The American Ceramic Society

43rd International Conference & Exposition on Advanced Ceramics and Composites

ABSTRACT BOOK

January 27– February 1, 2019
Daytona Beach, Florida

The American Ceramic Society
www.ceramics.org

Introduction

This volume contains abstracts for over 975 presentations during the 43rd International Conference & Exposition on Advanced Ceramics & Composites in Daytona Beach, Florida. The abstracts are reproduced as submitted by authors, a format that provides for longer, more detailed descriptions of papers. The American Ceramic Society accepts no responsibility for the content or quality of the abstract content. Abstracts are arranged by day, then by symposium and session title. An Author Index appears at the back of this book. The Meeting Guide contains locations of sessions with times, titles and authors of papers, but not presentation abstracts.

How to Use the Abstract Book

Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

MEETING REGULATIONS

The American Ceramic Society is a nonprofit scientific organization that facilitates the exchange of knowledge meetings and publication of papers for future reference. The Society owns and retains full right to control its publications and its meetings. The Society has an obligation to protect its members and meetings from intrusion by others who may wish to use the meetings for their own private promotion purpose. Literature found not to be in agreement with the Society's goals, in competition with Society services or of an offensive nature will not be displayed anywhere in the vicinity of the meeting. Promotional literature of any kind may not be displayed without the Society's permission and unless the Society provides tables for this purpose. Literature not conforming to this policy or displayed in other than designated areas will be disposed. The Society will not permit unauthorized scheduling of activities during its meeting by any person or group when those activities are conducted at its meeting place in interference with its programs and scheduled activities. The Society does not object to appropriate activities by others during its meetings if it is consulted with regard to time, place, and suitability. Any person or group wishing to conduct any activity at the time and location of the Society meeting must obtain permission from the Executive Director or Director of Meetings, giving full details regarding desired time, place and nature of activity.

Diversity Statement: The American Ceramic Society values diverse and inclusive participation within the field of ceramic science and engineering. ACerS strives to promote involvement and access to leadership opportunity regardless of race, ethnicity, gender, religion, age, sexual orientation, nationality, disability, appearance, geographic location, career path or academic level.

Visit the registration desk if you need access to a nursing mother's room or need further assistance. For childcare services, please check with the concierge at individual hotels for a listing of licensed and bonded child care options.

The American Ceramic Society plans to take photographs and video at the conference and reproduce them in educational, news or promotional materials, whether in print, electronic or other media, including The American Ceramic Society's website. By participating in the conference, you grant The American Ceramic Society the right to use your name and photograph for such purposes. All postings become the property of The American Ceramic Society.

During oral sessions conducted during Society meetings, **unauthorized photography, videotaping and audio recording is prohibited.** Failure to comply may result in the removal of the offender from the session or from the remainder of the meeting.

Registration Requirements: Attendance at any meeting of the Society shall be limited to duly registered persons.

Disclaimer: Statements of fact and opinion are the responsibility of the authors alone and do not imply an opinion on the part of the officers, staff or members of The American Ceramic Society. The American Ceramic Society assumes no responsibility for the statements and opinions advanced by the contributors to its publications or by the speakers at its programs; nor does The American Ceramic Society assume any liability for losses or injuries suffered by attendees at its meetings. Registered names and trademarks, etc. used in its publications, even without specific indications thereof, are not to be considered unprotected by the law. Mention of trade names of commercial products does not constitute endorsement or recommendations for use by the publishers, editors or authors.

Final determination of the suitability of any information, procedure or products for use contemplated by any user, and the manner of that use, is the sole responsibility of the user. Expert advice should be obtained at all times when implementation is being considered, particularly where hazardous materials or processes are encountered.

Table of Contents

Plenary Session

Plenary Session 15

Special Focused Session on Diversity, Entrepreneurship, and Commercialization

Diversity, Entrepreneurship and Commercialization 15

8th Global Young Investigator Forum

Advanced Ceramics and Coatings for Structural, Energy, Environmental and Functional Applications 16

Frontiers in Ceramic Materials: Advances and Challenges in Novel Materials Design, Synthesis, Performance, and Reliability I 17

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects and Thermo-mechanical Performance 18

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Environmental Barrier Coatings - Materials, Processing & Properties I 20

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Progress in SOFC and SOEC Technology 22

SOC Stacks and their Integration in the Systems 23

S4: Armor Ceramics - Challenges and New Developments

Terminal Ballistics / Quasi-Static and Dynamic Behavior I 23

Terminal Ballistics / Quasi-Static and Dynamic Behavior II 24

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li Batteries I 26

Thermoelectrics I 26

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Sintering Technologies I 28

S11: Advanced Materials and Innovative Processing Ideas for Production Root Technologies

Sustainable Energy Concepts and Applications 30

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Novel Applications and Device Fabrication I 32

Novel Applications and Device Fabrication II 32

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Ceramic Fuel Materials, Technologies, and Characterization 34

Novel Ceramics and Composites for Nuclear Systems I 35

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials I 36

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Stereolithography I 38

Stereolithography II 39

Stereolithography III 39

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced Nanostructured Materials for Photovoltaics and Solar Fuels I 40

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Precursor Chemistry and Applications 42

Solution Procesing and Rare Earth Materials 43

40th Anniversary Richard M. Fulrath Award Symposium on Frontiers of Ceramics for Sustainable Society

Fulrath Session I 44

Fulrath Session II 46

8th Global Young Investigator Forum

Frontiers in Ceramic Materials: Advances and Challenges in Novel Materials Design, Synthesis, Performance, and Reliability II 48

Novel Characterization Tools and Methods of Ceramics and Composites 48

Careers in Science, Technology, Engineering and Mathematics (STEM) 49

Ceramic Hybrid Materials and Composites for Aerospace, Armor, Biomedical, Electronics, Sensors and Actuators, Energy Conversion and Storage, Photo-catalysis, and Environmental Applications I 49

Ceramic Hybrid Materials and Composites for Aerospace, Armor, Biomedical, Electronics, Sensors and Actuators, Energy Conversion and Storage, Photo-catalysis, and Environmental Applications II 50

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Photocatalysis and Photovoltaics 51

Molecular Precursor Approaches for Vapor-phase Synthesis (ALD, CVD) of Materials 52

Gas Phase Depositions and In-Situ Characterization 53

Solution Procesing and Photocatalysts 54

S1: Mechanical Behavior and Performance of Ceramics & Composites

Fibers, Matrices, Coatings, and Interfaces. 56

Processing - Microstructure - Mechanical Properties Correlation I 57

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Environmental Barrier Coatings - Materials, Processing & Properties II 59

Thermal Barrier Coatings - Materials, Processing & Properties I 60

Thermal Barrier Coatings - Materials, Processing & Properties II 61

CMAS Degradation of EBC/TBC: Effects and Mitigation Strategies I 62

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Novel Processing 63
Sealants and Mechanical and Thermomechanical Aspects of Manufacturing 63
Electrolytes 64
Stack / Cell Performance and Durability 65

S4: Armor Ceramics - Challenges and New Developments

Materials Characterization I 66
Materials Characterization II 67
Materials Characterization III 68
Materials and Process Modeling I 68

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li Batteries II 69
Thermoelectrics II 70
Beyond Li Batteries I 71
Li Batteries III 72

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Sintering Technologies II 73
Advanced Manufacturing and Processing I 74

S11: Advanced Materials and Innovative Processing Ideas for Production Root Technologies

New Concepts and Emerging Technologies for Enhanced Product Performance I 76
New Concepts and Emerging Technologies for Enhanced Product Performance II 78

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Boride Properties and Oxidation 79
Carbide Properties and Oxidation I 81
Progress on Mxenes and Their Composites 81
Novel Processing of Mxenes and Their Composites I 82

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Joining and Technologies for Reactor Components. 83
Coating Technologies for Reactor Components 84
Novel Ceramics and Composites for Nuclear Systems II 84
Modelling Nuclear Ceramic Fuels and Structures 85

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials II 86
Semiconductors and Dielectrics I 87
Semiconductors and Dielectrics II 88

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Direct Writing 89
Fused Deposition 90
Ink Jet Printing I 91
Ink Jet Printing II 92

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced Nanostructured Materials for Photovoltaics and Solar Fuels II. 93
Advanced Nanostructured Materials for Photovoltaics and Solar Fuels III 94

Poster Session A 96

40th Anniversary Richard M. Fulrath Award Symposium on Frontiers of Ceramics for Sustainable Society

Fulrath Session III. 111

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Precursor Chemistry and Polymer Derived Ceramics I. 112
Precursor Chemistry and Polymer Derived Ceramics II 113

FS4: Green Technologies and Joining of Ceramics

Materials Processing from Ceramic, Plastic, Metallic, and Wastes I 114
Environmental Technologies 115
Materials Processing from Ceramic, Plastic, Metallic, and Wastes II 116
Ceramic Joining for Ambient and Extreme Environmental Applications 117

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation II. 117
Processing - Microstructure - Mechanical Properties Correlation III 119

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

CMAS Degradation of EBC/TBC: Effects and Mitigation Strategies II. 121
Multifunctional Protective Coatings: Processing, Microstructure and Properties I 122
Multifunctional Protective Coatings: Processing, Microstructure and Properties II. 123

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Air Electrode Performance and Durability 124
Fuel Electrode Performance and Durability. 125
Interconnects and Coatings. 126
HT Electrolysis. 127

S4: Armor Ceramics - Challenges and New Developments

Materials and Process Modeling II. 128
Synthesis and Processing I. 129
Synthesis and Processing II 130

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Beyond Li Batteries II 132
Thermoelectrics III. 133
Beyond Li batteries III. 134
Li Batteries IV. 134

S7: 13th International Symposium on Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental, and Health Applications

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures I 136

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures II 136

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Manufacturing and Processing II 137

Joining Technologies and Polymer-based Processing. 139

S9: Porous Ceramics: Novel Developments and Applications

High SSA Ceramics 140

Innovations in Processing Methods and Synthesis of Porous Ceramics I 141

S10: Ceramics Modeling, Genome and Informatics

Functional Ceramics I. 142

Functional Ceramics II 143

Structural Ceramics I 144

Structural Ceramics II 144

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Carbide Properties and Oxidation II 145

High Entropy UHTCs. 146

Structure and Bonding in MAX Phases 147

Novel Applications and Device Fabrication III. 148

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Corrosion of Nuclear Ceramics 149

Material Technologies for Enhanced Accident Tolerance LWR Fuels 150

Radiation Damage, Defect Production, Evolutions, and Interactions I. 151

Radiation Damage, Defect Production, Evolutions, and Interactions II 152

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Characterization Tools I . . . 153
Characterization Tools II . . . 154
Emerging Technologies . . . 155
Discussion Panel: Opportunities & Challenges in Ceramics Additive Manufacturing . . . 155

S16: Geopolymers, Inorganic Polymers and Sustainable Materials

Synthesis, Processing and Microstructure . . . 156
3-D Printing . . . 157
Composites . . . 158
Sustainable Materials . . . 159

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Multi-functional Materials I . . . 159
Multi-functional Materials II . . . 161

Poster Session B . . . 162

FS1: Bio-inspired Processing of Advanced Materials

Mechanical Properties of Natural and Bioinspired Materials . . . 174
Processing of Biomorphic and Biomimetic Materials . . . 175

FS2: Image based Characterization and Modelling of Ceramics by Non-destructive Examination Techniques

Characterization NDE Technologies for Sintering Analysis, Stress, Void and Distribution I . . . 177
Characterization NDE Technologies for Sintering Analysis, Stress, Void and Distribution II . . . 178
Influence of Inhomogenity . . . 178

FS4: Green Technologies and Joining of Ceramics

Future Directions of Materials Innovation and Joining Technology . . . 179

S1: Mechanical Behavior and Performance of Ceramics & Composites

Design, Life Prediction and Tribological Performance 180

Mechanics, Characterization Techniques, and Equipment 182

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Air Electrode Performance 184

Air Electrode: Powders, Fabrication, Contacting 185

Proton Conducting Fuel Cells I 186

Proton Conducting Fuel Cells II 186

S5: Next Generation Bioceramics and Biocomposites

Bioceramics and Biocomposites I 187

Bioceramics and Biocomposites II 189

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li-O2 and Li-S I 191

Li-O2 and Li-S II 191

S7: 13th International Symposium on Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental, and Health Applications

Nanomaterials for Energy Conversion and Storage and Catalysis 192

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures III 193

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures IV 194

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures V 195

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Functional Materials and Composites 196

S9: Porous Ceramics: Novel Developments and Applications

Modeling and Mechanical Properties of Porous Ceramics 198
Innovations in Processing Methods and Synthesis of Porous Ceramics II 199
Innovations in Processing Methods and Synthesis of Porous Ceramics III 199
Properties of Porous Ceramics 200

S10: Ceramics Modeling, Genome and Informatics

Structural Ceramics III 202
Structural Ceramics IV 202
Structural Ceramics V 203
Structural Ceramics VI 204

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Synthesis, Processing, and Densification 206
Ultra-High Temperature Composites I 207
Ultra-High Temperature Composites II 208
Novel Applications and Device Fabrication IV 208
Novel Processing of MXenes and Their Composites II 209

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Mechanical Properties and Test Methods 210

S16: Geopolymers, Inorganic Polymers and Sustainable Materials

Phosphates and Other Inorganic Materials 212
Alkali Activated Cements and Materials I 212
Alkali Activated Cements and Materials II 213
Novel Applications 214

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Multi-functional Materials III 214

FS1: Bio-inspired Processing of Advanced Materials

Bioinspired Materials for Functional Applications 216

FS2: Image based Characterization and Modelling of Ceramics by Non-destructive Examination Techniques

Use of NDE Techniques for Detection of Local Microstructural Changes and Damage Characteristics in Ceramic Matrix Composites I 217

S5: Next Generation Bioceramics and Biocomposites

Bioceramics and Biocomposites III 218

S10: Ceramics Modeling, Genome and Informatics

Structural Ceramics VII 220

Structural Ceramics VIII 221

Monday, January 28, 2019

Plenary Session

Plenary Session

Room: Coquina Salon D
Session Chairs: Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST); Surojit Gupta, University of North Dakota

8:50 AM

(ICACC-PLEN-001-2019) Renewable Energy: Role of Ceramics and Composites

D. Singh*[1]

1. Argonne National Laboratory, Applied Materials Division, USA

Extreme environments and operating conditions of power generation from renewable energy sources is necessitating development of components and systems using advanced materials. This presentation will discuss the opportunities and challenges in various renewable energy technologies including solar, wind, and geothermal. Role of engineered ceramic materials in fulfilling the gaps and/or meeting the material technological challenges will be discussed. Attributes of ceramics and their composites, vis-à-vis to metals, that make them the materials of choice are their high-temperature mechanical properties, corrosion and creep resistance, etc. As part of the presentation, specific example will presented that will outline the development of a ceramic composite system for high temperature thermal energy storage from bench to prototype scale. Finally, the need for techno-economic analysis to demonstrate the viability of the advanced ceramic materials for renewable energy applications will be discussed.

9:30 AM

(ICACC-PLEN-002-2019) Processing of complex ceramic materials by rapid high-energy techniques

J. Lis*[1]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Poland

The presentation is prepared based on author experience and the results obtained by AGH University of Science and Technology research group working in the field of ceramic materials synthesis using selected rapid high-energy techniques (RHET). Two RHET methods are described in details namely: Combustion Synthesis is also called Self-Propagating High-Temperature Synthesis (SHS) and Laser Rapid Manufacturing (LRM). Those approaches lead to technology enable to use strong high-energy sources for synthesis of different compounds associated with local consolidation of materials. These techniques should be considered as harvesting energy methods because reaction is initiated locally, then process goes in self-sustaining regime and chemical energy is generated from ambient surrounding powdery bed to provide an uninterrupted synthesis. Considering materials science point of view, physico-chemical processes occurring in the micro-regions undergoing rapid temperature rise with of next flash cooling resulted in very effective and untypical in nature phenomena compare to more conventional heating. Such combination effects lead to preparation new materials having interesting properties. Examples of such phenomena occurring in conditions of strong sources of chemical energy (SHS) or laser energy (LRM) used to prepare ceramic materials are analysed.

10:40 AM

(ICACC-PLEN-003-2019) Crystalline Oxide Semiconductor (IGZO Ceramics)- Based Devices for Artificial Intelligence (AI) and Internet of Things (IoTs)

S. Yamazaki*[1]

1. Semiconductor Energy Laboratory Co., Ltd., Japan

In 2009, we discovered c-axis aligned crystalline indium-gallium-zinc-oxide (CAAC-IGZO), which is a crystalline oxide semiconductor material. CAAC-IGZO is layered, and has a novel crystal structure. It is highly aligned in the c-axis direction and is not aligned in the a-b plane direction, but has no clear crystal grain boundaries. CAAC-IGZO is a ceramic material that can be applied to active devices, which can be applied to hardware such as a graphics processing unit (GPU), a central processing unit (CPU), a dynamic random access memory (DRAM), a 3D-NAND flash, and a field-programmable gate array (FPGA). AI chips are fabricated using the hardware listed above, and they are fabricated using Si semiconductor material. More DRAM chips are on an AI chip more than any other chip, and they consume power more than any other chip. This technology enables extreme reduction of AI chip's power consumption. Ceramics play key role in various critical developments in AI technology. In future crystalline oxide semiconductor will be the key technology to make AI prevalent throughout the world. This presentation will go across boundaries and introduce the applications of IGZO ceramics in an active device for AI technology.

11:20 AM

(ICACC-PLEN-004-2019) Drug, Device, or Diagnostic? Engineering in a new world of medicine

M. Cima*[1]

1. Massachusetts Institute of Technology, Department of Materials Science and Engineering, USA

Medical technologies are evolving at a very rapid pace. Portable communications devices and other handheld electronics are influencing our expectations of future medical tools. The advanced medical technologies of our future will not necessarily be large expensive systems. They are just as likely to be small and disposable. In addition, the lines between drugs, devices, diagnostics, and procedures are being blurred. This talk will review how microsystems and microdevices are already impacting health care as commercial products or in clinical development. Example systems include point of care diagnostics (POCT), patient monitoring tools, systemic drug delivery, local drug delivery, and imaging tools are described. These technologies are moving care from hospitals to outpatient settings, the physician's office, community health centers, nursing homes, and the patient's home.

Special Focused Session on Diversity, Entrepreneurship, and Commercialization

Diversity, Entrepreneurship and Commercialization

Room: Coquina Salon E
Session Chairs: Surojit Gupta, University of North Dakota; Valerie Wiesner, NASA Glenn Research Center

1:30 PM

(ICACC-DIV-001-2019) Integrated design of ceramic coatings for accident-tolerant fuel cladding in LWRs (Invited)

J. Zhang*[1]; J. Wang[1]

1. Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics, China

Nuclear energy is regarded as an important resource supplying low-carbon electricity at stable and affordable costs. The reliable and safety operation is essential for the application of nuclear

energy. Currently, the worldwide focus in LWRs is the development of accident-tolerant Fuels (ATF) with enhanced behavior under design-basis accident and severe-accident conditions, along with improved performance under normal operating condition. The cladding coating strategy is economically attractive, so-called near-term concept. In our work, PVD technique is employed for ceramic coating synthesis with temperature friendly to Zircaloy cladding. Moreover, the extremely harsh nuclear environments and high reactivity of Zircaloy require integrated design of coating composition and structure. For nano-laminated MAX phases, which display high resistance to oxidation and ion irradiation, multilayered coating structure is optimized and their feasibility for ATF application is evaluated. Besides, gradient ceramic coating system with combined merits of feasible performance and chemical compatibility is designed and characterized. It is expected that the safety margin of the fuel cladding system in LWRs could be enhanced by applying ceramic coating.

2:00 PM

(ICACC-DIV-002-2019) Effect of deposition parameters on cubic TiC and hexagonal Ti phase formation of thin films deposited by magnetron sputtering (Invited)

K. Balazsi*[1]

1. Centre for Energy Research HAS, Thin Film Physics, Hungary

Modern methods of vacuum deposition provide great flexibility for manipulating material chemistry and structure, leading to films and coatings with special properties. These new special properties of nanocomposites are often unachievable in bulk materials. A combination of pure carbon-based thin films with metallic nanoparticles can enhance certain physical properties in a nanocomposite. In this presentation, the effect of deposition temperature on the formation of TiC / Ti phases and mechanical properties of magnetron sputtered TiC based coatings will be showed. The thin films were deposited by DC magnetron sputtering at various temperatures from 25°C to 800°C in ultrahigh vacuum from two targets (Ti and C). The deposition parameters were chosen in order to synthetize amorphous, nanocrystalline and columnar TiC as well. The hardness of films with various nanostructures was found between 7 and 26 GPa, modulus of elasticity between 135 and 219 GPa. The films with pure cubic TiC phase exhibited two times higher hardness than films with the softer hexagonal Ti phase.

2:30 PM

(ICACC-DIV-003-2019) Nano to Bulk Scale Ceramic Processing and Structure Control for Enhanced Properties (Invited)

L. M. Rueschhoff*[1]

1. Air Force Research Lab, Materials and Manufacturing Directorate, USA

Historically, both inherent processing difficulties and catastrophic brittle failure in ceramics have limited their use in high stress, critical applications. In this talk I will give an overview of my research with an insight to ceramic structure-properties-processing relationships on all length scales. Traditional powder processing limitations can be overcome through the use of both preceramic polymers and ceramic powder aqueous suspensions. Both can be rheological designed and modified to be tailored for a variety of advanced processing techniques, with a special focus given to direct ink writing additive manufacturing. In recent years, manipulation of ceramic structure on the nanoscale has led to the discovery of new properties and behaviors that are distinct from the bulk scale. For example, ceramic mechanical metamaterials have been designed that exhibit ductile-like deformation and strain recovery due to their tailored nanostructure design. Final remarks of the talk will address the importance of networking and mentoring in personal and project success, along with opportunities available for involvement within ACerS.

3:00 PM

(ICACC-DIV-004-2019) GrainBound – A Perspective Into Starting a "Consulting" Company (Invited)

C. J. Marvel*[1]

1. GrainBound, Inc., USA

GrainBound was founded in 2016 and we consider ourselves as a solution providing company. We aim to help our clients adapt manufacturing strategies to better control microstructural evolution and to also improve scalability of their products. In particular, our modus of operandi is to engineer solid interfaces in collaboration with our clients, most often grain boundaries, using a combination of state-of-the-art material characterization techniques and data analytics. Hence the name GrainBound. It is also important to us that we truly guide our clients using our results, and over 100 years of grain boundary expertise between the technical staff, to improve their processes, rather than supply data without scientific backing or forward-thinking manufacturing strategies. As a new company, we still have a strong entrepreneurial mindset. We are always seeking new strategies to grow our client base, develop business proposals, improve marketing strategies, and advance our technical approaches to provide the best return on investment for our clients. This talk will be my brief perspective into our story, our vision, and the lessons that we have learned as we continue to grow in the "consulting" company market.

8th Global Young Investigator Forum

Advanced Ceramics and Coatings for Structural, Energy, Environmental and Functional Applications

Room: Coquina Salon G

Session Chair: Manoj Mahapatra, University of Alabama at Birmingham

1:30 PM

(ICACC-GYIF-001-2019) Sintering of Advanced Ceramics by Plastic Deformation as Dominant Mechanism (Invited)

W. Ji*[1]; Z. Fu[1]

1. Wuhan University of Technology, China

Dense and fine grain structure is the goal of ceramic sintering. However, common sintering processes with high sintering temperature and long soaking time lead to inevitable grain growth. A new ceramic sintering approach employing plastic deformation as the dominant mechanism is proposed, at low temperature close to the onset point of grain growth and under high pressure. High performance Boron Cabide ceramics with full density without grain growth were fabricated based on the technology. This idea and method provide both time and energy efficient ways for B_4C, and also facilitate preparation of other advanced ceramics such as nano-ceramics for practical applications.

1:50 PM

(ICACC-GYIF-002-2019) Airborne Impurities Assisted SOFC Cathode Degradation and Mitigation Approaches (Invited)

A. Aphale*[1]; M. Reisert[1]; B. Hu[1]; S. Belko[1]; S. Heo[1]; J. Hong[1]; P. Singh[1]

1. University of Connecticut, Materials Science and Engineering, USA

Solid oxide fuel cells (SOFC) experience long term structural, chemical and electrochemical performance degradation due to the poisoning of the cathode exposed to ambient air containing trace levels of both intrinsic (H_2O,CO_2,SO_x) and extrinsic (CrO_x,$CrO_x(OH)_x$,Si(OH)x for e.g) impurities. Experimental observations show that while the exolution of A-site alkaline earth dopants from the perovskite lattice becomes prevalent in the presence of moisture, trace levels of gaseous chromium and sulfur species lead to reaction product formation at free electrode surface

and electrolyte-electrode interface resulting in the blocking of the triple phase boundary (TPB) sites for oxygen reduction reaction (ORR). Findings from transpiration and electrochemical cell tests, thermochemical modeling, computational simulation and chemical and morphological characterization studies, along with electrode poisoning mechanisms will be presented. A novel approach to mitigate chromium poisoning by reducing the overall chromium flux ingested into the electrochemically active stack will be outlined and recent computational and experimental results will be presented. Development of cost effective "Getters", for the capture of trace impurities, synthesized using low cost alkaline earth and transition metal oxides, will be presented. Approaches involving alloy surface modification to reduce Cr evaporation will also be discussed.

2:10 PM

(ICACC-GYIF-003-2019) Micro-plasma based enhancement in dielectric and piezoelectric properties of ZnO based multifunctional composite thin films by surface modification (Invited)

H. Brar[1]; E. Leal-Quiros[1]; S. Ahmed[2]; S. Banerjee*[1]

1. California State University, Fresno, Mechanical Engineering, USA
2. SUNY Buffalo State, Mechanical Engineering, USA

Atmospheric pressure and ambient temperature based micro-plasmas have been used in polarization and alignment of dipoles in ferroelectrics. The same phenomenon can be used to enhance the surface energy and surface characteristics of composite multifunctional thin films by means of surface modification. A significant increase in non-thermal atmospheric plasma applications, such as dielectric barrier discharge (DBD) and corona discharge plasmas have been steadily increasing in industry and in the research literature. The current work involves the use of DBD plasma for surface modification of ZnO based multi-functional and flexible thin film devices towards enhancement in surface bonding characteristics and variation in surface wettability and surface energy characteristics. The parameters being investigated in the experiments include plasma device characteristics such as voltage, current, and frequency, as well as other significant parameters such as displacement between thin film and DBD/Corona discharge source, treatment time, and temperature of the plasma. The modified surface micro-structure is analyzed using a scanning electron microscope and the bulk electrical and dielectric properties are characterized using impedance spectroscopy.

Frontiers in Ceramic Materials: Advances and Challenges in Novel Materials Design, Synthesis, Performance, and Reliability I

Room: Coquina Salon G

Session Chairs: Yoshiki Sugimoto, National Institute of Advanced Industrial Science and Technology (AIST); Giorgia Franchin, University of Padova

3:20 PM

(ICACC-GYIF-004-2019) Progress and Challenges in Graphene Reinforced Ceramic Matrix Composites (Invited)

A. Nieto*[1]

1. Naval Postgraduate School, Mechanical and Aerospace Engineering, USA

This talk will present some of the most promising progress made in the field of graphene reinforced ceramic matrix composites (CMC) over the last half-decade or so. The outstanding functional and mechanical properties of graphene have been shown to impart ceramics with highly desirable properties such as higher electrical conductivity and improved damage tolerance and fracture toughness. In addition, unlike their CNT counterparts, graphene nanoplatelets (GNP) have shown excellent compatibility in biological environments thus far. This talk will provide a mechanistic overview of the current understanding of the mechanisms associated with graphene reinforcement for both mechanical and functional properties. Several challenges remain for advancing GNP-CMCs as an engineering material, including the difficulty in attaining consistently uniform particulate distribution, size and thickness dependence of GNP properties, and control of the GNP/ceramic interface. Future scope of GNP-CMC research will be discussed from both the perspective of ongoing challenges as well as applications where GNP-CMCs offer intrinsic advantages over conventional ceramics and fiber reinforced CMCs.

3:50 PM

(ICACC-GYIF-005-2019) Compressive response of ice-templated ceramic-polymer composites both in quasistatic and dynamic regimes of strain rate

S. Akurati*[1]; N. Tennant[1]; D. Ghosh[1]

1. Old Dominion University, Mechanical and Aerospace Engineering, USA

In recent years, bioinspired ceramic-polymer composites with multilayered architecture have drawn significant attention because of the possible synergy of strength and damage-tolerance. Polymer infiltration of ice-templated ceramics has emerged as a promising and versatile technique to develop this class of novel composites, which can be utilized for a number of structural applications including in high-strain rate environments. In spite of the growing interests, there is limited understanding of compressive mechanical response of ice-templating based multilayered ceramic-polymer bulk composites and investigation on their dynamic behavior is almost non-existent. Moreover, for this class of materials there is a need to understand the orientation-dependence of properties. In this study, our goal is to understand the effects of composition (ceramic to polymer ratio) and morphology of the ceramic scaffolds on the macroscopic response of the composites. Moreover, these composites will be subjected to uniaxial compressive loading along different orientations. A split-Hopkinson pressure bar (SHPB) will be utilized to investigate the dynamic response of the composites.

4:10 PM

(ICACC-GYIF-006-2019) Effects of particle size and morphology on the dynamic compressive response of ice-templated ceramics with directional porosity

M. Banda*[1]; J. E. John[1]; D. A. Terrones[1]; B. B. Laredo[1]; D. Ghosh[1]

1. Old Dominion University, Mechanical and Aerospace Engineering, USA

Quasistatic compressive response of ice-templated ceramics with directional porosity is influenced by solids loading, freezing front velocity, particle size and morphology. However, the dynamic compressive response of ice-templated ceramics is still to be explored. Our recent studies revealed a marked improvement in the compressive strength and energy absorption of ice-templated ceramics processed with an aqueous ceramic suspension that contained two different particle morphology. The enhancement in these mechanical properties is even higher when the ice-templated ceramics subjected to dynamic compressive loading. In this presentation, first we will demonstrate the unique changes in microstructure of ice-templated sintered ceramics (porosity, lamellar bridge density, pore size and aspect ratio) by introducing different particle morphology. Next, we will present the uniaxial quasistatic and dynamic compressive response of these porous structures. Finally, we will discuss the correlations among particle size and morphology, microstructural features, and dynamic compressive response of ice-templated ceramics. Our present work can be helpful in design and development of high strength-lightweight materials for impact protection and energy absorption applications.

4:30 PM

(ICACC-GYIF-007-2019) Synthesis and Characterization of Novel Lignin-Metal Composites

G. Ellis*[1]; M. Dey[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

Lignin is an important source of aromatic compounds which has a huge commercial potential. However, due to its heterogenous chemical nature there are many issues in its succesful commercialization. In this poster, we report some of the recent results in the development of lignin-metal composites. More particularly, we will report detailed microstructure and mechanical behavior characterization of these composites.

4:50 PM

(ICACC-GYIF-008-2019) Synthesis of Al_4SiC_4 by the self-propagating high-temperature synthesis method

Y. Nakashima*[1]; H. Hyuga[1]; R. Kamiya[2]; S. Hashimoto[2]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan
2. Nagoya Institute of Technology, Japan

As one of the promising high-temperature ceramics, aluminum silicon carbide (Al_4SiC_4) is known as a promising material for high-temperature ceramics. However, Al_4SiC_4 is synthesized at high temperatures with long reaction time by an electric furnace. Self-propagating high-temperature synthesis (SHS) is a promising synthesis technique because of energy-efficient, time-saving and mass production technique. Therefore, in this experiment, Al_4SiC_4 was produced from a mixture pellet of Si, Al and carbon black with the addition of poly(tetrafluoroethylene) (PTFE) as an exothermic promoter by SHS method, and the effect of the atmosphere, gas pressure, and amount of PTFE were investigated. The argon was the ideal atmosphere, because it was not reacted with raw materials (Al, Si) and the gaseous material could be kept in the mixture pellet. The gas pressure also important factor for synthesizing Al_4SiC_4, because the gaseous material could be more kept in the mixture pellet by higher gas pressure. The amount of PTFE was affected on the formation of SiC, because it was worked as the promotor for the reaction between Si and carbon black via the formation of SiF_4. As the result, the high purity Al_4SiC_4 could be synthesized from Al, Si, and carbon black with 20 wt.% PTFE at 3.0 MPa argon atmosphere.

5:10 PM

(ICACC-GYIF-009-2019) Calorimetric Measurements of the Thermodynamic Properties of Gas-Ceramic Coatings and Ingested CMAS Corrodents (Invited)

G. Costa*[1]; B. J. Harder[1]; V. L. Wiesner[1]; N. P. Bansal[1]; K. N. Lee[1]; D. Kapush[2]; S. Ushakov[2]; A. Navrotsky[2]

1. NASA Glenn Research Center, USA
2. University of California, Davis, Peter A. Rock Thermochemistry Laboratory and NEAT ORU, USA

The thermodynamic properties of ceramic coatings and their reaction products are crucial to develop more durable materials for gas-turbine engines. An example involves the corrosion studies of thermal (TBC) and environmental (EBC) barrier coatings of gas turbines by molten silicate debris consisting of CaO-MgO-Al_2O_3-SiO_2 system (CMAS). Here, we discuss some results measured by high temperature drop solution calorimetry, drop-and-catch calorimetry (DnC) and differential thermal analysis (DTA) techniques to obtain the thermodynamic properties of ceramic coatings for gas-turbine engines and their corrosion products. The enthalpies of solution of $Y_2Si_2O_7$ and $Yb_2Si_2O_7$ and 31YSZ, 16RESZ based coatings and apatite reaction products are moderately positive. However, 7YSZ shows somewhat different behavior. Apatite formation is only favorable over coating dissolution in terms of enthalpy for 7YSZ. The enthalpies of mixing between the coatings and the molten silicate are less exothermic for $Yb_2Si_2O_7$ and $CaYb_4Si_3O_{13}$ than for 7YSZ, indicating lower energetic stability of the latter against molten silicate corrosion. We also report for the first time the calorimetric measurements of the enthalpy of formation of rare-earth apatites (rare-earth, RE = Y, Yb, Gd and Sm). Implications of these results on predicting CMAS induced corrosion are discussed.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects and Thermo-mechanical Performance

Room: Coquina Salon D

Session Chairs: Jonathan Salem, NASA Glenn Research Center; Marina Ruggles-Wrenn, Air Force Institute of Technology

1:30 PM

(ICACC-S1-001-2019) Creep of a Nextel™720/alumina ceramic composite containing an array of small holes at 1200° C in air and in steam (Invited)

M. Ruggles-Wrenn*[1]; S. Minor[1]; C. P. Przybyla[2]; E. L. Jones[2]

1. Air Force Institute of Technology, Aeronautics & Astronautics, USA
2. Air Force Research Lab, USA

Creep behavior of an oxide/oxide composite containing an array of small circular holes was evaluated. The composite consists of a porous alumina matrix reinforced with Nextel™720 alumina-mullite fibers woven in an eight harness satin weave. Test specimens contained an array of 17 small holes with 0.5-mm diameter drilled using a CO_2 laser. Tensile creep behavior was examined at 1200°C in air and in steam for creep stresses ranging from 38 to 140 MPa. The presence of the laser-drilled holes accelerates the creep rates and significantly degrades creep performance of the composite. Creep run-out, defined as 100 h at creep stress, was achieved for stresses < 60 MPa in air and for stresses < 40 MPa in steam. Composite microstructure, as well as damage and failure mechanisms were investigated. The degradation of tensile properties and creep resistance are attributed to damage caused to composite microstructure by laser drilling.

2:00 PM

(ICACC-S1-002-2019) Modeling Oxidation Embrittlement of SiC/SiC Ceramic Matrix Composites

V. Collier*[1]; M. Begley[2]; W. Xu[1]; F. W. Zok[1]; R. M. McMeeking[2]

1. University of California, Santa Barbara, Materials, USA
2. University of California, Santa Barbara, Materials and Mechanical Engineering, USA

The oxidation embrittlement of SiC/SiC ceramic matrix composites (CMCs) at intermediate temperatures is a critical aspect of CMC durability that is not satisfactorily described by existing models. Consequently, a model has been developed to investigate three major oxidation phenomena, namely: (i) diffusion of oxygen and water vapor along a pre-existing matrix crack; (ii) recession of BN interphase via reaction with water and oxygen and subsequent diffusion of gaseous boron hydroxide species; and (iii) growth of an oxide scale on the surfaces of the matrix crack and on the fiber as a function of time. Scaling arguments suggest key rate-limiting species, e.g. the scale growth is dominated by water vapor transport and production of HBO2 is negligible in comparison to the other boron hydroxide reaction products: H3BO3 and H3B3O6. Accordingly, the model only tracks the concentration distributions of oxygen, water, and relevant boron hydroxide species. Furthermore, the feedback between transport-oxidation and mechanics is explored by calculating fiber-bridging stresses for the oxidized state while accounting for the effect of BN recession by adjusting the shear sliding length of classical fiber bridging models. The results highlight key sensitivities to temperature and atmospheric conditions and inform how chemistry changes fiber stress distributions in CMCs.

2:20 PM

(ICACC-S1-003-2019) Oxidation behavior of $HfSi_2$ with boron addition

T. Tsunoura*[1]; K. Yoshida[2]; T. Yano[2]; T. Aoki[3]; T. Ogasawara[4]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan
2. Tokyo Institute of Technology, Laboratory for Advanced Nuclear Energy, Japan
3. Japan Aerospace Exploration Agency, Aeronautical Technology Directorate, Japan
4. Tokyo University of Agriculture and Technology, Department of Mechanical Systems Engineering, Japan

SiC fiber-reinforced composites have received attention for high temperature components in aero-engines. Recently, Si eutectic alloys such as Si-$HfSi_2$ have been used to fabricate and joint SiC composites due to their low melting point and excellent infiltrability. In our previous work, $HfSi_2$ showed poor oxidation resistance in dry and wet condition. In this study, oxidation behavior of $HfSi_2$ with boron addition to improve oxidation resistance was evaluated. B_4C was used as boron additive. $HfSi_2$ with and without B_4C additive were fabricated by spark plasma sintering. The $HfSi_2$-B_4C composites consisted of $HfSi_2$ and HfB_2. Oxidation tests were carried out at 800-1200°C for 100 hours in humid air. $HfSi_2$ without boron addition showed catastrophic oxidation behavior called pest oxidation after wet oxidation test at 800-1000°C. Oxidation thickness of $HfSi_2$ was about 100 μm after oxidation test at 800°C. On the other hand, $HfSi_2$-10vol%B_4C showed thin and uniform oxidation layer around 10 μm after oxidation test at 800-1000°C. It is because that protective layer by B_2O_3 was formed by oxidation of boride in $HfSi_2$-10vol%B_4C. Oxidation rate of $HfSi_2$ was able to be improved and controlled using boron additive.

2:40 PM

(ICACC-S1-004-2019) Mechanical Characterization of SiC/SiC Ceramic Matrix Composites under a Unique Combustion Facility

R. Panakarajupally*[1]; M. J. Presby[1]; J. Zhou[2]; M. Kannan[1]; G. N. Morscher[1]; G. G. Chase[2]

1. The University of Akron, Mechanical Engineering, USA
2. The University of Akron, Chemical Engineering, USA

Future gas turbine engines are aimed for higher efficiency with lower exhaust emissions. Efficiency of the gas turbine engine increases with an increase in turbine inlet temperature (TIT). Current Nickel based super-alloys are operating at their maximum temperatures and cannot withstand an increase in temperature. Ceramic matrix composites (CMC's) evolved as the choice materials because of their low weight, high temperature capability and high specific strength. But these materials are prone to oxidation followed by surface recession in high temperature water vapor containing environments. In order to successfully implement CMC's in jet engines one has to characterize these materials in similar jet engine conditions. A unique burner rig facility capable of simulating coupled mechanical loading along with combustion environment was developed. SiC/SIC CMC's are investigated under burner rig conditions to study the effect of combustion environment on the mechanical properties. Non-Destructive Evaluation (NDE) techniques such as Electrical Resistance (ER) is used to monitor damage and a Forward Lean Infrared Camera (FLIR) is used to monitor the front and back surface temperature of the specimen. Similar tests are performed in isothermal furnace for comparison.

3:20 PM

(ICACC-S1-005-2019) Low temperature mechanical properties and oxidation behavior of melt-infiltrated SiC/SiC ceramic matrix composites

K. Detwiler*[1]; J. Pierce[2]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA
2. University of Dayton Research Institute, USA

SiC/SiC ceramic matrix composite (CMC) turbine engine components will experience a wide range of temperatures, environments and stresses, dependent upon the part's location in the engine. The present work is focused on a lower temperature, higher stress regime where water vapor is present. Of specific interest is the effect of applied stress on the oxidation mechanisms for SiC/SiC CMCs. Monotonic tensile tests were conducted to specimen failure in lab air to measure baseline mechanical properties at relatively low temperatures of 400°C, 600°C, and 800°C. Acoustic emission was utilized during tensile testing to track the onset of matrix cracking within the composite. Oxidation kinetics were separately evaluated using thermogravimetric analysis (TGA) to track weight change of specimens with exposed fibers on machined edges during low temperature exposures in both dry and wet oxygen. Resulting microstructures for both the tensile and TGA specimens were characterized via scanning electron microscopy. Based on these results, a test matrix to evaluate the coupling of the thermochemical and thermomechanical behavior will be presented.

3:40 PM

(ICACC-S1-006-2019) Multi-Physics Computational Modeling of High-Temperature Oxidation Damage in Ceramic Matrix Composites

P. Prabhakar*[1]; V. Damodaran[1]

1. University of Wisconsin, Civil and Environmental Engineering, USA

The main objective of this paper is to establish the structural integrity of fiber reinforced ceramic matrix composites (FRCMCs) subject to extreme temperatures in oxidizing environments. These composites retain exceptional thermal and mechanical properties at elevated temperatures in inert environments, however, degrade rapidly at temperatures as low as 450°C in oxidizing environments for Carbon fiber reinforced in Carbon matrix (C/C) composites. This paper focuses on developing an experimentally validated multi-physics (thermo-chemical-mechanical) finite element modeling framework that captures the extent and spatial distribution of degradation due to oxidation in FRCMCs at the microscale. Under extreme temperatures, interacting degradation modes manifest due to high temperature gradients, oxidizing environments, mismatch in physical properties of constituents, etc. Therefore, it is critical to relate and establish the two-way coupling between the thermo-chemical evolution to the mechanical degradation upon exposure to high temperatures. This computational framework will enable the identification of key degradation features and failure mechanisms due to thermal, chemical and mechanical interactions, in view of complex internal micro architecture of the fiber bundles.

4:00 PM

(ICACC-S1-007-2019) A deformation map for WC

B. J. Currie[1]; L. J. Vandeperre[1]; S. A. Humphry-Baker*[1]

1. Imperial College London, Materials, United Kingdom

WC ceramics and their composites are employed in tools for energy extraction and manufacturing. They are also candidate plasma-facing materials in nuclear fusion reactors. In both applications, materials are exposed to extreme thermal and mechanical excursions. However, the understanding of high temperature deformation is not well understood. Underlying this understanding – both in monolithic and in composite structures – is the behaviour of individual WC grains. However, the existing literature data for pure WC is sparse; no creep measurements exist and high temperature

hardness measurements are widely scattered, most likely due to excessive porosity. We have studied the deformation of fully dense WC fabricated by spark-plasma sintering. Multiple methods are employed, including warm nanoindentation; high temperature cross-wedge indentation; and compressive creep. Combining our results with the existing literature, we generate for the first time a deformation mechanism map for the compound WC. The map can enhance our fundamental understanding of WC composite deformation, and enable the design of high performance materials.

4:20 PM

(ICACC-S1-008-2019) Exploration of the Coefficient of Thermal Expansion of Rare Earth Silicates Using Dilatometry and High Temperature X-ray Diffraction

C. G. Parker*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA

Rare earth silicates exhibit predominately highly anisotropic monoclinic crystal structures. Measurement of the coefficient of thermal expansion (CTE) of these materials by traditional dilatometry is therefore inadequate to fully describe their expansion behavior. Rare earth silicates are used as environmental barrier coatings on ceramic matrix composites and applied using the Air Plasma Spray (APS) method, leaving an amorphous coating with multiple phases present. In this work, thermal expansion of phase pure Y_2SiO_5, $Y_2Si_2O_7$, Yb_2SiO_5, and Yb_2SiO_5 obtained by dilatometry was compared to results from high temperature X-ray diffraction (XRD) performed at the Advanced Photon Source at Argonne National Laboratory. The high temperature XRD data were analyzed using Rietveld refinement to accurately describe the lattice parameters and interplanar spacings of each phase. Lattice parameters were used to calculate CTEs in each crystallographic direction. Plane spacings were used for analysis in the Coefficient of Thermal Expansion Analysis Suite, software developed by the Kriven group at University of Illinois, to represent expansion in three dimensions and determine eigenvalues of the expansion tensor. Thermal expansion of APS $Y_2Si_2O_7$ was also analyzed using dilatometry to understand the effect of thermal cycling and phase content on CTE of APS coatings.

4:40 PM

(ICACC-S1-009-2019) Impact of Irradiation-Induced Point Defects on Fracture Mechanisms in Ceramic Nanocomposites

C. E. Athanasiou*[1]; T. Baba[2]; C. Ramírez[1]; W. Zhang[1]; I. Szlufarska[2]; B. Sheldon[1]

1. Brown University, School of Engineering, USA
2. University of Wisconsin, Department of Materials Science & Engineering, USA

The incorporation of carbon nanotubes (CNTs) in ceramic matrix composites produces materials with a wide range of mechanical properties. More specifically, increased fracture toughness on the order of 50-200% is now well documented. However, the influence of defects on the fracture toughness is unclear. Detailed study of fracture mechanisms in these materials is challenging, because of the small length scales involved. In this work, we experimentally induce controlled point defects in the nanocomposite using high energy carbon and proton ions. The defect density was controlled by varying the radiation exposures, and the mechanical response of the material was measured with nanoindentation and microcantilever fracture measurements. Surprisingly, the increased defect densities result in higher fracture toughness. In addition to presenting these experimental results, possible mechanisms that link the defect density with the material toughness will be discussed.

5:00 PM

(ICACC-S1-010-2019) Erosion of a Gas-Turbine Grade Ceramic Matrix Composite: Experimental Characterization and Multi-Scale Modeling

M. J. Presby*[1]; G. N. Morscher[1]; C. Godines[2]; D. Huang[2]; A. Eftekharian[2]; F. Abdi[2]

1. University of Akron, Mechanical Engineering, USA
2. AlphaSTAR Corporation, USA

A key design requirement for use of ceramic matrix composites (CMCs) in gas turbine engines is resistance to solid particle erosion. Despite this importance, little systematic work has been performed on the erosion behavior of CMCs. Owing to their unique architectural configurations, the erosion behavior of CMCs is markedly different than that observed in monolithic ceramics materials. In this study, the erosion behavior of an N720/alumina oxide/oxide CMC was characterized at ambient temperature using spherical glass beads as the erodent. The erosion rate and damage morphology were determined and characterized as a function of particle size and velocity. Post-erosion residual strength was performed in flexure to quantify the effect of the damage. The experimental erosion degradation was simulated by computational multi-scale progressive failure analysis (MS-PFA) using LS-Dyna in conjunction with AlphaSTAR's GENOA material characterization and qualification (MCQ) module.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Environmental Barrier Coatings - Materials, Processing & Properties I

Room: Tomoka B

Session Chairs: Douglas Wolfe, Pennsylvania State University; Bryan Harder, NASA Glenn Research Center

1:40 PM

(ICACC-S2-001-2019) Slurry-Based Environmental Barrier Coatings (Invited)

K. N. Lee*[1]; B. J. Harder[1]; J. Setlock[2]; B. J. Puleo[1]

1. NASA Glenn Research Center, Materials, USA
2. University of Toledo, USA

Increased fuel efficiency is obtained through increased thermal efficiency of turbine engines by increasing the overall pressure ratio (OPR). Increased OPR requires increased turbine inlet temperature, which is paced by advances in turbine hot section materials. SiC/SiC Ceramic Matrix Composites (CMCs) are the most promising materials to enable a quantum leap in temperature capability. Environmental Barrier Coatings (EBCs) are an enabling technology for CMCs by protecting them from water vapor-induced recession. The first EBC-coated CMC component in a commercial engine entered into service in 2016. The temperature capability of current CMCs is ~1300°C. Research has been underway to develop next generation CMCs with 2700°F (1482°C) temperature capability. The silicon bond coat in current EBCs limits their upper use temperature to the silicon melting point (1414°C). As such the viability of 2700°F CMCs is contingent upon the successful development of EBCs that replace the silicon bond coat. NASA has recently developed next generation EBCs with a 2700°F-capable bond coat using a slurry coating process. This paper will discuss the performance of slurry-based EBCs in laboratory test furnaces and a combustion rig test.

2:00 PM

(ICACC-S2-002-2019) Implications of rapid quenching and chemical composition shift in Plasma Sprayed $Yb_2Si_2O_7$ Environmental Barrier Coatings

E. Garcia Granados*[1]; H. Lee[1]; S. Sampath[1]

1. Stony Brook University, Center for Thermal Spray Research, USA

Environmental barrier coatings (EBCs) are the envisioned solution to protect ceramic matrix composites (CMC) components in forthcoming power generation and aircraft/spacecraft turbine engines from Si volatilization caused by the combustion atmosphere. The most promising candidates for this application are atmospheric plasma sprayed (APS) rare earth silicates and among them $Yb_2Si_2O_7$ has gained consideration in the last few years. APS rare earth silicates present two main drawbacks; the volatilization of SiO_2 which shift the original feedstock composition and favors the development of Yb_2O_3 enriched phases and the amorphous nature of the as deposited coatings. The present work aims to understand the role of the amorphous character of the as sprayed coatings and Yb_2SiO_5, detected after annealing treatments, on the microstructure and properties of plasma sprayed $Yb_2Si_2O_7$ coatings, assessing the crystalline phases (XRD, DTA, CTE), microstructure (SEM) and chemical composition of the obtained coatings before and after post-spraying treatments.

2:20 PM

(ICACC-S2-003-2019) Effect of stress/strain distribution on quantitative measurement of delamination toughness in oxide EBCs on SiC/SiC substrate system

Y. Arai*[1]; Y. Aoki[2]; H. Hatta[1]; Y. Kagawa[1]

1. Tokyo University of Technology, Japan
2. The University of Tokyo (Currently Kobe steel, Ltd.), Japan

A simple technique to measure interfacial delamination toughness between environmental barrier coatings (EBCs) and CMC substrate has been developed. Recent research has revealed that intensive distributions of residual stresses have developed especially in the substrate made of woven fabric reinforcement and coating on it. In the present study, in order to elucidate the effect of the stress distribution on the delamination toughness, model materials were prepared, and interfacial delamination toughness was evaluated. A simple model was proposed to explain the effect of the stress distribution.

2:40 PM

(ICACC-S2-004-2019) Oxidation Performance of Doped and Undoped Environmental Barrier Coatings Deposited Via Plasma Spray–Physical Vapor Deposition (Invited)

B. J. Harder*[1]; K. Lee[1]; B. Kowalski[1]

1. NASA Glenn Research Center, USA

Next generation turbine engines will incorporate silicon-based ceramic matrix composites for efficiency benefits attributed to their higher temperature capability, reduced weight and cooling requirements over traditional superalloys. However, environmental barrier coatings (EBCs) are needed to protect these materials in combustion environments. Future operating temperatures target 1482°C, which may require advanced processing of EBCs to provide durability in these aggressive conditions. Plasma Spray- Physical Vapor Deposition (PS-PVD) is a hybrid technique that can tailor microstructures and compositions to optimize performance. PS-PVD deposited EBCs of doped and undoped $Yb_2Si_2O_7$ composition were deposited on SiC substrates and cycled in 90% H_2O/O_2 at 1426°C to evaluate the oxidation performance in a steam environment. Coating composition, phase, and microstructure were tracked with X-ray diffraction and electron microscopy was used to measure thermally grown oxide thickness in order to determine the effect of doping on the oxidation rate.

3:30 PM

(ICACC-S2-005-2019) Effect of EBC porosity on performance at >1400°C in steam (Invited)

B. A. Pint*[1]; S. Sampath[2]

1. Oak Ridge National Laboratory, Materials Science and Technology, USA
2. Stony Brook University, USA

The next generation of ceramic matrix composites will target operation above 1400°C, therefore, an environmental barrier coating (EBC) without a Si bond coating will be needed. To begin to understand EBC performance under those conditions, initial experimental work is evaluating the cyclic oxidation performance of two ytterbium silicate coatings with different levels of porosity on CVD SiC substrates at 1425°C in flowing steam. The reaction products will be evaluated to determine if coating density affected the protective role of the EBC under these conditions. Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Turbine Program.

4:00 PM

(ICACC-S2-006-2019) Chemical Vapor Deposition of Ytterbium Silicate Coatings for SiC Ceramic Matrix Composite

A. Ito*[1]; T. Hara[1]

1. Yokohama National University, Environment and Information Sciences, Japan

SiC-fiber-reinforced SiC ceramic matrix composite (SiC-CMC) has been developed for next generation gas turbine engine, and thermal and environmental barrier coatings (T/EBCs) shall be developed for SiC-CMC to assure its reliability. Requirements for T/EBC materials are phase stability, low thermal conductivity, low mass loss at elevated temperatures, and resistance to CMAS sand debris. Ytterbium silicate is candidate material, which exhibits a low mass loss at elevated temperatures than current T/EBCs candidate materials. Chemical vapor deposition (CVD) is a coating process via vapor phase and exhibits excellent step coverage. Microstructure of coatings can be controlled by changing deposition parameters. In this talk, preparation of ytterbium silicate coatings on SiC fiber for SiC-CMC will be presented. This work was supported in part by KAKENHI, Japan Society for the Promotion of Science, and Cross-ministerial Strategic Innovation Promotion Program (SIP), "Structural Materials for Innovation, SM^4I (Funding agency: JST)".

4:20 PM

(ICACC-S2-007-2019) Characteristics of Ytterbium Disilicate-based EBCs Fabricated by Suspension Plasma Spray

S. Kim*[1]; Y. Oh[1]; S. Lee[1]; H. Kim[1]; Y. Sohn[2]; O. Guillon[2]; R. Vassen[2]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Engineering Ceramics Center, Republic of Korea
2. Forschungszentrum Juelich, IEK-1, Germany

Rare-earth disilicates, such as $Yb_2Si_2O_7$ and $Y_2Si_2O_7$, have been investigated as one of the candidate materials for environmental barrier coating (EBC) applications to protect silicon (Si)-based ceramic matrix composites from combustion atmospheres in advanced gas turbines. EBCs, as diffusion barriers for water vapor, are required to be dense, crack-free, uniform, and with well-matched CTE compared to Si-based substrates. In this study, the fabrication of ytterbium-disilicate-based environmental barrier coatings by using suspension plasma spray are reported. Characteristics of these EBCs are represented in terms of density and phase formation with different spraying and feedstock conditions. The possibility of these coatings as environmental barrier application is also discussed.

4:40 PM

(ICACC-S2-008-2019) Phase Transformation of Mixture Ytteribium Silicate / Mullite in the Environmental Barrier Coating

N. Yamazaki*[1]; S. Kanazawa[1]; K. Kubushiro[1]; T. Nakamura[1]

1. IHI Corporation, Japan

To apply CMC to aircraft engine, development of EBC (Environmental Barrier Coating) technology is indispensable because CMC shows significant water vapor thinning. As for coating material for EBC, mixture of Yb_2SiO_5/Mullite is promising due to its oxygen diffusion barrier properties and good volatility under high temperature steam. For deposition method of EBC, though APS (Air Plasma Spray) is gathering more and more attention, failures such as cracks and pores are unavoidable for coatings deposited by APS. In this study, in order to fill the failures, we deposited mixtures of Yb_2SiO_5/Mullite by APS, and conducted annealing on them. It was found out that phase transformation occurred during the annealing process. Before annealing, as deposited Yb_2SiO_5/Mullite mixtures were formed by Yb_2O_3 phase and amorphous Mullite phase while Garnet phase, $Yb_2Si_2O_7$ phase, and Yb_2SiO_5 phase were observed after the annealing. It was also found out that failures occurred during APS were filled by annealing above 1473 K.

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Progress in SOFC and SOEC Technology

Room: Crystal

Session Chair: Mihails Kusnezoff, Fraunhofer IKTS

1:30 PM

(ICACC-S3-001-2019) Overview of DOE Office of Fossil Energy's Solid Oxide Fuel Cell Program (Invited)

P. Burke*[1]; S. D. Vora[1]

1. National Energy Technology Laboratory, U.S. Department of Energy, USA

The mission of the U.S. Department of Energy is to ensure America's security and prosperity by addressing its energy, environmental and nuclear challenges through transformative science and technology solutions. Supporting this mission is the Office of Fossil Energy's Solid Oxide Fuel Cell (SOFC) Program. Administered by the National Energy Technology Laboratory, the SOFC Program is committed to developing efficient, low-cost electricity from natural gas or coal with intrinsic carbon capture capabilities for distributed generation (DG) and utility-scale applications, maintaining cell and core technology research to increase the reliability, robustness, and durability of cell, stack, and system technology, and providing the technology base to permit cost-competitive DG applications. The SOFC program has a two-pronged approach to complete the maturation of the SOFC technology from its present state to the point of commercial readiness: Core Technology Research & Development (CTR&D) and Systems Development (SD). The CTR&D element identifies technical and economic barriers and develops solutions to those barriers. The SD component validates those solutions through multi-cell stack tests, proof-of-concept and prototype system tests. The status of these research programs, the status of the program's integrated systems tests, and the roadmap to deploy a MWe-class natural gas fueled DG system, will be presented.

2:00 PM

(ICACC-S3-002-2019) Recent Achievements and Challenges of SOFC Power Generation Systems (Invited)

Y. Kawabata*[1]; Y. Matsuzaki[3]; K. Sasaki[2]

1. Tokyo Gas Co., Ltd., Application Technology Research Institute, Japan
2. Kyushu University, Faculty of Engineering, Japan
3. Tokyo Gas Co., Ltd., Fundamental Technology Department, Japan

Solid oxide fuel cells (SOFCs) have great potential of efficient and clean power generation in various applications from residential co-generation and commercial-use through industrial-use and power generation plants. In this paper, we will show our practical achievement and future challenges of SOFC power generation systems. For recent achievements of large-scale SOFC power generation systems, results of practical evaluation of SOFC-Micro Gas Turbine (MGT) hybrid power generation system are shown. Basic performance, long-term-durability and reliability in outside condition, installation and usability have been evaluated, which leads to market introduction of the SOFC-MGT hybrid power generation system. For challenges towards low-carbon society, a concept and feasibility study of efficient CO2-capture proton ceramic fuel cells (PCFCs) power generation system are also shown. The results indicate that PCFCs and SOFCs have great potential which enables extremely high efficient power generation and efficient CO2-capture with simple additional equipment. The technical issues for practical-use of proposed systems are also shown as our future challenges of development of PCFCs and SOFCs.

2:30 PM

(ICACC-S3-003-2019) Solid Oxide Cells Technology Development at Taiwan Institute of Nuclear Energy Research (Invited)

C. Liu*[1]; R. Lee[1]; Y. Cheng[1]; W. Hong[1]; S. Wu[1]; T. Lin[1]; C. Chang[2]; N. Hsu[3]

1. Institute of Nuclear Energy Research, Nuclear Fuels and Materials Division, Taiwan
2. Institute of Nuclear Energy Research, Physics Division, Taiwan
3. Institute of Nuclear Energy Research, Chemistry Division, Taiwan

Taiwan Institute of Nuclear Energy Research (INER) has committed to developing solid oxide fuel cell (SOFC) technologies and applications over the past decade. We have made remarkable progress in manufacturing of membrane electrode assembly (MEA), assembling of stack, and integrating of power system. For instance, to date, we have established the fabrication processes separately for making a full size (10×10 cm^2) of planar type of anode-supported cell (ASC) and metal-supported cell (MSC) to reach a power density over 500 mW/cm^2 and degradation rate less than 1%/kh. Moreover, INER's SOFC technologies, including MEA, stack, reforming catalysts, and power system have been technical transferred to the domestic industry companies. It is worth mentioning that the SOFC industry chain in Taiwan is budding and there are many state-run and private companies investing in SOFC technologies. Furthermore, solid oxide electrolysis cell (SOEC) is the reverse operation of SOFC and can produce hydrogen by feeding water and electricity. Therefore, a SOC combined SOFC and SOEC will potentially become one of the most promising new energy conversion and storage devices in the future. In this paper, we showed the state of the art of SOEC technology developments and accomplishments at INER such as high efficiency, stable configuration, and spalling-proof cathode of our home-made cells.

3:00 PM

(ICACC-S3-004-2019) Selection, Characterization, and Validation of Materials for Solid Oxide Electrolysis Operation (Invited)

S. Elangovan*[1]; J. Hartvigsen[1]; D. Larsen[1]; T. Hafen[1]; M. Adams[1]

1. OxEon Energy, LLC, USA

Solid oxide electrolysis devices operate at high efficiencies. Early work focused on steam electrolysis to produce H_2. Since then, co-electrolysis of CO_2 and steam is recognized as a practical method

to reuse carbon dioxide and store renewable energy using carbon as the backbone. Specialized application such as electrolyzing Mars atmosphere carbon dioxide to produce oxygen is also under development. High temperature operation puts high demand on physical and thermochemical properties of materials to accommodate temperature variations, thermal cycles, pressure differential, and long term performance stability. Desire to operate electrolysis stacks in fuel cell mode adds additional constraints on materials and stack design. Application specific operating conditions impose additional requirements on materials properties. Examples include thermal management in fuel cell operation, C deposition and oxidation of fuel electrode during CO_2 electrolysis and Ni coarsening during steam electrolysis. Delamination of air electrode during electrolysis is another well-known phenomenon. Seal integrity is critical in maintaining product purity and enabling high pressure operation. An overview of OxEon Energy's approach in the design, materials selection, and operation of electrolysis stacks will be presented. Support by the State of Utah through USTAR program and by NASA SBIR program is acknowledged.

SOC Stacks and their Integration in the Systems

Room: Crystal

Session Chair: Jeffry Stevenson, Pacific Northwest National Lab

3:50 PM

(ICACC-S3-005-2019) Industrial scale SOFC manufacturing challenges and achievements: The experience of SOLIDpower SpA (Invited)

D. Montinaro*[1]

1. SOLIDpower SpA, R&D Materials and Process, Italy

Solid Oxide Fuel Cells (SOFC) are one of the most effective technologies for energy conversion, recognised for high efficiency, low emissions and their ability to operate on all kinds of available fuels. Despite their technical advantages, SOFC require a significant reduction in manufacturing costs in order to achieve a significant market penetration. The cost of fuel cell systems is mainly related to the core component: the SOFC stack. SOLIDpower SpA is an Italy-based industry that has acquired HTceramix SA in Yverdon (Switzerland) in 2007 and the assets and team of Ceramic Fuel Cells Germany GmbH in Heinsberg in 2015, and operates also an office in Melbourne, Australia. During more than 18 years experience, SOLIDpower validated competitive manufacturing technologies by extensive lab testing and demonstration in a pilot line, assessing the main environmental and cost reduction benefits. This work presents the experience of SOLIDpower on the implementation of conventional ceramic manufacturing technologies on the large scale production of SOFC and stack components and gives an overview on the most innovative technologies considered as a potential step to the industrialization of next generation Solid Oxide Cells.

4:20 PM

(ICACC-S3-006-2019) Status of Stack and system development at Sunfire (Invited)

C. Walter*[1]; C. Geipel[1]; T. Strohbach[1]; F. Mittmann[1]; O. Poszdiech[1]

1. sunfire GmbH, Stacks, Germany

Sunfire develops and produces high-temperature fuel cell (SOFC) and electrolyzer (SOEC) applications. SOFCs convert fuels and gases into electricity and heat for residential, commercial and industrial applications. SOECs convert water and/or carbon dioxide with preferably renewable electricity into hydrogen and carbon monoxide. Both processes can also be combined in a single device: a reversible Solid Oxide Cell (rSOC) system. With these technologies, sunfire addresses a multitude of challenges in our energy systems. Sunfire started with the production of stacks and small systems mainly for residential CHP (Sunfire-Home) and offgrid power applications (Sunfire-Remote) with outputs of less than 5kW. By expanding the product portfolio to systems for commercial CHP (Sunfire-PowerPlus) and hydrogen production (Sunfire-Hylink), larger modules up to 25 kW SOFC power output and 150 kW SOEC power were developed. Within those larger modules up to 96 stacks are combined into one system requiring a sophisticated technical design. Sunfire's SOC technology is continuously being improved to achieve the optimal balance between high reliability, low manufacturing costs and high electrical efficiency. This contribution focusses on the industrialization of our stack design but also shows results on further optimization on degradation, power density and stack costs. Furthermore, results of systems running in the field will also be presented.

4:50 PM

(ICACC-S3-007-2019) Development and operation of Saint-Gobain's all-ceramic Solid Oxide Fuel Cell Stack

J. Pietras*[1]; Y. Takagi[1]; B. Feldman[1]; S. Megel[2]; J. Schnetter[2]; S. Hielscher[2]

1. Saint-Gobain, USA
2. Fraunhofer IKTS, Germany

Energy generation through solid oxide fuel cells (SOFCs) is a long-term strategic project for Saint-Gobain, a global leader in ceramic materials and components. Our unique all-ceramic SOFC stacks are designed to meet the reliability and cost targets for micro-combined heat and power (μCHP) systems and distributed energy commercial applications. Significant operational stability improvement and manufacturing cost reduction is achieved through extensive engineering of ultra-thin ceramic interconnects, simplified monolithic stack-supported design and a multi-cell co-firing process. Saint-Gobain's SOFC stacks have demonstrated an outstanding durability under long term operation, and has been shown to withstand a number of thermal cycles, power cycles and start-stop cycles designed for μCHPs and distributed power systems. In this presentation, the design and operational characteristics of Saint-Gobain's newest generation SOFC stack and hot box module will be reported. The hot box is newly developed in collaboration with Fraunhofer IKTS, in order to optimize the performance and reliability of the all-ceramic SOFC stack. It includes the electrical current collection mechanism, gas delivery manifolds and related compression mechanism, as well as other BOP functions. Operation characteristics under system simulated fuel compositions and fuel / air utilizations will be presented.

S4: Armor Ceramics - Challenges and New Developments

Terminal Ballistics / Quasi-Static and Dynamic Behavior I

Room: Coquina Salon F

Session Chair: Brady Aydelotte, US Army Research Laboratory

1:30 PM

(ICACC-S4-001-2019) Modeling ceramics using different failure mechanisms in compression and tension (Invited)

T. Öst*[1]; P. Lundberg[1]

1. FOI - Swedish Defence Research Agency, Sweden

We present simulations of projectile impact on ceramics using a model that incorporates failure mechanisms in compression and tension that are different using the finite element analysis software IMPETUS Afea. A pressure dependent shear resistance is used that gradually decreases with increased compressive, or crushing, damage. The crushing damage is evolved from the deviatoric inelastic shear strain and the model includes inelastic dilatation. In addition to the crushing damage there is a brittle tensile criterion combined with node splitting. A fracture initiates depending on the evolution of a tensile damage parameter that is a function

of the first principal stress, a spall stress parameter and the level of crushing damage that has occurred. An optional initial defect within the material may also be incorporated by scaling the spall stress using a random distribution function. Cracks propagate if the stress intensity factor is larger than the fracture toughness of the material (mode I). We present simulations of different impact conditions. These are edge-on impact experiments with a notched ceramic, sphere impact experiments on both bare ceramics as well as ceramics with composite backing and simulations of long-rod penetration of pre-stressed ceramics. Results such as crack pattern, crack velocity, cone formation and pressure dependency obtained in the simulations are presented.

2:00 PM

(ICACC-S4-002-2019) Steel Spheres Impact on Alumina Ceramic Tiles: Experiments and Finite Element Simulations

G. Toussaint*[1]; I. Polyzois[1]

1. Defence Research and Development Canada, Canada

Finite element (FE) simulations can be very useful for assessing and optimizing the design of advanced armor systems, but they require to capture the mechanisms of damage and failure that occur in composite-backed ceramic tiles when subjected to shock impact. The damage that occurs, namely the comminution and the formation of radial and conical cracks, is complex. Therefore, the first steps towards understanding these mechanisms are to simplify the problem. In this work, impact experiments using spherical projectiles were conducted on bare alumina ceramic tiles of two different thicknesses. Observations of the damage were then used to investigate the capability of numerical codes to capture the damage mechanisms occurring at various impact velocities. The smooth particle hydrodynamics (SPH) formulation in LS-DYNA FE code was used to model the projectile and target. Two constitutive models were analyzed for the alumina based ceramic, namely the Johnson-Holmquist model 2 and the pseudo-rheological Karagozian & Case Concrete model – Release III. The radial and conical cracking patterns as well as the cone dimensions and residual velocities obtained from simulations were compared with experimental measurements. The numerical results obtained using the SPH method demonstrated the potential of this approach to capture the damage produced by the impact of steel spheres on alumina ceramic tiles.

2:20 PM

(ICACC-S4-003-2019) Dynamic Bulking in Advanced Ceramics

B. Koch[1]; C. Lo[1]; T. Sano[2]; J. D. Hogan*[1]

1. University of Alberta, Edmonton, Mechanical Engineering, Canada
2. US Army Research Laboratory, USA

Microcrack models of failure form the foundation of understanding the fracture and fragmentation of brittle materials such as advanced armor ceramics. As these microcracks occupy volume, their growth or collapse requires that the volume of the material not be conserved, a phenomenon called bulking. Under uniaxial strain conditions, the simplest way of tracking the degree of volume conservation is the Poisson's ratio, which requires multidimensional strain measurement. Through use of digital-image-correlation (DIC), one can track 2D strain optically and thus make inferences on the internal evolution of microcracks. Furthermore, DIC coupled with high-speed video allows for the measurement of 2D strains under dynamic conditions. This presentation will discuss the evolution of bulking behavior in advanced ceramics across a range of strain rates, and how this phenomenon relates to ballistic impact situations.

2:40 PM

(ICACC-S4-004-2019) Dynamic Compression Strength of Ceramics: Preliminary Results from a Round Robin Exercise

J. Swab*[1]; G. D. Quinn[2]

1. Army Research Laboratory, USA
2. National Institute of Standards and Technology, USA

Knowing the compression strength of advanced ceramics at high strain rates is of interest for many applications. The most common method of obtaining a dynamic compression strength value is the split-Hopkinson pressure bar (SHPB) method. Unfortunately a standard test methodology with a standard specimen geometry does not exist for ceramic materials. This leads to questions about data consistency and validity. A three laboratory round robin exercise was conducted to assess the strength of a commercial alumina using the SHPB method and a dumbbell-shaped specimen. These results will highlight the various SHPB parameters used by each round robin participant, determine if the dumbbell-shaped specimen is the appropriate geometry for testing ceramics and show if a consensus strength value was achieved. It will also highlight any issues encountered and propose potential solutions.

Terminal Ballistics / Quasi-Static and Dynamic Behavior II

Room: Coquina Salon F
Session Chairs: Jerry LaSalvia, U.S. Army Research Laboratory; Jonathan Ligda, US Army Research Laboratory

3:20 PM

(ICACC-S4-005-2019) A Comparison of Long Rod Penetration Data with Continuum Scale Simulations (Invited)

B. Aydelotte*[1]; J. Niederhaus[2]

1. US Army Research Laboratory, USA
2. Sandia National Laboratories, USA

Numerical simulations of the dynamic behavior of brittle materials are important for a number of applications. In order to have confidence in such simulations, it is desirable to validate them by comparison against well-diagnosed experiments. Reverse ballistic impact experiments of a silicon carbide cylinder against a tungsten heavy alloy long rod were conducted using proton radiography to diagnose the experiments, yielding high-resolution images of the penetration process. These images reveal a complex penetration process and provide a rich data set for model validation. In this work, a detailed comparison is made between a reverse ballistic impact experiment and simulation predictions.

3:50 PM

(ICACC-S4-006-2019) Compression Strength Anisotropy of Hot-Pressed Boron Carbide

J. J. Pittari*[1]; J. Swab[2]

1. U.S. Army Research Laboratory, Material Response and Design Branch, USA
2. U.S. Army Research Laboratory, Ceramic and Transparent Materials Branch, USA

An accurate measure of the compressive strength of hot-pressed ceramics is vital to modeling and experimental efforts to understand the complexity of ballistic impact events. It is well understood that uniaxial hot-pressing induces anisotropy in the finished plate due to the lack of confinement pressure perpendicular to the pressing direction. Hence, testing of specimens cut parallel to the plate surface may not result in an accurate depiction of the compressive strength of a material. Prior research has shown that the compressive strength of hot-pressed boron carbide decreases by 15-25% for specimens produced with the long-axis parallel to the pressing direction compared with specimens from the perpendicular alignment. It can be difficult to machine an appropriate test specimen geometry

through the thickness of hot-pressed boron carbide plates, but the use of miniature dumbbell-shaped specimens facilitates the production and testing of through-thickness specimens (i.e., perpendicular to impact surface). Specimens were produced with the major axis aligned at 0°, 45°, and 90° to the surface of the plate to investigate the intrinsic anisotropy of the hot-pressed part. Specimens were tested at quasi-static, intermediate, and high strain rates to discern the presence of rate effects on compressive strength and the fracture behavior and mechanisms.

4:10 PM

(ICACC-S4-007-2019) Influence of stress states during amorphization of single crystal boron carbide

J. Ligda*[1]; J. LaSalvia[1]; B. Schuster[1]

1. US Army Research Laboratory, USA

Spherical nanoindentation was performed on single crystal boron carbide to delay the on-set of in-elastic deformation. A spherical tip geometry creates a well-defined transition from elastic to in-elastic deformation in the ceramic, and by performing tests to different maximum loads the initiation of in-elastic deformation is controlled. Identifying the in-elastic damage as a result of cracking or amorphization is done using Raman spectroscopy and scanning electron microscopy. The degree and location of any amorphous bands under the indents are characterized by Raman spectroscopy and transmission electron microscopy. The stress states underneath the indent are modeled to identify if the orientation of the damage bands follows a crystallographic direction or stress trajectories.

4:30 PM

(ICACC-S4-008-2019) Onset Conditions to Induce Amorphization in Doped Boron Carbides in a Diamond Anvil Cell

M. C. Schaefer*[1]; R. A. Haber[1]; V. Domnich[1]

1. Rutgers University, USA

Boron carbide is a great armor material owing to its extreme hardness and low density. However, the material fails unexpectedly in ballistic testing due a lack of ductility and a drop in shear strength. The reduction in shear strength has been linked to the formation of amorphous bands in boron carbide, which are observed in the samples impacted beyond certain critical velocities. It is theorized that doping boron carbide with excess boron, or silicon, could show a reduction in such amorphization. In this study, we aim to observe the onset conditions of amorphization of boron-rich and silicon-doped boron carbides in a Diamond Anvil Cell (DAC). High pressure measurements will be made using a DAC and in situ Raman spectroscopy. Stoichiometric boron carbide (B4C) has already been investigated in this manner, but doped boron carbides have yet to be investigated. To investigate the effect of deviatoric stresses on the onset of amorphization, measurements will be recorded using a DAC, both with and without a pressure transmitting medium.

4:50 PM

(ICACC-S4-009-2019) Static and Dynamic Properties of B_4C-BAM Composites

R. A. Riera*[1]; M. DeVries[1]; G. Subhash[1]

1. University of Florida, Mechanical and Aerospace Engineering, USA

Due to their exceptional properties, including high hardness and low density, Aluminum Magnesium Boride (BAM) ceramics show great promise in wear resistance, low friction, and armor applications. However, the inability to produce large quantities of BAM, due to complex processing, limits the experimental study on its bulk mechanical properties. In the current investigation, quasi-static and dynamic tests are conducted on four compositions of BAM to ascertain their material and mechanical properties: $AlMgB_{14}$ with 0% B_4C, 10% B_4C, 20% B_4C, and 50% B_4C. These materials were produced by spark plasma sintering (SPS). The quasi-static and dynamic compressive strength, hardness, and fracture toughness are determined experimentally and compared to values found in literature for BAM and commercial boron carbide, silicon carbide and boron suboxide. Microstructure and composition are investigated using scanning electron microscopy and energy dispersive spectroscopy. Raman spectroscopy is performed on BAM before and after deformation to study amorphization behavior and determine its feasibility as an effective armor ceramic.

5:10 PM

(ICACC-S4-010-2019) Extreme Fast Granular Flow of Boron Carbide by Pressure Shear Plate Impact

X. Sun*[1]; A. Tonge[2]; J. LaSalvia[2]; K. Ramesh[1]

1. The Johns Hopkins University, Mechanical Engineering, USA
2. US Army Research Laboratory, USA

As an advanced structural ceramic, boron carbide is drawing more attention as a promising candidate material for amour protection with its low density and excellent mechanical strength. Extreme fast granular flow is triggered by brittleness of boron carbide during high strain rate (10^5 - $10^6 s^{-1}$) and high pressure (several GPa) impact and has critical effects on ceramic ballistic performance. However, granular flow at such high strain rate has not been well characterized due to the experimental complexity. To understand extreme fast granular flow under different levels of pressure and strain rate, we designed and performed multi-axial loading experiments of pressure shear plate impact on a commercially available boron carbide powder with an average grain size of 0.7 micron. The granular boron carbide powder is deformed at a shearing rate as high as 4×10^4 s^{-1} with a superimposed hydrostatic pressure up to 2.6GPa. The granular flow shear stress is ~430MPa under such pressure and shear strain rate. From all plate impact data, shear stress of granular material increases with increasing pressure, showing a strong pressure effect, which has been confirmed by other's experiments and simulations. Post-mortem TEM characterization provides useful insights of mechanisms such as grain fracture or amorphization during the deformation.

5:30 PM

(ICACC-S4-011-2019) Aluminum-dodecaboride-, boroncarbide-based and silicon carbide lightweight ceramics

T. Prikhna*[2]; P. Barvitskyi[2]; V. Moshchil[2]; R. A. Haber[1]; V. Domnich[1]; S. Dub[2]; M. Karpets[2]; V. Muratov[3]

1. The State University of New Jersey, USA
2. Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
3. Institute for Problems in Material Science, NAS Ukraine, Ukraine

The correlations between structures and mechanical characteristics of a-AlB_{12}-, $AlB_{12}C_2$-, B_4C-based lightweight ceramics and composites synthesized or sintered by hot pressing (at 30 MPa) and SiC-based ceramics obtained by reactive sintering are compared. The effect of C, TiC and SiC additions on the properties of the resultant composites and the particularities of the ceramics destruction under shock loading will be discussed. The performed ballistic tests of 10 mm thick plates from the developed ceramic with 2.63 g/cm^3 density having composition according to X-ray diffraction analysis 78 wt.% of B_4C and 22 wt.% of SiC and which stoichiometries according to SEM microprobe X-ray analysis $B_{3.64}CSi_{0.01}$ and $SiC_{1.07}$, respectively, showed that it can withstand the shot from 10 m distance of B32 bullet with kinetic energy of 3.7 kJ.
Acknowledgements: The work was performed in the framework of the NATO Science for Peace G7050 project.

5:50 PM

(ICACC-S4-012-2019) Failure and Fragmentation Process of Al_2O_3 and SiC under Quasistatic and Impact Loadings

Q. Zhang[1]; Y. Zheng[1]; F. Zhou*[1]

1. Ningbo University, Engineering Mechanics, China

The compressive failure tests for the alumina (Al_2O_3) and the silicon carbide (SiC) cylindrical specimens were conducted using a Universal test machine and a Split Hopkinson Pressure Bar (SHPB) apparatus. In the strainrate range from 10^{-3} 1/s to 10^{3} 1/s, the measured failure strengths of both specimen exhibit rate-dependency, which is also associated with the material's porosity. The alumina material having more intrinsic defects exhibits a larger dynamic/static strength ratio. All specimen experienced explosive fragmentation after failure. Most of the fragments were collected after testing, the size of which were statistically analyzed. The average fragment size decreases with the increase of the failure strength. A theoretical model was proposed to estimate the average fragment size using the failure strength, the material parameters, and the loading rate. This theoretical model gives reasonable well predictions of the experimental data. It is shown that the static compressive strain energy stored within the specimen prior to failure plays an important role controlling the fragment sizes. The effect of the kinetic energy in the dynamic compression process is minor, compared with the strain energy effect.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li Batteries I

Room: Tomoka A

Session Chairs: Palani Balaya, National University of Singapore; Olivier Guillon, Forschungszentrum Juelich

1:30 PM

(ICACC-S6-001-2019) Lithium metal/lithium ion conducting ceramics composite electrode for high energy density batteries (Invited)

N. Imanishi*[1]; S. Watanabe[1]; S. Taminato[1]; D. Mori[1]

1. Mie University, Chemistry, Japan

High energy density storage batteries are strongly demanded to meet requirements for EV and grid applications, in order to solve the energy problems. Lithium metal anode is a key to develop such a high energy density battery, because it shows the lowest electrode potential and quite high specific capacities. However, lithium metal is a quite reactive material due to the strong reducibility. In a battery, a reaction readily takes place by contact with an electrolytic solution, which causes various problems such as low coulombic efficiency. To avoid the unwanted reactions, so-called protected lithium electrode "PLE" was studied. It is a composite electrode of lithium metal covered with a ceramic sheet which conducts only lithium ions. In this configuration, lithium metal can be coupled with any other electrode systems. In this presentation, oxide materials for the ceramics sheet were studied to improve the ionic conductivity. We also investigated plating/stripping mechanism of the lithium metal anode under the presence of the ceramic protective layer. Lithium-oxygen/water batteries are examined as application examples of the PLE. They have potential to become a low-cost storage battery. A pouch-type test cells produced higher energy densities than conventional lithium ion batteries.

2:00 PM

(ICACC-S6-002-2019) Microscopic Insights into Solid Electrolytes-Electrode Interfaces (Invited)

M. Chi*[1]

1. Oak Ridge National Lab, USA

Solid-state electrolytes are considered as a critical component in future-generation lithium battery systems, which includes their use as the primary electrolytes in all-solid-state batteries, and the interfacial separation layer for Li-air or aqueous batteries. An ideal solid electrolyte material must be highly ionically conductive and exhibit desirable stability with metallic lithium. However, unexpected high interfacial resistivity is often observed and is the major limitation in realizing the practical application of these materials. Elucidating the fundamental origin of high interfacial impedance is crucial but challenging to both experiment and theory, due to spatial confinement and structural and chemical complications. In this presentation, I will talk about our recent efforts in probing interfacial phenomena in solid electrolytes, by using in situ and atomic-resolution scanning transmission electron microscopy and electron energy loss spectroscopy. Oxide solid electrolytes, including $Li_{0.33}La_{0.55}TiO_3$ and Al-$Li_7La_3Zr_2O_{12}$, and LIPON, are used as prototype materials. Several effective strategies to form a conductive and stable interface between a solid electrolyte and lithium metal, will be demonstrated and discussed, including the formation of a passivation layer though chemical reactions or through instinctive phase transformation, and the exploitation of oxide coating.

2:30 PM

(ICACC-S6-003-2019) Improved Li- and Na-ion Storage Capacity of Organic Cathodes Based on Surface-Controlled Charge Storage Mechanism (Invited)

B. Lee[1]; T. Liu[1]; M. J. Lee[1]; S. Lee*[1]

1. Georgia Institute of Technology, Mechanical Engineering, USA

Organic electrode materials have been attracting considerable attention for energy storage devices due to their sustainability, environmental benignity, and high theoretical capacity. Despite these advantages, organic electrode materials suffer from poor cycling stability due to the dissolution of active molecules into the electrolyte. A promising strategy to overcome the stability issue is to polymerize redox-active molecules onto conductive carbon matrix. Recently, we have demonstrated that polydopamine on the CNT or graphene substrates can exhibit the stable and fast redox reactions between the carbonyl groups in polydopamine and Li/Na-ions. We also introduce the shape-controlled 2D carbon materials with the high capacities for Li/Na-ion storage. Based on these high-capacity carbon cathodes, we demonstrate hybrid supercapacitors with significantly enhanced energy density.

Thermoelectrics I

Room: Tomoka A

Session Chairs: Emmanuel Guilmeau, CNRS CRISMAT; Jon Goldsby, NASA Glenn Research Center

3:20 PM

(ICACC-S6-004-2019) Thermoelectric oxides: An environmentally friendly solution (Invited)

F. Delorme*[1]; C. Chen[2]; F. Giovannelli[3]

1. University of Sheffield, Department of Materials Science and Engineering, United Kingdom
2. BAM Federal Institute for Materials Research and Testing, Germany
3. University of Tours, France

The ideal thermoelectric material should be stable in an oxidizing atmosphere in the targeted temperature range, easy to produce in large quantities, cheap and readily available, not toxic for environment and human health and of course presenting high efficiency.

This material does not exist. Most of the efficient thermoelectric materials are only stable at low temperature (tellurides), composed by rare or expensive elements (Te, Ge, …) or even toxic elements (Pb, Te …). Oxides are considered as potential thermoelectric materials since the discovery in 1997 of a large thermopower and power factor in the metallic oxide Na_xCoO_2. However, their efficiency as ceramics needs to be improved, mostly due to high thermal conductivity values. The potential influence of doping or nanostructuring will be reported. But the focus will be given to new oxide compositions that present promising thermoelectric properties especially a new family of cobalt oxide compounds that presents the CdI_2 structure of well-known Na_xCoO_2 or $Ca_3Co_4O_9$ but with Co(II) and Co(III) rather than Co(III) and Co(IV) and also cobalt in a tetrahedral environment. Synthesis, processing, shaping, as well as structural and microstructural features will be reported, together with the electrical and thermal properties.

3:50 PM

(ICACC-S6-005-2019) Tailoring electronic and thermal properties of bulk $Cu_{26}M_2(Ge,Sn)_6S_{32}$ colusite through defects engineering and functionnalization of the conductive network (Invited)

E. Guilmeau*[1]

1. CNRS CRISMAT, France

Colusite, $Cu_{26}M_2(Ge,Sn)_6S_{32}$, represents a prototypical complex sulfide (i.e.large unit cell with 66 atoms and light mass elements) with low lattice thermal conductivity. It has been recently studied but the origin of the low thermal conductivity is not understood and the full potential of $Cu_{26}M_2(Ge,Sn)_6S_{32}$ as an advanced thermoelectric material has not been fully explored. We present here a complete study of the bulk properties of colusite including the characterization of the band structure and the vibrational dispersions from first principles calculations. We pinpoint the special role played by Cu in low frequency optic modes and linked such an effect with electronic properties. Our results also address the spectacular role of ion substitution on the vanadium site on the electronic properties, leading to outstanding power factors. More importantly, we prove that the TE transport properties of colusite are also dramatically influenced by the densification temperature and method, and suggest strategies to control the formation of specific defects. Transport properties and TE efficiency are rationalized within these novel findings in order to provide guidance for the design of TE materials based on tailoring the role of defects and chemical bonding.

4:20 PM

(ICACC-S6-006-2019) Nanostructuring and defect engineering for enhanced thermoelectric properties in ZnO-based ceramics (Invited)

S. Bernik*[1]; A. Rečnik[1]; T. Tian[2]; G. Li[2]; E. Guilmeau[3]

1. Jozef Stefan Institute, Department for Nanostructured Materials, Slovenia
2. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China
3. Laboratoire CRISMAT, France

ZnO is a promising oxide thermoelectric material, having a high S of about -400mV/K and excellent charge-carrier transport properties that are easily tunable via doping, resulting in a reported zT value of 0.45–0.65 at 1000°C. Being inexpensive, nontoxic and stable in air to high temperatures are also advantages for applications of ZnO. Doping with In_2O_3 and Ga_2O_3 causes nanostructuring in the ZnO wurtzite structure with the formation of multiple planar defects. Our results showed that these defects are formed in some ZnO grains already for additions of In and Ga much below 1 at%, causing a strong increase of σ to several 100S/cm and a decrease of κ to about 7.5W/mK, and the effects of the percolation mechanism on S, σ and κ. Electrostatic Schottky barriers at the grain boundaries are responsible for the strongly decreased σ of the ZnO sintered in air. Our results showed that the sintering of doped ZnO in a reducing atmosphere or under vacuum in an SPS eliminates the acceptor states at the grain boundaries and increases the solubility of the dopants (Al, Mg, Ti) in ZnO, resulting in a σ of $1.9x10^3$S/cm, a maximum power factor of $8.2x10^{-4}$W/mK and due to the large concentration of point defects, a similar κ. Obtaining much higher zT values requires the simultaneous optimization of the composition, structure, microstructure and point defects, which represents great challenge.

4:50 PM

(ICACC-S6-007-2019) High Temperature Thermoelectric Power Studies of Cadmium Substituted Cobalt Ferrite Nanoparticles (Invited)

D. Ravinder*[1]

1. Osmania University, Department of Physics, India

Thermoelectric power studies of Cadmium substituted cobalt ferrite nanoparticles with a chemical formula of $Cd_xCo_{1-x}Fe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 & 0.6) were investigated from room temperature to well beyond the Curie temperature by the differential method. It is observed that all the samples show similar thermal variation with Seebeck coefficient. The value of Seebeck coefficient increases with increase temperature up to a particular temperature called transition temperature. But, beyond the transition temperature the Seebeck coefficient decreases. At low temperature, positive value of Seebeck coefficient shows p-type semiconducting nature of the prepared ferrite samples. Initially, Co-ferrite behaves like p-type semiconductor at low temperature (300 K). With increasing the temperature and Cd-content, the Seebeck coefficient also increases. Beyond the transition temperature, the Seebeck coefficient start decreasing with increase in temperature. Then sample behavior is changed to n-type semiconductor behavior. The probable conduction mechanisms in the spinel nanoferrites system under investigation are $Fe^{2+} \leftrightarrow Fe^{3+}+e^-$ (n-type or electron exchange mechanism). If hole exchange mechanism dominates over the electron exchange mechanism, the ferrite composition might conduct as p-type semiconductor and vice versa.

5:20 PM

(ICACC-S6-008-2019) Thermal stability of thermoelectric mechanically alloyed ZnSb

C. M. James*[1]; M. S. Wickleder[1]; W. E. Mueller[2]

1. University of Cologne, Inorganic Chemistry, Germany
2. DLR - German Aerospace Center, Institute for Material Research, Germany

Due to its promising thermoelectric (TE) properties, ZnSb is subject of current research. Arising from the abundance and low toxicity of zinc and feasible synthetic routes, this semiconductor is a desirable p-type TE material for mass production. ZnSb has its main application at intermediate temperatures of 420 - 650 K. Even though the thermal conductivity of bulk-ZnSb is larger compared to state-of-the-art TE compounds, e.g. Bi_2Te_3 or PbTe, it can be lowered significantly through micro structuring (e.g. ball-milling). Yet, it has been shown, that binary compounds in the system of zinc and antimony inherently exhibit a defect structure, dominated by zinc deficiency sites. Investigation of bulk-ZnSb with XRD showed decomposition at 573 K, attributed to Zn evaporation. In this work, we investigated ZnSb from a mechanical alloying (MA) synthesis using element powders of Zn and Sb. On executing thermoelectric characterisation of consolidated pellets of the as-milled microscopic MA-ZnSb powder in a temperature cycle (300 - 600 K), we found hysteresis behaviour in the values of Seebeck coefficient and electrical conductivity. We thus investigated the MA powder in an in situ temperature resolved XRD studies, demonstrating decomposition of the material already at 423 K. We conclude, that in micro-particulate ZnSb the transport of Zn is facilitated, due to the high concentration of grain boundaries compared to bulk-ZnSb.

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Sintering Technologies I

Room: Coquina Salon A

Session Chairs: Alexander Mukasyan, University of Notre Dame; Thanh Son Nguyen, Kushiro National College of Technology

1:30 PM

(ICACC-S8-001-2019) Attainment of Low Temperature and High Strain Rate Superplastic Flow in Structural Ceramics by Application of Strong Electric-field (Invited)

H. Yoshida*[1]; Y. Sasaki[2]

1. National Institute for Materials Science (NIMS), Japan
2. Tokyo University of Science, Dept. Materials Science and Technology, Japan

High-strength structural ceramics are known to be brittle, with limited plastic deformability, even at high temperatures above 1000°C. However, some ceramics with grain sizes of 1 μm or less exhibit superplasticity, i.e., tensile elongation exceeding 100% via grain boundary sliding (GBS). Superplasticity has been expected to be new forming and manufacturing technology for ceramics, but in typical superplastic ceramics such as Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (TZP), superplastic deformation only occurs at high temperatures (>1400°C) and low strain rates ($<10^{-4}$ s^{-1}). Such high temperatures and low strain rates hinder industrial application of superplasticity in structural ceramics. We demonstrate that low temperature and high speed superplastic flow in structural ceramics was achieved by applying a strong electric field during deformation. The application of a direct-current field of 190 Vcm^{-1} led to superplastic deformation in Y_2O_3-stabilised tetragonal ZrO_2 polycrystal with a total tensile elongation of >150% at 800°C and an initial strain rate of 2×10^{-3} s^{-1}. The field-activated plasticity was attributed to highly-accelerated self-diffusion induced not only by temperature rise but also by a field effect.

2:00 PM

(ICACC-S8-002-2019) Transparent Er:YAG ceramics with doping gradient processed by SPS (Invited)

M. Lagny[1]; A. Katz[1]; J. Boehmler[1]; Y. Lorgouilloux[2]; S. Lemonnier[1]; S. Bigotta[1]; A. L. Leriche*[2]

1. ISL, France
2. University de Valenciennes, France

In recent years, transparent polycrystalline ceramics have been used in various domains, such as medicine, industry, defense and security. The current subject is to develop a Er^{3+}:YAG Solid State Heat Capacity Laser (SSHCL), which exhibits an emission at 1.6 μm ("eye-safe" emission). One of the current limitations of single crystals as laser gain medium is the thermal lens effect, which affects the laser beam, output performances and moreover might lead to cracks. One solution is to replace the single crystal, by a polycrystalline ceramic, which induces better thermo-mechanical performances. The powder metallurgy approach reduces the production time and consequently the cost of development of gain medium and opens the possibility of doping gradients. In a first study, Er^{3+}:YAG SPS sintered ceramics have been tested in a laser cavity (slope efficiency of ≈31%). In order to improve the laser performances, the present work focuses on realization of doping gradients. Different approaches have been tested to make ceramics with doping gradient starting either from powders, pre-sintered samples or fully dense ceramics, by assembling within a SPS apparatus. All these approaches will be compared to select the most efficient technique to obtain highly transparent ceramics with the desired doping profile.

2:30 PM

(ICACC-S8-003-2019) Fabrication and Microstructure of B_4C-TiB_2-SiC composites with improved mechanical properties (Invited)

W. Wang*[1]; Q. He[1]; A. Wang[1]; W. Ji[1]; Z. Fu[1]; H. Wang[1]

1. Wuhan University of Technology, China

B_4C-TiB_2-SiC composites were fabricated via hot pressing using ball milled B_4C, TiB_2, and SiC powder mixtures as the starting materials. The impact of ball milling on the densification behaviors, mechanical properties, and microstructures of the powder mixtures were investigated. The results showed that the ball milling processing could promote the sinterability of the B_4C-TiB_2-SiC powder mixtures, resulting in the improvement of the mechanical properties and microstructures. Moreover, the formation of a liquid phase during the sintering process was considered to be an important contribution to the sintering of the composites. The typical values of relative density, hardness, bending strength, and fracture toughness of the composites reached 99.20%, 32.84 GPa, 858 MPa and 8.21 MPa $m^{1/2}$, respectively. Crack deflection, crack bridging, and crack branching are considered to be the potential toughening mechanisms in the composites. Furthermore, numerous nano-sized intergranular/intragranular phases and twin structures were observed in the B_4C-TiB_2-SiC composite.

3:20 PM

(ICACC-S8-004-2019) Highly Porous Hardystonite Glass-Ceramics by Direct Foaming or Digital Light Processing and Sinter-Crystallization

H. Elsayed[1]; M. Picicco[2]; J. Kraxner[3]; D. Galusek[3]; E. Bernardo*[1]

1. University of Padova, Department of Industrial Engineering, Italy
2. CETMIC, Argentina
3. FunGlass – Centre for Functional and Surface Functionalized Glass Alexander Dubček University of Trenčín, Slovakia

Hardystonite (Ca2ZnSi2O7) ceramics represent one of the most promising class of biomaterials. The shaping into highly porous bodies, however, generally depends just on the sintering of pre-processed ceramic powders. In the present investigation we propose a glass-based route to hardystonite ceramics, previously unexplored. Glasses corresponding to the stoichiometry of hardystonite solid solutions (Ca2Zn0.85Mg0.15Si2O7 and Ca1.4Sr0.6Zn0.85Mg0.15Si2O7) were first sythesized and reduced in the form of fine powders (<50 μm). Highly crystallized samples were achieved by sinter-crystallization, in air, at 1000 °C, starting from highly porous bodies (porosity >70%) obtained by direct foaming or stereolithography. More precisely, homogeneous foams were obtained by gelation of alkali activated suspension of glass powders, owing to the formation of calcium silicate hydrated compounds, followed by intensive mechanical stirring, with the help of a surfactant. Stereolithography, on the other side, was used to form highly regular scaffolds, with the help of an UV-curable sacrifiical binder. The intensive crystallization caused an excellent retention of the shape assigned at room temperature. The uniform microstructures, all comprising quite dense struts, favoured the mechanical properties (with crushing strength well exceeding 2 MPa).

3:40 PM

(ICACC-S8-005-2019) Processing of Multi-Layered Composite Coatings for Corrosion and Wear Applications

E. Medvedovski*[1]

1. Endurance Technologies Inc., Canada

The multi-layered composite coatings on steels and ferrous alloys have been produced and analyzed. They consist of 2-3 coating layers based on borides, aluminides, chromides obtained through thermal diffusion technology, and new coating options may have an additional top layer based on selected oxides or non-oxides. The coating

architectures and total thickness varied from ~25 to 250 μm or greater depend on the metallic substrate, type of thermal diffusion coating, process parameters, as well as the application requirements. Diffusion-related bonding between the layers promotes the integrity of the coatings. Nano-size starting materials provide a high level of consolidation of the top coating layer with a nano-crystalline structure. The proposed composite coatings are successfully employed for corrosion and/or wear high-temperature applications.

4:00 PM

(ICACC-S8-006-2019) Reaction products of late-stage oxidation of Zircaloy-4 in nitrogen-rich atmosphere

T. Do*[1]; V. Do[3]; Y. Matsumoto[1]; T. Ogawa[2]; T. Nakayama[4]; H. Suematsu[1]

1. Nagaoka University of Technology, Nuclear System Safety Engineering, Japan
2. Japan Atomic Energy Agency, Japan
3. Hitachi-GE Nuclear Energy, Japan
4. Nagaoka University of Technology, Japan

The products of extensive oxidation of Zircaloy-4 in nitrogen-rich atmosphere at temperatures 800 - 1100°C were studied in order to supply database for the management of air-ingress accident debris of the light water reactor fuels. The composition of products consisting of monoclinic ZrO_2, tetragonal ZrO_2 and ZrN were studied as a function of the oxidation progression. Tetragonal ZrO_2 and ZrN persisted even to high degree of oxidation. The characteristic features of the late-stage oxidation in nitrogen-rich atmosphere were discussed in view of the Zr-O-N ternary diagram. Zircaloy-4 plates (10 x 20 x 0.5 mm) were placed in a quartz boat. Oxidation was done in an electric furnace in the ambient air, (N_2+10%O_2) or (Ar+H_2O) mixed gas at temperatures ranging from 800 to 1100°C for 1 to 12 hours. Another oxidation test was at 1100°C for 8 hours in Mo/MoO_2-buffered nitrogen, so the reaction will be take placed in 10^{-14} atm of oxygen partial pressure. The analysis of quantitative phase composition was made by using Rietveld refinement. The quantitative compositional point analysis was made by electron probe microanalysis. The phase had higher values of (1.5N+O) might be the valence of nitride in t-ZrO_2 as produced in the reactions. Besides, the area that ZrN is in equilibrium with m-ZrO_2 and t-ZrO_2 was found.

4:20 PM

(ICACC-S8-007-2019) Adaptive Ceramic Processing Via Real-Time Monitoring and Intelligent System Control

J. Hollenbach*[1]; M. C. Golt[2]

1. Drexel University, USA
2. US Army Research Laboratory, USA

The microstructures of ceramic armor materials determine their properties and performance. During manufacturing, slight variations in the input, such as the powder lot, ball milling, and green body formation can cause significant changes in the final microstructure. This unwanted variability can be minimized through the application of costly quality control measures on the inputs and output of the manufacturing process. However, if the densification progress was monitored and the processing of these materials was adaptive to changes in the input, ideal output microstructures could be consistently found. For example, the work applied during heat treatment can be calculated and considered with the observed densification rate to determine the effective activation energy of the part. From this information, a process control algorithm can form a prediction of the future densification path and determine an optimal processing route to obtain a consistent output. This study attempts to manufacture consistent grain size, densification, and microstructure via in situ characterization and adaptive processing techniques. We show that utilizing displacement during hot uniaxial pressing, it is possible to estimate density and use this as real-time feedback for dynamic control over furnace temperature and hold time, giving the ability for automated processing for desired microstructures.

4:40 PM

(ICACC-S8-008-2019) Vacuum furnaces for advanced ceramics - Case history

A. Fiorese*[1]

1. TAV VACUUM FURNACES SPA, R&D, Italy

In the last decades, with the progress of knowledge on the links between properties and structure of traditional ceramic materials, a new generation of ceramic materials, called “advanced” ones, has been born. For advanced ceramics we mean those inorganic, non-metallic and polycrystalline products equipped with relevant structural and / or functional performances. Injection moulding is the often used technology to produce small size products and complex shapes. The ceramic powder is added with a polymeric binder to obtain a high fluidity of the mass during the mould filling. Hence, the consequent need to obtain the final component is to carry out a heat treatment for debinding and sintering. Among many applications, the most common one for the process described above concerns brackets made of translucent alumina for the construction of orthodontic appliances. For aesthetic reasons and final properties of the material, debinding and subsequent sintering of the alumina brackets necessarily require the use of a furnace capable of operating in vacuum at high temperatures. The development of this type of vacuum furnace, accompanied by a careful optimization of the sintering parameters by the end users, has led to the achievement of completely translucent brackets with high mechanical characteristics.

5:00 PM

(ICACC-S8-009-2019) Effect of External Electric Field/Current on Grain Growth: A Case Study of Bi_2O_3-doped ZnO

J. Nie*[1]; J. Luo[1]

1. University of California, San Diego, USA

This presentation will discuss about our recent study on the grain growth behavior of Bi_2O_3-doped ZnO at liquid-phase sintering temperature under external electric field/current. Specifically, enhanced grain growth was observed along -E direction in polycrystal-(11-20) single crystal-polycrystal sandwich specimens. In contrast, specimens without external electric field/current showed similar grain growth on both sides of the single crystal. Aberration-corrected STEM images reveal that the fast-moving grain boundaries (along -E) are highly ordered, and the slow-moving grain boundaries (along E) are more disordered. Grain boundaries of reference specimen (without electric field/current) are also disordered. Additionally, abnormal grain growth was observed at locations near the negative electrode. EBSD micrographs clearly show the preferred orientations of these abnormal grains. External electric field/current are expected to affect the space charge layers near grain boundaries and further affect the grain boundary disordering and the grain growth behavior.

S11: Advanced Materials and Innovative Processing Ideas for Production Root Technologies

Sustainable Energy Concepts and Applications

Room: Ponce de Leon
Session Chairs: Sungwook Mhin, Korea Institute of Industrial Technology; Hyuksu Han, Korea Institute of Industrial Technology

1:30 PM

(ICACC-S11-001-2019) Amorphous-crystal semiconductor junction: A new class of charge-separating semiconductor system

H. Han*[1]; S. Mhin[1]; H. Choi[2]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Universität zu Köln, Germany

Amorphous phases of semiconductors are in most applications, expected to degrade the charge transport and catalytic reactivity, due to low carrier mobility. However, being in small portion, amorphous semiconductors have high potentials to effectively improve charge separations and electrochemical reactivity because of band offsets induced by phase transitions in junction with crystalline phase. In this study, we demonstrated that crystal-amorphous (c-a) semiconductor junction can be well utilized in charge separation, similarly to conventional p-n or heterojunctions of semiconductors. Compared to p-n or heterojunctions, c-a junctions can be fabricated by much more facile and simple processes thanks to homogeneous chemical compositions in crystalline and amorphous phases. We expect that a newly developed c-a junction in this work has high potentials to replace conventional p-n or heterojunctions and thus can pave a way for the next generation of materials in the fields of (photo)electrochemistry.

1:50 PM

(ICACC-S11-002-2019) Oxygen evolution reaction of Co-Mn-O electrocatalyst

S. Mhin*[1]

1. Korea Institute of Industrial Technology, Heat Treatment R&D Group, Republic of Korea

Oxygen evolution/reduction reactions (OER/ORR) play an important role in metal-air battery, fuel cells and etc. Commonly, noble metals are used for improving the OER/ORR, which is scarce and expensive. Therefore, exploiting highly efficient non-precious metal catalysts for oxygen evolution reaction (OER) is desirable. In this study, OER electrocatalytic properties of Co-Mn-O (CMO) catalysts are investigated. CMO nanopowders were prepared via different processing routes; gel coumbustion method and coprecipitation method. Different synthetic routes result in different composition and morphology, which provides different electrochemical properties of the CMOs. Mechanism of the OER depending on the processing routes is discussed.

2:10 PM

(ICACC-S11-003-2019) Synthesis of porous geopolymer for hydrogen recombination catalyst supports in wet radioactive waste containers (Invited)

H. Suematsu*[1]; T. Utsumi[1]; T. Do[1]; I. Kudo[2]; K. Takase[3]; T. Nakayama[1]; T. Ogawa[4]

1. Nagaoka University of Technology, Extreme Energy-Density Research Institute, Japan
2. Nagaoka University of Technology, Technical Development Center, Japan
3. Nagaoka University of Technology, Department of Nuclear System Safety Engineering, Japan
4. Japan Atomic Energy Agency, Collaborative Laboratories for Advanced Decommissioning Science, Japan

After the Fukushima Daiichi Nuclear Power Station accident, it is required to develop containers for radioactive slurry with water. In the containers, radiolysis of water forms hydrogen gas, which should be recombined with oxygen to prevent explosion. Some hydrogen recombining catalysts are developed and are including utilization of those for nuclear power plants and automobiles. For cost reduction and waste soil utilization, geopolymer is a candidate material for the catalyst support. In this study, synthesis of porous geopolymer and the pore size/density control were carried out. Raw materials of microsilica and metakaoline powders were mixed with potassium silicate and potassium hydroxide solution to form slurry. The slurry was stirred at 70 °C for 0-20 min and then poured and cured in a mold. In some experiments, the mold was capped with a breathable filter. After the curing at 70 °C for 48 hours, the sample was removed from the mold. The sample was dipped in tetranitric acid platinum solution and heated at 500 °C in air for 3 hours. The heat treated sample was observed by transmission electron microscopy. In the lattice image, many Pt particles with diameters of 2-3 nm were seen. From these results, it was concluded that a Pt hydrogen recombining catalyst on porous geopolymer was successfully developed.

2:30 PM

(ICACC-S11-004-2019) Lithium Recovery from Used Li-ion Batteries by Innovative Electrodialysis using a Lithium Ionic Conductor Membrane (Invited)

T. Hoshino*[1]

1. National Institutes for Quantum and Radiological Science and Technology (QST), Breeding Functional Materials Development Group, Department of Blanket Systems Research, Rokkasho Fusion Institute, Fusion Energy Research and Development Directorate, Japan

In recent years, the industrial importance of lithium (Li) has increased due to its use in Li-ion batteries. I have developed a method for the recovery of Li from seawater using a Li ionic superconductor functioning as a Li-ion separation membrane (LISM). This innovative method involves the use of an LISM whereby only Li ions in a solution of used Li-ion batteries permeate from the positive electrode side to the negative electrode side during electrodialysis; the other ions, including Co, Al, and F, do not permeate the membrane. $Li_{0.29}La_{0.57}TiO_3$ was selected as the LISM. The positive side of the dialysis cell was filled with used Li-ion battery solution. Then the negative side was filled with distilled water. The applied dialysis voltage was 5 V, and electrode area was 16 cm^2. The Li recovery ratio increased with electrodialysis time. Then, Co, Al, and F were not permeated. After electrodialysis, CO_2 gas was bubbled in the Li recovery water to produce lithium carbonate (Li_2CO_3) as a raw material for Li-ion batteries. The Li_2CO_3 deposition was easily generated by the reaction of CO_2 gas and the Li recovery solution as a lithium hydroxide (LiOH) solution. This new method for recycling Li-ion batteries shows good energy efficiency and is easily scalable. Thus, this electrodialysis method is suitable for the recovery of Li from used Li-ion batteries.

3:10 PM

(ICACC-S11-005-2019) Intrinsic properties of $LaCoO_3$ from First-Principles Density Functional Theory Calculations (Invited)

D. Lee*[1]

1. Pohang University of Science and Technology(POSTECH), Materials Science and Engineering, Republic of Korea

Lanthanum cobaltite, $LaCoO_3$, a mixed ionic and electronic conductor, is a promising material for various applications, such as Solid Oxide Fuel Cells (SOFCs), electrolysis membranes, catalyst, gas sensor and thermoelectric (TE) devices. Especially, it has shown superior electronic and ionic conductivity when it is doped with other ionic species such as Sr, Ca, Ba and other transition metals. However, there are still a couple of issues that need to be taken cared for $LaCoO_3$ to be used for various industrial applications. In this study, first-principles density functional theory calculations are employed to understand the relationship between spin state of Co ions and electronic structure of $LaCoO_3$. Our study shows that the variation of spin state of Co ions significantly affects the electronic structure of $LaCoO_3$ and thus affect the electrical conductivity. Our calculation results will be a cornerstone for controlling the electronic properties of $LaCoO_3$ by using various dopants.

3:40 PM

(ICACC-S11-006-2019) Economic discovery and processing optimization of commercializable functional materials using quantum mechanical computations

H. Choi*[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Satisfying both high functionalities and production economy of new emerging materials is very difficult and rare. Synthesis and processing conditions of inorganic nanomaterials significantly changes the phase, morphology, properties and functionality. Therefore, exact fundamental understanding must be given to materials processing and discovery to draw desirable properties. Density functional theory (DFT) calculations are known to provide us with exact values of thermodynamic parameters for inorganic materials quickly. In this talk, recent achievements of accelerated discoveries and processing optimization guided by quantum mechanical computations are introduced in various application fields: memory device, hydrogen-fuel catalysts, and solar cell materials.

4:00 PM

(ICACC-S11-007-2019) Solvent-deficient method for the sustainable synthesis of advanced functional ceramics (Invited)

S. Zeljkovic[2]; H. Maruyama[1]; J. C. Nino*[1]

1. University of Florida, MSE, USA
2. University of Banja Luka, Department of Chemistry, Bosnia and Herzegovina

Synthesis of nanopowders of advanced functional ceramics is of fundamental interest to industry and there are numerous methods currently employed including sol-gel, solvothermal, combustion reaction, microwave, sonochemical, co-precipitation, electrospraying, solution evaporation, molten salt, etc. These methods vary substantially in their simplicity, capital and operating expense, and their overall environmental hazard and safety. Therefore, there is significant interest in developing new, environmentally benign and more efficient methods for obtaining high purity nanopowders of advanced ceramics. Here we describe a solvent deficient method for the synthesis of high surface area metal oxide nanomaterials that does not employ traditional organic solvents during the mixing the reagents, and does not require a complex apparatus or setup. Based on the solid mixture of nitrate precursors and ammonium bicarbonate, the synthesis process involves low energy and time consumption. We show the solvent deficient synthesis of nanoparticles of CeO_2, Gd-doped CeO_2, and $BiFeO_3$. The synthesis reactions and kinetics investigated by simultaneous thermogravimetric analysis-differential scaning calorimetry, and x-ray diffraction will be discussed. Moreover, the powder morphology, sintering behavior, resulting micorstructure, and the electrical and magnetic properties of the compounds will be presented.

4:30 PM

(ICACC-S11-008-2019) Tape casting porous and textured lead-free piezoelectrics for ultrasound transducers (Invited)

A. B. Haugen*[1]; K. Andersen[1]; N. Van Nong[1]; E. Ringgaard[2]; F. Levassort[3]

1. Technical University of Denmark, Energy Conversion and Storage, Denmark
2. Meggitt A/S, Denmark
3. University of Tours, GREMAN UMR, France

Piezoelectric ceramics can reach properties close to those of single crystals if they are made with aligned grains (texture). Compared to a bulk ceramic made by uniaxially pressed and sintered powder, this texture requires extra processing steps with shear forces to align anisometric template particles seeding directional grain growth. In addition to investigate texture to replace single crystals, it is therefore interesting to introduce texture to ceramics already made by shaping techniques with shear forces, such that texture can improve them without significant extra costs. One such process is tape casting of thin and multilayered piezoelectrics. In this talk, I will present results on tape casting of $(Li_{0.06}(K_{0.52}Na_{0.48})_{0.94})(Nb_{0.71}Ta_{0.29})O_3$ doped with 0.25 mol% Mn (KNNLTM). KNNLTM is a promising lead-free composition for ultrasound transducers, due to its high coupling coefficients as a single crystal. Using $NaNbO_3$ anisometric seeds crystals, 85 % $(100)_{pc}$ texture could be introduced, with a 50 % increase in the piezoelectric response to a k_t of 0.34 and a d_{33} of 170 pC/N. KNNLTM also provides lower acoustic impedance (21 MRayl) than lead-based transducers (>30 MRayl). After careful process control, KNNLTM multilayers for high-frequency ultrasound transducers could be obtained, with a thin, dense, piezoelectric active KNNLTM layer supported on a porous KNNLTM backing.

5:00 PM

(ICACC-S11-009-2019) Single-Source-Precursor Synthesis and Processing of Silicide-Containing Polymer-Derived Ceramic Nanocomposites (Invited)

E. Ionescu*[1]

1. Technical University Darmstadt, Materials Science, Germany

In the present talk, the synthesis and processing of ceramic nanocomposite materials consisting of transition metal silicides TMS (i.e., Fe_3Si, $PdSi_2$ and Mn_5Si_3) which are in-situ generated upon ceramization of suitable polymeric single-source precursors as homogeneously distributed nanoparticles in a polymer-derived silicon oxycarbide matrix will be addressed. The single-source precursors will be introduced in detail concerning their synthesis and structural characterization as well as their conversion into the TMS/SiOC nanocomposites. The TM-Si-O-C system is shown to be thermodynamically controlled with respect to its phase compositions obtained at high temperatures. Within this context, suitable design tools to tailor/adjust the phase composition in the presented systems will be introduced and critically discussed. Furthermore, selected properties of the prepared nanocomposites materials such as soft magnetic or catalytic properties will be highlighted.

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Novel Applications and Device Fabrication I

Room: St. Johns

Session Chairs: Michel Barsoum, Drexel University; Thierry Cabioch, University of Poitiers

1:30 PM

(ICACC-S12-001-2019) Tracking Phase Changes in Cr_2AlC by in-situ Resistivity Measurements (Invited)

B. Stelzer[1]; P. Bliem[1]; X. Chen[1]; J. M. Schneider*[1]

1. RWTH Aachen University, Materials Chemistry, Germany

The resistivity changes of magnetron sputtered, amorphous Cr_2AlC thin films were measured during heating in vacuum. Based on correlative X-ray diffraction (XRD), selected area electron diffraction (SAED) and differential scanning calorimetry (DSC) data it is evident that the resistivity changes at 552 ± 4 and 585 ± 7 °C indicate the phase transitions from amorphous to a disordered hexagonal solid solution and from the latter to MAX phase, respectively. We have shown that phase changes in Cr_2AlC thin films can be revealed by in-situ measurements of resistivity.

2:00 PM

(ICACC-S12-002-2019) Microstructure and surface preparation effects on the oxidation behavior of Ti_3AlC_2 and Ti_2AlC MAX phases (Invited)

V. Gauthier-Brunet*[1]; E. Drouelle[2]; B. Levraut[1]; J. Cormier[1]; P. Villechaise[1]; P. Chartier[1]; S. Dubois[1]; P. Sallot[2]

1. Institut PPRIME, Physique et Mécanique des Matériaux, France
2. SAFRAN, CRT, France

For several decades, the lightening of structures has become a major issue for transport industries. In this context, Ti_3AlC_2 and Ti_2AlC phases deserve to be considered. Although the high-temperature mechanical properties of these materials have been poorly investigated, many studies have shown the ability of MAX phases containing aluminum to form a protective α-Al_2O_3 layer at high temperatures. In this study, Ti_3AlC_2 samples were produced by performing spark plasma sintering (SPS) onto home-made Ti_3AlC_2 powder. The selected operating parameters (Ti_3AlC_2 powder purity and densification step parameters) were varied to modify the Ti_3AlC_2 microstructural characteristics (porosity, grain size, nature and content of secondary phases). Ti_3AlC_2 oxidation resistance was investigated in air in the temperature range 800-1000 ° C. Fine-grained and coarse-grained Ti_2AlC samples were respectively synthesized using SPS onto home-made Ti_2AlC powder and hot isostatic pressing starting with elemental powders. The effect of the grain size, the surface roughness influence and the Ti_2AlC crystalline orientation role were investigated after short-term oxidation at 1000°C. The effect of both the oxidation conditions and the MAX phases microstructural characteristics were studied via the observation of the oxide layers morphology and the study of the oxidation kinetics.

2:30 PM

(ICACC-S12-003-2019) Breakaway oxidation in wedge-shaped Ti_2AlC MAX phase

Y. Chen*[1]; Z. Zhan[1]; T. Duong[1]; A. Talapatra[1]; R. Arroyave[1]; A. Srivastava[1]; M. Radovic[1]

1. Texas A&M University, Materials Science & Engineering, USA

Ti_2AlC MAX phase has promising applications at high temperatures due to excellent oxidation resistance. Wedge-shaped Ti_2AlC samples were prepared with a 3-4° taper and exposed to oxidation in 1000-1200 °C range for different times. SEM, EDS and EBSD reviled three different regions on the oxidized wedge-shaped Ti_2AlC sample: (i) breakaway oxidation region containing Al_2O_3 + TiO_2 (ii) intermediate region having continuous oxide layer with large Al_2O_3 + TiO_2 small nodules; (iii) region having thin protective Al2O3 oxide layer. The results of this study indicate that Al deficient of approximately 4% in Ti_2AlC leads to the breakaway oxidation, i.e. formation of Al_2O_3+TiO_2 oxide, instead of protective Al2O3 oxide layer. The outcomes of this study expected to be contributing towards the research and development of advanced Ti_2AlC MAX phase with good oxidation resistance behavior.

2:50 PM

(ICACC-S12-004-2019) Oxidation of Ti_2AlC/Ti-Al composites with Nb or Mo additions

G. A. Hug*[1]; A. Jankowiak[2]; S. Mellac[1]; K. Piven[1]

1. ONERA, LEM, France
2. ONERA, DMAS, France

Two-phased composite materials consisting of one MAX (Ti2AlC) ceramics and an intermetallic compounds are produced by reactive sintering and Spark Plasma Sintering (SPS) and studied for high temperature application. The oxidation resistance and the mechanical strength are further optimized by doping at the M site with several elements. The oxidation behavior is studied by cyclic oxidation experiments. It is observed that the addition of Nb improves the oxidation resistance by promoting the formation of a thin and adherent Al2O3 layer. Although it helps the synthesis of the 211 phase, the addition of Mo does not lead to the same beneficial effect on oxidation resistance. The oxidation mechanisms as studied by SEM will be presented.

Novel Applications and Device Fabrication II

Room: St. Johns

Session Chairs: Miladin Radovic, Texas A&M University; Gilles Hug, ONERA

3:20 PM

(ICACC-S12-005-2019) Environmental resistance of MAX phases under aggresive working conditions (Invited)

J. Gonzalez-Julian*[1]; T. Go[1]; D. Mack[1]; G. Mauer[1]; R. Vassen[1]

1. Forschungszentrum Juelich, Germany

MAX phases are a relative new family of materials with high potential for high temperature applications due to their unique combination of properties, bridging the gap between ceramics and metals. However, due to the novelty of these materials, more research regarding processing and properties under realistic environmental working conditions is required to transfer MAX phases to final applications. One of the most potential application of MAX phases is as coatings in order to protect metals and superalloys against high temperature (> 1000 °C) and oxidizing environments. Unfortunately, the development of these coatings (thickness > 70 μm) has not been strongly developed by two main reasons: i) the availability of large quantities of highly pure powders, and ii) difficulties to deposit the powders by thermal spray technologies. In this work, processing of dense Cr_2AlC materials and highly dense Cr_2AlC coatings by thermal spray technologies (cold spray and High Velocity – Atmospheric Plasma Spray) will be shown. The environmental response of these structures under long-term experiments (few days) and high temperature (1200 °C) will be analyzed and characterized in detail. Furthermore, the possibility to use MAX phases as bond-coats in Thermal Barrier Coatings (TBCs) will be explored, increasing the number of potential applications.

3:50 PM

(ICACC-S12-006-2019) A description of (211) MAX Phases Electronic Structure based on Rigid Band Models (Invited)

D. Pinek*[1]; T. Ito[2]; M. Ikemoto[3]; T. Ouisse[1]

1. Grenoble INP, France
2. Nagoya University, Japan
3. Nagoya University Synchrotron Radiation Research Center, Japan

We report a study of the electronic structure of 211 MAX phases and how relatively simple rigid band models can equally describe the band structures (BSs) and Fermi surfaces (FSs) of those compounds. Rigid band structures were built up from Density Functional Theory (DFT) calculations, but their applicability and limits have been tested by comparing their outcomes with experimental results from Angle Resolved Photoemission Spectroscopy (ARPES) on Cr_2AlC, V_2AlC and Ti_2SnC. The charge transfer between A, M, and X atoms was also assessed. A remarkable agreement is found between theory and experiment, therefore confirming the applicability of rigid band models to describe MAX phases electronic structure. From those results, we propose a new classification of the 211 MAX phases.

4:20 PM

(ICACC-S12-007-2019) Compatibility of Zr_2AlC MAX Phase with Liquid Lead-Bismuth Eutectic (LBE) and Lead (Pb)

B. Tunca Altintas*[1]; T. Lapauw[2]; R. Delville[1]; J. Hadermann[3]; A. Marshal[4]; K. Pradeep[5]; J. M. Schneider[4]; E. Caspi[6]; J. Vleugels[2]; K. Lambrinou[1]

1. SCK-CEN, Nuclear Materials Science Institute, Belgium
2. KU Leuven, Materials Engineering, Belgium
3. University of Antwerp, Department of Physics, Belgium
4. RWTH Aachen University, Materials Chemistry, Germany
5. Indian Institute of Technology, India
6. Nuclear Research Centre-Negev, Physics Department, Israel

MAX phase-coated stainless steel fuel clads are a candidate near-term technology targeting the good compatibility of the fuel clad with the inherently corrosive heavy liquid metal (HLM) coolants (lead or lead-bismuth eutectic) of Gen-IV lead-fast reactors (LFRs). Various MAX phases have shown excellent liquid corrosion resistance when exposed to liquid LBE/Pb under aggressive test conditions, i.e., high temperatures ($T \leq 750°C$), low HLM oxygen concentrations ($C_O << 10^{-8}$ mass%), and high HLM flow velocities ($v \approx 8$ m/s). Zr_2AlC is a candidate coating material for Gen-IV LFR fuel clads, due to the small neutron cross-section of Zr. This work discusses the interaction between Zr_2AlC and oxygen-poor ($C_O < 10^{-8}$ mass%) static liquid LBE/Pb, at 500°C, for up to 2000 h. Post-test material characterisation was based on scanning electron microscopy, electron backscatter diffraction, transmission electron microscopy, and atom probe tomography. The exposure of Zr_2AlC to liquid LBE/Pb formed in-situ a $Zr_2(Al,Pb/Bi)C$ MAX phase solid solution at the HLM/Zr_2AlC interface and was also accompanied by vacancy ordering in the specimen bulk. The crystal structure of this new solid solution was studied by neutron diffraction on bulk $Zr_2(Al_{0.5},(Pb,Bi)_{0.5})C$ made by reactive hot pressing. A mechanism explaining the Zr_2AlC/HLM interaction is also proposed here.

4:40 PM

(ICACC-S12-008-2019) Compatibility of candidate MAX phase coating materials for accident-tolerant fuel clads with water and high-temperature steam

K. Van Loo*[1]; C. Bail[3]; R. Bosch[3]; M. Grosse[2]; J. Vleugels[1]; K. Lambrinou[3]

1. KULeuven, Department of Materials Engineering, Belgium
2. Karlsruhe Institute of Technology, Germany
3. Nuclear Materials Science Institute, SCK-CEN, Belgium

The Fukushima Daiichi event in 2011 has demonstrated the need for safer nuclear energy, a goal that can be reached by the development of accident-tolerant fuels (ATFs), which are expected to address the technical shortcomings of the standard zircaloy/UO_2 fuels. Candidate ATF cladding materials must outperform the commercial zircaloys in nominal and transient/accidental operation conditions; first and foremost, this implies a good clad compatibility with the coolant in all its states (water, steam). An ATF cladding material concept currently under evaluation envisages the deposition of a phase-pure MAX phase coating with the appropriate composition and microstructure (grain size, texture) on a zircaloy substrate. For this purpose, screening cladding/coolant interaction tests have been performed on a wide range of MAX phase ceramics (Ti_2AlC, Ti_3SiC_2, Cr_2AlC, $(Ti,Nb)_2AlC$, $(Zr,Ti)_2(Al,Sn)C$, Maxthal® 211 and 312, etc.). Testing assessed material resistance to aqueous corrosion (330°C, 30 days, PWR-like water) and high-temperature steam oxidation (≤1200°C, 1 hour, steam), thus evaluating the suitability of MAX phase ceramics for the ATF application. This work reports on the resistance of the tested MAX phases to aqueous corrosion and steam oxidation, comparing their performance to the benchmark performance of commercial zircaloys tested simultaneously.

5:00 PM

(ICACC-S12-009-2019) Thermal expansion of MAX phases solid solutions

T. Cabioch*[1]; P. Chartier[1]; B. Tunca[2]; J. Vleugels[2]; K. Lambrinou[3]

1. University of Poitiers, France
2. KULeuven, Belgium
3. SCK-CEN, Belgium

The structures and the properties of ternary compounds such as MAX phases can be modified, and even tuned, by introducing a fourth, or more, element into their structures. It is now well established that isostructural solid solutions can be obtained on the M, A and/or X sites and this compositional degree of freedom has been exploited by some to tailor the MAX phases' properties. Recently, new quaternary MAX phases were obtained with an out-of-plane ordering (o-MAX) and in-plane ordering (i-MAX). This contribution focuses on the evolution of thermal expansion coefficients of $M_{n+1}AX_n$ compounds by using in-situ High Temperature X-Ray Diffraction when isostructural solid solutions are obtained on the M, A or X sites for various values of n. Thermal expansion of novel o-MAX and i-MAX will also be dicussed on the basis of results obtained by the same technique.

5:20 PM

(ICACC-S12-010-2019) High temperature water vapor oxidation of Cr_2AlC coatings on Zircolay-4 claddings for Accident tolerant fuels (ATFs)

Y. Lei*[1]; J. Zhang[1]; J. M. Schneider[2]; J. Wang[1]

1. Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics Division, China
2. RWTH Aachen University, Materials Chemistry, Germany

Accident tolerant fuel (ATF) is proposed after the accident in Fukushima Daiichi in 2011, aiming to improve the margin of safety when accidents happen. Protective coatings are fabricated on zirconium-based alloys, as one of ATF strategies, requiring good high-temperature oxidation resistance in water vapor. MAX phases are believed to be attractive coating candidates, for they possess the combined excellent properties, including high modulus, high thermal conductivities, excellent high temperature corrosion resistance and easy machinability. In this work, phase pure Cr_2AlC coatings are synthesized by magnetron sputtering on Zircaloy-4 cladding tubes, and specimens are oxidized in water vapor at 900 to 1200 °C for 1 h. The weight gains of one-side Cr_2AlC coatings decrease by 20% from that of uncoated cladding after oxidation in water vapor at 1100 and 1200 °C for 1 h, while at 1000 °C, breakaway oxidation occurs. Meanwhile, outward and inward diffusion of alumina occur simultaneously during the oxidation. For further application in ATFs, a buffer layer should be introduced.

5:40 PM

(ICACC-S12-011-2019) Microwave Absorption Study of $SrFe_{12}O_{19}/Ti_3SiC_2$ Nanocomposites

A. Garg*[1]; N. Kumari[2]; S. Tyagi[1]

1. Central Scientific Instruments Organisation, Chandigarh, india, Ubiquitous Analytical Techniques, India
2. Central Scientific Instruments Organisation, Chandigarh, Thin Film Divison, India

Microwave absorbing medium comprising strontium hexaferrite and titanium silicon carbide, $SrFe_{12}O_{19}/Ti_3SiC_2$ has been synthesized. The Strontium hexaferrite ($SrFe_{12}O_{19}$) has been synthesized by auto combustion method. The 'as synthesized' hexaferrite powder is observed to have low coercivity (255.09 G) and high saturation magnetization (45.1 emu/g). The titanium silicon carbide (Ti_3SiC_2) has been synthesized by the heat treatment of the precursors (Ti/Si/TiC) at 1100ºC. A microwave absorbing material is developed by mixing followed by heating $SrFe_{12}O_{19}$ and Ti_3SiC_2 composite at 200ºC in different weight ratios. The maximum reflection loss of -24.62 dB at 9.37GHz is observed for the composite containing 40% Ti_3SiC_2 and 60% $SrFe_{12}O_{19}$ powder with 2 mm thickness. This suggests, developed material to be a potential stealth material for defense applications.

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Ceramic Fuel Materials, Technologies, and Characterization

Room: Coquina Salon H
Session Chair: Yutai Katoh, Oak Ridge National Laboratory

1:30 PM

(ICACC-S13-001-2019) UCO TRISO Fuel Particle Performance Demonstration (Invited)

P. A. Demkowicz*[1]

1. Idaho National Laboratory, USA

The US DOE Advanced Gas Reactor program has demonstrated the fabrication and irradiation performance of high-quality low-enriched uranium oxycarbide (UCO) tristructural isotropic (TRISO)-coated particle fuel. This is a spherical, layered composite fuel form consisting of pyrocarbon and SiC layers that retain fission products within the particles and is a key component of the functional containment licensing strategy for high-temperature reactors. The fuel has been irradiated to peak burnup of 19.5% FIMA and time-average peak temperatures as high as 1360°C with excellent performance in terms of particle coating layer failure rates and fission product retention. Post-irradiation, high-temperature accident safety testing of the fuel demonstrates the robustness of the fuel form at temperatures up to 1800°C for several hundred hours. The relatively low cesium release under these conditions compared to UO_2 TRISO fuel highlights one of the key advantages of UCO in reducing CO(g) formation in the kernel and eliminating the associated CO corrosion of the SiC layer which results in significantly higher cesium release from UO_2 fuel. Extensive post-irradiation examination of fuel particles has elucidated various kernel and coating behaviors, including coating fracture and the causes of individual layer failures. This performance demonstration serves as a foundational basis for the use of these particles in a variety of HTR designs.

2:00 PM

(ICACC-S13-002-2019) Characterization of TRISO fuel particles with modified multilayered SiC shells

R. Seibert*[1]; M. Balooch[2]; D. Schappel[3]; B. Jolly[1]; K. Terrani[1]

1. Oak Ridge National Laboratory, USA
2. University of California, Berkeley, USA
3. University of Tennessee, USA

Three novel designs of silicon carbide (SiC) and pyrocarbon (PyC) are considered to replace the SiC coating layer of tristructural-isotropic (TRISO) nuclear fuel particles. The SiC layer of TRISO fuel provides structural integrity and acts as the primary fission product release barrier. To date, these particles are high performing, with the exception of localized SiC attack by fission products that can lead to cracking and possible particle failure. Due to their success, modified forms of the particles are under consideration for use in other reactor technologies. The designs proposed in this work were created with the intent to increase SiC coating layer resistance to cracking and fission product attack during operation and accident scenarios. The designs were produced using fluidized bed chemical vapor deposition system. Characterization of the particles was conducted using electron microscopy, while mechanical properties of the modified SiC region were studied by nanoindentation. These studies indicated that the mechanical properties were unchanged in the modified designs, but the resistance to crack propagation was greatly increased compared to the reference monolithic design. Finite element analysis of stress distribution and evolution in the SiC coating layer of the fuel particles during normal operation did not show significant changes between the modified designs and the reference structure.

2:20 PM

(ICACC-S13-003-2019) Spark plasma sintering of ceramic nuclear fuels from sol-gel feedstock

A. M. Raftery*[1]; J. W. McMurray[1]; M. Trammell[1]; K. Terrani[1]

1. Oak Ridge National Laboratory, USA

Ceramic materials, including uranium nitride and uranium carbide, have been used as practical nuclear fuels due to their stability over a range of temperatures and conditions. Traditional fabrication routes for ceramic fuels involve powder processing and sintering in a conventional furnace for hours at high temperatures. Alternative methods for fabrication of nuclear fuel pellets are gaining recognition due to potential advantages in comparison to the conventional approach. The sol-gel processing route for the production of feedstock has the benefit of eliminating the use of radioactive powder and allowing fine control of the chemical composition of the resulting ceramic microspheres. In addition, spark plasma sintering (SPS) can provide sintering in much less time (minutes) and at significantly lower temperatures than conventional sintering methods. This work intends to demonstrate the fabrication of uranium nitride and uranium carbide pellets via spark plasma sintering of sol-gel microspheres. A parametric study is performed to elucidate the sintering behavior of the high density ceramic fuel materials based on the feedstock properties and sintering parameters.

2:40 PM

(ICACC-S13-004-2019) Demonstration of Fuel as Fiber LCVD Concept Using Uranium Disilicide

S. Harrison*[1]; J. Pegna[1]; J. L. Schneiter[1]; K. L. Williams[1]; R. K. Goduguchinta[1]; E. G. Vaaler[1]

1. Free Form Fibers, USA

Fuel as Fiber (FAF) is a laser-driven chemical vapor deposition (LCVD) concept for forming nuclear fuel in fiber format in a controlled array pattern referred to as a fiber forest. Free Form Fibers demonstrated FAF in collaboration with MCL, Inc. in Oak Ridge, Tennessee using depleted uranium-based precursor gas to form uranium disilicide fibers on a substrate. The resulting fabricated

fibers were analyzed for crystalline and chemical content with the goal to produce the U_3Si_2 composition. The utility of uranium-based fibers either as stand-alone nuclear fuel raw material or as part of a fuel pellet design will be discussed. In addition, a review of the FAF approach and the LCVD technology will be provided.

Novel Ceramics and Composites for Nuclear Systems I

Room: Coquina Salon H

Session Chair: Paul Demkowicz, Idaho National Lab

3:20 PM

(ICACC-S13-005-2019) New Silicon Carbide Matrix Compositions for Fully Ceramic Microencapsulated Fuels

Y. Kim*[1]; Y. Kim[1]; S. Lee[2]; K. Lim[2]

1. University of Seoul, Dept. of Materials Science & Engineering, Republic of Korea
2. KEPCO Nuclear Fuel, Materials Development Group, Republic of Korea

Fully ceramic microencapsulated fuels (FCM) consist of tristructural-isotropic (TRISO) fuel particles embedded in a SiC matrix. The SiC matrix offers potential advantages including improved irradiation stability and enlarged safety margin. Material issues to attack for the successful development of FCM includes (1) low temperature sintering, (2) additive compositions without Al or with a minimal Al content, (3) corrosion resistance, (4) irradiation resistance, (5) mechanical properties, (6) thermal shock resistance, (7) thermal conductivity, and (8) cost. The main focus of this presentation is to report recent progress in SiC matrix development for FCM. The following efforts will be presented: exploration of new additive compositions for developing SiC matrix without Al or with a minimal Al content, and investigation of factors affecting thermal conductivity of SiC matrix. Specifically, SiC ceramics with sintered densities above 99% were successfully obtained at a temperature as low as 1850°C via a hot-pressing route without Al additives. Typical flexural strength, fracture toughness, and thermal conductivity of the hot-pressed SiC ceramics with a new additive system were >800 MPa, 4.7 $MPam^{1/2}$, and >100 W/mK at room temperature, respectively. Preliminary data on the processing of FCM via hot-pressing route will be presented.

3:40 PM

(ICACC-S13-006-2019) Multiphysics modeling of SPS based manufacturing of SiC-matrix FCM pellet

G. Singh*[1]; C. K. Ang[1]; Y. Katoh[1]; L. Snead[2]

1. University of Tennessee, USA
2. Stony Brook University, USA

A fully coupled electro-thermo-mechanical analysis of Spark Plasma Sintering (SPS) of fully ceramic microencapsulated (FCM) pellet with silicon carbide matrix was performed using the finite element (FE) method to map the temperature distribution and densification in the pellet. The relative sensitivities of the temperature and density field to several manufacturing parameters were evaluated. The dependence of the material properties on temperature and pressure have been incorporated. The FE model was validated by comparing the predicted results with the experimental data. In addition to mapping the temperature and density in pellet the FE model can be used to optimize the parameters including die design for manufacturing a pellet with uniform density and regularly arrangement fuel particles.

4:00 PM

(ICACC-S13-007-2019) Consolidation mechanism of SiC matrix hosting nuclear fuel kernels

C. K. Ang*[1]; Y. Katoh[1]; G. Singh[1]; L. Snead[2]

1. University of Tennessee, Nuclear Engineering, USA
2. Stony Brook University, Old Engineering Bldg, USA

The development of Fully Ceramic Microencapsulated (FCM) fuels requires the synthesis of a composite material containing non-shrinking fuel kernels in a shrinking SiC matrix. First, candidate SiC matrices were examined as a function of powder size. The densification of SiC was assessed via constant heating rate and isothermal shrinkage models. Densification initiated at 1800K due to reduction of apparent activation energy caused by Al_2O_3-Y_2O_3 additives. A moderate independence of final density to powder size illustrated the sensitivity of surface transport mechanisms on the sintering process. Next, selected SiC powders were used to form FCM pellets, which demonstrated successful closed porosity needed for high-performance fuel. Transport of the SiC matrix between hosted fuel kernels was apparent, and matrix densification was accounted for by modified shrinkage models. However, in larger size parts, predicted local shrinkage is found to be critically dependent on temperature and pressure distribution within the graphite tooling.

4:20 PM

(ICACC-S13-008-2019) Cold sintering of iodate-substituted calcium hydroxyapatite (IO-HAp)

M. ul Hassan*[1]; H. Ryu[1]

1. Korea Advanced Institute of Science and Technology (KAIST), NQE-NFML, Republic of Korea

Reprocessing of spent nuclear fuel (SNF) is one of the important parts of the nuclear fuel cycle. Among the waste stream of SNF, I-129 is a volatile and long-lived radionuclide having high mobility and low adsorption. Low-temperature glass, zeolites, sodalities, cement, and apatites have been investigated to capture and immobilize iodine. These options are shown good adsorption and durability, however; high processing temperature, use of toxic reagents, strict synthesis conditions and use of sophisticated tools and techniques for the conditioning make them less viable. In this study, we have applied the cold sintering technique for densification of dried IO-HAp and achieved up to 97% sintered relative density at 200 °C only. The sintered matrix was nano-structured with the good compressive strength of 172 MPa and a hardness value of 3.2 GPa. The sintering parameters have shown no effect on the stability of the iodates. The product consistency test (PCT) shown promising low values for the leaching of Iodine (10^{-3} $g/m^2/d$), Calcium and Phosphorous (10^{-6} $g/m^2/d$). Therefore, the novel cold sintering was proposed as a simple, cost-effective method for the conditioning of IO-HAp.

4:40 PM

(ICACC-S13-009-2019) Sintering of YH_2 for nuclear reactor moderator applications

A. P. Shivprasad*[1]; J. T. White[1]; T. A. Saleh[1]; J. R. Wermer[2]; D. Rao[3]

1. Los Alamos National Lab, Materials Science and Technology, USA
2. Los Alamos National Lab, Sigma Division, USA
3. Los Alamos National Lab, Civilian Nuclear Programs, USA

Because of their small size, low capital cost, and low power, very small modular reactors (vSMRs) could be integrated into hybrid microgrids, for which current generation nuclear power plants are ill-suited. In particular, vSMRs could be designed to be inherently self-regulating in that the reactor power varies to meet power needs without requiring active controls or a cadre of on-site operators. One such proposed vSMR is a high-temperature reactor that uses metal hydrides as the moderator due to their high hydrogen density, allowing enhanced fuel utilization and cost-effectiveness while keeping the core transportable. Yttrium dihydride (YH_2) is

a promising candidate for this application due to its high thermal stability and the stability of the oxide layer that forms on the surface, even at temperatures exceeding 1200 K. Despite these advantages, it is difficult to produce YH_2 in geometries required for reactor design concepts. In this study, YH_2 pellets were fabricated using powder metallurgical methods so as to ensure dehydriding did not occur. Thermogravimetric analysis was used to determine mass change as a function of temperature and sintering environment. Pellets were then analyzed for thermal diffusivity, coefficient of thermal expansion, and heat capacity to determine thermal conductivity. Results will relate the thermophysical properties of the sintered pellets with those of hydrided monoliths in literature.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials I

Room: Tomoka C

Session Chairs: Kenji Toda, Niigata University; Romain Gaume, University of Central Florida

1:30 PM

(ICACC-S14-001-2019) Correlation between variation of network and luminescence properties of glasses (Invited)

H. Masai*[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Department of Materials and Chemistry, Japan

Since oxide glass is a metastable solid state material obtained from the supercooled liquid state, the glass structure and physical properties of the glass depend on various parameters, such as chemical composition, the preparation method, and annealing process. In the case of phosphor application with doped activators, the local coordination states in glass will be important for the advancement of glass science from both scientific and industrial perspectives. In the study, the relationship between the structural ordering of oxide glass and the luminescent properties of the activators in glass is examined. Although it is conventionally recognized that glass is quite different from crystalline materials, a relationship between structural ordering and luminescence will be useful for understanding the crystalline phosphor. By using several different analysis techniques, the structural parameters of glass are quantified in order to discuss the relationship between the structure and luminescent properties.

1:50 PM

(ICACC-S14-002-2019) Sintered Glass Ceramics for High-Power White-Light-Emitting Diodes

A. Longato[1]; S. Picco[1]; M. Buffolo[2]; N. Trivellin[2]; C. De Santi[2]; L. Borgato[2]; M. Meneghini[2]; A. Martucci*[1]

1. University of Padova, Industrial Engineering, Italy
2. University of Padova, Information Engineering, Italy

Due to the weak thermal and chemical stability of organic resins which are used for conventional white LEDs to embed phosphors, inorganic color converters such as phosphor ceramics and phosphor-in-glasses are currently being used to replace conventional color converters based on organic materials, especially for high power and high brightness applications. In this paper we report on the study of sintered glass ceramics based on low melting glass in which commercial YAG:Ce3+ phosphors are embedded. A low Tg is necessary to avoid high temperature sintering which can damage the optical properties of the embedded phosphors. Two different types of glass have been studied: borosilicate and tellurite. The compositions have been optimized in terms of stability, sintering efficiency and thermal conductivity. Selected samples were optical charterized using a GaN high power multimode 450 nm Laser Diode, with a maximum output power of 1.6 W at 1.5 A. We investigated both the effect of high irradiation density and high operating temperature, as well as their color-rendering index. The sintered glass ceramic based on borosilicate glass showed better high power stability because of its higher thermal conductivity.

2:10 PM

(ICACC-S14-003-2019) Design of novel phosphors with narrow f-f emission by band-gap engineering

Y. Sato*[1]; J. Odahara[1]; T. Iwamoto[1]; Y. Iwashita[1]; M. Kakihana[2]

1. Okayama University of Science, Department of Chemistry, Japan
2. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, Japan

In this study, we investigated the photoluminescence of Pr^{3+}-acitvated $CaX_xTa_{1-x}O_{2+x}N_{1-x}$ (X: Zr, Hf) phosphors with the range from 0.0 to 1.0. The solid-solution systems can be expected that the wavelength of maximum exciation is widely adjusted along with bandgap energy between valence and conduction bands by the control of the O/N and Zr/Ta (or Hf/Ta) ratios. Thus, the sharp emission peak from Pr^{3+} in the solid-solution system can be excited by near-UV or blue lights if the width of bandgap energy is adujusted from 2.8 to 3.2 eV. All the sample were prepred by polymerizable complex method. The obtained precursors were heat-treated under NH_3 gas flow at 900-1100°C. XRD patterns indicated that all the samples were of single phase perovskite structure. The absorption attributed to the band gap excitation shifted to high-energy sides with increasing Zr^{4+} or Hf^{4+} concentration. Especially, the bandgap energy were sucessfully adjusted from 2.8 to 3.2 eV while the x was changed from 0.60 to 0.90 by the control of the Zr^{4+}/Ta^{5+} (or Hf^{4+}/Ta^{5+}) and O/N ratios. Furthremore, the solid-solution systems showed the intriguing photoluminous behavior. The single emission peaks were observed at 612 nm when the bandgap enegries were adjusted at around 3.0 eV for the samples with x from 0.55 to 0.70, The red emission peak can be assigned to the electron transition between $^1D_2$ and $^3H_4$ levels of Pr^{3+} ions.

2:30 PM

(ICACC-S14-004-2019) Preparation of Transparent $MgAl_2O_4$ Ceramics for LED Applications

Z. Lences*[1]; M. Radwan[1]; P. Sajgalik[1]

1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Ceramics Department, Slovakia

During the last decade there is a growing R&D interest in the development of transparent ceramics as inorganic phosphors for high-power LED applications, e.g. the sintered Lumiramic phosphor wafers developed by Philips based on transparent YAG:Ce and translucent $M_2Si_5N_8$:Eu phosphors. This work presents the preparation and characterisation of transparent $MgAl_2O_4$ spinel ceramics doped with both transition and rare-earth metals. Aqueous dispersion of the initial spinel powder was optimized using Darvan C-N as a surfactant, followed by freeze casting in a liquid nitrogen and freeze drying in vacuum. Highly transparent $MgAl_2O_4$ ceramics were successfully fabricated by green compaction using cold-isostatic pressing (CIP) followed by two-steps sintering approach using pressureless pre-sintering (PLS) in air and hot-isostatic pressing (HIP) in a pressurised argon gas. The real in-line optical transmission (RIT) of the polished dense spinel samples measured in the visible spectrum of light reached 76% (approx. 87% of the theoretical transmittance limit). This work was supported by SASPRO 1329/03/02-b, APVV-14-0385 and VEGA2/0164/18 projects.

2:50 PM

(ICACC-S14-005-2019) Polycrystalline transparent ceramics fabrication by a combination of Spark Plasma Sintering (SPS) and Hot Isostatic Pressing (HIP) processes

S. Cohen*[1]; B. Ratzker[1]; M. Sokol[2]; S. Kalabukhov[1]; N. Frage[1]

1. Ben-Gurion University of the Negev, Materials Engineering, Israel
2. Drexel University, Materials science&engineering, USA

SPS is a rapid and cost-effective advanced sintering technique, highly promising for the fabrication of transparent polycrystalline ceramics. However, using this approach for large and/or thicker parts is difficult due to limited tooling dimensions, applied force and non-homogeneous temperature distribution. In the present study we suggest to combine the SPS process under vacuum of 10^{-2} mbar with a subsequent HIP treatment in Ar atmosphere to obtain relatively large (40 mm diameter) transparent ceramic parts. $MgAl_2O_4$ nano-size powders, were firstly densified by SPS to obtain translucent parts with about 1-2% of residual close porosity. HIP treatments was conducted in the1500-1800°C temperature range, under 2000 atm for durations from 120 to 600 minutes. Fully dense samples with transparency of about 84% in the 600 nm wavelength (4-8 mm thickness samples) were obtained already after HIP at 1500°C for 120 minutes. Microstructure and mechanical properties will be discussed.

3:20 PM

(ICACC-S14-006-2019) Fabrication of transparent magneto-optical YIG ceramics

C. French[1]; M. Julian[1]; A. Schülzgen*[1]; R. M. Gaume[1]

1. University of Central Florida, CREOL, USA

Due to its superior Verdet constant, Yttrium Iron Garnet (YIG) has long been recognized as an important magneto-optical material, particularly in the field of high-power infrared isolators. When processed in bulk polycrystalline ceramic form, the transmission of this material is greatly affected by the presence of pores and deviation from stoichiometry. This work investigates the densification of phase-pure YIG ceramics by way of Conventional Solid-State Reactive Sintering (CSSRS) and specifically addresses the role played by the atmosphere and sintering additives on the microstructure and densification kinetics. We show that infrared-transparent bulk-sized ceramics can be obtained with a 3 μm grain size under optimal sintering conditions.

3:40 PM

(ICACC-S14-007-2019) Investigation of storage luminescent materials for radiation detectors (Invited)

T. Yanagida*[1]; N. Kawaguchi[1]

1. Nara Institute of Science and Technology, Japan

Storage phosphors have been used in many application fields. One of the interesting and important applications of storage phosphors is a detection of ionizing radiation. When ionizing radiation is irradiated to the storage phosphor materials, many secondary electrons (carriers) are generated, and some of these carriers are captured at localized trapping centers. Upon the stimulation by thermal or optical energy, these trapped carriers are re-excited, and some of them can recombine at localized luminescence center to show luminescence. The luminescence intensity depends on the irradiated dose, and we can evaluate the absorbed dose. When the stimulation is done by the thermal energy, we call the phenomenon thermally stimulated luminescence (TSL), and done by optical energy, we call it optically stimulated luminescence (OSL). If the change of the charge valence occurs by ionizing radiation irradiation, and such ions with changed valence show a photoluminescence, such a phenomenon is called radiophotoluminescence (RPL). Up to now, we have proved that these ionizing radiation induced storage luminescence shows an anti-correlation relationship with scintillation. In the conference, I will overview common storage phosphor materials for ionizing radiation detectors, and introduce our recent research results on TSL, OSL and RPL materials.

4:10 PM

(ICACC-S14-008-2019) Analysis of the relaxation processes of excited states in self-activated scintillators using transient absorption spectroscopy (Invited)

M. Koshimizu*[1]; Y. Muroya[2]; S. Yamashita[3]; H. Yamamoto[4]; T. Yanagida[5]; Y. Fujimoto[1]; K. Asai[1]

1. Tohoku University, Department of Applied Chemistry, Japan
2. Osaka University, Japan
3. The University of Tokyo, Japan
4. National Institutes for Quantum and Radiological Science and Technology, Japan
5. Nara Institute of Science and Technology, Japan

The development of novel scintillators with high light yields is of considerable interest. Most scintillators are composed of an insulator host with dopants as the luminescence centers. In contrast, some scintillators exhibit efficient scintillation without such dopants. These scintillators are called self-activated. Notable examples of self-activated scintillators include $CdWO_4$ (CWO) and $Bi_4Ge_3O_{12}$ (BGO). The occurrence of large Stokes shifts in these scintillators suggests that the scintillation occurs through radiative transitions of self-trapped excitons. However, based on the light yields of CWO and BGO, most of the initially produced excited states in these systems do not lead to scintillation, but instead, experience quenching. Little is known about the quenching process despite its importance. In this study, we analyzed the excited states of CWO and BGO single crystals using transient absorption spectroscopy with the aim of better understanding the quenching process. Based on transient absorption measurements in the pico and nanosecond time scales, we concluded that quenching initially occurs within 1 ns.

4:40 PM

(ICACC-S14-009-2019) Synthesis and Properties of $Gd_3(Ga,Al)_5O_{12}$:Ce Transparent Ceramics

Y. Wang*[1]; J. Glodo[1]; U. Shirwadkar[1]; C. Brecher[1]; D. Chartier[1]; N. Cicchetti[1]; K. Shah[1]

1. Radiation Monitoring Devices, Inc., Research, USA

Gd-containing mixed garnet ceramics such as $(Gd,X)_3(Ga,Al)_5O_{12}$:Ce especially $Gd_3(Ga,Al)_5O_{12}$:Ce (GGAG) get increasing interest recent years since they offer excellent optical and scintillation properties such as high gamma ray stopping power, high light yield as well as fast decay which make these materials potential candidates for future radiation detection. The relative low densification temperatures employed for ceramic processing offer an alternative to single crystal growth in obtaining less expensive scintillators. In current study, optically transparent GGAG:Ce ceramic was synthesized by ceramic process. The relationship between ceramic stoichiometry and phase structure and microstructure evolution was studied. The influence of ceramic processing conditions such as densification temperature, dwelling time and atmosphere on microstructure and morphology were investigated in order to optimize the transparency and understand the densification mechanism. The scintillation evaluation indicates that the light yield and decay of the GGAG ceramic were very sensitive to the Gd/(Ga+Al) ratios. Transparent GGAG:Ce ceramic with a high light yield of 66,000 Ph/MeV was obtained which make it promising candidate for future scintillation detection applications.

5:00 PM

(ICACC-S14-010-2019) Borate glass scintillators for charged-particle detection (Invited)

N. Kawaguchi*[1]; T. Kato[1]; G. Okada[1]; Y. Fujimoto[2]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Graduate School of Materials Science, Japan
2. Tohoku University, Japan

Scintillators emit ultraviolet or visible light in response to incident radiation and are used for radiation detectors. A typical radiation detector consists of a single crystal scintillator and a photomultiplier tube (PMT) operating in the photon-counting mode. To develop simpler detector system for charged-particle detection, we studied Eu^{3+} ions doped borate glass scintillators coupling with a silicon image sensor operating in the integration mode. In general, the production cost of glass materials is lower than that of single crystals. In addition, borate glasses have both the relatively lower melting temperature and the higher chemical stability. Borate glasses doped with the Ce^{3+} ion, which is the most conventional luminescent center for oxide single crystal scintillators, often have low quantum efficiencies. In contrast, the luminescence from Eu^{3+} ions in borate glasses, which are originated from inner shell 4f-4f transitions, can show high quantum efficiencies. Scintillation properties of the Eu^{3+} ions doped borate glasses and the result of the alpha-particle imaging test will be shown at the conference.

5:20 PM

(ICACC-S14-011-2019) Effects of Gd^{3+} doping on luminescence properties of (Gd,Ce):SrF_2 nanopowders and transparent ceramics

I. Milisavljevic*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

With a considerable expansion of transparent ceramics research in the past decade, however, there have been noticeably less reports on transparent ceramic materials with emissions in the UV range. In this work, (Gd,Ce):SrF_2 transparent ceramics were fabricated via vacuum hot pressing method, by using the co-precipitated Gd,Ce:SrF_2 nanopowders with a fixed concentration of Ce^{3+} and different concentrations of Gd^{3+}. XRD analysis showed that all the powder samples had a single cubic SrF_2 phase, while the shift of all diffraction peaks to smaller angles indicated incorporation of dopants. The photoluminescence and time decay measurements of powders revealed that the co-doping of Ce^{3+} and Gd^{3+} ions not only gave emission in the UV range, but also increased the luminescence emission intensity of Ce^{3+} due to the energy transfer. Furthermore, the spectroscopic and microstructural features of the obtained Gd,Ce:SrF_2 transparent ceramics have been investigated.

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Stereolithography I

Room: Coquina Salon B

Session Chair: Soshu Kirihara, Osaka University

1:30 PM

(ICACC-S15-001-2019) New applications of hybrid ceramic multi-materials and smart design (Invited)

R. Gaignon*[1]

1. CEO, France

3D printing lets users push back production limits. Ceramics are no exception to the rule. To open up this technology to a wider spread of professionals 3DCeram is sharing its maker experience to propose smart design (multi-function parts such as 3Doptic system for space application) and multi-material solutions (presentation of the H2020 project Cell3Ditor). Thus the new Ceramaker Hybrid is able to print several material at the same time and can manufacture smart design parts. With 3DCeram, 3Dprinting is just not repeating what we can do with other production technology but is going a step forward.

2:00 PM

(ICACC-S15-002-2019) Multi-ceramic additive manufacturing based on novel digital light processing technology (Invited)

H. Yun*[1]

1. Korea Institute of Materials Science, Engineering Ceramics Department, Republic of Korea

Additive manufacturing (AM) technologies have attracted huge attentions and have advanced remarkably in the last decade. However, there are still limitations both in selecting materials and in controlling part performance. Notably, for most ceramics, the functionality of structure was controlled by modelling the 3D architectures although we can expect much advanced functionality of 3D part by using multi-materials for AM process. To this purpose, our group has developed an original digital light process (DLP) based system, which has been designed specifically to overcome the complications of typical vat-type DLP system that use ceramic suspension. Our new system consists of multi-film type material feeding system with a 180°-horizontally rotatable stereolithography module and unique washing module to prevent contamination between materials, for structures with multi-ceramic distribution. The fabrication system and processing has been successfully optimized for various types of materials for fine control over the end product. We could co-print multi-component in one structure using less amount of ceramic suspension with high resource efficiency. We have confirmed multi-material printability of both the functionally graded materials structures and the core-shell structure. We believe that this new technology may provide big turning point to overcome limitation of ceramic forming process.

2:30 PM

(ICACC-S15-003-2019) Establishment of Stereolithographic Additive Manufacturing for Fine Ceramic Production (Invited)

T. Houki*[1]; Y. Fujii[2]; S. Kirihara[3]

1. SHASHIN-KAGAKU Co., Ltd., Development, Japan
2. SK FINE Co., Ltd., President, Japan
3. Osaka University, Joining and Welding Research Institute, Japan

Stereolithographic additive manufacturing (STL-AM) systems using nanoparticles resin paste were newly developed to form the very high definition structured model applying optical modeling method. After removal of the photo-curable resins and sintering, the high density ceramics sample is provided. The made ceramic parts by our equipment are used as a parts for thermometry in semiconductor process, and as the supporting structures in chemical reaction. We will introduce our devices and the process technology in this conference. The 'SK FINE' is a bland-new company for producing ceramic AM equipment and the materials. 'SK FINE' was founded by SHASHIN-KAGAKU Co., Ltd. and OSAKA University Venture Capital Co., Ltd. in October 2018. But the history of the AM equipment technology for 15 years is succeeded in this company. SHASHIN-KAGAKU had been developing AM equipment and OSAKA University had been developing the process for ceramic AM. 15 years ago, Dainippon Screen Mfg. Co., Ltd. had developed finest resolution AM equipment with resolving power of 1 micron. Dainippon Screen Mfg. was born from SHASHIN-KAGAKU in 1943. The development of AM technology was continuing in SHASHIN-KAGAKU.

Stereolithography II

Room: Coquina Salon B
Session Chair: Hui-suk Yun, Korea Institute of Materials Science

3:20 PM

(ICACC-S15-004-2019) Lithographic additive manufacturing of silicon carbide ceramics

M. Schwentenwein*[1]; A. Altun[1]; J. Homa[1]

1. Lithoz GmbH, Austria

This work focuses on new developments concerning lithographic additive manufacturing (AM) of non-oxide ceramics. Lithographic AM techniques show advantages when it comes to the fabrication of highly precise and strong ceramic parts; however, the available material portfolio is significantly smaller than for powder bed processes or extrusion-based techniques, mainly due to difficulties associated light absorption and scattering as it is especially for non-oxide ceramics such as silicon carbide (SiC). By using highly reactive binder systems it was possible to realize photocurable SiC suspensions with solids loadings up to 50 vol% that could successfully be shaped using the lithography-based ceramic manufacturing (LCM) technique. By doing conventional sintering under argon atmosphere liquid-phase sintered (LPS)-SiC was obtained; moreover, by using silicon infiltration reaction-bonded (RB)-SiC components could be successfully prepared. This study presents first results regarding the mechanical and structural characterization along with fractography of the printed SiC components. The results indicate that the lithographic AM route can also be a viable method for making functional SiC parts, especially for small or complex shaped SiC components this lithographic AM can be a capable method to develop new designs and applications.

3:40 PM

(ICACC-S15-005-2019) Lithography based additive manufacturing of Mg stabilized zirconia

E. Adolfsson*[1]; E. Johansson[1]; G. Llanos[1]

1. Swerea IVF AB, Sweden

When additive manufacturing are applied on ceramics, the layer by layer manufacturing and the burn out process can easily introduce additional defects in the green body that are not removed during the sintering process. These defects may cause a significant reduction of the mechanical performance. A lithography based additive manufacturing process with Mg stabilized zirconia was thus investigated with the aim to obtain dense and reliable materials without large process related defects. Additional powder processing was performed before the resin based suspension was prepared. An optimum resin composition was developed with a solids loading of 45vol% and suitable rheological characteristics for the printing process. The printing parameters on the Cerafab 7500 (Lithoz) printer were adjusted according to the suspension characteristics. Various post-processing steps and binder burnout procedures were evaluated in order to reduce the time and the formation of cracks. The densification and the microstructure of the sintered materials were evaluated. The results obtained showed that the resin composition developed allows additive manufacturing of components with a uniform microstructure, high density and good dimensional accuracy.

4:00 PM

(ICACC-S15-006-2019) 3D printing of complex alumina components by DLP: A comparison between 'bottom-up' and 'top-down' approaches utilizing the same slurry and light source

O. Santoliquido*[1]; G. Bianchi[1]; A. Ortona[1]

1. SUPSI, MEMTi, Switzerland

A systematic study with bottom-up and top-down stereolithography for the production of complex ceramic objects has been performed using the same DLP light source and photosensitive ceramic slurry. The formulation consists in alumina particles dispersed in an acrylic resin mixed with a photo initiator. Two identical DLP projectors were mounted on two commercial 3D printers. Cylindrical periodic architectures consisting in a lattice of rotated cubes as elementary cells were printed with the two machines. Thanks to mechanical testing, density measurements and morphological analysis (micro and macro structure) a quantitative and qualitative assessment of each technique capabilities was performed. In the Bottom-up approach the periodic detachment introduces stresses and deformations in the component which lead to several problems. The advantage, however, lays in the higher precision of the printed components. Concerning the Top-down method, the main issue is that the thickness of the printed slices is not precise and constant during printing. Since this parameter is difficult to control, less accurate and detailed components can be obtained. The main advantage is that the printed object is stress-free and thus its micro and macro features are more consistent.

4:20 PM

(ICACC-S15-007-2019) DLP Stereolithography of Zirconia Dental Restorations

E. Willems*[1]; F. Zhang[1]; B. Van Meerbeek[2]; J. Vleugels[1]

1. KULeuven, Department of Materials Engineering, Belgium
2. KULeuven, Department of Oral Health Sciences, BIOMAT and UZ Leuven, Dentistry, Belgium

Zirconia is one of the most commonly used materials for dental restorations because of its good mechanical properties and high aesthetic potential. Currently, dental restorations are created by subtractive manufacturing, wasting a lot of material during the milling step. In additive manufacturing, stereolithography is one of the most promising techniques for ceramic oxides because of the high resolution and good surface finish. It is able to produce near dense and accurate designs within a reasonable time frame. This study uses mask exposure (DLP) stereolithography to manufacture 3 mol% yttria stabilized zirconia (3Y-TZP) ceramics. It is essential to manage and optimize the diverse steps of the process to obtain high quality dental restorations that can compete with the subtractive manufacturing process. The control of the density and accuracy of the ceramic green part, via the use of optimal printer settings, is of utmost importance to obtain high quality sintered ceramics. The influence of varying exposure times and led intensities during printing on the microstructure of the green bodies and sintered ceramics will be discussed. Furthermore, the slurry composition and post processing steps are critical to obtain pore and crack-free, dense ceramics. The influence of the slurry properties and debinding cycles will be highlighted.

Stereolithography III

Room: Coquina Salon B
Session Chair: Martin Schwentenwein, Lithoz GmbH

4:40 PM

(ICACC-S15-008-2019) Ceramic components additively manufactured by vat photo polymerization

U. Scheithauer*[1]; E. Schwarzer[1]; T. Moritz[1]; H. Klemm[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Shaping, Germany

Additive Manufacturing technologies for ceramic components which bases on photo-curable suspensions are currently the best choice concerning the realizable resolution and surface quality. Highly ceramic particle filled photo-curable suspensions are used and selectively cured by light. This opens the door to realize ceramic components with complex geometries for different applications, like micro reactors or heat exchanger. The next step will be the integration of sensors and actuators, which becomes possible by the combination of AM and printing technologies, like Aerosol printing. To increase the field of possible applications further, the material portfolio has to be extend. Silicon nitride is a very interesting

material, especially for high temperature applications. For all of these points different demonstrators will be presented to show the current state of research concerning the vat photo-polymerization processes for ceramic components.

5:00 PM

(ICACC-S15-009-2019) Additive Manufacturing of Polymer-Derived Ceramic Composites

T. Schaedler*[1]; K. A. Porter[1]; P. P. Bui[1]; M. R. O'Masta[1]; J. M. Hundley[1]; Z. C. Eckel[1]

1. HRL Laboratories, USA

We report advances in ceramic stereolithography using resins based on UV curable preceramic monomers. Ceramic particles and microfibers were added to the resins in volume fractions of 10 - 50% and the effects on mechanical properties were investigated. In contrast to conventional ceramic particle filled resins and inks, the liquid resin does not leave the material on heat treatment, but pyrolyzes to a ceramic matrix embedding the particles or microfibers. The resulting composites exhibit substantially higher bending strength and fracture toughness than the un-reinforced ceramic. Novel preceramic resin formulations were synthesized to reduce the oxygen content in the silicon oxycarbide ceramic and increase high temperature properties. Potential applications for this technology will be presented, including selected results of a NASA program on additively manufactured ceramic rocket engine components.

5:20 PM

(ICACC-S15-010-2019) 3D Printing of ceramic-based porous structures using stereolithography

A. Dieraert*[1]; C. Sanchez[2]; P. Belleville[1]

1. CEA, Le Ripault, France
2. Université Pierre et Marie Curie (Paris VI), Collège de France, Chimie de la Matière Condensée de Paris, France

Stereolithography-based additive manufacturing (AM) is increasingly becoming the technology of choice for the small series or single unit production. Although the spectrum of available 3D-printed materials has been widened in recent years, there is still a lack of ceramic-based materials which can be processed with stereolithography on a routine basis. The extremely high melting point of many ceramics adds challenges to additive manufacturing as compared with metals and polymers. Because ceramics cannot be cast or machined easily, three-dimensional (3D) printing enables a big leap in geometrical flexibility and microstructured architecture. We report work on synthesis new ceramics from preceramic monomers or inorganic powder loaded resins that are cured with ultraviolet light in a stereolithography 3D printer. After a thermal debinding and sintering step the part turns into a dense ceramic open structure and gains its final properties, with uniform shrinkage and porosity control. The paper discusses the critical process parameters that influence the properties of the final ceramic. Currently it is possible to print 3D-structures with a spatial resolution down to 200 µm, with complex shape and cellular architecture. Experimental characterization and performances of the AM ceramic parts will be discussed with regard to high temperature super insulation material application, exhibiting high-stiff properties.

5:40 PM

(ICACC-S15-011-2019) Polymer-derived SiC-SiOC ceramic matrix composites fabricated via stereolithography 3D printing

S. A. Brinckmann*[1]; J. Yao[1]; R. S. Fertig[1]; C. Frick[1]

1. University of Wyoming, Mechanical Engineering, USA

Due to complicated manufacturing methods and lack of machinability, the use of engineering ceramics is limited by the manufacturing processes used to fabricate parts with intricate geometries. Additive manufacturing of polymers that can be pyrolyzed into functional ceramics has recently been used to significantly expand the range of geometries that can be manufactured, but large shrinkage during pyrolysis has the potential to lead to cracking. In this work, a method to 3D print particle-reinforced ceramic matrix composites is described. Stereolithography is used to crosslink a resin comprised of acrylate and vinyl-functionalized siloxane oligomers with dispersed SiC whiskers. After crosslinking, the part is pyrolyzed to amorphous SiOC while the SiC whiskers remain unaffected. During pyrolysis, composite ceramics shrink 37% while unreinforced parts shrink 42%; this reduction in shrinkage improves part stability. Importantly, these ceramic matrix composites contain no visible porosity nor cracking on the microstructural level. Printed ceramic porous structures, gears, and components for turbine blades are demonstrated. Applying stereolithographic techniques to ceramic matric composites, this work may improve processing and properties of ceramics for applications that require complex geometries.

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced Nanostructured Materials for Photovoltaics and Solar Fuels I

Room: Halifax A/B

Session Chairs: Haiguang Zhao, Qingdao University; Rafik Naccache, Concordia University; Alberto Vomiero, Lulea University of Technology

1:30 PM

(ICACC-S17-001-2019) 2-D oxides optimized for energy storage and sensing: Key roles of surfaces and defects (Invited)

S. T. Misture*[1]

1. Alfred University, MSE, USA

Vanadate, titanate, niobate and MnO_2 2-D nanosheet assemblies have been studied in detail to define the effects of charged defects and surface area on charge storage and sensing properties. We find a direct link between charged defects and the optical, chemical, photochemical and electrochemical function. We focus our studies on 2-D nanosheets obtained by exfoliation or hydrothermal synthesis, and on defects on the metal sublattice; that is, we introduce aliovalent substituents or reduce or oxidize some of the metal cations using suspension pH or gas-phase reduction. The results demonstrate improvements in charge storage and charge transfer by as large as a factor of 10, and improvements in alcohol oxidation, for example. In general, we find clear links of activity with defect content, demonstrating that the defects modifying the surface features are critical in improving performance.

2:00 PM

(ICACC-S17-002-2019) Plasmonics of 2D molybdenum sulfides and oxides (Invited)

K. Kalantar-zadeh*[1]; J. Ou[2]

1. University of New South Wales (UNSW), School of Chemistry, Australia
2. RMIT University, School of Engineering, Australia

Plasmonics of 2D materials have attracted significant attention due to their desirable dispersion relation as according to the 2D dispersion equation, the cutoff frequency limit is eliminated. Their large tuneability, high doping range, and the existence of favorable depolarization factors allow for their better control. Among 2D materials, molybdenum sulfides and oxides are good candidates for plasmonics. Here tunable plasmon resonances in suspended 2D molybdenum oxide and molybdenum sulfide flakes are demonstrated. The 2D configuration generates a large depolarization factor and the presence of ultra-doping produces visible-light plasmon resonances. The ultra-doping process is conducted by reducing the semiconducting 2D oxide flakes. The generated plasmon resonances

are controlled by the doping levels and the flakes' lateral dimensions, as well as by exposure to a model protein. Alternatively, by electrochemically intercalating lithium into 2D molybdenum disulfide nanoflakes, plasmon resonances in the visible and near UV wavelength ranges are achieved. These plasmon resonances are controlled by the high doping level of the nanoflakes after the intercalation, producing two distinct resonance peak areas based on the crystal arrangements. The system is also benchmarked for biosensing. This work provides a foundation for developing future 2D molybdenum sulphide and oxide based biological and optical units.

2:30 PM

(ICACC-S17-003-2019) Hollow Multi-shelled Structures: Synthetsis and Applications (Invited)

D. Wang*[1]

1. Institute of Process Engineering/CAS, State Key Laboratory of Biochemical Engineering, China

Hollow multi-shelled structures (HoMSs) with hollow interior and multiple shells have been recognized as one type of promising material for applications in in energy conversion and storage, sensors, catalysis, electromagnetic absorption and drug delivery, etc. However, compared to their single- or double-shelled counterparts, the synthesis of HoMSs is much more challenging due to the increased complexity of the structure. Our group proposed a general and widely usable sequential templating approach (STA) to prepare HoMSs by utilizing carbonaceous spheres as templates to adsorb metal ions and heating them to remove the template and generate multiple shells. Numerous HoMSs of metal oxides, metal sulfides, and also heterogeneous mixed metal oxides have been successfully prepared using STA. The breakthrough of synthetic methodologies for HoMSs also provides opportunities to acquire unique physical or chemical properties and performance in specific applications by manipulating their geometric structures, such as shell numbers, shell thickness, inter-shell space as well as shell composition and morphology. Many successful examples have been well demonstrated in the specific fields, including dye-sensitized solar cells, lithium ion batteries, gas sensors etc.

3:20 PM

(ICACC-S17-004-2019) Optical Gas Sensors Based on Localised Surface Plasmon Resonance (Invited)

A. Martucci*[1]

1. University of Padova, Industrial Engineering, Italy

Au nanoparticles (NPs) dispersed in an oxide matrix represent an effective design for a gas sensor's active material owing to their catalytic and localised surface plasmon resonance (LSPR) properties. Noble metal NPs can exhibit catalytic properties and hence modify the chemical interactions between the oxide surface and the target analyte, thereby improving the sensing process. Moreover, if the metal NPs show an LSPR peak in the visible range, the nanocomposites can be used as selective optical gas sensors. TiO_2 thin films with embedded Au and/or Pt NPs have been obtained by synthesising high-quality metal and metal oxide colloids. These Au-TiO_2 samples show rapid, highly sensitive, and reversible changes in optical absorption when exposed to H_2 and CO species at 200°-350°C. More importantly, Au-Pt-TiO_2 thin films showed room-temperature responses to H_2. Thin films comprised of Au NPs dispersed in an NiO-TiO_2 mixed-oxide matrix were obtained by spin coating a sol-gel solution on a glass substrate and subsequent thermal annealing. These samples show high responses to H_2S down to a few ppm, with nearly nil interference in response during simultaneous exposure to CO or H_2. More recently dark field microscopy (DFM) has been used for direct observation of the kinetics of H_2 gas interaction with single gold nanorods (NRs) coupled with Pt NPs and/or in metal oxide matrices.

3:50 PM

(ICACC-S17-005-2019) Halide/oxide perovskites for efficient hybrid optoelectronic devices (Invited)

R. Nechache*[1]

1. Ecole de technologie Superieure, Electrical Engineering, Canada

Since the discovery of the bulk photovoltaic effect in ferroelectrics, there has been a growing interest in perovskite (PE) materials for energy related applications, including PV and water splitting. In such materials, the spontaneous polarization-induced electric field promotes the required separation of photo-excited carriers and allows photovoltages higher than their bandgap, which lead to efficiencies that can exceed the maximum possible in a semiconductor p–n junction solar cells. Among these materials, Bi2FeCrO6 is highly promising because it exhibits a conversion efficiency of about 8.1% under 1 Sun in thin film form. Other perovskites can be hybrid, if the cation A is replaced with an organic radical. This is the case for halide PE compounds (CH3NH3PbX), with X=Br, Cl, I, found recently to possess excellent light absorption in the VIS-NIR spectrum. The use of these materials in solar cells had led to a rapid increased of the photovoltaic conversion efficiency in the last year exceeding 22 %. Our study deals with the major challenges related with the implementation of functional PE oxides in organometallic PE based optoelectronic devices. The optimization of the properties of such hybrid systems and the performance of their related devices will be also discussed.

4:20 PM

(ICACC-S17-006-2019) Carbon dots as hybrid hole-transporting material and downshifting layer for highly efficient and stable inverted perovskite solar cells

D. Benetti*[1]; E. Jokar[2]; H. Zhao[3]; A. Vomiero[4]; E. Diau[2]; F. Rosei[1]

1. Institut National de la Recherche Scientifique, Énergie Matériaux Télécommunications, Canada
2. National Chiao Tung University, Department of Applied Chemistry, Taiwan
3. Qingdao University, College of physics, China
4. Lulea University of Technology, Engineering Sciences & Mathematics, Sweden

We report the effect of the integration of carbon dots (Cdots) in high-performance inverted planar-heterojunction (PHJ) perovskite solar cells (PSCs). Exploiting the excellent opto-electronic properties of Cdots, we show that an optimal amount of Cdots in a composite material with graphene oxide (GO) nanosheets can significantly improve hole extraction from perovskite films at the interface with GO/ITO. The increased hole-transport property at the interface of ITO/GO/perovksite increases the short-circuit current density (J_{SC}) and open-circuit voltages (V_{OC}), yielding a maximum efficiency of 16.2%, as opposed to a PCE of 14.7% obtained from the GO-based perovskite device. When applying Cdots with an engineered absorption only in the UV range as downshifting layer, the device performance was further improved, to attain a maximum PCE of 16.8% and, at the same time, the stability of the device was also enhanced. Kelvin-probe force microscopy (KPFM) and cyclic voltammetry (CV) are employed to analyze the electronic band alignment at the interface between GO/Cdots and the perovskite film. Photoluminescence (PL), transient PL decays, transient photovoltage (TPV) decays and electrochemical impedance spectroscopy investigated the charge-transfer kinetics and proved the delay of charge recombination.

4:40 PM

(ICACC-S17-007-2019) Energy related devices based on bismuth ferrite (BFO) nanomaterial

S. S. Bouzidi*[1]; P. Fourmont[1]; S. G. Cloutier[1]; R. Nechache[1]

1. Ecole de technologie supérieure, Génie électrique, Canada

The low dimensional and functional materials, such as thin films and nanomaterials, have gained tremendous attention over the last decades. As a functional material, bismuth ferrite (BiFeO3 or BFO) is one of the few multiferroic materials that exists at room temperature. Indeed, its perovskite structure allows it to show promising properties for electronic devices and more widely energy related applications. Over the two last decades, this material has gained research interest due to the coexistence of ferroelectric and antiferromagnetic orders over a wide range of temperatures. Nowadays, there is a tendency to integrate this material in electronic devices such as highly efficient optoelectronic devices and nanogenerators. Here we will introduce the influence of the BFO nanomaterials morphology on the optoelectronic performances of their devices. BFO nanostructures were synthesized by means of different methods and their properties were studied for integrating them in photodetector devices. The relationship between microstructural, optical and electrical properties and their effect on the photodetector performance will be also presented and discussed.

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Precursor Chemistry and Applications

Room: Coquina Salon C

Session Chairs: Sanjay Mathur, University of Cologne; Emanuel Ionescu, Technical University Darmstadt

1:30 PM

(ICACC-FS3-001-2019) Energy Landscapes and Thermodynamic Control of Synthesis Pathways in Complex Ceramics (Invited)

A. Navrotsky*[1]

1. University of California, Davis, Peter A. Rock Thermolab and NEAT ORU, USA

Many complex ceramic materials can be synthesized in a variety of structural states, with polymorphism, grain size, and order-disorder on several length scales among the parameters desriable to be controlled. Such control can be achieved by choosing appropriate initial synthesis conditons and progressing downhill iin free energy by appropriate thermal treatment. Understanding the relations among structure, processing, and thermodynamic driving forces versus kinetic barriers is critical to choosing a path to desried products. This talk shows how calorimetric study of the closely spaced energetics of various intermediate states provides insight and control into the products formed. Three very different examples illustrate common underlying thermodynamic principles of control. The first is polymrphism and synthesis of new structures in mechanochemical synthesis of metal organic frameworks. The second is control of order-disorder linking pyrochlore, weberite, defect fluorite, and amorphous structures, with radiation damage, grinding, and low and high temperature processing as variables. The third is particle size control at the nanoscale in producing thermodynamic crossovers of polymorph stability in simple oxides. In each case, new materials with distinct and interesting properties can be produced by stopping the reactions at intermediate states.

2:00 PM

(ICACC-FS3-002-2019) Block Copolymer Directed Advanced Ceramics and Composites (Invited)

U. Wiesner*[1]

1. Cornell University, Materials Science and Engineering, USA

The use of organic molecule self-assembly to structure direct various inorganic materials into nanostructured ceramics and composites is an area of intense research activity world-wide. Low cost solution assembly renders these approaches particularly interesting for applications ranging from separation and catalysis all the way to energy storage and conversion. In this talk progress in the field will be described with work by the Wiesner group at Cornell University. Examples will focus on the use of block copolymers as structure directing agents for various nanostructured ceramics and composites using equilibrium as well as non-equilibrium processes. The talk will describe efforts to develop a fundamental understanding of the respective structure formation processes supported by early stage formation studies as well as theoretical and simulation work. Finally, after describing the degree of structural control achievable in various materials classes ranging from oxides to non-oxide ceramics and from metals to semiconductors and from homogeneous structures to hierarchical and graded mesoporous structures, focus will turn to the study of entirely new and emerging property profiles of such materials that are a direct result of the achievable structure control on the nanoscale.

2:30 PM

(ICACC-FS3-003-2019) Hybrid Halide Perovskites: New Optical Materials for Energy Conversion Devices (Invited)

J. Vela*[1]

1. Iowa State University, Department of Chemistry, USA

Halide perovskites have quickly become one of the most interesting semiconductors for photovoltaics, reaching power conversion efficiencies of over 22% [1-5]. We were among the first to synthesize colloidal $CH_3NH_3PbX_3$ (X = I, Br) nanocrystals with different morphologies (dots, rods, wires, sheets) [4]. At the single particle level, these nanostructures show shape-correlated PL emission across whole particles, with little photobleaching observed and very few off periods [3]. We are particularly interested in mixed-halide perovskites such as $CH_3NH_3PbX_{3-a}X'_a$ (X, X' = I, Br, Cl) because of their enhanced moisture stability, and band gap tunability. Using a combination of optical absorption spectroscopy, powder X-ray diffraction (XRD) and, for the first time, ^{207}Pb solid state nuclear magnetic resonance (ssNMR), we have probed the extent of alloying and phase segregation in these materials [2]. ^{207}Pb ssNMR reveals that nonstoichiometric dopants and semicrystalline phases are prevalent in samples made by solution phase synthesis. We have shown that these nanodomains are persistent after thermal annealing up to 200 °C. Our observations are consistent with the presence of miscibility gaps and spontaneous spinodal decomposition at room temperature, and underscore how strongly different synthetic procedures impact the nanostructuring and composition of organolead halide perovskites.

2:50 PM

(ICACC-FS3-004-2019) Chemically Engineered Functional Nanostructures for Energy and Health Applications (Invited)

S. Mathur*[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Chemical nanotechnologies have played, in the past few decades a major role in the convergence of life, physical and engineering sciences leading not only to simple collaboration among the disciplines but to a paradigm shift based on true disciplinary integration. The successful synthesis, modification and assembly of nano building units such as nanocrystals and wires of different materials have demonstrated the importance of chemical influence

in materials synthesis, and have generated great expectations for the future. Implications of chemistry as an innovation motor are now visible for knowledge leap forward in various sectors such as materials engineering for energy, health and security. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude. This talk will present how chemically grown nanoparticles, nanowires and nanocomposites of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies. The examples will include microwave-assisted synthesis of surface-functionalized nanoparticles for drug delivery applications and chemically controlled production of heterostructures for energy harvesting and energy storage applications.

Solution Procesing and Rare Earth Materials

Room: Coquina Salon C

Session Chairs: Javier Vela, Iowa State University; Uli Wiesner, Cornell University

3:30 PM

(ICACC-FS3-005-2019) Upconversion Nanoparticles in Nanobiomedicine (Invited)

J. A. Capobianco*[1]

1. Concordia University, Chemistry and Biochemistry, Canada

The field of upconversion in ion doped system can be traced back to an idea of Bloembergen in 1959. Bloembergen proposed that IR photons could be detected and counted through sequential absorption (ESA) within the levels of a given ion in a solid. Role of energy transfer in upconversion was recognized by Auzel in 1966. Medical science has begun to focus their attention on the use of nanomaterials to improve diagnosis and treatment of diseases with the ultimate goal of moving into personalized medicine. The need to develop more efficient drug delivery procedures motivated us to propose novel nano-carrier based on lanthanide upconverting nanoparticles (Ln-UCNPs). They offer significant advantages in biological applications, particularly the extension of the system applicability to deep tissue regions of the body, a reduced scattering of the excitation wavelength, reduction of autofluorescence, and decrease in photodamage to the system under study. We will discuss relevant biological applications of these upconverting nanoparticles as a platform for drug delivery, imaging and nanothermometry.

4:00 PM

(ICACC-FS3-006-2019) Chemical formation and PL properties of β-SiAlON:Eu^{2+} phosphors derived from single source precursors (Invited)

D. Hamana[1]; J. Iihama[1]; J. Duclère[2]; T. Asaka[1]; Y. Daiko[1]; S. Honda[1]; S. Bernard[2]; T. Hayakawa[1]; Y. Iwamoto*[1]

1. Nagoya Institute of Technology, Japan
2. Univ. Limoges, CNRS, IRCER, France

Single source precursors for β-SiAlON:Eu(II) phosphors were designed and synthesized by chemical modification of perhydropolysilazane (PHPS) with $Al(OiPr)_3$ and $EuCl_2$ (Al/Si = 0.09, Eu/Si = 0.01). The in-situ GC-MS analysis for the reaction of PHPS with $Al(OiPr)_3$ in xylene at 140 °C showed evolution of iPrOH. The subsequent TG-MS analysis for the pyrolysis up to 1000 °C resulted in the detection of the residual xylene, propene and propane at 200 to 400 °C, while the elimination of HCl was observed above 800 °C. The single source precursor were successfully converted to β-SiAlON:Eu^{2+} by pyrolysis at 1000 °C under flowing N_2 for 1 h, and subsequent heat treatment at 1800 °C in N_2 (920 kPa) for 1 h. The polymer-derived β-SiAlON:Eu^{2+} phosphors exhibited a typical green emission peak centered at around 540 nm when excited at 420 nm, and the emission peak intensity was apparently higher than that evaluated for the samples synthesized by the conventional powder metallurgy method. Further study on the chemical composition controlling at molecular scale level and the related PL properties will be shown and discussed aiming to develop novel silicon oxynitride-based phosphors through polymer-derived ceramics (PDCs) route.

4:20 PM

(ICACC-FS3-007-2019) Low valent uranium: Perspectives of a forgotten element (Invited)

M. S. Wickleder*[1]

1. University of Cologne, Department of Chemistry, Germany

In contrast to the 4f elements the analogous 5f metals display a significantly larger range of oxidation states. Among these elements, uranium is certainly the best investigated because its radioactivity is low and it can be handled in an ordinary lab. Uranium exhibits the oxidation state +VI as the most common one, usually stamped by the appearance of the uranyl cation $[UO_2]^{2+}$. However, with respect to the properties the lower oxidation states are of interest because of the partially filled f orbitals of U^{5+} (f^1), U^{4+} (f^2), U^{3+} (f^3), and U^{4+} (f^4). These unique electron configurations may lead to interesting properties and functions, e.g. in luminescence and catalysis. We have started to prepare uranium compounds with different anionic ligands and we tried to address different oxidation states for the same ligands.[1-3] In this contribution we will discuss the synthesis and the properties of different compounds and their relation to their analogous lanthanide compounds. We have investigated especially the halides of uranium, e.g. UCl_4 and UI_3, for spectroscopic measurements doped into appropriate host lattices ($ZrCl_4$, LaI_3). Furthermore, a number of oxoanionic compounds could be gained, for example the sulfate $U(SO_4)_2$.

4:40 PM

(ICACC-FS3-008-2019) Chemical Processing of Nanostructured Uranium Oxides- Investigations on Structural and Electronic Properties

J. Leduc*[1]; M. Frank[1]; T. Fischer[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Uranium oxides (e.g. UO_2, U_3O_7, U_3O_8, UO_3) belong to a promising family of new materials for heterogeneous catalysis and light harvesting applications as a result of their interesting photonic and electronic properties as well as their redox-active surface chemistry. However, due to limited information and knowledge on the phase-selective preparation of uranium oxides, convenient synthetic access to thin film fabrication of UO_x phases is lacking. Moreover, contradictory reports in the literature on electronic properties of uranium oxides and their correlation with U:O stoichiometries as well as the dearth of reference materials and data for interpretation of experimental findings that necessitate complementary analytical techniques pose additional challenges. Therefore, new well-defined starting materials (precursors) for the direct synthesis of uranium oxides with coherent structural and compositional control are required. In addition, experimental studies and modelling of the electronic band structure and their correlation to photoabsorption and photocatalytic behaviors are needed. In this work, the integrated approach of precursor development, material synthesis and characterization via advanced spectroscopic methods in combination with computational modeling and application of uranium oxide materials in heterogeneous catalysis is presented.

5:00 PM

(ICACC-FS3-009-2019) Sol-gel rare-earth-doped glasses and glass-ceramic materials for optical applications (Invited)

F. Enrichi*[1]

1. Centro Studi e Ricerche E. Fermi (Italy) and Luleå University of Technology (Sweden), Italy

Sol-gel technique is commonly used for the preparation of a variety of optical materials. Moreover, rare earth doping can be easily obtained, providing suitable spectroscopic properties for many optical applications, such as phosphors for lighting and light-emitting devices, light amplifiers, lasers, spectral up- and down-conversion layers, and optical biomarkers. Furthermore, by controlling the composition and the annealing conditions, glass-ceramic nanocomposites can be synthesized, which combines the advantages of glasses with the better spectroscopic properties of the crystals. In this presentation I will discuss the synthesis of rare earth doped glasses and glass-ceramics by sol-gel route, like for example Tb-Yb co-doped silica-hafnia and silica-zirconia coatings. Furthermore, the introduction of Ag by ion-exchange in silica-zirconia-soda and silica-soda films will also be discussed, demonstrating a broadband and efficient sensitization of most of the rare earth ions, with high potential impact for applications.

5:20 PM

(ICACC-FS3-010-2019) Dinuclear lanthanide complexes as multifunctional magneto-optical systems

R. Marin*[1]; M. Murugesu[1]; E. Hemmer[1]

1. University of Ottawa, Department of Chemistry and Biomolecular Sciences, Canada

Lanthanide complexes are currently subject of intense research owing to their unique optical and magnetic properties. Indeed, lanthanide-based single-molecule magnets (SMMs) hold great promise for their future application in miniaturized data storage devices, while luminescent lanthanide complexes are suitable candidates in applications as optical sensing, illumination and optical thermometry. Among other systems, we are presently exploring the potentiality of a ligand combination (biprymidine and trifluoroactylacetonate) that enables the preparation of multifunctional dimeric lanthanide complexes $\{Ln_2\}$ featuring exciting optical and magnetic properties, depending on the lanthanide ion of choice. Here we give an overview of the potential applications of this simple, yet elegantly resourceful, family of compounds. Specifically, upon harnessing the optical and magnetic properties of $\{Dy_2\}$, we report for the first time an SMM possessing optothermometric properties, envisioning the development of a class of ultraminiaturized self-monitored components for the preparation of magneto-electronic devices. Also, we show how these complexes can be amalgamated with upconverting nanoparticles to prepare hybrid systems with augmented optical properties, benefiting from the synergy between the features singularly showcased by these moieties.

Tuesday, January 29, 2019

40th Anniversary Richard M. Fulrath Award Symposium on Frontiers of Ceramics for Sustainable Society

Fulrath Session I

Room: Coquina Salon E
Session Chairs: Mrityunjay Singh, Ohio Aerospace Institute; Yoshihiko Imanaka, Fujitsu Laboratories Ltd.

8:40 AM

(ICACC-FUL-001-2019) The Unprecedented Promise of Perovskite Solar Cells for Cheap, Efficient and Clean Energy for a Sustainable Future (Invited)

N. P. Padture*[1]

1. Brown University, School of Engineering, USA

Solution-processed thin-film perovskite solar cells (PSCs), where the record efficiency has rocketed from ~4% to ~23% — comparable to commercial silicon-based solar cells — in just nine years, offer unprecedented promise of low-cost, high-efficiency renewable electricity generation. Organic-inorganic halide perovskites (OIHPs) at the heart of PSCs have unique structures, which entail rotating organic cations inside inorganic cages, imparting them with desirable optical and electronic properties. To exploit these properties for PSCs application, the reliable deposition of high-quality OIHP thin films over large areas is critically important. The microstructures and grain-boundary networks in the resulting polycrystalline OIHP thin films are equally important as they control the PSC performance and stability. Fundamental phenomena pertaining to synthesis, crystallization, coarsening, and microstructural evolution involved in the processing of OIHP thin films for PSCs will be discussed with specific examples. The overall goal of our research is to have deterministic control over scalable processing of tailored halide perovskite thin films with desired compositions, microstructures, and grain-boundary networks for large-area, high-efficiency, and stable PSCs.

9:10 AM

(ICACC-FUL-002-2019) A new ceramic capacitor for energy storage (Invited)

T. Tsurumi*[1]

1. Tokyo Institute of Technology, Japan

Energy storage devices will be a key component for solving energy problems in the world. Lithium ion battery is currently regarded as the most promising devise for this purpose but its energy density is theoretically limited below 250 Wh/kg. We believe that capacitors are more suitable for energy storage devices than batteries. The energy density of a battery is determined by the performance of electrode materials, while the energy density capacitors can be increased by reducing thickness of dielectric layers. The capacitance density (energy density) of MLCC increased 100 million times from the discovery of barium titanate. However the dielectric constant of the barium titanate ceramics has been almost the same from the discovery to current compositions used in latest MLCCs. The increase of capacitance density has been done by reducing thickness of dielectric layers and producing multi-layered structure. We are aiming the same strategy to increase the energy density of new ceramics capacitors. We need huge dielectric constant caused by polarization that is determined by the dipole momentum given by the product of charge and distance. To produce huge polarization, we employed long range ionic motions in solid electrolytes. The new capacitor is called as Solid State Ionic Capacitor (SSIC). I will introduce the process and performance of SSIC in the presentation.

9:40 AM

(ICACC-FUL-003-2019) Hydrogen-selective Si-based inorganic-organic hybrid membranes for solar hydrogen production via photoelectrochemical water-splitting (Invited)

Y. Iwamoto*[1]

1. Nagoya Institute of Technology, Japan

Recently, increasing attention has been directed to a novel H_2 production system using photoelectrochemical water-splitting cells. This system essentially requires separation process for H_2 and co-produced O_2, and membrane separation is one of the candidate processes. Since the H_2 separation process is operated at low temperatures (below 373 K) in the presence of water, there are several technical issues in the conventional H_2-selective membranes such as water-induced swelling of polymer membranes and blockage of H_2-permeable micropore channels by water condensation within the hydrophilic microporous amorphous silica membranes. In this paper, our recent study on the polymer-derived Si-C-(O)-H inorganic-organic hybrid membranes will be presented. The water vapor adsorption-desorption isotherm analysis at 298 K revealed that the hybrids showed excellent hydrophobicity compared to sol-gel derived SiO_2 and γ-Al_2O_3 which have been often used for ceramic membranes. The hybrid membranes showed a good H_2-selectivity under dry condition as well as under various water partial pressures up to RH=100% at 323 K. These results will be shown and discussed aiming to develop novel hydrogen separation membranes for solar hydrogen production systems.

10:20 AM

(ICACC-FUL-004-2019) The photochemical reactivity of Polar surface domains on non-polar surfaces (Invited)

G. Rohrer*[1]

1. Carnegie Mellon University, USA

Polar semiconductors have recently received significant attention because their internal fields separate photogenerated electron-hole pairs and reduce recombination. On surfaces with polar domains, electrons are attracted to positively terminated domains where they promote reduction reactions and holes are attracted to negatively charged domains where they promote oxidation. We have found that polar domains can be created on the surfaces of non-polar materials, including BiVO4, WO3, and SrTiO3. In the cases of WO3 and BiVO4, polarity arises from the flexoelectric effect. On SrTiO3, polarity arises from polar terminations on different terraces. For SrTiO3, it is possible to control the fraction of the surface terminated by positive or negative charges by annealing the surfaces in environments with an excess or deficit of strontium. In this talk, the use of polar domains to control photochemical reactions on the surfaces will be described.

10:50 AM

(ICACC-FUL-005-2019) Growth and characterization of novel single crystals for electro-optical applications (Invited)

K. Shimamura*[1]; V. Garcia[1]

1. National Institute for Materials Science, Japan

Electro-optical technology progress in a wide range of applications, and still demands the further development. Here, recent activities of our group related with novel single crystals with advantageous characteristics will be reviewed. A new concept of high-brightness white LEDs based on Ce:YAG single crystal phosphor plates (SCPPs), which can overcome the conventional temperature- and photo-degradation problems, is proposed. SCPPs demonstrated excellent thermal stability with no temperature quenching, high values of luminous efficacy and increased quantum efficiency. $Tb_3(Sc_{1-x}Lu_x)_2Al_3O_{12}$ (TSLAG), CeF_3 and PrF_3 single crystals have been designed and grown for high-power laser machinery. They showed a higher visible-UV transparency and a larger Faraday rotation than $Tb_3Ga_5O_{12}$. They are therefore very promising material in particular for new magneto-optical isolator applications in the UV-VIS-NIR wavelength. Lead-free single crystals are attracting much attention for various piezoelectric applications due to their relatively high piezoelectric coefficient and high Curie temperature. In this work, some of the dielectric single crystals were successfully grown. The properties of grown crystals were systematically studied. Authors would like to thank to Koha Co., Ltd., and Fujikura Ltd., for the collaboration.

11:10 AM

(ICACC-FUL-006-2019) Development of Glass-Based Solid Electrolyte for All-Solid-State Lithium and Sodium Batteries (Invited)

A. Hayashi*[1]

1. Osaka Prefecture University, Department of Applied Chemistry, Japan

All-solid-state rechargeable lithium and sodium batteries attract much attention because of their high safety, long cycle life, versatile geometry and high energy density. Development of superior inorganic solid electrolytes is important for realize those rechargeable batteries. In addition, mechanical properties are of great significance to solid electrolytes for forming favorable solid-solid interfaces in all-solid-state batteries. We have developed sulfide and oxide glass-based electrolytes with both high conductivity and good deformability. Glass electrolytes were prepared via mechanochemistry using a planetary ball mill, and this process has a big merit to give glasses with high alkali-content. Glass electrolytes are useful as a precursor for precipitating metastable crystalline phases, which are difficult to prepare by a conventional solid phase reaction. Several metastable phases such as $Li_7P_3S_{11}$ and cubic-Na_3PS_4 are crystallized from glassy state and the prepared glass-ceramic electrolytes exhibit higher conductivities than their mother glasses. Crystallization of oxide glasses in the system Li_3BO_3-Li_2SO_4 also increases their conductivity and the prepared electrolytes show favorable ductility like sulfide glass electrolytes. Glass-based electrolyte materials with high conductivity and good ductility are useful for application to all-solid-state rechargeable batteries.

11:30 AM

(ICACC-FUL-007-2019) Additive Manufacturing for Aerospace Applications (Invited)

M. C. Halbig*[1]; M. Singh[2]

1. NASA Glenn Research Center, USA
2. Ohio Aerospace Institute, USA

The next generation of materials and structures targeted for use in future aerospace applications will require new processing and fabrication methods to obtain optimized properties and unique designs. Additive manufacturing offers new capabilities for achieving benefits over conventional approaches such as tailored material properties and unique structures as well as components that are more geometrically complex, compact, multi-material, innovatively cooled, integrated, and multifunctional. Various materials to include metals, ceramics, and polymers are being used in additive manufacturing to develop components for aeronautics and space applications. An overview will be provided on the efforts at NASA Glenn Research Center to apply additive manufacturing toward components for hot sections, turbine engine components, heat exchangers, acoustic panels, inlet guide vanes, electric motors, and multi-functional panels and structures.

11:50 AM

(ICACC-FUL-008-2019) Effect of synthesis routes on the enhancement in conductivity of cathode material $PrBaCo_2O_{6-\delta}$: SSR vs ACR (Invited)

P. Singh*[1]

1. Indian Institute of Technology(BHU), Department of Physics, India

In the present work, the PBCO sample is synthesized through auto-combustion route (ACR) and solid state route (SSR) at different sintering temperatures. The optimized sintering temperatures are found to be 1150 and 1050 ˚C for auto-combustion route and solid state route, respectively. The calcined powders were taken for thermogravimetric measurements and showed a continuous mass loss along with a kink for SSR at 413 ˚C and for ACR at 273 ˚C. The selected area electron diffraction patterns show that the crystals have grown very well in both the synthesis techniques. The peaks for Co in XPS spectra are observed to shift towards left i.e. low binding energy in ACR sample. This shifting is correlated to the decrease in oxidation states i.e. decrease in oxidation state of Co from Co^{+4} to $Co^{+3+\delta}$. The conductivity observed for SSR sample was found to be higher than that of ACR sample. The conduction mechanism has been understood in the terms of structural and thermal analyses.

Fulrath Session II

Room: Coquina Salon E

Session Chairs: Gregory Rohrer, Carnegie Mellon University; Takaaki Tsurumi, Tokyo Institute of Technology

1:30 PM

(ICACC-FUL-009-2019) Seeing the Invisible: Dynamic Interfacial Phenomena in Energy Materials (Invited)

V. P. Dravid*[1]

1. Northwestern University, Materials Science and Engineering, USA

Surfaces and interfaces are integral part of materials microstructure. Their dynamic behavior, especially under external stimuli such as thermal, electrical or mechanical, underpin great number of materials phenomena; ranging from mechanical behavior to charge transport. A detailed understanding of the dynamics of surfaces and interfaces, across hierarchical length-scales, holds the key to improved materials properties; as in energy conversion, storage and transport. The presentation will cover several examples of emerging nanostructures and associated interfacial phenomena in energy materials. It will introduce novel chalcogenide thermoelectrics which reversibly convert (waste) heat into useful electricity, and Li and Na-based electrochemical storage systems which show remarkable stability and sustained energy release enabled by nanoscale interfacial phenomena. The role of advanced and in-operando electron microscopy will be highlighted in unravelling the hierarchical architecture of the constituents and their intimate interplay in governing key phenomena in energy conversion and electrochemical storage. It will be argued that static and dynamic microscopy have pivotal role in understanding spatio-temporal phenomena in surface and interfacial phenomena in energy materials.

2:00 PM

(ICACC-FUL-010-2019) Why Soft Processing(=Low-Energy Production) of Advanced Materials is Difficult but Necessary for Sustainable Society? (Invited)

M. Yoshimura*[1]

1. National Cheng Kung University, Mater. Sci. & Eng., Taiwan

Modern our society has been developed with various advanced materials. Most of advanced materials, Metallurgical materials, Semiconductors, Ceramic materials and Plastics have been used in wide area of applications. Most of them except for bio-polymers & bio-minerals have never been produced via Biological systems. Thus they have generally been fabricated artificially and/or industrially by so-called high-technology, where high temperature, high pressure, vacuum, molecule, atom, ion, plasma, etc. have been used for their fabrications, then consumed huge amount of resources and energies thus exhausted huge amounts of wastes: materials, heats and entropy. They are completely against Biological system based upon Water Cycle in Mother Nature. Considering the lowering of total energy consumption and wastes, we have challenged to fabricate those advanced inorganic materials with desired shape/size/location, etc. directly in low energetic routes using (aqueous) solutions since 1995 an innovative concept and technology, "Soft Processing" or "Soft Solution Processing". In addition to several oxides, the preparation of Graphene and functionalized Graphene under ambient temperature and pressure conditions will be talked.

2:20 PM

(ICACC-FUL-011-2019) State of Play in the Developing Story of Cold Sintering (Invited)

C. Randall*[1]; X. Zhao[1]; J. Guo[1]; K. Wang[1]; T. H. de Beauvoir[1]; B. Li[1]; A. Ndayishimiye[1]; J. Seo[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

Cold sintering is the ability to densify ceramics and ceramic composites through the use of a transient liquid phase at intermediate temperatures and pressures. Since the early reports of the ability to synthesize many materials with this process, we have gained new insights into the mechanisms that underpin or limit the densification process. In this presentation, we will review both our own work, as well as the work of others that is emerging over the last two to three years. We will critically review areas of agreement, as well as many of the unknowns and challenges that still need to be resolved. We will also highlight a number of the application areas that seem most appropriate for cold sintering. In particular, we have been developing methods to redesign grain boundaries in ceramics with secondary phases. These include thin polymer interfaces, as well as nanomaterials, such as 2-D materials, that could all be included to create new microstructures and very unusual composite properties. We will highlight characteristics ranging from electrochemistry, dielectric and semiconducting properties, mechanical properties, and thermal properties. The ability to make composites with high volume fractions of ceramic, but also nanometer scale polymer and 2-D materials in grain boundaries, is a unique advantage of cold sintering.

2:40 PM

(ICACC-FUL-012-2019) Solvothermal Synthesis of Barium Titanate Nanocubes and Their Assembly (Invited)

S. Wada*[1]

1. University of Yamanashi, Material Science and Technology, Japan

To enhance physical properties, it is known well that polarization rotation mechanism is very important for dielectric and piezoelectric materials on the basis of "interface engineering". To apply the polarization rotation mechanism for property enhancement, a new material design using different complex oxide nanocubes was proposed. In this study, barium titanate ($BaTiO_3$, BT) nanocubes was prepared by a simple and conventional solvothermal method without surfactants or capping agents. The obtained BT nanocubes were confirmed as ones with a size of around 100 nm. Then, for a dispersion of BT-nanocubes, electric double-layer mechanism was applied and as a result, well dispersed BT nanocubes were clearly observed. Finally, the well-dispersed BT nanocubes were accumulated with sizes over 10 x 10 mm by capillary force at room temperature to measure dielectric properties. The detailed experimental procedure and dielectric properties will be reported at the conference.

3:20 PM

(ICACC-FUL-013-2019) Ceramics to metal joining for next generation power deviecs (Invited)

K. Suganuma*[1]

1. Osaka University, Japan

SiC and GaN, wide bandgap power semiconductors, have been expected to provide many benefits by replacing the conventional Si power devices such as energy saving, increasing power density, shirinkage of power module, and long life time. On the other hand, the increasing power density leads temperature increase beyond 200 degree C at the semiconductor junctions. Thus, not only SiC/GaN die-attach itself, insulating ceramic substrates such DBC and DBA must possess good heat-resistance and heat-shock resistance. Temperature range will be from -50 degree C to 250 degree C, which is quite severe for Al2O3 substrates with copper metal plates. In our group, while DBA was established in 1990s, new design rules of die-attach and insulating substrate have been explored to realize the reliable SiC/GaN power devices. It was found that DBAs of AlN, Si3N4 and Al2O3 can survive even in severe thermal shock test. Sevre metal surface deformation is the cause of serious degradation of the assembly. The properties of surface plating has a key to surpress this surface deformation. A nondestructive inspection method by using AE monitoring has been proposed to understand the degradation of module during thermal cycling.

3:50 PM

(ICACC-FUL-014-2019) Engineered Refractory Ceramic Materials for Energy and Environmental Efficiency (Invited)

J. G. Hemrick*[1]

1. Reno Refractories, Inc., Research and Development, USA

Although refractory ceramic products are often viewed as merely "dirt in a bag", these materials are in actuality highly engineered systems. Through a combination of chemical composition, microstructure, and thermos-physical properties; these complex ceramics can be utilized to improve the energy efficiency and decrease the environmental impact of the various industrial processes that our manufacturing-based society is dependent on. This talk will explore how refractory ceramic technology can lead to a more sustainable industrial footprint and preserve our resources and environment while maintaining our standard of living.

4:10 PM

(ICACC-FUL-015-2019) Femtosecond laser-fabricated three-dimensional structures for medical applications (Invited)

R. Narayan*[1]

1. NC State University, USA

We have utilized two photon polymerization to create microneedle arrays for transdermal drug delivery and sensing. The two photon polymerization technique involves temporal and spatial overlap of photons to initiate reactions that lead to material hardening within well-defined volumes; devices with microscale and sub-microscale features can readily be prepared using this approach. Two photon polymerization provides many advantages over conventional methods for fabricating microneedles and other small-scale medical devices. A variety of photosensitive materials, including organically-modified ceramic materials, may be used for two photon polymerization. In addition, two photon polymerization can be set up in a conventional environment that does not include cleanroom equipment. Finally, two photon polymerization of microneedles is a straightforward process. In this presentation, mechanisms for creating solid and hollow microneedles will be considered. The results of in vitro studies involving the materials used in two photon polymerization will be presented. Finally, the results of application-specific studies involving two photon polymerization-fabricated microneedles will be provided. Our results suggest that two photon polymerization offers many advantages for fabrication of microneedles and other small-scale medical devices.

4:30 PM

(ICACC-FUL-016-2019) Epsilon-WO3: Ferroelectric Poling and Ferro-Chromic Effects (Invited)

P. Gouma*[1]

1. The Ohio State University, MSE, USA

This work focuses on the processing and characterization of epsilon-WO3, a widely unknown low temperature polymorph of WO3 which we have stabilized at RT in nanopowder form using a rapid solidification process. The acentric structure of the epsilon phase provides the material with ferroelectric characteristics. Although directly characterizing the ferroelectric properties of this nanomaterial has been challenging, evidence is shown here that ferroelectric poling is responsible for the material's selectivity to polar molecules and also for a ferro-chromic effect observed upon polarization switching. These findings open the pathway for advanced applications such as non-invasive detection of diabetes or envoronmental friendly color changing windows and displays.

4:50 PM

(ICACC-FUL-017-2019) 3D printing of Ceramics for biomedical applications: Opportunities and challenges (Invited)

S. Bose*[1]

1. Washington State University, Department of Chemistry, USA

There are an estimated one million bone grafting procedures performed annually in the U.S. and a few million worldwide to repair bone defects, tumors, hip and knee replacements. Role of 3D printing (3DP) or additive manufacturing (AM) is becoming important in those cases of patient matched implants due to lower cost and shorter lead time to manufacture. However, additively manufactured components are still questioned for their reproducibility, machine to machine part quality variations and process specific material properties. Establishing process property relationships for different AM techniques are vital towards successful implementation of 3DP in biomedical devices. Hard biomaterials, e.g., calcium phosphate (CaP) ceramics show significant promise towards bone implant applications, in both 3DP tissue engineering scaffolds and surface modified hip and knee replacement devices. We have used 3DP CaP scaffolds, for bone tissue engineering to control their degradation kinetics, mechanical strength, and biological properties with improved osteogenesis, angiogenesis and as drug delivery vehicle. An additional coating of polymer on both CaP scaffolds and hip / knee implant devices helped improve mechanical and biological properties while controlling the drug release kinetics. The presentation will include opportunities and challenges towards the use of 3DP or AM in developing biomedical devices.

5:10 PM

(ICACC-FUL-018-2019) Development of Low Thermal Cordierite Porcelain Cook wares (Invited)

L. K. Sharma*[1]

1. CSIR-Central Glass & Ceramic Research institute, India

Cookwares are used to keep eatables in warm condition through LPG burner flames during social functions throughout world. Investigations were carried out to develop Cookwares formulations by using dead burnt primary clay grog from eastern part of India, Talc, Calcined Aluminum oxide & Raw Secondary clay in different proportions. Transparent glaze of matching Thermal Expansion was developed to avoid the defects of crazing etc. Different shapes were jiggered by using Roller Head. Shapes were Bisque fired at 1350 degree Centigrade at soaking of 4 hours. Glost firing was done at 1000 degree centigrade. Test bars were taken for further studies of Linear Thermal Expansion, Apparent Porosity, Water Absorption, Thermal Shock Resistance and Bulk Density. Products were also

tested for Thermal Shock resistance. 9% MgO based formulation was found to be best suitable with thermal expansion of 2.09x10-6/ degree Centigrade. Fritted glaze was found to be suitable for the body formulations. Wares were found to pass 20nos Thermal Shock Cycles from 500 degree centigrade to Air Quenching. XRD studies showed good cordierite peaks.

8th Global Young Investigator Forum

Frontiers in Ceramic Materials: Advances and Challenges in Novel Materials Design, Synthesis, Performance, and Reliability II

Room: Coquina Salon G
Session Chair: Ryan Paul, GrafTech International Holdings Inc.

8:30 AM

(ICACC-GYIF-010-2019) Eu/Y:Al_2O_3 films and powders from alkoxide precursors

M. Ek*[1]; G. Westin[1]

1. Uppsala University, Chemistry Ångström, Sweden

Alumina is a high melting, hard, thermally conductive material with high transparency over a large optic window, which makes it useful for many applications in hard and optical materials. Here alkoxide based processing of films and powders with low doping of the Lanthanide-ions, Y and Eu is presented. The Ln concentration studied were below 5% and the precursors used were; $Al_4(OiPr)_{12}$, $EuAl_3(OiPr)_{12}$ and $YAl_3(OiPr)_{12}$. The phase evolution on heating the gel like materials obtained to 1000°C was monitored by; TG/DTA, IR and Raman spectroscopy, XRD, XPS, SEM and TEM.

8:50 AM

(ICACC-GYIF-011-2019) Modelling and design of Thermal protection system for hypersonic space vehicles using UHTC

C. Zuccarini*[1]

1. Kingston University London, Mechanical and Aerospace Engineering, United Kingdom

This paper shows the conceptual design and modelling of a Thermal Protection System that can be used to protect the sharp leading edge of the Space Shuttle. The Protection system has been designed using composite materials based upon ultra high temperature ceramics for a sharp edge exposed to exit speed, hypersonic and re-entry conditions. Using numerical modelling based upon Naiver-Stoke Equations an initial estimation of heat flux and pressure distribution has been calculated and validated using convergence analysis. These results have then been used for finite element modelling of the protection system in order to find the maximum allowable heat flux to have the minimum possible deflection This thermal protection system is modelled as a three-layer system, with a middle layer of Reinforced Carbon Composite (RCC) sandwiched between two layer of Zirconium Bicarbonate (ZrB2). Temperature distribution, stress tensor and displacement across the whole shield have been analysed to ensure the best possible thermo-structural stability. This designed protection system can contain stresses of up to 41 MPa generating a displacement of just 0.57 mm during cruise flight and re-entry. The establishment of those limits as well as the aerodynamic analysis are now leading to a new way to find the most suitable material using optimization principles based on predictive analytics.

9:10 AM

(ICACC-GYIF-012-2019) Electrolytic deposition of protective coating for solid oxide fuel cell interconnects

M. K. King*[1]; M. Mahapatra[1]

1. University of Alabama at Birmingham, Materials Science and Engineering, USA

Electrochemical deposition is a cost effective method for developing protective coatings on solid oxide fuel cell (SOFC) interconnects. Metallic coatings transform to ceramic coatings during SOFC fabrication and operation. We have investigated various deposition parameters (current density, current type, and electrolyte bath composition) on the quality of nickel coating on AISI 430 alloy. It has been found that lowering deposition current density improves the coating uniformity and its adhesion with the substrate but longer time is required to obtain a thick (> 5 μm) coating. However, deploying cyclic voltammetry to identify the deposition voltage eliminates the need to optimize the deposition parameters by trial and error method.

9:30 AM

(ICACC-GYIF-013-2019) Nowotny Phase $Mo_{4.8}Si_3C_{0.6}$ Dispersed in a Porous SiC/C Nanocomposite Matrix: A Novel Catalyst for Electrochemical Water Splitting (Invited)

Z. Yu*[1]

1. Xiamen University, China

Electrochemical water splitting is one of the most efficient ways to produce hydrogen due to its renewability and environmental-friendliness, which urgently requires novel active catalysts for the hydrogen evolution reaction (HER). In this lecture, we report on the in-situ formation of a nano-sized Nowotny phase (NP) $Mo_{4.8}Si_3C_{0.6}$ embedded in a porous SiC-based matrix via a polymer-derived ceramic (PDC) approach. The advanced features of our NP/C/SiC nanocomposite are as follows: i) in-situ formed catalytically active NP nanoparticles within an in-situ generated SiC/C-based matrix to avoid aggregation of the nanosized NP and ii) the simultaneous formation of carbon-rich phases improving the electric conductivity, which significantly increases the charge transfer rate during the HER process. As a result, the NP/C/SiC-based nanocomposites exhibit excellent HER activity in acidic media. The analyzed electrocatalytic performance exceeds that of most Mo_2C-based electrocatalysts. Moreover, our electrocatalytic system shows outstandingly high stability ratio. To the best of our knowledge, this is the first time that a NP is discovered to possess electrocatalytic activity and excellent durability in terms of the HER, which extends and broadens the potential applications of PDCs in the field of energy materials.

Novel Characterization Tools and Methods of Ceramics and Composites

Room: Coquina Salon G
Session Chair: Matthew Appleby, The University of Akron

10:20 AM

(ICACC-GYIF-014-2019) Molecular Design and External Magnetic Field Effects on Structure Formation in Chemical Vapor Deposition

D. Stadler*[1]; T. Brede[2]; D. Bialuschewski[1]; A. Moellmann[1]; T. Fischer[1]; C. A. Volkert[2]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany
2. Georg-August-University, Institute of Materials Physics, Germany

The phase pure formation of materials, may it be macroscopic or in the nano regime requires a good mixing, short diffusion paths and large temperatures. Even though smaller grain sizes are accessible by e. g. ball milling, the formation of secondary phases or undesired side products remains a challenge. A solution for this problem is the design of molecules having the right stochiometric ratio on atomic

scale and the subsequent decomposition to the desired material. In this context, temperature dependent properties, like electronic conductivity and magnetism can be used to further influence the texture and morphology of the sample during preparation. By combining the advantages of molecular design with field assisted processing could lead to new insights in nanostructure formation in magnetic fields. We would like to report on a magnetic field assisted cold wall CVD setup to study film formation of magnetic materials in external magnetic fields. We were able to demonstrate morphological influences in case of iron deposition and suppression of crystal orientation in case of magnetic ceramics during film formation. Different field orientations and strengths were applied during the film growth and will be described comparatively during this presentation.

10:40 AM

(ICACC-GYIF-015-2019) Determination of intrinsic strength of carbon fibers (Invited)

Y. Sugimoto*[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

In the process of developing carbon fibers (CF) from new sources or through new production methods, it is often a matter of great concern to assess the potential ability of the fiber under development. In this study, such a value is called intrinsic strength and has been determined from the strength of bluntly notched CF by taking account of the orthotropy in the mechanical properties of the CF. The finite element analysis showed that the orthotropy in the mechanical properties causes marked increase in the stress concentration at the notch tip. The orthotropic mechanical properties of the CF including the tensile, transversal compression, and torsional moduli were determined on single fibers. A blunt notch was introduced on the surface of CF using a focused ion beam milling machine and the tensile tests were performed on the notched fibers. Using point stress criterion, the intrinsic strength of carbon fibers were determined.

11:10 AM

(ICACC-GYIF-016-2019) Synthesis and Characterization of Novel PEEK-MAX Composites

S. Javaid*[1]; M. Dey[1]; N. Kaabouch[2]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA
2. University of North Dakota, EE, USA

MAX Phases are novel ternary carbides and nitrides bestowed with unique properties like machinability, hardness etc. Recently, we showed that it is possible to reinforce polymer and metal matrices with MAX Phases. In this presentation, we will present recent progress on the synthesis and characterization of PEEK-MAX composites (namely, Ti_3AlC_2, Ti_3SiC_2, and Cr_2AlC). Detailed microstructure and mechanical behavior of these composites will be presented. In addition, we will also report the wettabiliy behavior of these composites.

Careers in Science, Technology, Engineering and Mathematics (STEM)

Room: Coquina Salon G

Session Chair: Matthew Appleby, The University of Akron

11:30 AM

(ICACC-GYIF-017-2019) Navigating from PhD to Industry: Some Best Practices (Invited)

R. M. Paul*[1]

1. GrafTech International Holdings Inc., Technology, USA

Although a PhD is often considered as preparation for an academic career, more and more young professional PhD earners are finding employment in industry. This is in part due to the large gap in available academic positions versus the growing number of PhD earners each year. The goal of this talk is to highlight the lessons learned during my transition from academic to industrial materials scientist, and then to R&D manager. I would like to show which academic skills are well transferred to industry, and which skills may needed to be picked up outside of school. Both academic and industry jobs require a balance of technical and non-technical (e.g. communication) skills. There are several parallels, for example, academics write grant proposals while industry professionals write business cases. I will highlight a few ways to successfully make the industry transition, as well as some decision criteria that may help to guide whether an industry job would be a good fit. The talk should be of interest to students both starting and finishing graduate school, those in post doc or other early career positions, and those who are seeking or already chosen an industry job.

Ceramic Hybrid Materials and Composites for Aerospace, Armor, Biomedical, Electronics, Sensors and Actuators, Energy Conversion and Storage, Photo-catalysis, and Environmental Applications I

Room: Coquina Salon G

Session Chair: Daniele Benetti, INRS

1:30 PM

(ICACC-GYIF-018-2019) Advancing Development of Environmental Barrier Coatings Resistant to Attack by Molten Calcium-Magnesium-Aluminosilicate (CMAS) (Invited)

V. L. Wiesner*[1]; B. J. Harder[1]; A. Garg[1]; N. P. Bansal[1]

1. NASA Glenn Research Center, Materials and Structures Division, USA

Ceramic matrix composites (CMCs) are a leading material system to replace metal-based parts in the hot-section of air-breathing turbine engines to improve fuel efficiency in aircraft engines. CMCs have higher temperature capabilities and lower density compared with traditional metallic structural materials. However, silicon-based CMCs are susceptible to oxidation in the harsh combustion environment encountered in turbine engines. Consequently, environmental barrier coatings (EBCs) are being developed to protect CMC components to improve durability and extend service life of CMCs. Sand, volcanic ash and other particulate debris, which are generally comprised of calcium-magnesium-aluminosilicate (CMAS) and other trace oxides, are routinely ingested by aircraft engines. At temperatures above 1200°C, CMAS particulates melt. Near target operating temperatures (~1500°C) of future CMC-based aircraft engines, molten CMAS behaves like a viscous melt that can infiltrate and chemically interact with protective coatings. These interactions can cause premature failure of the EBC system and ultimately the overall CMC engine component. Degradation of candidate EBC materials by molten CMAS will be presented with a focus on recent work, as well as methods of evaluating the complex high-temperature materials interactions, underway at NASA Glenn Research Center.

2:00 PM

(ICACC-GYIF-019-2019) The emerging roles of carbon dots in solar energy devices

D. Benetti*[1]; Y. Zhou[1]; H. Zhao[3]; A. Vomiero[2]; F. Rosei[1]

1. INRS, EMT, Canada
2. Luleå University of Technology, Sweden
3. Qingdao University, College of Physics, China

To reduce our dependence on fossil fuels and control the greenhouse emissions, it is necessary to transit to more sustainable sources of energy. This challenge may be addressed by using carbon Dots (Cdots) which represent an emerging class of semiconducting nanomaterials. Cdots are exclusively composed of non-toxic elements (C, N and O) and can be synthesized in large quantities via a simple

solvothermal approach. Compared to conventional semiconducting quantum dots (QDs), carbon dots (Cdots) have superior advantages of non-toxicity, environmental friendliness, low-cost and simple preparation using abundant carbon based feedstock. Recently they have been used successfully in different solar applications and also as catalyst material for hydrogen production in combination with different heterostructures. Exploiting the ability to tune the optical and electrical properties of Cdots by changing the synthetic methods, we synthesized different types of Cdots, with absorption and emission spectra in the range 380 nm to 650 nm. The as-prepared Cdots are employed for realizing different devices such as Luminescent Solar Concentrator and Perovskite Solar Cells.

2:20 PM

(ICACC-GYIF-020-2019) Development of regenerative catalyst containing spinel oxide for reforming hydrocarbons

S. Yamaguchi*[1]; T. Ozaki[1]; T. Suyama[1]

1. Osaka Research Institute of Industrial Science and Technology, Applied Material Chemistry, Japan

When reforming hydrocarbons using catalysts for a long term, their active metals agglomerate and the activity decreases irreversibly. To suppress the activity loss, regenerative catalysts by reduction and oxidation (Red-Ox) cycles have been focused. In this study, catalysts composed of spinel oxide containing Ni (NSO) and NSO added with Ru (RNSO) were examined for their repeated regenerative function and catalytic activity of reforming hydrocarbons. The regenerative function of NSO and RNSO were evaluated by temperature programmed reduction and oxidation repeatedly. The crystalline change of NSO and RNSO reduced and oxidized were analyzed by X-ray diffraction and Scanning Transmission Electron Microscopy. When the NSO reduced by hydrogen at over 750 °C, fine particles of Ni were appeared and highly dispersed. When the reduced NSO was oxidized, at 350 °C, Ni was oxidized to NiO and at over 750 °C NiO dissolved in the spinel structure again. Further, the reducing rate of RNSO was faster at lower temperature than NSO. Even after several times Red-Ox cycles, the regenerative function of RNSO was not decreased, compared to that of NSO decreased. Additionally, the catalytic activity of reforming hydrocarbons of NSO and RNSO showed higher than Pt based catalyst. The number of active site of reduced NSO and RNSO were considered to be highly dispersed and more than that of Pt catalyst.

2:40 PM

(ICACC-GYIF-021-2019) Freestanding Nitrogen Doped d-Ti_3C_2/GO Films for High Performance Supercapacitors

W. Zheng*[1]; L. Yang[1]; P. Zhang[1]; J. Chen[1]; W. Zhang[1]; W. Tian[1]; Y. Zhang[1]; Z. Sun[1]

1. Southeast University, School of Materials Science and Engineering, China

A facile method is developed to prepare nitrogen doped delaminated Ti_3C_2/GO (N-d-Ti_3C_2/GO) freestanding film as high-performance binder-free supercapacitor electrodes by vacuum filtration. The results show that the N-d-Ti_3C_2/GO film exhibits a high specific capacitance of 247 F g^{-1} (~420 F cm^{-3}) at 1 A g^{-1} in 6 M KOH. Furthermore, this electrode showed excellent cycling stability, retaining 95% of its initial capacitance after 10000 cycles at 10 A g^{-1}. In addition, the flexible symmetric supercapacitor assembled with N-d-Ti_3C_2/GO films as electrodes is also studied. It delivers a maximum energy density of 15.7 W h kg^{-1} (at 309 W kg^{-1}) and a power density 3738.7 W kg^{-1} (at 11.05 W h kg^{-1}) in PVA/H_2SO_4 gel, which is comparable to carbon and graphene based supercapacitors. This impressive electrochemical performance can be attributed to the following: (1) the nitrogen functionalities not only enhance the conductivity but also afford MXene a high pseudocapacitance; (2) the insertion of GO nanosheets between MXene layers effectively inhibits the self-restacking of MXene layers.

Ceramic Hybrid Materials and Composites for Aerospace, Armor, Biomedical, Electronics, Sensors and Actuators, Energy Conversion and Storage, Photo-catalysis, and Environmental Applications II

Room: Coquina Salon G

Session Chairs: Daniele Benetti, Institut National de la Recherche Scientifique; Valerie Wiesner, NASA Glenn Research Center

3:20 PM

(ICACC-GYIF-022-2019) In situ grown metal nanoparticle catalysts: Properties and control (Invited)

T. Oh*[1]

1. Auburn University, USA

The ability to produce supported metal nanoparticle catalysts via exsolution from a perovskite type oxide support under reducing conditions has been known for some time and is used in some formulations of automotive emissions control catalysts. The ability to re-dissolve and exsolve the metal via redox cycling has led to these systems being referred to as smart or regenerable catalysts. While this phenomenon is well known, the mechanism by which the transition metal is exsolved from the oxide host is still poorly understood. The relationships between the exsolution process and the resulting structure of the metal nanoparticles are also not well understood. In this talk we will discuss our recent mechanistic studies of the exsolution process. In this work we have used well-defined model systems and detailed structural analysis using electron microscopy and atomic force microscopy to characterize the nucleation and exsolution of Ni particles from Ni-doped strontium titanate. These studies show how exsolution produces unique surface structures consisting of metal particles partially submerged in pits on the oxide surface. We will show that this particle-in-a-pit morphology imparts unusually high thermal stability as well as significantly decreased carbon filament formation. Metal exsolution control will be discussed for host oxide lattices in thin film form.

3:50 PM

(ICACC-GYIF-023-2019) Graphene-like clay hybrid materials for environmental and energy applications (Invited)

C. Ouellet-Plamondon*[1]; P. Nguyen-Tri[1]; K. Jhimi[1]

1. ÉTS, Construction, Canada

Clay based materials can be functionalized for a variety of purposes, including environmental, energy and building materials. Hybrid materials from commonly available resources, clay and sugar, are synthesized into a graphene-like materials. The challenges of this research is to characterize the material's properties, to understand the coupling between chemical, mechanical and electrical phenomena, and to study the adsorption of pollutants. The transformation of sugar into a graphene sheet is characterized using Raman and broadband dielectric spectroscopy, X-ray diffraction, thermogravimetric methods, X-ray photoelectron spectroscopy and transmission microscopy. The zeta potential measurement revealed the amphoteric nature of the graphene-like materials, according to acidic and basic properties of the suspensions. The contact angle measurements revealed that the clay graphene-like was hydrophilic. The graphene-like clay was effective for the removal of sodium pentachlorophenate, insecticide and herbicide which used as a wood preservative, rhodamine B and methylene blue. The graphene-like clay also shows good potential for copper and arsenic sorption. This graphene-like clay is promising material to adsorb environmental pollutants. The graphene-like clay is also being investigated for energy applications in polymer composites for underground extruded power cables.

4:20 PM

(ICACC-GYIF-024-2019) Nd^{3+} doped single band nanothermometry and its integration within decoupled theranostics

A. Skripka*[1]; T. Cheng[1]; A. Morinvil[1]; G. Jarockyte[2]; V. Karabanovas[2]; R. Rotomskis[2]; F. Vetrone[1]

1. Institut National de la Recherche Scientifique, Canada
2. National Cancer Institute, Lithuania

Near-infrared (NIR) light for optical bioimaging enables us to peer deeper inside tissues, as it is less absorbed or scattered by tissue constituents than visible light. However, the shift to NIR wavelengths, requires efficient NIR light absorbing and emitting contrast agents. As such, rare earth based nanoparticles (RENPs) provide a versatile platform possessing the desired optical properties, which can be fine-tuned to create NIR imaging probes applicable within a biological milieu. Nd^{3+} doped RENPs are regarded as highly potent contrast agents with their multiple photoluminescence bands spanning a wide NIR region. In addition to imaging, these bands can be used for non-invasive optical temperature sensing, granting an additional layer of information "in one shot". Hence, Nd^{3+}doped RENPs can be used not only to image a target but also to investigate it from a thermodynamic viewpoint, or to monitor in real-time the development of heat based therapies locally – minimizing damage to the surrounding healthy tissues. Here, we investigate Nd^{3+} doped Li-based RENPs as NIR optical contrast agents and nanothermometers. Additionally, we are exploring the integration of these properties within the context of decoupled theranostics, creating multifunctional RENPs where their optical response is wavelength dependent to prompt therapy or diagnostics.

4:40 PM

(ICACC-GYIF-025-2019) Novel Methods for Designing Carbonate Ceramics

M. Ahmann*[1]; M. Alshaya[1]; A. Miles[1]; A. Minhas[1]; M. Abdulrahman[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

Grand Challenge Scholar Program (GCSP) is a novel approach by National Academy of Engineering to train next generation engineers. In this paper, we will present Undergraduate Research as a part of this program and senior design where we will analyze some of the recent issues with CO2 sequestration, and report progress in manufacturing novel materials by CO2 sequestration. We will present detailed microstructure and mechanical performance analysis of novel carbonate ceramics by reinforcing them with biofibers. It is expected that these materials can be used be for various multi-functional applications.

5:00 PM

(ICACC-GYIF-026-2019) In-Situ Phase Diagram Determination of the HfO_2-Ta_2O_5 Binary Up to 3000 °C

S. J. McCormack*[1]; K. Tseng[1]; R. Weber[2]; S. Ushakov[3]; D. Kapush[3]; A. Navrotsky[3]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Materials Science and Engineering, USA
2. Materials Development, Inc., USA
3. University of California, Davis, Peter A. Rock Thermochemistry Laboratory and NEAT-ORU, USA

Ceramic equilibrium phase diagrams have proven to be difficult to produce for materials above 1500 °C. We demonstrate that in-situ X-ray diffraction on laser-heated, levitated samples can be used to elucidate phase fields. In these experiments, solid spherical samples were suspended and rotated by a gas stream through a conical nozzle levitator, heated by a 400 W CO_2 laser at beamline 6-ID-D of the Advanced Photon Source at Argonne National Laboratory. X-ray diffraction patterns suitable for Rietveld refinement were collected at 100 °C temperature intervals and were used to determine the phase fraction of phases present. The temperature of each phase was determined based on thermal expansion data collected by powder diffraction in conjunction with the Quadrupole Lamp Furnace (QLF) at beamline 33-BM-C. The liquidus temperature was determined from recoalescence. The crystal structures of new phases were solved using the charge flipping method from powder diffraction data. The HfO_2-Ta_2O_5 binary was investigated as an example system due to its high melting points and application in refractories and electronics.

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Photocatalysis and Photovoltaics

Room: Coquina Salon C

Session Chairs: Graziella Malandrino, Universita' degli Studi di Catania; Mats Boman, Institute of Chemistry - Angstrom

8:30 AM

(ICACC-FS3-011-2019) Stability Enhancement in Perovskite Solar Cells with Functional Nanocomposites (Invited)

Y. Hahn*[1]

1. Chonbuk National University, School of Semiconductor and Chemical Engineering, Nanomaterials Processing Research Center, Republic of Korea

Solar cells based on organic-inorganic halide perovskites have been a hot topic in photovoltaic industry, but long-term stability should be insured for the practical use of perovskite solar cells (PSCs). It is known that the stability problems attributed to air-induced, thermal and light instabilities and ions migration are critical issues for practical use of perovskite solar cells. In order to solve such problems, we developed composite-based PSCs, using perovskite/silver nanoparticles-anchored reduced-graphene oxide (perovskite/Ag-rGO) and perovskite/NiO nanoparticles composites. The graphene sheets in the perovskite/Ag-rGO composite in active layer not only impede the destructive ions diffusion in perovskite phase but also accelerate the charge transport in the active layer. The thermally-aged cells based on the perovskite/Ag-rGO composites sustained 93.4 % of the initial value of power conversion efficiency (PCE), while the pristine PSCs showed 39 % decrease in initial PCE due to degradation. More importantly, the long-term stability of the composites-based PSCs was exceptional, retaining almost 100 % of the initial values of performance parameters over 330 days under ambient condition (25-30 °C, 45-57% humidity).

8:50 AM

(ICACC-FS3-012-2019) Functional Applications ZnO Tetrapod Nanomaterials made by Flame Transport Synthesis (Invited)

Y. K. Mishra*[1]; L. Siebert[1]; F. Schütt[1]; F. Ceynowa[1]; M. Mintken[1]; S. Shree[1]; I. Paulowicz[1]; O. Lupan[1]; S. Kaps[1]; R. Adelung[1]

1. Kiel University, Institute for Materials Science, Germany

Applications of ZnO tetrapods in: Nanoelectronics, Optics, Composites, Sensing, 3D Materials, Biomedical, and in many other directions, will be briefly presented in this talk. ZnO material with n-type conductivity, bandgap of ~3.37 eV, hexagonal-wurtzite crystal structure, is among pioneering materials towards nanostructuring and broad range of applications. A wide variety of ZnO nanostructural shapes have been synthesized and utilized in many applications but the role of structural aspects, e.g., complex shape, still needs to be addressed. Inspired by unique capabilities of ZnO, we recently developed a flame transport synthesis, which offers very simple and mass-scale fabrication of tetrapod shaped ZnO structures. The 3D shape feature enables these tetrapods to be used as unique building blocks for fabricating highly porous and flexible ceramic materials for advanced technologies as well as used as templates for synthesizing hybrid and new 3D porous nanomaterials.

9:10 AM

(ICACC-FS3-013-2019) The role of gold clusters on electron transfer reactions for hydrogen production over rutile TiO_2(110) single crystal (Invited)

K. Katsiev[2]; G. Thornton[1]; G. T. Harrison[3]; H. Idriss*[2]

1. University College London (UCL), Center for Nanotechnology, United Kingdom
2. King Abdullah University of Science and Technology (KAUST), SABIC Corporate R&D, Saudi Arabia
3. King Abdullah University of Science and Technology (KAUST), KAUST Solar Center, Saudi Arabia

Electron transfer reactions in the photocatalytic hydrogen production rely on the presence of metals of cluster or nanoparticle nature dispersed on top of a semiconductor. Among the most promising methods for the photo-catalytic water splitting are those involving modified ultra-high concentrated solar cells. At very high photon flux, the kinetics of the reactions are expected to be different because of possible cluster sintering and changes in electron transfer rates. In order to explore part of this complex kinetics, H_2 production rates of an electron donor, such as ethanol, over Au clusters with different sizes and coverage deposited on single crystal rutile TiO_2(110) were studied by scanning tunnelling microscopy, online mass spectrometry and complemented by femto second pump probe spectroscopy. The key determining factor appears to be the Au inter-particle distance. Increasing this distance resulted in an increase in the normalized reaction rate. These results are explained in terms of competition between particles for excited electrons to reduce H^+ (of surface OH groups) to H_2. The fact that metal inter-particle distances directly affect the reaction rate indicates that nanostructured synthesis is needed in photocatalyst manufacturing for future technologies.

9:40 AM

(ICACC-FS3-014-2019) Solution-processing of nanostructured materials for solar energy conversion (Invited)

J. Wu*[1]

1. National Cheng Kung University, Department of Chemical Engineering, Taiwan

Conversion of the solar energy into chemical fuel has been realized using photocatalytic processes in which a sequence of steps, i.e., light harvesting, charge separation, and charge injection, take place in the photocatalysts. Charge recombinations occurring in the bulk and at surface states of the photocatalysts are the competing steps with charge separation and charge injection, respectively, which degrade the performance of the photocatalyst. To improve the charge separation efficiency, the morphology and configuration of the photocatalysts need to be well-controlled. Solution-processing of the nanostructured photocatalysts for efficient solar energy conversion will be reported in the presentation. Through the strategies of morphology and interfacial energetic controls, superior photocatalytic performances have been demonstrated in TiO_2-based dual-staggered-heterojunction nanodendrite (ND) arrays and $BiVO_4$-based heterojunction ND arrays. The details of which will be reported in this presentation.

Molecular Precursor Approaches for Vapor-phase Synthesis (ALD, CVD) of Materials

Room: Coquina Salon C

Session Chairs: Hicham Idriss, SABIC; Yogendra Mishra, Kiel University

10:20 AM

(ICACC-FS3-015-2019) Synthesis of functional hard materials by homogeneous and heterogeneous decomposition of molecular precursors (Invited)

M. Boman*[4]; L. von Fieandt[1]; M. Halvarsson[2]; H. Larsson[3]; T. Larsson[5]; O. Bäcke[2]; A. Forslund[3]

1. Sandvik Coromant AB, Sweden
2. Chalmers University of Technology, Sweden
3. Royal Institute of Technology, Sweden
4. Uppsala University, Dep. of Chemistry Angstrom, Sweden
5. Seco Tools AB, Sweden

In thermally activated chemical vapor deposition, the chemical identity of the precursors interacts with the processing parameters, and together they will define several of the properties of the final coating. During the deposition process, precursors undergo chemical reactions on or in the vicinity of the substrate surface, i.e. either heterogeneously and homogeneously. In both cases, such chemical reactions will influence the character of the deposit. By a proper choice of the precursor and the accompanying CVD parameters, for example total pressure and deposition temperature, the properties of the deposit can be tailored. I will in my talk give some recent examples of how the hardness and wear resistance of CVD-coatings can be deliberately affected. One specific example illustrates that almost single crystalline thin films of super-hard Ti(C,N) were deposited and could be optimized by applying a proper combination of precursors and processing parameters. As a result, coatings with better performance were obtained. The CVD coatings were characterized by several materials analysis techniques, including HR-SEM, HR-TEM, ERDA, nano-indentation, several XRD-techniques and AFM. Using DFT, thermodynamic modeling and consideration of kinetics, the investigation gained a more in depth view of the how the coatings were formed on a molecular level.

10:50 AM

(ICACC-FS3-016-2019) Crystalline metal-organic thin films by ALD/MLD: fundamentals and potential applications (Invited)

M. Karppinen*[1]

1. Aalto University, Finland

The ALD/MLD technique is strongly emerging as a highly viable technology for the fabrication of new types of hybrid metal-organic thin films. It is derived from the ALD (atomic layer deposition) thin-film technology commercially used for the fabrication of high-quality inorganic thin films, and from its much less exploited counterpart for purely organic thin films, i.e. MLD (molecular layer deposition). In ALD/MLD the hybrid thin film is grown from gaseous precursors through surface-saturated reactions; this may result in novel bonding schemes and molecular assemblies. Recently we moreover discovered that the technique has the capacity to yield in-situ crystalline metal-organic structures similar to those known for coordination polymer or metal-organic framework materials synthesized from solutions, or even entirely new compositions/structures. An exciting example is the lithium quinone thin films grown from lithium hexamethyldisilazide and hydroquinone precursors. The structure contains coordinatively unsaturated Li^+ sites, which explains why this compound can not be synthesized through conventional solution synthesis. Most excitingly, the material turned out to be a promising cathode material for a Li-ion microbattery. In this lecture, I discuss the fundamentals and future application possibilities of ALD/MLD grown crystalline metal-organic thin films.

11:10 AM

(ICACC-FS3-017-2019) Atomic Layer Deposition of Functional Complex Oxides - A Necessary Challenge (Invited)

H. H. Sønsteby*[1]

1. University of Oslo, Department of Chemistry, Norway

Atomic layer deposition (ALD) of functional complex oxides attracts increasing attention due to the possibility of obtaining chemically and structurally conformal films on substrates with challenging morphology. This presentation will focus on two different complex oxides systems, $La_{2-x}Sr_xCuO_{4-y}$ (LSCO) and $KTa_{1-x}Nb_xO_3$ (KTN) and discuss different challenges and approaches for ALD of highly crystalline films of these materials. LSCO is a superconductor at approximately 30 K, and is the mother structure of most high-T_c superconductors. A major challenge in ALD of LSCO is controlling the copper chemistry via choice of precursor and precursor conditions. Copper oxide can catalytically decompose metalorganic precursors, and this effect must be limited to obtain proper self-limiting growth. We will show an approach for controlling this, while still maintaining control of the total stoichiometry. We will then discuss the properties of the films, and how they can be improved further. KTN is an important paraelectric/ferroelectric with a strong electro-optical behaviour useful for creating efficient integrated photonics optical modulators. The challenge is that very few synthesis techniques produces the material with good stoichimetric control. We will use this example to show how ALD can be used to produce highly uniformal KTN films, building on that to discuss alkali containing complex oxide ALD in general.

11:30 AM

(ICACC-FS3-018-2019) Full vapor phase MOCVD/MLD approach to hybrid metalorganic-inorganic systems (Invited)

A. Pellegrino[1]; G. G. Condorelli[1]; A. Speghini[2]; G. Malandrino*[1]

1. Universita' degli Studi di Catania, Dipartimento Scienze Chimiche, Italy
2. Università degli Studi di Catania, Dipartimento di Biotecnologie, Italy

The metalorganic-inorganic hybrid systems are very appealing due to their potential applications in several fields such as optoelectronic devices, sensors and dye sensitized solar cells (DSSCs). In this perspective, anchoring of appropriate molecular systems on the metal oxide surface allows the development of multifunctional materials, due to the combination of the molecular and oxide functionalities. Up to date, most of the synthetic approach to prepare hybrid systems have applied solution self-assembly routes. In this presentation, we report a full vapor phase approach based on the MOCVD of the inorganic component, NiO films, and the molecular layer deposition (MLD) to assemble the metalorganic monolayer component of the type Eu(β-diket)$_3$L. The present approach is based on the pre-activation of the NiO nanostructured films with water or ozone and the subsequent anchoring of the Eu(β-diket)$_3$L complex through a ligand-exchange reaction between one or two β-diketonato ligands and the terminal –OH groups of the NiO surface. X-ray photoelectron spectroscopy characterization confirmed the covalent anchoring onto nanostructured transparent NiO films of the luminescent europium(III) adduct. Optical properties of the obtained hybrid NiO/Eu(III) system are evaluated by UV/Vis and fluorescence spectroscopy.

11:50 AM

(ICACC-FS3-019-2019) Consolidation of diamond powders with CVD-coated ceramic layers

H. Katsui*[1]; T. Goto[2]; N. Kondo[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Structural Materials Research Institute, Japan
2. Tohoku University, New Industry Creation Hatchery Center, Japan

Dimond has the highest hardness and thermal conductivity, which can be applied for cutting tools and thermal management materials. For consolidating diamond powders to dense compact, sintering should be carried out under ultra-high pressures above several GPa to avoid transformation from diamond to graphite at high temperatures. This study demonstrated the synthesis of diamond-based composites via sintering under moderate pressures of 100 MPa by using diamond powders coated with SiC layers. Staring diamond powders were coated with conformal SiC thin layers with thickness of several tens nanometers by chemical vapor deposition, resulting in core (diamond) /shell (SiC) powders. The core/shell powder mixed with SiO2 powder were rapidly consolidated to fully dense compacts by spark plasma sintering at 1873 K under 100 MPa for 600 s. The coated SiC layers played an important role to form the dense diamond/SiC/SiO2 interface structure without transformation of diamond to graphite during the sintering. As the compacts contained the diamond constituent of 59 wt%, the resultant diamond-based compacts exhibited high hardness up to 36 GPa. The effects of sintering conditions and counterpart materials to diamond on the sintering behavior, microstructure, and mechanical properties will be discussed.

Gas Phase Depositions and In-Situ Characterization

Room: Coquina Salon C

Session Chairs: Samuel Bernard, CNRS IRCER; Ravi Kumar, IIT BHU

1:30 PM

(ICACC-FS3-020-2019) 3D nanoarchitectures for energy technologies and bio-medical sensing - enhancing functionality through correlative microscopy (Invited)

S. Christiansen*[1]

1. Helmholtz Center for Materials and Energy, HZB, Germany

Complex nano-architectures of various material combinations (e.g. Si-nanostructures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications. In this context we will show nano-material choices for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in electrical devices such as resistors. Materials and device optimization will rely on advanced correlated electron microscopy and optical spectroscopy (CORMIC) containing electron beam induced current (EBIC) measurements, I-V characterization with and without illumination (with tunable power and wavelength) inside a scanning electron microscope (SEM), cathodo-, photo- luminescence as well as in-SEM micro-Raman spectroscopy and time-of-flight mass spectrometry (TOF-MS).

2:00 PM

(ICACC-FS3-021-2019) In-situ and in-operando characterization in CVD processes (Invited)

T. Fischer*[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

The full potential of Chemical Vapour Deposition (CVD) techniques can be maxed when using tailored molecular precursors with a predefined arrangement of atoms on the molecular level, thus facilitating solid phase formation at relatively low temperatures. Moreover by changing the ligand sphere in precursor molecules alternate decomposition pathways can be followed resulting in non-stoichiometric or even meta-stable phases for coatings and/or fabrication of nanostructured materials. Only a precise control over the reaction conditions (i.e. temperature, pressure, flow, etc.) as well as an analysis of the ongoing reaction in the gas phase as well as at the solid/gas interface gives access to a complete understanding of the whole deposition processes vital to a full process control. The following presentation will highlight the aspects of controlling

precursor chemistry, reactor design as well as process conditions for the synthesis and integration of nanostructured films of various metal oxides and showcase how in-situ diagnostics using i.e. mass spectrometric analysis and in-operando electrical characterization can support the process development in gas phase deposition reactions.

2:20 PM

(ICACC-FS3-022-2019) X-ray based in situ studies of the ALD growth and thermal stability of Pt nanoparticles (Invited)

E. Solano*[2]; R. K. Ramachandran[1]; M. Minjauw[1]; G. Portale[5]; D. Hermida-Merino[4]; A. Coati[3]; C. Detavernier[1]; J. Dendooven[1]

1. Ghent University, Solid State Sciences, Belgium
2. ALBA Synchrotron Light Source, SWEET-NCD beamline, Spain
3. Synchrotron SOLEIL, SixS beamline, France
4. ESRF European Synchrotron, DUBBLE beamline, France
5. University of Groningen, Macromolecular Chemistry & New Polymeric Materials, Netherlands

We aim to demonstrate that in situ X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) can offer unique insights in the ALD growth and thermal stability of metal nanoparticles (NPs), offering approaches towards superior size and coverage control, and improved stability, as required for applications in catalysis. In a first study, the $Me_3(MeCp)Pt$ precursor is combined with O_2 gas and N_2 plasma to grow Pt NPs, and in situ XRF and GISAXS measurements provide the evolution of Pt loading, NP dimensions and spacing, revealing that the choice of reactant has a significant impact on the NP morphology. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage. A second systematic in situ GISAXS study investigates the coarsening behavior of the Pt NPs and it is found that bigger and more widely spaced NPs as well as larger O_2 partial pressures induce a higher onset temperature for coarsening. These results shed light on the surface oxidation and reduction processes governing Pt NP coarsening. Finally, the influence of Al_2O_3 overcoats on the stability of Pt NPs is probed. The overcoat thickness required to stabilize the NPs is investigated for different Pt NP coverages and sizes, highlighting the challenges of this approach for closely packed Pt NPs.

2:40 PM

(ICACC-FS3-023-2019) High Activity Heterogeneous Catalysts by Plasma-assisted Chemical Vapor Deposition of Volatile Palladium Complexes on Biomorphic Carbon

M. Frank*[1]; L. Czympiel[1]; T. Fischer[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Novel palladium complexes based on allyl and alkenolate ligands were synthesized and structurally characterized. Combination of delocalized allylic sp^2-hybridized carbon centers and a strongly binding N^O chelating unit (e.g. 3,3,3-trifluoro(pyridin-2-yl) propen-2-olate) offered a promising combination of high volatility and thermal lability not commonly observed in noble metal precursors. Application of the new Pd compounds in thermal metal-organic (MOCVD) as well as plasma-enhanced chemical vapor deposition (PE-CVD) demonstrated their clean and efficient decomposition pathways, which in conjunction to their intriguing air stability made them efficient precursors for Pd films and clusters. PE-CVD of the palladium compounds on biomorphic carbon used as a porous substrate with high surface area and inter-connected channels delivered recyclable carbon-supported Pd catalysts (Pd@BioC), which showed excellent selectivity, stability and recyclability in C-C coupling reactions.

Solution Procesing and Photocatalysts

Room: Coquina Salon C

Session Chairs: Silke Christiansen, Helmholtz-Zentrum für Materialien und Energie Berlin (HZB); Thomas Fischer, University of Cologne

3:20 PM

(ICACC-FS3-024-2019) Crosslinking chemistry of liquid preceramic polymers toward processable precursors of functional Si-based carbides, carbonitrides and nitrides (Invited)

D. Lopez-Ferber[1]; A. Lale[1]; M. Schmidt[1]; M. Wynn[1]; S. Bernard*[1]

1. CNRS IRCER, France

A very convenient precursor route to produce high-tech ceramics including SiC and Si_3N_4 is the polymer derived ceramics (PDCs) route. The implementation of the PDCs route is motivated by the possibility to generate ceramics without undesirable elements, complex compositions and micro-/nanostructures and to process materials in particular shapes as well as specific textures (dense or porous) that are difficult, or even impossible to obtain by conventional routes. The shaping potential of polymers is closely related to their chemistry and in particular to their degree of crosslinking, the type of bonds that link monomeric units as well as the nature of the functional groups attached to the elements composing the polymer backbone. Crosslinking chemistry offers precise control over the crosslinking reactions of liquid preceramic polymers. In this presentation, we describe an effective and a simple approach that consists of tailoring the crosslinking degree of liquid polysilazanes and polycarbosilanes with low molecular weight metal and metalloid-based species. This strategy allows synthesizing preceramic polymerswhich are shown to develop and extend the processability of neat polysilazanes/polycarbosilanes while forming ceramics with tailored functionalities according to their composition, shape, structure and texture.

3:50 PM

(ICACC-FS3-025-2019) Highly porous $TiNb_2O_7$/carbon microtube composites as a novel anode material for lithium-ion batteries

R. Kumar*[1]

1. Indian Institute of Technology-Madras (IIT Madras), Department of Metallurgical and Materials Engineering, India

$TiNb_2O_7$ (TNO) has been considered as a promising intercalation type anode material in recent times for lithium-ion batteries (LIBs), which satisfy high theoretical capacity (~388 $mAhg^{-1}$) and high discharge voltage (~1.6 V). However, the practical application of TNO is limited by its poor rate capability resulting from low electronic conductivity and poor ionic diffusivity. Herein, we report a simple method to overcome the above disadvantage by preparing a porous $TiNb_2O_7$/ carbon micro-tube (TNO/CMT) composites using precursor route. The porous TNO is synthesized by reacting niobium ethoxide with titanium isopropoxide (molar ratio=2:1) and F127 as surfactant via sol-gel method, followed by heating at 800°C under ambient atmosphere. CMTs are prepared from the pyrolysis of chicken feathers under nitrogen atmosphere. X-ray diffraction analysis (XRD) results revealed the formation of $TiNb_2O_7$ as crystalline phase with no mixed oxide phases and possessing high surface area. Scanning electron microscopy (SEM) confirms the microtube morphology of the carbonized chicken feather with diameter ranging from 20 to 50 μm. The preliminary results exemplify great potential for TNO/CMT composites as an anode material for LIBs.

4:10 PM

(ICACC-FS3-026-2019) DFT-guided design of heterojunctioned photocatalysts (Invited)

H. Choi*[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

In spite of synthetic complexity, heterojunctioned or heterostructured nanomaterials are widely developed for photocatalytic activity enhancement. The activity enhancement of photocatalysts having heterojunctions are mostly comes from the effective separations of photoexcited electron and hole pairs. However, it is time-consuming work to measure the band alignments of each materials and phases in advance of synthesis. Density functional theory (DFT) calculation is capable of predicting band alignments of nanomaterials and thermodynamic stabilities of solid phases. In this study, I will present how DFT calculations can be utilized to develop and discover photocatalytic materials in heterojunctions with combinations of theoretical predictions and experimental verifications.

4:30 PM

(ICACC-FS3-027-2019) Nano-structured sponges through solution chemistry (Invited)

G. Westin*[1]

1. Uppsala University, Sweden

There is a strong demand for tailored materials for sensors, catalysts, solar-cells and energy storage for renewable energy areas. Typical features of these materials are; a large interface to the surrounding liquid electrolyte, reaction liquid, or gas phase, surface modification for e.g. band structure and corrosion control, and catalysis. Often a high conductivity is required to get generated electrons out to the surface or electrode which implies materials of high crystalline quality with controlled dopant positioning, as well as a good connectivity though the structure. Here we present new salt-based synthesis routes yielding oxide sponges of various contents at down to 200°C, 3min. Systems such as doped and non-doped ZnO and MgO will be discussed in detail from the solution to the final products, as well as some of their properties. The sponges obtained at 200°C typically consist of highly porous bread-like structures built up from well connected, ca 10 nm crystallites. These structures do not sinter together, even on heating to 900°C, but from ca 500°C, a reproducible grain growth took place within the sponge structures allowing for tuning of crystal sizes. The processes and products were studied with; TG/DTA/DSC, XRD, IR and Raman spectroscopy, SEM-EDS, TEM-EDS/ED, and XPS.

4:50 PM

(ICACC-FS3-028-2019) Application of Water-soluble Titanium Complexes for Synthesis of Titania Nanocrystals (Invited)

M. Kobayashi*[1]; H. Kato[1]; M. Kakihana[1]

1. Tohoku University, Japan

In the synthesis of materials containing titanium by solution methods, chlorides, sulfates or alkoxides are often employed as raw materials due to its high hydrolysis nature. They can be actually used only under limited experimental conditions, and one must suffer from the difficulty of their handling because of their toxicity and instability. We have developed a series of water-soluble titanium complexes, which do not undergo a hydrolysis under ambient conditions and in a wide range of pH. Application of water-soluble titanium complexes led to success in selective synthesis of titania polymorphs by a hydrothermal treatment of the complexes. Only by changing ligand and/or additive, anatase, rutile, brookite, and TiO_2(B) were obtained as a single-phase material without post treatments such as annealing. Moreover, morphologies of titania polymorph particles were controlled by the hydrothermal treatment of the complexes in the presence of given simple molecules. Recently, we found that synthesis of titania crystals with high energy facets was achieved using this approach. In addition, a molecular dynamics simulation was conducted to elucidate the conformation and dynamics of organic molecules as a molecular control agent. In our presentation, we will summarize our results on selective synthesis and morphological control of titania polymorphs using a series of water-soluble titanium complexes.

5:10 PM

(ICACC-FS3-029-2019) Semiconductor Nanoheterostructures for Photoconversion Applications (Invited)

Y. Chiu[1]; M. Kuo[1]; T. Lai[1]; P. Hsieh[1]; Y. Hsu*[1]

1. National Chiao Tung University, MSE Department, Taiwan

With the inherently high degree of complexity, nanoheterostructures composed of two or more materials joined in unique architectures may exhibit superior synergetic properties that are difficult or impossible to acquire from their individual constituents. For semiconductor nanoheterostructures, the relative band alignment of the constituents promotes effective charge separation to bring them desirable properties for photoconversion applications. Several representative works from our lab, including Au-decorated ZnO nanocrystals, Ti-Nb-Ta-Zr-O Nanotubes, Au@Cu_2O core@shell nanocrystals and Au@Cu_7S_4-decorated TiO_2 nanowires, will be introduced to demonstrate the promising potentials of semiconductor nanoheterostructures.

5:30 PM

(ICACC-FS3-030-2019) Facile precursor-mediated synthesis of binary and ternary G11 metal selenide-based nanomaterials for improved photocatalysis

S. Mishra*[1]; S. Gahlot[1]

1. University of Lyon, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), France

Titanium dioxide (TiO_2) is one of the most promising photocatalysts due to its low cost, non-toxicity, chemical stability and high catalytic activity. However, it mainly absorbs in the UV region of the solar spectrum which represents only ~3.5% energy of the total solar light. Its catalytic efficiency is further reduced by a relatively easy recombination of the photogenerated electrons/holes. To overcome these limitations, the current research focuses mainly on decreasing the band gap of TiO2 by introducing some defects. This usually increases the wavelength range for the absorption but only at the cost of a decreased activity for TiO_2. To improve the efficiency of TiO_2, we are currently focusing on its nanocomposites with low bandgap metal chalcogenide semiconductors. This talk deals with precursor-mediated synthesis of binary and ternary G11 metal selenide nanoaprticles under mild conditions. It will describe different reaction conditions which lead to different reactivities of the starting reagents, affording either molecular complexes or inorganic nanoparticles directly. The factors governing the divergent reactivity and the structures of the molecular species trapped during the course of the reactions will be discussed and photocatalytic efficiency of nanocomposites of these metal chalcogenides with TiO_2 will be presented.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Fibers, Matrices, Coatings, and Interfaces

Room: Coquina Salon D
Session Chairs: Emmanuel Boakye, UES Inc.; Craig Smith, Ohio Aerospace Institute

8:30 AM

(ICACC-S1-011-2019) The Effect of Grain Size on Creep Resistance of Silicon Carbide Fiber

K. Wada*[1]; M. Oakmura[1]; M. Takeda[1]

1. NGS Advanced Fibers Co., Ltd., Japan

Silicon carbide fibers have good heat resistance and high modulus. They are provided with flexible, multi-filament yarn. Recently, CMC Shrouds reinforced by SiC fibers were applied in commercial jet engine, "LEAP". New factory of SiC fiber production with capacity 10ton per year was established at NGS Advanced Fibers Co. in Toyama, Japan. For further industrial application, e.g. aerospace, power generator and nuclear power, SiC fiber with improved creep resistance at high temperature would be required. This presentation discusses the results of recent studies aimed SiC fibers with improved creep resistance at high temperature more than 1500 degree C. SiC fibers were annealed at high temperature in order to grow SiC crystal. After annealing, tensile strength at room temperature and bend stress relaxation (BSR) test were performed for these fibers. The microstructure was analyzed with X-ray diffraction (XRD) and scanning electron microscopy (SEM). As a result, enhanced creep resistance of fiber was achieved with larger grain size, as compared with current Hi-Nicalon TypeS.

8:50 AM

(ICACC-S1-012-2019) Effect of Amorphous SiC fiber degradation on mechanical properties of Ceramic Matrix Composites

S. Kanazawa*[1]; N. Yamazaki[1]; K. Kubushiro[1]; T. Nakamura[1]

1. IHI Corporation, Materials, Japan

SiC-based fibers are classified into two groups, expensive Crystallite SiC-based fiber and cheap Amorphous SiC-based fiber. Crystallite SiC-based fiber has higher strength properties at elevated temperatures compared to Amorphous SiC-based fiber. On the other hand, Amorphous SiC-based fiber has excellent ductility and its productivity of CMC is superior to Crystallite SiC-based fiber. Therefore, a good understanding of influencing factors on strength properties of Amorphous SiC-based fiber and use of Amorphous SiC-base fiber in un-degradation conditions enable to manufacture a cheap and high strength CMC. In this study, in order to clarify the Amorphous SiC-based fiber degradation effects on the mechanical properties of CMC composed of Amorphous SiC-based fiber, the fibers and CMC were exposed at different heat treatment conditions and tensile tests were conducted.

9:10 AM

(ICACC-S1-013-2019) Innovative manufacturing process of the new SILAFIL® silicon carbide fiber

W. Humbs*[1]; M. Rothmann[1]

1. BJS Ceramics GmbH, Germany

An update on the status of our own silicon carbide fiber development will be presented. We use a dry spinning technique to process our own unique polysilane precursor. Tuning of rheological properties is the key to a stable spinning process. Finally, we yield a 200tex ceramic SiC fiber by effective high-temperature treatment. The influence of various processing parameters on the fiber properties will be discussed. We will also give an overview of the competitive room and high- temperature properties of our new SILAFIL® SiC fibers. The mechanical properties have been determined by single filament tensile tests. The composition of the ceramic was measured by hot gas extraction methods. Finally, we will present an outlook on the transfer of our lab-scale technology into pilot-scale, which will start from mid 2019.

9:30 AM

(ICACC-S1-014-2019) Rare earth disilicate fiber coatings for SiC/SiC CMCs

E. E. Boakye*[1]; P. Mogilevsky[1]; T. A. Parthasarathy[1]; T. Key[1]; M. Cinibulk[2]; R. Hay[2]; S. Opeka[1]

1. UES Inc., Materials Science, USA
2. Materials Directorate AFRL, USA

Rare-earth disilicates ($RE_2Si_2O_7$) are potential oxidation-resistant alternatives to carbon or BN fiber coatings for SiC/SiC CMCs. Our prior work experimentally demonstrated that rare earth disilicates may work as a weak interface in fiber-reinforced SiC/SiC CMCs. However, the effect of oxidation, especially in water vapor, on their functionality as a weak interface has not yet been tested. In this work, SiC/SiC mincomposites with $Y_2Si_2O_7$ interface were exposed to steam at 1000°C/10h and tensile tested. Minicomposites with BN interfaces were used as control. The effect of steam on the functionality of the two interface coatings was studied and will be reported.

10:10 AM

(ICACC-S1-015-2019) Development of fiber-matrix interface for non-oxide CMC for gas turbine applications

C. Steinborn*[1]; H. Klemm[1]; A. Michaelis[1]

1. FhG IKTS Dresden, Germany

Caused by the steady increasing energy price and the stronger requirements in environmental protection the main focus of future generations of gas turbines will be emphasized on an increased efficiency with a simultaneous reduction of the emissions. From technical point of view these goals can be obtained only by higher operating temperatures in the system in combination with lower amount of cooling air. Ceramic matrix composites (CMC) offer a high potential for applications as structural parts in advanced gas turbines. During recent years, significant progress in material development of oxide and non-oxide CMC has been achieved, however, there are still considerable deficits in their behavior at elevated temperatures in hot gas conditions. The present study is focused on the damage tolerance behavior of non-oxide CMC. Several new fiber coating systems were developed and fabricated by chemical vapor deposition. The functionality of the fiber coatings was characterized on model composites with different matrices by single fiber push-out test (micro-indentation). Based on comprehensive microstructural investigations general concepts for the development of fiber coatings with high stability at elevated temperatures will be provided.

10:30 AM

(ICACC-S1-016-2019) The Role of Heat Treatment on Mechanical and Thermal Properties of Carbon-Silicon Carbide Hybrid Nano-Fibers

S. Nabat Al-Ajrash*[1]; K. Lafdi[1]

1. University of Dayton, Chemical and Materials Engineering, USA

A hybrid Carbon - Silicon Carbide (C-SiC) nano-fibers were fabricated using polyacrylonitrile (PAN) and Silicon (Si) nanoparticles as precursors. A uniform nano-fibers with few silicon nanoparticles on the fibers skin were observed using SEM and TEM characterization techniques. The microstructural properties of the material at different temperatures and holding times were examined using X-Ray diffraction. The complete transformation of Si to SiC occurred at 1250 °C. However, below 1000 °C three phases (Si, C, and SiC) were observed as a result of incomplete transformation of Si to SiC. The effect of the microstructural changes, due to

the heat treatment, on the oxidation resistance was determined using thermal gravity analysis (TGA). Furthermore, the char yield showed an exponential growth with increasing the carbonization temperature from 850 ºC to 1250 ºC. The holding times at higher temperatures showed a massive increase in fibers thermal properties because of SiC grain growth. At higher holding times, the SiC has the function of coating and reinforcing phase. Such structural changes were related to fibers mechanical properties. The highest tensile strength was recorded for carbonized fibers at 850 ºC, while the modulus kept increasing its value with increasing carbonization temperature.

10:50 AM

(ICACC-S1-017-2019) Properties of BN-coated SiC fibers in SiC-based matrices

E. B. Callaway*[1]; F. W. Zok[1]

1. University of California, Santa Barbara, Materials Engineering, USA

Mechanical properties of SiC-SiC composites are critically dependent on the properties of the fiber coatings, typically BN. In the present study we examine the coating properties in several representative composites using fiber push-in tests. Analyses of the test results reveal two distinct behaviors: one in which a crack forms suddenly within the coating or at one of the interfaces with neighboring phases, followed by interface sliding; and another in which yielding of the BN precedes cracking. Micromechanical models are used to interpret the two behavioral types and to determine the pertinent properties. The results indicate that the shear yield stress of the BN coating may fundamentally change the nature of the failure processes in SiC-SiC composites, especially the characteristics of load transfer between fibers and matrix in the vicinity of cracks.

11:10 AM

(ICACC-S1-018-2019) Evaluation of tensile strength distribution of SiC fiber filaments within a multifilament tow

S. Okuizumi*[1]; T. Aoki[2]; Y. Asakura[1]; T. Ogasawara[1]

1. Tokyo University of Agriculture and Technology, Graduate School of Engineering, Japan
2. Japan Aerospace Exploration Agency, Japan

This study examined the tensile strength distribution of crystalline SiC fibers (Tyranno SA, Hi-Nicalon Type S) and amorphous SiC fibers (Tyranno ZMI, Nicalon, Hi-Nicalon) using multifilament tows. The experimental results for Hi-Nicalon Type-S fibers under a constant displacement rate of 0.6 mm/min at room temperature were reasonable. However, the sudden load drop (unstable failure) after reaching the maximum load was observed for ZMI,Nicalon and Hi-Nicalon fibers under the same loading condition, resulting in considerable scattering in the strength and rupture strain. Although the unstable failure after reaching the maximum load was not observed in Tyranno SA fibers, the maximum loads exhibited considerable scattering. Decreasing the displacement rate to be 0.12 mm/min, stable fiber breakages were observed except Hi-Nicalon fibers. Furthermore, raising the test temperature to be 210 ºC, the stable fiber failures were achieved even for Hi-Nicalon fibers. These experimental results imply that the sizing agent (poly vinyl alcohol, PVA) contribute the load transfer between fibers. Therefore, it was suggested that reducing the viscosity of the sizing agent might be effective to obtain reasonable results.

11:30 AM

(ICACC-S1-019-2019) Effects of Boria on Rare Earth Silicate Environmental Barrier Coatings

R. Guarriello*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA

SiC/SiC CMCs (Silicon Carbide Ceramic Matrix Composites) have recently come into use for hot section components of turbine engines. It is important to understand any reactions between the composite substrates and the Environmental Barrier Coatings (EBCs) used to protect them in high temperature combustion environments. These CMCs are comprised of SiC fibers surrounded by a BN (boron nitride) interphase in a SiC matrix. The BN oxidizes at high temperatures to form B_2O_3 (boria) on the surface of the CMC. Boria is a strong glass-former when in contact with other oxides such as the Ytterbium DiSilicate (YbDS) currently used as an EBC. Little is known about phase equilibria and reactions in the Yb_2O_3-SiO_2-B_2O_3 system. This project seeks to understand these issues through two complementary studies; the first focusing on interfacial reactions in the system and the second being the determination of phase diagrams for this complex oxide system. One of these studies is an idealized interface test between the oxide constituents. Wells are drilled into Spark Plasma Sintered or Air Plasma Sprayed samples of the YbDS material and then filled with plugs of pure boria glass. After heat treatment, multiple reaction zones appear showing formation of previously unexplored phases. These reaction products will inform the phase diagram and help to understand the interactions between the EBCs and the boria formed from the CMC.

Processing - Microstructure - Mechanical Properties Correlation I

Room: Coquina Salon D
Session Chairs: Yogesh Singh, The University of Akron; Michael Presby, University of Akron

1:30 PM

(ICACC-S1-020-2019) High Temperature Fatigue Property of SiC/SiC CMC Manufactured from Low Temperature Melt Infiltration Process

K. Kubushiro*[1]; S. Kanazawa[1]; N. Yamazaki[1]; T. Nakamura[1]

1. IHI Corporation, Japan

Melt Infiltration (MI) process, one of the Ceramic Matrix Composites (CMC) manufacturing process, can form the dense matrix in short time compared to the other process. However Amorphous SiC-based fibers are degraded during MI process because of the high process temperature over 1414ºC which is the melting point of Si. Therefore decreasing process temperature and inhibiting fiber degradation is necessary without loss of MI process merits. Recently it is reported that Si alloy with low melting point can decrease the process temperatures, called Low Temperature Melt Infiltration (LMI). High UTS and strain at failure of CMC by Low Temperature Melt Infiltration Process (LMI-CMC) indicated beneficial. Though information of fatigue property for LMI-CMC is almost nothing. The purpose of this work is to clarify fatigue property of LMI-CMC and investigate the degradation mechanism.

1:50 PM

(ICACC-S1-021-2019) Net shape CMC components obtained by pyrolysis and reactive melt infiltration of continuous carbon fibers and PEEK matrix preforms produced by composite flow molding

G. Bianchi*[1]; A. Vodermayer[2]; A. Ortona[1]

1. SUPSI, MEMTi, Switzerland
2. icotec, Switzerland

This work shows how to produce net shape ceramic matrix composites (CMC) artefacts by a modified injection moulding technique called composite flow molding (CFM) followed by pyrolysis and reactive silicon infiltration. The peculiarity of the produced components stands in their microstructure which is characterized by fibres crossing the part without interruption. This new method will open the use of CMCs to complex geometries for structural applications because they can be produced to net shape without machining and thus interrupting the fibres. A net shape CMC screw was manufactured, but other shapes, such as: bolts, nuts, rivets, springs and even turbine blades can be easily produced.

2:10 PM

(ICACC-S1-022-2019) Composites elaborated with acid-based geopolymers

V. Mathivet*[1]; H. Celerier[1]; J. Jouin[1]; S. Rossignol[1]; M. Parlier[2]

1. Laboratoire IRCER, France
2. ONERA, France

To reduce the cost of current ceramic matrix composites, geopolymers could be used as new matrices. However, alkali-based binders are not suitable due to fibers degradation induced by remaining alkali ions. Consequently, acid-based geopolymers are a promising alternative with improved mechanical properties and formation of refractory phases as $AlPO_4$ with increasing temperature. This study focuses on the selection of the formulation of an acid-based geopolymer matrix to obtain a suitable impregnation of fibers. The studied matrices were elaborated with various water contents. The impact of the concentration on the geopolymer structure was studied by Fourier Transform Infrared spectroscopy, X-ray diffraction, thermal analyses and rheological study. Composites were elaborated with different formulations to determine the most suitable matrix and were characterized by Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy. The addition of water in the formulation leads to an important decrease of the viscosity accompanied by a decrease of water resistance and an increase of fire resistance of the geopolymer matrix after consolidation. The addition of water modifies the structure of the geopolymer. A formulation was determined for a suitable impregnation of the fibers.

2:30 PM

(ICACC-S1-023-2019) Coherency Strains and Strengthening of Bulk Polycrystalline MgO-based 'Ceramic Alloys'

L. Gurnani*[1]; U. Kumar[1]; A. Mukhopadhyay[1]

1. IIT Bombay, Metallurgical Engineering and Materials Science, India

The present research explores the influences of coherency strains at precipitate/matrix interfaces on the relative improvements in mechanical properties of bulk polycrystalline 'age-hardened ceramic alloys' containing uniformly dispersed coherent intragranular precipitates, as obtained here upon aging of sintered supersaturated ceramic solid solutions of MgO-7wt.%Fe_2O_3 and MgO-3wt.%Cr_2O_3 (systems selected due to different coherency strains and matrix/precipitate interfaces). The 'aging' treatments led to uniform precipitation of nanosized second phase particles ($MgFe_2O_4$ and $MgCr_2O_4$ for the respective alloys), with the intragranular precipitates being coherent with the MgO matrix. The alloys exhibit improved hardness (by ~52% for MgO-$MgFe_2O_4$ and ~84% for MgO-$MgCr_2O_4$) and indentation toughness (by ~35% for MgO-$MgFe_2O_4$ and ~45% for MgO-$MgCr_2O_4$) w.r.t. monolithic MgO. Improvements in abrasive wear resistance and compressive strengths have also been recorded with the alloys. Of more interest here is that the experimentally observed hardness increments agree best with those estimated based on strengthening due to coherency strains. Hence, despite lesser content of second phase particles, the greater hardness increment for MgO-$MgCr_2O_4$ alloys w.r.t. MgO-$MgFe_2O_4$ alloys (by ~32%) is attributed to higher coherency strains (~1%) at MgO- $MgCr_2O_4$ interface, as compared to ~0.4% at MgO-$MgFe_2O_4$ interface.

3:10 PM

(ICACC-S1-024-2019) Fracture, Fatigue, and Wear in Alumina/Graphene Nanocomposites

Q. Wang*[1]; C. Watts[1]; O. López[2]; A. L. Ortiz[2]; N. P. Padture[1]

1. Brown University, Engineering, USA
2. Universidad de Extremadura, Spain

Graphene, known for its exceptionally high strength and stiffness, is a promising reinforcement material for improving a variety of mechanical properties of advanced ceramics. Here we show that the incorporation of aligned graphene-based reinforcements in alumina matrix can result in significant toughening due to crack-wake bridging. We have used in situ scanning electron microscopy characterization to elucidate the anisotropic toughening mechanisms in these nanocomposites. We have also investigated the sliding-wear of these nanocomposites, considering that the 2-D graphene layers are expected to provide built-in lubrication for improved wear-resistance. While this effect is demonstrated in certain orientation of the graphene-based reinforcements, there are some countervailing effects that lead to reduction in the wear-resistance. Finally, we have discovered that, in contrast to conventional ceramic composites toughened by fibers or whisker where the efficacy of the crack-wake bridging degrades in cyclic-fatigue, the graphene-based reinforcements are relatively immune to fatigue degradation. All these results are discussed in the context of achieving ceramic/graphene nanocomposites that are tough, and are also resistant to sliding-wear and cyclic-fatigue.

3:30 PM

(ICACC-S1-025-2019) Evaluation of Mechanical and Micro-Failure Sensing of Composites via Pencil Led Drawing Paper Sensor and Electrical Resistance Mapping

J. Park*[1]; H. Park[1]; P. Shin[1]; J. Kim[1]; Y. Baek[1]; L. K. DeVries[2]

1. Gyeongsang Natl University, Materials Eng. & Convergence Technology, Republic of Korea
2. The University of Utah, Dept of Mechanical Engineering, USA

Graphite pencil led drawing paper sensor (PLDPS) is an innovative flexible and wearable sensing device. It can be a new concept sensor that offers many potential advantage for a variety of applications, as a flexible damage or strain sensor on microfailure mechanisms and deformation of different shaped structural composites. Highly responsive, sensitive, low cost, easy-to-handle graphite pencil led in paper made of cellulose pulp fibers from wood are inexpensive nature-friendly materials. Sensing effects on 3 different papers (plane, Hwasun, Han papers) based on the properties of PLDPS were compared by combined with FT-IR, wettability, various mechanical tests, surface observation and the change in electrical resistance (ER). The mechanical properties of neat epoxy and glass fiber (GF)/epoxy composites were evaluated for micro-failure damage and strain sensing. The ER mapping using PLDPS was plotted correspondently during impact, flexural, and interlaminar shear strength (ILSS) testing. The optimum type of paper used as the adherend of the PLDPS was a plane paper. As the neat epoxy and GF/epoxy composites were damaged stepwise, the ER changes of PDPS were responded consistently well. Acknowledgement: This work was supported by National Research Foundation of Korea (NRF) grant funded by Korea government (MOE) (No.2016R1D1A1B01012620), 2016-2022.

3:50 PM

(ICACC-S1-026-2019) Fabrication of SiC/silicides composites by melt infiltration method

T. Tsunoura*[1]; N. Hayama[2]; K. Yoshida[3]; T. Yano[3]; T. Aoki[4]; T. Ogasawara[5]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan
2. Tokyo University of Science, Department of Mechanical Engineering, Japan
3. Tokyo Institute of Technology, Laboratory for Advanced Nuclear Energy, Japan
4. Japan Aerospace Exploration Agency, Aeronautical Technology Directorate, Japan
5. Tokyo University of Agriculture and Technology, Department of Mechanical Systems Engineering, Japan

Melt infiltration method is one of the most reasonable methods to fabricate SiC-based composites for high temperature components. One of the disadvantages of the composites is low heat resistance because Si in matrices of the composites melts above the melting point of Si around 1400oC. We focused on silicides instead of Si. Some silicides have higher melting point than Si. Hence, it is

expected that SiC/silicides show the higher melting point. In this study, SiC/silicides were fabricated by melt infiltration method, and mechanical properties of the composites were evaluated. The reactivity of silicides with SiC was evaluated, and silicides were classified as reactive silicides such as $TiSi_2$ and non-reactive silicides such as $CrSi_2$. The silicides were infiltrated into SiC preform. Then, the melting point of the composites was evaluated, and bending test was carried out up to 1400oC. SiC/reactive silicides showed low heat resistance below melting point of Si because the composition of matrices of the composites was changed to Si-rich composition due to reaction with SiC. On the other hand, SiC/non-reactive silicides showed high melting point as the silicides. The SiC/non-reactive silicides were stiff at high temperature.

4:10 PM

(ICACC-S1-027-2019) SiC_f/Eutectic silicon alloy matrix composites fabricated by melt-infiltration processing

T. Aoki*[1]; T. Tsunoura[2]; K. Yoshida[2]; T. Ogasawara[3]

1. Japan Aerospace Exploration Agency, Advanced Composite Research Center, Institute of Aeronautical Technology, Japan
2. Tokyo Institute of Technology, Japan
3. Tokyo University of Agriculture and Technology, Japan

Silicon melt infiltration is a practical processing employed for matrix formation of SiCf/SiCs. Principally, this processing requires the temperatures above the melting point of Si, i.e., >1414°C. At such high temperatures, amorphous SiC fibers undergo pyrolysis and crystallization that degrade their original strength. Therefore, crystalline SiC fibers are preferred as the reinforcement for the processing. However, utilization of expensive crystalline fibers increases the price of the components. The objective of this study is to propose a cost effective processing for forming a dense matrix for amorphous-SiC-fiber composites. Attentions have been placed upon the binary Si alloys with low melting points. For example, Si alloys loaded with 18at.%Y, 16at.%Ti, 10at.%Zr and 8.5at.%Hf exhibit lower melting points than pure Si by 80-175°C. It is therefore expected that the melt infiltration with these Si alloys inhibits degradation of the reinforcing fibers while keeping high productivity. This study presents the effects of adding elements such as Hf, Ti, Co, Fe, etc. in silicon alloys on the mechanical and oxidation behaviors of amorphous-SiC-fiber/silicon alloy matrix composites. Moreover, mechanical properties of the binary alloys were investigated at elevated temperatures to discuss suitable adding elements from the view points of the strength and oxidation resistance.

4:30 PM

(ICACC-S1-028-2019) Fabrication of SiC/ternary silicon alloy matrix composites by melt infiltration method

N. Hayama*[1]; S. Ogihara[1]; R. Kitamura[1]; T. Tsunoura[2]; T. Aoki[3]; T. Ogasawara[4]

1. Tokyo University of Science, Japan
2. Tokyo Institute of Technology, Japan
3. Japan Aerospace Exploration Agency, Japan
4. Tokyo University of Agriculture and Technology, Japan

SiC-fiber-reinforced SiC matrix composites (SiC_f/SiC) fabricated by silicon melt infiltration are expected as high-temperature structural materials because of the excellent stability at elevated temperatures. However, heat resistance of the composites is limited at temperatures bellow 1400°C due to the presence of free Si in the matrix. In order to improve the heat resistance, the present authors are paying attention to ternary silicon alloys as the matrix of SiC-fiber-reinforced composites. In this study, ternary silicon alloys having the melting points higher than 1500°C and low reactivity with SiC were selected with the aide of a thermodynamic calculation. The candidate alloys were then melt-infiltrated to a porous SiC preform to evaluate the melting point and mechanical properties. Microstructural observations revealed that several Si-V-Cr alloys showed a limited attack to the SiC phases in the preform and excellent infiltration ability. Moreover, Si-V-Cr alloy matrix showed load bearing capability even at temperatures exceeding 1400°C.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Environmental Barrier Coatings - Materials, Processing & Properties II

Room: Tomoka B
Session Chair: Kang Lee

8:30 AM

(ICACC-S2-009-2019) Development of environmental barrier coatings for non-oxide ceramic matrix composites (Invited)

H. Klemm*[1]; W. Kunz[1]; B. Gronde[1]; K. Schönfeld[1]

1. FhG IKTS Dresden, Germany

Ceramic matrix composites (CMC) offer a high potential for applications as structural parts in advanced gas turbines. During recent years, significant progress in material development of oxide and non-oxide CMC has been achieved, however, there are still considerable deficits especially in the long-term behavior of the materials in hot gas conditions. The present study is focused on the environmental stability of the materials. Caused by the high water vapor pressure in combination with high temperatures and gas velocities, corrosion processes at the surface and inside the materials were observed resulting in significant material degradation and mass loss. Hence, environmental barrier coatings (EBC) have been presented to be the solution to protect the surface of the ceramic materials. Systematic studies on the hot gas corrosion of non-oxide CMC have been performed with and without EBC. Based on a detailed understanding of the processes in the whole system, EBC and the ceramic base material during application in hot gas environments at elevated temperatures, general concepts for the development of environmental barrier coatings will be discussed.

9:00 AM

(ICACC-S2-010-2019) High Temperature, High Velocity Water Vapor Stability of the Oxides and Silicates in the Y_2O_3 – SiO_2 System

C. G. Parker*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA

Recent updates in the high temperature steam jet technique allow for the observation of the reaction between SiO_2 and $H_2O(g)$ to form $Si(OH)_4(g)$ at temperatures above 1200°C, velocities of ~200 m/s, and in silicates with SiO_2 activities below 0.3. These advancements have enabled systematic determination of thermochemical stability towards $H_2O(g)$ across all phases in the Y_2O_3 – SiO_2 system. Steam-jet experiments were conducted on Y_2O_3, Y_2SiO_5, $Y_2Si_2O_7$, and SiO_2 for times between 1 and 125 hours and temperatures of 1200-1400°C. Volatility of Y_2O_3 was not observed indicating minimal formation of any $Y(OH)_x(g)$ species. Phase pure Y_2SiO_5 showed evidence of SiO_2 loss at 1400°C after 60h of steam-jet exposure. Previous testing of $Y_2Si_2O_7$ at 1200°C showed formation of a porous Y_2SiO_5 surface layer due to SiO_2 depletion; however, new results obtained at 1400°C show a dense product layer on top of or instead of this porous layer under some conditions, pointing to previously unobserved mechanisms at play. The mechanisms and kinetics of the reaction between SiO_2 and $H_2O(g)$ to form $Si(OH)_4(g)$ in Y_2SiO_5, $Y_2Si_2O_7$, and SiO_2 will be discussed.

9:20 AM

(ICACC-S2-011-2019) Residual stress distribution of Si bond coat layer in Mullite/Si/RB-SiC EBC system after heat exposure above melting point of Si

Y. Arai*[1]; M. Sato[1]; H. Hatta[1]; Y. Kagawa[1]

1. Tokyo University of Technology, Japan

Residual stress of Si bond coat layer in Mullite/Si/RB-SiC model EBC system after high temperature heat exposure has been measured by micro-Raman spectroscopy. After the heat exposure, above the melting point of Si (1414°C), Si bond coat layer becomes fully dense Si and formed coarse grains connect with free Si in the reaction-bonded SiC substrate. The average residual stress measured by Raman spectroscopy becomes nearly constant throughout the dense Si bond coat layer. The level is explained thermal stress induced by thermal expansion mismatch of constitute layers. Then, crack growth behaviors within the dense Si bond coat layer is strongly affected by the existence of residual stress. Stress distribution appears near a reaction product within the dense Si bond coat layer. This local stress distribution reflects phase transformation of the reaction product (cristobalite). Discussions are made on the effects of residual stress on crack propagation path in the dense Si bond coat layer.

9:40 AM

(ICACC-S2-012-2019) Mass transfer in $Yb_2Si_2O_7$ under oxygen and water vapor potential gradients at high temperatures

M. Wada*[1]; T. Matsudaira[1]; N. Kawashima[1]; D. Yokoe[1]; T. Ogawa[1]; S. Kitaoka[1]; M. Takata[1]

1. Japan Fine Ceramics Center, Japan

High-temperature oxygen permeation tests of a polycrystalline $Yb_2Si_2O_7$ (YDS) film, which served as a model for an environmental barrier coating, were conducted under dry and wet conditions in the presence of an oxygen potential gradient. Under dry conditions, oxygen permeation of YDS was controlled by interdiffusion of Yb and oxide ions along grain boundaries (GBs). The addition of water vapor to the high oxygen partial pressure (P_{O2}(hi)) side clearly promoted GB diffusion of these ions, but no oxygen permeation to the low oxygen partial pressure (P_{O2}(lo)) side was detected. Under wet conditions, significant growth of Yb_2SiO_5 (YMS) occurred on both the P_{O2}(hi) and P_{O2}(lo) surfaces. In addition, YMS precipitates were formed along the GBs inside the film. However, no segregation of silicon was observed. Subsequently, when dry conditions were reintroduced, the YMS regions both on the P_{O2}(hi) surface and inside the film converted back to YDS, without any oxygen permeation of the film occurring. The formation of YMS on the P_{O2}(lo) surface was mainly caused by reaction of oxygen that had permeated through the film from the P_{O2}(hi) side with ambient H_2 gas, which was introduced into the lower chamber to reduce the P_{O2}(lo) value.

Thermal Barrier Coatings - Materials, Processing & Properties I

Room: Tomoka B

Session Chair: Eric Jordan, University of Connecticut

10:20 AM

(ICACC-S2-013-2019) Mechanical properties of different YSZ and $Gd_2Zr_2O_7$ thermally sprayed thermal barrier coatings (Invited)

R. Vassen*[1]; B. Lu[1]; D. Koch[1]; E. Bakan[1]; R. Muecke[1]

1. Forschungszentrum Juelich, IEK-1, Germany

Atmospherically sprayed thermal barrier coatings can have different microstructures as micros-cracked/porous, segmented or columnar. These microstructures often have due to their strain tolerance a positive influence on the performance of TBCs under thermal cyclic loading. Correlated with the performance of such TBCs are their Youngs moduli and also their viscosity values. In addition, the development of these mechanical properties during annealing is also of importance. In this paper, the results of the evaluation of free-standing YSZ coatings by bending tests and also by indentation testing (including constraint systems) will be presented. Depending on the microstructure, as-sprayed properties and evolution of them during annealing are observed to be different. Additionally, Gd2Zr2O7 coatings were tested and their properties were compared with that of YSZ coatings especially with respect to the often claimed higher sintering resistance of Gd2Zr2O7 coatings.

10:50 AM

(ICACC-S2-014-2019) Crack Formation and Propagation Phenomena in Air Plasma Sprayed Ceramic Coatings

S. V. Shinde*[1]; E. J. Gildersleeve[1]; S. Sampath[1]

1. Center for Thermal Spray Research, SUNY Stony Brook University, NY, Material Science, USA

Segmentation cracks in Air Plasma Sprayed top-coats have been industrially successful owing to their ability together to impart a higher in-plane strain tolerance and fracture toughness to the coatings which enhances their durability. In terms of processing, the formation of the vertical cracks have been associated with the enhanced inter-splat bonding facilitating the growth of coherent columnar grains through the coating thickness. This study seeks to elucidate the intricacies of vertical macro-crack formation in ceramic coatings produced by Air Plasma Spray Techniques. In particular, the behavior of incoming molten droplets upon a pre-cracked surface is examined through advanced characterization techniques to identify the conditions at which the coherent columnar growth amongst grains is promoted. Furthermore, through established beam curvature measurement techniques, the corresponding mechanical properties of the deposited coatings is dynamically monitored; and an attempt to categorize these coatings by the conditions facilitating formation of segmentation cracks is proposed.

11:10 AM

(ICACC-S2-015-2019) Investigation of the bond coat surface topography effect on TBC lifetime

J. P. Martins[1]; P. Xiao*[1]; Y. Chen[1]; G. Brewster[2]; R. McIntyre[2]

1. University of Manchester, School of Materials, United Kingdom
2. Rolls Royce plc, Surface Engineering – Materials Engineering, United Kingdom

The application of thermal barrier coatings (TBCs) systems in gas-turbine engines has played an instrumental role in the evolution of the transportation, energy and defence sectors over the last decades by allowing them to expand the limits of engine service operation. As these systems are utilised in high temperature oxidising environments, they undergo a continuous and evolutionary degradation process that limits their lifetime and is usually attributed to cumulative thermo-chemical and mechanical degradation processes. Even though the effect of bond coat (BC) interfacial roughness has been investigated as a significant factor in the thermal cyclic fatigue performance of Air Plasma Sprayed (APS) TBC systems, the full impact of BC interface topography and the mechanisms involved are still not fully understood. Therefore, this study focused on quantitatively assessing whether the BC interface topography played a significant role in influencing the lifetime of the TBC system via alteration of the ceramic topcoat microstructure and its mechanical properties. Confocal and electron microscopy were used in conjunction with complementary mechanical testing to characterise the BC interface topography and establish a relationship with TBC system thermal cyclic fatigue lifetimes.

11:30 AM

(ICACC-S2-016-2019) Temperature Mapping at the Thermal Barrier Coating/Bond Coat Interface by Luminescence Lifetime Imaging Using Integrated Erbium-Doped Sublayers

J. I. Eldridge*[1]; A. C. Wroblewski[1]; D. E. Wolfe[2]

1. NASA Glenn Research Center, USA
2. Pennsylvania State University, USA

Full-field temperature mapping of thermal barrier coated components by either infrared thermography or phosphor thermometry has been limited to surface temperature mapping even though temperature mapping at the thermal barrier coating (TBC)/bond coat interface is more relevant for evaluating the TBC thermal protection performance. For the first time, 2D temperature mapping at the TBC/bond coat interface has now been achieved by full-field luminescence lifetime imaging measurements of emission from a thin erbium-doped yttria-stabilized zirconia (YSZ) sensing layer integrated into the TBC below the overlying undoped YSZ. This new capability was applied to map temperatures at the TBC/bond coat interface for TBC-coated specimens subjected to a heat flux produced by the NASA Glenn high heat flux laser facility. In particular, thermal gradients at the TBC/bond coat interface were mapped in regions where the TBC was subjected to erosion or to mechanically induced delamination crack propagation. Finally, temperature mapping of the TBC/bond coat interface was used to evaluate the effectiveness of surface air film cooling at the TBC/bond coat interface.

Thermal Barrier Coatings - Materials, Processing & Properties II

Room: Tomoka B

Session Chair: Robert Vassen, Forschungszentrum Juelich

1:30 PM

(ICACC-S2-017-2019) Yttrium Aluminum Garnet (YAG) Coatings in Relation to Currently Used TBCs (Invited)

E. H. Jordan*[1]; M. Gell[2]; C. Jiang[2]; R. Kumar[2]

1. University of Connecticut, Mechanical Engineering, USA
2. Solution Spray Technologies LLC, USA

The broad array of coating types and geometries i n current aero and industrial applications will be discussed. A study of currently used TBCs reveals that TBCs with a broad range of properties are currently in use, where important properties often vary by a factor of 10. In an ideal case, a winning TBC system would exhibit superiority in all aspects. However, the nature of the existing applied coatings shows that instead each coating has its unique set of properties and meets the need for a specific application area. In this context, the properties and related issues for solution precursor sprayed yttrium aluminum garnet (YAG) will be discussed, including the latest advancements in processing and properties.

2:00 PM

(ICACC-S2-018-2019) Process-Induced Architectural Variations in Plasma Sprayed Thermal Barrier Coatings and Their Implications on Performance in a Thermal Gradient Environment with and Without Siliceous Debris

E. J. Gildersleeve*[1]; S. Sampath[1]

1. Stony Brook University, Materials Science, USA

The continued drive for higher gas turbine operating temperatures in the interest of increased efficiency has brought about new obstacles to the performance of typical Thermal Barrier Coating (TBC) systems. For instance, with increasing operating temperatures comes the possibility for ingested siliceous debris (CMAS) to become molten and adhere to the surface of the TBC. Depending on the coating material and deposition methods employed (which also influences the microstructure & property of the coating), these molten debris can flow freely into the entirety of the microstructure or arrest at the surface. In each of the cases, beyond their unique interaction with CMAS, the inherent microstructure of the coating will have an added role on the movement and flow of the melt. For example, coatings with high porosity (>15%) or coatings which are dense with vertical cracks (DVC) will have different infiltration mechanisms, only further aggravated in a thermal gradient scenario. To evaluate the differences in performance with respect to the microstructure, several types of single and multilayer TBCs were produced using distinct processes and exposed to CMAS through varying experimental scenarios. Results indicate a potential dependence on the process-induced microstructure and the CMAS interaction.

2:20 PM

(ICACC-S2-019-2019) Beyond YSZ: Aluminate-zirconate composite coatings for enhanced durability of next-generation high temperature TBCs

M. Schmitt*[3]; J. Stokes[1]; A. K. Rai[2]; D. E. Wolfe[1]

1. Pennsylvania State University, USA
2. UES, Inc.", USA
3. HAMR Industries LLC, USA

Three factors are critical for advancement beyond yttria stabilized zirconia (YSZ) thermal barrier coatings (TBCs): thermochemical stability beyond 1400°C, thermal conductivity values adequately low to enable these high temperatures, and sufficiently high erosion durability to maintain coating longevity in a thermomechanically demanding environment. At this stage, no individual material has demonstrated improvements in each category with respect to YSZ including gadolinium zirconate (GZO) whose poor erosion durability limits the benefits of its high temperature stability and low thermal conductivity. Previous work has demonstrated that composite TBCs incorporating a secondary toughening phase can provide significant enhancement in the durability of GZO. This work describes the first potential materials system capable of operating at temperatures of 1400°C and beyond without sacrificing durability or thermal insulation with respect to YSZ. This was accomplished by using thermodynamically compatible aluminate-zirconate composites. Dense pellets and air plasma spray coatings were utilized in this study to confirm the material properties and coating performance. Mechanical properties and thermal conductivity were evaluated while elevated temperature stability, erosion resistance and thermal cycling were demonstrated.

2:40 PM

(ICACC-S2-020-2019) Extending the lifetime of T-EBC coatings during thermal cycling above 2400°F

J. Deijkers*[1]; H. Wadley[1]

1. University of Virginia, Materials Science & Engineering, USA

Growth of a cristobalite thermally grown oxide in silicon-based EBCs results in mud cracking and eventual delamination of the EBC system due to high thermal stresses. A proposed composite bond coating of silicon and hafnia will be used to transform excessive cristobalite growth upon oxidation into hafnon (hafnium silicate), which is thermally stable and compatible with the currently longest-lasting EBC system (silicon bond coat, ytterbium disilicate (YbDS) top coat). Silicon-hafnia powder mixtures have been consolidated using spark plasma sintering (SPS) to demonstrate the growth of hafnon during oxidation of this system at temperatures between 1150°C and 1350°C in a compacted powder specimen. Subsequently, cristobalite-hafnia powder mixtures have been consolidated using SPS and annealed in air and argon, demonstrating the growth rates of hafnon in different oxygen environments. Silica volatility reduces the YbDS to YbMS, forming a volatile silicon hydroxide gas. HfO_2 and stabilized HfO_2 TBCs have been deposited on the YbDS using EB-DVD, growing a columnar microstructure in an attempt to reduce silica volatility. The evolution of the coating structure has

been observed during steam cycling, showing sintering and subsequent cracking of the HfO_2-based TBC, and a reaction between the HfO_2 and the YbDS diffusion barrier during the steam cycling of these coatings.

CMAS Degradation of EBC/TBC: Effects and Mitigation Strategies I

Room: Tomoka B
Session Chair: Hagen Klemm, FhG IKTS Dresden

3:20 PM

(ICACC-S2-021-2019) Effects of CMAS Deposits on Delamination and Damaging Mechanisms in Thermal Barrier Coatings and Gas Turbine Engine Components

K. Chen*[1]; V. Pankov[1]; L. Jiang[1]; P. Patnaik[1]

1. National Research Council Canada, Aerospace Research Centre, Canada

This work studies the degradation of thermal barrier coatings (TBCs) produced by electron beam physical vapour deposition (EB-PVD) under attack by volcanic ash. A delamination map of the EB-PVD TBC top coat due to volcanic ash penetration was established based on fracture mechanics and thermal gradient conditions. The effect of CMAS infiltration on thermal stresses generated in YSZ EB-PVD coating was experimentally investigated in the temperature range of 25ºC – 600ºC using X-ray stress analysis. It was found that CMAS infiltration deteriorates the tolerance of EB-PVD TBCs to thermal stresses. A mechanism for this deterioration effect was identified. The behaviour of volcanic ash particles in a gas turbine combustor and nozzle guide vanes was numerically investigated. It was revealed that the ash capturing efficiency of the nozzle guide vane (NGV) external wall dramatically increases as the turbine inlet temperature approaches that of the metal melting point. Furthermore, the majority of the ash particles entering the NGV were found to be trapped within the cooling flow passages. This may represent a new volcanic ash damage mechanism for internally cooled gas turbine components.

3:40 PM

(ICACC-S2-022-2019) Interaction of $Yb_2Si_2O_7$ and Yb_2SiO_5 environmental barrier coating materials with CMAS melts

R. Webster*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science & Engineering, USA

Calcium Magnesium Alumino-Silicate (CMAS) attack is a pressing issue in the development of Environmental Barrier Coatings (EBCs) for Ceramic Matrix Composites (CMCs). CMAS originates as siliceous debris such as sand, dust, or volcanic ash, which can be ingested into aircraft turbine engines on takeoff, landing, or in flight. At temperatures greater than approximately 1200°C, CMAS melts and can penetrate EBC materials, causing premature coating failure. Current generation EBC materials include Rare Earth (RE) silicates, $Yb_2Si_2O_7$ and Yb_2SiO_5. These materials are typically deposited by Air Plasma Spray (APS), which results in a heterogeneous coating containing multiple phases. The influence of secondary phase content on CMAS resistance in $Yb_2Si_2O_7$ and Yb_2SiO_5 was investigated in the current study. Spark Plasma Sintering (SPS) was used to prepare dense Yb-silicates for testing. $Yb_2Si_2O_7$ and Yb_2SiO_5 were prepared as standalone materials and were also mixed with 10-30 and 5-15 vol % Yb_2SiO_5 and Yb_2O_3, respectively. Samples were sectioned and polished and were exposed to CMAS at 1300°C for up to 200 h. Following heat treatment, samples were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS). The thickness and phase constitution of the reaction interface was monitored. CMAS mitigation strategies will be discussed.

4:00 PM

(ICACC-S2-023-2019) Thermal Environmental Barrier Coating Ceramics Based on Rare-Earth Pyrosilicates and their High-Temperature Interactions with Calcia-Magnesia-Alumino-Silicate (CMAS) Glass

L. R. Turcer*[1]; H. Sternlicht[1]; C. Watts[1]; M. Koval[1]; H. Garces[1]; N. P. Padture[1]

1. Brown University, Engineering, USA

Ceramic-matrix-composites (CMCs) are replacing metallic hot-section components, which allow for higher operating temperatures in gas-turbine engines. In the presence of water vapor active-oxidation is prevalent, therefore, dense environmental barrier coatings (EBCs) are needed to protect CMCs. At temperatures above 1200 °C, silicate particles (sand, volcanic ash, fly ash, etc.) that enter the engine melt on the hot surfaces and form calcia-magnesia-alumino-silicate (CMAS) glass deposits. These molten glass deposits can react with the EBCs and/or penetrate grain boundaries, which can lead to premature coatings failure. New EBC ceramics are needed that are resistant to CMAS attack. Optical basicity has been used to predict the reactivity between CMAS and potential EBC ceramics. Several potential EBC ceramics have been identified, including rare-earth (RE) pyrosilicates ($RE_2Si_2O_7$, RE = Yb, Y, Sc, Lu). Low thermal conductivity binary solid-solutions of these RE pyrosilicates (e.g. $Y_xYb_{(2-x)}Si_2O_7$) are also being considered that can serve as new thermal environmental barrier coatings (TEBCs). Their high-temperature interactions with CMAS are studied, and the nature of these interactions, damage mechanisms, and their mitigation are discussed.

4:20 PM

(ICACC-S2-024-2019) Dissolution and Diffusion of Thermal Barrier Oxides in Molten Silicates

C. S. Holgate*[1]; D. L. Poerschke[2]; C. G. Levi[1]

1. University of California, Santa Barbara, Materials, USA
2. University of Minnesota, Chemical Engineering and Materials Science, USA

The degradation of thermal barrier coatings (TBCs) by molten silicates (CMAS) is a significant barrier to increasing the operation temperature of gas turbine engines and their fuel efficiency. Novel TBC chemistries that show resistance to CMAS attack are needed, requiring a rapidly dissolving TBC that is reactive with the melt to form favorable crystalline products capable of arresting melt penetration; however, the kinetics of TBC-CMAS interactions remains understudied in the literature. In the presented work, dense single and polycrystalline thermal barrier oxides (TBOs) were placed into a semi-infinite, 1D diffusive contact with model silicate compositions, which enabled the quantification of the TBO dissolution rate into and diffusion rate within the silicate melt. The dissolution mechanism was ascertained and the significance of the melt temperature, melt composition, and TBO composition on the dissolution and diffusion rates were compared. Furthermore, the results yielded qualitative insight on the reaction product morphology and mechanism of attack for polycrystalline and single crystalline TBOs. The gathered kinetic data was also incorporated into finite element models that afford insight on infiltration, dissolution, and diffusion behavior on model TBC geometries.

4:40 PM

(ICACC-S2-025-2019) Complex Melting Behavior of Si-lean, Fe-Ti-CMAS and its Effects on the Recession of EB-PVD Gadolinium-Zirconate TBC

P. Mechnich*[1]

1. DLR - German Aerospace Center, Institute of Materials Research, Germany

First and second stage high-pressure turbine blades of aeroengines are typically made of Ni-based superalloys protected by thermal barrier coatings (TBC). In operation, state of the art EB-PVD

ZrO_2 TBC experience severe degradation by airborne inorganic particles commonly referred to as CMAS (CaO-MgO-Al_2O_3-SiO2). CMAS particle ingestion, deposition, and subsequent melt infiltration is a major reason for premature TBC failure. A promising way to overcome the CMAS problem is the use of highly reactive TBC/EBC materials which can trigger rapid crystallization of CMAS melts, thus mitigating melt infiltration. A variety of new TBC materials such as rare-earth zirconates having low thermal conductivity exhibit such promising resistance against simplified CMAS compositions. However, partial or incongruent melting of CMAS constituents lead to complex reaction and infiltration scenarios. Such kinds of effects were studied on EB-PVD $Gd_2Zr_2O_7$ coatings and synthetic Si-lean, Fe,Ti-rich CMAS mimicking deposits on ex-service turbine blades. It turns out that such Si-lean, fully crystalline CMAS deposits are exhibiting phase equilibria, stepwise melting, and reactions which are very sensitive to their respective bulk chemical composition, thus making it difficult to assess the corrosion resistance and operation limits of new TBC materials.

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Novel Processing

Room: Crystal
Session Chair: John Pietras, Saint-Gobain

8:30 AM

(ICACC-S3-008-2019) Supported films for SOFC applications (Invited)

A. Sanson*[1]; A. Gondolini[1]; E. Mercadelli[1]

1. CNR-ISTEC, Italy

The production of SOFC and SOEC hugely relies on the deposition of either dense or porous thin films onto suitable substrates. The film produced must shows the wanted microstructural and functional properties and be compatible with the substrate in which is printed. Among the different techniques for film deposition, screen printing and wet powder spray are the most considered for the low cost and easy scalability. This work will highlight and examine the different issues connected with the deposition of films used either as electrode or electrolyte with these techniques, and will propose different approaches that can be applied to overcome possible hurdles. Focusing on the processing steps, the work will show the importance of the nature of the surface used for the deposition, in terms of chemistry and morphology, and the suspension/ink used for the deposition demonstrating their role on the performances and variability of results that can be found in literature.

9:00 AM

(ICACC-S3-009-2019) 3D Printing of Ceramics for Application in Solid Oxide Fuel Cells (Invited)

A. Morata[1]; A. Hornés[1]; V. Esposito[2]; M. Rosa[2]; C. Chaput[3]; G. Le Meillour[3]; L. Hernández[4]; F. Ramos[5]; J. Guimbao[5]; C. Crawshaw[6]; A. Ansar[7]; D. Lieftink[8]; A. Tarancón*[1]

1. IREC, Spain
2. DTU, Denmark
3. 3DCERAM, France
4. ULL, Spain
5. FAE, Spain
6. Promethean Particles, United Kingdom
7. SAAN Energi, Sweden
8. HyGEAR, Netherlands

A Solid Oxide Fuel Cell (SOFC) is a ceramic-based multilayer device that currently involves expensive and time-consuming multi-step manufacturing processes including tape casting, screen printing, firing, shaping and several high-temperature thermal treatments. This complexity of the manufacturing process leads to long production times and high costs. The Cell3Ditor project aims at developing a 3D printing process for mass production of monolithic SOFC stacks without joints and sealing to manufacture SOFC stacks in only two production steps (printing and sintering) thereby reducing manufacturing complexity and increasing cost effectiveness and reliability. Within the project a multi material 3D printer is being developed to enable mass production of whole SOFC stacks in a single printing step. This printer combines stereolithography and robocasting printing in a single machine for a sequential application of different materials during the printing process. State of the art materials are being used and inks and slurries based on ceramic nano materials are being optimised for 3D printing to reach the required thicknesses, gas tightness, porosity and reactivity of the respective layers within the stack. This contribution will give a snapshot of the current status of the project in terms of the printing process itself as well as the functionality of the printed parts.

9:30 AM

(ICACC-S3-010-2019) Artificial intelligence for automatic optical inspection of multilayered solid oxide membranes

R. Hoeppener*[1]; A. Litke[2]; P. Martens[2]; G. Norsworthy[1]

1. Haiku Tech Inc., USA
2. Haiku Tech Europe BV, Netherlands

Large scale implementation of SOFC technology is limited by the high cost per kW power. Production of the SOFC MEA's is the major part of the system cost. This price component can be reduced through scale up, automation, and optimization of the manufacturing process. Mass production requires automatic quality control methods to reliably detect functional defects early in the production cycle. Multiple types of defects ranging in size from mm to few microns, which are randomly located on the surface of the ionic conductive membrane, push the limits of conventional imaging hardware and challenge reliability and productivity of classical algorithms for visual data analysis. In this regard, Artificial Intelligence (AI) offers a much higher degree of freedom for feature detection and classification. In this study we evaluate the feasibility of detection and classification of functional defects in fired solid oxide membranes with a custom-developed AI system. The optical inspection was developed for high-speed imaging of solid oxide membranes at 3.5 mm/pixel resolution in a production environment with 100% inspection. The high-resolution images of SOFC plates were used for automated recognition of several classes of functional defects like craters, hairs, cracks and pinholes down to 10 micrometer size. The system showed high rates of correct defect detection.

Sealants and Mechanical and Thermomechanical Aspects of Manufacturing

Room: Crystal
Session Chair: Federico Smeacetto, Politecnico di Torino

10:10 AM

(ICACC-S3-011-2019) New Silver-Based Alloys for Solid Oxide Cell Brazing and Circuit Patterning (Invited)

Q. Zhou[1]; Y. Ma[1]; T. R. Bieler[1]; J. D. Nicholas*[1]

1. Michigan State University, Chemical Engineering and Materials Science, USA

Silver based brazes are the most common solid oxide cell (SOC) brazes used today. Unfortunately, the copper additions used in conventional Ag-CuO Reactive Air Brazes (RABs) to promote silver wetting result in porosity during SOC manufacture and use. This talk will discuss two new silver-based brazes systems, Ag-Ge and Ag-Ni, that allow dense, resilient stainless steel to ceria or stainless steel to yttria stabilized zirconia brazes to be produced at ~800 and 1000ºC, respectively. Initial tests on these new braze systems suggest

they have several performance benefits compared to conventional RABs. For instance, dual atmosphere rapid thermal cycling and dual atmosphere 750ºC isothermal tests on Ag-Ni brazes show that they exhibit less degradation than conventional Ag-3CuO brazes. Further, by patterning the porous Ni layers used to promote Ag wetting, it is possible to produce dense, well-adhered thick film silver wires on various ceramic substrates. Lastly, the lower brazing temperature of Ag-Ge brazes, compared to the ~950ºC brazing temperature of conventional RABs, make them more compatible with nanostructured electrodes that experience unwanted microstructural changes at high temperature.

10:40 AM

(ICACC-S3-012-2019) Modelling of local interfacial failures in solid oxide cell stacks

X. Miao*[1]; M. Navasa[1]; H. L. Frandsen[1]

1. Technical University of Denmark, Denmark

The commercialization of solid oxide cell (SOC) technology puts forward high requirements on long-term performance, efficiency and reliability of SOC stacks. Particularly, the reliability must be ensured over the expected lifetime of SOC stacks. SOC stacks have many geometric features and are subjected to multiphysics processes (electrochemistry, mechanics, heat transport, flows, etc.). To describe the overall behaviour of full stacks under the interactions of multiple physical fields, highly computational models are needed. We use "homogenized" stack model to perform fast full stack simulations. Ceramic materials in SOC are brittle and susceptible to fracture caused by induced stresses under the operating conditions. Fractures in the contact layer between the electrodes and the metallic interconnect will result in loss of contact, which can significantly influence the conduction of electrical current. The homogenization modelling framework of SOC stacks is extended to describe local mechanical failure. A novel concept of linking the stresses in homogenized model to local values of J-integral analytically is developed. The J-integral can be evaluated at every point in the stack at every instance in time. The approach will be demonstrated based on simulation results from fully coupled multiphysics model run for operation scenarios >20,000 hours to determine if mechanical failure would occur through operation.

11:00 AM

(ICACC-S3-013-2019) Torsion test for joined SOFC components

S. De La Pierre*[1]; A. Sabato[1]; H. Javed[1]; F. Smeacetto[2]; J. Malzbender[3]; M. Ferraris[1]

1. Politecnico di Torino, DISAT, Italy
2. Politecnico di Torino, DENERG, Italy
3. Forschungszentrum Jülich, Germany

The shear strength of SOFC joined parts (interconnect/cell) is an important information for design and prediction of their behavior in working conditions. Most of the currently used test methods are based on lap-shear configurations, useful for comparison purposes, but unsuitable to provide pure shear strength for design and modelling purposes. Torsion tests on glass-ceramic joined steel specimens have been used to obtain their shear strength at room and working temperature. The steel is a Crofer22APU and the glass-ceramic joining materials have typical sealant compositions based on silica containing SrO and-or BaO as modifiers. Torsion test on hourglass shaped joined samples confirmed the suitability of this test to measure the shear strength of joined components. The results for joined samples of different size and with adhesive or cohesive behavior were compared with SEM on fracture surfaces to understand the measured results.

Electrolytes

Room: Crystal

Session Chair: Olivier Guillon, Forschungszentrum Juelich

1:30 PM

(ICACC-S3-014-2019) Enhanced grain boundary conductivity in Gd doped CeO_2 through solvent deficient synthesis method

H. Maruyama*[1]; S. Zeljkovic[2]; J. C. Nino[1]

1. University of Florida, Materials Science and Engineering, USA
2. University of Banja Luka, Chemistry, Bosnia and Herzegovina

Gadolinium doped ceria has been used as an electrolyte for solid oxide fuel cells due to its high ionic conductivity. High sintering temperature typically leads to high grain boundary (GB) resistance due to dopant segregation and oxygen deficiency along the GBs. Reducing the particle size is an effective way to reduce sintering temperature since the surface area significantly increases. Recently, a novel technique to synthesize nanoparticles without a liquid solvent, known as solvent deficient method (SDM), had been developed. In this study, 10 mol% Gd doped CeO_2 (10GDC) was synthesized using SDM to examine its sinterability and electrical properties. To produce 10GDC nanoparticles, cerium nitrate hexahydrate, gadolinium nitrate hexahydrate and ammonium bicarbonate were mixed and calcined at 300-500°C. To sinter 10GDC, a modification on the recently developed cold sintering process (CSP) was employed and 91% of the theoretical density was achieved. Although the grain conductivity for the samples (8.0×10^{-3} S/cm at 500°C, and 3.3×10^{-2} S/cm at 700°C) is on par with the highest reported values, the measured total conductivity (3.9×10^{-3} S/cm 500°C, and 2.5×10^{-2} S/cm at 700°C) is about 10 times higher than that of 10GDC, pointing to the effectively lower GB impedance. The nanoparticle synthesis, sintering optimization, and effect of GB on the conductivity will be discussed in detail.

1:50 PM

(ICACC-S3-015-2019) Flash sintering of oxygen ion and mixed conductors and characteristics for application in SOFC

H. Charalambous*[1]; S. K. Jha[1]; K. H. Christian[1]; J. Okasinski[2]; T. Tsakalakos[1]

1. Rutgers University, Materials Science and Engineering, USA
2. Argonne National Lab, Advanced Photon Source, USA

Solid oxide fuel cells (SOFC) hold tremendous potential in replacing the internal combustion engine with a high efficiency engine that can convert chemical energy directly into electrical energy. The main challenge, however, remains in the limited ionic conductivity of solid electrolytes, high temperature operation requirements, and fabrication methods. Flash sintering offers a new route for fabrication and co-sintering of electrolytes, anodes and cathodes with higher ionic grain-boundary conductivity. 8YSZ, pure CeO_2 and Gd-doped CeO_2 have been sintered to high density using the flash sintering technique. In our study, we analyses the effect of electric field in changing the conduction mechanism during in situ study using energy dispersive X-ray diffraction (EDXRD) on these two systems.

2:10 PM

(ICACC-S3-016-2019) A scalable protonic ceramic fuel cells

H. An*[1]; H. Lee[1]; B. Kim[1]; J. Son[1]; K. Yoon[1]; H. Kim[1]; D. Shin[2]; H. Ji[1]; J. Lee[1]

1. Korea Institute of Science and Technology, Republic of Korea
2. Hanyang University, Republic of Korea

Proton conducting ceramic electrolyte possesses attractive features – higher ionic conductivity and lower activation energy – and enables SOFCs to operate at lower temperatures (400 – 600ºC). However, crucial technical challenges on cell fabrication, especially establishing a chemically homogeneous and physically thin electrolyte layer, have been limiting its commercial implementation. These challenges mainly stem from the refractory nature of the proton-conducting electrolytes. It makes the densification behavior of the electrolyte in PCFCs difficult to control and in most cases, negatively impacts

on its ionic conductivity. As a result, protonic ceramic fuel cells has been demonstrated a frustrating performance and scalability (an anode support size of at most 3cm^2). Here, we present breakthroughs in the performance and scalability of PCFCs: a high peak power density of 1.3 W/cm^2 was obtained at 600°C, resulting in a 20.8 W per single cell with a size of 5x5 cm^2. The advances stem from an internal supply of sintering aid from the anode to the electrolyte as well as an excess shrinkage force driven by the anode promote the densification of electrolyte at temperature of 1350°C, leading to an area-specific ohmic resistance of 0.09 Ωcm^2. Furthermore, since all of the utilized fabrication processes are cost-effective, consistent, and readily scalable, our results fulfill the requirements for achieving commercial feasibility of PCFCs.

2:30 PM

(ICACC-S3-017-2019) Barium Zirconate Based Electrolyte Densification Using Reactive Sintering Aids

B. Hu*[1]; M. Reisert[1]; A. Aphale[1]; S. Belko[1]; O. Marina[3]; J. W. Stevenson[3]; D. Ding[2]; U. Pasaogullari[1]; P. Singh[1]

1. University of Connecticut, Center for Clean Energy Engineering, USA
2. Idaho National Laboratory, USA
3. Pacific Northwest National Laboratory, USA

Observed higher proton conductivity at low to intermediate temperatures provides promising opportunities for barium zirconate based electrolyte for use in solid oxide electrolyzers, fuel cells, and gas separation membrane applications. The above electrolyte, however, requires very high sintering temperature to achieve full densification. This study describes experimental approach to lower the sintering temperature of barium zirconate based proton electrolytes (BZCY-Yb) by using a reactive and nano-sized sintering aids. The electrolyte pellets were made by isostatic pressing after mixing of electrolyte and sintering aids. The electrolyte was sintered in oxygen atmosphere in the temperature range of 1523-1723 K. The densification and morphologies of the sintered electrolyte were examined by scanning electron microscopy and focus ion beam-transmission electron microscopy (FIB-TEM). The bulk and surface structure evolution during high-temperature sintering was studied by in situ X-ray diffraction technique. The conductivity of the sintered electrolyte with and without sintering aids was measured by 4-probe technique. Dense BZCY-Yb electrolyte has been achieved at 1623 K in oxygen atmosphere with a total conductivity of >0.01 S/cm^2 at 973 K in 3% H_2O/air.

Stack / Cell Performance and Durability

Room: Crystal

Session Chair: Mihails Kusnezoff, Fraunhofer IKTS

3:10 PM

(ICACC-S3-018-2019) Online health monitoring of SOFCs and accelerated degradation (Invited)

V. Subotic*[1]; M. Preininger[1]; B. Stoeckl[1]; M. Kusnezoff[2]; C. Hochenauer[1]

1. Graz University of Technology, Institute of Thermal Engineering, Austria
2. Fraunhofer IKTS, Germany

Main issues that hinder commercial application of solid oxide fuel cells (SOFC) are durability and stability against failure modes. The electrochemical impedance spectroscopy (EIS) gives insight into processes that occur during the SOFC operation, the measurement of which takes several minutes up to one hour. However, during the measurement procedure undesired failure modes can intensify SOFC degradation and eventually cause its damage. To detect and prevent the onset of preventable irreversible system changes, redesign of the conventional characterization methodologies into an advanced online-monitoring system is necessary. To this purpose, the present study focuses on: (1) application of THD (total harmonic distortion) methodology to identify failures at very beginning, and (2) acceleration of degradation in industrial-sized SOFCs. The THD method reduces the measurement time down to several seconds, and provides accurate information on specific failure modes whereas conventional methods fail. The long-term experiments performed under real operating conditions showed great stability of the SOFCs used, even under harmful operating conditions, compared to which other SOFC cell types were damaged after only several hours of operation under same conditions. Using conventional techniques critical operation could not be observed, while the THD approach provided relevant data at the early degradation stage.

3:40 PM

(ICACC-S3-019-2019) Accelerated testing of CFY stacks / Degradation analysis of CFY-stacks

S. Rothe*[1]; S. Hielscher[1]; C. Folgner[1]; V. Sauchuk[1]; S. Megel[1]; M. Kusnezoff[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Germany

Accelerating tests for SOC stacks are necessary to make a clear prediction of lifetime for SOC stacks. With estimated operation times of 40-80.000 h it is impossible to test all component generations for stacks. It is necessary to select the specific operation parameters inside the permitted operation window to accelerate the degradations without any changes of effects. Degradation analysis is very sensitive to several boundary conditions. Selected tolerances will be considered and presented with examples. A guideline for gaining reliable test results will be given with a focus on test hardware, operation mode and parameter set for reference points. For fast loop development, special sample tests are necessary parallel to stack for picking the right source of degradation and conduct accelerated sample tests for single components. All examples are given with MK35x CFY stacks. A 20.000 h test of a 10-cell stack shows a linear degradation of $\Delta P/P_0$<0.6 %/1.000 h (ΔASR=16 mΩcm^2/1.000 h) and defines the baseline of the state of the art MK35x technology. By changing one test parameter the difference of the degradation rate can be converted into an acceleration factor. The main focus is set to the post mortem analysis to predict the right point of sampling for comparing all effects of aging. This is shown for higher temperature, current density and humidified air.

4:00 PM

(ICACC-S3-020-2019) Degradation of gasified biomass-fueled SOFC

O. Guillon*[1]; H. Jeong[1]; M. Geis[2]; S. Fendt[2]; S. Herrmann[2]; N. H. Menzler[1]

1. Forschungszentrum Juelich, IEK-1, Germany
2. TU München, Germany

One major advantage of a HT-fuel cell is its fuel flexibility. Within a cooperation project between TU Munich and Jülich, the interaction of synthetic syngas and real bio-syngas from a biomass gasifier with an SOFC are characterized. The synthetic syngas consists of H_2, H_2O, CO, CO_2 and CH_4. To examine the interaction of typical impurities in real bio-syngas (e.g. sulfur or tar) with the SOFC in a controlled manner, such impurities are added to the synthetic syngas. The tests are conducted on single cell level (10x10 cm2) or in real stacks. The characterization ranges from electrochemistry to post-test analysis of the cells and the stack components. Here we report on the electrochemical and chemical interactions of bio-syngas containing tars with the SOFC. It was found that different tar species show different interactions: The first one is mainly electrochemical and influences the cell performance, while the second one is chemical and deteriorates the anode support. Macroscopic erosion of the anode support is observed in only a few hundred hours, dramatically limiting the expected lifetime of an anode-supported cell in bio-syngas containing tars. In addition, the deposition of carbon was detected in spite of the high humidity in the fuel gas. The results obtained underline the necessity of a gas cleaning system or resistant anode materials.

4:20 PM

(ICACC-S3-021-2019) Electrochemical characterization and performance assessment of SOC stacks in electrolysis mode

M. Preininger*[1]; V. Subotic[1]; B. Stoeckl[1]; R. Schauperl[2]; C. Hochenauer[1]

1. Graz University of Technology, Institute of Thermal Engineering, Austria
2. AVL List GmbH, Fuel Cell Systems, Austria

High temperature electrolysis (HTE) of steam, CO_2, and steam and CO_2 for highly efficient generation of hydrogen, carbon monoxide as well as syngas was investigated for four solid oxide cell stacks, all supplied by different stack manufacturers. The SOCs employed within the stacks were planar, and electrolyte or electrode supported with an industrial size between 80 and 128 cm^2. A comprehensive electrochemical characterization of both stacks and individual cells within the stacks was conducted by means of electrochemical impedance spectroscopy and polarization curve measurement. Detailed performance analyses showed the highest efficiency when operating the stack under H_2O electrolysis, followed by co-electrolysis and eventually CO_2 electrolysis. Subsequently, the stacks were operated under reversible system-relevant steady-state conditions, thus varying the working temperatures, the current density and the gas inlet flow. For that purpose both the conversion rate and fuel utilization were set to be between 70% and 80%. All stacks were operated for long-term periods of >1,000 h, during which degradation monitoring was applied. The results obtained within the present study allow a better understanding of the electrochemical processes that occur during reversible operation and especially HTE, and provide a guideline for optimized operation of a fully autonomous rSOC system.

4:40 PM

(ICACC-S3-022-2019) Development of Metal-Supported Solid Oxide Fuel Cell Fabricated by Atmospheric Plasma Spraying in INER

C. Chang*[1]; C. Tsai[1]; C. Fu[1]; C. Yang[1]; S. Yang[1]; R. Lee[2]

1. Institute of Nuclear Energy Research, Physics Division, Taiwan
2. Institute of Nuclear Energy Research, Taiwan

Institute of Nuclear Energy Research (INER) has been developing fabrication method for metal-supported solid oxide fuel cell operating in the 600-750 temperature range. The planar MS-SOFC cell with 10x10 cm^2 in size composed of a permeable Ni-based plate as a support, a NiO-YSZ layer as an anode, a $Ce_{0.6}Mn_{0.3}Fe_{0.1}O_{2-d}$ (CMF) layer as a buffer layer, a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-d}$ (LSGM) layer as an electrolyte and double layers with different contents of $Sm_{0.5}Sr_{0.5}CoO_{3-d}$-$Sm_{0.2}Ce_{0.8}O_{2-d}$ (SSC-SDC) composite layers as a cathode were fabricated by atmospheric plasma spraying (APS). The measured powers of the MS-SOFC in cell test achieve 55, 44.6 and 28 W at 0.8 V and 750, 700 and 650ºC, respectively. The power outputs of MS-SOFC single-cell stack are 54.7 and 44.3 W at 0.7 V and 750 and 700ºC, respectively. The durability tests of the MS-SOFC cell had performed for 3,900 hours at the test condition of 400 mA/cm^2 and 700ºC. The measured degradation rate is less than 1 %/1000hr, which indicates that the plasma-sprayed MS-SOFC cell made by INER reveals an inspired performance.

S4: Armor Ceramics - Challenges and New Developments

Materials Characterization I

Room: Coquina Salon F
Session Chairs: Lionel Vargas, US Army Research Laboratory; Anthony DiGiovanni, US Army Research Laboratory

8:30 AM

(ICACC-S4-013-2019) A Brief History of Industrial Diamond Materials and Technology: Converting Fantasy to Fact and Profit (Invited)

A. A. DiGiovanni*[1]

1. US Army Research Laboratory, USA

The history of synthetic diamond and its use as an industrial material is both an inspiring tale of scientific achievement and a disconcerting allegory to the pitfalls of high-stakes technology development. High pressure studies during WWII by Bridgeman enabled the first experiments in the US and Sweden during the 1950's into high-pressure conversion of carbon into synthetic diamond. Initially held as a state secret by the US government, the machine responsible for successfully growing synthetic diamond materials heralded a new era of materials synthesis. Subsequent development and commercialization of synthetic diamond materials and various composites, including combinations with silicon carbide, have had an almost immeasurable impact on modern industrial processes and technology development. Low-pressure investigations into vapor phase and shock synthesis produced additional useful forms of diamond that continue to this day to find ever more inroads to advanced technology development in a broad spectrum of disciplines, including mining, machining, optics, electronics, and medicine. This talk will address a broad spectrum of diamond technologies, their origins, and focus on the development of bulk materials and their composites.

9:00 AM

(ICACC-S4-014-2019) SiC-bonded diamond materials – Superhard materials for a wide range of applications (Invited)

M. Herrmann[1]; B. Matthey[1]; S. Kunze*[1]; M. Zins[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Germany

One of the core activities of the Fraunhofer IKTS is the development of hard, wear-resistant materials, especially transparent oxide materials which can also be used for armor applications. A new, extremely wear-resistant and superhard material are SiC-bonded diamond ceramics, which can be manufactured by reaction bonding of diamond by liquid silicon infiltration similar to the SiSiC process. Using this approach, components can be produced cost-effectively in large sizes and with complex shapes. They can also be produced as layered materials with SiC-bonded diamond only in areas where it is required. Due to the strong chemical bonding between silicon carbide and diamond, the new material shows excellent properties: hardness (HK) > 45GPa, strength values between 450 and 600 MPa (biaxial test), K_{IC} of 4-5 $MPam^{1/2}$ and thermal conductivity up 500-600 W/mK depending on the microstructure. The content of free silicon can be reduced to < 5vol.%. Therefore, more than 90% of the initial strength can be maintained even after corrosion in 20 % NaOH (at 90°C 500 h). An overview concerning correlations between preparation, microstructure and properties of the new class of materials is given.

9:30 AM

(ICACC-S4-015-2019) Reaction Bonded (SiC & SiC/B_4C) + Diamond Composites: Uniform and Graded Structures (Invited)

S. Salamone*[1]; G. Evans[1]; M. Aghajanian[1]; C. R. Baker[2]

1. M Cubed Technology, Inc., USA
2. US Army, Soldier Protection and Individual Equipment Program Executive Office Soldier, USA

The addition of diamond particles has been shown to be beneficial to the impact performance of reaction bonded composites. Initial development focused on homogenously mixed diamond particles and an increase in performance was found with increasing diamond content, from 0 to approximately 50 volume percent diamond in the composite. Recently, it has been surmised that there might be an advantage to preferentially concentrating the diamond particles in the vicinity of the impact surface. Two paths were explored in regards to these graded structures: heavily loaded diamonds at and near the surface and a more gradually graded diamond structure throughout. Currently, 14 to 21 volume percent diamond particle systems were developed to create gradually graded diamond structures with reaction bonded SiC/B_4C composites. Properties, performance and microstructures will be discussed.

Materials Characterization II

Room: Coquina Salon F

Session Chair: Christopher Marvel, Lehigh University

10:20 AM

(ICACC-S4-016-2019) Interfacial characteristics and properties of a reaction bonded SiC/diamond composite (Invited)

Y. Zhang[1]; J. Wynn[2]; M. Aghajanian[3]; P. Koindikar[3]; C. Ni*[1]

1. University of Delaware, Materials Sci.&Eng., USA
2. TA Instruments, USA
3. II-VI M cubed Technologies Inc., USA

Reaction bonded SiC/diamond composites are the top candidates among premier materials employed in the extreme environment requiring ultrahigh strength and modulus, exceptional thermal transport behavior and unique structural stability and integrity. This study evaluates the structure-property details of a reaction bonded SiC/diamond composite. The diamond content has a strong correlation with the thermal transport. At the room temperature, the thermal diffusivity exhibits approximately 2-fold increase from about 0.8 to 1.5 cm^2/s as the diamond content increases from 17.5 wt% to 70 wt%. Analysis on the reaction formation of phases reveals a reaction zone existing surrounding the diamond grains. TEM imaging further determines that the reaction zone includes a graphite layer of up to 50 nm next to diamond, nanocrystalline SiC and significant micro-twins in some of the SiC grains, and a few minor phases such as residual Si and impurities. The effects of this reaction zone on the thermal and mechanical properties are investigated via systematic experiments and computations. In-situ TEM heating test suggests that adequate annealing and/or optimized fabrication parameters can lead to a structural improvement especially in the reaction zone that may potentially enhance the composite properties.

10:50 AM

(ICACC-S4-017-2019) Characterization of Al-doped boron carbide

S. Xiang[1]; B. Yang[2]; C. Hwang[2]; R. Haber[2]; K. Y. Xie*[1]

1. Texas A&M University, Materials Science and Engineering, USA
2. Rutgers University, Materials Science and Engineering, USA

Boron carbide suffers a loss of ballistic strength against high-speed threats due to the formation of amorphous shear bands. Numerous effort has been devoted to suppress the phase transformation via atomic-level doping such as Si, Al, etc. Here, we observed a surprisingly high solubility of Al in boron carbide. We also noted Al alloying reduced the surface energy of boron carbide. In this presentation, we will also investigate the effect of Al-doping on the lattice parameter, microstructure and amorphization resistant in boron carbide. Cs-corrected STEM and EELS results regarding the Al atomic occupancy in the boron carbide lattice will also be discussed.

11:10 AM

(ICACC-S4-018-2019) Characterization of residual stresses: Implications on failure of B_4C/SiC armors

T. Shoulders*[1]; A. A. DiGiovanni[1]; L. Vargas[1]

1. US Army Research Laboratory, USA

Multi-phase materials are now the norm for the ceramic "strike face" in body armor systems. To aid further development, a multi-disciplinary approach that includes obtaining a full microstructural description, experimentally probing failure at relevant scales, and modelling the failure behavior at multiple length scales is currently underway. A model study of a series of hot-pressed, particulate-reinforced, boron carbide/silicon carbide (B_4C/SiC) ceramics with compositions spanning the entire range between the two pure endpoints in 10 wt% increments is presented. While multiple efforts, including quantitative stereology, are ongoing in the microstructural characterization of these samples, the focus of this investigation is on the analysis of residual stresses by both x-ray diffraction and Raman spectroscopy. Measurements are related to quasi-static performance through Knoop indentation hardness and ultrasonic resonance measurements of the elastic properties. Initial findings within the global scope of understanding and improving the failure of multi-component armors are discussed.

11:30 AM

(ICACC-S4-019-2019) Fabrication of dense B_4C-SiC composite via preceramic polymer route

C. Hwang*[1]; Q. Yang[1]; S. Xiang[2]; V. Domnich[1]; A. U. Khan[1]; K. Xie[2]; K. Hemker[3]; R. A. Haber[1]

1. Rutgers University, Dept. of Materials Science and Engineering, USA
2. Texas A&M University, Department of Mechanical Engineering, USA
3. Johns Hopkins University, Department of Mechanical Engineering, USA

We fabricated dense B_4C-SiC composite (relative densities > 99%) via the preceramic polymer (PCP) route combined with pressure-assisted sintering by controlling surface oxide on B_4C powder and pyrolysis conditions for PCP coated powder. We elucidate i) the microstructure and phase developments observed in the process of fabricating dense B_4C-PCP derived SiC composites and ii) the mechanical properties and crack deflection behavior of dense bodies along with mechanisms to explain the trends and behavior observed. The incorporation of PCP derived SiC to B_4C decreases hardness because of the smaller hardness value of SiC compared to B_4C and the residual carbon accompanied by SiC formation. On the other hand, the PCP derived SiC improved indentation fracture toughness, for which the main toughening mechanism is not the typical crack deflection at B_4C-SiC interface caused by residual stress but a combination of crack impeding by SiC grains and crack deflection within SiC grains due to the presence of subgrains or layered structure in PCP derived SiC grains.

Materials Characterization III

Room: Coquina Salon F
Session Chair: Kristopher Behler, U.S. Army Research Lab

1:30 PM

(ICACC-S4-020-2019) Structure and Chemical Quantification of Grain Boundaries in a Boron Carbide and Silicon Hexaboride Diffusion Couple (Invited)

C. Marvel*[1]; A. M. Etzold[2]; V. Domnich[2]; K. D. Behler[3]; J. LaSalvia[3]; R. Haber[2]; M. P. Harmer[1]

1. Lehigh University, Materials Science and Engineering, USA
2. Rutgers University, Materials Science and Engineering, USA
3. US Army Research Laboratory, WMRD, USA

Doping boron carbide with silicon (Si) has been shown to mitigate stress-induced amorphization. However, it is unclear how Si is distributed throughout the microstructure (i.e. bulk lattice, grain boundaries, and second phases). This work aimed to explore grain boundary and bulk thermodynamics of Si-doped boron carbide by analytical electron microscopy (AEM) and chemical quantification using the ζ-factor approach. A diffusion couple of boron carbide and silicon hexaboride was hot-pressed using 50 MPa applied pressure at 1600 °C for 24 hours, and thin AEM specimens were extracted from multiple locations within the diffusion zone to enable direct comparisons of microstructures with varying Si concentrations. Overall, it was observed that the maximum Si solubility in boron carbide was approximately 2.0 at.% and that grain boundaries exhibited maximum excess coverages of Si of 3 atoms/nm^2 near the boron carbide / silicon hexaboride interface. The carbon concentration of boron carbide was also quantified across the diffusion zone and ranged between approximately 10 at.% and 20 at.%. Experimental procedures and results will be presented and discussed.

2:00 PM

(ICACC-S4-021-2019) Solute-Acceleration and Microstructural Evolution of Alumina (Invited)

R. Moshe[1]; W. D. Kaplan*[1]

1. Technion - Israel Institute of Technology, Dept. of Materials Science and Engineering, Israel

The influence of CaO on the evolving microstructure of alumina was studied for a range of concentrations below the solubility limit. The amount of Ca in the alumina was determined by conducting fully standardized wavelength dispersive spectroscopy, and the change in grain boundary mobility as a function of the amount of dopant was characterized using scanning electron microscopy to determine the grain size as a function of annealing time at 1600°C. Annealing experiments were conducted in a graphite furnace under flowing He, and the mobilities were compared to samples annealed in air. Unlike segregating dopants which reduce grain boundary mobility by solute-drag (such as MgO), CaO increases the rate of grain growth, and a trend of increased mobility with increasing dopant level was shown. The increased mobility with Ca segregation is believed to be due to an increase in vacancy concentration in the vicinity of the grain boundaries, thus facilitating faster grain boundary motion.

2:30 PM

(ICACC-S4-022-2019) Alignment development α-Alumina Platelets Formed via Shear/Elongational Flows of Thermoplastic Polymer and Ceramic Blends for Improved Transparency

W. J. Costakis*[1]; A. Schlup[1]; R. Trice[1]; J. P. Youngblood[1]

1. Purdue University, Materials Engineering, USA

Transparent ceramics are typically used in military applications where the combination of optical and ballistic properties are desirable. Alumina is a potential candidate due to the inexpensive raw material cost and its transparent properties in single crystal form. A cost-effective processing approach will require the use of powders leading to a final polycrystalline ceramic material were the introduction of grain boundaries will inhibit the final transparency. However, it has been shown that the alignment of α-alumina platelets can improve the transparency, but this is typically done through the use of a strong magnetic field. It is proposed that the use of shear and elongational stresses during forming can be a practical means to align α- alumina platelets. Thermoplastic polymer and α-alumina blends where developed and formed into sheets through the use of pressure through a heated hydraulic press. The effects of the processing parameters on the alignment of the α-alumina were investigated through rocking curve analysis. The fugitive binder systems was removed and final pieces were sintered via hot pressing.

2:50 PM

(ICACC-S4-023-2019) Hot Pressing Platelet Morphology α-Al_2O_3: Effect of Particle Alignment and Processing Parameters

A. Schlup*[1]; W. J. Costakis[1]; R. Trice[1]; J. P. Youngblood[1]

1. Purdue University, Materials Engineering, USA

Transparent polycrystalline ceramics have many useful military applications where ballistic protection and optical transparency are required, such as blast shields and radomes. The high hardness of alpha-alumina (α-Al_2O_3) makes it a promising candidate for these applications, but the birefringence that results from its hexagonal crystal structure limits transparency in the visible spectrum. One solution is to align the alumina particles along the same crystallographic direction prior to sintering to improve the optical properties. In the present work, shear and elongational flows in a thermoplastic polymer are utilized to align platelet α-Al_2O_3 particles along their basal planes. Subsequent polymer burnout and hot-pressing are used to densify the final part. Our processing method will be discussed, as well as how particle alignment and hot-pressing parameters influence the density and transparency of the α-Al_2O_3 samples.

Materials and Process Modeling I

Room: Coquina Salon F
Session Chairs: Shawn Coleman, US Army Research Laboratory; Jennifer Dunn, U.S. Army Research Laboratory

3:30 PM

(ICACC-S4-024-2019) A Data Fingerprint for Ceramic Design (Invited)

K. Rajan*[1]

1. University at Buffalo-the State Univ. of NY, Materials Design and Innovation, USA

In this presentation we present new ways to apply recent advances in some of our latest work in fusing computational chemistry techniques with statistical learning methods to unravel interrelationships between molecular geometry and bonding in complex crystal chemistries. We describe application of Topological Data Analysis (TDA) to capture the "shape" of data in a multiscale manner to probe for hidden correlations between crystallographic structure and electronic structure. Our work reveals new information on how chemical site occupancy within molecular nanocluster units defines groupings of chemical homologues in chemically complex ceramics. Through the application of TDA methods we develop a new genre of structure maps to visualize the classifications in chemical crystallography which we are terming as a "Material Barcode" that serves a data fingerprint for designing ceramics

4:00 PM

(ICACC-S4-025-2019) Hardness Prediction in Icosahedral Boron Rich Ceramics

A. Cheenady*[1]; A. Awasthi[1]; G. Subhash[1]

1. University of Florida, Mechanical Enginnering, USA

Hardness has been identified as the most relevant property for identifying promising ceramics in ballistic applications. Icosahedral boron rich ceramics are sought for these applications because of their low density and high hardness. In this work, the Bond Strength (BS) model and Electronegativity (EN) model are utilized to evaluate the theoretical hardness of this class of materials. These models provide estimates of the intrinsic hardness of covalent and polar covalent crystals, given their unit cell parameters and bonding environment. Boron carbide with its several polymorphs, boron suboxide, and aluminum magnesium boride ("BAM") are analyzed using these models. This analysis is extended to study the influence of dopants, such as silicon and nickel, in the cage spaces of their crystal lattice on the hardness of these crystals. Inferences are gained on the propensity of various icosahedral crystals to amorphization, a local loss of crystalline order under conditions of high pressure, and on ways to mitigate this deleterious mechanism. This study thus establishes connection between bonding characteristics, crystal structure and hardness of icosahedral ceramics, with the hope of providing valuable insight into the search for new amorphization-resistant ultra-hard materials.

4:20 PM

(ICACC-S4-026-2019) Ceramics under high pressures: Compression characteristics of B4C using molecular dynamics

A. Awasthi*[1]; M. DeVries[1]; G. Subhash[1]

1. University of Florida, Mechanical and Aerospace Engineering, USA

Boron carbide (B4C) is a highly sought icosahedral ceramic being pursued because of low density, superhard properties and economic mass-production. Its pressure-volume characteristics derived experimentally, having been investigated experimentally for several decades, have speculated the presence of phase change during conditions of high compressive stresses. Additionally, thermodynamical arguments predict melting events at high volumetric compression. Exact atomistic mechanisms revealing origin of rise in temperature and its connection with compressive pressure, have remained undetermined. In the present work, we present molecular dynamics modeling of volumetric compression of B4C using the ReaxFF potential. The atomistic system is subjected to incremental levels of volumetric compression, while pressure, temperature, and relative volume changes are monitored along with atomic configurations within the crystalline lattice. Results give new insights when compared with experimentally obtained shock behavior of B4C compiled about two decades ago, and provide a new platform to assess amorphization, a deleterious mechanism that hinders true application potential of B4C.

4:40 PM

(ICACC-S4-027-2019) Atomistic response of boron carbide under shock impact conditions using molecular dynamics

M. DeVries*[1]; A. Awasthi[1]; G. Subhash[1]

1. University of Florida, Mechanical and Aerospace Engineering, USA

The outstanding mechanical properties of boron carbide promote applications in structures, abrasives, and armor. However, when subjected to high pressures, boron carbide undergoes a deleterious loss of crystalline order known as amorphization, drastically reducing its effectiveness in such applications. Occurring via shock impact testing, indentation, and scratching, amorphization of boron carbide has been investigated extensively using these experimental techniques. Both computational as well as experimental studies have led to several theories for the mechanism of amorphization in boron carbide. In the present work, we perform molecular dynamics (MD) simulations of shock impact of boron carbide using the ReaxFF potential. The MD studies reveal that shock conditions can raise the temperature of the ceramic to that of its melting point and may be a cause for initiation of amorphization. The shock Hugoniot of the boron carbide system is discussed from both experimental and computational perspectives, and influence of defects is being examined to investigate influence of stress concentration and thermodynamic effects on amorphization. Finally, atomic deformation of the system is tracked to shed light on possible structural collapse mechanisms of amorphization in boron carbide.

5:00 PM

(ICACC-S4-028-2019) Modeling of Influence of Structural Defects in Cubic SiC on its Interaction with Shock Waves

I. Kartuzov*[1]

1. IPMS NASU, Ukraine

Silicon carbide is commonly used in modern industry as armor material. With respect to this, it is of interest to study an interaction of silicon carbide with shock waves. This effort is to investigate the properties of shock waves in cubic SiC with nonideal crystal structure. The work employs the molecular dynamics (MD) method which uses Tersoff's interatomic potentials. The main purpose is to elucidate the influence of presence of point defects (vacancies and interstitial atoms) on emergence of samples fractures resulting from shock waves, as dependent on defects concentration and loads intensity. High concentration of defects can be observed in samples subjected to intense ionizing radiation. In numerical simulations, we obtained the dependencies of threshold loads causing samples fracture versus defect concentration. In addition, the effects of shock wave propagation in SiC due to deviation from the exact stoichiometric composition, namely, in a solid solution of SiC-C, were considered. As shown in experiments, the excess of carbon in this system can form either uncorrelated point defects or ordered planar carbon defects in SiC lattice which significantly increase impact resistance of a material. The obtained results are used to explain the microscopic mechanisms of fracture of SiC ceramics subjected to shock loadings.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li Batteries II

Room: Tomoka A

Session Chairs: Valerie Pralong, CNRS ENSICAEN; Do Kyung Kim, Korea Advanced Institute of Science and Engineering (KAIST)

8:30 AM

(ICACC-S6-009-2019) Electrochemical thermodynamics of lithium batteries and their materials (Invited)

H. J. Seifert*[1]; W. Zhang[1]; D. Li[1]

1. Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

The thermodynamics of lithium battery materials has a major influence on the electrochemical performance of the operating systems. CALPHAD modeling (Computer coupling of phase diagrams and thermochemistry) allows calculated predictions regarding energy density, capacity, open circuit voltage as well as thermal behavior and safety. The phase diagrams indicate possible heterogeneous reactions during the synthesis of individual battery materials and their interactions in electrochemical cell operation. The thermodynamics of cathode materials (e.g. spinel-type; layered oxides) were investigated by combination of experimental and theoretical studies. Various types of calorimetry (drop solution, differential scanning, accelerating rate calorimetry) were used to measure heat capacities,

enthalpies of formation and enthalpy increments. Experimental data and ab initio results were then used as input for CALPHAD-type modeling of oxide systems. Here the Li-Mn-O (LMO) spinel electrode is introduced as an example to describe the composition–structure–property–performance relationships and evaluate the performance of the spinel compounds for battery applications. Cell cyclability was evaluated to find the compounds with higher electrochemical stability and suppression of the Jahn-Teller distortion. The energy density was evaluated according to the cell voltage and capacity.

9:00 AM

(ICACC-S6-010-2019) ARTISTIC Project: modeling-driven prediction of optimal rechargeable battery manufacturing parameters (Invited)

A. A. Franco*[1]

1. Université de Picardie Jules Verne, Laboratoire de Reactivité et Chimie des Solides, UMR CNRS 7314, France

In this talk i present our efforts within the ERC-funded "ARTISTIC" project [1] which aims at developing a computational platform, available in Internet and devoted to predict optimal manufacturing parameters of lithium ion batteries. The platform combines, within a multiscale simulation framework, Coarse Grained Molecular Dynamics, Lattice Boltzmann and 3D Continuum models to describe the electrode slurries, their coating process, the electrolyte impregnation and the resulting performance at the cell level. Together with the use of machine learning algorithms and an in house database built from systematic experiments, the platform is being designed to perform direct and reverse predictions. Predictions regarding the manufacturing of cells containing graphite, silicon and NMC materials are in particular discussed in connection with experiments. The novel use of immersive Virtual Reality to analyze the results is also presented. Expected implications of our efforts at the industrial level are finally discussed. [1] ERC Consolidator Project ARTISTIC (PI: Prof. Alejandro A. Franco), grant agreement #772873 (Project website: https://www.u-picardie.fr/erc-artistic/ ; European Research Council website: https://erc.europa.eu/).

9:30 AM

(ICACC-S6-011-2019) In quest of high voltage insertion compounds for Li-ion and Na-ion batteries (Invited)

M. Reynaud[1]; A. Wizner[1]; N. Katcho[1]; M. Galceran[1]; J. Carrasco[1]; T. Rojo[1]; M. Armand[1]; M. Casas-Cabanas*[1]

1. CIC energigune, Spain

A salient aspect of research in batteries is the discovery of new materials or novel properties of existing compounds. In this quest, the traditional approach is to focus on archetype compounds in which a desirable property was first observed, stimulating further investigations. This has been the innovation pathway of many battery materials. Indeed, most Li-ion cathode materials belong to a handful of structural families: layered oxides, spinel, and olivine. Yet this trial-and-error exploratory research based on extrapolating known solutions to new compositional spaces has high demands in terms of synthesis and characterization times that hinder the emergence of new, disruptive compounds. In this contribution we will present the strategies that have allowed us to develop new high-voltage materials based on the analysis of structural descriptors. Following this approach our recent results related to the nitridophosphate family ($Na_3TM(PO_3)_3N$), where N assists inductive effect induced high redox potential, will be shown. Within this family, $Na_3V(PO_3)_3N$ has been found to be the Na-ion cathode material with the highest operation voltage for the V^{IV+}/V^{III+} redox couple together with $Na_7V_3(P_2O_7)_4$. Strategies to further lower the cost and improve the safety of these systems will be discussed.

Thermoelectrics II

Room: Tomoka A

Session Chairs: Michitaka Ohtaki, Kyushu University; Olivier Delaire, Duke University

10:20 AM

(ICACC-S6-012-2019) Atomic Dynamics and Strong Anharmonicity in Thermoelectrics and Superionics (Invited)

O. Delaire*[1]

1. Duke University, USA

A detailed understanding of anharmonic lattice dynamics (phonons) is needed to refine microscopic theories of thermal transport and thermodynamics, and is of practical interest for the design of new functional materials. For example, in thermoelectrics and ferroelectrics, phonons are strongly anharmonic near lattice instabilities responsible for structural phase transitions, which directly impacts thermal conductivity or ferroelectric behavior. In superionic compounds, fast diffusion is critical for solid-state electrolytes in future all-solid batteries, but the atomic dynamics leading to large ionic mobility remain insufficiently understood and strongly debated. Our group combines advanced neutron and x-ray scattering studies with first-principles simulations to elucidate the atomic dynamics responsible for useful properties in materials for thermal energy conversion and rechargeable energy storage. In this presentation, I will discuss the results of our neutron scattering measurements in SnSe and SnS thermoelectrics, combined with first-principles simulations, revealing the strongly anharmonic behavior of acoustic and optic phonons, and explaining the ultralow thermal conductivity. I will also discuss the atomic dynamics in superionic conductors, which have recently emerged as a new class of "phonon liquid / electron crystal" thermoelectrics ($Cu_{2-x}Se$, $CuCrSe_2$ and $AgCrSe_2$).

10:50 AM

(ICACC-S6-013-2019) Rapid densification of thermoelectric compounds by flash sintering (Invited)

M. Mikami*[1]; Y. Kinemuchi[1]; K. Kubo[2]; N. Uchiyama[2]; H. Miyazaki[3]; Y. Nishino[3]

1. National Institute of Advanced Industrial Science and Technology, Japan
2. Atsumitec Co., Ltd., Japan
3. Nagoya Institute of Technology, Japan

In various kinds of functional material, its properties can be controlled by microstructure refinement in order to optimize its performance. Especially for a thermoelectric material, the reduction of thermal conductivity and the improvement of mechanical strength by the microstructure refinement can enhance its utility for thermoelectric energy conversion devices. For the fabrication of a fine-grain sintered body, a powder metallurgical technique is commonly used. In particular, electric current activated/assisted sintering (ECAS) is an effective means of microstructure refinement in sintered body because of its rapid densification of finely powdered material. Recently, flash sintering (FS), which is defined as sintering with a duration in the order of seconds, is expected as an energy efficient sintering technique. In addition, from an application viewpoint, the high production rate of FS is expected to bring improved productivity to mass production of sintered parts. In this study, FS of typical thermoelectric compounds, such as Bi_2Te_3 and Sb_2Te_3 was examined by the sintering apparatus specially designed for FS. In addition, near-net-fabrication of millimeter-sized sintered body for a thermoelectric module was also conducted using the Heusler Fe_2VAl alloy. The microstructure and transport properties of the sintered compacts will be presented.

11:20 AM

(ICACC-S6-014-2019) Developing specialty glasses as anti-sublimation barrier for thermoelectric materials

Y. Sadia*[1]

1. Ben-Gurion University of the Negev, Material Engneering, Israel

One obstacle to the widespread use of thermoelectric materials in generators is the degradation of thermoelectric materials at their most efficient temperatures. The need to choose between high efficiency and high reliability limits the technology. One solution to this problem is mitigating the degradation by creating anti-sublimation barriers. The PbO-SiO_2 system seems to be of interest in this regard allowing for a glass transition temperature of ~500-600°C. In addition, PbO should allow for better adherence and higher coefficient of thermal expansion in the glass. In this work we explored the properties of $(PbO)_{0.3}(SiO_2)_{0.7}$ glass. The glass was doped by up to 5% of Na_2O and B_2O_3 to map the possible glass transition temperatures and coefficients of thermal expansion possible in these glasses. While both Na_2O and B_2O_3 reduced the glass transition temperature of the material, sodium has a more profound effect on the transition temperature. The resulting transition temperatures ranged from 530°C for the undoped sample to ~440°C to the sample doped with 5% of both Na_2O and B_2O_3. In addition thermal expansion coefficients in the order of 6-10 ppm were obtained depending on the exact composition. These results would allow for a better tailoring of glasses for thermoelectric coating in different applications.

11:40 AM

(ICACC-S6-015-2019) Growth of flexible, nanoporous and transferable $Ca_3Co_4O_9$ thin films for thermoelectrics

P. Eklund*[1]; B. Paul[1]

1. Linkoping University, Dept. of Physics, Chemistry, and Biology, Sweden

Nanoporous thin film materials are promising for low power thermoelectric applications (e.g. to power wearable electronics, on-chip cooling, etc.), as they offer the scope for tailoring both electronic and phononic properties in a single material systems, leading to the drastic enhancement of thermoelectric efficiency. Here, we present growth of nanoporous and transferable thermoelectric Ca3Co4O9 thin films by a simple and scalable sequential sputtering-annealing method. In this method, the multilayered CaO/CoO films are first sequentially deposited on sapphire and mica substrates by rf-magnetron reactive sputtering from metallic targets of calcium and cobalt, followed by annealing under oxygen flow at 700 degrees Celsius to obtain the final phase of Ca3Co4O9. This thermally induced phase transformation is accompanied by a volume contraction over 20 %, resulting in the formation of nanopores in the film. The thermoelectric properties of the nanoporous films are tunable by controlling the porosity of the films, and thus the lowest electric resistivity ~ 7 mOhm.cm is achieved, which results in high power factor, 2.32 x 10^-4 mW/mK2 near room temperature. Furthermore, due to the weak adhesion of the films with the substrates via nanopillars they are simply transferable to other arbitrary polymer substrates by physical dry transfer.

Beyond Li Batteries I

Room: Tomoka A

Session Chairs: Shyue Ping Ong, University of California, San Diego; Nobuyuki Imanishi, Mie University

1:30 PM

(ICACC-S6-016-2019) Studies on Next Generation Battery Materials (Invited)

M. Doeff*[1]

1. Lawrence Berkeley National Laboratory, USA

Ni-rich NMC ($LiNi_xMn_yCo_zO_2$; x ≥ y+z) cathodes have high practical capacities making them an excellent choice for lithium ion batteries intended for vehicular applications. The thermal stability of these materials at high states-of-charge is, however, a concern. We have conducted bulk and surface studies on NMC-622 and NMC-811 at various levels of delithiation to understand how phase changes occur during heating. The lower the lithium content and the higher the nickel content, the lower the temperature at which phase changes occur, and the more likely that oxygen release is involved, a concern for safety. Phase changes involving loss of oxygen, such as transformation to M_3O_4 spinel or rock salt structures require overall reduction of transition metals, but there is evidence that some oxidation actually occurs, especially at particle surfaces. Nanotomography experiments show that Ni migrates throughout particles upon exposure to even low levels of heat, which may explain this observation. Ultimately, utilizing these materials in all solid-state batteries with ceramic electrolytes may mitigate issues associated with thermal instability, because there are no flammable components. For vehicle applications, however, innovative composite cathode designs are required to maximize energy density, such as one approach we will discuss during this presentation.

2:00 PM

(ICACC-S6-017-2019) Rechargeable sodium-ion batteries utilizing amide-based ionic liquid electrolytes (Invited)

T. Yamamoto*[1]; K. Matsumoto[2]; R. Hagiwara[2]; T. Nohira[1]

1. Kyoto University, Institute of Advanced Energy, Japan
2. Graduate School of Energy Science, Kyoto University, Japan

Ionic liquids (ILs) have several unique characteristics such as negligible volatility, nonflammability, and good electrochemical stability. Thus, they have been applied as the electrolytes of various energy storage devices including batteries and capacitors. Recently, many researchers are working on the development of the large-scaled energy storage devices in order to promote the utilization of intermittent renewable energy resources. Although the current lithium-ion batteries possess high energy densities, we have to carefully consider the limited resources of lithium and cobalt, and the potential safety issues of flammable organic solvent-based electrolytes. Under the current circumstances, we have focused on the sodium-ion batteries with ionic liquid electrolytes containing amide-based anion, bis(fluorosulfonyl)amide (FSA). In particular, Na[FSA]-[C_3C_1pyrr][FSA] (C_3C_1pyrr$^+$ = N-methyl-N-propylpyrrolidinium) binary system is promising as an electrolyte of sodium-ion batteries. We demonstrated that various kinds of positive and negative electrode materials exhibit good charge-discharge performance in this electrolyte. We also evaluated the performance of the sodium-ion full-cell composed of hard carbon (HC) negative electrode and $NaCrO_2$ positive electrode, and obtained superior rate capability in the ionic liquid electrolytes with higher sodium ion concentrations.

2:30 PM

(ICACC-S6-018-2019) A Nanotube-structured $Na_2V_3O_7$ Cathode Material for Sodium-Ion Batteries with High-rate and Stable Cycle Performances (Invited)

N. Tanibata*[1]; Y. Kondo[1]; S. Yamada[1]; M. Maeda[1]; M. Nakayama[1]; A. Kitajou[3]; S. Okada[2]

1. Nagoya Institute of Technology, Advanced Ceramics, Japan
2. Kyushu University, Japan
3. Yamaguchi University, Japan

Sodium ion batteries meet the demand for large-scale energy storage as in electric vehicles due to the material abundance of sodium and the possibility of high sodium diffusivity. In the present paper, nanotube-type $Na_2V_3O_7$ is proposed as a cathode material in terms of fast sodium diffusivity, thorough the investigation of ~4300 candidates via a high-throughput computation using the bond valence force field approach. The $Na_2V_3O_7$ electrode exhibited a reversible capacity of about 90 mAh g^{-1} at a constant current density of 0.1 C. The capacity corresponded to almost half of the theoretical capacity.

Remarkably good capacity retention of ~65% was obtained even at 10 C, which indicated high sodium diffusivity in the $Na_2V_3O_7$ active material suggested by the high-throughput computations. Galvanostatic intermittent titration technique (GITT) and AC-impedance measurements were conducted to investigate why the observed reversible capacity was limited to half of the theoretical value. In the GITT curves of the charge process, the voltage was sharply increased in the highly desodiated region, $x > 1$ in $Na_{2-x}V_3O_7$. AC impedance spectra showed that the abrupt increase was attributed to the diffusion process, which was also suggested by the variation of MD-derived diffusion coefficients of sodium versus composition x.

Li Batteries III

Room: Tomoka A

Session Chairs: Alejandro Franco, Université de Picardie Jules Verne; Montse Casas-Cabanas, CIC energigune

3:20 PM

(ICACC-S6-019-2019) Achieving full capacity in multi-electron $LiVOPO_4$ polymorphs (Invited)

S. Ong*[1]; Y. Lin[1]; M. Hidalgo[2]; A. Grenier[3]; D. Xiao[2]; R. Tran[1]; F. Omenya[2]; I. Chu[1]; Z. Wang[1]; X. Li[1]; N. Chernova[2]; K. Chapman[3]; G. Zhou[4]; M. Whittingham[2]

1. University of California, San Diego, Department of NanoEngineering, USA
2. Binghamton University, Department of Chemistry, USA
3. Argonne National Lab, Advanced Photon Source, USA
4. Binghamton University, Department of Mechanical Engineering, USA

The $LiVOPO_4$ polymorphs are promising multi-electron, high-voltage cathodes for rechargeable lithium-ion batteries. In this talk, we will discuss the insights into the thermodynamics and kinetics of $LiVOPO_4$ polymorphs obtained from a multi-modal approach involving density functional theory (DFT) calculations, synthesis and in operando characterization. We will demonstrate how the major polymorphs of $LiVOPO_4$ can be synthesized in a controlled manner from a single precursor and explain the observed phase transformations using DFT calculations. We will also show how the different electrochemical performances of the various polymorphs may be explained by their different Li migration topologies and barriers. Using these insights, we have achieved full capacity, i.e., two-electron, cycling in $LiVOPO_4$ by carefully optimizing synthesis and processing.

3:50 PM

(ICACC-S6-020-2019) Spectroscopic study of charge compensation in Li_3MO_4 (M=Ru, Ir) during electrochemical cycling (Invited)

J. Cabana*[1]

1. University of Illinois at Chicago, Chemistry, USA

Current battery electrode materials are unable to reversibly accommodate redox changes of more than one electron per total transition metal content. The formal activity of transition metal centers is traditionally employed to account for chemical changes during these redox reactions. In oxides, recent studies suggest that bands with a large oxygen character can supply additional charge beyond the amount compensated at transition metal centers. The descriptions of the associated modifications of electronic structure remain deficient, and so is the understanding of the role of the specific transition metal. This talk will describe the electronic changes undergone by Li_3MO_4 (M=Ru, Ir) upon reactions of Li intercalation, using a suite of measurements of X-ray absorption spectroscopy. These systems were chosen as models of compounds with transition metals in a very high formal oxidation state in their pristine state, but that are also active toward further oxidation. A comprehensive picture of the fundamental chemical and structural changes will be produced to assess charge and chemical reversibility. The goal of the talk will be to move away from ionic models to describe battery electrodes, and develop a nuanced framework of charge compensation.

4:20 PM

(ICACC-S6-021-2019) Polymer-derived Ceramic Fiber-based Electrodes for Electrochemical Energy Storage (Invited)

R. Cuccato[2]; S. Mukherjee[1]; G. Franchin[2]; P. Colombo[2]; G. Singh*[1]

1. Kansas State University, Mechanical and Nuclear Engineering Dept., USA
2. University of Padova, Industrial Engineering, Italy

Molecular precursor derived ceramics (PDCs) have garnered intense research interest as potential standalone as well as composite electrode materials for rechargeable alkali metal-ion batteries and supercapacitors. PDC based electrodes offer high surface area, improved electrical conductivity by heteroatom modification, and mechanical toughness along with added value of mass production. Here, we will present data on recent success in direct fabrication of self-standing molecular precursor-derived silicon oxycarbide (SiOC) ceramic battery and supercapacitor electrodes by two different routes--electrospinning and additive manufacturing. We will show that micro and nano-structuring of PDCs is an effective strategy in improving PDC's electrochemical cycleability toward alkali metal ions and first cycle efficiency. In addition, we will discuss the effect of PDC chemical interfacing with graphene on electrode's electrical conductivity and capacitance.

4:50 PM

(ICACC-S6-022-2019) Discussing the Homogeneity of Aluminum Distribution in $LiCo_{1-y}Al_yO_2$ for Low Doping Amounts ($y \leq 0.04$)

M. Duffiet*[1]; M. Blangero[2]; K. Song[2]; P. Cabelguen[3]; C. Delmas[1]; D. Carlier[1]

1. ICMCB-CNRS, France
2. Umicore, Republic of Korea
3. Umicore, Belgium

Although $LiCoO_2$ (LCO) has now been used for decades as positive electrode material in Li-ion batteries, only 60 % of its theoretical capacity is utilized in commercial cells. Cycling LCO at higher cutoff voltages (> 4.3 V) would be required to access more capacity, but electrolyte degradation, structural instabilities and cobalt dissolution have always led to a poor cycling performance - and prevented industrial applications. Better capacity retention was reported for Al-doped LCO, as the substitution of Co^{3+} with Al^{3+} is believed to help maintaining the layered structure of the material over cycling at high voltage. Various preparation methods have been reported for $LiCo_{1-y}Al_yO_2$, and the homogeneity of Al doping may differ from one route to another – affecting the electrochemical performance of the material in Li ion batteries. However, this aspect is rarely addressed in the literature, especially for low doping amounts. In this talk, we will discuss the homogeneity of aluminum distribution in 4% Al-doped LCO phases obtained from different solid state syntheses. A special focus will also be given to the relation between the homogeneity of the Al-doping and the electrochemical performances of the materials used as positive electrode in Li cells.

5:10 PM

(ICACC-S6-023-2019) Hierarchical structured inorganic oxides@ graphene nanocomposites as anodes for lithium/sodium ion batteries

J. Chen*[1]; H. Xu[1]; D. Wang[1]; P. Zhang[1]; W. Zhang[1]; W. Tian[1]; Z. Sun[1]

1. Southeast University, School of Materials Science & Engineering, China

Hierarchical nanostructured materials possess unique characteristics such as hierarchical pores, high surface area, large accessible space and low density, which are beneficial for electron and ion transport, mass loading and diffusion, thus endowing them with significant potentials in high-performance lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs). Herein we report our recent work on design and develop several novel hierarchical nanocomposites

including hierarchically porous carbon-coated SnO_2@graphene, yolk–shell SnO_2@graphene with multi-point contact, ternary (0D, 1D and 2D) Fe_3O_4/Co_3O_4/graphene and MOF-derived TiO_2@graphene composites. These fabricated nanocomposites deliver extraordinary electrochemical properties as anode materials for LIBs or NIBs, such as the ultralong cycle life, ultrahigh specific capacities and rate capability. The excellent lithium/sodium storage performance is attributed to the hierarchal design yielding a stabilized electrochemical interface, 3D continuous conductive networks and open diffusion channels.

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Sintering Technologies II

Room: Coquina Salon A

Session Chairs: Suk-Joong Kang, KAIST; Ralf Goller, University of Applied Sciences

8:30 AM

(ICACC-S8-010-2019) MoO_3 porous materials for neutron irradiation targets for production of ^{99}Mo/^{99m}Tc (Invited)

H. Suematsu*[1]; M. Seki[1]; T. Do[3]; M. Nanko[2]; T. Suzuki[3]; D. V. Dong[1]; T. Nakayama[1]; K. Niihara[1]

1. Nagaoka University of Technology, Extreme Energy-Density Research Institute, Japan
2. Nagaoka University of Technology, Department of Mechanical Engineering, Japan
3. Nagaoka University of Technology, Department of Nuclear System Safety Engineering, Japan

^{99m}Tc is a radioactive isotope which emits a gamma ray and yields after decay of ^{99}Mo. ^{99}Mo has been produced by nuclear fission in highly enriched uranium fuel. However, because of the security reason, other methods have to be developed. Nuclear reaction of $^{98}Mo(n,g)^{99}Mo$ is an alternative method but this requires repeated cycles of sintering, neutron irradiation and dissolution of MoO_3 targets. We are now developing a novel method to produce ^{99}Mo utilizing hot atoms by just pouring water onto the irradiated porous MoO_3 targets. As a method to prepare the porous MoO_3 targets, in this study, MoO_3-NaCl composite materials were prepared and washed by water to obtain porous MoO_3 targets. Powders of MoO_3 was mixed with 20-70 vol. % of NaCl powder and sintered in air at 500 °C for 0.5-4 hours. The sintered body was washed by water to remove remaining NaCl to form porous MoO_3. After the sintering, SEM observation revealed a core-shell structure and the core was removed by the washing. This result indicate the water went through the shell to form porous Mo-O sintered body.

9:00 AM

(ICACC-S8-011-2019) Microwave Synthesis of Red-Emitting $Ca_2Si_5N_8:Eu^{2+}$ Phosphor and its Photoluminescence Properties for White-LEDs

W. Chou[1]; C. Chang[1]; S. Huang[1]; T. Hsieh[1]; S. Chung*[1]

1. National Cheng Kung University, Chemical Engineering, Taiwan

A microwave synthesis method has been developed for synthesis of $Ca_2Si_5N_8:Eu^{2+}$ phosphor and its photoluminescence properties were investigated. Ca, Si, and Eu_2O_3 powders were used as the reactants serving as the sources of the Ca, Si and Eu. Addition of NaN_3, NH_4Cl and Si_3N_4 powders was found to increase significantly the product yield. These powders were mixed and pressed into a compact which was then embedded in AlN powder inside a BN crucible. The crucible was then placed at the center of the microwave cavity (TE103 single-mode). The microwave synthesis was performed at a microwave power (2.45GHz) of 600 W for 1 hour in a flowing 90%N_2-10%H_2 gas at one atmosphere. The synthesized $Ca_2Si_5N_8:Eu^{2+}$ phosphor absorbs light in the region of 240-520 nm and shows a single broad band emission in the region of 500-750 nm (peaking at 602 nm). The effects of process parameters on the product yield and photoluminescent properties were investigated. The peak emission intensity at an optimized Eu_2O_3 molar ratio (0.03) was measured to be ~106% of the commercial YAG:Ce^{3+} (P46-Y3) phosphor.

9:20 AM

(ICACC-S8-012-2019) In-situ coagulation casting of ceramic suspension via Dispersant Removal

K. Gan*[1]; Y. Lu[1]; X. Zhang[1]; J. Yang[1]; Y. Huang[1]

1. Tsing Hua University, Materials Science and Engineering, China

We report a novel shape forming method for advanced ceramic. Usually high solid loading and low viscosity ceramic suspension need to be prepared with dispersant. Most previous researches focused on the effect of dispersant on the dispersion and rheological properties of the suspension. However, few people notice that it can also achieve the in-situ coagulation of the suspension after the dispersant losing dispersion. Generally, stable mechanism of ceramic suspension includes electrostatic, steric, electrosteric, depletion and semisteric stabilization. In our work, we prepared four kinds of the suspension above using silicon nitride (Si3N4), silicon carbide (SiC), alumina (Al2O3) and yttria-stabilized zirconia (YSZ) powder employing tetramethylammonium hydroxide (TMAH), polymine (PEI), oleic acid (OA), sodium tripolyphosphate (STPP) etc. as dispersant, and fabricated the ceramics with good mechanical properties via dispersant reaction, hydrolysis, crosslink method and so on. We call these methods as Dispersant Removal Coagulation Casting (DRCC). We believe that, due to the numerous ceramic dispersant types, DRCC method with immense development potential can be widely applied in the ceramic colloidal forming process.

9:40 AM

(ICACC-S8-013-2019) Highly-efficient preparation of anisotropic ZrB_2-SiC powders and dense ceramics with outstanding mechanical properties

J. Liu*[1]; H. Zhang[1]

1. Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, China

Highly-dense ZrB_2-SiC composite ceramics with excellent mechanical properties including Vickers hardness of 24.5 GPa and fracture toughness of 4.8 $MPa \cdot m^{1/2}$ were successfully prepared, by spark plasma sintering of its counterpart powders synthesized by a novel molten-salt and microwave co-assisted boro/carbothermal reduction (MSM-BCTR) method. Compared with the processing conditions required by the conventional reduction method for synthesis of ZrB_2-SiC, the present MSM-BCTR method possessed a variety of significant merits including the cheaper raw materials, lower processing temperature (1200°C) and dramatically higher efficiency (soaking time as short as 20 min). More importantly, the ZrB_2-SiC powder product of MSM-BCTR was verified to have single-crystalline nature and uniform well-grown anisotropic morphologies (nano-scale rod and micron-scale hexagonal plate for ZrB_2 and SiC, respectively) as well as the resulting great potential in mechanical-property enhancement of corresponding bulk material. This great achievement was mainly ascribed to the specific MSM-BCTR conditions characterized by microwave heating and molten-salt medium.

10:20 AM

(ICACC-S8-014-2019) Processing of Novel Spinel Transparent Ceramics through Aqueous Gel-casting Technique (Invited)

H. Wang*[1]; X. Zong[1]; H. Zhang[1]; Z. Liu[1]; L. Ren[1]; W. Wang[1]; Z. Fu[1]

1. Wuhan University of Technology, China

Spinel transparent ceramics with disorder solid solution structure, e.g. aluminum oxynitride (γ-AlON), magnesium aluminate ($MgO•nAl_2O_3$), and magnesium aluminum oxynitride (MgAlON), have already been regarded as important candidates for sapphire, due to their outstanding optical and mechanical properties. In order to fit the increasing requirements in various application fields, components with large sizes and complex shapes are highly demanded. In this work, some transparent ceramics have been prepared through aqueous gel-casting shaping technique. The effects of pH value, dispersant, ball-milling time and solid loading on the viscosity of slurries were investigated. The influences of monomer concentration, MAM/MBAM ratio and solid volume fraction on the bending strength and relative density of green bodies were studied. Finally, slurries with high solid loading (>50vol%) and low viscosity (<500mPa•s) were prepared through all above optimized parameters. After casting and calcining, the obtained samples were densified by pressureless sintering and further hot isostatic pressing. The sintered transparent ceramics showed high in-line optical transmittance. The microstructure of green bodies and sintered samples were investigated.

10:50 AM

(ICACC-S8-015-2019) Densification in Ionic Materials Nanoparticulate System under Simultaneous Applied Electric and Thermal Fields: An in situ time-resolved line broadening study using energy dispersive x-ray diffractometry with an ultrahigh energy synchrotron probe (Invited)

I. Savkliyildiz*[1]; E. Akdogan[2]; T. Tsakalakos[2]; Z. Zhong[3]; H. Bicer[4]

1. Konya Technical University, Turkey
2. Rutgers University, USA
3. Brookhaven National Laboratory, USA
4. Dumlupinar University, Turkey

As the temperature is raised from RT-905 °C, the superposition of a nonisothermal field and a 215 V/cm dc E-field on the 8% Y_2O_3-ZrO_2 nanoparticulate system leads to an anisotropic and abrupt increase in (101) and (110) coherently diffracting domain size (CDDS) from 32 and 21 nm to 88 and 128 nm, and a decrease in d-spacing variation (DSV) from 0.72% and 0.64% to 0.44% and 0.52%, respectively, while burst mode densification to 97% of theoretical is observed. The CCDS and DSV exhibit time-dependent relaxation/recovery to their initial state upon cool down from 905 °C to RT under zero E-field. The results provide direct proof of oxygen vacancy transport as well as rearrangement in the crystal lattice under the action of the simultaneous fields causing burst mode densification.

11:20 AM

(ICACC-S8-016-2019) Macroscale internal structure and density distribution in powder compact made by granule die-pressing

S. Tanaka*[1]

1. Nagaoka University of Technology, Materials Science and Technology, Japan

In order to attain the homogeneous packing structure, it is necessary to understand the realistic phenomena of the forming process. In this study, the deformation of granules and packing homogeneity in the powder compact were evaluated macroscopically by the liquid immersion method with a confocal scanning laser fluorescent microscope (LI-CSLFM), and the influence of granules characteristics and pressure were examined on the packing structure in the powder compact. The granules were prepared from slurries with organic binder by a spray-drying. The size distribution of granules was controlled to be narrow in the range of 63-75 μm. The granules characteristics such as binder-segregation, relative density, and compressive strength were evaluated. The powder compacts were fabricated with uni-axial pressure 20-100 MPa. The results show that the granules near the punch deformed anisotropically, whereas those deformed isotropically at the center. It indicates that the isotropic pressure was applied to the granules at center part. The relative density distribution of the powder compact was estimated from the deformed shape of each granule. The relative density increased at the center part. Thus, local relative density was also changed by the characteristics of granules. Deformability and stress transference may affect the packing structure of powder compacts.

Advanced Manufacturing and Processing I

Room: Coquina Salon A

Session Chairs: Anne Leriche, University of Valenciennes; Hao Wang, Wuhan University of Technology

1:30 PM

(ICACC-S8-017-2019) Hybrid SHS-based Technologies to Fabricate Advanced Ceramics and Composites (Invited)

A. Mukasyan*[1]

1. University of Notre Dame, Chemical and Biomolecular Engineering, USA

Combustion synthesis (CS) or Self-propagating High-temperature Synthesis (SHS) is a unique approach to produce a wide variety of advanced materials in forms of powders, bulk solids and net shape articles. CS is based on the fundamental ability of the exothermic reactions to occur in self-sustained manner, reaching extremely high heating rates (up to 10^6 K/s) and temperatures (2000-4000 K). Ceramics were among the first materials manufactured by SC. The goal of this paper is critically discussed the recent results for direct CS of the ceramics. Special attention is paid to the last achievements in the field of hybrid processing, including combustion synthesis + spark plasma sintering; combustion synthesis + high-energy ball milling; combustion synthesis + shock wave. It is also an attempt to prove that combustion-based technologies provide an efficient route for productions of variety of ceramics, which is difficult tofabricate by other methods.

2:00 PM

(ICACC-S8-018-2019) Si_3N_4/graphene nanocomposites for tribological applications

C. Balazsi*[1]; K. Balazsi[1]

1. HAS Centre for Energy Research, Hungary

The main aim of this work is to develop novel, highly efficient tribological systems on the basis of ceramic/graphene nanocomposites as well as to prove their superior quality and to demonstrate their suitability for technical applications e.g. for slide bearings and face seals in aqueous media. Current research in the field of ceramic nanocomposites shows that is possible to make ceramic materials with improved mechanical and tribological properties by incorporating graphene into the Si_3N_4 structure. Multilayered graphene (MLG) was prepared by attritor milling at 10 hours intensive milling of few micrometer sized graphite powders. The large quantity, very cheap and quick preparation process are a main strengths of our MLG. Si_3N_4 / MLG nanocomposites were prepared by attritor milling and sintered by hot pressing (HP). The Si_3N_4 ceramics were produced with 1wt%, 3wt%, 5wt% and 10wt% content of MLG. Their structure was examined by transmission electron microscopy (TEM). The tribological behavior of composites in different environments was investigated and showed the decreasing character of wear at increased MLG content. This new approach is very promising, since ceramic microstructures can be designed with high toughness and provide improved wear resistance at low friction.

2:20 PM

(ICACC-S8-019-2019) Evaluation of the carbon fiber orientation in the composites materials by using X-ray

Y. Sugimoto*[1]; Y. Hotta[1]; D. Shimamoto[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Carbon fiber reinforced plastics (CFRPs) are high strength and high modulus and lightweight materials and used in wide range filed from aerospace application to sports gears. The property of the composites is determined by various factors: fiber property, matrix property, fiber/matrix interface property, and composites architecture. So, evaluating these factors is important. Carbon fibers are anisotropically ceramic material and controlling fiber orientation which is related to the composites architecture is especially important. In the case of the composites using the glass fibers, X-ray CT can evaluate internal structure clearly. Owing to the recent computer calculation power, not only global orientation distribution but also local orientation distribution can easily be obtained. On the other hand, in the case of CFRPs, the density difference between carbon fiber and matrix is very small. It is very hard situation to distinguish single fibers by X-ray CT at present stage. It is known that carbon fiber has nano-voids and they scatter the X-ray in the perpendicular direction to the fiber. This scattering pattern can be measured by small angle X-ray scattering (SAXS). In this study, using SAXS, carbon fiber orientation in CFRPs was measured. Using cylinder symmetry assumption and orientation function, orientation distribution was determined.

2:40 PM

(ICACC-S8-020-2019) Development of the Production Process of a Prepreg for BN Particle Dispersion SiC/SiC Composites without Fiber/Matrix Interface

S. Ogitani*[1]; K. Kamoshida[1]; A. Kato[1]; S. Taguchi[1]; K. Toujinbara[1]; S. Aratani[1]; N. Miwa[1]; K. Ashitaka[1]; K. Shimoda[3]; T. Kanayama[4]; K. Yamaoka[4]; A. Edano[4]; K. Igawa[4]; T. Hinoki[2]

1. Fujimi Incorporated, Advanced Technology Research Center, Japan
2. Kyoto University, Japan
3. National Institute for Materials Science (NIMS), Japan
4. Marui Orimono Co., Ltd., Japan

Several manufacturing methods for SiC/SiC composites have been being investigated. However, currently available technologies still need to reduce its high production cost like BN coating on the SiC fiber surface while improving oxidation resistance. The objective is to develop the production process of a prepreg which consists of a 2D woven SiC fabric without fiber coating and matrix material containing BN particles. A yarn path guide and a weft insertion device were designed based on the curvature radius of SiC fibers. The effects of the dispersion of BN particles in SiC matrix and the compatibility of plasticizers with a binder resin on the uniformity of the matrix were studied by the SEM observation of the matrix. The modified loom successfully enabled us to obtain 30cm wide and 150m long SiC fabric with little damage to SiC fibers. It was found that non-uniformly dispersed particles created many large voids in the matrix, and that diethylene glycol was the best choice among evaluated plasticizers to obtain homogeneous matrix. By combining the 2D woven technique and uniform matrix fluid, the prepreg production process has become ready to go industrial stage. This work was supported by METI, Japan for the Advancement of Strategic Core Technologies, "Development of Production Process of SiC/SiC composites for High Efficiency Aircraft Engine"

3:20 PM

(ICACC-S8-021-2019) Effect of machining on surface quality of Oxide Ceramic Matrix Composites - OCMCs (Invited)

R. Goller*[1]

1. University of Applied Sciences, Mechanical Engineering, Germany

Oxide Ceramic Matrix Composites (OCMCs) are promising materials for high temperature applications for gas turbines. The implementation of these materials is necessary to further increase the energy efficiency of turbine machines. However there are many challenges on the way to industrial production. One important step is the final machining of the components. Although the parts are produced near net shape a final finishing is required to reach dimension tolerances and topography for coating. the machining is done with diamond tools of different grain sizes and diamond cutting tool with polycrystalline diamond (PCD) inserts at different process parameters. The presented work will show the influence of machining on surface roughness and damage of a commercial OCMC.

3:50 PM

(ICACC-S8-022-2019) Fabrication of Three Dimensional Nanostructures by Two-Photon Polymerization Method and Their Motion Control in Electric Field (Invited)

T. Nguyen*[1]; T. Nakayama[2]; T. Takahashi[1]; Y. Tokoi[3]; H. Suematsu[2]; M. B. Mohd Pauzi[1]; K. Moriya[2]; K. Niihara[2]

1. Kushiro National College of Technology, Department of Creative Engineering, Japan
2. Nagaoka University of Technology, Japan
3. Nagaoka National College of Technology, Japan

The development of two-photon polymerization method in nanoscale 3D printing has enabled the ability to create micromachines with feature size smaller than 100 nm. These micromachines, then can be driven using pressure, fluid, magnetic field, and especially electric field because of its high precision in motion control. In this research, firstly a micromachine system with piston and filter for cracking bacterial cells and recovering useful precious chemical substances inside was fabricated by the above method. Then, the micromachine was put into an experimental setup prepared for the electric-field-induced motion of the piston. The movement of the piston destroyed the bacterial cell to release the precious matter. The useful matter was passed through the filter and collected at the other end of the system for other research purposes. The structure of the created micromachine was analyzed with a scanning electron microscope, and in-situ observation of the motion of the system was conducted with a digital microscope.

4:20 PM

(ICACC-S8-023-2019) Understanding the Electrical properties of epoxy MoS_2 nanocomposites

N. Peddamallu*[1]; K. Sridharan[1]; T. Nakayama[2]; S. Ramanujam[1]

1. IIT Madras, Electrical Engineering, India
2. Nagaoka University of Technology, Japan

In recent times, epoxy nanocomposites are gaining importance as an insulant because of its enhanced electrical, thermal and mechanical properties. The use of MoS_2 as nano filler with epoxy resin have indicated good thermal and mechanical properties. It is essential to understand the dielectric properties of epoxy MoS_2 nanocomposites with different filler concentration, at different temperatures. The results of the study indicate that tuneable dielectric constant with low dielectric losses can be achieved by varying the filler content. In addition, theoretical models are used to predict to achieve the required dielectric properties of composites. As a part of the study, surface charge accumulation characteristics and trap charge analysis of the nanocomposites are studied. Resistance to electrical discharges of developed nanocomposites are analysed by carrying out experiments adopting IEC (b) electrode configuration. Also the hardness of the material and resistance to electrical discharges are correlated.

4:40 PM

(ICACC-S8-024-2019) Innovative manufacturing technique for ceramic fiber and particle reinforced aluminum components

M. Jiménez Martínez*[1]; R. Gadow[1]

1. University of Stuttgart, Institute for Manufacturing Technologies of Ceramic Components and Composites, Germany

The excellent strength and stiffness of Metal Matrix Composites (MMC) enable new lightweight solutions for structural applications. Further functionalities, such as improved wear resistance or reduced thermal expansion, can be also tailored by dispersion of particles in the metallic matrix. Most MMC manufacturing routes are based on liquid state processes, whereby fibers come in direct contact with molten metal. This exposure can lead to undesirable chemical reactions at the fiber-matrix interface damaging the filaments and impairing the mechanical strength of composites. For this reason, cost-intensive ceramic fibers are traditionally selected as reinforcement. This fact means a distinct handicap of competitiveness of this material-class for applications in the automotive sector. An innovative manufacturing technique, based on the semi solid forming and consolidation of thermally sprayed pre-impregnated products, enables the production of MMC components in a cost-effective way. The key enabling factor is the reduced processing temperature, which implies an increase of thermal efficiency and a reduction of fiber damage, allowing the introduction of carbon fibers as reinforcing material and thereby improving the competitiveness of the material. This presentation will discuss material characterization, industrial applications and future potential for upcoming industrial challenges.

5:00 PM

(ICACC-S8-025-2019) SiC_f/SiC Ceramic Matrix Composites using Microwave Enhanced Chemical Vapour Infiltration

M. Porter*[1]; A. D'Angio[2]; J. Binner[1]; M. Cinibulk[3]

1. University of Birmingham, Metallurgy and Materials, United Kingdom
2. National Composites Centre, United Kingdom
3. Air Force Research Lab, USA

High-temperature ceramic matrix composites (HT-CMCs), specifically SiC_f /SiC, have been identified as candidates to operate in the hostile aero-thermo-chemical environments experienced in service without compromising structural integrity, whilst keeping mass at a premium. Chemical vapour infiltration (CVI), is an effective advanced manufacturing route capable of creating near fully dense CMCs with a very refined microstructure with no fibre preform degradation and minimal residual stresses. CVI's challenges, however, are threefold; i) processing is typically 2 – 3 months; ii) premature surface pore closure occurs preventing great than 90% densification; iii) subsequently associated costs are very high and the resulting products very expensive. Microwave energy (MCVI) has been proposed as a potential solution to heat the SiC fibre preform for CVI; it produces an inverse temperature profile, which initiates densification at the centre of the sample, thus avoiding porosity closure. It is expected that the use of MCVI could yield near fully dense products in as little as 72 – 96 hours. An update will be provided on the latest results with respect to the densification profile developed within the SiC preform, the stoichiometry and crystal structure of the resulting SiC deposit; the modelling and simulation of the gas flow through the preform and the properties of the resultant composite.

S11: Advanced Materials and Innovative Processing Ideas for Production Root Technologies

New Concepts and Emerging Technologies for Enhanced Product Performance I

Room: Ponce de Leon

Session Chairs: Kyoung Il Moon, KITECH; Tadachika Nakayama, Nagaoka Univ of Tech

8:30 AM

(ICACC-S11-010-2019) Synthesis and signal detection of pressure sensor for IoT application (Invited)

T. Nakayama*[1]

1. Nagaoka Univ of Tech, Japan

Competition for development of various IoT devices is spreading. Sensor development is one of the important research themes among them. In this paper I developed the IoT system on pressure through development of a pressure sensor and transferring information obtained from this sensor to a smartphone. The pressure sensor has a structure in which carbon particles are dispersed in silicone rubber. We investigate the influence of carbon dispersion amount and presence mode on sensor characteristics.

9:00 AM

(ICACC-S11-011-2019) Microstructural Evolution of Polymer Precursor-derived SiC on Core/Rim Structure (Invited)

L. Ji Hwoan*[1]; J. Byung-Koog[1]

1. Kyushu University, Interdisciplinary Graduate School, Republic of Korea

To overcome the low sinterability of silicon carbide (SiC), polymer precursor (Polycarbosilane (PCS)) and spark plasma sintering (SPS) were employed. The densification of PCS-derived SiC ceramics was conducted without sintering additives using SPS at 1700 ~ 1900°C under 40 or 80 MPa pressure. In the SiC discs sintered at 1800 and 1900°C under the 80 MPa, the microstructure consisted of core, intermediate and rim regions: porous microstructure with only a β-SiC in the rim region; dense microstructure with α-SiC, graphite, and amorphous SiO_2 in the core region; denser microstructure with similar components in the intermediate region. The amorphous SiO_2 located in the SiC samples as well as free carbon played a key role on the final grain and pore sizes and porosity of the sintered body. The reduction and evaporation of SiO_2 led to vapor transport mechanism and resulted in high porosity with coarser microstructure. The presence of amorphous SiO_2 in the core and intermediate regions resulted in a higher densified microstructure with finer grains and pores. The reactions with introduced carbon and oxygen and characteristics (short time for reaction, different loaded pressure) of SPS were multiply applied to core/rim structure.

9:20 AM

(ICACC-S11-012-2019) Electrically and Thermally Conductive Liquid-Phase Sintered Silicon Carbide Ceramics (Invited)

Y. Kim*[1]; Y. Kim[1]

1. University of Seoul, Dept. of Materials Science & Engineering, Republic of Korea

Electrically and thermally conductive liquid-phase sintered SiC ceramics (LPS-SiC) were developed by hot-pressing SiC and Y_2O_3-Sc_2O_3 powder mixtures. X-ray diffraction data indicated that the specimens consisted mostly of β-SiC as a major phase and traces of α-SiC and $(Sc,Y)_2Si_2O_7$ phases. The LPS-SiC showed both high electrical conductivity on the order of $\sim 10^1$ $(\Omega cm)^{-1}$ and high thermal conductivity (≥200 W/mK). Growth of N-doped SiC grains contributed to increase the electrical conductivity of the LPS-SiC. The high thermal conductivity of the LPS-SiC was attributed to

(1) oxygen pick-up of the Y_2O_3-Sc_2O_3 additives in SiC lattice by forming $(Y,Sc)_2Si_2O_7$ phase, (2) the lack of solubility of Y in SiC lattice, and (3) the suppression of the β→α phase transformation of SiC during hot pressing in a nitrogen atmosphere. According to the Wiedemann–Franz law, the electron contribution to the thermal conduction in the present specimens was negligible (~0.003%). The electrically and thermally conductive LPS-SiC ceramics could be successfully used as a die material for spark plasma sintering.

9:40 AM

(ICACC-S11-013-2019) Fractography of Al_2O_3 and Si_3N_4 Ceramics Fractured in Torsion (Invited)

F. Feng*[1]; K. Yasuda[1]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan

Torsion fracture is one of the most important fracture modes, however, there is a little investigation on it in ceramics because torsion tests need special jigs. Recently, an easy-to-use torsion test method has been developed, and applied to Al_2O_3 and Si_3N_4 ceramics by the present authors. Torsion strength was slightly different from bending strength of the same ceramics, however, by calculating the characteristic strength σ_0 of Weibull distribution, reasonable agreement was seen between torsion and bending data in both ceramics. It means that torsion fracture is also controlled by tensile mode fracture microscopically by normalizing the volume effect. In this presentation, fracture surfaces of Al_2O_3 and Si_3N_4 ceramics were observed to find the fracture origins made by torsion fracture, and discuss the differences in size and shape of the origins between bending fracture and torsion fracture.

10:20 AM

(ICACC-S11-014-2019) The development of CFRTP having both high mechanical properties and high recyclability (Invited)

T. Irisawa*[1]; Y. Tanabe[1]; N. Nagao[1]; S. Kobayashi[1]

1. Nagoya University, Japan

Carbon fiber reinforced thermoplastics (CFRTPs) get a lot of attention for their high production rate, and some commodity thermoplastics have been chosen as the matrix polymer in terms of cost. However, it is also concerned that these CFRTPs are insufficient in terms of mechanical and thermal properties. Therefore, this study focuses on CFRTPs made with the aromatic thermoplastic such as polyethersulfone (PES) as the next generation CFRTPs. Firstly, in this study, CFRTPs made with PES were investigated in terms of the mechanical properties and thermal stability for aircraft and automotive applications. If the CFRTPs can be used for their applications, they contribute to the realization of sustainable society. Therefore, this study deals with CFRTPs made with PES as sustainable CFRTPs. Furthermore, it is thought that the CFRTPs themselves should be sustainable materials, if they are used for the realization of sustainable society. Therefore, the recyclability of the CFRTPs were also discussed in this study. This study finally will report about the extremely high mechanical properties and good thermal stability of CFRTPs made with PES. Moreover, this study will discuss the good recyclability of them.

10:50 AM

(ICACC-S11-015-2019) The two-stage crack-healing reaction in Yttrium titanate-TiC composite (Invited)

H. Iwasawa*[2]; S. T. Nguyen[1]; W. J. Paulo[2]; A. Okawa[2]; T. Nakayama[2]; K. Sugiya[2]; H. Suematsu[2]; T. Suzuki[2]; K. Niihara[2]

1. National Institute of Technology, Kushiro College, Japan
2. Nagaoka University of Technology, Japan

In this research, we report not only the formation of oxides, but also the two-step repair reaction that reacts the formed oxides with the matrix phase. Yttrium titanate (Y_2TiO_5, $Y_2Ti_2O_7$) was selected for the matrix phase and TiC was selected as the filler. The repair process of this material is first, TiC dispersed in the Matrix phase is reacted with TiO_2, next, the produced TiO_2 is reacted with Y_2TiO_5 contained in the parent phase. Finally, it is aimed at making single phase $Y_2Ti_2O_7$. In this report, after making a sample in which Y_2TiO_5 is included in $Y_2Ti_2O_7$ as a matrix, TiC is mixed with Y_2TiO_5 so that the molar ratio is 1: 1. The volume ratio of TiC was to the matrix phase 5% and 6%. After sintering the mixed sample by hot pressing. The sample surface with Vickers indentation introduced was observed by scanning electron microscope (SEM). After that, performed an annealing to indented sample at 450 °C, 500 °C, and 550 °C in the air, and the state of the indentation was compared before and after the annealing. The composition of that sample was confirmed using X-ray diffraction (XRD) and Energy dispersive X-ray spectrometry(EDS). As result, we could confirm dispersion of TiC in sintering sample and crack filling by annealing.

11:10 AM

(ICACC-S11-016-2019) Recovering the crack-healing agents in the self-repairing nanocomposites and their high-temperature strength (Invited)

T. Nguyen*[1]; T. Nakayama[2]; H. Suematsu[2]; K. Niihara[2]; K. Sugiya[2]; H. Iwasawa[2]

1. Kushiro National College of Technology, Department of Creative Engineering, Japan
2. Nagaoka University of Technology, Japan

Ytterbium silicate ($Yb_2Si_2O_7$) is a promising candidate material for the uppermost layer of the environmental barrier coating, which is important for protecting the underneath SiC/SiC gas turbine blade against hot gas and oxidation. The reinforcement of SiC nanofillers into the ceramic has proven that not only improve the tensile strength but also enable the crack healing ability of the ceramic. However, the bending strength and crack-healing behavior of this composite during operation at high temperature are still unknown. Here, we introduce a hybrid material prepared by dispersing both SiC particles and SiC whisker into $Yb_2Si_2O_7$ ceramic with various volume content (0 to 15%). Then the crack healing behavior and bending strength of the hybrid at high temperatures (up to 1373 K) are evaluated by conducting high-temperature bending strength tests for smooth, indented, and healed specimens. In addition, a heat-treatment process for recovering the healing agent of environmental/thermal barrier coatings to continuously employ this useful property is also introduced in this paper.

11:30 AM

(ICACC-S11-017-2019) Effect of TiC addition on $Y_2Ti_2O_7$-Y_2TiO_5 ceramics on their mechanical properties and promotion of a self-healing process (Invited)

A. Okawa*[1]; S. T. Nguyen[2]; W. J. Paulo[1]; H. Iwasawa[1]; T. Nakayama[1]; K. Sugiya[1]; H. Suematsu[1]; T. Suzuki[1]; K. Niihara[1]

1. Nagaoka University of Technology, Japan
2. National Institute of Technology, Kushiro College, Japan

This work evaluates the effect of TiC addition on $Y_2Ti_2O_7$-Y_2TiO_5 (YT75) ceramics on their mechanical properties and promotion of a self-healing process. Several $Y_2Ti_2O_7$-Y_2TiO_5-TiC composites (YT75C) were fabricated by using solid state reaction and hot-press sintering at 1500°C for 1 h in Ar at 25 MPa. All YT75C composites were annealed at 1200°C in air for 6 h to promote the oxidation of TiC into TiO_2, and then, induce a chemical reaction between Y_2TiO_5 and TiO_2 to form new $Y_2Ti_2O_7$ phase, evidencing a self-healing process. X-ray diffraction (XRD) was used to characterize the phase transformations before and after annealing, whereas scanning electron microscope (SEM) was used for observing TiC distribution on the YT75C surface. Vickers hardness and fracture toughness of YT75 and YT75C composites were evaluated at different TiC additions. Results confirmed the promotion of a self-healing process in YT75C composites after annealing. It is expected that an adequate amount of TiC addition could enhance the mechanical properties of YT75 ceramics and promote a self-healing process in YT75C composites, simultaneously.

New Concepts and Emerging Technologies for Enhanced Product Performance II

Room: Ponce de Leon

Session Chairs: Giovanni Ramirez, Bruker Nano Surfaces; Sungwook Mhin, Korea Institute of Industrial Technology

1:30 PM

(ICACC-S11-018-2019) Enhancement of tribological surfaces by tribocatalysis (Invited)

G. Ramirez*[1]; O. Eryilmaz[2]; A. Erdemir[2]

1. Bruker Nano Surfaces, USA
2. Argonne National Laboratory, USA

PVD coatings are commonly in use to increase the durability of the surfaces on mechanical components and tools. However, surfaces that can provide booth wear resistance and friction control are not easy to achieve. In this work, we present the concept of tribocatalysis of coatings/thin films that when interacting with lubricating oils, can enable the increase in wear protection while decreasing the friction by at least 20%. We will describe how this tribocatalysis events empowers the formation of a lubricious carbon based tribofilm, which is formed directly from hydrocarbon molecules of the oil. The metal catalysts that compound the coating enable the process that breaks the hydrocarbon molecules of the lubricant and under pressure and temperature, produces different forms of carbon nanostructures. In this work, tribological tools and advanced characterization techniques (such as Raman Microscopy, TOF-SIMS and HR-TEM) help to elucidate the presence of such amorphous carbon-based tribofilms. With the help of MD and ab-initio molecular dynamic simulations we will be able to prove our tribo-catalysis theory that allows the in-operando formation of a protective tribofilm.

2:00 PM

(ICACC-S11-019-2019) Development and characterization of Zr Based multi component nanocomposite coating for low friction applications (Invited)

K. Moon*[1]; H. Lee[1]; H. Yoon[1]

1. KITECH, Republic of Korea

There are increasing demands on the development of new nano composite coatings with high thermal stability, high hardness, and low friction coefficient for automobile engine systems. For this, various phase should be formed in nano-range, That is, nanocomposite should be formed. According to the alloy design rules for the nanocomposite coating, it is not easy to make the alloying target. Thus, nanocomposite coating is made with multiple targets. This results in the complex of equipment and process for nanocomposite coating. So, if a single alloying target with homogeneous compositions and high toughness could be prepared, it is considered that the mass production of nanocomposite coating would be easier than before. Previously, various single allying targets with the composition of Mo-Cu-X and Zr-Cu-X, and Ti-Al-X have been tried to be made by powder metallurgy methods such as atomization, mechanical alloying, and Spark Plasma Sintering (SPS). In this present, update data on the tribo-properties of Zr based nanocomposite coating will be summarized.

2:20 PM

(ICACC-S11-020-2019) Overstoichiometric $TMN_{x>1}$ transition metal nitrides: New generation of coatings (Invited)

S. Kos*[1]; J. Musil[1]; G. Remnev[2]

1. University of West Bohemia, Czechia
2. Tomsk Polytechnic University, Russian Federation

The overstoichiometric $MeN_{x>1}$ nitride coatings represent a new class of coatings with unique properties. They are created by a reactive sputtering in magnetron discharges generated in an ionized mixture of Ar + N_2 gases. These nitrides are created at atomic level from TM atoms sputtered from the magnetron target and N atoms of dissociated and ionized N_2 gas, i.e. $TM + xN \rightarrow TMN_x$, condensing on the substrate surface. To form $TMN_{x>1}$ films the deficiency of N atoms must be removed. In principle there are two ways how it can be achieved: (1) A strong increase of the ionization of sputtering gas and (2) A reduction of the number of TM atoms to a value corresponding to the stoichiometry x of the $TMN_{x=2}$ dinitride film, i.e. $N_N = 2\ N_{TM}$. A technique combining both ways was used in our experiments described in Refs [1,2]. Formation of overstoichiometric $ZrN_{x>1}$ and $TiN_{x>1}$ and their properties are reported in detail.

2:40 PM

(ICACC-S11-021-2019) The effect of element addition on the mechanical properties of AlCr-based coatings (Invited)

H. Lee*[1]; H. Yoon[1]; K. Moon[1]

1. KITECH, Heat Treatment Technology R&BD Group, Republic of Korea

For tool and aerospace parts and manufacturing, materials with high hardness and tribo characteristics are needed. In order to improve the durability and abrasion resistance of current tools, many thin films having excellent mechanical properties such as AlCrN, TiN, and TiAlN are being applied. In this study, AlCrFe based ternary and quaternary alloys were designed for thin films with high hardness and high heat resistance. An AlCr-based powder was prepared for target production, and a sputter targets were prepared using the hot press process. In order to prepare an AlCr-based powder, addition of an Fe element is inevitable. Therefore, various elements were added to the AlCrFe powder to prepare a sputtering target. AlCrFe based coatings with various elements were deposited by sputtering. For application as a tool coating, the hardness, adhesion and heat resistance of the coatings were analyzed.

3:20 PM

(ICACC-S11-022-2019) Effect of electric current on grain refinement during solidification in aluminum

M. Kim*[1]; J. Choi[1]; M. La[2]; D. Kim[1]; K. Choe[1]

1. Korea Institute of Industrial Technology, Liquid Processing & Casting Technology R&D Group, Republic of Korea
2. Korea Institute of Industrial Technology, Molds & Dies R&D group, Republic of Korea

Weight reduction is the most cost-effective mean to reduce fuel consumption from the transportation sector. The use of lightweight alloys such as aluminum and magnesium alloys is one way to satisfy requirement of weight reduction in automotive industry. Also, as the safety standards become stricter, the mechanical property including strength should be also guaranteed or improved for using lightweight alloys. Various methods have been used for enhancing the strength of alloys, such as the solid-solution strengthening, strain hardening, precipitation hardening, and strengthening through grain refinement, etc. Especially, grain refinement has been suggested effective method for improving property of metal alloy. Several methods to obtain fine grains have been used in casting process such as adding grain refiner, ultrasonic vibration, electromagnetic vibration, electromagnetic stirring, and electric current (EC) technique. In this work, effect of electric current on grain refinement during solidification in pure aluminum under the application of electric current is investigated based on the microstructural analysis. The value of applied electric current and duration are set as variables for experiment and effect of electric current during solidification is discussed to understand the mechanism of grain refinement by applying electric current during solidification.

3:40 PM

(ICACC-S11-023-2019) Cast bonding of Aluminum-Cast Iron bimetals for automotive applications

D. Kim*[1]; T. Kim[1]; J. Yang[1]; J. Shin[1]

1. Korea Institute of Industrial Technology, Republic of Korea

In the automotive industry, various methods have been studies in order to simultaneously achieve high strength and light weight. The conventional manufacturing methods such as fusion bonding, pressure bonding, diffusion bonding, friction welding methods and so on have been developed for bonding different kinds of metal. However, due to the limitation on the shape of the component, productivity and interfacial bonding strength, the use is still limited. The casting technology has an advantage that complex shapes can be manufactured with high production speed. In addition, since the ferrous metals such as cast iron and carbon steel can cast a part close to the final shape while having high strength, it is expected to be a great advantage when combining with light materials having high castability. In the point of view of the materials, aluminum-cast iron bimetal is one of the most interesting materials for the high strength and light weight automotive parts. In the meantime, many researches have been performed on the combinations of carbon steels or alloy steels and aluminum, but the studies on bonding between cast iron having high industrial utilization and aluminum alloys with excellent castability have not been fully studied. In this presentation, the cast bonding process to improve interfacial bonding strength of aluminum and cast iron via the surface treatment and casting method are introduced.

4:00 PM

(ICACC-S11-024-2019) Material characteristics and clinical performance of a newly-developed calcium-based bone void filler (Ezechbone®Granule) (Invited)

J. Chern Lin*[1]; C. Ju[1]; B. Yang[1]; J. Lee[2]; W. Hong[3]; S. Chiou[5]; C. Lin[4]; C. Li[4]

1. National Cheng-Kung University, Materials Science and Engineering, Taiwan
2. National Cheng-Kung University Medical College and Hospital, Surgery, Taiwan
3. Wei-En Dental Clinic, Taiwan
4. Joy Medical Devices Corp, Taiwan
5. Livingstone Dental Clinic, Taiwan

A series of synthetic, inorganic, highly osteoconductive and fully resorbable calcium-based bone substitute material (Ezechbone®Granule) has been developed by a joint research project of National Cheng-Kung University and Joy Medical Devices Corporation of Taiwan. The porous granular product is uniquely featured by its high resorption/healing rate. Safety and efficacy of the device were confirmed by a series of chemical/ physical characterization and biocompatibility tests such as cytotoxicity, sub-chronic toxicity, intracutaneous reactivity, skin sensitization, ocular irritation, endotoxin test, hemolysis test, genotoxicity and implantation. Animal models for implantation tests include SD rat femur body, New Zealand white rabbit femur condyle and mandible, Lanyu pig mandible, and osteoporotic goat spine. The histopathologic examination indicates that the implant is always intimately integrated with surrounding bone tissues. Majority of Ezechbone® Granule is readily resorbed and replaced by new bone as early as 4W post implantation. The early-stage new bone formation of Ezechbone® Granule is faster than autologous group by >10 times. Clinical cases include ridge augmentation, sinus lift, etc. The research was funded by Southern Taiwan Medical Device Industry Cluster (CY-08-09-60-106).

4:20 PM

(ICACC-S11-025-2019) Densification Optimization of Ceramics Using Dilatometer Results and Kinetic Analysis (Invited)

E. Post*[1]

1. NETZSCH Geraetebau GmbH, Germany

Ceramics are often produced by sintering a green body that contains some amounts of organic or inorganic binder. After burn-off of the binder, the sintering process follows. The burnout and sintering parameters have significant influence on the quality of the ceramics. Sintering and density changes of ceramics are traditionally studied by dilatometry. Dilatometer measurements are usually performed at linear heating rates. In practice, kilns with certain different temperature zones or certain temperature programs are applied for the production of ceramics. This is often a result of reams of trial and error experiments with loaded ovens. This contribution shows the sintering curves and kinetic analysis results for zirconia and further oxides measured by dilatometry. With this data, optimum sintering parameters can be predicted with regard to the final density.

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Boride Properties and Oxidation

Room: St. Johns

Session Chairs: William Fahrenholtz, Missouri University of Science & Technology; Bai Cui, University of Nebraska, Lincoln

8:30 AM

(ICACC-S12-012-2019) Ablation behavior of ZrB_2 based ceramics and composites at ultra-high temperature (Invited)

J. Zou*[1]; W. Hillman[1]; J. Binner[1]

1. University of Birmingham, School of Metallurgy and Materials, United Kingdom

Although ZrB_2-SiC ceramics have been extensively researched for applications at ultra-high temperatures (>2000°C), it is well known that at these temperatures the SiC oxidises actively yielding a gaseous sub-oxide, SiO. On the other hand, due to their intrinsic brittleness, monolithic ceramics are suspected to thermal shock failures when they were subjected to rapid changes in temperature. These limit the high-temperature range of SiC-bearing ceramics for ultra-high temperature applications. The presentation will focus on the thermoablative resistance of ZrB_2 based ceramics and composites at ultra-high temperatures. For the former part, results show that the addition of 5 vol% WC effectively eliminated the active oxidation of SiC in ZrB_2-SiC ceramics. The significantly improved ablation resistance of ZrB_2-SiC-WC ceramics is mainly attributed to a competitor transition from tungsten boride (WB) to metallic tungsten, which retards the occurrence of the active oxidation of SiC. In the second part of the presentation, the ablation behavior of porous, particulate based composites fabricated from the infiltration of ZrB_2 or HfB_2 powders into Cf preform will be reported. Apart from a detailed microstructure analysis near the as-ablated zone, the possible effects of the molten oxides that formed during the ablation will also be discussed by analysing their properties, e.g. viscosity at high temperatures.

9:00 AM

(ICACC-S12-013-2019) Evaluation of Rare-Earth Elements Co-Dopants (Sm and Er) on theTotal Hemispherical Emittance of ZrB_2/SiC Composites

A. A. Pena*[1]

1. Purdue University, Materials Science and Engineering, USA

Hypersonic aircraft need a high emissivity coating (HEC) to mitigate the aerodynamic heating effect produced by the sharp leading edges. Recent work has shown that small amounts of Sm dopant added to zirconium diboride/silicon carbide coatings can increase their emittance in the visible to near infrared wavelength range important for the temperature ranges experience during hypersonic flight. In the work reported here, the effect of an additional dopant (Er) on the emittance as a function of wavelength is being investigated. In this study, sintered billets with five different combinations of Sm:Er ratios were prepared and evaluated. Emittance as a function of temperature and wavelength were measured and will be reported.

9:20 AM

(ICACC-S12-014-2019) Oxidation Behavior of Ultra-High Temperature Ceramics Fabricated by Colloidal Processing Routes

K. Mueller*[1]; J. Slagle[1]; D. Pinnisi[1]; N. Craft[1]; K. Gjata[1]; E. J. Opila[1]; C. Tallon[1]

1. University of Virginia, USA

Ultra-High Temperature Ceramics (UHTCs) are materials proposed for use in extreme environments due to their melting points above 3000°C, but current manufacturing methods (Spark Plasma Sintering (SPS) and Hot Pressing (HP)) require extensive post-densification machining to produce complex geometry components. Colloidal processing followed by pressureless sintering has been proven to produce near-net shaped UHTC components without the need for high pressure techniques, yielding parts with physical characteristics similar to those from pressure methods. However, the oxidation resistance of UHTCs fabricated using this new approach needs to be evaluated to determine if this method is a true alternative to SPS and HP. This work examines the oxidation resistance of zirconium diboride (ZrB_2) prepared by two shaping and sintering approaches: i) state-of-the-art SPS method; ii) colloidal routes and pressureless sintering. Sintered samples (densities 80-95% of theoretical, with and without sintering aids), were oxidized at 1500°C in air for up to 30 minutes, characterized using SEM before and after oxidation, and compared in terms of density, microstructure (grain and pore size) and presence of secondary oxide phases after testing. Preliminary oxidation results on zirconium diboride specimens prepared by both approaches indicate that specific weight gain agrees well with existing literature.

9:40 AM

(ICACC-S12-015-2019) In Situ Oxide Scale Investigation of Sm-Doped ZrB_2/SiC Billets

A. Brenner*[1]; R. Trice[1]

1. Purdue University, Materials Engineering, USA

Samarium-doped zirconium diboride/silicon carbide (Sm-ZBS) ceramics possess emissive properties of 0.9 at 1600°C and develop oxide scales that have excellent ablation performance. This study investigates the oxide scale development of 3 mol% doped Sm-ZBS. The sintered billets were prepared via chemical infiltration and pressureless sintering in an argon (Ar) atmosphere. The samples were then oxidized for 10, 60, and 300 s respectively by rapidly heating using an oxyacetylene torch. XRD was used to observe pre-oxides of ZrO2 and Sm2O3 which were first formed which proceeded to combined to form a c1-Sm0.2Zr0.8O1.9 oxide which has a melting temperature exceeding 2500°C. SEM and EDS were also used to investigate the microstructural formation of the oxide scale.

10:00 AM

(ICACC-S12-016-2019) Intrinsic Thermal Properties of ZrB_2 and HfB_2

A. Stanfield*[1]; W. Fahrenholtz[1]; G. Hilmas[1]

1. Missouri University of Science & Technology, Material Science and Engineering, USA

Zirconium diboride with low Hf content and hafnium diboride with low Zr content were synthesized to study their intrinsic thermal properties. Ceramics were reactive hot pressed from high purity raw powders. Thermal diffusivity and heat capacity were measured from 25 °C to 2000 °C and used to calculate thermal conductivity. Electrical resistivity was measured from 25 °C to 2000 °C to calculate the electrical contribution to thermal conductivity. Transition metals such as Hf, Ti, and Y were added individually to nominally phase pure ZrB_2 to study the effects on thermal properties. These properties are compared to ceramics synthesized from commercial ZrB_2 powders, containing natural Hf abundance. The intrinsic thermal properties of ZrB_2 and HfB_2 will be discussed as well as the effect of transition metal additions on the high temperature thermal properties of ZrB_2 with low and naturally abundant quantities of Hf.

10:20 AM

(ICACC-S12-017-2019) Understanding and predicting the thermomechanical behavior of multiscale porous UHTCs via microstructure-properties using Material Point Method

S. Povolny*[1]; G. Seidel[1]; C. Tallon[2]

1. Virginia Tech, Aerospace and Ocean Engineering, USA
2. Virginia Tech, Materials Science and Engineering, USA

Ultra high temperature ceramics are ideal candidates for material systems operating in extreme environments, like leading edges on hypersonic vehicles. Design of such systems requires an understanding of UHTC properties and behavior in such environments. The time and monetary costs of testing motivate a need for computational characterization as a tool to pair material system performance with microstructure. In this work we analyze multiscale porous TiB_2 and ZrB_2 with porosities ranging from 50-90% and two distincts pore sizes: macroporosity (50-500um) from the processing route and interparticle porosity (0.5-5um) due to partial sintering. We aim to predict effective properties (such as elastic modulus and thermal conductivity) along with material behavior (such as damage initiation and propagation during compressive loading, buckling of slender microstructure features, and self-contact) as a function of microstructure geometry, and to correlate computational and experimental results. In lieu of the finite element method (typical choice for property prediction) the material point method (MPM) is proposed as a tool to capture the aforementioned phenomena. MPM discretizes a body using particles and incrementally updates their states using a background grid to solve equations of motion, which eliminates worries about mesh degradation.

10:40 AM

(ICACC-S12-018-2019) Synthesis and Properties of $(Zr,Ta)B_2$ Ceramics

A. N. Dorner*[1]; W. Fahrenholtz[1]; G. Hilmas[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

Zirconium diboride containing solid solution additions of tantalum ranging from 0 to 6 at% were synthesized by reactive hot pressing of zirconium and tantalum hydrides and amorphous boron. Microstructural analysis demonstrated that the $(Zr,Ta)B_2$ ceramics reached nearly full relative density and were nominally phase pure. Analysis of x-ray diffraction data revealed that tantalum was fully incorporated into the ZrB_2 structure and that the lattice parameters decreased with increasing tantalum addition. The mechanical properties that were measured included Vickers' hardness, flexure strength, fracture toughness, and elastic modulus. The thermal

properties measured included thermal diffusivity, heat capacity, and coefficient of thermal expansion. Properties were tested from room temperature up to 2000°C. Changes in properties were analyzed to determine the effects of tantalum content on ZrB_2 and to guide future studies into the effects of additives and impurities on the processing and properties of diboride-based ultra-high temperature ceramics.

Carbide Properties and Oxidation I

Room: St. Johns

Session Chairs: Bai Cui, University of Nebraska, Lincoln; William Fahrenholtz, Missouri University of Science & Technology

11:00 AM

(ICACC-S12-019-2019) The zeta phase in the transition metal carbides and nitrides: Structure, microstructure and properties (Invited)

C. R. Weinberger*[1]; H. Yu[2]; G. Thompson[3]

1. Colorado State University, Mechanical Engineering, USA
2. Drexel University, Mechanical Engineering and Mechanics, USA
3. University of Alabama, Department of Metallurgical and Materials, USA

The structure and stability of the zeta phase in the transition metal carbides and nitrides has been widely debated for decades. Neither the crystal structure nor the chemistry has been completely determined. There has been renewed interest in this problem because high volume fractions of the zeta phase in the tantalum carbides has shown exceptional fracture toughness. In this talk we review the mechanical properties, microstructure and phase stability of this phase in the transition metal carbides and nitrides, with a focus on the tantalum carbides and hafnium nitrides. For each case, we examine how modern computational tools can provide insight into this unique problem. Specifically, we show how bonding can regulate fracture, how relative energetics can predict microstructure and how computational search tools can, for the first time, concretely identify the structure and chemistry of the zeta phase. Our results not only connect phase stability to properties, but firmly estalblish the zeta phase as a low temperature thermodynamically stable phase in the tantalum carbides. Its stabity in the nitrides is much more complicated, but also discussed.

11:30 AM

(ICACC-S12-020-2019) Thermal and Mechanical Properties of Zeta Phase Tantalum Carbide

E. C. Schwind*[1]; G. Hilmas[1]; W. Fahrenholtz[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

High purity zeta phase tantalum carbide (ζ-Ta_4C_{3-x}) was synthesized and densified using reaction hot pressing for measurement of thermal and mechanical properties. Billets of >95% purity and >96% density were produced. The microstructure of ζ-Ta_4C_{3-x} was analyzed using optical microscopy and SEM and grains were found to have an aspect ratio of ~2 and a major axis of 13.6 μm. X-ray diffraction coupled with Rietveld refinement were used to study phase composition and purity. Fracture toughness and flexure strength were measured from room temperature to 2000°C. Thermal diffusivity was also measured from room temperature to 2000°C while electrical resistivity was measured up to 800°C. The values obtained from this study will be compared with known properties of other phases in the Ta-C system.

11:50 AM

(ICACC-S12-021-2019) Composite NbC as a model material for fuel matrices in Nuclear Thermal Propulsion

C. K. Ang*[1]; K. Bennesky[3]; S. J. Zinkle[1]; P. Venneri[2]

1. University of Tennessee, Nuclear Engineering, USA
2. USNC, Advanced Systems, USA
3. NASA Marshall, Space Flight Center, USA

Nuclear thermal propulsion (NTP) requires hydrogen compatible refractory materials for both fuel matrix and structural components. Ultra-high temperature ceramics (UHTCs) are matrix candidates due to corrosion-resistance and tolerable design strains. However, sintering and densification of UHTCs with fuel components limits available process temperature or pressure. A composite approach of NbC-SiC using <1 wt% sintering additives was densified at 2100K with ~10 MPa applied pressure. Densification is dominated by enhanced SiC grain boundary migration, and XRD/SEM indicated a two-phase material, confirming limited interface reactions. However, testing in H_2 at <2500K of NbC-SiC, CVD SiC and sintered SiC indicated grain boundary removal of sintering additives, accelerated by porosity. Parabolic mass loss was observed, and at higher temperatures, a transition to para-linear mass loss from intergranular phases and additives. The feasibility of composite approach for NTP reactor cores will depend on acceptable mass loss and fission product containment requirements.

Progress on Mxenes and Their Composites

Room: St. Johns

Session Chair: Vadym Mochalin, Missouri University of Science & Technology

1:30 PM

(ICACC-S12-022-2019) MXenes: A progress report (Keynote)

M. Barsoum*[1]

1. Drexel University, Materials Science and Engineering, USA

The 2D early transition metal carbides known as MXenes - obtained by etching the A-layers from the MAX phases - discovered in 2011 and now constituting more than 30 members, with new ones discovered on a regular basis, have generated substantial interest in the scientific community because of their potential in an ever-expanding host of applications. Unlike hydrophobic graphene, MXenes are hydrophilic and behave as 2D metals or "conductive clays", a hitherto unknown combination. In this talk I will focus on our current understanding of their processing and how the processing influences the properties. Lastly, I will overview, some of the potential applications for MXenes, with an emphasis on those that are likely to be commercialized in the near future.

2:00 PM

(ICACC-S12-023-2019) MXenes and their Composites for Energy Storage (Invited)

Z. Sun*[1]; W. Zheng[1]; L. Yang[1]; H. Zhang[1]; P. Zhang[1]; J. Chen[1]; W. Tian[1]; W. Zhang[1]; Y. Zhang[1]

1. Southeast University, School of Materials Science and Engineering, China

Herein we report our recent work on MXenes and their composites for energy storage applications such as Li-ion batteries (LIBs) and supercapacitors (SCs). Firstly, we developed a facile route to the synthesis of CNTs@MXene nanostructures, in order to overcome the problems of re-stacking and collapse of MXenes. CNTs were grown on MXene in only 40 seconds assisted by microwave irradiation. At a high rate, the capacity of as-prepared CNTs@MXene anodes exceeds commercial graphite and most reported MXenes systems in LIBs. Secondly, a three dimensional (3D) SnO_2@C/d-Ti_3C_2 (S-TCS) network architecture was fabricated by employing a sol-gel method to anchor the core-shell SnO_2@C onto the d-Ti_3C_2 xerogel framework. Typically, 3D S-TCS delivers reversible specific

capacity of 520 and 492 mA h g^{-1} at the current density of 1.0 and 2.0 A g^{-1}, respectively, after 1000 times charge-discharge cycles. Thirdly, binder-free Ti_3C_2 MXene-carbon nanotubes (Ti_3C_2-CNTs) composite films were successfully deposited onto graphite substrate by electrophoretic deposition (EPD). The as-prepared Ti_3C_2-CNTs electrode exhibited enhanced specific capacitance, with excellent cycling stability. Finally, we will report our latest progress on the research of MXenes for energy storage at the conference.

2:30 PM

(ICACC-S12-024-2019) Assembling 2D MXenes into supercapacitor electrodes with high energy and power densities (Invited)

M. Beidaghi*[1]; A. VahidMohammadi[1]; J. Orangi[1]; E. Kayali[1]

1. Auburn University, USA

Two-dimensional (2D) transition metal carbides/nitrides (MXenes) have shown promise for a range of applications due to their unique physical and chemical properties. The high electrical conductivity, 2D and layered structure, and rich surface chemistry of MXenes have sparked great interest in their properties as electrode materials for energy storage devices. However, similar to other 2D materials, the applications of MXenes in batteries and supercapacitors is dependent on their assembly into electrode structures with high electrical and ionic conductivities. The main focus of this talk is our group's recent research on the assembly of MXene flakes into electrode structures with high energy and power densities. We have found that the electrochemical properties of MXene electrodes are highly dependent on the size of MXene flakes used in their fabrications. Controlling the flake size in the electrode structures leads to significant improvements in their specific capacitance and rate capability. These properties are also improved by assembling MXene flakes into porous 3D structures. A method for fabrication of 3D MXene aerogels with ordered structures and the effects of ordering on the electrochemical properties of the aerogels will be discussed. In addition, our work on increasing the electrochemical stability of MXene electrodes through unconventional assembly methods will be discussed.

Novel Processing of Mxenes and Their Composites I

Room: St. Johns

Session Chairs: Zhengming Sun, Southeast University; Majid Beidaghi, Auburn University

3:20 PM

(ICACC-S12-025-2019) Discovery of new MAB phase and 2 D nanosheets in Cr-Al-B system (Invited)

Y. Zhou*[1]; H. Zhang[1]; H. Xiang[1]; F. Dai[1]; Z. Zhang[2]

1. Aerospace Research Institute of Materials & Processing Technology, China
2. Beijing Jiaotong University, School of Mechanical, Electronic and Control Engineering, China

MAB phases, wherein M is a transition metal, A is Al or Si, and B is boron, are appealing due to the unique properties that they display. From structure point of view, they have layered crystal structure and anisotropic chemical bonding; from property point of view, they exhibit good electrical and thermal conductivities, moderate modulus, being resistant to thermal shock and oxidation, and tolerant to damage like MAX phases. The combination of these properties makes them promising for high and ultra-high temperature applications. Up to now, the theoretically and experimentally studied MAB phase include $(CrB_2)_nCrAl$ (n=1, 2, 3), W(Mo)AlB, M_5Si_3B, $Y_5Si_2B_8$ and $YAlB_4$. Among them, compounds in Cr-Al-B system can be described as alternating stacking of $(CrB_2)_n$ and CrAl layers along a specific crystallographic direction. Recently, a new compound Cr_4AlB_4, which is formed by alternatively stacking of $(CrB)_2$ layer and Al layer, was discovered by the authors' group. In this presentation, the process for the discovery of this new MAB phase and its crystal structure, electronic structure and elastic and thermodynamic properties will be introduced. The discovery and characteristics of the 2D CrB prepared from Cr_2AlB_2 will also be presented.

3:50 PM

(ICACC-S12-026-2019) Chemistry and Applications of 2D Transition Metal Carbides (MXenes) (Invited)

V. N. Mochalin*[1]

1. Missouri University of Science & Technology, USA

Large family of two-dimensional transition metal carbides and nitrides (MXenes) raises interest for many applications due to their unique properties. However, their chemistry that is key to development of these applications, still remains largely terra incognita. In this presentation we will discuss recent progress in understanding MXene chemistry and harnessing it for development of applications. For example, during delamination and storage in ambient air, spontaneous oxidation of MXene flakes leads to formation of TiO_2, a process that can be harnessed for simple, inexpensive, and environmentally benign manufacturing MXene-titania composites for optoelectronics, sensing, and other applications. Other selected examples illustrating connections between understanding MXene chemistry and development of their applications will also be considered.

4:20 PM

(ICACC-S12-027-2019) Layer-by-Layer Processing of Surface Agnostic MXene/Polymer Coatings for Sensing Applications

H. An[2]; T. Habib[2]; S. A. Shah[2]; H. A. Gao[3]; M. Radovic*[1]; M. J. Green[2]; J. L. Lutkenhaus[2]

1. Texas A&M University, Materials Science & Engineering, USA
2. Texas A&M University, Chemical Engineering, USA
3. Texas A&M University, Mechanical Engieering, USA

MXene sheets as conductive two-dimensional nanomaterials are promising for many applications including flexible electronics and sensing, but it is still extremely difficult to form surface-agnostic MXene coatings that can withstand extreme mechanical deformation. Herein, we report on surface-agnostic MXene multilayer coatings that can undergo large-scale mechanical deformation while maintaining a conductivity as high as 2000 S/m. MXene multilayers are successfully deposited onto flexible polymer sheets, stretchable poly(dimethylsiloxane), nylon fiber, glass, and silicon using Layer-by-Layer (LbL) technique. The coating shows a recoverable resistance response to bending (up to 2.5-mm bending radius), stretching (up to 40% tensile strain) and change in humidity, which was leveraged for sensing. We anticipate that this discovery will allow for the implementation of MXene-based coatings for sensing motion and humidity as well as other environmental stimuli.

4:40 PM

(ICACC-S12-028-2019) Synthesis of 2D transition metal carbide (MXenes) with randomly distributed vacancies by etching of their solid solutions MAX phases

J. Halim*[1]; J. Palisaitis[1]; J. Lu[1]; j. Thornberg[1]; E. Moon[2]; M. Precner[3]; P. Eklund[1]; P. Persson[1]; M. Barsoum[2]; J. Rosen[1]

1. Linkoping University, Department of Physics, Chemistry and Biology, Sweden
2. Drexel University, USA
3. Slovak Academy of Sciences, Institute of Electrical Engineering, Slovakia

Introducing point defects in 2D materials can alter or enhance their properties. It was shown that by selective etching of Al and Sc atoms from the parent 3D MAX phase $(Mo_{2/3}Sc_{1/3})_2AlC$ with in-plane chemical ordering of Mo and Sc, ordered vacancies can be introduced in MXenes. This vacancy-ordered MXene showed a three order of magnitude higher conductivity and an enhancement in the volumetric capacitance of 65% compared to its counterpart, Mo_2C

with no vacancies. However, not all quaternary parent MAX phases form the in-plane chemical ordering of the two M metals, thus the synthesis of the vacancy-ordered MXenes is restricted. We present a new method to obtain MXene flakes with disordered vacancies, that can be generalized to all quaternary MAX phases. As a proof of concept, we chose Nb-C MXene, as Nb_2C has shown a promise in several applications, including energy storage, photothermal cell ablation and photocatalysts for hydrogen evolution. We demonstrate how etching a $(Nb_{2/3}Sc_{1/3})_2AlC$ quaternary MAX phase, of both the Sc and Al atoms, results in a 2D $Nb_{1.33}C$ material with a large number of vacancies and vacancy clusters. This method is applicable to any quaternary, or higher, MAX phase wherein one of the transition metals is more reactive than the other and could be of vital importance in applications such as catalysis and energy storage.

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Joining and Technologies for Reactor Components

Room: Coquina Salon H

Session Chair: Takaaki Koyanagi, Oak Ridge National Laboratory

8:30 AM

(ICACC-S13-010-2019) Laser Supported Joining of SiC_f/SiC Claddings for the Application in Nuclear Reactors (Invited)

M. Herrmann*[1]; M. Graffé[1]; W. Lippmann[1]; A. Hurtado[1]

1. Technische Universität Dresden, Institute of Power Engineering, Germany

Silicon carbide fiber reinforced silicon carbide (SiC_f/SiC) is one of the candidate cladding materials for the development of Accident Tolerant Fuel (ATF). The application of SiC_f/SiC clads in light water reactors requires the development of joints fulfilling extreme chemical, thermal and radiation demands what is still an unsolved problem. At TU Dresden laser beam as heating source for the joining of SiC components is used. The local heat input permits the sealing of components independent from the lengths what is applicable to the joining of approx. 4 m long SiC_f/SiC clads. The aim of the presentation is to show that this approach minimizes the heat input on the fuel inside the cladding. In addition, the short processing time allows the heating of the SiC_f/SiC-components to temperatures necessary for the joining process in seconds respectively few minutes. The formation of the microstructure inside the joints during short processing will be demonstrated using Zr-based alloys as filler material for SiC_f/SiC materials. The results offer the potential of the technology for the application in other ceramics. Moreover, the presentation will outline the activities for the joining and testing of SiC_f/SiC-clads in the European R&D project IL TROVATORE.

9:00 AM

(ICACC-S13-011-2019) Characterization of Fusion Welds in the SiC-ZrB_2-ZrC System

J. Jarman*[1]; W. Fahrenholtz[1]; G. Hilmas[1]; J. Watts[1]; D. King[2]

1. Missouri University of Science & Technology, Department of Material Science and Engineering, USA
2. UES, Inc., USA

Previous research has shown that ceramics with sufficient electrical conductivity, specifically boride based ceramics, can be fusion welded. In the current study, Plasma Arc Welding (PAW) and Gas Tungsten Arc Welding (GTAW) were used to join composites in the SiC-ZrB_2-ZrC system. Various compositions of SiC-ZrB_2-ZrC were synthesized to study their weldability and to determine the maximum SiC content that was still weldable. Specimens were produced via hot pressing, machined into 12 mm x 31 mm x 4 mm coupons, and welded via PAW and GTAW methods in an inert argon atmosphere. Welding parameters for both PAW and GTAW welds were varied to determine conditions required to achieve high quality welds. The fusion zone of welded coupons was cross sectioned and analyzed using optical microscopy and scanning electron microscopy (SEM). The weldability and weld quality of various SiC-ZrB_2-ZrC compositions will be discussed, as well as the effect of welding parameters and composition on the microstructures formed. Ideal welding parameters for various compositions will also be discussed.

9:20 AM

(ICACC-S13-012-2019) Development of joining process technology for SiC core materials

S. Suyama*[1]; M. Ukai[1]; M. Akimoto[1]; H. Sato[1]; H. Heki[1]

1. Toshiba Energy Systems & Solutions Corporation, Japan

Recently, SiC/SiC composites have been shown to be promising structural materials for use in nuclear reactor cores, such as fuel cladding and channel boxes, in order to enhance safety. We have been developing manufacturing process technology for (1) thin-walled and elongated SiC/SiC composite based tubes, (2) bottom-end plugs of SiC/SiC composite based tubes, and (3) upper-end plugs of SiC/SiC composite based tubes. This work describes the joining process technology to seal a SiC/SiC composite based tube with a SiC-ceramic upper-end plug after putting fuel pellets in it. We selected an optimum joining process and designed its joining structure for the SiC fuel cladding. Furthermore, we fabricated one type of joining specimen, a silver eutectic alloy brazing and screw-on structure, and evaluated the hermetic sealing property. This combination of a joining process and its structure is expected to meet one of application requirements with a good hermetic seal.

9:40 AM

(ICACC-S13-013-2019) Fabrication of SiC-SiC joints in representative cladding geometries

S. Gonderman*[1]; E. Song[1]; K. Shapovalov[1]; G. Jacobsen[1]; H. Khalifa[1]; T. Koyanagi[2]; C. Petrie[2]; C. Deck[1]

1. General Atomics, NTM, USA
2. Oak Ridge National Lab, USA

General Atomics (GA) is developing SiGA^{tm} silicon carbide matrix composite (SiC-SiC) cladding for accident tolerant fuel (ATF) applications and advanced reactor concepts. GA's SiGA^{TM} cladding tubes must be joined to a SiC endplug to form a sealed rod, and these joints must maintain strength and leak tightness throughout the full fuel cycle. To investigate this, a Department of Energy Nuclear Science User Facility (NSUF) funded collaboration between GA and Oak Ridge National Lab (ORNL) has been initiated, to survey the mechanical and hermetic response of several promising SiC joint formulations before and after irradiation in the High Flux Isotope Reactor (HFIR). Several joint types are being explored including oxide, trans-eutectic phase (TEP), and GA's hybrid SiC (HSiC) joints. These methods were selected because they have demonstrated strength resilience under irradiation in planar geometries. Initial efforts at fabricating both one-end sealed tubular and planar geometries for all joint types will be presented, including a more detailed update on the GA's localized joint processing to seal and backfill rodlets. Pre-irradiation thermal, mechanical, and leak tightness data will be reported. The data obtained in this work will address a key knowledge gap, enabling more accurate modeling of joints in SiC-based components for nuclear applications.

Coating Technologies for Reactor Components

Room: Coquina Salon H
Session Chair: Marion Herrmann, Technische Universität Dresden

10:20 AM

(ICACC-S13-014-2019) Development of Hydrothermal Corrosion Resistant Coating Technology for Silicon Carbide Fuel Cladding (Invited)

R. Ishibashi*[1]; T. Kondo[1]; S. Yamashita[2]; T. Fukahori[2]

1. Hitachi-GE Nuclear Eneargy, Japan
2. Japan Atomic Energy Agency, Japan

To improve the corrosion resistance of silicon carbide (SiC) for accident tolerant fuel (ATF) in boiling water reactor (BWR) environments, corrosion resistant coating technology to SiC substrates and joint portions are being developed. One critical issue left for the practical application of SiC fuel cladding and a fuel channel box is hydrothermal corrosion. In hydrothermal light water reactor (LWR) coolant environments, the silicon in SiC undergoes oxidation and produces silica that readily dissolves in water. Silica concentration in the coolant of BWRs should be kept low because silica deposited on turbine vanes might decrease efficiency. Therefore, coating technology which suppresses silica dissolution into the coolant needs to be developed. Performance of the coating technology using candidate corrosion resistant metals of Ti, Zr and Cr in unirradiated high purity water at high temperatures was evaluated by laboratory tests. The Ti coating was superior to others in protective performance in oxygenated high temperature water. The coating processes were physical vapor deposition followed by heat treatment for SiC substrate and vacuum plasma spraying for joint portion. The results indicate that Ti coating applied on SiC substrates and joint portions is potentially effective as an environment barrier coating in oxygenated high temperature water.

10:50 AM

(ICACC-S13-015-2019) Evaluation of SiC/SiC Coating Technologies for Accident-Tolerant LWR Fuels

Y. Katoh*[1]; T. Koyanagi[1]; P. J. Doyle[2]; X. Hu[1]; S. S. Raiman[1]; C. Petrie[1]; C. K. Ang[2]; P. Xu[3]; C. Deck[4]

1. Oak Ridge National Laboratory, USA
2. University of Tennessee, USA
3. Westinghouse Electric Company, USA
4. General Atomics, USA

Using silicon carbide (SiC) composite as fuel cladding is an attractive approach to make light water reactor (LWR) drastically tolerant against severe accidents. However, fission product gas containment and irradiation-assisted hydrothermal corrosion remain as outstanding concerns for use of SiC composites in LWR cores. Application of a coating on the external surface with a hermetic and corrosion-resistant material is a potential approach to mitigate these two issues at the same time. In this work, some of the candidate coating materials and technologies were evaluated. The presentation will focus primarily on new results from selected coated SiC/SiC samples following neutron irradiation in inert environment. In addition, pathway toward development of the coated SiC/SiC technologies for use in LWR cores will be discussed based on the latest technical progress. This work is supported by DOE Office of Nuclear Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:10 AM

(ICACC-S13-016-2019) Coatings for SiC based components for light water reactors

V. Casalegno*[1]; M. Salvo[1]; P. Gianchandani[1]; F. D'Isanto[1]; L. Manna[1]; M. Ferraris[1]

1. Politecnico di Torino, DISAT, Italy

Recently, SiC/SiC materials have been the focus of an extensive research activity for several nuclear applications. In particular, they can be used in nuclear fuel cladding in light water reactors (LWRs). One of the key feasibility items for SiC/SiC based components is the hydrothermal corrosion of SiC-based materials in LWRs coolant environments. The present work reports on several coatings for SiC-based components: refractory metals, metal glasses, silicone-based resins and glass-ceramics. Coated SiC based components have been tested in autoclave at 320 °C, in high purity water, under 15 MPa pressure for 8 hours, in order to simulate the corrosion in coolant at normal operating conditions for SiC-based cladding. The major development activities and outcomes in autoclave corrosion testing through the morphological and compositional analysis of coating and interfaces between coating and substrates are discussed. Acknowledgement The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 740415 Project "IL TROVATORE - Innovative Cladding Materials for Advanced Accident-Tolerant Energy Systems".

11:30 AM

(ICACC-S13-017-2019) Effect of Dry Neutron Irradiation on SiC Coated with TiN, CrN, or Cr

P. J. Doyle*[1]; K. Terrani[2]; Y. Katoh[2]; C. K. Ang[1]; S. S. Raiman[2]; S. J. Zinkle[1]

1. University of Tennessee, Nuclear Engineering, USA
2. Oak Ridge National Lab, USA

SiC-based materials have good potential for use as accident-tolerant fuel (ATF) cladding due to their low neutron absorption cross-sections, excellent stiffness and mechanical strength, excellent oxidation resistance in high temperature steam, and radiation damage resistance. However, SiC may corrode too quickly in the presence of liquid water, a problem which is exacerbated by impurities from manufacturing (in non-CVD variants), and any dissolved oxygen. Three variants of SiC, high resistance chemical vapor deposited (CVD), low resistance CVD, and a ceramic matrix composite (CMC) with Tyranno SA3 fibers were coated with TiN, CrN, and Cr as potential corrosion mitigation coatings, and irradiated at the MIT reactor to a final damage level of 0.5 dpa between 270 and 340^{0}C. Samples were examined by optical and electron microscopy for surface cracks, coating through-cracks (by cross-sectioning), and delamination. Multilayer CrN samples showed extensive cracking, Cr showed some cracking, and the TiN samples were free of cracks. TEM confirmed, the Cr samples were substantially debonded as a result of extensive void formation. Some local cracking on the interface was observed for CrN coatings, while the TiN was fully adherent. Transmission Kikuchi Diffraction was performed to identify the grain character and local straining of the lattice as function of distance from the interface in each coating.

Novel Ceramics and Composites for Nuclear Systems II

Room: Coquina Salon H
Session Chair: Young-Wook Kim, University of Seoul

1:30 PM

(ICACC-S13-018-2019) 3D Printing and Densification of Silicon Carbide Components with Complex Geometry

B. Jolly*[1]; M. Trammell[1]; K. Terrani[1]; A. Schumacher[1]

1. Oak Ridge National Laboratory, USA

By combining advanced manufacturing (3D printing) methods and chemical vapor infiltration (CVI) techniques, SiC parts with highly complex geometries that would be difficult or impossible to form with traditional SiC processing routes can be fabricated. The specific 3D printing method uses SiC powder to result in an open-pore structure suitable for densification with SiC CVI. This densification process strengthens the part and can be tailored to provide a hermetic seal or leave residual open porosity. The flexibility of this advanced manufacturing process combined with the excellent high temperature mechanical properties, corrosion resistance and radiation tolerance of SiC makes these parts suitable for a wide range of

applications such as chemical processing, heat exchangers, accident tolerant nuclear fuel and components, etc. Complex SiC parts have been produced using this methodology and work is ongoing at the Oak Ridge National Laboratory to study this fabrication process and the thermophysical properties of the resulting SiC-based materials. This work was funded by U.S. Department of Energy's Office of Nuclear Energy, Advanced Methods for Manufacturing.

1:50 PM

(ICACC-S13-019-2019) ZrC materials for nuclear applications produced by additive manufacturing methods

M. Trammell*[1]; B. Jolly[1]; A. Schumacher[1]; K. Terrani[1]

1. Oak Ridge National Lab, USA

The properties of ZrC make it an excellent material component for high temperature nuclear fuel forms for both high burnup applications and harsh environments such as hot hydrogen systems for Nuclear Thermal Propulsion (NTP). ZrC has demonstrated attractive properties for these nuclear systems including the resistance to hydrogen corrosion, the ability to withstand ultrahigh temperatures, irradiation stability, fission product retention, as well as the ability to produce solid solution $U_xZr_{1-x}C_y$. A room temperature additive manufacturing technique that can be used to produce low density materials from powder is utilized in this study. ZrC material made with this method has an open pore structure that may then be infiltrated with additional ZrC by a chemical vapor infiltration (CVI) process to produce higher density and structurally sound materials with complex geometry and composition. This ongoing work includes the exploration of additive manufacturing process parameters to produce ZrC parts, CVI infiltration process development, and the characterization of resulting materials. This work was funded by the U.S. Department of Energy's Office of Nuclear Energy, Advanced Methods for Manufacturing.

2:10 PM

(ICACC-S13-020-2019) Low Temperature Synthesis Zirconium Carbide Powders by Solid State Reaction

Y. Zhou*[1]; W. Fahrenholtz[1]; G. Hilmas[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

The low temperature synthesis of zirconium carbide (ZrCx) powders was systematically studied. Zirconium hydride (ZrH2), carbon black and phenolic resin were used as precursor for solid state reactions. The decomposition temperature of ZrH2 was measured by thermal gravimetric analysis (TGA). X-ray diffraction (XRD) was used to study the phases present at different temperatures. Nominally pure ZrCx was obtained at 1200 celsius. Microstructures and morphology of the ZrCx powders were characterized by transmission electron microscope (TEM) and scanning electron microscope (SEM). Rietveld refinement was used to determine the lattice parameters and crystallite sizes for each synthesis condition. Carbon stoichiometry and oxygen contents for the ZrCx powders synthesized at different temperatures were measured. Intrinsic properties of ZrCx powders for increasing synthesis temperatures and hold times will be discussed in this presentation.

2:30 PM

(ICACC-S13-021-2019) Development of YSZ environmental barrier coatings for the molten salt fast reactor

L. J. Espinoza Perez[1]; F. Cano[1]; S. Esquivel[1]; E. Lopez-Honorato*[1]

1. CINVESTAV, Mexico

The Ni alloys generally used for the construction of the molten salt fast reactor can be prone to corrosion attacks and deleterious thermal effects on their mechanical properties at temperatures above 700°. In order to reduce corrosion and thermal damage, we are currently studying the deposition of YSZ coatings by sol-gel/dip-coating and plasma enhanced chemical vapor deposition. Sol-gel derived coatings are prone to develop cracks due to internal stresses produced during drying. However, by controlling the drying and coating speed it was feasible to produce crack-free coatings with a 90% cubic phase content with 20 mol% yttrium, a hardness of 3 GPa and a 60% increase on wear resistance compared to the original metal. Furthermore, we show that it is feasible to produce ZrO_2 by the use of zirconium acetylacetonate as precursor, at temperatures below 800 °C by PE-CVD. Deposition efficiency increased with temperature and oxygen concentration resulting in coatings with a monoclinic phase. The formation of tetragonal phase without the use of any dopant was observed by increasing the plasma power above 200 watts. Corrosion resistance was tested with FLiNaK salt.

2:50 PM

(ICACC-S13-022-2019) Validation of tungsten carbide ceramics as a neutron shielding material

S. A. Humphry-Baker*[1]

1. Imperial College London, Materials, United Kingdom

The neutron energy attenuation of WC has been modelled by Hong (2011), Menard (2016) and Windsor (2018). All studies predict excellent performance. This has critical implications to the development of compact fusion reactors, where the shield thickness is a key parameter in defining the overall size of the reactor. However, theoretical neutronics studies are so far accompanied with little practical development. Fusion-relevant properties of WC-based materials remain poorly understood, and optimised microstructures and composites are yet to be explored. These shortfalls are addressed: Firstly, high temperature property measurements of monolithic WC are presented. Included in this are thermal conductivity, thermal shock behaviour and creep deformation. The key result is that modern powder-consolidation methods have enabled dramatic property improvements, which shows promise. Secondly, a composite material, WC-FeCr, is introduced. The metallic FeCr matrix enables enhanced manufacturability and toughness. The microstructural space of this composite is explored via a structure property map. Recent results of its accident tolerance and irradiation behaviour are reviewed.

Modelling Nuclear Ceramic Fuels and Structures

Room: Coquina Salon H

Session Chair: Nicholas Brown, Pennsylvania State University

3:30 PM

(ICACC-S13-023-2019) Modeling Nuclear Fuel Performance of Accident Tolerant Fuel Cladding Concepts (Invited)

B. Wirth*[1]; R. Sweet[1]; D. Schappel[1]

1. University of Tennessee, USA

The necessary short development time and testing of accident tolerant fuel concepts for light water reactors requires the incorporation of computational modeling and analysis that can quantify performance in normal and transient conditions. This presentation will focus on a multiscale approach to developing a first principles understanding for the development of key material behavior and constititutive models for radiation-induced degradation, and then apply these models into the engineering scale fuel performance code BISON to assess concept performance. Particular emphasis in this presentation will be on the radiation strengthening of FeCrAl alloys, as well as the radiation-induced swelling of SiC composite cladding, especially in cases where the experimental database is incomplete at this time. BISON fuel performance modeling assessments will be discussed that assess the performance of FeCrAl or SiC fuel rods, and identify ways to improve the ATF design.

4:00 PM

(ICACC-S13-024-2019) Multi-Physics Simulation of SiC/SiC Composite Cladding

K. Shirvan*[1]; W. Li[1]

1. Massachusetts Institute of Technology, USA

In the previous studies, the multi-layered cladding performance of SiC/SiC composite material in nuclear reactor under steady state and postulate accident conditions were simulated. It was found that the nuclear reactor environment imposes significant tensile stresses in the cladding material that needs to be more closely analyzed. In this work, we investigate the coupled fuel and multi-layer cladding performance with 1.5D fidelity on full core level and 2D/3D fidelity on single rod bases. The simulations cover a wide range of conditions including steady state, power ramp, loss-of-coolant accident, control rod ejection accident and station blackout scenario for pressurized water reactors and boiling water reactors. The fuel performance simulations are informed by lab-scale experiments and system-level response to produce accurate and realistic behavior of SiC/SiC material in the reactor core. Of particular interest, the SiC/SiC composite layer with a CVD SiC overcoat and SiC/SiC composite layer with PVD Cr overcoat were modeled. The full core simulation results infer that thermal conductivity of UO_2 fuel needs to be increased either through material additives such as BeO or a switch to a higher conductivity ceramic such as U_3Si_2 or UN. The 2D/3D FEA simulations revealed the ability of SiC/SiC composite material to retain coolable geometry during the postulated accident scenarios.

4:20 PM

(ICACC-S13-025-2019) Deformation Analysis of SiC-SiC Channel Box for BWR Applications

G. Singh*[2]; J. Gorton[3]; D. Schappel[2]; N. Brown[3]; Y. Katoh[1]; B. Wirth[2]; K. Terrani[1]

1. Oak Ridge National Lab, USA
2. University of Tennessee, USA
3. Pennsylvania State University, USA

SiC-SiC composites are being considered for channel boxes in BWRs to improve accident tolerance. In the reactor environment, channel box will be exposed to neutron and other radiation damage and temperature gradients. To ensure reliable and safe operation of a SiC-SiC channel box, it is important to assess its deformation behavior under in-reactor conditions including the expected neutron flux and temperature distributions. In particular, this work has evaluated the effect of non-uniform dimensional changes caused by spatially varying neutron flux and temperatures on the deformation behavior of the channel box over the course of one cycle of irradiation. The dependence of dimensions and thermophysical properties on fast flux and temperature has been incorporated into the material models. These initial results indicate significant bowing of the channel box with a lateral displacement greater than 6.5 mm. The bowing behavior gradually recovers during the course of the operating cycle as the swelling of the SiC-SiC material saturates. However, the bending relaxation due to temperature gradients does not fully recover and residual bending remains after the swelling saturates in the entire channel box.

4:40 PM

(ICACC-S13-026-2019) Stress and bowing analysis of a SiC/SiC channel box irradiation experiment in the High Flux Isotope Reactor

C. Petrie*[1]; J. Burns[1]; C. Deck[2]; Y. Katoh[1]

1. Oak Ridge National Lab, USA
2. General Atomics, USA

Silicon carbide (SiC)-based ceramic matrix composites have long been considered for a variety of nuclear applications due to their high temperature strength retention, their dimensional stability under irradiation, and their reduced steam oxidation kinetics. One of these applications is to replace current zirconium-based channel boxes in boiling water reactors (BWRs). One of the critical issues facing SiC-based channel boxes for BWR applications is the lateral bowing due to differential radiation-induced swelling resulting from a non-uniform power profile. To address this issue, Oak Ridge National Laboratory is performing thermomechanical modeling to predict the extent of the lateral bowing and experimental irradiation testing to validate these models. This work describes an irradiation experiment that is being performed in the reflector of the High Flux Isotope Reactor, where there exist significant radial gradients in the fast neutron flux. Detailed neutronic calculations were performed to provide three-dimensional profiles of the displacement damage rate within the channel box. These results are used as input to structural simulations that predict the amount of bowing and the resulting stress in the channel box. The bowing calculations will be validated by laser profilometry measurements performed before and after irradiation.

5:00 PM

(ICACC-S13-027-2019) Validation of Mesoscale Simulations of UO_2 fuel behavior by Comparing to Separate Effects Data

M. R. Tonks*[1]; C. Bhave[1]; X. Wu[1]; Y. Zhang[1]; J. Lian[2]

1. University of Florida, Materials Science and Engineering, USA
2. Rensselaer Polytechnic Institute, USA

The MARMOT tool, under development by the US Nuclear Energy Advanced Modeling and Simulation (NEAMS) program, predicts the behavior of various reactor materials. For example, MARMOT predicts grain growth, and fracture in UO_2 and the degradation of the thermal conductivity of irradiated UO_2. These mesoscale simulations are used to assist in the development of macroscale materials models for fuel performance codes such as BISON, also under development by the NEAMS program. However, before they can be trusted, the models for UO_2 need to be validated. New separate effects data from UO_2 that has been collected at RPI is being used along with statistical uncertainty quantification to validate these MARMOT models for UO_2. In this presentation, we demonstrate the model validation.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials II

Room: Tomoka C

Session Chair: Takayuki Yanagida, Nara Institute of Science and Technology

8:30 AM

(ICACC-S14-012-2019) Post-processing of CVD-grown ZnSe ceramics for three-wave mixing applications (Invited)

R. M. Gaume*[1]; X. Chen[1]

1. University of Central Florida, CREOL, USA

Random quasi-phase-matching is an efficient nonlinear scheme for three-wave mixing in transparent ceramics of non-centrosymmetric cubic materials. This process is controlled by the average grain-size and distribution and the nonlinear conversion efficiency is maximized when grain size of ceramics is close to the coherence length. In this work, solid-state grain-coarsening was used to fabricate ZnSe ceramics with desired grain size. The effect of different atmospheres (selenium vapor, zinc vapor and vacuum) on the grain size control of ZnSe ceramics at 850°C and 1000°C as a function of time is investigated. Random quasi-phase-matching of second-harmonic generation process is investigated theoretically in ZnSe samples with experimentally-determined grain-size distributions. Selenium atmosphere helps to increase the grain growth and control the grain size distribution. The narrow grain size distribution achieved under selenium atmosphere helps to get 21% higher second harmonic generation intensity compare with that under other atmospheres.

9:00 AM

(ICACC-S14-013-2019) Synthesis of Fe:ZnSe nanopowder by co-precipitation method for sintering transparent ceramics (Invited)

S. Yu*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

Fe:ZnSe nanopowders were synthesized by the co-precipitation method. All of FexZn1-xSe (0≤x≤0.06) powders calcined at 400 oC had pure cubic ZnSe phase. The impurity phase ZnO appeared in the powders calcined at 500-600 oC and it was found that acid washing could effectively remove ZnO from Fe:ZnSe powders. The lattice parameter of a-axis was monotonically increased when Fe2+ doping content was increased. The highest doping content of Fe2+ was about 3.3×10-20 cm-3. The average grain size of Fe:ZnSe powders was increased from several nanometers to hundreds of nanometers when calcination temperature was increased from 80 oC to 600 oC. Fe:ZnSe transparent ceramics with pure ZnSe phase could be sintered at 950 oC for 30 min under presser 60 MPa by SPS. This work demonstrated the scheme of synthesis of Fe:ZnSe nanopowders by co-precipitation method for sintering transparent ceramics.

9:20 AM

(ICACC-S14-014-2019) Sapphire characterization and development at II-VI Optical Systems (Invited)

M. Seitz*[1]

1. II-VI Optical Systems, Project Engineering, USA

II-VI Optical Systems (II-VI OS) is currently growing sapphire via a heat exchanger method and an edge fed growth method. The heat exchanger method yields up to 13″ diameter a-plane window blanks, but boules can also be oriented to yield c-plane, m-plane, and r-plane windows at a smaller size. The edge fed growth method yields a-plane crystals approximately 12″ x 24″ x 0.250″ thick. These crystals are being ground, polished, and shaped at II-VI OS for use in demanding aerospace applications. Over the last 4 years, II-VI OS has performed material characterization studies on its sapphire to better understand the expected range of material performance and to provide the most accurate and up-to-date information for II-VI OS customers. During this presentation, Mrs. Seitz will discuss the material studies II-VI OS has completed. This has included measurements of the coefficient of thermal expansion, Knoop hardness, modulus of elasticity, rupture modulus, index of refraction and index homogeneity. Additionally, II-VI OS is investing in further development of its sapphire technology, including material characterization specific to high energy laser applications, and in process development to improve yields and provide larger sapphire substrates to the aerospace industry.

9:50 AM

(ICACC-S14-015-2019) Development of Laser Sintering Process of Alumina using Nd:YAG Laser (Invited)

T. Kimura*[1]; S. Suehiro[1]

1. Japan Fine Ceramics Center, Japan

For laser sintering of alumina, two important elemental techniques have been developed in this study: (a) drying/dewaxing technique of slurry layer, and (b) effective laser heating technique. An alumina slurry containing sub-micron alumina powder was used as a starting material. By controlling temperature distribution in the painted slurry layer using a hot-plate heating, the slurry layer was dried and dewaxed without crack, and densely packed alumina powder layer was obtained. The dense powder layer was also obtained by spraying the slurry onto the pre-heated substrate. Nd:YAG laser (wavelength:1064 nm) was employed in this study as a heating source, but alumina poorly absorb this laser. We introduced a graphite layer on the alumina powder layer as an absorption aid to enhance the laser heating of the alumina layer, and 300 micron-thick layers was successfully sintered by 10 seconds irradiation at power density of 250 watt/sq-cm. We also examined laser sintering of bulk alumina. After 60 seconds laser irradiation to a pressed alumina pellet, the pellet was sintered and became translucent. The Vickers hardness was about 1800. In this translucent alumina, huge alumina grains of several hundreds microns in size were formed, and anisotropic grain growth was observed.

Semiconductors and Dielectrics I

Room: Tomoka C

Session Chair: Tetsuo Tsuchiya, National Institute of Advanced Industrial Science and Technology (AIST)

10:20 AM

(ICACC-S14-016-2019) Photocatalyst anode using nanoparticle deposition for artificial photosynthesis system (Invited)

Y. Imanaka*[1]; T. Anazawa[1]; T. Manabe[1]; H. Amada[1]

1. Fujitsu Laboratories Ltd., Japan

Artificial photosynthesis technology known as Honda-Fujishima effect which produces oxygen and hydrogen or organic energy from sunlight, water, and carbon dioxide, is an ultimate energy and environmental technology. The key device for the higher efficiency of this reaction system is the anode electrode, generally composed of a photocatalyst formed on glass substrate with an electrically conductive Fluorine doped Tin Oxide (FTO). To obtain the highly efficient electrode, the dense film composed of nano particulate visible light responsible photocatalyst having usually complicated multi-elements composition need to be deposited and adhered on the FTO. In this study, we discovered a method capable of controlling electronic structures of a film by controlling the aerosol-type nano particle deposition (NPD) condition and thereby forming films of materials with a smaller band gap than prepared raw material powder, and succeeded in extracting a higher current from the anode electrode. As a result, we confirmed that a current approximately 100 times larger than currents produced by conventional processes could be obtained using the same material. This effect can be adopted to any photocatalyst, particularly materials of solid solution compositions. Besides that, the new computer architecture: digital annealer technology will be introduced.

10:50 AM

(ICACC-S14-017-2019) Simple Fabrication of Nanostructured Hybrid Semiconductor Materials Photodetector

D. M. Gedamu*[1]

1. École de technologie supérieure (ETS), Department of Electrical Engineering, Canada

Simple and low-cost photodetectors are in high demand currently since the current photodetectors in the market which are commonly based on silicon or semiconductor alloys require costly and complex fabrication processes. The photodetectors are also expected to cover a wide range spectral response ranging from UV-Vis to the near infrared (NIR) which makes them attractive for a wide variety of applications including image sensing, chemical/biological sensing, communication and other high-speed photodetectors. Based on 0D, 1D and 2D materials, efficient photodetectors have been fabricated from a single or hybrid semiconductor materials. In here we will demonstrate an efficient and stable broad-spectrum photodetector based on nanostructured ZnO/PbS hydbrid materials deposited micro-patterned Au electrodes. The use of nanostructured hybdrid materials network greatly facilitated in improving the device performance due to a larger surface-to-volume ratio. A simple drop casting technique is used to integrate ZnO nanostructures in to lithographically patterned gold electrodes in a simple experimental strategy followed by PbS QDs deposition on the ZnO nanostructures at ambient air condition. The excellent photo detector capability in the UV range which is further widened to encompass the NIR though the incorporation of PbS quantum dots will also be presented.

11:10 AM

(ICACC-S14-018-2019) Controlled Assembly of 2D Materials for Electrical Applications (Invited)

M. Osada*[1]

1. Nagoya University, Japan

We review the progress made in the synthesis, characterization and properties of 2D oxide nanosheets, highlighting emerging functionalities in electronic applications. A variety of oxide nanosheets (such as $Ti_{1-d}O_2$, $Ti_{1-x}Co_xO_2$, MnO_2, and perovskites) were synthesized by delaminating appropriate layered precursors into their molecular single sheetsviasoft-chemical process. These oxide nanosheets have distinct differences and advantages compared with graphene because of their potential to be used as insulators, semiconductors, and even conductors, depending on their composition and structures. Another attractive aspect is that oxide nanosheets can be organized into various nanoarchitecturesby applying solution-based layer-by-layer assembly. We utilized oxide nanosheets as building blocks in the LEGO-like assembly, and successfully developed various functional nanodevices such as all nanosheet FETs, high density capacitors, artificial ferroelectrics/multiferroics, spinelectronic devices, magneto-plasmonic materials, Li-ion batteries, actuator crystals, etc. Our work is a proof-of-concept, showing that new functionalities and nanodevicescan be made from nanosheet architectonics.

11:40 AM

(ICACC-S14-019-2019) Synthesis of Nano Materials by a Novel Selective Dissolution Method (Invited)

K. Toda*[1]

1. Niigata University, Japan

In this study, we synthesized the nanostructure inorganic materials by the selective dissolution methods from the layered perovskite compounds. For example, nano tantalate sheet was synthesized by the selective dissolution process of the single layered tantalate of Bi_4TaO_8Cl. This precursor is a member of the sillen phase and have the two-dimensional bismuth oxyhalide sheets. The Bi_4TaO_8Cl powders were successfully synthesized by a conventional solid state reaction. The powders were treated with 3 M HCl. The completion of the selective dissolution was confirmed by the ICP analysis of the solution. The decomposition of water into H_2 and O_2 using semiconductor photocatalysts has been intensively investigated for solar energy conversion and storage. The photocatalytic decomposition of water was performed with a gas-closed circulating system. A high-pressure mercury lamp (400 W) was employed as light source. The powder XRD analysis of as-prepared and the acid-treated Bi_4TaO_8Cl confirmed that the long-range order of nano-sized powder was lost by the acid treatment. The hydrated nanosheet tantalate $HTaO_3$ was highly effective than anhydrous as-prepared Bi_4TaO_8Cl. In the case of hydrous layered tantalates, the photogenerated electrons and holes may be easily transferred to the interlayer and thus the water in the interlayer space can be effectively decomposed.

Semiconductors and Dielectrics II

Room: Tomoka C

Session Chairs: Minoru Osada, National Institute for Materials Science; Yoshihiko Imanaka, Fujitsu Laboratories Ltd.

1:30 PM

(ICACC-S14-020-2019) Fundamental study of highly reactive chemical vapor deposition of AlTiN films (Invited)

T. Ishigaki*[1]

1. Mitsubishi Materials Corporation, Central Research Institute, Japan

Recently, Aluminum Titanium Nitride (AlTiN) films deposited by thermal CVD method (CVD-AlTiN) have attracted attention as novel wear resistant coating having superior performance and surprising limit of Al ratio of higher than 0.80 as fcc phase compared to the conventional PVD method. The AlTiN films deposited by PVD method have cubic structure in the Al ratio lower than about 0.67, while they begin to contain softer hexagonal structure in the range of higher Al ratio. In this presentation, our works on CVD-AlTiN films with wide range of Al content will be shown. We focused on the characteristics and growth mechanisms of metastable fcc phase of these films. From the result of EBSD, misorientation in grains of CVD-AlTiN was observed and the average value of Grain Orientation Spread (GOS) was higher than that of conventional wear resistant coatings. Also, nano-lamellae structure was observed in the cross-section by SEM. In the growth process of CVD-AlTiN films, some interesting phenomena were observed which would be caused by high reactivity of ammonia gas as a nitrogen source. The growth rate of CVD-AlTiN films were apparently faster than that of TiN and AlN also using ammonia gas. From these results, we surmise that the superior performance of CVD-AlTiN film would be derived from these unique characteristics different from conventional films.

2:00 PM

(ICACC-S14-021-2019) Diffusion Properties of Dopants during Sintering Process of $BaTiO_3$ Ceramics (Invited)

Y. Iwazaki*[1]

1. TAIYO YUDEN CO., LTD., Research and Development Laboratory, Japan

The diffusion of low-concentration dopants during the sintering process of $BaTiO_3$ ceramic was examined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). An analytical sample which consisted of two pellets of $BaTiO_3$ with different concentrations of Manganese (Mn) and Holmium (Ho) was prepared and measured by LA-ICP-MS to evaluate distributions and concentrations of the dopants to examine their diffusion properties. The experimental results suggest that the diffusion of Mn was much faster than Ho during the sintering process of $BaTiO_3$ ceramics. The results obtained in this study show the effectiveness of LA-ICP-MS for the future improvement of ceramic devices such as multi-layer ceramic chip capacitor (MLCC).

2:30 PM

(ICACC-S14-022-2019) Development of Novel Soft Chemistry (Invited)

K. Toda*[1]

1. Niigata University, Japan

Progress of the solid state reaction required to fulfill two conditions; Thermodynamics (Is a reaction favored?) and Kinetics (How fast is a reaction?). If the reaction rate based on the defect thermodynamics is extremely slow, we cannot observe final products at low temperature. Many researchers claimed that ionic-diffusion in ionic crystal is very slow at low temperature. In addition, final product layer spatially separates the raw materials at the interface in the course of solid state reactions. The mass transport of raw materials occurs through the thermodynamically stable product layer. Observed data of ionic-diffusion are not true diffusion rate. Therefore, the ceramic materials are generally synthesized at high temperature. To overcome the problem of the kinetics (slow reaction rate), we developed a novel low-temperature synthetic technique (water-assisted solid-state reaction (WASSR)) for the nano inorganic compounds. The WASSR method is a very simple and can synthesize the nano inorganic materials just by mixing or storing of raw materials with a small amount of water at low temperature (below 573 K). For example, Nano $BaTiO_3$ (under 20 nm) can be synthesized at 357 K for 6 h just by storing of $Ba(OH)_2$ hydrate and TiO_2 with a small amount (10 wt%) of water in the container. Our original WASSR method is a promising process for the industrial mass production. In this study, we present the machanism of the WASSR method.

3:20 PM

(ICACC-S14-023-2019) Development of flexible oxide thin films by using photo-reaction of hybrid solution process (PRHS) (Invited)

T. Tsuchiya*[1]; Y. Uzawa[1]; T. Nakajima[1]; J. Nomoto[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Considering the recent global interest in reducing energy consumption, SiC power electronics technology is now ready to enable the step to the next plateau for efficiency standards. In most case, SiC power modules are designed to work at operating temperatures around 250 °C. Therefore, a comical available electronic components such as resistor, cannot use for the SiC modules because the electrode and resistor materials and substrate is deterioration in the temperature. To overcome this problem, we developed new thin film resistor by using a photo reaction of hybrid solution (PRHS) process. By using ELAMOD and PRHS process, flexible RuO_2 film was successfully prepared. Lowest resistivity of the RuO_2 film was $8.8\times10^{-5}\Omega$cm. The resistance change was 2.4% at the temperature range from 300 to 25°C. In addition, at the time of implementation, flexible resistor would be expected to relax the crack that comes from the difference in the thermal mechanical properties. In addition, by using PRHS, patterned resistor film was formed by UV irradiation using the photomask after leaching the solvents. So PRPS process is effective for not only crystallization but also patterning. In this presentation, we will explain the ELAMOD and PRHS process for the RuO_2 and other oxide thin film and its electrical properties.

3:50 PM

(ICACC-S14-024-2019) Lithium-ion Battery Management IC using C-Axis Aligned Crystalline In–Ga–Zn–O FETs

S. Harada[1]; Y. Okamoto*[1]; K. Takahashi[1]; T. Ishizu[1]; R. Tajima[1]; K. Nei[1]; T. Takeuchi[1]; M. Kozuma[1]; T. Matsuzaki[1]; T. Ikeda[1]; S. Yamazaki[1]

1. Semiconductor Energy Laboratory Co., Ltd., Japan

The lithium-ion battery, with its high voltage and capacity, is used in various mobile devices. Outside the range of its safety operating voltage, however, it may cause serious accidents. To operate safely and reliably, the lithium-ion battery requires a battery management (BTM) IC that prevents over-charge, over-discharge, and over-current. The proposed BTM IC is composed of the FET using c-axis aligned crystalline In–Ga–Zn–O (CAAC-IGZO) as its active layer. CAAC-IGZO FETs have three features: extremely low off-state current, which enables retaining analog voltage levels by memory configured with one CAAC-IGZO FET and one capacitor; current-temperature characteristics different from those of SiFETs, higher on-state current with higher temperature; and high drain breakdown voltage due to the large bandgap of IGZO. To detect voltage abnormity such as over-charge, BTM ICs constantly compare battery voltage and reference voltage. With the proposed BTM IC, the power consumption of the reference voltage generation circuit is reduced by memory using CAAC-IGZO FETs, which maintains the reference voltage for a long time. The current-temperature characteristics of CAAC-IGZO FETs allow adjustment of charge current according to the temperature. Furthermore, the high breakdown voltage of CAAC-IGZO FETs would achieve stable operation of the BTM IC, even when a series connection causes high battery voltage.

4:10 PM

(ICACC-S14-025-2019) Dynamic Photoresponse Enhancement of Zinc-Tin Oxide (ZTO) Thin Film Transistor via Gate Voltage Pulse

J. Chen*[1]; C. Chang[1]; T. Lin[1]

1. National Cheng Kung University, Materials Science and Engineering, Taiwan

In this work, a zinc tin oxide (ZTO) film prepared by a solution route is applied as the active semiconductor layer in a thin film transistor (TFT) with SiO_2 dielectric and Si gate. The spin-coated ZTO film is about 4-6 nm and exhibits nanocrytalline feature. With light illumination of 405 nm wavelength, the light responsibility of ZTO TFT reaches around 800 A/W. However, the dynamic photoresponse of TFT drain current to pulsed light illumination is rather slow and it shows a significant persistent photoconductivity (PPC) effect. This PPC effect phenomenon can be successfully minimized by applying a positive gate voltage pulse as the light pulse is switched off. In addition, as the light pulse is switched on, the rise time constant can be significantly reduced from 15.8 s to 0.87 s by applying a short negative gate voltage pulse. The dynamic photoresponse improvement can be attributed to the separation of positively ionized oxygen vacancies and photoelectrons generated by light illumination and the mechanism will be discussed in details.

4:30 PM

(ICACC-S14-026-2019) Microstructure-Electrical Properties Correlation of Pressureless Sintered Al_2O_3-$CaTiO_3$ Nancomposites

P. K. Mallik*[1]; J. K. Sahoo[1]; S. Mallick[1]; S. C. Patnaik[1]

1. Indira Gandi Institute of Technology Sarang, Metallurgical and Materials Engineering, India

Alumina (Al_2O_3) is a biologically inert ceramic that limits the bone growth in vitro and in vivo. But its good mechanical properties enables for load-bearing hard tissue replacement. In contrast, calcium titanate ($CaTiO_3$) is a good bioactive, osseeointegration and osteoinductivity than HA. Our main objective is to determine the microstructure–electrical properties correlation of Al_2O_3-$CaTiO_3$ (ACT) composites using impendence analyser. A range of ACT composites was developed by pressureless sintering process. Phase identification and microstructural analysis were carried by XRD and SEM. AC conductivity and permittivity were carried out by using impendence analyser as the function of frequency and temperature from 100 KHz–1MHz and RT to 200°C. As a result, 98% theoretical density was achieved for ACT composite sintering temperature at 1200°C for 2 hours. XRD analysis was revealed the absence of $CaAl_2O_3$ phase. Impendence analysis indicates that the conduction process is thermally activated. The activation energy was calculated from an Arrhenius plot indicates a non-Debye type relaxation due to the long-range motion of mobile charge carriers. The grain conduction effect was not observed from the complex impedance analysis due to the linerity in Nyquist plot. Finally, It can be sugested that the developed nanocomposite could be used for the eletronic and biomaterial applications.

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Direct Writing

Room: Coquina Salon B

Session Chair: Paolo Colombo, University of Padova

8:30 AM

(ICACC-S15-012-2019) Dense powder beds for powder-based additive manufacturing of ceramics (Invited)

J. Guenster*[1]; A. Zocca[1]

1. BAM Federal Institute for Materials Research and Testing, Germany

Many of the most successful and precise additive manufacturing (AM) technologies are based on the deposition layer-by-layer of a flowable powder. Since the first pioneering work at the end of the 1980th many developments have been introduced, greatly extending the use of different materials, improving the physical properties of the components built and enhancing the accuracy of the process. Still very important issues remain nowadays, hampering a completely autonomous production of parts and even restricting the

freedom of design by means of these technologies. One of the major issues is the low density and stability of the parts during the building process, which implies the need of support structures: The powder bed surrounding the part has an essential role, since it should support the structure during building, until it's ready for removal. Moreover, the microstructure of the powder bed is a template for the microstructure of the part produced. In this context, the use of submicron ceramic powders is still a challenge. Three approaches for the stabilization and densification of powder beds will be presented: The Layerwise Slurry Deposition process LSD, the gas flow assisted powder deposition and the Laser Induced Slipcasting (LIS) of ceramic powder compacts.

9:00 AM

(ICACC-S15-013-2019) Direct ink writing of advanced ceramics: Process design for dense components

G. Franchin*[1]; A. Borgna[1]; N. Mondin[1]; S. Diener[2]; N. Katsikis[2]; P. Colombo[1]

1. University of Padova, Industrial Engineering, Italy
2. H.C. Starck Ceramics GmbH, Germany

One of the main factors limiting the industrial impact of Additive Manufacturing (AM) processes is the potential to fabricate fully dense, monolithic ceramics with high values for the mechanical properties. Deposition in a filament fashion such as in Direct Ink Writing (DIW) has so far shown its limitations as it generates rough surfaces and voids at the interface between layers and filaments, affecting the mechanical properties of the produced components. In this work, aqueous-based suspensions of Si_3N_4 and SiC were optimized for use as inks for DIW; their rheological properties were characterized and proved suitable for fabricating both porous, unsupported structures and dense components. It was possible to formulate printable inks with high solid loading exhibiting the desired Bingham shear thinning behavior. The printing process was investigated with the aim of identifying the source of strength limiting defects; particular interest was given to how layers are stacked on top of each other (aligned stacking of filaments, hexagonal build-up, Bouligand structures) and on the surface finish of the samples (as fired or post-processed). Densities and other properties of the samples were characterized and compared with conventional components.

9:20 AM

(ICACC-S15-014-2019) A workflow for formulating printable direct-ink write suspensions of various advanced armor ceramics

C. A. Marsico*[1]; N. Ku[2]; L. Vargas[2]

1. University of Washington, Materials Science and Engineering, USA
2. US Army Research Laboratory, Weapons and Materials Research Directorate, USA

Additive manufacturing can be an enabling technology for development of ceramics with multi-scale, three-dimensional structural features. To exploit direct-write processing for ceramics, the rheology of the ceramic suspension must be optimized to ensure appropriate nozzle flow and minimize slumping during printing. However, this is challenging when working with multiple material systems since each is generally optimized independently. Here, a general workflow for developing ceramic suspensions for direct-ink writing was investigated enabling the production of aqueous ceramic slurries with high solids loading (50–58 vol.%) stabilized by small additions (<5 wt.%) of polymeric dispersants invariant of powder feedstock. In this study, several common binders were assessed for use with several powder variants of advanced armor ceramics (B_4C, SiC, and Al_2O_3). Proficient binders were identified through zeta potential measurements, and the effect of powder type, solids loading, and binder content on slurry rheology were assessed resulting in the rapid formulation of printable suspensions for multi-material additive manufacturing.

9:40 AM

(ICACC-S15-015-2019) Shaping of high performance porous structured ceramics by 3D micro-extrusion

M. Rombouts*[1]; J. Lefevere[1]; V. Middelkoop[1]; B. Michielsen[1]

1. Vito, Sustainable Materials Management, Belgium

Additive manufacturing by 3D micro-extrusion of highly viscous, powder loaded pastes allows for the creation of complex shaped ceramic products. After 3D printing, the products are generally post processed by thermal treatment to remove the organic binder and/or strengthen the material. 3D printing offers the possibility of tailoring the macro-porous architecture with a high level of freedom of design. In view of optimal heat and mass transfer properties, in combination with a low pressure drop, this enables the improvement in the efficiency of sorption and catalytic processes. In fields of application such as adsorption and catalysis, both the direct printing of the active (sorbent/catalytic) material as well as the coating of the active material onto an inert 3D printed support will be demonstrated. The paste formulation (powder, (in)organic binder, rheology modifier, dispersants,…), extrusion conditions and thermal post-processing conditions have an impact on the structural properties, mechanical strength and catalytic performance (selectivity and yield of conversion) in specific reaction conditions (e.g. CO2 methanation). The strength of the developed 3D printing technology lies in its easy scalability and the wide variety of materials (metals, zeolites, oxide ceramics, carbon-based,…) that can be processed.

Fused Deposition

Room: Coquina Salon B

Session Chair: Jens Guenster, BAM Federal Institute for Materials Research and Testing

10:20 AM

(ICACC-S15-016-2019) 3D Printing of mullite-based ceramics from preceramic polymers and alumina with Fused Deposition Modelling (FDM)

R. Tonello[2]; L. Gorjan[2]; G. Franchin[1]; S. Tutu[2]; P. Colombo*[1]; F. Clemens[2]

1. University of Padova, Industrial Engineering, Italy
2. Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Switzerland

For the first time, a thermoplastic filament based on a preceramic polymer containing alumina powder was developed for Additive Manufacturing of lightweight mullite honeycomb structures using Filament Deposition Modeling (FDM). For lightweight structures, mullite is an interesting material because of its low thermal extension coefficient, high creep resistance, and low density. To obtain mullite, stoichiometric ratio between the alumina powder and the polysiloxane was used. Three different alumina powder were investigated to obtain mullite conversation at low temperatures. Using coarse alumina powder, the reaction of mullite did not state at temperatures below 1300°C, while using fine powder resulted in highly cracked pieces after debinding and sintering. A temperature above 1550°C was needed to fully convert the alumina powder into pure mullite. Different printing settings were tested, and the best ones enabled to obtain high-quality parts after firing.

10:40 AM

(ICACC-S15-017-2019) On the Development of Novel MAXPOL Composites by Fused Deposition Modelling (FDM)

K. Hall*[2]; C. Matzke[1]; Y. Ji[2]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA
2. University of North Dakota, Chemical Engineering, USA

In this presentation, we report for the first time the synthesis and characterization of novel Ti_3SiC_2 and MoAlB reinforced polymer matrix composites by 3D printing. Novel Ti_3SiC_2-PLA and MoAlB-PLA composites were designed by adding 1 wt% and

2 wt% Ti_3SiC_2 (Resin-2%312Si) particulates in the PLA matrix. Initially, filaments were extruded in the Filabot extruder. Thereafter, the extruded filaments were printed by using a Afina printer. Microstructure studies by SEM studies showed that the Ti_3SiC_2 and MoAlB particulates are well dispersed in the resin matrix. Finally, we will report the detailed mechanical and tribological characterization of these composites.

11:00 AM

(ICACC-S15-018-2019) Ceramic matrix composites fabricated by Fused Filament Fabrication (FFF)

H. Klemm*[1]; J. Abel[1]; A. Michaelis[1]; M. Singh[2]

1. FhG IKTS Dresden, Germany
2. Ohio Aerospace Institute, USA

Ceramic matrix composites with SiC short fibers have been fabricated by Additive Manufacturing (AM) using a thermoplastic approach. By means of Fused Filament Fabrication (FFF) or Fused Deposition Modelling (FDM) a ceramic part is shaped layer by layer using a thermoplastic filament which is extruded through a heated nozzle. According to the degrees of freedom for movement of the printing head (and printing bed) green bodies with complex geometries can be fabricated. In this study a ceramic feedstock with SiC fibers (Hi Nicalon, UBE SA3), SiC powder and a thermoplastic binder system was used. Tailored filaments with approximately 1.8 mm in diameter were developed, fabricated by extrusion and printed by FFF to achieve CMC with short and long SiC-fibers. After binder burnout ceramic matrix composites were fabricated by polymer infiltration and pyrolysis (PIP) and liquid silicon infiltration (LSI). Various composites with unidirectional fiber orientation and different geometries were obtained. Finally, the materials fabricated were characterized regarding their microstructure and mechanical properties.

11:20 AM

(ICACC-S15-019-2019) Thermoplastic-based Additive Manufacturing of multi-functional and multi-material ceramic components

U. Scheithauer*[1]; J. Abel[1]; S. Weingarten[1]; T. Moritz[1]; H. Klemm[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Shaping, Germany

Within the Additive Manufacturing technologies for ceramic components direct working thermoplastic based AM technologies have outstanding advantages. Highly ceramic particle filled suspensions or filaments are used as a semi-finished product which are molten and deposited to manufacture green components with a high green density additively. This allows the complete densification during the final sintering process. The consolidation of the material resulting from cooling of the molten thermoplastic matrix allows the processing of all powders which can be dispersed within the thermoplastic binder system. And the selective deposition of the materials opens the door to the AM of multi-functional and multi-material ceramic components. The presentation will describe the two AM technologies Ceramic Thermoplastic 3D Printing (CerAM T3DP) and Ceramic Fused-Filament-Fabrication (CerAM-FFF). CerAM FFF is a low cost approach bases on filaments which are used to produce large and complex components quickly. CerAM T3DP bases of the selective deposition of single droplets and shows in comparison to CerAM FFF a lower productivity, but a much higher resolution. In the presentation different multi-functional (e.g. combination of dense & porous zirconia or black & white zirconia) and multi-material components (metal-ceramic components) additively manufactured with these technologies will be shown.

11:40 AM

(ICACC-S15-020-2019) Glass material for Directed Energy Deposition

F. Spirrett*[1]; I. Ashcroft[1]; E. Saleh[1]; K. C. Datsiou[1]; R. Goodridge[1]

1. University of Nottingham, United Kingdom

Additive manufacturing (AM) of glass material is potentially of high value to many industries owing to the combination of properties such as high chemical resistance, durability, transparency, interesting electrical and thermal properties, and the ability to make more geometrically complex shapes than available with traditional glass making methods. However, the high local temperatures required to process glass by AM, together with the sensitivity of glass to thermal-stress induced cracking, makes glass additive manufacturing very challenging. Through optimisation of glass feedstock and laser processing parameters, this work investigates the processing of glass by Directed Energy Deposition (DED), an AM process in which powdered or wire material is fed to a focused energy source. In the paper we demonstrate the consolidation of soda lime silica and borosilicate glasses using a laser based DED system. Processing parameters were optimised to enable the consolidation of soda lime silica powder to form glass structures without cracking. Glass fibre feedstock was also produced for DED processing, and the consolidation of soda lime silica glass fibres onto a glass substrate is demonstrated for decorative glass. This work introduces glass material for DED processing and outlines the necessary work for future widespread adoption of DED processing of glass material in industry.

Ink Jet Printing I

Room: Coquina Salon B
Session Chair: Andrea Zocca, BAM Federal Institute for Materials Research and Testing

1:30 PM

(ICACC-S15-021-2019) Inkjet technology for ceramic products: Influence of some process variables on ink penetration (Invited)

J. Amorós[1]; A. Moreno*[1]; E. Blasco[1]; J. Pérez[2]; S. Navarro[2]; S. Reverter[2]

1. University Jaume I, Instituto de Tecnología Cerámica, Spain
2. Color Esmalt S.A., R&D, Spain

Inkjet technology has become very popular in recent years and is nowadays widely used for decorating ceramic products. This has led to in-depth study of the operating principles and process variables involved. These notably influence the properties of the deposited ink layers, as do the physicochemical properties of the applied inks and of the glazes on which the inks are deposited. The problems associated with these factors are further heightened when inks with complex formulations designed to obtain special effects and specific surface properties are used. This study examines the characteristics of the interface that developed on applying an ink on a certain type of glaze, as well as the surface properties of the final product. The relationship of the amount of ink applied per unit area and the particle size distribution of the glaze on which it was deposited to ink penetration into the glaze layer was also investigated. The study was performed on several fired glaze layers obtained by modifying the above process variables. The resulting microstructures were observed by SEM, while the variation of glaze layer composition with distance to the surface was determined by SEM-EDS. The results obtained were successfully correlated with the porous texture of the raw glaze (determined by SEM and mercury porosimetry) and with raw glaze particle size distribution.

2:00 PM

(ICACC-S15-022-2019) Additive Manufacturing for Achieving Innovative Electric Motor Designs

M. C. Halbig*[1]

1. NASA Glenn Research Center, USA

Additive manufacturing enables new, non-conventional fabrication capabilities for achieving innovative electric motors designs. The design benefits offered by additive manufacturing include compact designs, complex geometries, multi-material components, innovative cooling, and optimally designed and manufactured components compared to the currently obtainable designs from the more standard fabrication methods. Motors with higher power densities and/or efficiencies can be achieved compared to the current state-of-the-art motors. Optimized stators concepts are being pursed in one design in which advanced conductive 3-phase coils are fabricated using direct printing of optimized silver pastes and in a second stator design which 3D prints a substrate in conjunction with automated wire embedding. Additional additive manufacturing methods are also being used to achieve structural components for the motor to include the rotors, housing, and a stator cooling ring. The motor performance improvements from optimized materials and new component designs will be compared to baseline motor performance in dynamometer testing. Systems studies show that the higher performance and lower weight motors offer improved energy efficiency and reduced emissions.

2:20 PM

(ICACC-S15-023-2019) Direct Writing of Conductive Silver Pastes for Electric Motor Applications

A. C. Salem*[2]; H. S. Leonard[3]; M. Singh[1]; M. C. Halbig[1]

1. NASA Glenn Research Center, Materials and Structures, USA
2. Washington University in St. Louis, Engineering, USA
3. RIT, Engineering, USA

In recent years, commercially available silver conductive pastes have significantly improved. This improvement has ultimately increased the number of potential applications for printed electronics. Further modifications and improvements to commercially available silver pastes will help in the application of this technology and will benefit a broad range of industries. In this study, six commercially available silver pastes were directly printed using an nScrypt 3Dn-300 system and characterized for their electrical conductivity and thermal stability. The explored pastes varied highly in their microstructures and rheology creating a wide range of properties and printability/manufacturing challenges. Furthermore, the sintering conditions of each paste affected the electrical properties of printed coils. The thermal properties of each paste were analyzed using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Microstructural analysis of silver coils was carried out using Optical and Scanning Electron Microscopy. Resistivity measurements were taken using the 4-probe (Kelvin) method. Effect of processing parameters and sintering conditions on the microstructure and electrical properties will be discussed.

2:40 PM

(ICACC-S15-024-2019) Evaluation of Conductive Silver Coils in Additively Manufactured Axial Flux Electric Motors

H. S. Leonard*[1]; A. C. Salem[2]; M. C. Halbig[3]; M. Singh[4]

1. Rochester Institute of Technology, USA
2. Washington University in St. Louis, USA
3. NASA Glenn Research Center, USA
4. Ohio Aerospace Institute, USA

Electric motors have been traditionally plagued by inefficiencies due to low copper fill in windings and eddy current losses within their cores. One way to increase current and power densities of electric motors is to print conductive coils out of silver paste in smaller, more compact shapes than typically achievable with enameled copper wire. In this work, nScrypt 3D printer was used to print silver paste into machined troughs within Vespel substrates. These traces were subjected to testing under different electrical loads, cooling methods, and their resistances were compared. Thermal imaging camera was used to measure the temperature changes in the coils as a function of electric current. Optical and SEM analysis was used to evaluate the cross sections of coils before and after the testing and to identify any porosity in the traces. Experimental results indicate that high temperature silver pastes can be used for design optimized coils and a viable option in electric motor applications.

Ink Jet Printing II

Room: Coquina Salon B
Session Chair: Craig Smith, Ohio Aerospace Institute

3:20 PM

(ICACC-S15-025-2019) Layerwise Slurry Deposition for Additive Manufacturing of Ceramics

A. Zocca*[1]; P. Lima[2]; S. Diener[2]; T. Mühler[3]; J. Lüchtenborg[1]; J. Guenster[1]

1. BAM Federal Institute for Materials Research and Testing, Ceramic Processing and Biomaterials, Germany
2. H.C. Starck Ceramics GmbH, Germany
3. Clausthal University of Technology, Germany

In powder bed Additive Manufacturing (AM) technologies, a part is produced by depositing and piling up thin powder layers. In each layer, the cross section of the object to build is defined by locally consolidating the powder, by sintering/melting the material (powder bed fusion technologies) or by ink jetting a binder (binder jetting technologies). These are already leading AM technologies for metals and polymers, thanks to their high productivity and scalability. The application of these techniques to most ceramics has been challenging so far, because of the challenges related to the deposition of homogeneous powder layers when using fine powders. In this context, the "layerwise slurry deposition" (LSD) has been developed as a layer deposition method which enables the use of SLS/SLM and 3DP technologies for advanced ceramic materials. LSD consists in the layer-by-layer deposition of a ceramic slurry by means of a doctor blade. Each layer is deposited and dried to achieve a highly packed powder layer. The LSD offers high flexibility in the ceramic feedstock used, especially concerning material and particle size, and enables the production of parts with physical and mechanical properties comparable to pressed or slip-casted parts. In this presentation, the LSD technique will be introduced and several examples of application to porcelain, SiC and alumina products will be reported.

3:40 PM

(ICACC-S15-026-2019) Binder Jet Additive Manufacturing of Soft Magnetic Materials for Aircraft Electric Propulsion Systems

D. Oropeza Gomez*[1]; S. M. Geng[2]; M. C. Halbig[2]; A. Hart[1]; M. Singh[3]

1. Massachusetts Institute of Technology, USA
2. NASA Glenn Research Center, USA
3. Ohio Aerospace Institute, USA

Emerging global need to reduce aircraft noise and carbon emissions has led to growing interest in the use of electric motors as an alternative to turbine engines for aircraft propulsion systems. The development of lightweight electric motor components (e.g., rotor, stator, housing) is desirable for aircraft applications. Recent work on materials for stators has shown that the use of soft magnetic composite (SMC) materials, insulation-coated iron powder particles formed by compaction, to fabricate 3-dimensional stator designs can reduce the size and weight of electric motors while still providing high flux and low losses. Another possible powder-based fabrication technique for shaping 3-dimensional stators is binder jet additive manufacturing (AM). In this work, we developed processing parameters for soft magnetic iron via binder jet AM and characterized the material density, electrical and magnetic properties after sintering.

Magnetic properties of the binder jet iron materials have been compared to sintered iron, laminated iron, and SMCs. The effect of thermal profiles during sintering on the material properties have been evaluated. These results demonstrate the feasibility of using binder jet AM to process soft magnetic iron, provide a comparison with other stator materials, and showcase the possibility to tailor magnetic properties through porosity control during sintering.

4:00 PM

(ICACC-S15-027-2019) Reactive binders for mitigating distortion during sintering of 3D printed green bodies

L. O. Grant[1]; C. F. Higgs[2]; Z. C. Cordero*[1]

1. Rice University, Materials Science and NanoEngineering, USA
2. Rice University, Mechanical Engineering, USA

Binder jet 3D printing is an additive manufacturing process that yields near net-shaped green bodies held together by a binder. This binder is normally an organic compound that is removed during the sintering thermal cycle. Here we explore an alternative class of binders that decomposes on heating to form nanocrystalline inter-particle necks, which strengthen the brown body and help suppress slumping. Using TiO_2 as a model system, we demonstrate that this effort could launch a promising, new generation of multifunctional binders for preserving the shape of binder jet 3D printed objects during pressureless sintering.

4:20 PM

(ICACC-S15-028-2019) A Novel Method to Increase Density of Ceramic Parts in Binder Jetting Additive Manufacturing

W. Du[1]; G. Miao[1]; Z. Pei[1]; C. Ma*[1]

1. Texas A&M University, USA

Binder jetting additive manufacturing has demonstrated a significant potential in printing ceramic parts because it has little geometry limitation and is easy to scale up. Currently, the bulk density of ceramic parts by this process ranges from 40% to 68%, far below the requirement for load-bearing applications. The main cause comes from the contradicting requirements for the particle size of the feedstock powder: a large particle size (>5 μm) is required for a high flowability while a small particle size (<1 μm) for a high sinterability. A novel powder granulation method was investigated to address this contradiction. Nanosized alumina powder (~100 nm) was used to prepare microsized breakable granules (10–100 μm). In this way, the flowability of the powder was improved by the increased apparent size while the high sinterability of the starting nanosized powder was maintained. In addition, the low-strength granules were broken into the original nanoparticles while forming the power bed, eliminating the inter-granule void. With this method, a bulk density of 80–90% was achieved on printed and sintered alumina, breaking the record in the literature. A hardness of 16.7 GPa was obtained, close to the hardness of conventionally manufactured dense alumina (17–18 GPa). This powder granulation method could enable widespread applications of ceramic binder jetting additive manufacturing.

4:40 PM

(ICACC-S15-029-2019) Large scale additive manufacturing of artificial stone

F. Gobbin*[1]; G. Franchin[1]; P. Colombo[1]; A. Italiano[2]; A. Beretta[2]; A. Zecchini[1]; A. Cervesato[1]; G. Rangon[1]

1. University of Padova, Industrial Engineering, Italy
2. Desamanera, Italy

Large scale (meter-sized) non-structural object were fabricated by an indirect AM technique (powder bed). Printers and materials were developed by Desamanera Srl in collaboration with the Industrial Engineering Department of the University of Padova. The printer machine works with a mobile printing head, that starts by laying out the printing powders and then selectively depositing a liquid on it, layer after layer. The printing bed contains both fillers and reactive powders, and the activation liquid is simply water. The exothermic reaction between reactive powder and water generates in situ a hydraulic inorganic binder, that cements the other powders in the bed. The reaction parameters were controlled to achieve a fast setting, to enable rapid printing and building up of a structure at the macro-scale. Raw materials are selected to be economic, easy to use, local, eco-friendly and sustainable. The main characteristics of both raw materials and printing mixes - such as composition, density, particle size distribution, flowability - were analyzed. Density, porosity, mechanical properties, phase assemblage analyses were carried out on the consolidated material, and images of the morphology of the printed parts were collected as well.

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced Nanostructured Materials for Photovoltaics and Solar Fuels II

Room: Halifax A/B

Session Chairs: Alessandro Martucci, University of Padova; Riad Nechache, Ecole de technologie Superieure; Alberto Vomiero, Lulea University of Technology

8:30 AM

(ICACC-S17-008-2019) New Directions in Luminescent Nanoparticles (Invited)

C. Wickleder*[1]; A. Mattner[1]; L. Zimmermann[1]; J. Olchowka[2]; S. Lienenklaus[3]; S. Weiß[3]

1. University of Siegen, Chemistry/Biology, Germany
2. Université de Bordeaux, Chargé de Recherche CNRS, France
3. Hannover Medical School, Germany

In this talk several fast and mild synthesis routes for luminescent nanoparticles (NPs) are presented. Eu^{2+} containing NPs of varying host lattices can be obtained even in aqueous solution using Zn as reducing agents for Eu^{3+}. Moreover, its synthesis is also possible in ionic liquids with Eu^{2+} containing starting materials. In the latter case ionic liquids (e.g. $[Bmim][BF_4]$ or $[Bmim][PF_6]$) can also serve as a fluoride source for easy and "green" production of fluoridic NPs. On the other hand NPs of $CaWO_4$:Eu^{3+}, Sm^{3+} with a persistent afterglow are presented for the first time with the aid of the co-precipitation method in diethylene glycol followed by an annealing step to improve the crystallinity for an intense afterglow. They can be used for bio-imaging and -detection due to the preferred red emission of the doped Eu^{3+} ions. Another advantage is the possibility to excite the nanoparticles before injection to avoid the problems of low transparency of tissue and autofluorescence of cells.

9:00 AM

(ICACC-S17-009-2019) Solution based synthesis of advanced Ln doped materials; from molecules to materials (Invited)

G. Westin*[1]

1. Uppsala University, Sweden

There is an increasing demand for complex multi-functional materials of high elemental and structural complexity, often hierarchically structured with sizes down to a few nm. These structures also have to be of high quality and produced at low cost, which means few and fast processing steps why it is anticipated that molecular based solution processes will be the main route for fabrication. Although the last decade has seen a rapid development of solution based processing routes there is still a strong need for new molecular based processes, where there is a strong connection between the target composition and micro-structure and the precursor structure and process steps in-between. By using low temperature synthesis and proper molecules there are also great possibilities to achieve far from thermodynamically stable doping levels, composites and inorganic

materials built with memory of the molecular precursors. Here we will describe solution processes to Ln doped glasses and oxide sponges and connect the final structures with the precursors and steps in-between. Some examples showing scalability of the processes through applications and up-scalings will also be given. The processes have been studied with a large range of techniques including; TG, DSC, XRD, XPS, SEM-EDS, TEM-EDS, and IR spectroscopy

9:30 AM

(ICACC-S17-010-2019) Multifunctional Carbon Dots for Sensing Applications (Invited)

J. Macairan[1]; F. Yarur[1]; F. Victoria[1]; F. Noun[1]; R. Naccache*[1]

1. Concordia University, Chemistry and Biochemistry, Canada

Carbon dots have garnered significant interest as fluorescent materials with a vast potential in sensing and imaging applications, in optoelectronics, as well as energy conversion. Their ultra-compact size, low cytotoxicity, low photo-bleaching/blinking, tunable photoluminescence, combined with simple, environmentally-friendly and low-cost synthesis, makes them ideal candidates for study. We synthesize carbon dots via bottom-up methods such as microwave and hydrothermal syntheses, with simple organic precursors (e.g. citric acid, amino acids or sugars) as the carbon source. We passivate the surface of our carbon dots to achieve high fluorescence quantum yields. Here, our work focuses on exploiting the carbon dots' optical properties in order to design a myriad of sensors namely for sensitive detection of chiral analytes, heavy metal cations in water, as well as for temperature sensing applications in biological systems.

10:15 AM

(ICACC-S17-011-2019) Solution processed chalcogenides and oxides for solar cells and solar water splitting (Invited)

L. H. Wong*[1]

1. Nanyang Technological University, Singapore

The increasing need of energy consumption and concerns over global warming prompt the urgent quest of clean and renewable energy sources. To extend solar energy applications beyond the utilization of solar panels on the rooftops and solar field, a more advanced technology involving new materials, novel processing and fabrication techniques, are required. Fabrication of high quality semiconductor film and nanostructures using solution methods is one promising approach in the discovery of materials with new properties and functionalities. However most of the low band-gap semiconductor photoabsorber still needs major breakthrough in improving their charge transport properties. This is usually achieved by employing nanostructuring together with doping and surface passivation strategies. In this talk, I will give an overview of our work in improving the bulk optical and electronic properties of semiconductor photoabsorbers, fabricated using solution methods. In particular, I will share our strategy in producing solution processed Cu chalcogenide thin film solar cells with power conversion efficiency >10%. I will also review our activities in artificial photosynthesis using nanostructured metal oxide (Fe_2O_3, $BiVO_4$, Fe_2TiO_5, $FeVO_4$, etc), with emphasis on improving the charge transport and separation efficiency by doping, surface passivation and co-catalyst integration.

10:45 AM

(ICACC-S17-012-2019) Heterostructured Nanocrystals for Solar-driven Photoelectrochemical Hydrogen Production (Invited)

H. Zhao*[1]

1. Qingdao University, College of Physics, China

Mesoporous metal oxide sensitized with semiconducting nanocrystals is considered as a promising system for photoelectrochemical (PEC) hydrogen generation, in view of its low cost and high solar energy to fuel conversion efficiency. Various types of heterostructured quantum dots were used to sensitized metal oxide (eg SnO2 and TiO2) for PEC water splitting. We investigated the effect of the size and shell thickness and interfacial shell thickness and composition on the charge transfer and further the efficiency and long-term stability of PEC devices. The highest saturated photocurrent density reaches 16 mA/cm2, which is among the best of reported values.

11:10 AM

(ICACC-S17-013-2019) Surface Engineering of Nanostructured Functional Ceramics (Invited)

O. K. Varghese*[1]; R. Neupane[1]; M. Paulose[1]; B. Kandel[1]; A. Alex[1]

1. University of Houston, Department of Physics, USA

Nanostructured materials possess high surface area to volume ratio and hence, their surface properties play a crucial role in determining their performance in a wide range of applications. The surface of semiconducting oxides, in general, is sensitive to the environment due to their ability to form weak or strong bonds with the interacting molecules or radicals belonging to matter in any phase. This property is directly exploited in several applications; chemical sensing and solar photocatalytic fuel generation are just two examples. The nature of interaction of the surface with water molecules is of significant interest not only to these but also to various other applications involving superhydrophilic and superhydrophobic coatings. The degree of wetting can be manipulated by controlling the surface energy. We have recently discovered a general method to tune the wetting properties of ceramic surfaces. This presentation will give the details of this work in relation with the use of these materials in chemical sensing and solar energy conversion.

11:40 AM

(ICACC-S17-014-2019) A Mechanistic study of the Photoluminescence Blinking in $CsPb_2Br_5$ Perovskite Crystals

Z. Qin*[1]; L. Ouyang[2]; F. Lin[1]; S. Yue[1]; Z. Wang[1]; J. Bao[3]

1. University of Electronic Science and Technology of China, USA
2. Yunnan University, China
3. University of Houston, USA

Perovskite semiconductors have been widely fabricated for various optoelectronic applications, such as nanolasers, LEDs, and solar cells. The photoluminescence (PL) intermittency phenomenon has been reported in many quantum dots and in several perovskites nanocrystals. But, the blinking has never been observed in $CsPb_2Br_5$ crystal, to the best of our knowledge. Here, we first observed the PL blinking in inorganic $CsPb_2Br_5$ crystals under the UV light (365nm) illumination. The time tagged PL confirmed that the blinking is non-periodical. The PL blinking behavior was also studied under different UV light intensity. The motivation of this research is to investigate the mechanism of the PL blinking, which will be beneficial to understand the luminescence properties of perovskite crystals.

Advanced Nanostructured Materials for Photovoltaics and Solar Fuels III

Room: Halifax A/B

Session Chairs: Lydia Wong, Nanyang Technological University; Mauro Epifani, CNR-IMM; Alberto Vomiero, Lulea University of Technology

1:30 PM

(ICACC-S17-015-2019) Ultrafast exciton dynamics in PbS/CdS and CdSe/CdS nanocrystals and in coupled nanoparticle systems (Invited)

M. Zavelani-Rossi*[1]

1. Politecnico di Milano, Energy Department, Italy

A wide variety of materials with nanometric dimensions are increasingly explored. Among them semiconductor nanocrystals (NCs) are very promising for photovoltaics, sensing and optical sources. Key advantage is the control of their electronic structure by engineering

composition, size, and shape. Significant results have been obtained with CdSe/CdS and PbS/CdS heterostructures NCs. New potentialities are under investigations in coupled system, such as lead calcogenide-metal oxide and ZnO-metal nanostructures. In all these materials the photophysical processes occurring in the first picoseconds after excitation play a crucial role in the optoelectronic behavior. In this talk I will present studies carried out by ultrafast pump-probe spectroscopy techniques with 100-fs time resolution. I will show the photoinduced exciton dynamics in CdSe/CdS and PbS/CdS NCs optically active in the visible and near-infrared spectral region; these NCs show dual color photoluminescence emission, optical gain and laser emission and can be used as thermal sensor. The role of interface, dimension and shape in the relaxation pathway of excitons will be discussed, pointing out their influence for applications. I will also present exciton and charge dynamics in PbS/CdS NCs at the surface of TiO_2 nanoparticles and in ZnO nanowires decorated with silver nanoparticles.

2:00 PM

(ICACC-S17-016-2019) Tuned Metal Oxide Nanosurfaces and Hetero-Interfaces for Solar Energy Conversion (Invited)

S. Mathur*[1]; J. Leduc[1]; T. Fischer[1]

1. University of Cologne, Germany

In search of new energy sources, photoelectrochemical splitting of water to produce hydrogen is a viable approach to transform sunlight into chemical energy, which has triggered a quest for suitable photocatalysts. Among different semiconductor metal oxides, hematite (a-Fe2O3) has emerged as a promising photo-anode material for water oxidation since it is cheap, abundant, non-toxic and stable under photoelectrochemical conditions. Although it promises high theoretical photocurrent densities (11-14 mA/cm2), corresponding to a solar-to-hydrogen (STH) efficiency of 14-17 %, these values can hardly be attained since hematite suffers from high resistivity, short lifetime of the photoexcited charge carriers, and short hole diffusion length (2-4 nm). To overcome these limitations, we have focused on interfacial modification of metal oxide multilayered photoanodes (Fe2O3//TiO2, Fe2O3//U3O8) deposited by plasma enhanced chemical vapor deposition (PE-CVD). The effect of impurities (dopants) and interface modification were elaborated via in-situ oxygen K-edge X-ray absorption spectroscopy (XAS) and transient absorption spectroscopy (TAS) for a detailed understanding of the photoelectrocatalytic performance. Moreover, the underlying processes with respect to water splitting reactions were investigated via ab-initio DFT calculations.

2:30 PM

(ICACC-S17-017-2019) Flame Annealed TiO_2 and its Heterojunctions for the Production of Solar Fuels (Invited)

K. Shankar*[1]; S. Zeng[1]

1. University of Alberta, Electrical and Computer Engineering, Canada

Flame annealed TiO_2 received significant attention in the early 2000s as a method to improve the visible light responsivity of titania through the introduction of defects and dopants. In a highly cited but controversial paper, S.U.M. Khan and colleagues reported on highly efficient water-splitting using flame annealed TiO_2 thin films in the journal Science in 2002. Due to problems with the reproducibility of the reported results, spectral mismatch issues and potentially unphysical mechanisms, this line of research was abandoned. In the last few years, there has been a resurgence of interest in Black TiO_2, which is a defect rich form of reduced titania exhibiting visible light absorption over a broad spectral range. Recently, the Shankar Lab found that flame annealing anodically formed TiO_2 nanotube arrays produced an unusual morphological transition from circular to square-shaped cross-sections, which was accompanied by changes in the density of Ti^{3+} states and the phase composition. Using isotope-labeled mass spectrometry, we observed that flame annealed nanotubes significantly outperformed regular nanotubes in the photoreduction of CO_2 to methane while harvesting blue light. Flame annealed titania nanotubes also performed better than regular nanotubes in photoelectrochemical water splitting. This Invited Talk will focus on the use of flame annealed TiO_2 nanotubes for the production of solar fuels.

3:20 PM

(ICACC-S17-018-2019) Fluoride thin films for energy-conversion in photovoltaics: Pros and cons of MOCVD and sol-gel approaches (Invited)

A. Pellegrino[1]; A. Speghini[2]; G. Malandrino*[1]

1. Universita' degli Studi di Catania, Dipartimento Scienze Chimiche, Italy
2. Università degli Studi di Verona, Dipartimento di Biotecnologie, Italy

Recent years have witnessed an exponential growth of research activities to enhance the efficiency of photovoltaic (PV) devices. One promising strategy is to collect the radiation energy outside the absorption range of the photoactive material (usually silicon) through down-conversion (DC) or upconversion (UC) processes. In particular, the most efficient hosts for energy up-conversion consist of alkaline earth fluoride matrices, as CaF_2 and SrF_2, and multicomponent $NaYF_4$ phase. In the presentation, an overview will be given on recent results on the fabrication of Ln-doped fluoride thin films through two different chemical approaches: Metal-Organic Chemical Vapor Deposition (MOCVD) technique, applied to the deposition of CaF_2: Yb^{3+}/Er^{3+} and $NaYF_4$ and a combined sol-gel/spin-coating approach for the deposition of β-$NaYF_4$: Yb^{3+}/Er^{3+} and β-$NaYF_4$: Yb^{3+}/Tm^{3+}. Both synthetic approaches use fluorinated metalorganic β-diketonate compounds, which act as single-sources, and have the advantage of being very reliable and reproducible methods for the fast production of films with high uniformity degree over large areas.

3:50 PM

(ICACC-S17-019-2019) Materials Captured in Space and Time (Invited)

A. Yurtsever*[1]

1. Institut national de la recherche scientifique (INRS), Canada

Understanding matter at the dynamic and microscopic levels is fundamental for our ability to predict, control and ultimately design new functional properties for emerging technologies. Reaching such an understanding, however, has traditionally been challanging due to limited experimental methodologies that can simultaneously image both in space and time. Ultrafast transmission electron microscopy (UTEM), a newly emerging methodology, offers the means to overcome this limitation by merging the femtosecond domain of pulsed lasers with the nanoscale domain of transmission electron microscopes. With UTEM, it is possible to capture ultrafast events in real space, Fourier space and spectroscopy. In this presentation, I will overview some of our results pertaining to the dynamic behavior of nano-materials. In particular, I will elaborate on a picosecond-scale strain dynamics induced by ultrafast laser pulses. Time-resolved convergent beam electron diffraction patterns reveal the unit-cell distortions, as the material absorbs the optical energy and dissipates it in ultrafast times. In addition, I will present an inelastic scattering process between pulsed electrons and photons. When this inelastic signal is mapped in space and time, optically-induced nearfields of several nanostructures are revealed with combined spatiotemporal resolutions. These results exemplify the versatility of UTEM in probing the dynamic nature of materials.

4:20 PM

(ICACC-S17-020-2019) Color Tunable Hybrid Polymer Light Emitting Diodes using Electrospraying

X. Guo*[1]; J. A. Benavides[1]; D. Banerjee[1]; F. Roy-Moisan[1]; S. G. Cloutier[1]

1. École de technologie supérieure, Electrical Engineering, Canada

This paper presents a new paradigm in polymer light emitting diodes (PLEDs) fabrication using a uniform electrosprayed particle film as the active layer of the device. Electrospraying (ES) is a simple fabrication technique with many processing parameters; and it enables multi-layer fabrication of the polymer materials with similar solubility in common organic solvents. First, We have used design of experiment approach together with computational statistical methods to investigate the key parameters in affecting the electrosprayed particle layer. Then, based on the analyzed experimental parameters, red emitting PLEDs (MEH-PPV) with peak current density of 1.93A/cm^2 and ~6000 cd/m^2 and additional four types of PLEDs of different composition ratio between MEH-PPV and F8BT are fabricated. Together, devices with similar electrical characterizations but only varying in emission wavelenght are demonstrated.

4:40 PM

(ICACC-S17-021-2019) Enhancement of sensing though surface-induced deformation in silicon nanostructures

M. Nasr Esfahani*[1]; M. Jabbari[2]

1. University of Warwick, WMG, United Kingdom
2. University of Manchester, United Kingdom

Silicon nanostructures have found applications in various fields – especially in the field of nanoelectromechanical systems – through development of a series of new-generation sensors. A remarkable contribution of surface energy on physical properties of nanostructures is identified within theoretical calculations and experimental observations. In this study, the influence of surface energy on mechanical deformation of silicon nano-cantilevers are studied through molecular dynamics simulations. A twist deformation at the free-end of silicon nano-cantilever is observed for rectangular cross-sections. Deformation associated with the surface stress is computed for mass sensing purposes. An improvement on sensitivity is observed for nano-cantilevers with high length-to-thickness ratios.

Poster Session A

Room: Ocean Center

5:00 PM

(ICACC-GYIF-P001-2019) Fabrication and plasma corrosion behavior of yttrium oxyfluoride ceramics

T. Tsunoura*[2]; K. Miyashita[2]; R. Tahara[2]; K. Yoshida[3]; T. Yano[1]

1. Tokyo Institute of Technology, Research Laboratory for Nuclear Reactors, Japan
2. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan
3. Tokyo Institute of Technology, Laboratory for Advanced Nuclear Energy, Japan

Plasma resistant materials are strongly required for the semiconductor manufacturing industries. One of conventional plasma resistant materials is yttria. However, it was reported that yttria reacts with fluorine, and yttria become yttrium-based fluoride under fluorine plasma condition. Particle contamination is generated from the fluoride layer. Yttrium oxyfluoride have received attention for new resistant materials because the yttrium oxyfluoride are more stable than conventional resilient materials. In this study, dense yttrium oxyfluoride ceramics were fabricated, and their plasma corrosion behavior was evaluated. Yttrium oxyfluoride powder was supplied from Nippon Yttrium Co, Ltd. The yttrium oxyfluoride ceramics were fabricated by hot-pressing. The ceramics were exposed to fluorine plasma for 60 minutes with ICP-RIE. ICP and RIE power was 1500 W and 750 W, respectively. Then, the etching rate was measured with a profilometer. Finally, the cross-section of the ceramics after plasma exposure was observed by TEM. Yttrium oxyfluoride showed similar etching rate to a conventional plasma resistant material, yttria. Fluorine was detected at the surface of the yttria after fluorine plasma exposure. On the other hand, compositions of yttrium oxyfluoride after plasma exposure were not changed. It is summarized that the yttrium oxyfluoride ceramics were excellent plasma resistant materials.

(ICACC-GYIF-P002-2019) Unmanned Aircraft Systems Far-Field Laser Power Transfer

P. Carr[1]; P. R. Dougherty*[1]; N. Kaabouch[1]; S. Gupta[2]

1. University of North Dakota, EE, USA
2. University of North Dakota, ME, USA

This project aims to investigate laser power transfer systems to enable extended unmanned aircraft flight endurance and unmanned aircraft swarming formations. For this study several laser types and photoconductor configurations will be tested to determine the optimal system for energy transfer at altitudes up to the lower stratosphere. The desire to reduce visual signatures while avoiding atmospheric absorption requires operation in the near-ultraviolet or infrared spectrums with near-ultraviolet providing the greatest energy density. Current solar cell technology can effectively collect and convert infrared radiation to DC power. However, the near-ultraviolet spectrum is not currently exploited and changes to photoconductor cells will be necessary to effectively utilize the near-ultraviolet spectrum.

(ICACC-GYIF-P003-2019) Cyclic Voltammetry - A tool for selecting electrodeposition parameters

M. K. King*[1]; M. Mahapatra[1]

1. University of Alabama at Birmingham, Materials Science and Engineering, USA

Electrochemical deposition is a simple and cost effective coating technique, which finds various applications. Cyclic voltammetry plays a vital role to determine the optimal voltage or current density, one of the key parameters, for electrochemical deposition. The advantages and limitations of cyclic voltammetry to optimize the electrodeposition parameters will be discussed for selected materials as example.

(ICACC-GYIF-P004-2019) Dynamic response of ice-templated ceramics with directional porosity

D. A. Terrones*[1]; A. Grabowski[1]; S. Akurati[1]; M. Banda[1]; D. Ghosh[1]

1. Old Dominion University, Mechanical & Aerospace Engrg, USA

Highly porous ice-templated sintered ceramics behave akin to cellular ceramics under compression. As the total solids loading in the ceramic suspension increases, the total porosity decreases and the pore architecture can transition from lamellar to dendritic nature which can offer more resistance to lateral bending of lamella walls. The decrease in porosity can influence not only the peak strength, but also the post-fracture inelastic response of the porous materials, i. e. the characteristic of compressive response can change from graceful progressive failure to brittle-like failure. Also the compressive response of porous materials probably be influenced by the rate of loading due to the transition in the failure mechanisms from quasistatic to dynamic loading regime. In spite of growing research on structure-property correlation of ice-templated materials, there is a very limited knowledge on the post-fracture inelastic response and dynamic behavior. In this study, our goal is to evaluate the microstructure-mechanical response of ice-templated porous alumina ceramics in both quasistatic and high-strain rate regimes of loading. Our present work can be useful in design and development of lightweight materials for impact protection and energy absorption applications.

(ICACC-GYIF-P005-2019) REU Project: Design of Novel Sustainable Materials for Multifuntional Applications

M. Ahmann*[1]; A. Miles[1]; M. Abdulrahman[1]; A. Minhas[1]; M. Alshaya[1]; S. Gupta[1]

1. University of North Dakota, USA

In this poster, we will present some of the recent progress in our lab on the design of sustainable materials as a part of Undergraduate Research. The team will focus on fabricating novel materials by innovative manufacturing techniques like casting, 3D printing etc. Therafter, the correlation between microstructure and mechanics will be presented in detail. It is expected that these novel materials can be used for mutititude of commercial applications.

(ICACC-FS2-P006-2019) 3D Intermittent observation of coarse pore evolution during sintering in alumina ceramics prepared from spray-dried granules

S. Tanaka*[1]

1. Nagaoka University of Technology, Materials Science and Technology, Japan

Non-destructive examination techniques such as microtomography (μ-CT) has been developed recently, and the internal structure image with high resolution of ceramics could be obtained easily. We had demonstrated pore distribution in porous ceramics and the fractal analysis using images. Furthermore, the coarse pore evolution with sintering was also evaluated using μ-CT. The coarse pores were important for a reliability of engineering ceramics, because those govern the mechanical properties. The objectives of this study was to clarify the occurrence of coarse defects in alumina ceramic at the initial–middle stages of sintering. The ceramic made from die-pressing of granules was sintered with various time at a constant temperature. Their internal structures at the same position was observed with μ-CT intermittently. In practice, after heat-treatment of samples at 1200 °C with some duration time, it was quenched once. After μ-CT observation, the samples was heated in the furnace again. In the results, coarse pores which was derived from burnout of binder became large between the granules. Furthermore, the coarse pores developed by sintering at high temperature. Some of them at interface of granules were joined each other, and become to the largest pore with several tens μm.

(ICACC-FS3-P007-2019) Microstructures of silver molybdates for enhanced photochemical degradation under visible light irradiation

S. Adhikari[1]; D. Kim*[1]

1. Chonnam National University, School of Chemical Engineering, Republic of Korea

Since the past decades, research has been focused on the development of novel and unique self-assembled structures exhibiting semiconducting properties to be applicable massively in opto-electronic and biological sectors. In recent years, the ternary and quaternary oxides have grabbed lots of attention among researchers due to their significant structural conformation. Particularly, molybdates of silver have exhibited its potentiality in energy storage devices, antibacterial properties, photocatalytic activity, gas sensors and others due to its intrinsic electrical and photoluminescence properties. The present work designs different microstructures of silver molybdates by permutation and combination of the reaction parameters via a simple, one-step, and facile hydrothermal processing. The different morphologies and crystal structures of the as-synthesized silver molybdates were analyzed using analytical tools. Photochemical degradation of organic dyes was carried out to understand the effect of microstructures on the degradation efficiencies. A detailed study of the parameters like pH, amount of catalyst, dye concentration variation, oxidizer effect was performed for optimization of the catalytic process. Furthermore, trapping of the oxidative species was also experimented for apprehending the mechanism of the photochemical reaction.

(ICACC-FS3-P008-2019) NIR-Emitting Quantum Dots – Ideal Candidates for Bio-Imaging

M. Adlung*[1]; K. Schneider[1]; C. Wickleder[1]

1. Universität, Inorganic Chemistry, Germany

Quantum Dots (QDs) emitting visible radiation are very well investigated since many years and are already used for several applications. They are, however, not suitable for the demands in Bio-sensing because they are in general based on Cd-containing semiconductors, this element is known for its carcinogenic impact. Another problematic point is that their excitation and emission energies are located in the visible because of the extremely low penetration depth of tissue in this range. Much more suitable materials for these applications are QDs emitting radiation in the NIR range and are composed on non-hazard-free elements, e.g. Ag_2S and Ag_2Se. Especially the latter is a very promising candidate due to their emission in the "second biological window" between 1000 and 1700 nm depending on their particle size. Unfortunately, their synthesis is mainly performed in organic solvents leading to hydrophobic QDs which cannot be used for Bio-imaging. Here we present an improved synthetic route for Ag_2Se QDs of different sizes emitting in the NIR range. This improvement was achieved by the usage of different stabilisers and ammonia as a starting material, which is demonstrated by XRD, TEM, DLS and luminescence measurements.

(ICACC-FS3-P009-2019) High Temperature Pyrolysis of Polymer Precursor Hydridopolycarbosilane/Polymethylhydrosiloxane: A Reactive Dynamics Simulation Study

H. Gao*[1]; H. Wang[1]; X. Fan[1]; L. Su[1]

1. Xi'an Jiaotong University, China

SiC nanowires (SiCNWs) have attracted increasing attention for their excellence properties and wide potential applications in hash environments, including high temperature, high frequency, and high power operations. Chemical vapor deposition (CVD) as one of the most effective method for preparation of SiCNWs offers gas phases at high temperature, making the nanowires feature controllable compositions as well as high crystal integrity and clean faceted structures. However, preparation of SiCNWs from high temperature pyrolysis of polymer precursors involves a complicated process of chemical reactions that can be hardly tracked through experimental characterizations. Therefore, reactive molecular dynamics simulations with ReaxFF potential was utilized to study the pyrolysis behaviors of Hydridopolycarbosilane (HPCS)/Polymethylhydrosiloxane (PMHS) mixed polymer precursor at 3000, 3500, and 4000 K. From analyses of the time evolution of bonds and products during decomposition of the mixed polymer, CH_4 and H_2 were generated in the first pyrolysis stage; then C_2 hydrocarbons (e.g. C_2H_4) and CO were formed due to CH_4 decomposition; SiH_4 was also generated during the high temperature pyrolysis. The CO and SiH_4 can be regarded as C and Si sources for preparation of SiCNWs and their yields at 4000 K is higher than those at 3000 and 3500 K.

(ICACC-FS3-P010-2019) Femtosecond Laser Structuring of Metal Oxide Thin Films for Enhanced Optical Properties

D. Bialuschewski*[1]; J. Hoppius[2]; E. L. Gurevich[2]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic and Material Chemistry, Germany
2. Ruhr-University Bochum, Chair of Applied Laser Technology, Germany

Disordered Materials, which can either be chemical or physical, often result in new and unique properties. This is also true regarding light interaction and interference of ordered and disordered structures. In this work, ultra short femtosecond laser pulses are used to tailor specific properties in different metal and metal oxide materials. By optimizing parameters such as laser fluence, pulse duration or repetition rate, we modify substrates on a physical or/and chemical level. Additionally, we show that by inducing structural disorder

in metals, for example by creating laser induced periodic surface structures (LIPSS), light harvesting properties like absorption, photoconversion and overall photoelectrochemical water splitting performance can be increased compared to untreated samples. This influence was investigated with and without additional top coating, regarding their spectroscopic (UV-VIS), microscopic (SEM), crystallographic (XRD and EBSD) and compositional (XPS) properties. Enhanced properties of periodic patterning was attributed to the increased specific surface area and light trapping compared to flat surfaces. Ultra fast laser pulses were also used to induce crystallization in amorphous films, which were prepared by plasma-enhanced chemical vapor deposition (PE-CVD).

(ICACC-FS3-P011-2019) Design and Software Integration of a miniaturized CVD-reactor

M. Grosch*[1]; T. Fischer[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Sensors are becoming increasingly important in many devices used on a daily basis, like mobile phones (11 sensors; Samsung), cars (60-100 sensors) and even shoes (Adidas). The first step towards new sensing materials starts in a lab, where many sensor are already in use. A method that can benefit from additional sensors and more precise sensing is the chemical vapour deposition (CVD), where they already help to achieve processes with high reproducibility. These sensors allow monitoring several parameters, like Pressure, Temperature, gas flow). By incorporating an intelligent sensor network around a customized CVD reactor with an automated self-learning software, a highly automated system can be achieved. The gathered data will be evaluated by an analytic algorithm and presented in a compact overview for the user. This will bring a better overview on parameter influence, which in turn allows precise parameter adjustment and optimization for different depositions. We would like to present the performance of the current sensor network and how material synthesis benefits from it.

(ICACC-FS3-P012-2019) Phase and Morphology Engineering of Plasma CVD Grown Hexagonal Boron Nitride (h-BN)

A. Sutorius*[1]; D. Stadler[1]; R. Frohnhoven[1]; Y. Gönüllü[1]; Y. K. Mishra[2]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany
2. Kiel University, Germany

Two dimensional materials, namely graphene, MoS2 and hexagonal boron nitride (h-BN) went into focus of scientist all over the world during the last years, due to their interesting intrinsic properties (e. g. non-symmetric conductivity,) and the possibility of large scale processability. However, the preparation of these materials often requires metal templates, such as Cu, Pt, Ir and Pd. In case of h-BN, a variety of processing techniques is reported in literature, mostly through the gas phase. While borazine is already established as precursor molecule for the phase selective h-BN formation, formation of h-BN using commercially available starting molecules like dimethyl amino borane (CH3)2NBH2 are rather limited. Even though some reports exist on the transformation of this precursor into BN films using plasma enhanced CVD, most of the research is focused on the formation of cubic boron nitride. Furthermore, a film formation beyond the epitaxial growth still is a challenge. In this approach, we demonstrate the thin film formation of h-BN on a variety of temperatures and substrates, ranging from planar surfaces to three dimensional superstructures. Results from atomic force microscopy, Infrared and X-ray photoelectron spectroscopy, as well as transmission electron microscopy will be presented to demonstrate the feasibility of the presented approach.

(ICACC-S2-P013-2019) Oxidation behavior of MCrAlY bond coat in thermal barrier coating system

J. Tang*[1]; Y. Bai[2]

1. Xi'an Aeronautical University, China
2. Xi'an Jiaotong University, China

The purpose of the present study is to improve the oxidation resistance and thermal cycling life of thermal barrier coating system (TBCs). The microstructure of plasma-sprayed CoNiCrAlY or NiCrAlY coatings was optimized by a high-temperature oxidation test. A comparative study between SAPS-coating (high efficiency supersonic atmospheric plasma spraying, SAPS) and HVOF-coating (high velocity oxygen fuel spraying, HVOF) was conducted in order to analyze the microstructure-property differences between them. The results showed that an appropriate proportion of the internal oxides, especially those formed at the splat boundaries can act as the diffusion barrier layer that could reduce the thermally grown oxides (TGOs) growth rate to some extent. The unmelted particles increased the surface roughness of bond coat and subsequently were oxidized to be some oxide mixtures at high temperature, which gave rise to the localized stress concentration and the formation of catastrophic cracks. For the same chemical composition of bond coat, the thermal cycling lives of SAPS-coatings were two times as much as those of HVOF-coatings, however, the average growth rates of TGOs were reduced by more than 21 %.

(ICACC-S2-P014-2019) Characterisation of electrosprayed nanohydroxyapatite coatings on Si_3N_4 and CNT/Si_3N_4 ceramic composite

K. Balazsi*[1]; T. Zagyva[1]; C. Balazsi[1]

1. Centre for Energy Research HAS, Thin Film Physics, Hungary

Synthesized nanohydroxyapatite (nHA) has high bioactivity and biocompatibility. Using a bioactive and highly biocompatible coating on the implant's surface could help avoid the rejection from the body in the early few days, after the operation. The aim of this study was to produce thin nHA layer on silicon nitride (Si_3N_4) implant material with a cost-efficient electrospray deposition method. During the first experiments, continuous nHA layer could not form due to the high electrical resistance of the Si_3N_4 substrate. Therefore, the electrical conductivity of the Si_3N_4 substrate has been increased by the help of carbon nanotube (CNT) addition. As a result ~5 μm thick continuous and smooth nHA coating on the CNT/Si_3N_4 composite could have been realized.

(ICACC-S2-P015-2019) Synthesis and Thermal Properties of Multicomponent Rare Earth Monosilicates

M. J. Ridley*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA

Environmental Barrier Coatings (EBCs) for SiC-based Ceramic Matrix Composites (CMCs) are currently made of multi-layer coating systems including rare earth silicates to limit water vapor and CMAS corrosion of turbine parts at high operating temperatures. Rare Earth (RE) disilicates ($RE_2Si_2O_7$) are often materials of choice for EBCs due to their excellent thermal expansion match with SiC compared to rare earth monosilicates (RE_2SiO_5). Still, the monosilicates can show better chemical stability in combustion environments. This research investigated the mixing of rare earth cations to determine the impact on thermal properties. Study of individual and combinations of rare earth monosilicates has been conducted with high purity monosilicate powders densified via Spark Plasma Sintering. Thermal expansion, phase stabilization, and thermal conductivity were analyzed over a range of temperatures to determine how mixing of rare earth monosilicates could impact EBC performance.

(ICACC-S2-P016-2019) Study of Multiferroic Properties and Enhanced Magnetoelectric Coupling in (BFCO-PZT) Composites

A. Marzouki*[1]

1. Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupélec, CNRS-UMR8580, Université Paris-Saclay, France

Multiferroic materials that simultaneously exhibit both polar and magnetic orders have attracted an ever-increasing interest driven by the ability to couple magnetic and electric properties which allow for instance tuning the magnetization using an external electric field instead of a magnetic one. $BiFeO_3$ (BFO) exhibits simultaneously both ferroelectricity (Tc~1103 K) and anti-ferromagnetism (T_N~643 K) at room temperature which makes it a potential candidate in the field of information technology and optoelectronic devices. Solid solutions such as $BiFeO_3$-ABO_3 perovskite-based materials have been investigated to minimize the high electric leakage of BFO keeping strong polarization and enhance the magnetization value in order to achieve stronger ME response. Here, to achieve improvement of the ME response, a composite using perovskite 1-perovskite 2 like system made of 50% of Co-doped BFO we optimized for its ME properties, and 50% of the well-known ferroelectric-piezoelectric (PZT) was realized and studied in details. Magnetoelectric and magnetic measurements were performed and associated to structural characterizations using X-ray diffraction, Raman spectroscopy and scanning electron microscopy depending on the sintering temperature. A large improvement of the magnetoelectric coupling is observed in composite-like samples compared to that of BFCO alone.

(ICACC-S3-P017-2019) Modeling degradation due to chromium poisoning in solid oxide fuel cell cathodes

J. H. Mason*[1]; I. B. Celik[1]; H. Abernathy[1]; G. Hackett[1]

1. National Energy Technology Labratory, USA

Chromium poisoning is a primary cause of degradation in solid oxide fuel cells (SOFCs) when chromium-containing interconnects and balance of plant components are used. Deposition of chromium in the cathode leads to degradation by (i) reducing the effective triple phase boundary density, (ii) restricting gas-transport through pore phase, and (iii) modulating material properties (e.g., electronic/ionic conductivities, microstructure, etc.). A model for predicting degradation due to chromium poisoning in SOFC cathodes is developed and implemented into an existing multi-dimensional, multi-scale computer code. The effects that steam and oxygen concentrations, temperature, overpotential distribution and chromium source material have on the vaporization and deposition of chromium species are considered. Data from literature, including both thermodynamic calculations and experiments, are used to estimate/calibrate model parameters. Cell degradation induced by chromium deposition in the cathode is calculated as a function of time for various operating conditions and different interconnect materials. Preliminary results from present model-predictions are presented and discussed. Recommendations are made with regards to validation experiments and further improvements of the model.

(ICACC-S3-P018-2019) LSM/YSZ & LSCF Button Cell Tests in Cathode Air with Measured Cr Concentrations

J. S. Hardy*[1]; C. A. Coyle[1]; J. Neeway[1]; D. J. Edwards[1]; A. Devaraj[1]; N. L. Canfield[1]; J. W. Stevenson[1]

1. Pacific Northwest National Laboratory, Materials Science, USA

Electrochemical tests of cells with LSM/YSZ cathodes were performed in a fixture developed for testing anode-supported SOFC button cells downstream from a chromia pellet placed in the cathode air stream at a prescribed temperature to control volatilization of Cr vapor species. A porous alumina foam coated with Cr gettering Na_2CO_3 was placed downstream from the cell to capture Cr from the cathode air stream by reacting with Cr vapor species to form Na_2CrO_4. The mass of Cr collected by the coating was used to calculate the average concentration in the known volume of air that flowed past the cathode over the duration of the test. Multiple tests were performed with the chromia pellet at varying conditions of temperature and humidity to elicit various levels of Cr volatility. In LSM/YSZ cells, molar concentrations of Cr species in the cathode air of less than 165 ppt were found to cause ~4-5%/kh degradation in performance, while less than 45 ppt Cr was found to cause no significant degradation. These results will be compared to those of more recent LSCF cell tests. Post-test TEM, STXM, Microprobe, and APT results will be presented.

(ICACC-S3-P019-2019) Performance evaluation for solid oxide fuel cell by addition of tetragonal zirconia polycrystal in anode substrate

H. Kuo*[1]; T. Lin[1]; C. Yeh[1]; W. Kao[1]; Y. Cho[1]; C. Liu[1]; Y. Cheng[1]; R. Lee[1]

1. Institute of Nuclear Energy Research, Nuclear Fuels and Materials Division, Taiwan

In considering the requirements of the SOFC anode porosity in order to facilitate gas-solid reaction mechanism, it is unavoidable to sacrifice mechanical strength, resulting in the subsequent cell stack packaging prone to failure situations. With tetragonal zirconia polycrystal in anode cermet, the substrate toughness and mechanical strength enhance, thereby the anode porosity can substantially increase, eliminating the possible cracking upon packaging and testing, hence providing a stable operation in long-term test. The materials being used in cermet include NiO, 8YSZ and 3YSZ that mixed into slurry, formed into anodes by tape casting, sintered to form an anode substrate, and followed by thin electrolyte formation. The cathode is then formed on electrolyte. With 3YSZ in anode, the mechanical strength increases above 200 MPa, which is about 3 times higher than traditional anode substrate. The enhanced strength also effectively results in cell thickness reduction, providing short path for the fuel gas to penetrate into interfaces for reactions. The cell performance results show that the electricity generation efficiency may raise a percentage of 20 % and the maximum cell output power reaches 32 W at operation potential 0.8 V. Further performance evaluation in the short stack operation will be executed for commercial application demonstration.

(ICACC-S3-P020-2019) Influence of Calcium and Dysprosium co-doping on Enhancement of Electrical Conductivity of Samarium Doped Ceria Electrolyte

S. L. Reis[1]; E. N. Muccillo*[1]

1. Institute of Nuclear Energy Research, Brazil

Ceria-based solid solutions have been considered as promising electrolytes for intermediate temperature (600–800°C) solid oxide fuel cells (IT-SOFCs) due to their excellent oxygen-ion conductivity compared to yttria stabilized zirconia (YSZ). It is well-known that enhanced ionic conductivity and other properties may be accomplished by introducing a second dopant. In this work calcium and dysprosium ions were chosen as the second additive. $Ce_{0.8}Sm_{0.2-x}M_xO_{1.9-x/2}$ compounds, with M = Ca, Dy and x = 0, 0.025, 0.05, 0.1, 0.15 and 0.2, were prepared by solid-state reaction, and the influence of the co-dopant content on densification and ionic conductivity was investigated. All compounds were found to possess cubic fluorite-type structure. The sintered solid electrolytes achieved densities higher than 92% of the theoretical value after sintering at 1500°C/3 h. The highest ionic conductivity was found for $Ce_{0.8}Sm_{0.175}Ca_{0.025}O_{1.888}$ with relative density of 97%.

(ICACC-S3-P021-2019) Analysis of Infiltration on Performance Enhancement via Multi-step Oxygen Reduction Reaction Mechanism

T. Yang*[1]; S. Lee[2]; J. Liu[2]; W. Li[3]; X. Liu[3]; H. Abernathy[2]; G. Hackett[1]

1. U.S. DOE, National Energy Technology Laboratory, USA
2. AECOM, NETL, USA
3. West Virginia University, Mechanical and Aerospace Engineering, USA

Infiltration can enhance the performance and stability of solid oxide fuel cells by modifying the morphology and accelerating the reactions in electrodes. The present study focuses on the effects of infiltration on the performance enhancement via thorough analysis of oxygen reduction reaction (ORR) processes in cathodes with multi-step ORR mechanism. First, a comprehensive multi-physics numerical model, including charge conservation, species transportation, and a multi-step ORR mechanism with parallel pathways, is calibrated with experimental data of a baseline cell with LSM/YSZ composite cathode. The model is then extended to simulate the performance of cells with cathodes infiltrated with various materials, which is also verified with experimental data. The structural property changes due to the infiltrated nanoparticles are estimated with a geometrical model, and possible changes in the detailed reaction mechanism are proposed (e.g., inter-diffusion and/or the creation of new interfaces between backbone and infiltrated phases). By analyzing the effects of various materials, this study separates and quantifies the effects of morphological changes and reaction mechanism modifications resulting from the surface modification. Furthermore, thorough analysis of rate-limiting steps, reaction order, and resistance components of each step provides more insights of ORR processes.

(ICACC-S3-P022-2019) Electrical Power Generation Characteristics of SOFC Stack System with Nitrogen Compounds as Fuel

R. Morikawa*[1]

1. KRI, Inc., New Energy Device R&D Laboratory, Japan

As a new hydrogen energy carrier, a nitrogen compound such as carbon-free NH_3 is receiving increased attention. NH_3 has high hydrogen density, can be liquefied at normal temperature with low pressure, and transported and stored easily. However, NH_3 is toxic and concerned about safety in operation. Therefore, we focus on urea as an energy carrier that contains NH_3 molecules with safe operation. Urea is hydrolyzed to NH_3 and CO_2 by exhaust heat from diesel engine. NH_3 thermally decomposes to $H_2 + N_2$ on the SOFC electrode and uses it as fuel for SOFC. Also, off-gas from SOFC system can be reused as SCR. In this paper, the power generation and exhaust gas characteristics of SOFC with direct fuel supply were evaluated assuming NH_3 mainly generated after urea decomposition with automotive SOFC APU system using urea as fuel. As for the power generation of the SOFC with direct NH_3 supply, it was confirmed that equivalent output as H_2 power generation under Uf 70% to 75%. In characteristics of exhaust gas, NH_3 in off-gas is thermally decomposed almost the theoretical equilibrium level, and SCR of the system cannot be operated only by fuel cell off gas, so urea is distributed to SOFC and SCR, simultaneously. We will discuss the results of long-term operation test of NH_3 power generation, demonstration of power generation using actual hydrolyzed gas, and feasibility of the system.

(ICACC-S3-P023-2019) Performance and Thermal Properties of Ni/Mo Alloy-Supported Solid Oxide Fuel Cell

S. Yang*[1]; C. Tsai[1]; C. Chang[1]; C. Fu[1]; C. Yang[1]; R. Lee[1]

1. Institute of Nuclear Energy Research Atomic Energy Council, Physics Divison, Taiwan

In this study, both long term durability and thermal properties (e.g., Thermal conductivity and diffusivity) test are executed on a large area of 10×10×1.2 cm molybdenum (Mo)-containing nickel (Ni)-based alloy-supported solid oxide fuel cell (SOFC). The Ni/Mo porous alloy is produced by a series of fabricating process including spray drying, compression molding and sintering steps as a supporting component for metal-supported SOFC. The porous interconnected networks of Ni-Mo alloy are made of introducing pyrolyzable filler during fabrication processes. The functional layers of cell that consists of an $La_{0.75}Sr_{0.25}Cr_{0.5}$- $Mn_{0.5}O_{3-d}$ (LSCM) interlayer, a nano-structured $Ce_{0.55}La_{0.45}O_{2-d}$ (LDC) -Ni anode, an LDC isolation layer, an $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-d}$ (LSGM) electrolyte, a $Sm_{0.15}Ce_{0.85}O_{3-d}$ (SDC) barrier layer and a SDC-$Sm_{0.5}Sr_{0.5}CoO_{3-d}$ (SSC) cathode is prepared by using an atmospheric plasma spraying technology. The 10×10 cm^2 MS-SOFC with effective electrode area of 81 cm^2 shows the open circuit voltages is 1.09 V at 700°C. The measured maximum output powers (@0.8V) of this cell is 44.6 W at 700 °C respectively. In the long term durability test, the cell voltages are measured in a constant current mode (400 mA/cm^2) for ~2600 h at 700 °C. The thermal conductivity (@25–300°C) of porous alloy substrate (7.5% pyrolyzable filler) sintered at 1250°C is in the range of 9.8–12 W/m.K.

(ICACC-S3-P024-2019) Improvement of LSM/CeO_2 nano-composite cathode properties by optimizing interdiffusion between LSM and CeO_2

H. Sakuma*[1]; S. Suda[1]; M. Hase[3]; J. P. Wiff[2]

1. Shizuoka University, Japan
2. Nagaoka University of Technology, Japan
3. National Institute for Materials Science (NIMS), Japan

Co-sintering of SOFC cells or stacks is indispensable for fabricating high-efficient compact SOFC stacks. La1-xSrxMnO3 (LSM) shows preferable low-reactivity with fluorite electrolytes during sintering at high temperatures, but lower cathode properties than LSC or LCSF because of poor oxygen ionic conductivity. We then prepared nano-composite of a-site deficient LSM and CeO_2 to improve oxygen diffusion of LSM. Oxygen diffusion coefficient and surface reaction constant were estimated by electrical conductivity relaxation (ECR) method as well as cathodic polarization. Adequate glycine processes made nano-scale LSM/CeO_2 composites that have dense enough to estimate by ECR. Nano-dispersion of 10 mol% CeO2 in LSM improved oxygen diffusion, but easy La diffusion from LSM to CeO_2 altered LSM composition of the nanocomposite. We thus analyzed the detailed structure and compositions in the nanocomposite by both magnetic properties of LSM and lattice constant of CeO2. Preparation processes changed the interdiffusion between LSM and CeO2. The interdiffusion, as well as the oxygen diffusion, was controlled by optimization of preparation processes. The control of interdiffusion would improve cathodic properties of the nanocomposite and lead advanced SOFC performance regarding high-efficient small SOFC cells or stacks.

(ICACC-S3-P025-2019) Optimization of self-expansion vermiculite/talc composite seals for gas-tight sealing on rough substrate at high temperatures

J. Xu*[1]; S. Suda[1]

1. Shizuoka University, Electronics and Materials Science, Japan

Glass-free gas-tight compression seal is an essential and promising component for quick set-up and thermal-cycle durable SOFC system. Generally, mica is a candidate for SOFC compression seals. However, it requires large compression loads, and it would easily bring about gas leakage through the interface between swelled or rough substrate and the seals. We thus investigate novel vermiculite/talc composite seals that would expand themselves during heating at SOFC working temperatures and absorb the roughness of the substrate. Adequate calcined vermiculite would expand during heating irreversibly, and talc would enhance plastic properties to avoid large crack formation. Crack-free vermiculite/talc composites after sintering at 800°C were obtained by investigating the effects of calcining temperatures and vermiculite/talc mass ratios. The vertical

expansion rate of the composite seals was controlled in the range of 0.4% to 30.3 %. Gas leakage of the seal was generally increased with increasing roughness of the substrate, but the seal optimized by the particle size of vermiculite and expansion rate of the composite showed low gas leakage regardless of surface roughness of the substrate.

(ICACC-S3-P026-2019) Conductivity and Activation Energy of Polycrystalline Lanthanum Silicate in Intermediate-Temperature Range

S. Yagi*[1]; A. Mineshige[1]; M. Momai[1]; H. Hayakawa[1]

1. University of Hyogo, Japan

SOFC is a high efficiency energy conversion device to generate electricity. However, it is required to reduce the operating temperature into the intermediate-temperature range below 873 K to improve durability of the cell. Lanthanum silicate (LSO) shows higher ionic conductivity than YSZ in this temperature range. The aim of this study is to get a guideline for designing ionic conductor with low activation energy by elucidating the factors that determine ion conducting properties of LSO. $La_{10}(Si_{5.5}Fe_{0.5})O_{26.75}$ was prepared by a conventional solid state reaction method. Pelletized powder was sintered at 1873 K or 1973 K. Ionic conductivity was evaluated with DC and AC 4-probe method. To obtain grain boundary and bulk resistivities, the Nyquist impedance plots were fitted using an equivalent circuit model. It was found that activation energy of grain boundary resistance of the 1873 K-fired sample (1.21 eV) was higher than that of the 1973 K-fired sample (1.01 eV). According to the XRD results, the 1873 K-fired sample contained a small amount of La_2SiO_5 phase in addition to the main LSO phase. This shows that co-existing phase determines temperature dependency of ionic conductivity of LSO. From the above, it was concluded that to design secondary phase by controlling firing temperature is important for improvement in conductivity of LSO at the intermediate-temperature range.

(ICACC-S4-P027-2019) Unravelling the mystery of new Raman spectral features of amorphized boron carbide: An atomistic study

A. Awasthi*[1]; G. Subhash[1]

1. University of Florida, Mechanical and Aerospace Engineering, USA

For several years, the Raman spectral behavior of boron carbide, a highly investigated icosahedral ceramic, has been shrouded in mystery. When subjected to high pressures, e.g. shock and indentation etc., boron carbide undergoes a deleterious effect commonly called 'amorphization'. Amorphized boron carbide exhibits an interesting Raman spectrum, wherein new spectral bands appear in addition to crystalline peaks. Up to now, origin of these new spectral bands has been speculative, hypothesized as graphite and carbon particles. In all existing theories on amorphization, connections between underlying atomic structure and the resulting Raman spectra have not been made. The present work establishes a new rationale for deciphering the amorphization phenomenon in boron carbide and focuses on explaining atomic interactions in amorphous islands. DFT simulations evaluate impact of compressive pressure on Raman spectra, and molecular dynamics (MD) simulations of volumetric compression provide insight into thermodynamics of the amorphization phenomenon. We examine the role of non-bonded van der Waals forces in amorphized zones, demonstrating origins of residual pressure in surrounding crystalline matrix. Using these atomistic findings, a new theory of Raman spectrum of amorphized boron carbide is developed, postulating to comprise of spectra from compressed crystalline material.

(ICACC-S4-P028-2019) Elucidating Structure-Property Relations in Compositionally Varied B4C-SiC Composites Via Automated Quantitative Stereology

A. A. DiGiovanni*[1]; T. Shoulders[1]; L. Vargas[1]

1. US Army Research Laboratory, Ceramic and Transparent Materials, USA

Ballistic threats are ever advancing and to keep pace, body armor research has evolved engineered structures at length scales spanning the atomic to the macro-scale. Recent commercially produced armor blends of B4C and SiC at the micro-scale have demonstrated improvement over their traditionally monolithic counterparts. To augment the on-going development of these armor materials, a systematic and quantitative understanding of the physics and mechanics of ballistic failure at a microstructural level is required. This investigation seeks to enhance the understanding of these diverse interactions by generating a statistically meaningful database of microstructural characteristics from traditional microscopy based on quantitative stereology. Physical or topological attributes of interest are phase content, grain size, shape, distribution, and mean-free-path to name just a few. The advent of digital imaging with the aid of automated scripting by programs such as Matlab and Image J, allows one to now generate statistically meaningful trends that may be associated with property and processing characteristics. This work will highlight the initial findings of such an approach using a series of hot-pressed B4C-SiC composites with compositional variation between the monolithic ceramics in increments of 10 wt%. Structural and chemical characterization was performed.

(ICACC-S4-P029-2019) Static and Dynamic Response of B_4C-B_6O Composite

K. Ghaffari*[1]; S. Bavdekar[2]; G. Subhash[2]

1. University of Florida, Material Science and Engineering, USA
2. University of Florida, Mechanical and Aerospace Engineering, USA

Boron suboxide (B_6O) and boron carbide (B_4C) ceramics are promising for armor applications due to low density, high strength, and high hardness. These materials have similar atomic structures, and both have previously been shown to undergo amorphization at high pressures. While extensive literature is available for B_4C, literature for B_6O is limited due to difficulty of powder manufacturing and producing dense specimens, as the process is not optimized. However, B_6O has already been shown to be comparable to B_4C, even in a non-optimized state. The present study investigates the mechanical and amorphization behavior of monolithic B_6O, as well as a composite of B_6O and B_4C (30 wt.% B_4C, 70 wt.% B_6O). Quasi-static and dynamic uniaxial compression and hardness testing are performed to investigate mechanical properties, and scanning electron microscopy is used to characterize microstructure and fracture modes. Finally, Raman spectroscopy is utilized to probe the materials for presence of amorphization, as well as to investigate the presence of thermally induced residual stresses.

(ICACC-S4-P030-2019) Uniaxial compressive response of ice-templated ceramics with directional porosity: Effects of porosity, morphology and strain rate

D. Ghosh*[1]; M. Banda[1]; J. E. John[1]; D. A. Terrones[1]; B. B. Laredo[1]

1. Old Dominion University, Mechanical & Aerospace Engrg, USA

Due to high specific strength and energy absorption capacity, ice-templated ceramics with directional porosity are promising materials for nuclear warheads, armor systems, anti-mining, and impact protection. In these applications, materials are often subjected to mechanical forces within loading durations of tens of microseconds. Therefore, mechanical response of ice-templated ceramics measured in quasistatic regime may not truly represent their dynamic (high-strain rate) mechanical behavior. In this presentation, we will discuss our work on understanding the uniaxial compressive response of ice-templated sintered ceramics both in the quasistatic and dynamic regimes of strain rates. We utilized

ice-templated alumina as a model system and employed a split-Hopkinson pressure bar (SHPB) to measure the uniaxial dynamic compressive response. In the processed ice-templated ceramics, porosity, lamellar bridge density, microstructural morphology and other length-scale features were modified through the systematic variations of the intrinsic (solids loading of suspension, particle size and morphology) and extrinsic (freezing front velocity) variables. This study will help to decipher the effects of porosity, pore morphology and length-scale features on the compressive mechanical response of ice-templated ceramics at two widely different strain rate regimes.

(ICACC-S4-P031-2019) Sintering and mechanical properties of Boron suboxide (B_6O)-Iron Boride (FeB) composites

A. U. Khan*[1]; V. Domnich[1]; R. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

Boron rich compounds are attractive materials for armor related applications. Boron suboxide (B_6O) is recently in focus, owing to its low density and high hardness. However, its sintering has been challenging over the years, due to the loss of oxygen at higher temperatures. We successfully sintered in-house synthesized B_6O-FeB composite, in spark plasma sintering (SPS), using a graphite die, with BN sprayed on all surfaces in contact with the sample. Sintered pellets were characterized by X-ray diffraction, scanning electron microscope, and Raman spectroscopy. Elastic constants were measured by employing the ultrasonic wave method. Vickers hardness was also measured.

(ICACC-S4-P032-2019) Laser Shock Processing of Ceramic Materials

F. Wang[1]; X. Yan[1]; C. Zhang[2]; L. Deng[2]; Y. Lu[2]; M. Nastasi[1]; B. Cui*[1]

1. University of Nebraska, Lincoln, Mechanical & Materials Engineering, USA
2. University of Nebraska–Lincoln, Department of Electrical Engineering, USA

Laser shock processing (LSP) is a novel surface engineering technique, in which a nanosecond-pulsed laser irradiates the ceramic surface to generate a plasma. The explosive expansion of the plasma generates shock waves that penetrate the bulk material to a depth of more than 1 mm from surface. Compared to metals, LSP has not been widely applied to ceramics, and the fundamental mechanisms of LSP on ceramics are less understood. LSP of α-Al_2O_3 and SiC ceramics can induce localized plasticity, with a high-density dislocations near the surface and grain boundaries, at room temperature. The localized plasticity is generated through the physical interaction of laser-driven shock waves with the local microstructures of ceramics. Significant compressive residual stress is generated in ceramics due to the localized plastic deformation. The LSP-induced localized plasticity can be used to improve the mechanical properties and performance of ceramics, such as the cracking resistance.

(ICACC-S4-P033-2019) Titanium Diboride Reinforced Si-doped Boron Carbide prepared using Reactive Hot Pressing

Q. Yang*[1]; A. M. Celik[1]; A. U. Khan[1]; C. Hwang[1]; V. Domnich[1]; R. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

Silicon doping has been proven to be an effective strategy to mitigate amorphization in boron carbide. Contrary to DFT simulations, the incorporation of silicon does not improve the toughness and ductility of the boron carbide. In addition, silicon doping promotes grain coarsening by forming liquid phase during sintering. Titanium diboride has combination of excellent strength, hardness, toughness and has been used as a sintering aid for boron carbide. Furthermore, titanium diboride co-sintered with boron carbide has shown to pin the grain development, making it an ideal candidate as a reinforcement phase. In this work, we reactive hot pressed Si-doped boron carbide with titanium diboride to form a composite. Hardness and toughness of this composite will be presented. Microstructural details was revealed using a scanning electron microscopy (SEM). Raman spectroscopy was be used to illustrate the suppression of amorphization due to silicon doping.

(ICACC-S4-P034-2019) Advancing mechanical properties of boron carbide by titanium diboride addition

A. M. Celik*[1]; C. Hwang[1]; V. Domnich[1]; A. U. Khan[1]; R. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

Boron carbide is a significant hard ceramic due to its high hardness, low theoretical density and high Young's modulus. Titanium diboride is another important hard ceramic and it exhibits ultra-high melting temperature, good chemical stability and high fracture toughness. To combine these properties, B_4C-TiB_2 composites could be produced. Precursors of B_4C and TiB_2 powders were prepared and then were sintered using different parameters under inert atmosphere via Spark Plasma Sintering (SPS) method. Chemical analysis, phase determination (XRD), microstructure investigation (SEM), and mechanical property measurements were performed to evaluate composite samples. BC-TiB_2 composites with advanced mechanical properties were fabricated and results will be presented.

(ICACC-S4-P035-2019) Effect of Silica and Rare Earth Silicate Additives on Densification, Microstructure and Hardness in Boron Suboxide

K. D. Behler*[1]; J. LaSalvia[2]; C. Marvel[3]; J. S. Dunn[2]; S. D. Walck[1]; T. Shoulders[4]; M. P. Harmer[3]

1. US Army Research Laboratory (SURVICE Engineering), Ceramics and Transparent Materials Branch, USA
2. US Army Research Laboratory, Ceramics and Transparent Materials Branch, USA
3. Lehigh University, Material Science Engineering, USA
4. US Army Research Laboratory (ORAU), Ceramics and Transparent Materials Branch, USA

Silica (SiO_2) has been shown to be an effective sintering aid for boron suboxide (B_6O) as evidenced by a reduction in hot-pressing of at least 100°C and in small amounts has shown to increase the 2 kg Knoop hardness by ~12%. The effects of additive chemistries and hot-pressing temperature on the densification and microstructure of B_6O are reported. B_6O powder mixtures containing either silica (1-5 vol% SiO_2) or silica/rare-earth oxide (Y-, Yb-, and La-REO) sintering additives, were hot-pressed between 1750°C-1850°C for up to 3 hrs and up to 54 MPa of applied load. Using a rapid heating rate of 50°C/min, SiO_2 was shown to be an effective densification aid. At 1750°C, densities increased with increasing SiO_2 content, reaching full density at 5 vol%. At 1850°C, B_6O was fully dense with as little as 1 vol.% SiO_2 additive. Grain sizes were typically observed to be submicron and monomodal, with the exception of B_6O hot-pressed using 5 vol.% SiO_2 at 1850°C, where abnormal grain growth (AGG) was observed. AGG was not observed using 5 vol.% SiO_2 and a hot-pressing temperature of 1750°C. The addition of SiO_2-REO sintering additives at 1850°C also resulted in full densification. While Y_2O_3 and La_2O_3 containing materials showed no grain growth, those containing Yb_2O_3 exhibited AGG. Experimental procedures and additional results will be presented.

(ICACC-S4-P037-2019) Eutectic Ceramic Composites as Promising Materials with Increased Impact Resistance

I. Kartuzov[1]; V. Kartuzov*[1]

1. IPMS NASU, Ukraine

Ceramic eutectic composites produced by the methods of directional crystallization are nowadays used for production of powders with a fibrous microstructure followed by their consolidation into macroscopically isotropic composites, which, at the same time, have an anisotropic grain microstructure and, when fractured during impact loading, can provide a high level of strain hardening of the solid phase in comminuted material, that brings, as it was previously showed by the authors, to a significant elevation of value R_t which

characterizes materials penetration resistance in the formalism of Alekseevsky-Tate. A continuum model to form ceramic bi-component eutectic composites in the process of directional crystallization in the form of modified one-dimensional Stefan problem, in which boundary condition on crystallization front account for, both usual latent heat of crystallization, energy contributions associated with the formation of composite microstructure, such as a surface energy of interfaces, is suggested. Parameters of composite structures determine a high level of mechanical properties of these materials, which can provide a significant level of strain hardening of fractured material under impact loading. The results of calculations of the parameters of projectile penetration into such materials and their comparison with typical armor materials are presented.

(ICACC-S4-P038-2019) Diamond-Ceramic Composites by Reactive Hot-Pressing

J. LaSalvia*[1]; K. D. Behler[1]; A. A. DiGiovanni[1]; T. Shoulders[1]; S. D. Walck[1]; L. Vargas[1]

1. Army Research Laboratory, USA

Diamond possesses an excellent combination of properties making it attractive for structural, wear, and thermal management applications. Synthetic diamond is commonly synthesized under high-pressure, high-temperature conditions (> 5 GPa, 1500ºC) or by chemical-vapor deposition. Limitations with both synthesis methods preclude their use for the manufacture of large, complex-shaped, and low-cost diamond components. Efforts to develop diamond-based composites materials through lower pressure/temperature methods such as pressureless-sintering and reaction bonding have been explored. Reaction bonding under conditions which minimize diamond graphitization has resulted in low-cost diamond-SiC-Si composites with excellent mechanical and thermal properties. As further exploration of alternative manufacturing methods, an initial study on reactive hot-pressing of diamond-SiB_6 powder mixtures is reported. Diamond and SiB_6 powders with mean particle sizes of 100 mm and 80 mm, respectively, in 50/50 vol% proportions, were acoustically wet-mixed. After drying, powders were loaded into a BN-lined graphite die and green pressed at 48 MPa. Hot-pressing was conducted at 1600ºC and 1700ºC for 2 hrs under an oxygen-gettered Ar atmosphere, 48 MPa load, and 50°C/min heating rate. Resulting specimens were characterized for density (Archimedes), phases (XRD), and microstructure (SEM and TEM). Experimental procedures and findings will be discussed.

(ICACC-S4-P040-2019) DFT Study of Silicon and Rare Earth Adsorption on Oxygen Terminated (101) Boron Suboxide Surface

J. S. Dunn*[1]; K. D. Behler[1]; J. LaSalvia[1]; C. Marvel[2]; M. P. Harmer[2]

1. U.S. Army Research Laboratory, USA
2. Lehigh University, Materials Science and Engineering, USA

In this paper, we develop a first principles Density Functional Theory (DFT) model of an oxygen terminated (101) boron suboxide (B_6O) surface and study the structural and electronic reconstructions that result from the adsorption of silicon, lutetium, lanthanum and yttrium. To determine the effect of these different surface reconstructions on the chemistry and bonding behavior at the surface, we perform a qualitative analysis of the electron localization function (ELF), electron density difference (EDD), band structure, and partial density of states (PDOS). Finally, to validate the model, we compare model predictions to aberration-corrected Scanning Transmission Electron Microscopy (AC-STEM) with High-Angle Annular Dark Field (STEM-HAADF) measurements of the atomic positions for the surface adsorbed silicon and rare earths along B_6O grain boundaries.

(ICACC-S4-P041-2019) A multi-mechanism-based constitutive model for the dynamic failure of boron carbide

Q. Zeng*[1]; A. Tonge[2]; K. Ramesh[1]

1. The Johns Hopkins University, Hopkins Extreme Materials Institute, USA
2. US Army Research Laboratory, USA

A multi-mechanism-based constitutive model is developed to describe the dynamic failure of boron carbide under high loading rates, which incorporates microcracking, amorphization and granular plasticity as the basic deformation mechanisms. Microcracking is described with a micromechanics-based damage model. A novel amorphization model is proposed to incorporate the effect of amorphization during the failure process, which considers the initiation and evolution of amorphization bands and its contribution to the accumulated damage. When the damage introduced by microcracking and amorphization reaches the threshold, granular plasticity is activated which incorporates dilatation to account for the introduction of porosity as fragments pass over each other, pressure dependence, and compaction of the porosity introduced through prior dilatation. With this integrative model, we investigate the dominate deformation mechanisms in plate impact experiments on boron carbide. The simulated particle velocity profiles in plate impact with different configurations and loading conditions agree well with experimental results. Finally, sphere-cylinder impact experiments are simulated to demonstrate the ability of the proposed model in capturing the competition of multiple mechanisms in complex stress states and large-scale simulations.

(ICACC-S11-P042-2019) The study on process variables of SiC Radiant Tube including in situ Joining

Y. Kim*[1]

1. Inocera inc., LAB., Republic of Korea

This study is designed to investigate effects of process variables of SiC radiant tube. As it has many merits like high thermal efficiency and low pollutant emission, RBSC radiant tube will be used gradually for heat treat applications. Joining is inevitable to use RBSC tube for Radiant applications. Starting materials are composed of batch of SiC powders and thermo-set polymers. These powders were mixed with thermo-set polymer in a chamber at low temperature. Pouring it into the casting mold, tube was formed by centrifugal force and heat aid. As the formed bodies were degreased, Joining paste were put on each face and pressed by 10MPa. Joining is done with molten Si infiltration at 1500C in vacuum at the same time. It was studied how process conditions such as casting variables, joining paste, joining method, heat treatment variables and Si infiltration variables affect on materials properties. The flexural strength, density and porosity were measured and microstructures were observed using Optical Microscope and SEM.

(ICACC-S11-P043-2019) Load and speed effects on constant-speed sliding behavior of a semi-carbonized Cu/phenolic-derived semi-metallic friction material

C. Ju*[1]; J. Chern Lin[1]; W. Chuang[1]; K. Lee[2]

1. National Cheng-Kung University, Materials Science and Engineering, Taiwan
2. I-Shou University, Materials Science and Engineering, Taiwan

Reported in this presentation are the effects of load and speed on the constant-speed tribological behavior of a semi-carbonized copper/phenolic resin-derived semi-metallic friction material sliding against 410 stainless steel. The material used for the study was prepared by dry-mixing appropriate amounts of phenolic resin powder, pure copper fiber, pure copper powder, along with additions of graphite and vermiculite powders, followed by hot-pressing, post-curing and semi-carbonization. The constant-speed tribological performance of the material was evaluated using a disk-on-disk sliding wear tester at ambient temperature. Experimental results showed that, no matter under the same load with different speeds or under the same speed with different loads, the present semi-carbonized sample coded

consistently demonstrated a higher friction coefficient, lower disc wear and comparable pad wear than its commercial high temperature-sintered metallic counterpart. One other primary advantage of the present pad material over the commercial metallic pad is its dramatically reduced noise level during testing. The research is supported by the Ministry of Science and Technology of Taiwan, ROC (MOST 106-2221-E-006-070).

(ICACC-S11-P044-2019) Recovery of Glass Panel and Valuable Metal from Waste LCD

H. Hong*[1]; M. Kim[1]

1. Sungshin Women's University, Republic of Korea

The recycling of LCD waste is currently carried only to plastics and some common metals, that is iron and aluminum, therefore, a comprehensive process of waste LCD products is needed. In the present study, valuable materials such as glass and rare metals recycling technology is proposed for commercially and environmentally beneficial recovery. The purpose of the present study is to demonstrate an economically and technically feasible recycling technology for LCD wastes. Three major steps include disassembly, separation of glass panel of LCD, and recovery of rare metal from ITO in glass panels. The mainly recycled components are metals, printed circuit boards, plastics and glass and thin film sheets. Especially, the recycling process of indium from the glass in waste LCDs was studied.

(ICACC-S14-P045-2019) Synthesis of nanocrystalline $Al_2W_3O_{12}$ and the impact of gallium on its thermal expansion

V. L. Blair*[1]; I. Muller Costa[2]; K. O. Rose[3]; B. Marinkovic[2]

1. US Army Research Laboratory, Weapons and Materials Research Directorate, USA
2. Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Engenharia Química e de materiais, Brazil
3. University of North Texas, USA

The development of ceramics with low thermal expansion properties can lead to the production of materials with a high thermal shock resistance that are ideal for infrared-transparent window applications. $Al_2W_3O_{12}$ has been previously examined as a low or negative thermal expansion ceramic. However, varying the aluminum content by replacing with gallium could potentially bring the coefficient of thermal expansion (CTE) of the material closer to zero. Due to the anisotropy of the material, the final grain size in the ceramic must be much smaller than the incident wavelength of light. Therefore, a reverse strike precipitation technique is required to produce nanosized powders. This research effort is focused on synthesizing stoichiometric powders with nanometric primary particles. The powders have been characterized by differential scanning calorimetry, powder and high temperature X-ray diffraction, X-ray fluorescence, and microscopy. The pH of the precipitation bath and starting precursor salts are critical to the overall stoichiometry of the final powder, which in turn impacts the thermal expansion behavior.

(ICACC-S14-P046-2019) Local coordination state of rare earth in eutectic scintillators for neutron detector applications

H. Masai*[1]; T. Yanagida[2]; T. Mizoguchi[3]; T. Ina[4]; T. Miyazaki[5]; N. Kawaguchi[2]; K. Fukuda[6]

1. National Institute of Advanced Industrial Science and Technology (AIST), Department of Materials and Chemistry, Japan
2. Nara Institute of Science and Technology, Japan
3. University of Tokyo, Japan
4. Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), Japan
5. Tohoku University, Japan
6. Tokuyama Corporation, Japan

Atomic distribution in phosphors for neutron detection has not been fully elucidated, although their ionization efficiency is strongly dependent on the state of the rare earth in the matrix. In this work, we examine optical properties of Eu-doped 80LiF-20CaF_2 eutectics for neutron detector applications based on the Eu distribution. At low concentrations, aggregation of Eu cations is observed, whereas homogeneous atomic dispersion in the CaF_2 layer, to substitute Ca^{2+} ions, is observed in the eutectics at high concentrations. Eu L_{III} edge X-ray absorption fine structure (XAFS) analysis suggests that neutron responses do not depend on the amount of Eu^{2+} ions. However, transparency, which depends on an ordered lamellar structure, is found to be important for a high light yield in neutron detection. The results confirm the effectiveness of the basic idea concerning the separation of radiation absorbers and activators in particle radiation scintillation and present potential for further improvement of novel bulk detectors.

(ICACC-S14-P047-2019) X-ray induced luminescence of oxide glass-ceramics

H. Masai*[1]; G. Okada[2]; N. Kawaguchi[2]; T. Yanagida[2]

1. National Institute of Advanced Industrial Science and Technology (AIST), Department of Materials and Chemistry, Japan
2. Nara Institute of Science and Technology, Japan

Glass is a metastable solid-state material obtained from the supercooled liquid state. The structure and physical properties of the glass, therefore, depend on the preparation process. The most important point during the preparation process is a thermodynamically structural stabilization of the supercooled liquid, i.e. the crystallization of glass, above the glass transition temperature T_g. If the nominal chemical composition of glass is equal to the corresponding crystal, such structural stabilization is often observed even in the as-prepared glass prepared by rapid quenching. Structural ordering affects many parameters, such as the phonon vibration, energy propagation, and thermal stability of glass. In this study, we focus on the luminescence properties of several oxide glasses and the glass-ceramics. As luminescent properties, X-ray induced scintillation and stimulated luminescence were measured in addition to conventional photoluminescence. Since the X-ray induced luminescence inherently contains energy transfer from the host matrix, it is expected that the crystallization affects the luminescence properties. Several oxide glasses were prepared by melt-quenching method in an ambient atmosphere. The glasses with non-stoichiometric chemical composition exhibit luminescence due to the defect i.e. residual amorphous region. Transparency of the glass-ceramics affects the intensity of scintillation.

(ICACC-S14-P048-2019) Relaxation processes of electron–hole pairs in α-Al_2O_3 probed with transient absorption spectroscopy

M. Koshimizu*[1]; Y. Muroya[2]; S. Yamashita[3]; H. Yamamoto[4]; Y. Fujimoto[1]; K. Asai[1]

1. Tohoku University, Department of Applied Chemistry, Japan
2. Osaka University, Japan
3. The University of Tokyo, Japan
4. National Institutes for Quantum and Radiological Science and Technology, Japan

Self-trapped excitons or holes in insulators can influence defect creation by ionizing radiation. To clarify the effect of irradiation in insulators, analysis of the relaxation processes of electron-hole pairs or excitons is required. Herein, we chose α-Al_2O_3 because of its application in personal dosimetry or beam monitoring. We used transient absorption measurements in the pico–nanosecond regime to analyze the relaxation processes. While transient absorption behavior in nano the second time scale has been reported, we have extended the time scale to the picosecond regime. Transient absorption measurements were performed in the picosecond and nanosecond time ranges using electron linear accelerators at the University of Tokyo and Osaka University, respectively. The spectrum revealed a single broad band at ~600 nm. The energy associated with the band was in agreement with a previous report that ascribed the band to interstitial Al atoms. The absorption time profile revealed that the decay behavior had two decay components: a fast one with a decay time constant of several tens of picoseconds,

and a slow one with a decay time constant of several tens of nanoseconds. Thus, the electronic excitation in α-Al_2O_3 decays via two relaxation processes.

(ICACC-S14-P049-2019) Flash sintering of piezoelectric and ferroelectric oxide ceramics

H. Charalambous*[1]; E. Taghaddos[1]; L. Perez-Maqueda[2]; S. K. Jha[1]; M. A. Wassel[1]; T. Tsakalakos[1]

1. Rutgers University, Materials Science and Engineering, USA
2. University of Seville, Instituto de Ciencia de Materiales de Sevilla, Spain

Flash sintering has been demonstrated to result in densification of a variety of piezoelectric and ferroelectric oxide ceramics including $BaTiO_3$, $BiFeO_3$, KNN, and PZT. However, the electrical properties of the flash sintered specimens have undergone little study. We aim to further the study of flash sintering by comparing the sintering behavior of two piezoelectric one ferroelectric system: $BaTiO_3$, BNT-BKT-BLT, and $BiFeO_3$. Focus is placed on previously unreported electrical properties of the flash sintered specimens in comparison to conventionally sintered specimens. Characterization of the dielectric, piezoelectric, and electromechanical properties was performed using impedance analyzer, piezometer, impedance spectroscopy, and Sawyer-Tower circuit.

(ICACC-S14-P050-2019) Investigations of complex anion material for scintillators

T. Yanagida*[1]; N. Kawaguchi[1]

1. Nara Institute of Science and Technology, Japan

Phosphor materials have been used in radiation detectors, and these phosphors are classified into two types, such as scintillators and storage phosphors for dosimeters. The scintillator has a function to convert a high energy ionizing radiation photon/particle to hundreds of visible photons via energy transportation from the host matrix to emission centers immediately. On the other hand, storage phosphors for dosimeters accumulate the incident radiation energy as form of carrier trapping, and these storage phosphors are used in personal dose monitoring and imaging plate applications. Among storage phosphors for dosimeters, Eu-doped BaFBr (Eu:BaFBr) is one of the most common materials. Generally, Eu:BaFBr is used in a ceramic form for imaging plate, and studies on crystal form for scintillator are not common. In this study, we prepared Eu:BaFBr crystal by the Bridgeman method, and evaluated scintillation properties. Under X-ray irradiation, the emission peak appeared around 390 nm due to Eu^{2+} 5d-4f transition in radioluminescence spectrum. When we irradiated ^{137}Cs, the scintillation light yield of Eu:BaFBr was roughly 27000 ph/MeV. At 662 keV, the energy resolution was around 11%.

(ICACC-S14-P051-2019) Development of LuAG-based near infrared-emitting scintillator

T. Yanagida*[1]; N. Kawaguchi[1]

1. Nara Institute of Science and Technology, Japan

$Lu_3Al_5O_{12}$ (LuAG) single crystals co-doped with Nd and Ce were grown by the Floating Zone (FZ) method to evaluate their scintillation properties particularly in the near infrared (NIR) wavelength. When X-ray was irradiated, the scintillation due to Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition was observed at 1064 nm. By changing the irradiation dose from 10-1000 mGy, we evaluated the relation between the scintillation intensity and the X-ray dose, and the relation was approximately linear. The scintillation decay time profiles were approximated by two or three exponential decay functions. The observed decay times were100 ns due to Ce^{3+}, 0.6-1.0μs due to the garnet host and few μs due to Nd^{3+}.

(ICACC-S14-P052-2019) Fabrication of translucent AlN ceramics

H. Akimoto*[1]; J. Tatami[1]; M. Iijima[1]; T. Takahashi[2]; M. Yokouchi[2]; T. Okuda[2]

1. Yokohama National University, Japan
2. Kanagawa Institute of Industrial Science and Technology, Japan

AlN is characterized by high thermal conductivity, high electrical insulation and intrinsically high transparency in the visible to infrared region. However, conventional AlN ceramics prepared by liquid phase sintering with sintering aids were generally opaque because light scattering results from the difference in the refractive index between AlN grains, residual pores and secondary phases derived from sintering aid. This means that the transmittance of AlN ceramics should increase by optimizing the microstructure related to the fabrication process. In the present study, the influence of sintering aid and the firing conditions on translucency of AlN ceramics was investigated. Samples are fabricated by adding various quantity of Y_2O_3 and $CaCO_3$. Phases present of the samples were $Y_3Al_5O_{12}$, $YAlO_3$, or $CaYAlO_4$ depending on the quantity and the composition of the sintering aid. The total transmittance of the samples increased from about 260 nm with increasing wavelength, and it greatly depended on conditions of the sintering aid. The sample having lower reflectance has higher transmittance. The sample prepared by adding 0.1 mol% Y_2O_3 showed the highest transmittance. It was shown that the total reflectance was explained by the reflective index and the fraction of the secondary phase resulting from the quantity and the composition of the sintering aid. Moreover, transmittance of AlN ceramics was improved by performing HIP treatment after GPS.

(ICACC-S14-P054-2019) X-ray-induced Luminescence in Sn-doped Zinc Sodium Phosphate Glasses

N. Kawaguchi*[1]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Graduate School of Materials Science, Japan

Radiation measurement techniques have been used in a wide range of application fields such as medicine, security, environmental monitoring and personal dose monitoring. As ionizing radiation detectors, inorganic phosphor materials are often utilized, and a numerous number of studies have been performed for the past decades. These phosphor materials are mainly classified to two types: scintillators and storage phosphors. These two types of phosphors in practice are mostly single crystal or crystalline powder. On the other hand, glass materials have advantages of their high transparency, productivity and chemical stability. Despite the advantages, there are not so many studies on glass materials for radiation measurements, and there is still large room left for research. Recently, the H. Masai's group had shown that Sn-doped zinc-phosphate glasses exhibit high photoluminescence quantum yield (PLQY) exceeding 90%. In this study, we have investigated X-ray-induced luminescence properties of Sn-doped phosphate glasses. Sn-doped zinc sodium phosphate glasses were prepared by a conventional melt quenching method, and their properties were evaluated.

(ICACC-S14-P053-2019) Particle Synthesis for Textured, High Performance $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ Ceramics

O. S. Ates*[2]; M. Avci[1]; E. Suvaci[2]

1. ENTEKNO Materials Corp., R&D, Turkey
2. Eskisehir Technical University, Material Science and Engineering, Turkey

Piezoelectrics attract attention for their diversified potential applications, such as sensors and actuators. Commonly used lead-based piezoelectrics are very toxic for the environment. NBT-based lead free systems can exhibit high piezoelectric performance if their grains are oriented. However, textured ceramics may exhibit less depoling temperature which may be caused by lattice mismatch between matrix grains and templates that are used for inducing grain orientation. Therefore, the research objective of this study was to synthesize and characterize NBT-KBT-BT matrix powder and NBT, KBT, BT and NBT-KBT-BT plate-like templates that can be

later used for producing textured ceramics with high piezoelectric response and high temperature stability. Synthesis of the templates with various chemistries enable one to design experiments to investigate the relationship between degree of lattice mismatch between matrix powder and templates and high temperature stability and piezoelectric performance. In this study, NBT-KBT-BT matrix powder was synthesized by mixed-oxide technique to achieve equiaxed morphology, submicron size and uniform size distribution. The templates with controlled properties were synthesized by molten salt method. In this presentation, effect of processing parameters on particle characteristics such as size, size distribution, morphology and chemistry will be discussed.

(ICACC-S14-P055-2019) Sn-doped Gallium Oxide Single Crystals for Radiation Detection

N. Kawaguchi*[1]; D. Nakauchi[1]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Graduate School of Materials Science, Japan

Inorganic scintillators are a kind of fluorescent materials and have taken on an important role to detect ionizing radiation in various fields such as medical imaging, security, astrophysics, and well-logging. Typical inorganic scintillators are insulator or semiconductor. Many types of insulator-based scintillators are used in practice. In contrast, relatively few types of semiconductor-based scintillators are known. Among the semiconductor scintillators, ZnS:Ag has been known over several decades and used for charged particle detections. It has been typically used in a thin-film due to its opacity, the detection efficiency is low and the applications are limited. Recently, our group have reported properties of a transparent Ga_2O_3 single crystal as the novel semiconductor scintillator. It showed a notably high light yield (15,000 ± 1,500 ph/MeV) and fast decay time (8 ns). In this study, we focused on Sn-doped Ga_2O_3 single crystals. The Sn ions can be doped in Ga_2O_3, and can affect its energy band structure. Sn-doped Ga_2O_3 single crystals were grown by the FZ (Floating zone method) method, and scintillation properties of them were investigated.

(ICACC-S14-P056-2019) Development of Textured, High Performance $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ Ceramics

C. Askin*[1]; H. Tetik[1]; O. S. Ates[1]; A. Avci[2]; E. Suvaci[1]

1. Eskisehir Technical University, Materials Science and Engineering, Turkey
2. ENTEKNO Corp., Turkey

NBT based ceramics are important alternatives for toxic lead based ceramics due to their high piezoelectric performances and high reproducibility. KBT and barium titanate-BT modification of NBT ceramics results in superior electrical properties with relatively high phase transformation temperatures. In addition, texturing ceramics with desired crystallographic orientation is another approach to obtain considerably high piezoelectric responses from NBT based ceramics. Templated Grain Growth is commonly used technique to produce grain oriented ceramics via the orientation of anisotropically shaped templates in equiaxed matrix particles followed by heat treatments where the densification and grain orientation occur via the Ostwald ripening process. In this process, evolution of lattice mismatches between templates and oriented grains may cause low depoling temperatures. To test this effect, in this study, plate-like NBT, KBT, BT and NBT-BT-KBT templates were used for texturing NBT-BT-KBT ceramics. In this presentation, microstructure and texture development as a function of temperature, time and platelet type will be discussed. In addition, results of the electrical, electromechanical properties and depoling temperature measurements will be presented as a function of texture quality and platelet type and hence degree of matching between oriented grains and the templates.

(ICACC-S14-P057-2019) Scintillation properties of Eu-doped $SrBr_2$ transparent ceramics

H. Kimura*[1]; T. Kato[1]; N. Kawaguchi[1]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Japan

Scintillators have a function to immediately convert the absorbed energy of ionizing radiation such as X- and γ-rays into low energy photons, and they have been used the various field such as medical, security and environmental monitoring. Conventionally, most scintillator materials have been used mainly in a form of bulk single crystal because of their high optical qualities. On the other hands, transparent ceramics has attracted much attention as radiation detector applications because transparent ceramic samples (e.g. GAGG:Ce, LuAG:Ce) showed superior scintillation properties than those of single crystals with the same chemical compositions in past literatures. $SrBr_2$:Eu showed high light yield (20,000 ph/MeV) in the form of single crystal. However, there are no reports on scintillation properties of $SrBr_2$:Eu in the form of transparent ceramic. In this study, we have developed $SrBr_2$:Eu transparent ceramics with different concentrations of Eu by the spark plasma sintering method and investigated the scintillation properties. Regarding the scintillation spectrum, the $SrBr_2$:Eu (0.1%) ceramic shows the emission peak around 400 nm, which was consistent with the past report on $SrBr_2$:Eu single crystal. The origins of the emission is due to the 5d-4f transitions of Eu^{2+}.

(ICACC-S14-P058-2019) Scintillation and dosimetric properties of CsCl transparent ceramics and single crystal

H. Kimura*[1]; T. Kato[1]; D. Nakauchi[1]; N. Kawaguchi[1]; M. Koshimizu[2]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Japan
2. Tohoku University, Japan

Scintillators have been used for the various applications such as positron emission tomography, X-ray computed tomography and survey meter. In general, the required properties for scintillation detector are a fast decay time, a high light yield and a low afterglow. Among the various luminescence mechanisms in scintillators, auger-free luminescence (AFL) has attracted much attention because of the fast decay time. AFL is due to the recombination of electrons from the valence band with holes from the core band. In previous reports, CsCl single crystal showed the AFL at the wavelength around 240 and 270 nm. However, there are no reports on the AFL of CsCl transparent ceramics. Recently, we has reported that transparent ceramics show better performance for radiation detection than the single crystal counterpart, and similar results can be expected in CsCl. In this study, we have developed CsCl transparent ceramics by the spark plasma sintering and investigated the scintillation and dosimetric properties, in comparison with a CsCl single crystal. Regarding the scintillation properties, the X-ray induced emission spectra of CsCl transparent ceramic shows 270, 340 and 400 nm. The origin of the emission around 270 nm is AFL. The other emission origin could be assigned to the defects or oxygen impurities in from the analogy supported with the case of CsBr.

(ICACC-S14-P059-2019) Lead-free KNN single crystal and its piezoelectric properties

K. Shimamura*[1]; X. Fu[1]; V. Garcia[1]; Y. Kitanaka[2]; Y. Noguchi[2]; M. Miyayama[2]; N. Ohashi[1]

1. National Institute for Materials Science, Japan
2. University of Tokyo, Japan

Due to the toxic nature of Pb, in the recent decade, there is an increasing request to develop high performance Pb-free piezoelectric materials. $K_{1-x}Na_xNbO_3$ lead-free compounds, commonly called KNN, are being investigated due to their relatively high piezoelectric coefficient and high Curie temperature. They are considered to be potential candidates to replace Pb-based piezoelectric ceramics in various applications. In this work, KNN single crystals were grown,

and their properties, including crystal structure, optical and ferroelectric properties, are investigated. Grown KNN single crystal presents some cracks, and although it looks opaque by naked eye, the transmittance of a both side polished plate of 0.5 mm thickness is over 70%. This result contrast with the published in the literature, where KNN crystals are reported as simply opaque at room temperature, and it is indicative of the significant improvement in crystalline quality. On the other hand, the Curie temperature was measured to be 420°C by TG-DTA heating. The temperature dependence of the ferroelectric properties will be discussed in detail and the overall performance compared. This work has been partially supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Element Strategy Initiative to Form Core Center of Japan.

(ICACC-S14-P060-2019) Properties of molybdates phosphors heat-treated by hydrothermal and exposed to beta radiation

R. Künzel[2]; R. Mazin Latini[1]; N. K. Umisedo[3]; E. M. Yoshimura[3]; E. Okuno[3]; A. d. Marques*[1]

1. Universidade Federal de São Paulo, Chemistry, Brazil
2. Universidade Federal de São Paulo, Physical, Brazil
3. Universidade de São Paulo, Instituto de Física, Brazil

Molybdate, how $AMoO_4$, where A= Ba^{2+}, Ca^{2+}, Sr^{2+} and rare earth, has various applications as phosphors, scintillators, magnets, sensors, and catalysts. Hydrothermal treatments can affect morphology, particle size, crystallinity and electronic properties of materials. Thermoluminescence (TL) and optically stimulated luminescence (OSL) are important phosphorescence phenomenon and can provide important information on the electronic transitions related to structural defects in a material. In this work, the luminescent characteristics of $SrMoO_4$ powders, grown in a microwave-assisted hydrothermal (MAH) system, under beta radiation excitation, are investigated by means of TL, OSL, and photoluminescence. XRD and Raman studies of the $SrMoO_4$ powders provide evidence of a scheelite-type crystalline structure. Thermoluminescence (TL) and optically stimulated luminescence (OSL) measurements were performed with powdered samples previously irradiated with beta radiation. The trap depth, associated with trap levels located inside the band-gap, were determined from TL data using different methods of glow curve analysis. Acknowledgments This work was supported by CNPq and FAPESP (#2016/20578-5, 2013/07437-5).

(ICACC-S14-P061-2019) Single crystal phosphors for high-brightness lightening

V. Garcia*[1]; K. Shimamura[1]; D. Inomata[2]; I. Akira[3]

1. National Institute for Materials Science (NIMS), Japan
2. Tamura Corporation, Japan
3. Koha Co., Ltd., Japan

Since the development and commercialization of while light emitting diodes (WLEDs) for general lightening, there has been an increasing urge to implement this new technology in other kinds of applications involving high-brightness. The drawbacks of current technologies are mostly related to two interconnected issues: On the one hand the thermal quenching of emission in ceramic powder phosphors (CPPs), and on the other hand the low thermal conductivity of phosphor binders used on the top of the blue LEDs. In order to improve current technologies, in the recent years we have proposed a new approach, namely the use of single crystal phosphors (SCPs) instead of conventional CPPs. Compared with ceramic powders, the superior crystallinity of single crystals is crucial to achieve highest conversion efficiencies and thermal stability of phosphors. SCPs can be used as such single crystals, but also in powder form without degradation of the optical properties of original crystals. Furthermore, these SCP powders can be compacted without the use of any organic compounds, a binder-free phosphor that takes advantage of the high thermal conductivity of SCPs. The characteristics of basic SCPs, namely yellow Ce:YAG and green Ce:LuAG, and their superior performance will be presented.

(ICACC-S15-P062-2019) Regolith Materials for ISRU in Vacuum Conditions: Approximation of Micro-Gravity influence on materials processing for Additive Manufacturing in Space

C. Neal*[1]; L. Pohl[2]; T. S. Sakthivel[1]; D. Britt[2]; S. Seal[3]

1. University of Central Florida, Materials Science & Engineering, Nanoscience Technology Center, Advanced Materials Processing & Analysis Center, USA
2. University of Central Florida, Physics, USA
3. University of Central Florida, Materials Science & Engineering, Nanoscience Technology Center, Advanced Materials Processing and Analysis Center, College of Medicine, USA

Space exploration & development has traditionally been limited by the expense of transporting massive payloads into space. Recently, support for in situ resource utilization (ISRU) has grown substantially as a solution to this issue with respect to the production of building materials &tools in space environments. Asteroid & lunar/Martian regolith are abundant in certain minerals, metals, important non-metals, & carbonaceous materials. To successfully extract & process materials in these environments (in situ), micro-gravity's influence must be well characterized throughout each process. In the presented work, antigorite & cronstedtite samples were analyzed via differential scanning calorimetry for phase change behavior by heating to 1200 C (20 C/min) under N_2 gas flow (100 mL/min) or partial vacuum. The influence of dehydration was also investigated with respect to changes in crystal structure & composition, via X-ray photoelectron spectroscopy & X-ray diffraction. Mechanical properties & the formation of building materials from raw materials also depend strongly on sample granularity. Therefore, sample treatments & characterizations were performed on varied size fractions. The results of this study suggest that the influence of vacuum environment on ISRU processing techniques strongly influences endpoint products.

(ICACC-S15-P063-2019) Alignment of α alumina platlets for transparency through direct ink writing

C. Meisel*[1]; W. J. Costakis[1]; A. Schlup[1]; R. Trice[1]; J. P. Youngblood[1]

1. Purdue University, Materials Engineering, USA

An additive manufacturing technique, termed direct ink writing, was used to fabricate near-net shaped alumina samples at room temperature with aqueous suspensions. It is proposed that this direct writing technology can be used to deposit alumina suspensions loaded with α-alumina platelets in a layer by layer fashion to align the microstructure and fabricate samples that can be sintered to final densities to produce transparent parts. Printing was conducted with round and flat nozzles with varying inner diameters of 1.35-1.7 mm. The suspensions consisted of 54 vol% solids loading with α-alumina platelets composition varying by 0-20vol% with the remaining amount being equiaxed powder. After printing, samples were placed in humidity chambers at above 70% relative humidity for two days to ensure no drying defects. The green bodies underwent binder burnout and were subsequently sintered via hot pressing.

(ICACC-S15-P064-2019) Large scale AM of artificial stone: Printers and printed components

F. Gobbin*[1]; G. Franchin[1]; P. Colombo[1]; A. Italiano[2]; A. Beretta[2]; M. Bergonzoni[1]

1. University of Padova, Industrial Engineering, Italy
2. Desamanera, Italy

Large scale (meter-sized) non-structural objects were fabricated by an indirect AM technique (powder bed). Printers and materials were developed by Desamanera Srl, Italy, in collaboration with the Industrial Engineering Department of the University of Padova, Italy. In the poster, we will show the technology and the different printers developed, and some printed components and examples of application. The large printer (Desa1 150.150) has a printing envelope of 1.5 x 1.5 x 1.5 m^3, and the small one (Desa1 60.60) of

about 0.6 x 0.6 x 0.6 m^3. The printers have a theoretical resolution between 3 and 6 mm, which is a reasonable value for the scale of objects that have been developed. The printed components can be post-processed to smoothen defects and increase the level of detail. A new printer is currently under development, having in mind Industry 4.0 and IoT possibilities, embedding sensors in the printer and inside the material to monitor the print quality and offer additional features to the printed parts. Printed components could have specific characteristics and be applied in different sectors, such as: art and design, interior and outdoor architecture, coastal protection and cultural heritage. New applications and potentialities are continuously investigated and developed.

(ICACC-S15-P065-2019) Advances in additive manufacturing of 3Y-zirconia based on video projection

C. A. Fortulan*[1]; L. B. Amaral[1]; J. L. Paschoa[1]; C. R. Foschini[2]

1. University of Sao Paulo, Mechanical, Brazil
2. São Paulo State University, Mechanical, Brazil

The additive manufacturing (AM) of materials has developed greatly in the last 12 years. For ceramic materials class, the development was relatively slower, mainly because the porosity and the low mechanical resistance, which limited its advance for structural applications. However, in the last 5 years, techniques based on stereolithography have begun to emerge in the direction of obtaining dense pieces. The present work deals with the experimental study of the additive manufacturing of 3Y-zirconia based on mask video projection. For this purpose, the top-down system was set up with a mechanical spreader of the layered paste and the intense light exposure. Formulations developed with a ceramic powder supersaturated with a resin photo-polymerizable was printed. After printing, the specimens were burned for resin removal followed of sintering. The specimens were characterized by conventional metrology and by scanning electron microscopy (SEM). Low porosity zirconia pieces were obtained using mixtures with ceramic powder/resin concentration up to 50 vol%. The mask video projection on layers favors lamination, which for ceramics the continuous process of movement of the z-axis was necessary. The results were very promising and accredited the mask video projection process as a viable alternative to the additive manufacturing of ceramics

(ICACC-S17-P066-2019) Effect of using binder free titania paste on the efficiency of solar devices

V. More*[1]

1. Indian Institute of Technology Bombay, CRNTS, India

Conventional dye sensitized solar cells are mostly prepared by titania nano particle paste which has organic binder. For removing these binders and improving interconnectivity of titania nanoparticles in film, substrates are subjected to heating to higher temperature (more than 400°C). But such pastes are not useful for making flexible DSSCs as they require high temperature treatment. Compaction of particle, electrophoretic deposition, microwave heating, coagulation of titania particles by adjusting zeta potential and mixing various sizes of titania particles are listed in literature to get interconnected titania particles at the temperature lower than degradation temperature of flexible conducting substrate. All these procedures are complicated so in this study preparation of binder free paste and its impact is reported. Binder free paste was made by mixing titania nano-sol with commercially available titania (P25) using mortar pestle. Titania film made from these paste showed microstructure (well connected titania particles) similar to microstructure of sintered titania films (500°C) made from binder containing paste. 4.59% maximum efficiency was achieved in DSSCs made by using titania films prepared from binder free paste.

(ICACC-S17-P067-2019) Electrochromic performances using sol-gel processes with tungsten trioxide (WO3) on flexible transparent electrodes

H. Kim*[1]

1. Yeungnam University, School of Materials Science and Engineering, Republic of Korea

Sol-gel methods was used to fabricate tungsten trioxide (WO3) films for electrochromic devices. When WO3 films deposited were thermally treated in air at 150 °C, the majority of tungsten species in the films became W6+, which is important for the realization of an optically transparent bleached state. To establish the fabrication protocol of WO3 films at low temperature, the correlation between the annealing conditions of WO3 films and their EC performance were studied. While the as-spun WO3 was amorphous, a monoclinic crystalline structure developed after thermal treatment. Annealing atmosphere in addition to temperature is a very important factor in determining the properties of WO3 films. For highly transparent WO3 films with majority W6+ species, the required annealing temperature was 60 °C in vacuum, which is much lower than the softening temperature of the polymer substrates. Although a similar tungsten composition and film transparency could be achieved even in air at 150 °C, the EC performances deteriorated. It was found that a cracked and irregular morphology of the WO3 film was the origin of this poor EC behavior. The optimum annealing conditions of 60 °C in vacuum provide the opportunity to apply WO3 films to flexible electronics. The electrochromic performances with flexible transparent electrode will be discussed.

(ICACC-WW-P001-2019) Structural and Morphological Characterization of Persistent Phosphor of $Y_3(Al,Ga)_5O_{12}:Ce^{3+},Cr^{3+},Nd^{3+}$ Ceramics Fabricated from Nanopowders

Z. Dai*[1]; V. Boiko[1]; M. Markowska[1]; A. Gerus[1]; M. L. Saladino[2]; F. Ursi[2]; D. Hreniak[1]

1. The Institute of Low Temperatures and Structural Research, Polish Academy of Sciences, Division of Optical Spectroscopy, Poland
2. University of Palermo, Stebicef Department, Italy

Persistent phosphors have recently aroused great interest and play ever more important role in many areas of materials science and new applications. Among others, the YAGG:Cr^{3+} co-doped with Ce^{3+} and Nd^{3+} got a great deal of attention due to their interesting red and infrared persistent luminescence. In this work, YAGG:Ce^{3+},Cr^{3+},Nd^{3+} ceramics were fabricated by sintering method followed by hot isostatic pressing (HIP) from the nano-powders obtained by modified Pechini method. Structure and morphology of nano-powders were characterized by X-Ray Powder Diffraction (XRPD), Brunauere-Emmette-Teller method (BET), Infrared Spectroscopy (FT-IR) and Transmission Electron Microscopy (TEM). The average crystallite sizes and particle sizes were calculated from the Rietveld refinement data and TEM results, respectively. In addition, the microstructure and optical properties of YAGG:Ce^{3+},Cr^{3+},Nd^{3+} ceramics were also preliminarily investigated. For developing the ceramics of required quality, the influence of annealing temperature of nano-powders and sintering parameters on their optical properties was determined.

(ICACC-WW-P003-2019) The Impact of Ceramic Raw Materials Variation on Investment Casting Refractories

E. Jones*[1]; S. Blackburn[1]; R. Greenwood[1]

1. University of Birmingham, Chemical Engineering, United Kingdom

A key part of the investment casting of turbine blades is the production of the ceramic shell. Regarding the raw materials for the shell system, there are various grades available which can be purchased from different locations, each with particular material properties. By characterising commercially available ceramic powders, the effect of mining location and processing on fundamental physical and chemical properties can be understood. The main raw material properties

to be explored are particle size and shape, composition and chemistry. The effect of particle size will be studied by producing bespoke particle size distributions and observing what effect this has on the dimensional stability of the shell mould. Elemental analysis will be used to identify which impurities are present in the samples and to understand what effect they have on the shell system. The influence of calcination and radiation damage on the ceramic powder will also be explored as it will cause the samples to have different crystal structures, densities and hardness. These properties will then be related to the development of key shell properties and consequential effects on casting dimensions. Detailed understanding of the material's microstructural development through shell manufacture and subsequent casting will allow Rolls-Royce plc to drive improvements into the dimensional capability of their cast product.

(ICACC-WW-P004-2019) Effect of neodymium oxide doping on the properties of 3Y-TZP

E. Willems*[1]; F. Zhang[1]; T. Van Hout[1]; J. Vleugels[1]; B. Van Meerbeek[2]

1. KULeuven, Materials Engineering, Belgium
2. KULeuven, Department of Oral Health Sciences, BIOMAT and UZ Leuven, Dentistry, Belgium

3 mol% yttria-stabilized zirconia (3Y-TZP) ceramics are successfully used for dental restorations especially due to their natural appearance, transformation toughening induced fracture toughness and high strength. The use of dental 3Y-TZP ceramics however is limited by its risk of hydrothermal aging. The use of trivalent cation doping can improve the mechanical properties and improve the resistance towards hydrothermal degradation. Moreover, doping with a proper mix of cations could lead to a more natural coloration. In this study, we investigated the influence of 0.1-3 mol% Nd_2O_3 addition on the microstructure, mechanical properties, and hydrothermal stability of zirconia ceramics. Commercially available Zpex powder (3Y-TZP with 0.05 wt% Al_2O_3) was doped with Nd_2O_3 by $Nd(NO_3)_3$ coating. Nd_2O_3 could be used as a replacement for Co_2O_3 doping, since it generates a similar color. Nd_2O_3-doped 3Y-TZP could be co-doped with Er_2O_3 (pink shade) and Fe_2O_3 (yellow shade) to obtain a tuneable naturally looking colored ceramic with exceptional properties. The obtained Nd_2O_3-doped ceramics could be fully densified using a conventional sintering cycle, and an increasing Nd_2O_3 content was accompanied by an increasing amount of c-ZrO_2 phase and a concomitant increasing average grain size. The hydrothermal aging resistance also improved with the introduction of Nd_2O_3 into the Zpex 3Y-TZP.

(ICACC-WW-P005-2019) In Vitro Efficacy of Antimicrobial-releasing Mesoporous Ceramics for Load-bearing Implant Applications

C. D'Haeyer*[1]; K. Thevissen[2]; A. Braem[1]

1. KULeuven, Department of Materials Engineering, Belgium
2. KULeuven, Centre of Microbial and Plant Genetics, Belgium

Rough implant surfaces, used to achieve successful osseointegration, entail a high risk for colonization by microorganisms and subsequent development of biofilm associated infections, thereby burdening both patients and healthcare systems. Implants incorporating and locally releasing anti-infective molecules at their surface in a controlled manner are proposed as a possible antimicrobial strategy. Sol-gel derived mesoporous ceramics, e.g. silica or bioactive glass, are of interest as these materials exhibit tunable pore structures allowing adjusting the diffusion kinetics, and hence the release profile, of drug molecules through the pores. However, coating materials tend to be fragile and cannot be refilled risking premature depletion. Within this context, we developed a mesoporous diffusion barrier inside a high-strength porous Ti structure enabling a sustained drug release from an internal reservoir to the implant surface. A proof-of-concept was established for the continuous release of constant therapeutic concentrations of chlorhexidine, an antimicrobial agent commonly applied in mouthwashes, and this for a prolonged time. Efficacy of the released chlorhexidine against various pathogens was evaluated in a preventive as well as curative setting. We hypothesize that implants made out of such composite materials can take metal-based drug eluting systems to a clinical level.

(ICACC-WW-P006-2019) Studying the mechanism of reactive infiltration of silicon and eutectic Si-Zr alloy in carbon using innovative laser-ablated microchannels and radiography experiment

M. K. Naikade*[1]; L. Weber[2]; A. Ortona[1]; T. Graule[1]

1. Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Switzerland
2. EPFL, Mechanical Metallurgy Laboratory, Switzerland

The reactive infiltration mechanism of molten silicon and a eutectic Si-8 at. pct Zr alloy in vitreous carbon microchannels was investigated by radiography. The microchannels were manufactured by making 20 to 100 micron deep grooves on vitreous carbon plate by laser ablation technique and clamping it with another flat plate. The extent of infiltration was observed nondestructively by X-ray radiographs. SEM and EDX were used to study the reaction layer at the interface. The innovative technique allowed studying the mechanism of reactive infiltration in very long micron size capillaries. In addition, the effect of tortuosity can be easily studied by changing the geometry of the microchannels. X-ray radiographs not only provided the information about the extent of infiltration in the microchannels but also gave some ideas about change in reaction product along the length of the microchannel.

(ICACC-WW-P007-2019) The Conversion of Metal Chlorides to Cobalt-titanium-boron based Hybrid Nanostructures

S. Khoshsima[1]; Z. Altintas[1]; M. Somer[1]; O. Balci*[1]

1. Koc University, Turkey

The synthesis and characterization studies of metal boride ceramics moved to center of both scientific and industrial interest in recent years due to their superior physical, chemical and mechanical properties. Cobalt-titanium-boron based metal borides are highly valuable materials with a high application potential in wide range of multi-functional areas due to their magnetic and mechanical properties. In this study, an alternative route for obtaining crystalline metal boride hybrid structures was proposed at low temperatures by using the ternary system of $CoCl_{2(s)}$-$TiCl_{4(l)}$-$NaBH_{4(s)}$. The reactions were carried out in a sealed reactor under autogenic pressure, placed in a chamber furnace. After reaction, the unwanted NaCl phase was removed by hot water leaching. Effects of different amounts of precursors on the conversion yield of metal chlorides to borides and microstructure of the final powders were investigated. Powders were characterized by using X-ray diffractometer (XRD), X-ray fluorescence spectrometer (XRF), scanning electron microscope (SEM/EDX), differential thermal analyzer (DTA/TG) and Zetasizer dynamic light scattering technique. After a reaction of the stoichiometric amounts of precursors at 850°C in a sealed reactor under autogenic pressure, the full conversion of metal chlorides to CoB-TiB_2 hybrid nanostructures having an average particle size of 300-500 nm was achieved.

(ICACC-WW-P008-2019) Multisensor $Ti_3C_2T_x$ MXenes Array Gas-Analytical Chips

H. Pazniak*[1]; I. Burmistrov[2]; E. Kolesnikov[1]; A. Varezhnikov[2]; T. Inerbaev[3]; V. Sysoev[2]; D. Kuznetsov[1]

1. National University of Science and Technology "MISiS", Russian Federation
2. Saratov State University, Russian Federation
3. L.N. Gumilyov Eurasian National University, Kazakhstan

MXenes are a large family of 2D transition metal carbides/nitrides obtained by removing the A-layer element from MAX phase precursor via selective chemical etching. $Ti_3C_2T_x$ is one of the first and well-known member of MXene family with fully functionalized

surface and metallic conductivity. Here, we demonstrate the experimental results for testing $Ti_3C_2T_x$ MXenes as material for chemiresistive gas sensors. The vapors of acetone, ethanol, and methanol have been mixed with dry air in the concentration range of 2…10 ppm and have been considered as test gases. The gas response was defined as the change in the electrical resistance upon gas injection compared to the baseline resistance ($\Delta R/R_b$ (%)). $Ti_3C_2T_x$ sensors displayed a negative variation of resistance for test gases. In our experiments, the MXenes gas sensor have the highest sensitivity at 350ºC for acetone. Charge transfer from adsorbed molecules governs the sensing mechanism in 2D materials. Using DFT we calculate the redistribution of charge carrier density while adsorbing analyzed gases. The formation of thin titanium oxide layer on MXenes surface is a reason of high gas response.

(ICACC-WW-P009-2019) Strontium/carbonate co-substituted two-phase system of hydroxyapatite and octacalcium phosphate derived from cuttlefish bone

A. Ressler*[1]; M. Cvetnić[1]; M. Ivanković[1]; H. Ivanković[1]

1. University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia

Hydroxyapatite (HAp) is the most widely used calcium phosphate (CaP) for hard tissue applications due to its compositional similarity to biological apatite, biocompatibility and bioactivity. Along with HAp, other CaPs, such as octacalcium phosphate (*OCP*) and tricalcium phosphates (*TCP*), are gaining increasing attention. As bone apatite is a multi-substituted carbonated HAp containing trace elements, one of the used approach to improve the biological and physicochemical properties of CaPs is ionic substitution. In this study Sr-substituted CaPs, with varying Sr-dopant content, have been prepared by using cuttlefish bone as precursor of Ca^{2+} and various trace ions. The effect of the doping on phase composition, crystal structure, morphology and thermal stability of synthesized materials was studied. Mineralogical composition of the as-prepared powders and the heat-treated powders were determined using X-ray diffraction analysis. The lattice parameters, the cell volume and phase composition of prepared powders were determined by Rietveld refinement using software DIFFRAC.SUITE TOPAS V.5.0. The precipitated powders were composed of HAp, OCP and amorphous CaP. After heat treatment, crystalline phase of β-TCP was detected. The chemical composition of unsubstituted and Sr-substituted HAp/OCP powders were determined by inductively coupled plasma mass spectrometry.

(ICACC-WW-P010-2019) Electrochemical assessment of NiO-CGO nanocomposites as cermet precursors

J. Grilo*[1]; D. Macedo[2]; R. M. Nascimento[3]; F. Marques[1]

1. Universidade de Aveiro, Department of Materials and Ceramics Engineering, Portugal
2. Universidade Federal da Paraíba, Department of Materials Science and Engineering, Brazil
3. Universidade Federal do Rio Grande do Norte, Department of Materials Science and Engineering, Brazil

$NiO\text{-}Ce_{0.9}Gd_{0.1}O_{1.95}$ (NiO-CGO) nanocomposite powders were produced by a one-step chemical route. These composites, precursors of anode Ni-CGO cermets, were uniaxially pressed and fired at 1400 °C for 4 h. Ni-CGO cermets were obtained by reduction in H_2+N_2 gas mixtures. Composites with similar composition were obtained by conventional mechanical mixing of commercial powders and tested for comparison. X-ray diffraction (XRD), Transmission and Scanning Electron Microscopy (TEM & SEM), impedance spectroscopy (in air and several N_2+O_2 gas mixtures) or dc conductivity, were used in materials characterization. Crystallites of synthetic composites were nanosized according to the XRD patterns refinement results. Particles with approximately 20 – 30 nm were revealed by TEM. On the contrary, one-step derived composites showed submicrometric grains, as observed by SEM. Low temperature impedance spectra were used to obtain significant insight on microstructural characteristics, due to a variable role of NiO when shifting from a well percolated electronic (synthetic composites) conducting pathway to a dispersed ion-blocking phase (mechanical mixed commercial powders). The superior conductivity of one-step materials was due to the presence of a well-connected tridimensional network of homogeneously distributed NiO(/Ni) grains, as shown by SEM.

(ICACC-WW-P011-2019) Toughening mechanism of graphene in silicon nitride ceramics

E. Bodis*[1]

1. Institute of Materials and Enviromental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, Hungary, Hungary

In this work, Si3N4-based ceramics mixed with 1, 3 and 5 wt% multilayer graphene (MLG), respectively, were produced by SPS in order to improve the fracture resistance of the Si3N4 ceramic. The investigations of sintered bodies focused on understanding the relationships between their microstructure and mechanical properties, with a special attention to the intergranular phases between Si3N4 matrix and MLG reinforcement. We have found that even 1 wt% MLG addition increases the fracture toughness of Si3N4-based composites by 60% as compared to the MLG-free Si3N4. In 1 wt% MLG/Si3N4 samples local, but separated nanopores are observed at the Si3N4-MLG interface, which pores probably promote the MLG pull-out mechanism imparting a toughening effect on the composite. In addition, in the microstructure of 1 wt% MLG/Si3N4 samples, strong surface contact area between the Si3N4 grains and the MLG platelets are developed. The homogenous MLG distribution improves the surface contact area and the transfer of internal stresses from the matrix to the reinforcement on loading. In contrast, 3 and 5 wt% MLG content result in agglomerated MLG grains and excessive porosity at the Si3N4-MLG interfaces, leading to weaker matrix- graphene adhesion and thus lower fracture toughness.

(ICACC-WW-P012-2019) Preparation of nanoceramic materials by needleless electrospinning

I. Shepa*[1]; E. Mudra[1]; M. Vojtko[1]; V. Medvecka[2]; J. Dusza[1]

1. Slovak Academy of Sciences, Institute of Materials Research, Slovakia
2. Comenius University, Faculty of Mathematics, Physics and Informatics, Slovakia

Oxide ceramic materials such as aluminum oxide, zinc oxide, titanium, tin and zirconium dioxides and others are widely used as refractories, sensitive elements of sensors, catalysts, photocatalysts in dye-sensitized solar cells and water treatment. Due to the specific properties of nanofibers, such as high surface-area-to-volume ratio, high porosity, appreciable mechanical strength, these materials in nanofibrous form show better characteristics. In this study needle-less electrospinning was used for the production of oxide and non-oxide ceramic fibres from the same precursor material. The post spinning treatment is the key step for transformation of electrospun precursors to ceramic or composite fibers. For spinning solutions preparation polyvinylpyrrolidone (PVP), titanium isopropoxide (TTIP), ethanol and acetic acid were used. Influence of heat treatment type, atmosphere and temperature on the chemical/phase composition and grains size of the final fibers were studied. The calcination of the electrospun precursor fibres resulted in the formation of titanium dioxide nano/microfibers. In case of the heat treatment experiments in the inert atmosphere carbothermal reduction took place and composite carbon/oxide ceramics and titanium carbide fibres were produced. The last alternative treatment technique – low-temperature plasma resulted in the formation of the unique flexible oxide ceramic composite material.

Wednesday, January 30, 2019

40th Anniversary Richard M. Fulrath Award Symposium on Frontiers of Ceramics for Sustainable Society

Fulrath Session III

Room: Coquina Salon E
Session Chairs: Michael Halbig, NASA Glenn Research Center; Kiyoshi Shimamura, National Institute for Materials Science

8:30 AM

(ICACC-FUL-019-2019) Picometer scale metrology of complex oxides with electrons and Xrays (Invited)

V. Gopalan*[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

With tremendous advancements in recent years in the state-of-the-art electron microscopy, and coherent diffraction imaging Xray synchrotron techniques, it has become routine to image oxygen of oxides, achieve sub-angstrom resolution and a few picometers of precision. In this talk, I will present two such studies. The first is the imaging of polar Ruddlesden Popper structures to image competing polar phases, and compare them one-on-one with density functional theory predictions. This will include a polar insulator, $Sr_{n+1}Ti_nO_{3n+1}$, and a polar metal, $Ca_3Ru_2O_7$. the second example will be to reconstruct the three-dimensional electron density of a low symmetry oxide interface of $CaTiO_3$ on various substrates with complex oxygen octahedral tilt patterns on both sides of the interface. This reveals the power of tilt-epitaxy in stabilizing new non-equillibrium phases with emergent phenomena.

9:00 AM

(ICACC-FUL-020-2019) In-situ observation of sintering behavior in a ceramic powder compact by optical coherence tomography (Invited)

J. Tatami*[1]; F. Sakamoto[1]; M. Iijima[1]; T. Takahashi[2]

1. Yokohama National University, Japan
2. Kanagawa Institute of Industrial Science and Technology, Japan

It is well known that bonding of particles, decrease in surface area, and shrinkage of a powder compact occurs dynamically in sintering of ceramics. Although the internal structure of the ceramics have to be controlled to make better ceramcs, evolution of the internal structure during sinterin at high temperatures has not been clarified yet. In this study, in-situ observation of sintering behavior in a ceramic powder compact was carried out by optical coherence tomography (OCT). Commercially available Al_2O_3 powder was used as a raw material. After adding the small quantity of MgO and molding the powder mixture by dry pressing, the powder compact was set in the electric furnace. OCT observation was carried out through a glass window from the above of the furnace. The internal structure of the powder compact was clearly observed at high temperatures without the effect of any heat radiation as well as at a room temperature. It was also found that the powder compact shrunk gradually with heating. The inhomogeneous region existed before firing, but it disappeared in the initial stage of the sintering shrinkage. When the relative density was over 90%, contrast of the sea-island structure appeared because of the difference in the porosity. After the contrast faded out again, the different inhomogeneiety was observed, resulting from the coarsening of the pores.

9:20 AM

(ICACC-FUL-021-2019) Motion Control of Ceramics particles by electric field and its VTV analysis (Invited)

T. Nakayama*[1]

1. Nagaoka Univ of Tech, Japan

Electrochemistry of non-aqueous solution is a chemistry to deal electron transfer between materials in non-aqueous solutions and various phenomena associated with it. By using appropriate non-aqueous solvent or a mixed solvent other than water, it becomes possible to cause a new reactions or purpose reactions by material's dissolved state and the reactivity changes. Furthermore, electro-rheological fluid is a functional fluid application that the rheological properties change by applying an electric field. This paper is intended to develop a new ceramic structure control method by combining the electrochemical of non-aqueous and the ER fluid. The main purpose of this study is a driving control of micro-structure by electric field. In particular, the drive control of the micro-structure in a non-aqueous solution to control from the outside by the electric field, are considering applications such as metering pump in the non-aqueous solution.

9:40 AM

(ICACC-FUL-022-2019) Potential of melilite-type single crystals as piezoelectric devices (Invited)

H. Takeda*[1]; T. Hoshina[1]; T. Tsurumi[1]

1. Tokyo Institute of Technology, Japan

Aim of this study is to investigate a potential of melilite-type single crystals as piezoelectric devices. Among a plenty of melilite-type crystals, we have focused on calcium aluminate silicate $Ca_2Al_2SiO_7$ (CAS) single crystal. For pressure sensor use, we attemptted to synthesize modified CAS single crystals with higher mechanical strength by substitution. This is because the CAS single crystals with a clear cleavage plane may have low mechanical strength. Strontium substituted CAS (Sr-CAS) single crystals were successfully grown by Czochralski technique. The Sr-CAS crystal substrate with (XYt)25° rotation cut showed the rupture strength of 220 MPa, which is comparable to that of quartz. Electroacoustical constants of the CAS crystals were also evaluated for the acoustic wave device. The first-order temperature coefficients (TC) of all the constants were determined between -30 and 120 °C. The TC of piezoelectric modulus d_{14} value is negative and that of d_{36} was positive. This observation gives an opportunity to obtain a near-zero temperature coefficient of time delay in the appropriated cut directions in both bulk and surface acoustic waves. The Rayleigh SAW velocities for the fundamental cuts of the crystals were theoretically calculated. The results were supported by the SAW velocities measured for the cuts of the crystal, proving the accuracy of the electroacoustic constants determined in this study.

10:20 AM

(ICACC-FUL-023-2019) Reliability Study of Dielectric Ceramic Materials (Invited)

A. Ando*[1]

1. Murata Mfg. Co., Japan

Huge amount of functional ceramic components will be used in the future electronics. Multilayered ceramic capacitor (MLCC) is one of the most widely used electronic components, and its capacitance has been increased by decreasing its dielectric ceramic layer thickness under 1um. The future MLCCs will be used at various conditions including extremely harsh conditions, for example, at high temperatures, under high electric field, under high mechanical stresses, and so on. Dielectric materials used for MLCC should have high reliabilities against these harsh conditions. Reliability designs for these dielectric ceramic materials is one of the most important issues for the MLCCs. The degradation mechanism of the MLCCs and the high reliability design will be descussed there.

10:50 AM

(ICACC-FUL-024-2019) Low temperature ceramic processing to electronics and energy application (Invited)

Y. Imanaka*[1]

1. Fujitsu Laboratories Ltd., Japan

In general, low firing process for ceramics is attractive for reducing energy consumption, resulting in low cost. Besides this generic common benefit, this process is recognized as the key technology for producing new devices in electronics ceramics field. The electronics ceramic devices such as chip capacitor, circuit board, various electronic components and modules, are always incorporated with various materials for adding different functions: ceramics for LCR and sensing function, metal for conductor and heat dissipation function, and resin for low-cost, light-weighted, and flexibility function, and so forth. In other words, theses electronics ceramic devices are regarded to be the composite with different materials. Since every material possesses its own optimum process temperature: usually, that temperature of ceramics is highest, compared with other materials, such as metal and resin, the ceramic process is the bottle neck for creating new devices. Therefore, the low temperature process is always expected in this field. This paper addresses basic concept of low temperature process as well as several examples of low temperature process: the multi-layered circuit board using low-temperature fireable ceramics with copper conductor, ceramic capacitor embedded organic and flexible substrate. Also, energy application and the new computer architecture: digital annealer technology will be introduced.

11:10 AM

(ICACC-FUL-025-2019) Investigation on electronic Structure at metal/oxide interfaces (Invited)

N. Ohashi*[1]; S. Hirose[2]; T. Ohsawa[1]; S. Ueda[1]

1. National Institute for Materials Science (NIMS), Japan
2. Murata manufacturing Co., Ltd., Japan

Electroceramics is a key for development of novel devices, such as E-vehicles and ITC devices. To gain further higher reliability and functionality, understanding of not only origin of the functions but also mechanism of degradation is of great importance. In particular, grain boundaries and hetero-interfaces are very important in these aspects. In this presentation, we focus on the metal/oxide interface in terms of defect structures and functionalization. The electronic structures and functions at the metal/titanate interfaces have been investigated with [Au or Pt]/[$SrTiO_3$ or $BaTiO_3$] interfaces prepared by sputtering. Various sputtering conditions were employed in order to see the effect of defect formation, as ionic bombardment during sputtering deposition is regarded as a cause for defect formation at the interface. Properties of the junctions were examined by electric measurements, such as I-V characteristics, and the electronic structures were characterized by X-ray photoemission with conventional AlKα radiation and synchrotron radiation. Here, the synchrotron light source was used to obtain hard-x-ray photoemission spectra. As a result, we have clearly demonstrated that dielectric properties of titanates are strongly affected by the sputtering conditions, such as input power, and the migration of defects are crucial for appearance of junction properties, such as ReRAM behaviors.

11:30 AM

(ICACC-FUL-026-2019) Experimental and Theoretical Analysis of Dopants for the Improvement of MLCC Lifetime (Invited)

Y. Iwazaki*[1]

1. TAIYO YUDEN CO., LTD., Research and Development Laboratory, Japan

Multi-Layer ceramic capacitor (MLCC) based on $BaTiO_3$ ferroelectric material is one of the well-known applications of ferroelectric oxide. Dopants in MLCC dielectric material is one of the important techniques to enhance their electronic properties. In this presentation, we will talk about our experimental and theoretical analysis of dopants, such as transition metal (vanadium), rare earth (holmium) and their combinations, and talk about the mechanism how these dopants improve the lifetime of MLCCs.

11:50 AM

(ICACC-FUL-027-2019) Integrating Data Sciences into Ceramic Science and Engineering Education (Invited)

E. C. Dickey*[1]

1. North Carolina State University, Materials Science and Engineering, USA

"Big Data" is becoming more prevalent in materials research and development, especially as high-throughput computation, large synchrotron scattering sources, and in-situ characterization tools become more widely available to the research community. As such, materials scientists need to be better educated in statistical data sciences, while data scientists have growing opportunities to address application opportunities and data-science research challenges in the physical sciences. This talk will discuss contemporary trends in interdisciplinary graduate education that intend to capitalize on emerging research methods. To prepare students for a more data-intensive research and development environment, several pilot graduate programs are being developed with support from the National Science Foundation (NSF) Research Traineeship Program. One such program is the Science and Engineering of Atomic Structure Traineeship at North Carolina State University. This traineship integrates Bayesian statistics, uncertainty quantification and materials informatics into the academic curriculum and fosters collaborative interactions and fluency across several physical sciences and mathematical disciplines.
(Supported by: NSF Grant No. DGE-1633587)

FS3: Chemically Processing of Functional Materials: Understanding the Conversion of Molecular Structures to Solid-State Compounds

Precursor Chemistry and Polymer Derived Ceramics I

Room: Coquina Salon C

Session Chairs: Ralf Riedel, TU Darmstadt; Zhaoju Yu, Xiamen University

8:30 AM

(ICACC-FS3-031-2019) Structure, energetics and bioactivity of polysiloxane-derived silicon oxycarbide-based glasses with highly connected networks (Invited)

E. Ionescu*[1]; S. Sen[2]; G. Mera[1]; A. R. Boccaccini[3]; A. Navrotsky[2]

1. Technical University Darmstadt, Materials Science, Germany
2. UC Davis, USA
3. FAU Erlangen-Nürnberg, Germany

In the present work, magnesium and magnesium/calcium bearing silicon oxycarbide glasses were prepared from polysilsesquioxane-based single-source precursors and investigated concerning their network architecture and thermodynamic stability. The obtained alkaline-earth silicon oxycarbide glasses show extremely high network connectivities. Furthermore, rthe investigated glass compositions were shown to be bioactive despite of network connectivity values higher than 5, much higher than that of vitreous silica, which itself is not bioactive. Silicon oxycarbide glasses may serve as model compounds for developing advanced design concepts for highly-connected bioactive glasses, which may be exciting material candidates for e.g. load-bearing applications. Thus, it seems that strong carbon-for-oxygen substitution in these glasses significantly improves their thermal and mechanical properties due to very high network connectivity; whereas at the same time, the bioactivity can be provided via minor depolymerization of the network with e.g. alkaline earth metals in combination with an open network architecture. Such a rational design of these materials may allow for

significantly improving their performance and expand the scope of their applications, which at the present time are rather limited.

9:00 AM

(ICACC-FS3-032-2019) Dimensionality Matters: Molecular Approach Towards Novel 0D, 1D and 2D Nanocarbon-Based Ceramic Composites

G. Mera*[1]

1. TU Darmstadt, Materials Science, Germany

The possibility to incorporate an extremely high content of carbon into the microstructure is a particular characteristic of polymer-derived ceramics (PDCs). The concentration, organization as well as the interface bonding of the segregated carbon phase with the surrounding matrix has been shown to play an important role on the nanostructure of materials as well as on their functional properties. Applications such as energy storage, photoluminescence, temperature and pressure sensors, are directly related to free-C phase in PDCs. In order to study the effect of the free-C phase (i.e., content, organization, interfaces etc.), novel SiO_2- and Si_3N_4-nanocarbon ceramic composites were produced upon the pyrolysis of preceramic precursors consisting of a highly crosslinked polysiloxanes and polysilazanes covalently functionalized with 0D, 1D and 2D-nanocarbons. As the polymers deliver C-free SiO_2 and Si_3N_4 upon pyrolysis, the nanocarbons were the exclusive carbon source in the obtained ceramics. The nanocomposites were structurally characterized and their thermal stability against crystallization and decomposition was carefully analyzed. Furthermore, selected functional properties thereof will be highlighted and discussed within the context of prospective energy-related applications.

9:20 AM

(ICACC-FS3-033-2019) Robust and electrically conducting graphene-modified polymer derived ceramics (Invited)

C. Salameh*[2]; M. Boussmen[1]; D. Voiry[1]; P. Miele[2]

1. Institut Europeen Des Membranes Montpellier, France
2. Ecole Nationale Supérieure de Chimie de Montpellier, France

Polymer derived ceramics (PDCs), silicon- and/or nitrogen-based ceramics synthesized by the thermal decomposition of polymeric precursors, present numerous attractive properties such as excellent high-temperature stability, thermo-mechanical properties, high piezoresistivity and high chemical stability attributed to their unique composition and structure. The polymer-to-ceramic process enables the incorporation of various functional materials into the ceramics leading to complex-shaped composites and devices. Such properties have made these materials promising for applications in energy storage, electromagnetic energy absorption, and high temperature sensors. In this work, we investigate the embedding of graphene networks into non oxide PDCs. Si-based and N-based polymer derived ceramics reinforced with graphene aerogels have been synthesized. The composition of the preceramic precursor, the cross-linking, the gel drying, the ratio between the polymer and the aerogel as well as the pyrolytic behavior were investigated. The different composites show increased electrical conductivity at elevated temperatures combined with good mechanical strength. The high porosity, light weight, together with the good electrical and mechanical properties, open new application field to polymer-derived composite aerogels.

9:40 AM

(ICACC-FS3-034-2019) New pressure-less sintering process of SiC powder using well-designed interstices

R. Usukawa*[1]; T. Ishikawa[1]

1. Tokyo University of Science, Yamaguchi, Applied Chemistry, Japan

SiC-polycrystalline fiber was synthesized by a conversion process from amorphous Si-Al-C-O fiber to SiC-polycrystalline fiber via degradation and sintering processes. During the conversion process, the degradation reactions ($SiO+2C \rightarrow SiC+CO$ and $SiO_2+3C \rightarrow SiC+2CO$) and the subsequent sintering proceed in the inside of each filament. Here we describe a new pressure-less solid sintering process of SiC powder making the best use of the abovementioned conversion process; the similar densification phenomenon proceeds in the interstices between SiC particles. In our process, to create the self-sintering interstices, we used aqueous silica compound containing equivalent carbon (for the carbothermal reduction) and small amount of aluminum (as a sintering aid for SiC crystals); subsequent calcination creates the nearly stoichiometric SiC phase containing small amount of aluminum between SiC particles. As can be seen from the abovementioned description, our process does not need ball-milling process which is needed for powder mixing using powdery sintering aid: contamination of impurities can be effectively avoided during the mixing process. Accordingly, using our new process, very simple pressure-less sintering of SiC powder was achieved to create a dense SiC sintered body with high purity. In this paper, our new sintering process and the fine structure of the obtained SiC sintered body will be described.

Precursor Chemistry and Polymer Derived Ceramics II

Room: Coquina Salon C

Session Chairs: Chrystelle Salameh, Institut Europeen Des Membranes Montpellier; Gunnar Westin, Uppsala University

10:20 AM

(ICACC-FS3-035-2019) High-Pressure Multifunctional Inorganic Nitrides (Invited)

R. Riedel*[1]

1. TU Darmstadt, Materials Science, Germany

High-pressure synthesis routes are expected to enable the access to a broad variety of novel nitride-based materials with properties far beyond that of the state of the art. Binary and ternary nitrides or oxynitrides are in the focus of this presentation. Theoretical predictions of novel metal or non-metal nitride solid-state structures guide our experimental studies. The use of a large volume press (LVP) allows to produce new materials in amounts suitable for further mechanical and functional characterization. Molecular single source precursors are synthesized and transformed to inorganic solid nitrides as starting materials for our high-pressure studies. Special emphasis is placed on (i) fundamental questions regarding pressure-temperature phase relations, (ii) nitrides, which have been predicted but not synthesized yet, and (iii) nitride-based (nano) composites which combine at least two binary high-pressure phases in one material. The novel nitride families are explored with respect to their most challenging and technologically relevant structural and functional properties including (i) hardness; (ii) semiconducting and electronic behaviour; (iii) ferromagnetism, (iv) optical transparency and (iv) photo(electro)catalytic behaviour. The high-pressure research is highly challenging but the successful synthesis of high-pressure nitrides will open new horizons in the fields of structural and functional materials.

10:50 AM

(ICACC-FS3-036-2019) Ultra-high temperature ceramic nanocomposites: Molecular synthesis, tailorable microstructure and advanced functional properties (Invited)

Z. Yu*[1]

1. Xiamen University, China

Numerous efforts have been made to improve the thermo-mechanical properties, oxidation and corrosion resistance of ultra-high temperature ceramics (UHTCs). For the first time, we discovered that polymer-derived UHTCs based on SiC-TiC, SiC-HfC and SiC-HfTaC nanocomposites also possess outstanding dielectric properties and electromagnetic (EM) performance. In this presentation, the synthesis and molecular structure of

single-source-precursors suitable to form the above mentioned UHTCs as well as the tailorable microstructure and dielectric features of the SiC-based UHTC nanocomposites derived therefrom will be discussed. In case of Hf containing single-source-precursor derived SiC/HfC_xN_{1-x}/C nanocomposites, a unique HfC_xN_{1-x}@C core-shell nanostructure has been formed in-situ, which plays an important role in improving the dielectric and EM performance of the resultant nanocomposites. With the introduction of Ta, the thickness of the carbon shell and the resultant electrical conductivity of the SiC/$Hf_yTa_{1-y}C_xN_{1-x}$/C nanocomposites can be precisely tuned by the Hf/Ta atomic ratios. The discovery of this family of novel UHTC nanocomposites constitutes substantial progress beyond the state of the art and shows enormous potential for EM applications in harsh environments.

11:10 AM

(ICACC-FS3-037-2019) A novel synthesis route to luminescent silicon nanocrystals in an amorphous silicon nitride matrix

G. Soraru*[1]; M. Biesuz[1]; R. Campostrini[1]; P. Bettotti[3]; M. Bortolotti[1]; G. Speranza[2]; O. Ersen[4]; M. Bahri[4]; S. Bernard[5]

1. University of Trento, Industrial Engineering, Italy
2. FBK, Italy
3. University of Trento, Physics Dept., Italy
4. University of Strasbourg, IPCMS, France
5. CNRS, Centre Européen de la Céramique, France

In this work we report the growth of luminescent silicon nanocrystals embedded in an amorphous silicon nitride matrix through a novel synthesis route based on the high temperature (950 – 1250 °C) pyrolysis of a Si-containing polymer in inert atmosphere (PDC route). The obtained materials were characterized by XRD, XPS and TEM, pointing out the formation of Si-nc@a-SiN_x nanocomposites. The correlations between annealing temperature and their microstructural/structural properties has been investigated. The optical characteristics of the Si-nc@a-SiN_x nanocomposites were deeply analyzed by photoluminescence spectroscopy and nonlinear optical measurements. The chemical resistance of the materials in strongly acid and basic environments was studied, as well. The results point out that the polymer-derived Si-nc@a-SiN_x nanocomposites combine the easiness of fabrication with interesting optical properties and chemical resistance, thus making them suitable for optical devices working in harsh environments.

11:30 AM

(ICACC-FS3-038-2019) Revealing interface characteristics of sol-gel derived SiOC glasses through bulk and surface characterization (Invited)

A. Tamayo*[1]; F. Rubio[1]; A. Mazo[1]; J. Rubio[1]

1. Institute of Ceramics and Glass, CSIC, Spain

Due to the nanostructured character of the sol-gel and polymer derived ceramics and glasses, the understanding of their structure at the nanoscale level becomes fundamental to decipher the unique features of these materials. The distribution of the nanodomains will determine the wide range of phenomena observed such as ionic conductivity, mechanical properties, creep and viscoelasticity. A collection of sol-gel derived silicon oxycarbide glasses with different carbon contents and nanodomain distribution is presented. Here, bulk characterization is combined with surface or interface-related techniques to determine, not only their interfacial characteristics but the nanodomain bulk properties as well. Inverse Gas Chromatography has been revealed as a powerful technique to extract the energetic data of the surface of the materials. The different contributions to the surface energy can be obtained from the interaction of the surface of the SiOC glasses either with polar or apolar molecules and branched or linear alkanes. Information about the surface topography can be compared with that obtained through the analysis of the adsorption data. Its combination with the spectroscopic characterization provides a deep knowledge of the microstructure of the materials in terms of the nanodomain distribution, chemical bonds at the interfaces and energetics of the surface.

11:50 AM

(ICACC-FS3-039-2019) Molecular manipulations of commercial oligosilazanes for processing of ceramic fibers, functional coatings and catalytically active ceramics

G. Motz*[1]; O. Flores[1]; L. Ribeiro[2]; P. Furtat[1]

1. University of Bayreuth, Ceramic Materials Engineering, Germany
2. Federal university of Santa Catarina, Chemical Engineering, Brazil

Since the first commercial production of silazanes in the 1980s, prices have fallen remarkably. Meanwhile, these precursors are commercially available on a ton scale at a reasonable price from Merck KGaA (Germany), but the variety of different silazanes is strongly limited, which prevents further distribution as for many applications a tailored precursor is required. However, the most common silazanes (PHPS, Durazane 1800 and 1033) are liquids but possess reactive groups like Si-H, Si-vinyl, N-H, and Si-N bonds suitable for precursor modifications. This presentation gives an insight in our activities to tailor the commercial oligosilazanes for special applications. The use of tetra-n-butylammoniumfluoride (TBAF) as catalyst leads to selective cross-linking via N-H and Si-H groups resulting in a meltable polysilazane suitable for processing of ceramic SiCN fibers. Using the same catalyst, the reaction of the oligosilazanes with trifluoroethanol leads to F-modified polysilazanes for coating applications. Furthermore, a carbon rich C/Si_3N_4 fiber with extraordinary oxidation stability was developed using an acrylonitrile/oligosilazane hybrid polymer. Finally, the reaction of various metal-aminopyridinato complexes with silazanes led after pyrolysis to catalytically active M@SiCN ceramics for different applications.

FS4: Green Technologies and Joining of Ceramics

Materials Processing from Ceramic, Plastic, Metallic, and Wastes I

Room: Tomoka C

Session Chairs: Carolina Tallon, Virginia Tech; Khwaja Hossain, Mayville State University

8:30 AM

(ICACC-FS4-001-2019) Additive manufacturing of portland cement pastes with additions of ash waste

L. Vergara[1]; H. Colorado*[1]

1. Universidad de Antioquia, Colombia

The main goal in this investigation is to develop formulations of Portland cement pastes for additive manufacturing with addition of ash wastes as admixture. A combination of kaolin, superplastificant and calcium carbonate were used as additives. The 3D printing process used was the direct ink writing technique, an inexpensive-based extrusion technique. Several formulations were built, from which some were able for the printing parts. Cylindrical samples were printed in order to be tested in compression tests. Parts with complex geometries were also printed in order to see the versatility of the formulations for the process. In addition to compressive strength, the microstructure was characterized with scanning electron microscopy and X-ray difraction.

8:50 AM

(ICACC-FS4-002-2019) Glass-ceramic Foams by Weak Alkaline Activation of Waste, Gel-casting and Sintering: Towards Permanent Materials

E. Bernardo*[1]

1. University of Padova, Department of Industrial Engineering, Italy

Highly porous glass-ceramic foams represent interesting solutions for thermal and acoustic insulation, but their extensive use is negatively affected by the manufacturing costs. In the present investigation, significant savings are proposed, by use of partially crystallized vitreous waste materials, such as powders from the polishing of porcelain stoneware and vitrified asbestos-containing waste, and minimization of additives and processing temperatures. Suspensions of waste powders, mixed with glass cullet and subjected to weak alkali activation (NaOH not exceeding 2.5M), were found to progressively harden, by formation of C-S-H gel and carbonates. An extensive foaming was determined by simple mechanical stirring, with the help of a surfactant. Finally, once ceramized at 1000 °C, the foams did not exhibit any degradation of the cellular structure previously obtained, but achieved excellent strength-to-density ratios. The firing actually determined just minor changes in the phase assemblage, from the starting raw materials, so that the same processing may be envisaged also for the recycling of the present glass-ceramic products once dismantled.

9:10 AM

(ICACC-FS4-003-2019) On the Design of Novel Lignin based Composites

K. Hall[2]; S. Abu Aldam*[1]; Y. Ji[2]; M. Dey[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA
2. University of North Dakota, Chemical Engineering, USA

Sustainability has become an important component of materials research. There is a continued search for novel materials which are renewable. Lignin is a promising candidate for sustainable materials, however, due to its heterogenous chemical nature it has not been commercialized although it is one of the largest source of aromatic chemicals. In this presentation, we will present some of the recent results on the synthesis and characterization PLA-Lignin and PHA-Lignin composites by advanced and additive manufacturing methods.

9:30 AM

(ICACC-FS4-004-2019) Towards the use of primary battery wastes in Colombia on route for a circular economy model for SME

H. Colorado*[1]

1. Universidad de Antioquia, Colombia

In this investigation, primary battery waste from Colombia is analyzed, processed and used in two research lines: hydrometallurgy for metal recovery and waste used as admixture in Portland cement. The valorization of this waste is an effort to further implement the circular economy in small and medium business enterprises (SME). Primary battery waste is mostly composed of zinc, manganese and iron oxides. Upon mechanical grinding and classification, the metal oxides were processed via hydrometallurgy. The waste was also introduced in white ordinary Portland cement in different concentrations and further evaluated with diverse characterization techniques. Microstructure was evaluated by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

Environmental Technologies

Room: Tomoka C

Session Chair: Kathy Lu, Virginia Tech

10:20 AM

(ICACC-FS4-005-2019) Environmentally Friendly Coatings for Corrosion Protection (Invited)

W. Fahrenholtz*[1]; M. O'Keefe[1]

1. Missouri University of Science & Technology, Dept. of Materials Science and Engineering, USA

Chromates, cadmium, and other toxic materials are widely used for corrosion protection of structural metal alloys. This presentation will review research from our group on the use of abundant rare-earth materials and other environmentally-friendly coatings for corrosion protection applications. Three different research areas will be discussed in which coatings containing hazardous compounds were replaced to reduce the environmental impact by eliminating sources of hazardous waste. The deposition mechanisms and corrosion inhibition mechanisms for cerium-based conversion coatings will be discussed with emphasis on electrochemical interactions in the near-surface region. The second coating type is epoxy-polyamide primers in which a praseodymium-based inhibitor has replaced chromates. Research revealed that the coatings protect by a dissolution-reprecipitation mechanism driven by local electrochemistry. Finally, research on replacement of cadmium from aerospace electrical connectors will be discussed. In this case, coatings based on zinc-nickel alloys that utilize a passivating layer were examined. The presentation will also describe the commercialization of these technologies.

10:50 AM

(ICACC-FS4-006-2019) Lead free Tin Iodide based perovskite solar cells: Optimization of electron and hole transport layers by simulation and analysis towards development of tandem configurations

J. Harris[1]; S. Ahmed*[2]; S. Banerjee[1]

1. California State University, Fresno, Mechanical Engineering, USA
2. SUNY Buffalo Satte, Mechanical Engineering, USA

The advantages of using perovskite for the active layer include but are not limited to broad a light absorption spectrum, tunable band gaps, long charge carrier diffusion, and low fabrication cost. The current project involves the design and simulation of different configurations of Lead Iodide active layer based lead-free perovskite solar cell. The goal of the project is to develop a configuration that is non-toxic as well as stable in natural open air environments with a specific resistance to moisture. This design incorporates the use of organic and inorganic materials, as well as the efficient use of the perovskite crystalline structure that is produced by using the properties of Tin. Different economical hole transport layers has also been explored to evaluate the impacts on opto-electronics, and photon-to-current conversion efficiencies. The stacking structure is further modulated within the cell by progressively including a recombination-inhibiting thin TiO2 of a ZnO layer with the FTO, followed by an electron-transport layer (various oxides). This work is intended to build up to a broader project of selecting the most optimal low-toxicity perovskite cell to stack onto a Si or FTO bottom cell for tandem configurations.

11:10 AM

(ICACC-FS4-007-2019) $Ca_xM_yO_z$ Solid Sorbents for CO_2 Capture: An in Situ X-Ray Diffraction Study (Invited)

E. Hassani[1]; T. Oh*[1]

1. Auburn University, USA

Global climate change presents a constant challenge to humankind. The release of CO_2 to the environment, the main cause of climate change, is greatly exacerbated by industrial activity. One way to mitigate this problem is post-combustion CO_2 capture using solid

sorbents. Calcium oxide-based materials, an economically favorable option due to its abundance and high adsorption capacity, suffers from significant long-term surface area loss during the carbonation/regeneration cycles. A simple solution is to introduce inert second phase by mechanical mixing. This will minimize the sintering of the calcium containing particles by limiting direct contact among CaO or $CaCO_3$ particles. In this research, different kind of metals, such as Fe, Co, Cu, are used to synthesize single-phase calcium metal oxide in form of $Ca_xM_yO_z$, then this solid precursor will be decomposed to CaO and the derivatives of metal oxides by reduction under hydrogen. The former is used as sorbent for CO_2, and the latter is a support to resist sintering and facilitate heat transfer. The temperature dependent carbonation/regeneration kinetics and CO_2 capture capacity change over cycling are investigated by collecting in situ X-ray diffraction pattern. Phase quantification of the CaO-based sorbents and their conversion to $CaCO_3$ is carried out by Rietveld refinement.

11:40 AM

(ICACC-FS4-008-2019) Development and Performance of Zirconia Based Oxygen Transport Membranes for Carbon Capture Processes

S. Pirou*[1]; P. Hendriksen[1]; A. Kaiser[1]; R. Kiebach[1]

1. Danmark Technical University, Energy, Denmark

Oxygen Transport Membranes (OTMs) can facilitate a more sustainable society by supplying oxygen to combustion processes, leading for example to more efficient Carbon Capture and Storage (CCS) or cement production. OTMs are dense ceramic membranes that only allow the transport of oxygen via migration of oxygen vacancies. The transport of electrons occurs in the opposite direction. OTMs are typically formed by Mixed Ionic Electronic Conductors (MIEC). Dual-phase membranes are a good option for applications under harsh conditions (e.g. flue gas containing CO_2, SO_2, H_2O) because they consist of a composite of a stable ionic conductor and a stable electronic conductor, which can combine high oxygen flux and chemical stability at the same time. This work will describe the use and benefits of OTMs for carbon capture processes and present the development and performance of planar zirconia based dual-phase OTMs taking place at the Technical University of Denmark (DTU). Three composite materials based on the ionic conducting phase 10Sc1YSZ $((Y_2O_3)_{0.01}(Sc_2O_3)_{0.10}(ZrO_2)_{0.89})$: 10Sc1YSZ-$MnCo_2O_4$, 10Sc1YSZ-$Al_{0.02}Zn_{0.98}O_{1.01}$ and 10Sc1YSZ-$LaCr_{0.85}Cu_{0.10}Ni_{0.05}O_{3-\delta}$ were successfully prepared and characterized as planar dual-phase asymmetric OTMs for direct operation (4-end mode membrane module) in oxy-fuel combustion power plants.

Materials Processing from Ceramic, Plastic, Metallic, and Wastes II

Room: Tomoka C

Session Chairs: Milena Salvo, Politecnico di Torino; Surojit Gupta, University of North Dakota

1:30 PM

(ICACC-FS4-009-2019) SiSiC Ceramics based on Wood Polymer Composites (WPC) (Invited)

W. Krenkel*[1]; T. Liensdorf[1]

1. University of Bayreuth, Ceramic Materials Engineering, Germany

A novel approach to fabricate silicon infiltrated silicon carbide (SiSiC) ceramics, based on wood polymer composites, is described. WPCs are bio-based materials which are used in the automotive, construction and furniture industry and replace more and more tropical wood. The main advantages of this processing route in comparison to conventional processes are the high degree of formability and the absence of any hard particles (e.g. primary SiC) in the feedstock prior to the shaping of the green body, which can be done by injection molding, extrusion or warm pressing. Thermoplastics (e.g. polyethylene, polyamide and novolac) have been used as binding materials, which were subsequently pyrolized and siliconized at temperatures up to 1600°C. In order to maintain the shape and to reduce the shrinkage during the pyrolysis step, different additives and/or thermally pre-treated wooden particles were added to the WPC. The microstructure and the material's properties (flexural strength, porosity, density, etc.) in the different stages (green body, pyrolysate and final SiSiC ceramic) were studied. The phase compositions were analyzed by X-ray diffraction and Rietveld analysis and compared with conventionally manufactured SiSiC ceramic materials. The correlations between the chemistry, the microstructure, the properties, and the manufacturability of these new materials are discussed.

2:00 PM

(ICACC-FS4-010-2019) Silicon Oxycarbide Through Flash Pyrolysis (Invited)

K. Lu*[1]; L. Wang[1]; R. Ma[1]; D. Erb[1]

1. Virginia Tech, USA

For the first time, flash pyrolysis was carried out to fabricate polymer derived silicon oxycarbide (SiOC) ceramics. With the application of a DC electric field at a furnace temperature of only 780 °C or lower, the SiOC ceramics exhibit characteristics that usually have to be pyrolyzed at ~1300 °C. Both electric field and current density accelerate the SiOC microstructure development, causing carbon and SiC phases to form at >500 °C lower pyrolysis temperatures than conventional within the SiOC matrix. With higher electric fields, the samples experience greater mass loss and linear shrinkage, while also forming more SiC and a more ordered carbon phase. The SiC formation inversely impacts the carbon content, causing a decrease in electrical conductivity. Further, reducing current density, electric fields, and pyrolysis temperature results in significant carbon precipitation without SiC formation. This study provides a novel route to synthesize high temperature SiOC nanocomposites. The fundamentals can be explained based on increased nucleation rate by the electrical field, accompanied by Joule heating and electromigration. This work is the first to demonstrate the great potential of flash pyrolysis on accelerated phase separation of polymer derived SiOC and can be a much greener technology in producing high temperature materials.

2:30 PM

(ICACC-FS4-011-2019) Harnessing the Lignocellulosic Components of Wheat Bran to Develop Bio-composites for Industrial Usage (Invited)

K. G. Hossain*[1]

1. Mayville State University, Science and Mathematics, USA

The bio-based composites have emerged as potential alternatives to fossil-based composites because of their renewability, low density, biodegradability, low cost, and low toxicity while providing similar structural performance. A large array of fiber sources like wood, hemp, feather, and corn hull have been explored for composite usage. However, wheat bran fibers have not been utilized in composites. Wheat grain contains nearly 14.5% bran and millers dispose about 90% of bran as waste which causes environmental pollution. Each year, farmers lose over 31 million bushels of their produce as bran which could boost farmers return, rural economy, industries, and reduce environmental pollution if it was used as industrial resource. The chemical treatment of water-insoluble fiber exposes higher percentage of cellulose and can be utilized as reinforcing material. Our ultimate goal is to incorporate wheat bran in various industrial applications. Recently, we have analyzed wheat bran from different classes of wheat and identified a pretreatment method before using in bio-composite. In our work, we treated wheat bran with NaOH and prepared composites with polypropylene at varying fiber loading rates. The mechanical properties showed a 16.3% increase in flexural strength and comparable tensile strength with Polypropylene at 20% or more fiber loading rates.

Ceramic Joining for Ambient and Extreme Environmental Applications

Room: Tomoka C

Session Chairs: Henry Colorado, Universidad de Antioquia; Marion Herrmann, Technische Universität Dresden

3:20 PM

(ICACC-FS4-012-2019) Processing and characterization of advanced ceramic-based joined components (Invited)

M. Ferraris*[1]; M. Akram[1]; M. Bangash[1]; V. Casalegno[1]; S. De La Pierre[1]; P. Gianchandani[1]; A. Sabato[1]; M. Salvo[1]; F. Smeacetto[1]

1. Politecnico di Torino, Department of Applied Science and Technology, Italy

Innovation in processing and characterization of advanced ceramic-based joined components developed at GLANCE-Glasses, Ceramics and Composites research group at Politecnico di Torino, Italy (www.composites.polito.it) will be presented and discussed. Joined components for nuclear (fusion and fission), solid oxide cells and concentrated solar energy production, also in the form of sandwich structures have been designed, fabricated and characterized in simulated working conditions: recent results on each topic will be briefly reviewed. The combination of advanced design of interfaces and joining materials/technologies, selective matrix removal from the composite surface, laser structuring and mechanical machining of the composite/metal surfaces will be discussed and compared to existing solutions. The work done with the aim of developing reliable and user-friendly international standard test to measure the shear strength of joined components will be reviewed. Finally, J-TECH@POLITO, a recently funded Advanced Joining Technology research center at Politecnico di Torino, will be described together with collaboration actions and opportunities for common research activity on joining.

3:50 PM

(ICACC-FS4-013-2019) Surface pre-treatments to improve joint strength of ceramics (Invited)

M. Salvo*[1]; V. Casalegno[1]; M. Ferraris[1]; C. Wilhelmi[2]; M. Suess[2]

1. Politecnico di Torino, Department of Applied Science and Technology (DISAT), Italy
2. Airbus Defence and Space GmbH, Space Systems, Mechanical Products and Engineering GE, Germany

The full exploitation by the aerospace industry of the attractive and unique properties of ceramics and ceramic composites calls for effective joining technologies that may help to assemble them in complex shapes or to combine them with metallic parts forming hybrid structures. Surface pre-treatments are widely recognized as one of the key steps to producing robust and reliable bonds. Surface pre-treatments, using advanced techniques such as laser nano-structuring, plasma etching on SiC, Si_3N_4 and thermal selective removal on SiC based composites will be discussed. Pre-treated joined samples showed a higher mechanical strength than the reference value (lapped surfaces). Some reference and laser-treated similar and dissimilar joints were submitted to a severe cryo-cycling test (from room temperature to 50 K), and it was found that exposure at these extremely low temperatures did not affect the mechanical integrity of the joints.

4:20 PM

(ICACC-FS4-014-2019) Novel processing of SOFC glass-ceramic sealants based on the sintering of glass powders mixed with a reactive silicone binder

E. Bernardo*[1]; H. Elsayed[2]; H. Javed[2]; F. Smeacetto[3]

1. University of Padova, Department of Industrial Engineering, Italy
2. Politecnico di Torino, Department of Applied Science and Technology, Italy
3. Politecnico di Torino, Department of Energy, Italy

It is well known that sacrificial binders for glass powders may determine some defects in the final product directly, by incomplete decomposition at low temperature and gas evolution upon viscous flow sintering, or indirectly, by offering poor adhesion between particles, so that 'green' compacts may be easily damaged. The present investigation is aimed at exploring a novel concept for sintered glass-ceramics, based on the adoption of a silicone polymer as reacting binder, providing an abundant ceramic residue after firing. A glass belonging to the $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ system, already studied as a sealant in solid oxide fuel cell (SOFC) planar stack design, was reproduced in form of 'silica-defective' variants, featuring a SiO_2 content, in the overall formulation, reduced up to 15 wt%. The overall silica content was recovered by mixing powders of the new glasses with the silicone: upon firing in air, the interaction between glass powders and polymer-derived silica led to glass-ceramics with the same assemblage than those formed by the reference glass. The new approach has been successfully applied to the actual manufacturing of glass-ceramic joints.

4:40 PM

(ICACC-FS4-015-2019) Glass/glass-ceramics for joining of materials in energy sectors

M. Mahapatra*[1]

1. University of Alabama at Birmingham, Materials Science and Engineering, USA

Glass/glass-ceramics are gaining attention for joining similar and dissimilar materials. Various glass systems have been investigated for joining active and inactive components of high temperature electrochemical systems. Recent progress in glass joining will be reviewed. In addition, the potential of glass joining for other high temperature joining applications will also be discussed.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation II

Room: Coquina Salon D

Session Chairs: Jonathan Salem, NASA Glenn Research Center; Michael Jenkins, Bothell Engineering and Science Technologies

8:30 AM

(ICACC-S1-029-2019) Forty years after the promises of ceramic steel: Zirconia-based composites with a metal-like mechanical behavior (Invited)

J. Chevalier*[1]

1. INSA Lyon, Materials Science, France

40 years ago, Garvie and co-workers reported that the transformation of metastable tetragonal zirconia grains towards the monoclinic symmetry could give rise to a powerful strengthening mechanism. Their results even led them to consider zirconia systems as analogues of certain steels. This seminal paper created an extraordinary excitement in the ceramic community and is still the subject of extensive research. Transformation toughening is widely used in a series of zirconia materials and leads to an increase in strength when

compared to non-transformable ceramics, but the translation into tough, strong and sufficiently stable materials is not fully addressed. For most industrial applications, zirconia ceramics fail at low strains with a much larger scatter in the strength values than metals and statistical approaches of failure are required. Here we describe in details the mechanical behavior laws of ceria-doped Zirconia composites exhibiting a high degree of stress-induced transformation. They exhibit, in some extent, a mechanical behavior analogue to a metal with a significant amount of transformation-induced plasticity without damage, a very high flaw tolerance and almost no dispersion in strength data. Their potential use in new applications, where the advantages of ceramics were dampened by their failure properties, is critically discussed.

9:00 AM

(ICACC-S1-030-2019) Can we predict zirconia ageing from processing parameters?

L. Gremillard*[1]; C. Wei[1]

1. INSA-Lyon, MATEIS, France

Hydrothermal ageing of yttria-stabilized tetragonal zirconia ceramics can be one of the most important phenomena limiting the lifetime of zirconia devices. It is a transformation from the metastable tetragonal phase to the stable monoclinic one, in the presence of water, and that results in roughening and potentially microcracking of the near-surface. Ageing kinetics are often described by the Mehl–Avrami–Johnson equation, most often used as a phenomenological description. This work seeks to relate the parameters of MAJ equations (V_{max}, n, b_0 and Q) to key microstructural features of the zirconia material: grain sizes, Y_2O_3 partitioning, monoclinic, tetragonal and cubic phases ratio. To this end, samples with identical nominal composition of 3Y-TZP were prepared with different sintering parameters. A relationship between microstructural parameters and sintering cycles was first proposed, followed by a relationship between ageing parameters and microstructural parameters. A particular behavior (very low activation energy) was also detected in some materials. These results provide a convenient framework to better develop the sintering cycle of zirconia biomaterial in order to maximize their resistance to hydrothermal ageing.

9:20 AM

(ICACC-S1-031-2019) Reactive Melt Infiltration of carbon fibre reinforced ZrB_2 composites with Zr_2Cu

A. Vinci*[1]; M. Kuetemeyer[2]; L. Zoli[1]; D. Sciti[1]; D. Koch[2]

1. ISTEC-CNR, DSCTM, Italy
2. DLR - German Aerospace Center, Germany

Ultra-high temperature ceramics (UHTCs) are a class of materials characterized by very high melting points, ablation resistance and high thermal conductivity and are being considered for the application in extreme environments. The major drawbacks are low resistance to crack propagation and thermal shock. Conventional routes to the consolidation of UHTCs involve the sintering of raw powders by Hot Pressing or Spark Plasma Sintering. Previous studies have shown the capability of carbon fibres to increase the damage tolerance of UHTCs but their presence hinders sintering. An alternative process for the fabrication of these materials is the in-situ synthesis of the UHTC phase by reactive melt infiltration (RMI), which allows to obtain near fully dense materials at lower temperatures by filling the voids with the liquid melt. In this study, various carbon fibre reinforced ZrB_2 composites were produced by RMI with the Zr_2Cu melt at 1200°C. The microstructure was analysed by SEM – EDS and X-Ray diffraction and mechanical properties were evaluated. The microstructure is fully dense and characterized by the presence of coarse and fine ZrB_2 particles, ZrC, Zr_2Cu. Fibres show moderate signs of reaction in melt-rich regions owing to the formation of ZrC at the interface. The presence of residual Zr_2Cu must be addressed and reduced in order to not jeopardize the high temperature properties of these materials.

9:40 AM

(ICACC-S1-032-2019) Manufacturing of Damage Tolerant Fiber Reinforced Ceramic Composites with UHTC based Matrices via Reactive Melt Infiltration

M. Kuetemeyer[1]; A. Vinci[2]; D. Sciti[2]; D. Koch*[1]

1. German Aerospace Center, Institute of Structures and Design, Germany
2. ISTEC-CNR, DSCTM, Italy

Reactive melt infiltration is a manufacturing process used to fabricate ceramic matrix composites (CMC), achieving a dense microstructure without extensive reinfiltration cycles. As a first step a dense preform containing carbon fibers and a boron based matrix is manufactured. During pyrolysis, a capillary pore structure forms. In the final processing step, liquid alloy enters the porous structure and reacts exothermic with the porous matrix to form a new high temperature stable phase. With this process ultra high temperature stable ceramic matrix composites (UHTCMC) with boride based matrices are produced. In order to provide a damage tolerant behavior, the fibers need to survive this process. Therefore it is favorable for the fibers to be protected against the reaction. Critical issues of the manufacturing process are presented and the key issues are evaluated. The mechanical properties of these UHTCMCs and their high temperature potential are discussed and correlated with micromechanical characterization.

10:20 AM

(ICACC-S1-033-2019) Damage tolerant carbon fibre reinforced ZrB_2/SiC composites

A. Vinci*[1]; L. Zoli[1]; D. Sciti[1]; C. Gutierrez[2]; S. Rivera[2]

1. ISTEC-CNR, DSCTM, Italy
2. Nanoker Research S.L., Spain

Ceramic matrix composites (CMCs) based on C/C or C/SiC are characterized by excellent mechanical properties but are not suitable for temperatures above 1600°C due to significant oxidation and erosion of the material. To overcome these limits we are developing a new class of composites which combines the good fracture toughness of CMCs with the oxidation and ablation resistance of ultra-high temperature ceramics. The aim of this work is to demonstrate the possibility to produce damage tolerant UHTC composites and provide an overview of the mechanical properties of these materials. The evaluation of damage tolerance has been object of discussion in the past few years due to the difficulty to introduce a relevant defect in the composite and test their fracture toughness, and currently there are no validated standards for the testing of K_{IC} for these materials. In the present work three-point chevron notch bending tests were used to measure the work of fracture and give a rough idea of the damage tolerance of these materials. Flexural strength was evaluated by three-point bending tests. Results show an increase of the strain to failure and fracture energy for the sample reinforced with fibers at the expense of the ultimate flexural strength. Young modulus is much lower than the corresponding bulk ceramic which can be attributed to the higher porosity and the presence of damaged fibers.

10:40 AM

(ICACC-S1-034-2019) Preparation and Characterization of Pure SiC Ceramics via High Temperature Physical Vapor Transport Induced by Seeding with Nano SiC Particles

Y. Deng*[1]; J. Yang[1]; N. Zhang[1]; B. Wang[1]

1. State Key Laboratory for Mechanical Behavior of Materials, China

Silicon carbide has always played an important role in the high temperature fields, due to its high strength, good resistance to oxidation, and excellent thermophysical properties. The method of high temperature physical vapor transport(HTPVT)is an available approach to prepare high density and purity silicon carbide ceramics. In this work, HTPVT was employed to grow polycrystal SiC ceramics, induced by seeding with nano SiC particles. The

obtained SiC ceramics were identified as 6H-SiC with a mainly preferred orientation along (0006) plane, and an obvious refinement of grain size was demonstrated for the SiC seeds. Mean grain sizes of SiC ceramics were 112μm and 314μm, by using the SiC seeds with mean particle size of 50nm and 500nm, respectively, which were obviously smaller than 960 μm for the seed-free sample. The samples induced by seeding also demonstrated enhanced flexural strength and hardness, attributed to the reduced mean grain size. Furthermore, SiC ceramics without seeds via HTPVT exhibited a high thermal conductivity of 242W×(m×K)$^{-1}$ at room temperature due to the highly preferred orientation. While the degree of preferred orientation of seed-induced samples was lower, the thermal conductivity of SiC ceramics induced by seeding still maintained at least 200W×(m×K)$^{-1}$, this level was much higher than other most methods.

11:00 AM

(ICACC-S1-035-2019) Evaluating and Visualizing the Effect of Binders on the Green Strength of Dry-Pressed Spray-Dried Alumina

I. Maher*[1]; R. A. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

In this study, alumina was the system analyzed and was processed by spray drying alumina slurries with two varying binders, an acrylic emulsion binder and a polyvinyl alcohol (PVA) binder, to evaluate the adhesion differences between the respective spray-dried granules and green strengths. Green strength measurements were conducted using a 3 point modulus of rupture testing apparatus with an Instron mechanical tester. Moisture was added to certain granules to evaluate the difference of green strength with the addition of moisture as a plasticizer for the PVA binder. Image analysis was conducted to understand the fracture surface of the dry-pressed alumina green body by the use of a field emission scanning electron microscope. The plasticity of the spray dried granules on a compaction scale was used as a tool to determine the effects of binder and processing parameters on the density and microstructural uniformity of the compacts.

11:20 AM

(ICACC-S1-036-2019) Characterizing the influence of local microstructure on ferroelastic deformation in ceramics

C. S. Smith*[1]; J. A. Krogstad[1]

1. University of Illinois at Urbana-Champaign, Materials Science and Engineering, USA

Ferroelastic deformation is known to lead to increased toughness in many electroceramic and structural ceramic materials. However, the affect that different local microstructures may have on the extent of ferroelastic deformation and toughening is not yet understood. In this study, the mechanism of ferroelastic deformation and its behavior in various ceramic microstructures has been examined. Microindentation has been used to induce ferroelastic deformation in bulk polycrystalline ceramic microstructures. The local microstructure associated with regions of favorable ferroelastic deformation has then been examined using electron backscatter diffraction (EBSD). Furthermore, deformation of single crystal and polycrystalline ferroelastic ceramics has been done using in situ transmission and scanning electron microscopy respectively. In situ electron microscopy has been used to characterize stresses and strains associated with the ferroelastic deformations. Characterizing the influence of local microstructure on ferroelastic deformation may have implications for designing microstructures for high toughness in the future.

11:40 AM

(ICACC-S1-037-2019) Thermal Stability of the Mechanically Alloyed 2SiB$_3$CN Ceramic

P. Zhang*[1]; R. Yu[1]; B. Yang[1]; D. Jia[2]; Z. Yang[2]

1. Henan University of Science and Technology, School of Materials Science and Technology, China
2. Harbin Institute of Technology, China

By the mechanical alloying and hot pressing technique, the amorphous and nano 2SiB$_3$CN ceramics were prepared, whose thermal stability was investigated. Results show that, for the mechanically-alloyed (MA) amorphous 2SiB$_3$CN ceramic, the crystallization temperature lies between 1500ºC and 1800ºC, and the rapid densification temperature is about 1830ºC. For the nano 2SiB$_3$CN ceramic, the phase composition consists of α-SiC, β-SiC and BN(C), and SiC has an average grain size of 58.19 nm. Compressed the nano ceramic at 1400ºC and under a pressure of 125 MPa for 24 hrs, the steady-state creep rate and the creep strain of the sample is 5.5×10^{-10} /s and 0.27%, respectively. Annealed the nano ceramic at 1800ºC in nitrogen for 3 hrs, the ceramic crystallinity, the α-SiC content and the grain size is increased, while the mechanical properties are reduced. For the as-annealed 2SiB$_3$CN ceramic, the average size of SiC grains is increased to 86.75 nm. The bending strength, elastic modulus, fracture toughness and Vickers hardness is 286.9 MPa, 98.2 GPa, 2.74 MPa×m$^{1/2}$ and 5.44 GPa, respectively. Additionally, the as-annealed ceramic produces a weigh loss of 3.55% and a linear shrinkage of about 0.2-0.5%. In the MA-2SiB$_3$CN ceramic, SiC and BN(C) enclose each other, and those covalent compounds generally have small diffusion coefficient. This may be the main reason why the MA-2SiB$_3$CN ceramic has such high thermal stability.

Processing - Microstructure - Mechanical Properties Correlation III

Room: Coquina Salon D

Session Chairs: Emmanuel Maillet, GE Global Research; Dietmar Koch, Institute of Structures and Design

1:30 PM

(ICACC-S1-038-2019) Manufacturing of damage tolerant C/C-SiC composites by adjustment of fiber matrix interface during processing

D. Koch*[1]; B. Heidenreich[1]; J. Neraj[1]; M. Kosin[1]; Y. Shi[1]; M. R. Buchmeiser[2]; S. Horn[3]

1. German Aerospace Center, Institute of Structures and Design, Germany
2. DITF, Germany
3. University of Augsburg, Germany

The Liquid Silicon Infiltration (LSI) process is applied to manufacture carbon fiber based C/C-SiC composites. A fiber preform is infiltrated with a phenolic resin which is then converted to carbon during high temperature pyrolysis treatment. This step induces a high amount of porosity. The pore morphology varies from fine pores throughout the composite up to large pore channels with block-like, pretty dense C/C fiber matrix areas. These different crack formations mainly depend on the fiber matrix-bonding in the polymeric state. Depending on the pore morphology, the liquid silicon converts carbon to SiC either only along the large pore channels or throughout the composite. SiC formation throughout the composite leads to favorable frictional behavior, while block like C/C areas surrounded by SiC phases are preferred when damage tolerant failure behavior is required. In the present study, the crack formation during pyrolysis is simulated in a FE-model. This model evaluates the effects of layer thickness, fiber volume fraction, fiber matrix bonding and other essential microstructural properties on the formation of different cracks during shrinkage under thermal treatment. In parallel, real composites are manufactured via LSI with different surface treated fibers. Mechanical tests and microstructural investigations are used to characterize the resulting composites.

1:50 PM

(ICACC-S1-039-2019) Microstructure formation during C/C-SiC composite manufacturing as a function of carbon fiber surface modification

W. M. Mueller*[1]; M. Schulz[1]; B. Brueck[1]; T. K. Schneck[3]; F. Hermanutz[3]; B. Clauss[3]; B. Heidenreich[2]; M. R. Buchmeiser[3]; D. Koch[2]; S. Horn[1]

1. University of Augsburg, Germany
2. DLR - German Aerospace Center, Germany
3. DITF - German Institutes of Textile and Fiber Research, Germany

The Liquid Silicon Infiltration (LSI) represents an efficient process for manufacturing of ceramic matrix composites as lightweight structural materials with excellent mechanical properties and high temperature and thermo-shock stability. The damage-tolerant failure behavior of C/C-SiC composites relies on their well-adapted microstructure based on dense C/C bundles enclosed by a SiC network. Due to the lack of a fundamental understanding of the formation of this microstructure including the role of fiber-matrix interaction, the potential of this class of materials is not yet fully exploited. So far, the favorable microstructure can be generated only with carbon fibers of medium strength and modulus, and with only few empirically selected matrix precursors. In the present study a systematic variation of the fiber-matrix interaction based on variation of process parameters during anodic oxidation treatment of the fibers was performed. C/C-SiC composites were manufactured from differently surface-activated fibers, and were investigated along the entire process chain, starting from the carbon fiber surface, the CFRP greenbody and its carbonized C/C state, up to C/C-SiC. The analysis comprises AFM, XPS (fiber surface), single-fiber push-out test (fiber-matrix interaction), SEM, porosimetry (microstructure) and mechanical testing, and identifies relevant correlations.

2:10 PM

(ICACC-S1-040-2019) Effects of slurry concentration on the properties of SiC_f/SiC fiber-reinforced ceramic composites made by precursor impregnation and pyrolysis process

S. Lee*[1]; J. Gu[1]; H. Lee[1]

1. Korea Institute of Materials Science, Republic of Korea

SiC_f/SiC ceramic matrix composites (CMC) tubes with the size of Φ50×100×3mm were prepared by using PyC coated Tyranno-SA3 grade SiC fiber and liquid polycarbosiane (PCS) ceramic precursor. Ultra-fine SiC powder (d_{50}: 170nm), prepared by mechanical alloying process, was used to prepare aqueous SiC slurries with the solid loading of 20, 30, 40 and 60 vol%. By the optimization of the dispersion condition and the oxidation treatment of the SiC powder, SiC slurry up to 66 vol% solid loading was successfully prepared. The slurries were infiltrated into the fiber fabrics and the properties of the CMC prepared by precursor-impregnation & pyrolysis process (PIP) were analyzed. The slurries with high solid loading induced the formation of dense SiC layer at the surface of the fiber preforms, which suppressed the efficient infiltration of the slurry. The weight of the CMC prepared using 60vol% slurry increased linearly up to 4 PIP cycles and the mass gain became less efficient afterwards. High temperature treatment of the CMC after 6 PIP cycles helped to increase the mass gain of the CMC. The effect of the slurry concentration on the green density, PIP efficiency and mechanical properties of the CMC were analyzed.

2:30 PM

(ICACC-S1-041-2019) Mechanical Properties of SiC/SiC Minicomposite with Various Matrix Thicknesses at Elevated Temperatures

T. Kato*[1]; K. Kawanishi[1]; S. Muto[1]

1. IHI Corporation, Materials Technology Department, Japan

SiC based ceramic matrix composites reinforced by SiC continuous fibers (SiC/SiC) have been investigated for application to aircraft engines such as blades, vanes, liners, and shrouds. Because of their lower density, higher strength, and higher durability at high temperature compared to conventional metallic alloys, SiC/SiC composites are expected to improve the efficiency of aircraft turbine engines. Thus, the understanding of properties of their constituents such as fibers, matrix, and interface coatings is of great importance. Minicomposites or unidirectional composites with a single bundle of fibers are an appropriate way to investigate these properties due to their simple geometry compared to woven 2D or 3D CMCs, and they can be fabricated at a lower cost and a shorter time than woven CMCs. In the present study, the mechanical properties of SiC/SiC minicomposite with various matrix thicknesses fabricated via chemical vapor infiltration (CVI) were determined by monotonic tensile testing under the wide range of temperature (RT-1200C). They were compared with those of precracked minicomposites and the fiber bundles the same batches of whom were used for minicomposites. The shape of force-displacement diagram of precracked minicomposites differed from those of minicomposites but showed nearly the same as those of bundles.

3:10 PM

(ICACC-S1-042-2019) Microstructure-based modeling of the ultimate tensile strength of ceramic matrix composites

E. Maillet*[1]; D. Dunn[1]

1. GE Global Research, USA

Ultimate tensile strength (UTS) is a key mechanical property controlling performance. In ceramic matrix composites (CMCs), UTS depends on the strength of the reinforcing fibers, and on microstructural attributes that determine local fiber stress. These attributes include fiber radius, coating thickness, distance between fibers, fiber and matrix moduli, and interfacial properties. In the present approach, the stress on each fiber is estimated analytically based on local microstructural characteristics, and UTS is predicted with a progressive failure model. The model is used to identify the main factors affecting UTS, and to predict UTS of actual CMC microstructures.

3:30 PM

(ICACC-S1-043-2019) Microstructure-based modeling of the interlaminar tensile strength of ceramic matrix composites

M. Moscinski*[1]; A. Cerrone[1]; P. Meyer[1]; E. Maillet[1]; D. Dunn[1]

1. GE Global Research, USA

Interlaminar capability, resisting forces trying to peal apart the various layers of material, is one of the critical properties to understand when designing components with a layered composite material such as ceramic matrix composites (CMCs). Interlaminar capability is a strong function of the microstructural composition which includes the properties of the constituents as well as their relative spatial locations. The presentation will compare both a damage based FEA approach along with a geometry based simplified model for estimating the influence microstructural variations have on the resulting interlaminar strength properties. These variations include fiber size, coating thickness, fiber spacing along with the properties of the fibers, coatings and matrix material.

3:50 PM

(ICACC-S1-044-2019) Image analysis technique for estimating ceramic matrix composite properties

A. Cerrone*[1]; M. Moscinski[1]; A. Santamaria-Pang[1]

1. GE Global Research, USA

The microstructural character of a ceramic matrix composite (CMC) dictates its mechanical properties related to structural integrity and strength. Micrographs are commonly generated during manufacturing to provide initial assessments of quality; however, these images can further be used to quantify capability. The presentation will detail a computational technique which ingests these micrographs and interrogates them to assess fracture-related properties

of the material system. This technique is based on the fast marching method and operates on micrographs whose constituents have been segmented. This computationally efficient approach will be shown to compare favorably with more expensive finite element techniques.

4:10 PM

(ICACC-S1-045-2019) Microstructure-based modeling of the thermal-elastic properties of ceramic matrix composites

M. Moscinski*[1]; A. Cerrone[1]; P. Meyer[1]; E. Maillet[1]; D. Dunn[1]

1. GE Global Research, USA

One of the fundamental requirements of designing any mechanical component is understanding the basic thermal-elastic properties of the underlying material. Composite materials such as ceramic matrix composites (CMCs) create some additional complexities with determining these standard material properties. Variations in the microstructure of CMC material can have a significant influence in the elastic and thermal properties. The presentation will highlight an approach for extracting microstructure details from an existing CMC sample and using a generalized method of cells based tool for estimating the corresponding thermal elastic properties.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

CMAS Degradation of EBC/TBC: Effects and Mitigation Strategies II

Room: Tomoka B

Session Chair: Peter Mechnich, DLR - German Aerospace Center

8:30 AM

(ICACC-S2-026-2019) Understanding the Stability of the Garnet Phase in the Context of Reactions Between T/EBCs and Silicate Deposits

E. Godbole*[1]; S. Berens[1]; D. L. Poerschke[1]

1. University of Minnesota, Chemical Engineering and Materials Science, USA

Understanding the interactions between calcium magnesium aluminosilicate (CMAS) deposits and T/EBC materials is critical to develop coating materials resistant to degradation caused by these deposits. For segmented TBCs, lifetime can be increased through the formation of crystalline phases which can block the coating channels thus mitigating further melt penetration. For dense EBCs, it is desirable to minimize the reactions consuming the coating. A variety of crystalline reaction products are possible depending on the composition of the coating and deposit. However, while reaction product phases such as apatite have been studied extensively, less is known about the stability of the yttrium-containing aluminosilicate garnet phase. This work expands the understanding about the garnet solid solution field in this system. An understanding of crystal chemistry was used to derive the range of theoretical garnet solid solution stoichiometries. These were then synthesized, heat treated at different temperatures and analysed to determine the actual phase equilibria and temperature dependent solid solution fields. Complementary experiments were used to understand the transition from apatite to garnet formation depending on deposit composition. This experimental data was used to further develop thermodynamic databases supporting computational TBC and EBC design tools.

8:50 AM

(ICACC-S2-027-2019) Effect of initial composition, morphology, and feed rate of synthetic calcium-magnesium-alumino-silicate (CMAS) on the extent of damage to thermal barrier coatings

B. Jun*[1]; E. H. Jordan[2]; R. C. Cooper[2]; R. Dibiase[1]

1. University of Connecticut, Materials Science, USA
2. University of Connecticut, Mechanical Engineering, USA

Thermal barrier coatings (TBCs) are susceptible to reduced lifetimes due to the infiltration of calcium-magnesium-alumino-silicate (CMAS). CMAS can vary in composition by region and source and this can have implications in terms of the aggressiveness of the deposits. The present study investigates the variation in infiltration depth, extent of chemical attack, and mechanical damage on TBCs as a function of feed rate, initial composition, and morphology of the deposit using a flame-based thermal gradient rig. This behavior was examined at multiple fractions of full TBC spall life using primarily scanning electron microscopy

9:10 AM

(ICACC-S2-028-2019) Thermochemical Effect of Alternative Fuel Impurities on the Degradation of YSZ Thermal Barrier Coatings

J. H. Ramirez Velasco*[1]; H. Kenttämaa[2]; G. Kilaz[3]; R. Trice[1]

1. Purdue University, Materials Engineering, USA
2. Purdue University, Department of Chemistry, USA
3. Purdue University, School of Engineering Technology, USA

Biofuels are a renewable fuel source for use in gas turbines employed for energy generation or aviation applications. Even though biofuels composition is not as sophisticated as petroleum-based fuels, alternative fuels contain impurities in highly variable concentrations that include the individual, and as of yet, unreacted constituents found in calcium-magnesium-aluminum silicates or CMAS depending on the biomass harvesting process. Thus, critical turbine and combustion chamber components in a gas turbine engine burning biofuels are exposed to impurities that may hasten the degradation of protective ceramic coatings, and in the worst case scenario, lead to catastrophic failure. In this study, the individual CMAS constituents found in biofuels were sprayed onto air plasma spray (APS) thermal barrier coatings (TBCs) and subsequently exposed to heating and cooling cycles at temperatures similar to those of a gas turbine. In each case, microstructure investigations revealed hastened delamination of the yttria-stabilized zirconia (YSZ). Comparison of the EDS cross sections revealed different degradation mechanisms including mineralization, chemical reaction, and bond-coat corrosion.

9:30 AM

(ICACC-S2-029-2019) Corrosive Behavior of Yb_2SiO_5 by CMAS and Volcanic Ash for Environmental Barrier Coatings

B. Jang*[1]; S. Kim[2]; Y. Oh[2]; H. Kim[2]

1. Kyushu University, Interdisciplinary Graduate School of Engineering Sciences, Japan
2. Korea Institute of Ceramic Engineering and Technology (KICET), Republic of Korea

Non-oxide silicon-based ceramics, such as silicon nitride (Si_3N_4), silicon carbide (SiC), and SiC/SiC composites are of interest as materials that could replace metallic materials under ultra-high temperature conditions to improve the thermal efficiency in gas turbine system. However, since it is prone to hot corrosion in combustion environments, the development of EBCs is mandatory. Besides high melting point, low heat conductivity, ideal EBCs materials should have low oxygen diffusion, favorable chemical stability, match the coefficient of thermal expansion (CTE) and thermo-dynamically compatible with substrate. Bases on the above request, we had already reported that yttrium mono-silicate (Y_2SiO_5) is considered a potential EBCs material for protection of SiC substrate from oxidation and steam corrosion. The purpose of this study is to investigate the differences in corrosion behavior of volcanic ash and

CMAS on the sintered Yb_2SiO_5. Dense sintered Yb_2SiO_5 specimens were prepared using the spark plasma sintering method at 1400°C for 10 min. These specimens were subjected to a hot corrosive environment of molten Iceland volcanic ash and CMAS at 1400°C for 2 hr, 12 hr, and 48 hr. Different corrosion phenomena, i.e., continuous reaction with CMAS and weak reaction with the volcanic ash, were observed.

Multifunctional Protective Coatings: Processing, Microstructure and Properties I

Room: Tomoka B
Session Chair: Peter Mechnich, DLR - German Aerospace Center

10:10 AM

(ICACC-S2-030-2019) Fabrication of Molybdenum Nitride - Graphene Composite by Solution Precursor Plasma Spray for Supercapacitor Electrodes

H. Caouette-Fritsch*[1]; T. W. Coyle[1]

1. University of Toronto, Materials Science and Engineering, Canada

High porosity fine grain size Mo_2N deposits can be produced by solution precursor plasma spray (SPPS) deposition of MoO_3 followed by a conversion heat treatment. The effects of adding graphite and/or graphene to the Mo_2N on the performance of the deposit as a supercapacitor electrode were investigated. To minimize the oxidation and vaporization of the graphite and graphene during deposition, a combination of axial injection of the Mo salt solution and radial injection of a dispersion of graphite or graphene was utilized to deposit the composite material on the Ti substrate. Thereafter, the electrodes were subjected to an ammonia heat treatment to convert the molybdenum oxide phases to molybdenum nitride phases. The microstructure, phase and chemical compositions, and electrochemical behaviour of the electrodes were characterized using the following equipment and tests: SEM, XRD, XPS, BET surface area measurements, and cyclic voltametry. The electrodes produced from SPPS were composed of two phases: α-MoO_3 and $(NH_4)Mo_6O_{18}$. After the ammonia heat treatment, the electrodes had transformed to δ-Mo_2N, β-Mo_2N, and γ-Mo_2N phases. The addition of the graphite and graphene increased the electrical conductivity, and resulted in a more stable electrochemical window and a larger capacitance.

10:30 AM

(ICACC-S2-031-2019) Protective Coatings for Super-Critical Water-Cooled Reactor Corrosion Resistance Applications

E. Medvedovski*[1]; M. MacGregor[2]; J. Lyons[2]; W. Cook[2]

1. Endurance Technologies Inc., Canada
2. University of New Brunswick, Canada

The performance of steels and alloys in SCWR corrosion environments in power generation, particularly, in high pressure - high temperature steam, can be enhanced through the appropriate coatings. The ETI multi-layered protective coatings based on borides and aluminides obtained through the thermal diffusion technology on carbon steel and 316 stainless steel have been tested using UNB's SCW loop under sub-critical and supercritical conditions (steam adjusted with ammonia) at pH of 9.5 at temperatures of 300-450°C and pressure of 24 MPa for up to 500 hrs. The coatings demonstrated promising performance with no surface destruction even at 450°C. Their integrity, e.g. structure, thicknesses (~150–200 μm depending on the coating system) and micro-hardness, remained at the original level after corrosion testing. Slight surface oxidation (a few microns thick) of the corrosion resistant borides and aluminides promoted the healing of the coating surfaces without breakaway. The selected coating systems and technology are applicable to long lengths of tubing and complex shape components.

10:50 AM

(ICACC-S2-032-2019) Development of bioinspired SiC/C/Al coatings with superwettability

P. Hernandez[1]; E. Lopez-Honorato*[1]

1. CINVESTAV, Mexico

Corrosion and bio-incrustation are among the most important challenges on the development of structural materials for Ocean Energy. One route to reduce corrosion and bio-incrustation is through the use of bioinspired materials with superhidrophobicity. Ceramic materials with its inherent corrosion resistance are generally transformed from hydrophilic to hydrophobic by the use of fluoride based polymers. In this work we show that it is feasible to produce superhydrophobic ceramic coatings by the use of SiC, C and Al (all hydrophilic by their own), using polycarbosilane as polymer derived ceramic precursor. We show that although is possible to obtained superwettability using C nanoparticles, it is also feasible to obtain similar behavior with milled graphite. We show that although chemistry affects the surface interaction, surface roughness play a very important role to set the water contact angle. This opens the possibility to produce ceramic coatings with inherent superhydrophobicity.

11:10 AM

(ICACC-S2-033-2019) Tunable functionality of high entropy carbide thin films via carbon stoichiometry

C. M. Rost*[1]; T. M. Borman[2]; M. Hossain[2]; M. Lim[3]; S. Daigle[3]; Z. Rak[3]; D. Brenner[3]; J. Maria[2]; P. E. Hopkins[1]

1. University of Virginia, Mechanical & Aerospace Engineering, USA
2. The Pennsylvania State University, Materials Science & Engineering, USA
3. North Carolina State University, Materials Science & Engineering, USA

Materials science is challenged with developing new materials in order to meet the demands of technological innovation. Consequently, this opens the door to novel or complex properties awaiting exploration. High entropy carbides (HECs) demonstrate the viability of materials engineering using configurational entropy to aid in phase development and stabilization. Using two compositions, Hf-Nb-Ta-Ti-Zr-C (HEC3) and Hf-Mo-Ta-W-Zr-C (HEC6), we explore the structure-property relationship of these systems as carbon stoichiometry is varied. Using time domain thermoreflectance (TDTR), we measure thermal conductivity of both the HEC3 and HEC6 thin film series and then relate trends to other observed characteristics of each system. Total thermal conductivity systematically varies with increasing deposition flow rate of methane, resulting in higher carbon concentrations, while the electrical contribution to the thermal conductivity decreases. Results are discussed in terms of various scattering mechanisms, emphasizing understanding of thermal properties from both a local and a global structural and morphology perspective. In this talk we focus on the experimental process of elimination using several metrology techniques, including four-point probe, SEM, XPS, and nano indentation, in conjunction with TDTR to gain meaningful perspective on configurationally disordered, highly crystalline systems.

11:30 AM

(ICACC-S2-034-2019) Influence of pulsed high-intensity ion and electron beams on the optical and mechanical properties of Al-Si-N nanocomposite coatings

G. Remnev*[1]; J. Musil[2]; I. Egorov[1]; A. Kadyrov[1]; F. Konusov[1]; S. Pavlov[1]; V. Tarbokov[1]; S. Zenkin[1]

1. Tomsk Polytechnic University, Russian Federation
2. University of West Bohemia, Czechia

We present the results of a study of the influence of pulsed nanosecond ion and electron beams on the structure, mechanical and optical properties of Al-Si-N nanocomposite coatings. These coatings deposited by reactive magnetron sputtering have high hardness,

transparency in the optical range, flexibility, crack resistance and high-temperature oxidation resistance. In addition, these coatings are promising as radiation protective coatings due to the large volume fraction of grain boundaries that are drains for radiation defects. A change in the volume fraction of defects in the action of pulsed high-intensity ion beams on metal materials has previously been observed. In studies with Al-Si-N coatings, it has been found that the transparency of coatings is increased at certain absorbed doses of pulsed ionizing radiation. The parameters of ion irradiation were as follows: 250 keV ion energy, up to 350 keV electron energy, absorbed doses amounted to 1GGy per pulse for an ion beam and ~ 1 MGy for an electron beam. The optical properties of coatings were investigated on the basis of absorption spectra of radiation in the optical range. The report also presents the results of mechanical testing of coatings after the action of pulse fluxes of charged high-intensity particles. The work is supported by the Russian Science Foundation, Grant No. 16-19-10246.

11:50 AM

(ICACC-S2-035-2019) Tailoring the wettability of hydrophobic ceramic coatings fabricated by solution precursor plasma spray process

P. Xu*[1]; T. W. Coyle[2]; L. Pershin[1]; J. Mostaghimi[1]

1. University of Toronto, Department of Mechanical and Industrial Engineering, Canada
2. University of Toronto, Department of Materials Science and Engineering, Canada

Surface topographies and geometric structures have a significant effect on its wettability. In this work, hydrophobic Yb_2O_3 coatings were deposited via solution precursor plasma spray by a radial injection of $Yb(NO_3)_3$ solution into the plasma jet. Coatings with different microstructures, geometric structures, and surface topographies were fabricated via manipulating process parameters including the torch transverse speed, solution concentration, and torch re-scanning post-treatment. The hierarchical columnar-structured coatings, columnar-structured coatings with smooth surfaces, and dense coatings with relatively flat topography were fabricated and exhibited different wetting behaviors. The coating microstructures were characterized and compared, and the wettability of coatings was characterized by measuring the static water contact angle and roll-off angle. The wetting behaviors of various coatings were correlated with different coating structures and surface topographies.

Multifunctional Protective Coatings: Processing, Microstructure and Properties II

Room: Tomoka B

Session Chair: Eugene Medvedovski, Consultant

1:30 PM

(ICACC-S2-036-2019) Titanium dioxide coatings engineered by HVSPFS processing with optimized injectors and combustion chambers

M. H. Blum*[1]; R. Gadow[1]; A. Killinger[1]

1. University of Stuttgart, Institute for Manufacturing Technologies of Ceramic Components and Composites, Germany

Titanium dioxide coatings were deposited from titanium isopropoxide precursor by use of a high-velocity solution precursor flame spray (HVSPFS) process. TiO_2 is already well known and still of high interest for numerous environmental and mechanical engineering applications in industry. This study explores the effect of HVSPFS key hardware components on the properties of novel fine grained TiO_2 coatings. Two solutions with different precursor concentration, dissolved in isopropanol medium, were processed by setting up the HVSPFS torch with combustion chambers of different lengths and with different injection systems. DTA-TG of solutions showed the complete transformation of the initial precursor into the respective oxide. XRD of HVSPFS coatings confirmed the presence of TiO_2 phases and the ability to control the phase composition by optimzed spray parameters. Especially the injection of the solution has a key influence on the atomization, solution fragmentation and gas dynamics in the HVSPFS process. The usage of an atomizing injection system together with geometry optimized combustion chambers, promotes a better fragmentation of the original liquid feedstock stream and better homogenization with the hot gas flow. This in turn leads to more finely structured and denser functional coatings with a significantly higher performance

1:50 PM

(ICACC-S2-037-2019) Two-step Fabrication of F-Plasma Resistant YOF Coating with uniform chemical composition

S. Lee*[1]; Y. Oh[1]; S. Park[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Republic of Korea

The YOF coating with uniform chemical composition has been fabricated by a 2-step process using the technique of suspension plasma spray and subsequent heat-treatment. The YOF coating is being studied for the application for the silicon wafer processing equipment in the semiconductor industry. The coating contains the high amount of fluorine, so its reaction with F-plasma would be minimized. To fabricate the uniform YOF coating, we started from preparing the suspension of Y_2O_3 and YF_3 powder mixture. The first step was using suspension plasma spray in order to fabricate a dense coating. The coating consisted of a layered structure of splats with non-uniform F and O contents throughout splats. The second step was to heat-treat the coating to obtain a uniform distribution of chemical compositions as well as a more granular microstructure. The heat-treatment was conducted at the temperature as low as 500°C, but very effective to promoting the elemental diffusion, resulting in the coating with very uniform chemical composition.

2:10 PM

(ICACC-S2-038-2019) Processing of an organosilazane-based glass/ZrO_2 composite coating system by laser pyrolysis

A. C. Horcher*[1]; K. Tangermann-Gerk[2]; G. Barroso[1]; W. Krenkel[1]; G. Motz[1]

1. University of Bayreuth, Ceramic Material Enginerring, Germany
2. Bayerisches Laserzentrum GmbH, Germany

Protective ceramic-based coatings are frequently the most suitable solutions for engineering problems like corrosion, oxidation and wear. It has been shown, that the precursor technology is suitable for the preparation of ceramic coatings by pyrolysis in a furnace. However, the required high temperatures for the preparation of the ceramic coatings only allow the use of temperature-resistant substrates. A very innovative approach to overcome this restriction is the use of laser radiation as an energy source for the pyrolysis of the preceramic polymer. For this reason, a composite coating system composed of an organosilazane with ZrO_2 and glass particles as fillers was developed suitable for pyrolysis with a Nd:YAG laser. Mild steel substrates were dip-coated with a bond coat, onto which the composite coating slurry was applied by spraying. The laser pyrolysis led to the formation of a dense ceramic coating system with a thickness up to 20 mm in a short time. The resulting coatings were investigated by infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). To investigate the functionality of the laser-pyrolyzed coating as an environmental barrier coating, oxidation tests were performed in a furnace for 100 h in air. The corrosion resistance of the coatings was examined with salt spray test. The wear behavior was tested with pin-on-disc method.

2:30 PM

(ICACC-S2-039-2019) Sintering and hardness of glass–zircon GMC coatings

J. Amorós[1]; A. Moreno*[1]; E. Blasco[1]

1. University Jaume I, Instituto de Tecnología Cerámica, Spain

Many ceramic coatings consist of more or less complex glass matrix composites (GMCs). This study examines the sintering of glass–zircon composites, the development of their microstructural characteristics, and the hardness of the resulting material, as this a key property of these coatings. The study was conducted on composites containing different volume fractions of rigid (zircon) inclusions: Φ=0, 0.05, 0.11, 0.17, 0.32, 0.43, 0.53, and 0.65. The sintering curves of these materials and the variation of their most important microstructural characteristics (e.g. porosity, pore size, zircon grain size, and crystallite size) with firing temperature were experimentally determined. The zircon solution–reprecipitation mechanism was verified to operate only at temperatures above 950C. For composites with $\Phi \leq 0.43$ densification was completed via particle rearrangement by viscous flow. Sintering of these composites was interpreted based on zircon particle connectivity, using the percolation theory. Finally, the hardness and the modulus of rupture of these materials were determined by micro-indentation tests, and their values were related to their microstructural characteristics.

2:50 PM

(ICACC-S2-040-2019) Fabrication and Microstructure Development of Dense Double-layer γ-$Y_2Si_2O_7$/ Y_2O_3-Al_2O_3-SiO_2 Glass Coating on Porous Si_3N_4 Substrate

X. Fan*[1]; H. Wang[1]; M. Niu[1]; Y. Wang[1]

1. Xi'an Jiaotong University, China

Dense ceramic coating is usually fabricated on the surface of porous Si_3N_4 ceramic to improve the comprehensive performance. Liquid infiltration processing is an advanced technique for the preparation of dense coating on porous substrates. Dense double-layer γ-$Y_2Si_2O_7$ /Y_2O_3-Al_2O_3-SiO_2 glass coating was in-situ fabricated by a combined melt-infiltration /sintering (MIS) procedure on porous Si_3N_4 ceramic. Composite based on γ-$Y_2Si_2O_7$ particles with a low melting Y_2O_3-Al_2O_3-SiO_2 glass "binder" phase was formed as the surface layer. The intermediate layer was formed by the infiltration of Y-Al-Si-O melt into the pores of substrate. Sintering process of the surface γ-$Y_2Si_2O_7$ layer was analyzed combined with grain-growth kinetics calculation, and the value of activation energy was measured to be ~295.77 kJ/mol. Microstructure evolution of the double layer coating was revealed by analyzing the infiltration kinetic of Y-Al-Si-O melt in detail. Preliminary examination indicates that the melt infiltration kinetics approximate to parabolic at 1350~1450°C. Results indicate that the as-prepared coatings could improve the waterproof ability and surface Vickers hardness effectively. Water absorption was reduced from 41% to 2.7 ~4.9%, and the surface hardness was also significantly increased from 465±20MPa to ~4GPa.

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Air Electrode Performance and Durability

Room: Crystal

Session Chair: Alexander Opitz, Vienna University of Technology

9:00 AM

(ICACC-S3-023-2019) Enhancing SOFC Electrochemical Performance with Nanoceramics Prepared via in situ Carbon Templating

S. P. Muhoza[1]; S. Lee[3]; M. D. Gross*[2]

1. Wake Forest University, Chemistry, USA
2. Wake Forest University, Engineering, USA
3. DOE National Energy Technology Lab, USA

Improving solid oxide fuel cell (SOFC) electrochemical activity is key to achieving lower temperature operation. Here we report on a new processing method to prepare SOFC electrode materials with surface areas over 100 times greater than traditionally processed materials. The method consists of two steps. First, an organic-inorganic hybrid material is sintered at traditional SOFC sintering temperatures in an inert atmosphere. During this step, the organic component is pyrolyzed, forming a carbon template in situ, which mitigates coarsening of the inorganic component. In the second step, the carbon template is removed through low temperature oxidation, 700°C, in air which leaves behind the ceramic component. The following ceramics have been successfully processed with this technique: yttria-stabilized zirconia (YSZ), gadolinia-doped ceria (GDC), samaria-doped ceria (SDC), lanthanum strontium cobalt ferrite (LSCF) and lanthanum strontium manganite (LSM). In all cases, surface areas of 60 m^2/g^{-1} – 100 m^2/g^{-1} were achieved. Incorporating these high surface area materials into YSZ-LSF and YSZ-LSM electrodes resulted in performance improvements of up to 45% and 75%, respectively. These results demonstrate a new pathway to dramatically improve SOFC electrochemical activity.

9:20 AM

(ICACC-S3-024-2019) Degradation Mechanism Studies of Ba-Fe-O infiltrated LSM/YSZ Solid Oxide Fuel Cell Operated Under Humidified Air

Y. Fan*[1]; Y. Chen[2]; H. Abernathy[1]; R. Pineault[3]; X. Song[2]; K. Gerdes[3]; S. Lee[1]; T. Kalapos[1]; G. Hackett[3]

1. DOE National Energy Technology Laboratory, AECOM, USA
2. West Virginia University, Department of Mechanical and Aerospace Engineering, USA
3. DOE National Energy Technology Laboratory, USA

Solid oxide fuel cells (SOFCs) with Ba-Fe-O (Ba:Fe = 1:2) infiltrated into an LSM/YSZ composite cathodes were measured for extended periods to evaluate the impact of infiltration on the performance stability in steam-containing environments. Ba-Fe-O infiltrated cells showed much higher performance and less performance degradation than the uninfiltrated LSM/YSZ cell. TEM analysis shows that uninfiltrated LSM/YSZ cells tested under steam contain cracks along LSM/YSZ interfaces at the cathode/electrolyte interface associated with the formation of ZrO_x particles. Three different morphologies (nanoribbons, nanoparticles and nanolayers) of infiltrated materials were found in the original pore region of the cathode functional layer before testing. Fewer cracks and fewer secondary phase along the LSM/YSZ interface were found in the infiltrated cells, mitigating degradation under humidified air. EDS analysis showed significant reactions between the infiltrated Ba and Fe with the La and Mn from the LSM backbone. The microstructure and chemistry of the infiltrated layer evolved during long term operation under humidified air. Diffusion of Fe into the LSM backbone of the infiltrated cells

may improve cell performance and stability, while Mn precipitated from the LSM backbone in the form of MnO_x may contribute to long-term performance degradation.

9:40 AM

(ICACC-S3-025-2019) Electrochemical impedance spectroscopy of $(La_{1-x}Sr_x)Ni_{0.9}Mn_{0.1}O_{4+\delta}$

Y. Sadia*[1]; S. Skinner[2]

1. Ben-Gurion University of the Negev, Material Engneering, Israel
2. Imperial College, Material Engineering, United Kingdom

One of the biggest obstacles to intermediate temperature SOFCs is a good cathode which is compatible with common electrolytes. La_2NiO_4 (LNO) is such a cathode showing both chemical and mechanical compatibility with common electrolytes such as CGO and LSGM. However, any attempt to increase the performance on LNO by doping has proved insufficient, increasing one property but reducing another. In this study we attempt to elucidate the effect of changing the Sr content on Sr and Mn doped LNO. Samples containing 10-50% Sr were created using a citric acid sol gel route and their electrical properties have been studied. The impedance behaviour of half-cells was measured with LSGM electrolyte. While an increase in the impedance was measured in the increasing Sr content along all temperatures, different mechanisms come into play for each sample. The LNO, 20% and 30% samples showed very similar behaviour at similar frequency with only the magnitude having a major difference between them. As opposed to this the 10% sample showed shorter relaxation times then LNO which accounts for faster processes. The 40-50% samples showed very high impedance at low frequencies. These behaviours can be correlated to structural and electronic data to allow for further examination of future work on such electrodes.

Fuel Electrode Performance and Durability

Room: Crystal

Session Chair: Scott Barnett, Northwestern Univ

10:20 AM

(ICACC-S3-026-2019) Revisiting hydrogen oxidation kinetics on Ni/YSZ: Bridging the gap between pattern and cermet electrodes (Invited)

A. K. Opitz*[1]

1. Vienna University of Technology, Christian Doppler Laboratory for Interfaces in Metal-Supported Electrochemical Energy Converters, Austria

Ni/yttria-stabilized zirconia (Ni/YSZ) is the current state-of-the-art SOFC anode material, but developments of the recent years have brought this material back to the focus of research. Novel concepts such as metal-supported cells require processing changes, which affect the anode performance, or the degradation of Ni/YSZ in electrolysis mode brings up new questions. To answer these issues, a fundamental understanding on the relevant elementary processes is important, thus allowing a knowledge-based improvement of Ni/YSZ electrodes. In this contribution, patterned thin film electrodes were used in the first step, to revisit the reaction pathways on Ni/YSZ, since results from literature are found to be ambiguous. By variation of geometry, a triple phase boundary (TPB) and an area path could be clearly distinguished. Moreover, the properties of both pathways were characterized by variation of temperature, $p(H_2)$, $p(H_2O)$, and H_2S content in the feed gas. In the second step, findings from model experiments are transferred to the interpretation of the impedance of porous cermets. Therefor, a transmission line circuit is deduced considering the relationships of the relevant elementary processes on composite electrodes. This circuit, together with a well-defined variation of experimental parameters, allows a physically sound deconvolution of elementary processes on Ni/YSZ cermets.

10:50 AM

(ICACC-S3-027-2019) Development of Anodes with High Resistance to Coking for Solid Oxide Fuel Cells (Invited)

A. Manthiram*[1]; K. Lai[1]; D. Yoon[1]

1. University of Texas, Austin, Materials Science and Engineering, USA

Carbon deposition (coking) on the conventional Ni-cermet anode in solid oxide fuel cells (SOFCs) results in an irreversible performance degradation when a hydrocarbon fuel is directly employed. This presentation focuses on two strategies for the development of anodes with high coking resistance. First, the incorporation of 1 at.% W onto the surface of Ni-GDC cermet as a heterogeneous catalyst keeps the Ni surface clean without coking for continuous methane oxidation. $H_xWO_{3-\delta}$ formed by a reaction with water vapor during fuel oxidation reaction provides hydroxyl groups to facilitate the oxidation of carbon accumulated on Ni surface. Ni–$H_xWO_{3-\delta}$–GDC anode-supported SOFCs show more than 200 h of stable operation with direct methane fuel. Second, exsolved Co-Fe nanoparticles on the surface of perovskite oxides are utilized as an active catalyst for the fuel oxidation reaction. A consistent nanoparticle size distribution and high areal particle density before and after the redox process confirm the self-regeneration capability and provide a unique ability to recover and maintain high catalytic activity. Performance evaluations of $La_{0.3}Sr_{0.7}Cr_{0.3}Fe_{0.6}Co_{0.1}O_{3-\delta}$–GDC composite anode with exsolved Co-Fe nanocatalysts in SOFC with various fuels demonstrate good activity stability, coking resistance, and H_2S tolerance.

11:20 AM

(ICACC-S3-029-2019) Nanostructured anode with extremely low Ni content for RedOx cycle tolerance of SOFC

J. Park*[1]; J. Lee[1]; K. Yoon[1]; H. Kim[1]; H. Ji[1]; S. Han[2]; J. Son[1]

1. Korea Institute of Science and Technology, Republic of Korea
2. Korea Advanced Institute of Science and Engineering (KAIST), Republic of Korea

The operation of SOFC systems essentially accompanies reduction and re-oxidation (RedOx) of the anode. The most commonly used anode catalyst is nickel and the RedOx cycle induces substantial volume change of Ni, which leads to the generation of fatal cracks in the SOFC. In this study, a solution to the instability of the nickel-based anodes during the RedOx cycles is demonstrated through composition and microstructure engineering. The content of Ni is significantly reduced to less than 10 vol%, and the decrease of Ni amount is intended to be compensated by uniformly dispersing nanosize Ni particles in a mixed ionic-electronic conducting matrix, gadolinia-doped cereia, by using pulsed laser deposition method. It is expected that the extremely low Ni content and increased interparticle distance can prevent Ni agglomeration during RedOx cycles, which would secure the structural stability of the anode. To quantify the volume change due to the RedOx cycles, the residual stress of the anode film is measured by wafer curvature; and these results are correlated to the microstructural and electrochemical characteristics. Surprisingly, impressive anode performance is resulted in spite of the low Ni content. Moreover, as expected, remarkable RedOx stability is confirmed with the anode of the lowest Ni content (2 vol%), which demonstrates no performance deterioration after 100 RedOx cycles.

11:40 AM

(ICACC-S3-030-2019) The study of SOFCRoll with an exsolved nickel anode

K. M. Nowicki*[1]; P. Connor[1]; X. Yue[1]; J. Irvine[1]

1. University of St Andrews, Chemistry, United Kingdom

The SOFCRoll is a self-supporting SOFC based on a double spiral shape combining the advantages of the planar system manufacturing and robustness of the tubular design. For SOFCRoll preparation, all layers are tape cast, laminated, rolled and fired in a single step. Despite high energy generation and efficient manufacturing

method, SOFCRoll suffers from the low durability of the anode. The performance of Ni-YSZ anode drops due to agglomeration, carbon deposition and poisoning. This work investigates the incorporating of A-site deficient B-site nickel doped perovskite material into SOFCRoll. Under reducing conditions, nickel can be released to the surface as metallic nanoparticles with significant catalytical activity, and a low tendency to agglomerate or to generate carbon nanofibers. The studies show that the structural deffects could be limited by controlling the shrinkage of the individual layers by a variety of factors, e.g. particles size or amount of pore-formers, while still maintaining the required microstructure or composition of the ceramic layers. The preliminary tests with perovskite anodes show performance improvements due to the releasing of nanoparticles, while SEM images show a network of metallic particles on the ceramic support. The presented work will discuss the methodology of SOFCRoll manufacturing method with the recent performance tests, microstructure analysis and shrinking behaviour of the ceramic layers.

Interconnects and Coatings

Room: Crystal
Session Chair: Albert Tarancón, IREC

1:30 PM

(ICACC-S3-031-2019) Development of protective coatings for the hydrogen and oxygen side of SOFC/SOEC interconnects (Invited)

S. Molin*[1]

1. Gdansk University of Technology, Laboratory of Functional Materials, Faculty of Electronics, Telecommunications and Informatics, Poland

High temperature corrosion of steel interconnects in SOFC/SOEC stacks is an important cause of degradation due to the entailed increase of ohmic resistance and possible release of Cr vapor (at high pO_2). In order to slow down corrosion kinetics and possible chromium evaporation, protective coatings are developed. In this work coatings for both the hydrogen and the oxygen side of the interconnect were studied to offer a complementary solution to corrosion problems. For the low pO_2 side, coatings based on reactive elements (e.g. Ce, Y) were considered, whereas for the high pO_2 side, dual layer coatings consisting of an inner reactive element layer (< 100 nm thick) and an outer (10-30 μm) $MnCo_2O_4$ layer were investigated. A considerable effort is also directed towards the development of new, non-toxic materials for the oxygen side (e.g. replacing Co). Acknowledgment: This project is supported by National Science Centre Poland (NCN) Harmonia project number 2017/26/M/ST8/00438.

2:00 PM

(ICACC-S3-032-2019) Investigation of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_3$ as Cr Gettering Materials: Effect of La/Sr Ratio on Reaction and Validation in Stack Fixture Test

Y. Chou*[1]; J. Choi[1]; N. L. Canfield[1]; J. W. Stevenson[1]

1. Pacific Northwest National Lab, Materials, USA

Chromium poisoning has been known as the leading cause for cell degradation when metallic parts are used in SOFC. Mitigation by various coating have been extensively studied. In addition to coatings, Cr-gettering materials such as Sr-Ni oxides have recently been investigated as a supplementary to coating approaches. In this work we propose $(LaSr)(CoFe)O_3$ (LSCF) as a candidate for Cr-gettering materials. This is based on the observation that Sr tends to segregate out of the crystal structure and readily react with Cr to form $SrCrO_4$ in the cathode. A series of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_3$ with varying La/Sr ratios of 8/2, 6/4, 4/6, and 2/8 while Co/Fe ratio was fixed at 2/8 will be investigated. LSCF powders will be mixed with Cr_2O_3 to study the chemical reaction at 800, 900, and 1000ºC for time up to 500h. XRD will be used to characterize crystalline phases. LSCF compositions of high reactivity will be selected for validation in stack fixture test using LSM-based cell and uncoated SS441 metal as Cr source at 800ºC for 1000h with humid air. After the test, detailed microstructure analysis will be conducted on cathode and LSCF materials to assess the Cr-gettering capability.

2:20 PM

(ICACC-S3-033-2019) Co-deposition of Cu and Fe-doped MnCo spinels on metallic interconnects by electrophoretic method: Structural, compositional modifications and corrosion properties

F. Smeacetto*[1]; A. Sabato[2]; H. Javed[2]; E. Zanchi[2]; B. Talic[3]; S. Molin[4]

1. Politecnico di Torino, Energy, Italy
2. Politecnico di Torino, Applied Science and Technology, Italy
3. DTU, Energy Conversion and Storage, Denmark
4. Gdansk, University of Technology, Poland

Manganese cobaltite spinel coatings are considered as one of the best materials as protective coatings for metallic interconnects used in solid oxide cell devices. The doping of MnCo spinel with transition metals such as Fe and Cu has been previously evaluated. Cu or Fe doped MnCo spinel powders are usually prepared "ex-situ", i. e. before the deposition process. The use of EPD technique to simultaneously co-deposit the MnCo spinel and the dopant (Cu or Fe) by adding a controlled amount of the second phase (Cu or Fe precursors) to the suspension represents a novel approach. Though the EPD has been used for preparation of protective coating in a few studies, the co-deposition approach proposed in this work is a new and an interesting route. Cu and Fe-doped Mn-Co spinels are optimized to improve the Mn-Co-based coatings on both Crofer22APU and AISI 441, in terms of densification and electrical properties. Oxidation kinetics and area specific resistance long term tests up to 3500 hrs (at 750-800°C) in real conditions are evaluated to assess the efficacy of coating in providing oxidation protection. The performances of Fe-doped MnCo coated Crofer22 APU and AISI 441 were evaluated by post mortem advanced electron microscopy analyses; different reaction layers and diffusion mechanisms are reviewed and discussed.

2:40 PM

(ICACC-S3-034-2019) Influence of metal coatings on the morphology and the structure of interconnect surface in anode gas ambience

M. Kusnezoff*[1]; V. Sauchuk[1]; C. Folgner[1]; S. Molin[2]; M. Vinnichenko[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Germany
2. Gdansk University of Technology, Faculty of Electronics, Electrocommunications and Informatics, Poland

SOFC interconnect materials (IC) Crofer 22 APU, Crofer 22 H, AISI441 and CFY were tested in anode gas environment to investigate the influence of the metallic contact/protection coatings on oxidation properties. Three coatings were applied onto the surface of samples by different deposition techniques. Copper and Nickel were firstly deposited as CuO or NiO oxides by screen printing and further reduced to metallic state under H_2 ambience whereas a thin Yttrium (Y) film was directly deposited from liquid solution by an immersion method. The experiments were carried out at temperature 875 °C to simulate accelerated SOFC stack degradation conditions. Both gravimetric measurements and FESEM/EDX data, as well as polished cross sections were analyzed to characterize the interactions of deposited coatings and IC material constituents on the formation and the microstructure of the resulting layers and oxide scales. The diffusion depths of Ni and Cu into interconnect materials were estimated in dependence on temperature and the duration of the thermal exposure. It was found that the Nickel diffusion depth is higher than the one of Copper in all investigated materials. The influence of the thin Yttrium layer on the Ni-diffusion in IC/Y/Ni-multilayer structure, the mechanisms of components interactions and the composition variations at the surface of IC-materials are discussed.

3:00 PM

(ICACC-S3-035-2019) Corrosion of Iron Alloy Interconnects under Dual Atmosphere Exposure Conditions in Intermediate Temperature SOFC Systems

M. Reisert*[1]; A. Aphale[1]; A. Pandey[2]; P. Singh[1]

1. University of Connecticut, Materials Science & Engineering, USA
2. LG Fuel Cell Systems, USA

Lower operating temperatures for solid oxide fuel cells have enabled the use of easily manufactured and readily available stainless steels as interconnect materials. However, under a bipolar atmosphere where the interconnect is simultaneously exposed to a reducing gas on one side and an oxidizing gas on the opposing side, an accelerated corrosion phenomenon is observed. As this does not occur in singular atmospheres, it has been deduced that hydrogen is the driving factor in accelerated corrosion, yet the exact role hydrogen plays remains largely unknown. Furthermore, the interactions caused by hydrogen permeation result in rapid and overgrowth oxidation of iron, where iron oxide nucleates as nodules that grow further into platelet-type projections. To achieve a better understanding of this phenomenon, diffusion and transport mechanisms of species involved in dual atmosphere corrosion will be discussed. Experimental comparisons of austenitic and ferritic stainless steels are presented in order to reveal the effect of alloy compositions and microstructure with regards to dual atmosphere corrosion. Possible reactions within the corrosive oxide scale with regards to hydrogen, oxygen, and metal species will be reviewed. This will be accompanied by thermodynamic driving forces for oxide growth in dual atmosphere conditions at an intermediate temperature range.

HT Electrolysis

Room: Crystal
Session Chair: Christian Walter, sunfire GmbH

3:40 PM

(ICACC-S3-036-2019) Performance and Long-Term Stability of Electrolyte Supported Solid Oxide Cells in Steam Electrolysis Mode (Invited)

J. Schefold*[1]; A. Brisse[1]

1. European Institute for Energy Research, EIFER, Germany

In recent years, steam electrolysis with solid oxide cells (SOC) has evolved from the lab to a technology with prototypes in the >100 kW range. The main application driver for this fast development is the growing availability of (surplus) electrical energy from intermittent renewable sources for H_2 production. Though all electrolysis technologies benefit from this change, the SOC has the advantages of higher electrical energy-conversion efficiency, in particular if heat for steam generation is available from downstream reactions. EIFER performs long-term electrolysis cell (and stack) testing. In several tests, operation times of 10 to >23 kh were achieved with electrolyte supported cells. This provides reliable lifetime extrapolations for industrial systems for which lifetimes >50 kh are foreseen. The cells used show a high degree of SOFC/SOEC reversibility. The main research interest is on low degradation (U_{cell} degradation <0.5 %/kh). Other issues are (i), the capability of operation with power variation and (ii), either an increase in the current density to ≥1 Acm-2, or a decrease of the operation temperature. The latter development mainly relies on the availability of thinner electrolyte layers. In all tests, impedance spectroscopy is used as in-situ tool for performance and degradation analysis. An update of the mentioned testing activities will be given.

4:10 PM

(ICACC-S3-037-2019) Methane Synthesis from Water and CO_2 with Solid Oxide Electrolysis Cells (Invited)

H. Kishimoto*[1]; T. Ishiyama[1]; T. Yamaguchi[2]; R. Atsumi[3]; Y. Fujimaki[2]; K. Yamaji[1]; Y. Fujishiro[2]; H. Shimada[2]

1. National Institute of Advanced Industrial Science and Technology (AIST), Research Institute for Energy Conservation (iECO), Japan
2. National Institute of Advanced Industrial Science and Technology (AIST), Japan
3. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Methane synthesis from water and CO_2 is realized by using two-stage solid state electrolysis processes. This system can achieve a conversion efficiency from electricity to chemical energy as high as 90%. The first stage is a co-electrolysis process changing from water and CO_2 to H_2 and CO mixture gas. In this process, the cell composed of Ni-cermet support/YSZ/GDC/LSCF-GDC is operated at 700 ~ 750 °C and the operating voltage was about -1.4V, which is slightly larger than the thermal-neutral point for water vapor electrolysis. The following stage is the process for producing methane from the syngas. This process is operated at 400 °C with the same cell as that for the first stage. In this process, the conversion rate from the syngas to methane increases with applying voltage. This should be the same phenomenon so-called NEMCA (Non-faradaic electrochemical modification of catalytic activity) effect.

4:40 PM

(ICACC-S3-038-2019) Intelligent and Robust Nano-particles on Perovskite for Next Generation Solid Oxide Electrochemical Cells (Invited)

T. Shin*[1]; H. Kim[1]; K. Hwang[1]; M. Kim[1]; M. Oh[1]

1. Korea Institute of Ceramic Engineering & Technology, Republic of Korea

Nano-structured surfaces, such as supported nano-wires, nano-tubes, nano-rods, nano-sheets, or nano metal particles have considerable potential to solve several key challenges which catalysis and renewable energy are currently facing, provided that their morphology and hence catalytic activity can be controlled during preparation but also during operation. In particular, the use of nanoparticles in solid oxide electrochemical cells has been considered problematic because the nano-structured surface typically prepared by deposition techniques may easily coarsen and thus deactivate, especially when used in high temperature redox conditions. Recently we have shown that perovskite lattice defects could be used for an alternative active oxide electorde for SOFC/EC. Here we show that robust transition metal nano complex grown in situ from specifically designed nonstoichiometric perovskites or extreme nano ceria share a uniquely strong interaction with the parent support and form a well-functioning solid oxide electrolysis cell cathode, with good stability even after several redox cycles. In this study, it will be therefore concluded that novel method for robust ceramic electrode with nano complex could be used as an active cathode in solid oxide fuel cells and solid oxide electrolysis with excellent redox and coking tolerance.

5:10 PM

(ICACC-S3-039-2019) Performance and Degradation of Metal-Supported Solid Oxide Electrolysis Cells (MS-SOECs) with Infiltrated Catalysts

R. Wang*[1]; E. Dogdibegovic[1]; M. C. Tucker[1]

1. Lawrence Berkeley National Laboratory, Energy Conversion Group, Energy Storage and Distributed Resources Division, USA

Metal-supported solid oxide cells with a symmetric cell architecture were developed for high temperature electrolysis. The cell is comprised of a ScSZ electrolyte, sandwiched between porous ScSZ electrode backbones and metal supports on both sides. Due to the unique symmetric cell architecture, various nano-structured

catalysts can be infiltrated into both the oxygen and fuel/hydrogen electrodes. Cells with different catalyst materials were tested from 650 to 800 °C, with steam content from 3 to 75 vol.%. Performance of the MS-SOECs was characterized by voltage-current and impedance spectroscopy measurements. By optimizing the catalyst materials selections and their infiltration strategies, excellent electrolysis performance was obtained, showing current densities of -5.31, -4.09, -2.64, and -1.62 A/cm^2 at 800, 750, 700, and 650 °C, respectively, at 1.3 V and 50 vol.% steam content. In addition to initial performance, the durability of infiltrated electrodes was studied in both symmetric cell and full cell tests. The dependence of degradation rate on operating current density/voltage, steam content in hydrogen electrode, and temperature was evaluated. After electrochemical testing, cell microstructures were characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy. The degradation mechanisms of MS-SOECs are investigated and discussed.

5:30 PM

(ICACC-S3-040-2019) A Role of the Oxygen Electrode Overpotential on the Solid Oxide Electrolysis Cell Degradation

B. Park*[1]; Q. Zhang[1]; P. Voorhees[1]; S. Barnett[1]

1. Northwestern University, USA

Hydrogen has received much attention as an environmentally benign energy carrier, and the solid oxide electrolysis cells (SOECs) are promising electrochemical devices for producing hydrogen with high efficiency. However, degradation during long-term operation remains a critical question for the practical implementation of SOECs. Degradation of the oxygen electrode has been widely reported, and is known to become more severe with increasing current density. The effects of other operating parameters such as temperature, and the effect of electrode composition, are generally not known. Here we report results on the effect of temperature and current density on oxygen electrode degradation. The life tests are done on both symmetric cells and full cells with YSZ electrolytes with either porous or dense GDC barrier layers, with various electrode materials including $Sr(Ti_{0.3}Fe_{0.7})O_3$ (STF) $Sr(Ti_{0.3}Fe_{0.63}Co_{0.07})O_3$, and $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ (LSCF). The observed dependences on temperature, current density, and electrode type indicate that an oxygen electrode overpotential $\eta \geq 0.2$ V induces fracture in the oxygen electrode that causes an increase in cell ohmic resistance and eventual cell failure. For example, for cells with LSCF or STF electrodes, increasing the temperature below ~ 650 °C increases η above 0.2 V, causing degradation.

5:50 PM

(ICACC-S3-041-2019) Influence of distribution of oxygen partial pressure on the electrolyte degradation of solid oxide electrolyser cells

Q. Zhang*[1]; B. Park[1]; Q. Liu[1]; S. Barnett[1]; P. Voorhees[1]

1. Northwestern University, USA

A number of degradation mechanisms have been observed during the long term operation of solid oxide electrolysis cells, including oxygen bubble/pore formation within the electrolyte and fracture in the electrode and/or electrolyte. We have further developed the mathematical model originally developed by Jacobsen and Mogensen to investigate the distribution of oxygen partial pressure in the electrolyte for different materials, different structures, and different operating modes. It is found that there is an abrupt change in oxygen potential at the p-n junction that develops in mixed conducting oxides such as Yttria-stabilized Zirconia. We find that this transition is sensitive to the material properties of the electrolyte and the operating conditions. The distribution of oxygen partial pressure in the electrolyte is also strongly dependent on the electrode overpotentials. At the oxygen electrode, the maximum oxygen pressure occurs at the interface between a YSZ electrolyte and the electrode, explaining the fracture often observed at this interface. When a CGO barrier layer is present, a maximum in the oxygen pressure is found at the interface of the YSZ and CGO that can result in fracture. At the fuel electrode, extremely low oxygen partial pressures can result in degradation in the electrode and also grain boundary cavitation in the electrolyte.

S4: Armor Ceramics - Challenges and New Developments

Materials and Process Modeling II

Room: Coquina Salon F

Session Chair: Jerry LaSalvia, U.S. Army Research Laboratory

8:30 AM

(ICACC-S4-029-2019) A rate-dependent breakage model for granulated ceramics

M. Cil*[1]; R. Hurley[1]; L. Graham-Brady[1]

1. Johns Hopkins University, Hopkins Extreme Materials Institute, USA

Ceramics are promising candidates for personal and vehicle protection systems due to their unique combination of properties including high strength and low-density. Ceramics subjected to impact or blast loading exhibit a catastrophic brittle failure involving the sudden formation, growth, and coalescence of cracks. This fragmentation process transitions monolithic solids into densely packed granulated ceramic assemblies. The response of such damaged ceramics to dynamic loading strongly governs the resistance of the material to penetration. Thus, understanding and modeling the behavior of granulated ceramics is essential to accurately model the dynamic response of ceramics and to develop effective armor systems. A rate-dependent constitutive model is proposed for damaged ceramics based on the framework of breakage mechanics theory. The model is devised using micromechanics-inspired internal variables, relating microscopic governing dissipative processes with macroscopic material response. Rate-dependency is introduced by employing the overstress concept in viscoplasticity. The proposed constitutive modeling framework is shown to capture key characteristics of the behavior of brittle granular materials over a wide range of pressures including density- and stress-dependent dilative/contractive response, evolution of PSD due to breakage, steady state under shearing, and the competition between dilation and breakage.

8:50 AM

(ICACC-S4-030-2019) Fragmentation and granular phase transition in brittle ceramics

A. Bhattacharjee*[1]; L. Graham-Brady[1]

1. Johns Hopkins University, Civil Engineering, USA

Under impact events, the active competition between stable wing crack growth and rapid growth of shear cracks determines the geometry of the comminuted material. Thereafter as the comminuted material becomes mobile, it starts behaving as a granular medium, and granular mechanics determines the physics of the material. There are two open questions in modeling this comminution process: what is an appropriate criterion for determining the onset of granular mechanics; and, what is the initial geometry (fragment size and shape distribution) describing the granular material at the moment of comminution? The transition of a comminuted material into a granular phase is modelled in previous work by the authors using a simple damage based analytical model, where linear elastic buckling of micro-columns of material between parallel crack assemblies is thought to drive the transition. A crack-coalescence based fragmentation model that tracks the aforementioned active competition between wing crack growth and Mode II coalescence is proposed in the current work. The model determines the key initial conditions – fragment size, distribution, angularity and porosity, that are necessary for any granular flow constitutive model to predict

the post-transition mechanical response. Capturing this initial state accurately is critical, since the granular mechanics model is sensitive to these initial conditions.

9:10 AM

(ICACC-S4-031-2019) Indentation Induced Amorphization of Single Crystal Quartz

K. Andes*[1]; K. Ramesh[1]

1. Johns Hopkins University, Mechanical Engineering, USA

Single crystal quartz is a transparent and brittle material that undergoes solid state amorphization. To date, research on amorphization has been primarily focused on understanding the effects of pressure on the onset of amorphization. We are investigating the role of both shear and pressure on the onset and evolution of amorphization using static and dynamic indentation experiments. We have performed these experiments using different indenter geometries, including Vickers and spherical, at different loads and strain rates. We are currently building maps of amorphized regions in the indented specimens using post-mortem Raman spectroscopy. Using this data, we can match the locations of the amorphous zones to theoretical calculations of full-field stress states. This evaluation, for different geometries and loads, will expand our understanding of the influence of shear on amorphization.

Synthesis and Processing I

Room: Coquina Salon F

Session Chairs: Lionel Vargas, US Army Research Laboratory; Nicholas Ku, U.S. Army Research Laboratory

9:30 AM

(ICACC-S4-032-2019) Additive Manufacturing of Glass Optics (Invited)

R. J. Dylla-Spears*[1]; N. Dudukovic[1]; J. Destino[2]; K. Sasan[1]; M. A. Johnson[1]; T. D. Yee[1]; D. T. Nguyen[1]; L. L. Wong[1]; T. Fears[1]; A. Lange[1]

1. Lawrence Livermore National Laboratory, Optics and Materials Science & Technology, USA
2. Creighton University, USA

The capability to customize the structure or composition of an optical element gives designers access to previously unrealizable configurations that show promise for reducing costs as well as improving the size, weight, and power of optical systems. Techniques for three-dimensional (3d) printing of glass have opened the door to novel glass optics with both unconventional structures and tailored composition. An overview of the state-of-the art in glass 3d printing will be presented. Particular emphasis will be placed on the direct ink writing (DIW) technique, in which specially formulated silica pastes are extruded through a nozzle and deposited in the geometry of interest, forming low density green bodies. The green bodies are then converted to full density, optically homogeneous glass by a series of heat treatments. The 3d printed silica-based glass components have material and optical properties that rival conventionally prepared optical grade fused silica. In addition, glass optics that contain tailored gradients in composition, such as gradient index lenses, have been achieved by DIW by blending separate inks inline at the print nozzle and directly depositing the desired composition profile before forming the glass. Strategies are also being developed to reduce time to development of new materials and structures.

10:20 AM

(ICACC-S4-033-2019) Additive Manufacturing for Advanced Armor Ceramics: Techniques, Capability Gaps, and Paths Forward to Enable the Next Generation of Protection (Invited)

L. Vargas*[1]; M. C. Golt[1]; N. Ku[1]

1. U.S. Army Research Laboratory, Weapons and Materials Research Directorate, USA

Immense pressure has been placed onto the armor S&T community to develop solutions for both increased mass-efficiency (greater than 20% weight reduction), and for the manipulation of the physics of failure in brittle ceramic materials. The development of novel ceramic materials and microstructures continue to be an imperative for the S&T community. However, new ideas for hierarchical order in ceramics are being proposed that could provide a path for enabling new dynamic fracture and deformation mechanisms in armor materials surpassing that of intrinsic material behavior alone. Additive manufacturing (AM) of ceramics promises the ability for discrete mesostructural tailoring, enhancing mechanisms and leading to unsurpassed ballistic efficiency, but there remain materials' challenges that must be addressed to achieve optimal material properties (high hardness, theoretical density). This work serves to assess the feasibility of ceramic additive manufacturing processes (such as direct-ink write, stereolithography, pre-ceramic precursors, binder jetting) for the development of dense, hierarchical armor ceramics. It will also address the technical challenges associated with materials and processing and develop a path forward for academia, industry and government researchers to collaborate toward meeting the needs for the future Warfighter.

10:50 AM

(ICACC-S4-034-2019) Additive Manufacturing for Hierarchical Design in Next-Generation Armor Composites

J. Pelz*[1]; N. Ku[2]; C. A. Marsico[2]; L. Vargas[2]; M. A. Meyers[1]

1. University of California, San Diego, MATS, USA
2. US Army Research Laboratory, USA

Development of next-generation armor ceramics must explore creative design approaches to attain improved properties through extrinsic mechanisms, such as bio-inspired, hierarchal designs. By tailoring composition and micro/mesostructure, functionally graded parts can be produced that show improved properties over those of their individual constituents. Traditional ceramic forming techniques limit the design space available for exploring functional designs, so additive manufacturing (AM) by direct ink writing (DIW) was chosen to produce test parts. In this study, a custom print head and feed system were designed to allow simultaneous extrusion of multiple, highly-loaded ceramic suspensions through a single nozzle; enabling production of functionally graded parts in terms of both composition and geometry. The print head contains an auger that achieves in-line mixing and volumetric extrusion, enabling simultaneous extrusion of inks with varying rheology. Composite parts were made with SiC and B_4C due to their favorable material properties, including high hardness and low density. Printed parts were sintered and characterized for their density, micro/mesostructure, and mechanical properties. Following this workflow, the design space is explored to determine optimal design parameters to create functionally graded armor that shows improved properties by incorporating extrinsic mechanisms.

11:10 AM

(ICACC-S4-035-2019) Binder Jet Fabrication of Boron Carbide-Silicon Carbide Composites

C. L. Cramer*[1]; R. A. Lowden[1]

1. Oak Ridge National Laboratory, ETSD, USA

Boron carbide and silicon carbide are engineering ceramics with low densities and high hardness properties advantageous for use in armor applications. Individually these materials perform well

in ballistic applications; however, combining the two can result in materials with high strength and improved toughness. Because of the complexities of processing, ceramic armor is typically produced in simple geometries and sometimes as composites. To increase the complexity of the geometry and provide a composite with hard phase, reaction bonding of binder jet printed powder blends containing boron carbide, silicon carbide infiltrated with silicon and silicon/carbon were investigate.

11:30 AM

(ICACC-S4-036-2019) Producing Dense Boron Carbide Components Using Room Temperature Injection Molding and Pressureless Sintering

E. Weaver*[1]; R. Trice[1]; J. P. Youngblood[1]

1. Purdue University, Materials Science & Engineering, USA

Boron carbide is an ideal material for lightweight armor applications due to its excellent mechanical properties, such as low density, high hardness, and high Young's modulus. However, the poor pressureless sintering behavior of boron carbide currently limits its widespread use, and current efforts are limited to simple geometries. Room-temperature injection molding, combined with pressureless sintering, allows for the formation of complex, near net shaped components. High relative densities can be achieved in these parts by using combinations of sintering aids and processing parameters. Using these methods, boron carbide parts containing a variety of sintering aids have been formed. The effect of several sintering aids on the density, microstructure, and mechanical properties of the densified boron carbide parts is evaluated and discussed.

11:50 AM

(ICACC-S4-037-2019) Challenges in densifying armor ceramics produced by direct-ink-write additive manufacturing

N. Ku*[1]; C. A. Marsico[1]; R. Dunn[1]; J. Pelz[2]; L. Vargas[1]

1. U.S. Army Research Laboratory, USA
2. University of California, San Diego, MATS, USA

The use of SiC-B_4C composite structures have replaced monolithic ceramics as the state-of-the-art in body armor materials. However, engineering of these composite structures has been limited due to the stochastic nature of traditional powder mixing and processing. The use of additive manufacturing with multiple extruders can enable increased control of engineered structures and interfaces to maximize ballistic efficiency of ceramic armor. This work highlights the challenges in utilizing a direct-ink-write method to additive manufacture dense ceramics pieces with an engineered, internal composite structure. Aqueous ceramic suspensions of SiC and B_4C with a solids loading of greater than 50 vol.% were investigated. The rheological properties of the particulate suspensions were measured to determine the necessary flow properties of a "printable" material. Sample warpage presented a challenge during the subsequent drying and binder burnout of the additive manufactured parts and is discussed. The densification of both monolithic and composite parts are also presented.

Synthesis and Processing II

Room: Coquina Salon F

Session Chairs: Selva Vennila Raju, U.S. Army Research Laboratory; Kristopher Behler, U.S. Army Research Lab; Jerry LaSalvia, U.S. Army Research Laboratory

1:30 PM

(ICACC-S4-038-2019) Complex Shape Components by 3D Printing and Spark-Plasma Sintering (Invited)

E. A. Olevsky*[1]; G. Lee[1]; E. Torresani[1]

1. San Diego State University, USA

The advanced pressure assisted sintering techniques, such as spark plasma sintering, enable the consolidation of various powder materials with the possibility to control the microstructure of the final products. These techniques are very useful for the fabrication of high performance materials, but their main drawback are the difficulties to generate complex shapes. In most of these processes a certain level of post-processing porosity or structure non-homogeneity is present, when complex shapes' fabrication is attempted, due to the high complexity of the tooling involved in the production of these shapes. To address this problem a new processing approach enabling the integration of the advanced complex shapes-rendering methods of 3D printing and the high quality of the material microstructures obtained by the pressure assisted sintering techniques is developed. The advantages of the new powder shaping and consolidation technique include the possibility to generate fully dense very high complexity shapes based on the use of 3D printing, the possibility to fabricate high performance materials, using consolidation techniques like spark plasma sintering or hot pressing, and the possibility to generate multiple parts by sintering them simultaneously thereby considerably increasing the productivity of the method. Examples of the fabrication of complex shape components based on metallic or ceramic powders are provided.

2:00 PM

(ICACC-S4-039-2019) Effect of boron carbide composition on its densification behavior during spark plasma sintering (SPS)

N. Firshtman*[1]; S. Kalabukhov[1]; N. Frage[1]

1. Ben-Gurion University of the Negev, Materials Engineering, Israel

Boron carbide displays very promising properties, such as high hardness and Young's modulus along with low specific density. Unfortunately, due to its covalent bonding successful sintering may be conducted only at relatively high temperatures (higher than 2200°C) even when external pressure is applied. Many sintered additives were suggested to decrease sintering temperature, but all of them affect mechanical properties, namely, decrease hardness value. We suggest to examine the effect of boron carbide stoichiometry, which changes from B_4C to $B_{10}C$, on its sintered behavior. To obtain boron carbide of various stoichiometry B_4C powder were mixed with an appropriate fraction of TiO_2 and annealed under vacuum (10^{-4} mm Hg) at 1400°C for 4 hours. The resulting powder mixtures consisted of boron carbide of desired stoichiometry and a novel formed TiB_2 phase were densified by SPS apparatus. For comparison B_4C-TiB_2 powder mixtures were also sintered. It was established that stoichiometry of boron carbide significantly affects sintering temperature (200-250°C lower than that for stoichiometric boron carbide and its mixtures with TiB_2) and relative density of the sintered samples. Mechanical properties of the SPS-processed specimens will be discussed.

2:20 PM

(ICACC-S4-040-2019) Multi-Phase Armor Production and Characterization Involving B4C–SiC–TiC with SPS Technique

G. Uysal Sapanci*[1]

1. ROKETSAN, Ballistic Protection Center, Turkey

B4C is commonly used material for armor applications due to its light and high hardness. However, the high cost is one of the most important obstacles in the front. Sintering of B4C requires sintering with a HP at temperatures around 2200C to bring it to the theoretical density. However, the mechanical properties of monolithic B4C are not good to be used in industrial applications. Numerous studies have been carried out on the production of B4C-containing composite materials by the addition of different compounds such as SiC, TiC. The addition of these compounds improves both the properties and reduces the sintering temperature. In this study, optimum boron carbide-silicon carbide- titanium carbide multiphase ceramic composite compositions were designed and produced by SPS technique bearing in mind the hardness–toughness–cost–lightness-performance relationship. In addition, the effect of these carbides was also investigated by adding only TiC or SiC powders into pure B4C powder. The addition of SiC did not affect the hardness and toughness, but the addition of TiC resulted in increased toughness in spite of decreased hardness. When SiC and TiC were added together, hardness decreased whereas fracture toughness increased. Because of the fact that B4C is a light material, all the additives added increase the weight, while the costs were reduced because all the additives are cheaper than B4C.

2:40 PM

(ICACC-S4-041-2019) Studying the incorporation of WC to make B_4C-TiB_2 system more interesting for armour applications

S. Failla*[1]; L. Zoli[1]; D. Sciti[1]

1. National Research Council of Italy - Institute of Science and Technology for Ceramics (CNR-ISTEC), Italy

B_4C is a lightweight ceramic with a unique combination of physical and mechanical properties but also very difficult to densify, also under pressure, below 2000 °C. The mixture with TiB_2 is an advantageous combination because it improves the toughness and the fracture resistance making B_4C electrically conductive and suitable for EDM technique. However, this system needs very high temperature and pressure to achieve full densification. Our idea was to used WC as sintering aid to study the influence of the densification and properties for B_4C-TiB_2 system. We explored the effect of WC addition with several processing methods (soft ball milling, high energy milling, using grinding media WC for both, and addition powder of WC) studying 50v%B_4C / 50v%TiB_2 compositions. High energy milling seems very attractive due to the combination of contamination and reduction of mean grain size of the powder. Thanks to this process, the sintering temperature decreased to 1860 °C giving high values of hardness and strength, 860±40 MPa and 28.5±1.4 GPa respectively. Different mixtures of B_4C-TiB_2 spanning from B_4C-rich to TiB_2-rich compositions were studied using the high energy milling method. The highest value of hardness (32±1.8 GPa) was obtained for 75v%B_4C / 25v%TiB_2 composition while the highest value of fracture toughness (5.1±0.1 MPa $m^{0.5}$) was obtained for 25v%B_4C / 75v%TiB_2 composition.

3:00 PM

(ICACC-S4-042-2019) $SiB_{2.5}$ or Si_4B_{10} – Crystal structure model, electronic structure, and NMR parameters from theoretical calculations

H. Hillebrecht*[1]

1. University of Freiburg, Institute for Inorganic Chemistry, Germany

XRD single crystal data refinement reveal a composition $SiB_{2.5}$ or Si_4B_{10} with icosahedra $B_{10}Si_2$ connected to a 3D framework by Si_2 dumbbells. The equatorial position which is connected to the Si_2 unit is occupied only by boron atoms while the polar position contains one third Si. Following the nomenclature of carborane $B_{10}C_2H_{12}$ three isomers are possible, 1,2 with neighboring Si-atoms, 1,7 and 1,12 with Si in trans position. According to unit cell size and symmetry (Rm, a = 6.300, c = 12.296 Å) sc-XRD can't differentiate between the isomers. Theoretical calculations (DFT-GGA, GIPAW, Program package Espresso) reveal, the arrangement of the $B_{10}Si_2$ icosahedra must occur in a way that intericosahedral Si-Si bonds are avoided. Furthermore the 1,2 isomer is slightly favored (10 kJ/mol), while the energy of 1,7 and 1,12 isomers are comparable. The calculated ^{11}B-NMR spectra of all isomers are similar making a differentiation quite uncertain. In contrast, ^{29}Si-NMR spectra reveal different chemical shifts for the Si atoms of the Si_2 dumbbell) and for the Si-atoms on the polar sites for the different isomers. Additionally, band structures, Bader charges and vibrational spectra were calculated.

3:20 PM

(ICACC-S4-043-2019) Field-Enhanced Processing of Armor Ceramics: SiC-B_4C Composites (Invited)

S. Raju*[1]; M. Kornecki[2]; R. E. Brennan[3]

1. Oak Ridge Associated Universities, USA
2. SURVICE ENGINEERING, USA
3. U. S. Army Research Laboratory, USA

Processing of ceramic materials under applied electromagnetic (EM) fields can enable improved densification behavior through enhanced sintering mechanisms. Numerous field-assisted processing studies on metals and oxide ceramics have demonstrated novel densification behaviors; however, few studies showing similar utility for nonoxide ceramics have been reported. SiC-B_4C composites are of interest for armor applications due to their excellent combination of physical and mechanical properties. In this study, the effect of EM fields on the sinterability of SiC/B_4C/C green bodies has been investigated using a 2.45 GHz single-mode microwave system. Under pre-heating conditions, materials were subjected to various electric/magnetic field ratios, leading to different heating rates and maximum temperatures. Mixed-field and 100% H-field conditions resulted in higher temperatures at equivalent power. For 100% E-field condition, densification was achieved several hundred degrees lower than conventional sintering. As an alternative method for producing dense SiC/B_4C composites, Si/C/B_4C green bodies subjected to EM fields were also explored. Two phenomena were observed, including flash sintering near room temperature and reactive sintering at temperatures significantly lower than conventional reaction bonding. Background, experimental procedures, and results will be presented.

3:50 PM

(ICACC-S4-044-2019) Flash sintering as a new green sintering technique (Invited)

T. Tsakalakos*[1]; H. Charalambous[1]; J. Okasinski[2]

1. Rutgers University, Materials Science and Engineering, USA
2. Argonne National Lab, Advanced Photon Source, USA

Flash sintering is a new field assisted sintering technique (FAST). Flash sintering lowers both the sintering temperature and time in comparison to traditional sintering techniques as well as other FAST such as microwave and spark plasma sintering (SPS). This greatly lowering the energy requirements required to achieve densification. A review of flash sintering of a wide variety of oxide and non-oxide ceramics as well as the mechanisms responsible for the enhanced diffusion kinetics are explored. The presentation will cover the flash sintering results on 8YSZ, ceria, titania, and zinc oxide; and the techniques of impedance spectroscopy, in-situ diffraction and TEM.

4:20 PM

(ICACC-S4-045-2019) Effect of Excess B_2O_3 and Hot-Pressing time on the Density, Microstructure, and Hardness of Reactively Hot-Pressed Boron Suboxide

K. D. Behler*[1]; J. LaSalvia[2]; H. E. Payne[3]; C. Marvel[4]; S. D. Walck[5]; L. Vargas[2]; M. P. Harmer[4]

1. US Army Research Laboratory (SURVICE Engineering), Ceramic and Transparent Materials Branch, USA
2. US Army Research Laboratory, Ceramic and Transparent Materials Branch, USA
3. US Army Research Laboratory (CQL-Penn State University), Ceramic and Transparent Materials Branch, USA
4. Lehigh University, Materials Science and Engineering, USA
5. US Army Research Laboratory (SURVICE Engineeirng), Materials Development & Transition Branch, USA

Reactive hot-pressing (RHP) of boron suboxide, nominally B_6O, was performed using mixtures of amorphous boron (B) and boron oxide (B_2O_3) powders under rapid densification rates (up to 50°C/min), dwell temperatures between 1750°C-1850°C for up to 3 hrs, and an applied uniaxial load of up to 54 MPa. Due to significant oxygen deficiencies, which are known to occur at pressures less than a few GPa, oxygen in excess of stoichiometrically computed ratios were used to determine an optimal ratio based on observation of second phase and hardness. The effect of excess oxygen on the densification, microstructure, chemistry, stoichiometry, and hardness was investigated. Resultant densities were determined by Archimedes and image analysis. XRD and Rietveld analysis were used to determine the resulting phases and B_6O stoichiometries. Microstructures were characterized by SEM, EDS, ac-STEM, TEM, and EELS. Knoop hardness values (2 kgf) varied from 18.4±0.6 GPa to 19.8±0.8 GPa depending on the processing conditions. The measured hardnesses of many of the B_6O samples were equal to or greater than that of a fully dense hot-pressed and glass encapsulated hot-isostatically-pressed material (18.9±0.5 GPa). Experimental procedures and results will be presented.

4:40 PM

(ICACC-S4-046-2019) Development of Transparent Spinel Ceramics

R. Stocky*[1]; J. Boehmler[1]; Y. Lorgouilloux[2]; S. Lemonnier[1]; A. L. Leriche[2]

1. French-German Research Institute of Saint-Louis, France
2. University of Valenciennes and Hainaut-Cambrésis, France

The main challenge for armor systems is to optimize and enhance the protection against specific threats but also to reduce weight. These last years, one material is in the spotlight: the Mg-Al-Spinel. This ceramic has many advantages such as high transparency in the UV, visible and mid-IR, good mechanical weight. An improvement of these properties can be achieved by a fine control of the characteristics of the powder, which are crucial since they are directly influencing the sintering behavior. The aim of this work is to study and understand the influence of different treatments of a spinel powder on its characteristics and furthermore on its sintering behavior. Powder treatments can improve the process, in respect of rheological behavior, improve the green body properties by removing remaining voids, might lead to a decrease of sintering temperature and even increase mechanical properties. These changes are a result of modification of the morphology of the particles, modification of the specific area. Commercial spinel powder was submitted to a treatment. Evaluation of treatment effect was done, based on the rheological behavior of the powder and the modification of physical characteristics (particle size, compressibility, angle of repose) and on its sinterability. In the end, these treatments influence the size and homogeneity of the microstructure the sintering temperature, and finally the transparency.

5:00 PM

(ICACC-S4-047-2019) Optimization of Consolidation Parameters and Characterization of Bulk Silicon-Doped Boron Carbides

M. Gagnepain*[1]; A. U. Khan[1]; C. Hwang[1]; R. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

Previous work at Rutgers University has shown that silicon doping in boron carbide (BC) may mitigate the issue of amorphization in high pressure events. In the present study, iterative trials varying temperature, ramp rate, and dwell time in hot pressing of washed powder mixtures containing commercial boron carbide, silicon hexaboride and elemental boron were performed in an effort to create dense bulk Si-BC samples. Si-BC samples of high relative density were produced at various sizes to determine the viability of scaling up the synthesis process to industrial level production. The prepared samples were characterized by X-ray diffraction to determine their stoichiometries and possible changes in the lattice structure. Raman spectroscopy helped to confirm the stoichiometry and enabled us to probe Vickers micro-indentations for amorphization in the Si-BC system. A Field Emission Scanning Electron Microscope (FESEM) coupled with Energy Dispersive X-ray Spectroscopy was used to observe the microstructure of the samples and map elemental distribution. Optimization of the sintering protocol will lead to better understanding of the limits of Si doping in the BC system, and will help in obtaining a dense amorphization resistant boron carbide large enough to conduct dynamic compression tests.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Beyond Li Batteries II

Room: Tomoka A

Session Chair: Hans Seifert, Karlsruhe Institute of Technology

8:30 AM

(ICACC-S6-024-2019) Sodium reactivity on $Na_2M_3O_7$ (with M = Mn, V) (Invited)

V. Pralong*[1]; E. Adamczyk[1]

1. CNRS, Crismat, France

Among the cathodes of the sodium ion batteries, the manganese based oxide materials present many advantages due to their high energy density, low-cost and low-toxicity. In particular, numerous layered materials have been reported in the system Na-Mn-O. These materials are interesting because they show weak interlayer interactions with free space allowing sodium diffusion. Here, we report the electrochemical activity of $Na_2M_3O_7$. its structure consists of Mn-vacancy-$[Mn_3O_7]^{2-}$ layers built up with edge sharing MnO_6 octahedra, separated by NaO_6 and NaO_5 polyhedra. This material could insert reversibly two sodium at 2.1V leading to the formation of $Na_4Mn_3O_7$. Interestingly, an additional reversible redox process, corresponding to the extraction of 1.5 Na^+, is observed on oxidation at 4.1 V due to the oxygen redox activity. Thus, by cycling this material in the potential range 4.7-1.5 V, the reversible specific capacity reaches 200 mAh/g. In comparison, no oxygen activity has been observed for the vanadium based material $Na_2V_3O_7$. A reversible charge capacity of 80 mAh/g at 2.8 V vs Na^+/Na is due to the V^{5+}/V^{4+} redox activity. In addition, two sodium could be inserted in the material, leading to the formation of a Rock Salt type material. The mechanism of extraction as well as the structures of the as-prepared and oxidized phases will be discussed in this presentation.

9:00 AM

(ICACC-S6-025-2019) Operando X-ray study of Na and K ion intercalation in MnO_2 electrodes (Invited)

S. T. Misture*[1]

1. Alfred University, MSE, USA

X-ray total scattering was teamed with Raman and X-ray spectroscopy and related tools to probe both the mesostructure and the atomic defects of MnO_2 nanosheet assemblies, revealing a direct link between surface Mn3+ defects and charge storage. Nominally defect-free MnO_2 nanosheets were reassembled into 3-D porous structures, followed by controlled reduction of some of the tetravalent Mn. Electrophoretic deposition onto glassy carbon substrates was used to provide samples suitable for operando study using high energy synchrotron radiation. Data demonstrate that the nanosheets breathe in 2-D; in other words, the interlayer spacing between nanosheets remains invariant while the nanosheets expand and contract in the plane of the nanosheets by as much as 1% during charging. X-ray spectroscopy provides the Mn oxidation state which completes the picture of Mn redox. Overall, the study demonstrates that Mn3+ defects increase charge storage by 3X with improvement in charge transfer resistance of 10% and dramatically improved cycle stability.

9:30 AM

(ICACC-S6-026-2019) Alloying-type electrode materials for emerging K-ion and Mg-ion storage systems (Invited)

R. Berthelot*[1]; F. Murgia[1]; V. Gabaudan[1]; M. Sougrati[1]; L. Monconduit[1]; L. Stievano[1]

1. CNRS / ICGM (France), France

Lithium-ion batteries are today everywhere. They power our portable electronic devices and are now more and more integrated in electric vehicles. In half a century, this technology overtook the others in terms of energy density and lifetime. However, its sustainability is questionable, especially with the current production boost. It is thus important to investigate other types of electrochemical energy storage technologies. Recently, potassium-ion and magnesium-ion system have focused the interest of the research community as they can theoretically exhibit high energy density and meet sustainability requirements. Metals from the p-block elements are known to alloy with alkali or alkaline earth ions. As the reaction occurs at low potentials, these metals are of interest as active materials in negative electrodes, with particular formulations that can buffer the important volumetric expansion resulting from the electrochemical alloying. Here, we will first focus on the mechanisms of the electrochemical alloying of potassium and magnesium, thanks to operando characterization techniques such as X-ray diffraction and Mössbauer spectroscopy. Moreover, we will show how alloys can be used as a platform to investigate positive electrode materials when (electro)chemical issues do not ease classical half-cells tests. To illustrate the concept, preliminary results on Mg/S cells will be detailed.

Thermoelectrics III

Room: Tomoka A

Session Chair: Masashi Mikami, National Institute of Advanced Industrial Science and Technology

10:20 AM

(ICACC-S6-027-2019) Drastically Suppressed Lattice Thermal Conductivity of ZnO-based Thermoelectric Oxides with Extended Solubility Limit on Binary Doping (Invited)

M. Ohtaki*[1]

1. Kyushu University, Interdisciplinary Graduate School of Engineering Sciences, Japan

Zinc oxide has been one of the most promising n-type thermoelectric oxides with relatively large power factor competitive to major non-oxide candidates such as skutterudites and clathrate compounds. However, a quite high lattice thermal conductivity of ZnO has limited its ZTvalues below 0.7, despite a number of attempts to suppress the thermal conduction in the oxide. The ZnO samples doped with equimolar amounts (x at. % to Zn) of Al and Cu showed a significant peak shift in their XRD patterns, which has never been observed on single doping of Al or Ga. Moreover, the thermal conductivity of the samples at x = 8 was as low as 5 and 1.5 W/Km at room temperature and 800 °C, respectively. By comparing with the thermal conductivity of 40 and 8 W/Km for Al-doped ZnO at x = 2 at the corresponding temperatures, a drastic reduction of the thermal conductivity was obvious. An enhanced substitution of Zn with Al was clearly observed by ^{27}Al MAS solid state NMR as enriched Al in the 4-fold coordination, evidencing an extended solubility limit of Al into the ZnO lattice in the presence of Cu as a co-dopant. It should also be noted that the value at 800 °C is very close to the theoretical lower limit of 1.2 W/Km for ZnO above room temperature.

10:50 AM

(ICACC-S6-028-2019) First principles assessment of the thermoelectric performance of Pyrochlore ceramics for direct thermal to electrical energy conversion (Invited)

J. Goldsby*[1]

1. NASA Glenn Research Center, Chemistry and Physics, USA

Solid state power conversion devices, such as thermoelectrics, depend solely upon the temperature gradients for their operation. Aeronautic engines, gas turbine and futuristic hypersonic type vehicles, have temperature gradients throughout, due to the enthalpy processes of combustion, which offers the possibility of some conversion to electrical power for use in primary and secondary electrical systems in the aircraft. However, currently available thermoelectric materials do not have the environmental durability and performance levels necessary to realize these benefits. New materials must be developed that can meet the requirements to harvest waste enthalpy in oxidizing environments. The ceramic Pyrochlore series of compounds possesses a myriad of electrical properties from being insulators to degenerate semiconductors with the associated metal-like electrical conductivity. To determine their suitability as thermoelectric generators, virtual crystals and super-cell calculations were performed on the most promising systems. Variations in compositions to determine the effects of dopants were also performed. The calculations were carried out using a projector augmented wave (PAW) method employing a commercial code (Materials Design Inc.) MedeA incorporating the Vienna Ab-initio Simulation Package (VASP) as the computational engine.

11:20 AM

(ICACC-S6-029-2019) Plasma sprayed transition metal oxides and related multilayer devices for thermoelectric applications

F. R. Caliari*[1]; H. Lee[1]; S. Sampath[1]

1. Stony Brook University, Center for Thermal Spray Research, USA

Transition metal oxides (TMO) are potential candidates for thermoelectric (TE) applications. Thermal spray (TS) stands out as a feasible process route, enabling the processing of these high temperature materials under either reducing or oxidizing environment, and thus providing in-situ reactions and control of the oxide stoichiometry. Recent studies have shown reasonable thermoelectric properties in in-situ synthesized sub-stoichiometric TiO_2 producing an n-type TE material. In this study additional oxides with potential p-type response to enable fabrication of p-n junctions and resultant thermoelectric devices are approached. In addition, multilayer strategy along with patterning is invoked using the unique capabilities of plasma spray to assemble thermoelectric system which can directly be applied on heat engine components for waste heat power harvesting.

11:40 AM

(ICACC-S6-030-2019) Glass-ceramic oxidation protective coatings for manganese- and magnesium-based thermoelectric silicides

F. D'Isanto*[1]; M. Salvo[1]; F. Smeacetto[2]; F. Gucci[3]; K. Chen[3]; M. Reece[3]

1. Politecnico di Torino, DISAT, Italy
2. Politecnico di Torino, DENERG, Italy
3. Queen Mary University of London, Nanoforce Technology Ltd, United Kingdom

Higher manganese silicide (HMS) and magnesium silicide are considered promising thermoelectric materials to generate electricity from waste-heat recovery. However, a critical issue is their stability over time and their oxidation resistance at temperatures above 500°C. Glass-based materials, due to their low electrical and thermal conductivity, are good candidates as protective coatings. In this work, $MnSi_{1.74}$ and $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ substrates, densified by spark plasma sintering, were coated with silica-based glass-ceramic materials in order to provide oxidation protection. The thermal cycling stability (from room temperature to 600°C in air) of as-sintered and glass-ceramic coated HMS was studied, with respect to changes in their chemical composition and electrical properties. The formation of a Si-deficient layer on the uncoated HMS, due to the reaction between HMS and oxygen at 600°C, led to a higher electrical resistivity as well as a reduced power factor. The coated samples did not show variations in electrical properties compared to the as-sintered one, thus demonstrating that the use of a glass-ceramic coating is an efficient oxidation protective system during cyclic working conditions. Moreover, a new silica-based glass-ceramic coating for magnesium silicide was designed in order to improve the long-term reliability of the thermoelectric module and its efficiency.

Beyond Li batteries III

Room: Tomoka A

Session Chairs: Marca Doeff, Lawrence Berkeley National Laboratory; Olivier Guillon, Forschungszentrum Juelich

1:30 PM

(ICACC-S6-031-2019) Aluminum rechargeable batteries with chloroaluminate liquid salt electrolytes (Invited)

T. Tsuda*[1]; Y. Uemura[1]; H. Gofuku[1]; C. Chen[2]; H. Matsumoto[3]; S. Kuwabata[1]

1. Osaka University, Department of Applied Chemistry, Japan
2. AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory, Japan
3. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Based on many years of experiences in Al electroplating from chloroaluminate liquid salts, e.g., $AlCl_3$–1-ethyl-3-methylimidazolium chloride ($[C_2mim]Cl$) ionic liquid (IL) and $AlCl_3$–NaCl–KCl molten salt, we have created several types of Al rechargeable batteries so far. If appropriate carbon materials are employed as the cathode materials, certain Al batteries can be fabricated with relative ease. In the present study, we attempted to use commercially available expanded graphite and $LiCoO_2$ as the cathode active materials for the Al rechargeable battery with chloroaluminate liquid salt electrolytes. The expanded graphite cathode showed favorable cyclability and relatively-high capacity. Especially, the cathode performance was greatly enhanced, when $AlCl_3$–NaCl–KCl molten salt was employed as the electrolyte. At 393 K, the battery showed outstanding capacity (128 mAh g^{-1} at 100 mA g^{-1}) and rate capability (63 mAh g^{-1} at 8000 mA g^{-1}). As to the Al battery with the $LiCoO_2$ composite cathode, the discharge capacity exceeded 131 mAh g^{-1} in the LiCl added $AlCl_3$–$[C_2mim]Cl$ under the charge/discharge rate of 10 mA g^{-1} at 298 K. $LiCoO_2$ and its analogues will be key materials for creating high capacity Al rechargeable battery.

2:00 PM

(ICACC-S6-032-2019) Prototype structures enabling reversible electrochemical Al^{3+} intercalation (Invited)

D. Dambournet*[1]

1. Sorbonne Universités, University Pierre and Marie Curie, France

From the perspective of the ionic radius, Al^{3+} ion exhibits ionic radius (0.53 Å) that is inferior than that of Li^+ (0.76 Å), and thus the insertion of such a cation in host frameworks is, in principle, achievable. Other characteristics, however, must also be taken into account, in particular, the extent to which the cation interacts with the anionic sublattice. By comparing values of the polarizing power between Li^+ and Al^{3+} cations, we can expect an increasing interaction with the anionic sublattice moving from Li^+ (1.73) to Al^{3+} (10.68). As a consequence, the intercalation chemistry of Al^{3+} ions is expected to strongly differ from that typically encountered for the lithium-ion. So far, knowledge's on Al^{3+} intercalation chemistry remains poorly understood because of several limitations including a limited number of suitable frameworks that enabled Al^{3+} intercalation. Here, we will present and discuss two Ti-based compounds recently reported by us. These compounds that are based on 3D-anatase and layered-like lepidocrocite type structures have specific structural features that enabled to reversibly insert Al^{3+} ions at room temperature. The Al^{3+} electrochemical storage mechanism will be discussed in relation with the specific structural features.

2:30 PM

(ICACC-S6-033-2019) A low-cost intermediate temperature Fe/Graphite battery for large scale energy storage (Invited)

X. Ning*[1]

1. Xi'an Jiao Tong University, China

Due to their enormous storage/supply flexibility and physical compactness, batteries are excellent candidates for large scale energy storage applications. However, the widespread application of most batteries hitherto developed is hindered by their high cost. We developed an intermediate temperature Fe/Graphite battery that emphatically resolves this issue. Operated at 170 °C, the cell comprises of a Fe metal anode, NaCl saturated $NaAlCl_4$ electrolyte and an $AlCl_4^-$ intercalated graphite cathode in the fully charged state. It has a capacity retention rate of 85% after nearly 10,000 cycles and an average coulombic efficiency of 99.5%. After systematically characterizing the anode, it was determined that the absence of dendritic growth and the high reversibility of the Fe to $FeCl_2$ solid state transformation are responsible for alleviating capacity fading in this cell. Different capacity matching strategies were also discussed in the context of ensuring safe operation during overcharging. Finally, the overall cost of the Fe/Graphite cell was estimated to be 80.2 \$ kWh^{-1}, which potentially can meet the demands of the commercial energy storage market.

Li Batteries IV

Room: Tomoka A

Session Chairs: Damien Dambournet, Sorbonne Universités; Valerie Pralong, CNRS ENSICAEN

3:20 PM

(ICACC-S6-034-2019) Ionic and thermal transport properties of ceramic solid electrolytes

M. Rohde*[1]; H. J. Seifert[1]

1. Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

Within this work we have studied three NASICON (Na Superionic Conductor) structured ceramic systems, which are candidate materials for solid state electrolytes for Li-ion cells but also for systems beyond Lithium ion technology. Namely, LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, x»0.5), LATP ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, x»0.5) and NAGP ($Na_{1+x}Al_xGe_{2-x}(PO_4)_3$, x»0.5) substrates were prepared using a melt quenching route

and by applying different compaction methods. In order to develop a better understanding of the relationship between the specific microstructure and the ionic conductivity as well as the thermodynamic properties of the samples were characterized by scanning electron microscopy and x-ray diffraction. The ionic conductivity was measured using impedance spectroscopy while the thermal diffusivity and the specific heat were determined by Laser Flash technique and differential scanning calorimetry, respectively. Additionally, thermal analysis was performed in order to evaluate glass transition as well as the crystallization temperatures in order to characterize the thermal stability a higher temperatures and to identify the optimum temperature range of the thermal post-processing. The three ceramic systems were compared regarding their ionic conductivity and thermodynamic behaviour. A possible correlation between the ionic and thermal transport properties will be discussed.

3:40 PM

(ICACC-S6-035-2019) Impedance of grains and grain boundaries of Li ion conducting ceramic solid electrolytes

S. Seepalakottai[1]; P. Balaya*[1]

1. National University of Singapore, Department of Mechanical Engineering, Singapore

Ceramic solid electrolytes (CSEs) have gained huge interest among Li-ion battery (LIB) research community due to their unique advantages such as high thermal stability (safety), high chemical stability towards Li metal and/or lithiated graphite, appreciable ionic conductivity at room temperature, ease of preparation/handling and so on. One of the main challenges in using any CSEs in LIBs is their interfacial impedance between the solid electrolyte and cathode/anode material. This challenge may be addressed if the CSEs are prepared with high ionic conductivity (in the range of 10^{-2} to 10^{-3} S/cm) at both grains and grain boundaries. Measurement of impedance of CSEs using 2-probe measurement can hardly distinguish contributions of grains and grain boundaries. Whereas, 4-probe micro-contact impedance study is more sensitive and enable to distinguish thecontributions of grains and grain boundaries separately. In this presentation, we investigate the impedance of grains and grain boundaries of Li-ion conducting NASICON-structured CSEs at different temperature, DC bias, probe distance and atmosphere to highlight the crucial factors that affect the ionic conductivity at the grain boundaries.

4:00 PM

(ICACC-S6-036-2019) Engineering transport pathways and interfaces in composite ceramic electrolytes for all solid state batteries

F. Shen[1]; M. Dixit[1]; K. B. Hatzell*[1]

1. Vanderbilt University, Department of Mechnanical Engineering, USA

Li-metal batteries are the primary market for solid state batteries because the state-of-the-art liquid electrolytes are incompatible with Li-metal. Theoretical studies suggest that solid electrolytes with a modulus of 6 GPa can mitigate dendrite propagation and short circuiting in solid state batteries. However, there are still several significant challenges with the integration high voltage cathodes with solid electrolytes (i.e. transport at extrinsic interfaces). Crystal structure lattice mismatch, the existence of a Li+ deficient space charge layers, and the formation of chemically unstable interfaces are large responsible for high interfacial impedances in all solid state batteries. To mitigate this fact, there is a growing number of researchers investigating interfacial engineering and modification strategies. Strategies involve either coating the electrode material with a buffer ionic conductor, or coating the electrolyte with an electronic conductor. Herein, we decouple the effects intrinsic and extrinsic interfaces have on transport in composite solid electrolytes. The ultimate goal is to understand how to engineer extrinsic interfaces for strength and transport. Results elucidate the trade-offs between adhesion and elastic strength at extrinsic interfaces n charge storage.

4:20 PM

(ICACC-S6-037-2019) Investigation of Metallic Dendrite Growth in Solid Electrolytes

C. Lei*[1]; T. D. Sparks[1]; A. V. Virkar[1]

1. University of Utah, Materials Science and Engineering, USA

Sodium sulfur batteries have been widely used for energy storage. Also, sodium ion batteries operating at room temperature are under development. One of the modes of failure of these devices is the formation of metallic sodium dendrites. In this work, a two-phase material Na-β''-alumina+3YSZ has been used to investigate the sodium dendrite growth under electrolytic conditions. The mixed Na^+ ion and O^{2-} ion electrolyte is fabricated by vapor phase process. In this process, α-alumina and 3YSZ was mixed by ball-milling, then the copper wire with a thin layer coat of wax was embedded inside during the initial die-pressing stage. This allows a hole to form so wires can be inserted inside. After wax evaporation, the copper wire was extracted. The disc was then sintered in air at 1500°C for 3 hours. After sintering, the disc was buried in Na-β''-alumina powder and heat-treated in air at 1450°C for 10 hours to insure fully conversion. To make sure the light can transmit through, the disc was grinded down to about 0.8 mm in thickness. Subsequently, a small plastic tube with 1M $NaNO_3$ was put on the surface of the obtained disc. Silver wires were put into the $NaNO_3$ solution and the embedded hole, they were connected with an amperemeter, a resistor and a voltage generator. The disc was put under the microscope and the voltage of 2.0-3.5V was applied. In-situ formation of sodium dendrites was observed.

4:40 PM

(ICACC-S6-038-2019) X-Ray Tomography Studies of Dendrite Propogation in Ceramic Solid Electrolytes for Solid-State Battery Applications

F. Shen*[1]; M. Dixit[1]; K. B. Hatzell[1]

1. Vanderbilt University, Department of Mechnanical Engineering, USA

All solid-state batteries are promising solutions for high energy density storage devices. While theoretical studies suggested that solid electrolytes with shear modulus larger than 8.5 GPa can mitigate Li dendrite formation, recent experiments have shown contradicting results. So far, studies that probe this failure mechanism have primarily used surface based, destructive, or ex-situ techniques. Herein, we demonstrate an indirect way to probe structural transformations by dendrites in ceramic electrolytes using synchrotron X-ray tomography. A subvolume of 300 μm^3 captures the heterogeneity of the solid electrolyte microstructure while minimizing the computational intensity associated with 3D reconstructions. While the porosity decreases with increasing temperature, the underlying connectivity of the pore region increases. Solid electrolytes with interconnected pores short circuit at lower critical current densities than samples with less connected pores. These insights inform about some crucial aspects of the stability of the solid electrolytes and will help tailor better processing methods. The methodology used in the characterization is extremely versatile and can be leveraged to study a large variety of materials under extremely varied environmental conditions.

S7: 13th International Symposium on Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental, and Health Applications

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures I

Room: Coquina Salon C
Session Chair: Alberto Vomiero, Lulea University of Technology

1:30 PM

(ICACC-S7-001-2019) Solution-Grown Sodium Bismuth Dichalcogenides: Toward Earth-Abundant, Biocompatible Semiconductors (Invited)

J. Vela*[1]

1. Iowa State University, Chemistry, USA

Many technologically relevant semiconductors contain toxic, heavily regulated (Cd, Pb, As), or relatively scarce (Li, In) elements and often require high manufacturing costs. We have developed a facile, general, low-temperature, and size tunable (4–30 nm) solution phase synthesis of ternary APnE2 semiconductors based on Earth-abundant and biocompatible elements (A = Na, Pn = Bi, E = S or Se). The observed experimental band gaps (1.20–1.45 eV) fall within the ideal range for solar cells. Computational investigation of the lowest energy superstructures that result from "coloring", caused by mixed cation sites present in their rock salt lattice, agrees with other better-known members of this family of materials. Our synthesis unlocks a new class of low cost and environmentally friendly ternary semiconductors that show properties of interest for applications in energy conversion.

2:00 PM

(ICACC-S7-002-2019) From Lab to Industry: Story of a New Generation Particle Technology: MicNo® (Invited)

E. Suvaci*[1]; A. Koparal[2]; R. Demirel[2]

1. Eskisehir Technical University, Department of Materials Science and Engineering, Turkey
2. Eskisehir Technical University, Biology Department, Turkey

Nanoparticles are the most widely utilized group and they have been successfully utilized in many technological applications from electronics to medical industry. Fine size of nanoparticles brings unique properties that can not be achieved at larger sizes (i.e., in submicron or micron form). Although nanoparticles posses unique properties, their fine size may cause processing difficulties such as uncontrolled agglomeration, health and environmental problems. Consequently, when scientists deal with nanoparticles, they should not only focus on advantages of them and produce more and more of those particles but also be aware of the potential problems associated with such fine particles and develop new solutions to overcome such potential problems while maintaining unique properties of nanoparticles. Accordingly, our research group with the sponsorship of Entekno Materials, (www.enteknomaterials.com) developed innovative MicNo® Particle Technology, provides both safe and environmentally benign nanoparticle solutions. MicNo particles are designed, platelet shaped micron particles which are composed of nano primary particles. In this presentation, application of the MicNo particle technology to ZnO system and subsequently both optical and biological properties of MicNo®-ZnO particles will be discussed in detail. In addition, transition of MicNo®-ZnO particles to commercial applications will be presented.

2:30 PM

(ICACC-S7-003-2019) Surface Modification of Cathode Particles with Oxide Electrolyte Nanocoating for Interfacial Resistance Control in All Ceramic Li-ion Battery (Invited)

H. Suzuki*[1]; J. K. Padarti[1]; T. T. Jupalli[2]; T. Ohno[3]; S. Hirai[3]; T. Kawaguchi[2]; N. Sakamoto[1]; N. Wakiya[1]

1. Shizuoka University, Research Institute of Electronics, Japan
2. Shizuoka University, Graduate School of Integrated Science and Technology, Japan
3. Kitami Institute of Technology, Department of Materials Science, Japan

Herein, we demonstrated an innovative approach to address the huge interfacial resistance in all ceramic type Li-ion battery by nanocoating of Li-ion conductive cubic garnet $Li_7La_2Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) surface layer over a high-capacity Ni rich $LiCo_xNi_yMn_zO_2$ (LNMC) cathode through boundary engineering. A superior LNMC/LLZTO interface and/or cathode/electrolyte boundary have been achieved with simultaneous improvements in the interfacial contact, electrochemical and chemical stability for the better ionic conductivity, leading to a significantly improvedelectrochemical properties of the resulting all ceramic solid state cell. The boundary engineering for all-ceramic Li/LLZTO/LCO cell delivered an improved initial capacity of about 102 mAh g^{-1} (at 0.5C) with high cycling (50 cycles at 25 °C) stability as well as the capacity fade rate of about 0.196 $mAhg^{-1}$ per cycle, which is the best performance of the all-ceramic Li batteries, and therefore is a significant breakthrough toward the development of intrinsically safe, high-performance all-solid-state lithium ion batteries. Moreover, this approach is not limited to LNMC cathode but can also be applied to any other layered transition-metal oxide cathodes/anode, promoting the practical application of all-solid-state lithium-ion batteries.

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures II

Room: Coquina Salon C
Session Chair: Mauro Epifani, CNR-IMM

3:20 PM

(ICACC-S7-004-2019) Carbon-Metal Oxides Nanocomposites for Energy and Environmental Applications (Invited)

N. Pinna*[1]

1. Humboldt-Universität zu Berlin, Department of Chemistry, Germany

The combination of different nanobuilding blocks in a single heterostructure can lead to materials with improved properties by selecting components with the desired characteristics for a specific application. Carbon-based nanomaterials demonstrated to be highly suitable as support for the elaboration of heterostructures. Atomic layer deposition proved to be a technique of choice for the coating of nanostructured carbon materials. These heterostructures find applications in various areas such as electronics, sensors and energy storage and conversion. Because the chemical inertness of the graphitic carbon inhibits the initiation of ALD film growth, numerous surface functionalization approaches have been investigated in order to provide the required nucleation sites. The different strategies employed for the ALD onto carbon nanotubes, graphene, graphite and other nanostructured carbon materials (e.g. carbon black, fibers) will be described. The peculiarity of ALD for tailoring the chemical, structural and morphological properties of the deposited material will be discussed. Finally, in order to highlight the importance of this class of materials, possible applications in energy storage and conversion, catalysis and gas sensing devices are also reviewed.

3:50 PM

(ICACC-S7-005-2019) New generaton of chalcogenide and phosphide catalyst for water splitting and PEM fuel cells (Invited)

D. Chua*[1]

1. National University of Singapore, Materials Science & Engineering, Singapore

Electrocatalysts are critical to increase reaction rates and control selectivity in many electrochemical reaction. Rational design and synthesis of material with controlled structures and morphologies from nanoscale to microscale are of utmost importance in order to achieve optimal performances. Today's catalyst goes beyond traditional expensive noble metals such as gold and platinum, especially in the area of water splitting (or hydrogen evolution reaction), we shall like to report on a new generation of 0D, 1D and 2D nanocomposites in the chalcogenide and phosphide family are highly promising. As a part of this electrochemical system strongly depends on the catalyst support. We further show that the formation of hybrid core-shell nanostructures utilizing carbon materials and metal foams as a base template effectively enhance the performance and extend the range of applications. Other than HER, these applications include PEM fuel cells. For example, MoS2 coated graphene/carbon nanotubes formed excellent catalytical activity in HER and PEM fuel cell applications.

4:20 PM

(ICACC-S7-006-2019) Harnessing Light From Rare Earth Doped Nanoparticles for Diverse Applications in Nanomedicine (Invited)

F. Vetrone*[1]

1. Institut National de la Recherche Scientifique, Université du Québec, Centre Énergie, Matériaux et Télécommunications, Canada

In the last decade, the field of rare earth doped nanoparticles has progressed from the basic understanding of the photophysical properties governing their nanoscale luminescence to their use in a variety of applications, with considerable focus in nanomedicine. This interest stems primarily from the ability to stimulate these luminescent nanoparticles with near-infrared (NIR) light as well as their diverse emission wavelengths spanning the UV to the NIR regions. Therefore, with a single NIR excitation wavelength, it is possible to observe anti-Stokes emission, known as upconversion, or single photon (Stokes) NIR emission in the three biological windows (BW-I: 700-950 nm, BW-II: 1000-1350 nm, BW-III: 1550-1870 nm) where tissues are optically transparent. Here, we present the synthesis of these nanoparticles, demonstrate how their various emissions could be harnessed for applications in biology and nanomedicine, and show how their optical properties could be further improved through the rational combination with other optically active nanostructures.

4:50 PM

(ICACC-S7-007-2019) Novel Pt@TiO_2 core-shell nanoparticles as catalyst for application in intermediate temperature range fuel cells

P. S. Nbelayim*[1]; Y. Ashida[1]; G. Kawamura[1]; W. K. Tan[2]; H. Muto[2]; A. Matsuda[1]

1. Toyohashi University of Technology, Electrical and Electronic Information Engineering, Japan
2. Toyohashi University of Technology, Institute of Liberal Arts and Sciences, Japan

Fuel cells is an area of high interest among the various alternative sustainable and environmentally friendly energy sources with the key advantages of low-to-zero emissions, fuel usage flexibility, high efficiency, portability and facile operability. Proton exchange membrane fuel cells (PEMFCs) is dominating the field with Pt applied as the catalyst for both anode and cathode. An effective catalyst should exhibit good activity, selectivity, stability and poisoning resistance. Current research target is to fine tune the properties of Pt for optimal usage and performance with various approaches including alloying with, layering on or below and core-shell with other materials. In our work we have prepared 2-7 nm size (by XRD and TEM) Pt@TiO_2 core-shell particles via a nano-micelle emulsion approach with hot-water and heat treatments that control particle size growth, a major challenge in the catalysis sector of PEMFCs. Quantitative EDX evaluation showed 75, 9.1 and 6.9 wt.% Pt, Ti and O, respectively. Cyclic voltammetric characterization showed a stable and reversible redox activity. Thus, we think these novel core-shell nanoparticles will exhibit effective catalysis in PEMFCs especially in the areas of stability, selectivity and poisoning resistance.

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Advanced Manufacturing and Processing II

Room: Coquina Salon A

Session Chairs: Shaowei Zhang, University of Exeter; Ajayan Vinu, University of Newcastle

8:30 AM

(ICACC-S8-026-2019) High Temperature Mechanical Properties of BN Particle Dispersion SiC Composites Fabricated with Prepreg Technique (Invited)

T. Hinoki*[1]; K. Kawasaki[1]; F. Shinoda[1]; A. Hashimoto[1]; N. Tsurui[2]; S. Hokari[2]; K. Shimoda[3]

1. Kyoto University, Japan
2. Kobe Material Testing Laboratory Co., Ltd., Japan
3. National Institute for Materials Science (NIMS), Japan

Silicon carbide composites basically require weak fiber/matrix interphase like boron nitride (BN). However precise control is the critical issue in terms of large scale production and cost. The interphase is the weakest link for the environmental effects. The SiC composites were developed by applying BN particle dispersion in SiC matrix without the interphase. The prepreg technique was developed. The objective is to understand the high temperature mechanical properties of the SiC composites. Silicon carbide composites reinforced with satin weave Hi-Nicalon type-S were fabricated by liquid phase sintering using the prepreg sheet. The prepreg sheet consisted with SiC fibers, SiC and BN powders and Al_2O_3 as sintering additive. Mechanical properties were characterized by tensile and fatigue tests. The BN particle dispersion SiC composites had uniform microstructure through thickness. No significant degradation of strength wasn't observed at 1200C in air. Oxidation of the composites were limited to near surface. The composites didn't break following over 100 thousand cycles applying 140 MPa at 1200C in air. The specimens had no oxidation resistant coating like CVD SiC. This work was supported by METI, Japan for the Advancement of Strategic Core Technologies, "Development of Production Process of SiC/SiC composites for High Efficiency Aircraft Engine."

9:00 AM

(ICACC-S8-027-2019) SiC-bonded diamond materials: A superhard wear and corrosion resistant material

M. Herrmann*[1]; B. Matthey[1]; S. Kunze[1]; A. Kailer[2]

1. Fraunhofer IKTS, Germany
2. Fraunhofer IWM, Germany

A new, extremely wear-resistant and superhard material is SiC-bonded diamond ceramic, which can be manufactured by reaction bonding of diamond by liquid silicon infiltration similar to the SiSiC process. Using this approach, components can be produced cost-effectively in large sizes and with complex shapes. They can also

be produced as layered materials with SiC-bonded diamond only in areas where it is required. Due to the strong chemical bonding between silicon carbide and diamond, the new material shows excellent properties: hardness (HK) > 45GPa, strength values between 450 and 600 MPa (biaxial test), K_{IC} of 4-5 $MPam^{1/2}$ and thermal conductivity up 500-600 W/mK depending on the microstructure. SiC-bonded diamond materials exhibit a high corrosion resistance even in basic media due to a low Si content of. They contain 40-60 Vol% of diamonds, but exhibit a friction behavior similar to PCD materials. After a short explanation of the production technology correlations between the microstructure and mechanical properties and corrosion properties and wear behavior will be given.

9:20 AM

(ICACC-S8-028-2019) Study of phase transitions of zinc sulfide optical materials

Y. Li*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

The ZnS phase transition between cubic sphalerite and hexagonal wurtzite has been considered as a crucial factor for fabricating zinc sulfide (ZnS) optical ceramics. In the current research, the phase transformation behaviors of ZnS ceramics consolidated via hot pressing and pressureless sintering was investigated. Two ZnS powders with different particle sizes and morphologies were employed to study the influences of microstructural features of starting powder on the phase transition behavior of ZnS. XRD, SEM and EBSD analyses revealed that the phase transition temperatures of ZnS during sintering correlates to the particle size of the powders and the consolidation pressure applied to the samples. An applied uniaxial pressure during hot pressing sintering could lead to the reverse phase transformation from wurtzite to sphalerite along with twining, resulting in improved optical and mechanical performances of the ZnS optical ceramics.

9:40 AM

(ICACC-S8-029-2019) Direct formation of photocatalytic anatase TiO_2 on titanium metal (Invited)

T. Ishikawa*[1]; K. Tsujikura[1]; M. Deguchi[1]; A. Aoki[1]

1. Tokyo University of Science, Yamaguchi, Applied Chemistry, Japan

Titanium has been widely used in various fields because of specific properties such as exceptional resistance to corrosion and oxidation. These properties are attributed to the oxide film formed on the titanium. Generally, the abovementioned oxide film consists of a thermodynamically stable rutile phase, which does not show the sufficient photocatalytic activity. To form a photocatalytic anatase TiO_2 on titanium, relatively complicated process such as hydrothermal reaction and anodic oxidation have been performed. Here we describe a simple process for direct formation of photocatalytic anatase TiO_2 on titanium. In our process, at the first step, titanium was treated by a reduction agent to create a surface titanium hydride layer, which is thermodynamically stable compared to pure titanium; rutile-formation is effectively prevented by the existence of the abovementioned titanium hydride at room temperature. After that, the treated titanium covered with titanium hydride was immerged in an aqueous silica; subsequent calcination effectively generated the surface anatase layer. It's because the covered silica stabilized the formed anatase phase; at the interface between TiO_2 and SiO_2, atoms constructing TiO_2 are substituted into the tetrahedral silica lattice, forming tetrahedral Ti sites. In this paper, the photocatalytic activity of the obtained titanium covered with anatase TiO_2 will be also described.

10:30 AM

(ICACC-S8-030-2019) Novel Interfacial Exfoliation by Electrical Pulse Fragmentation for Reuse and High-Grade Recycling (Invited)

G. Granata*[1]; C. Tokoro[1]

1. Waseda University, Department of Resources and Environmental Engineering, Japan

Electrical pulse fragmentation (EF) is a comminution method to break samples selectively at the phase boundary between insulators and electrical conductors. The method was proven effective to detach parts from printed circuit boards and separate resins from copper wires. However, controlling the point to be irradiated by the electric pulses is crucial to dismantle the sample rather than damaging it. Thus, this work addressed the development of an innovative EF method that enables to control electrode position and irradiation point. The EF method was applied on screwed samples and three-layer samples consisting of steel plate, urethane resins and adhesive agents. Samples were dismantled by EF with and without control system. Experimental results highlighted that a larger number of pulses were required to dismantle the screws from the sample body without electrode position control while the three-layer sample could not be dismantled at all. In contrast, assisting EF with the control system produced an efficient dismantling of the screws from the body with only one or two pulses. The method was proven efficient also under open air atmosphere. The obtained results suggest that the EF with electrode position control system could be efficiently used to achieve reuse and high-grade recycling by promoting the selective localized detachment of parts from the targeted devices.

11:00 AM

(ICACC-S8-031-2019) Aqueous Tape Casting of Multilayer Transparent Nd:YAG Composite Ceramics

X. Chen*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

Aqueous tape casting and oxygen atmosphere sintering were successfully applied to process the transparent multilayers Nd:YAG ceramics. Homogenous and flexible green tapes could be obtained at room temperature with a relative humidity >60% for drying > 24h. The de-bindering and sintering process were combined into one process by using oxygen sintering technique. After sintering, transparent Nd:YAG ceramic composites were obtained without an annealing process. The average grain size was about 5μm after sintering at 1750oC. High transmittance with uniform microstructures of Nd:YAG ceramics were obtained. The optical transmittance at the laser emission wavelength was measured in UV–VIS regions with a transmittance of approximate 77%.

11:20 AM

(ICACC-S8-032-2019) Fabrication of c-axis oriented $(Sr,Ca)_2NaNb_5O_{15}$ in rotating high magnetic field with stereolithography

S. Baba*[1]; S. Tanaka[1]

1. Nagaoka University of Technology, Japan

Crystal-orientation using the colloidal processing in a high magnetic field is effective for improving property of the polycrystalline ceramics. We have examined on the colloidal processing with UV curable binder and reported the fabrication of a particle-oriented green sheet. The polymerization by the UV light could shorten the duration time in the magnetic field for several ten seconds. However, a green sheet prepared by polymerization is very thin because scattering of light cause within the slurry during forming. The objective of this study is to prepare a particle-oriented bulk ceramic by stereolithography in rotating high magnetic field. In the experiment, the well-dispersed slurry with solid loading of 55 vol% was prepared from the UV curable acrylic binder, photoinitiator, and dispersant.

The slurry was cast on a PET film and placed in magnetic fields with 10 T. After duration of various seconds, UV light was irradiated to the tapes in the magnetic field. The casting of the slurry on the film and polymerization was repeatedly performed. The key are preparation of well-dispersed slurry and formation of green body with homogeneous structure.

Joining Technologies and Polymer-based Processing

Room: Coquina Salon A

Session Chairs: Tatsuya Hinoki, Kyoto University; Toshihiro Ishikawa, Tokyo University of Science, Yamaguchi

1:30 PM

(ICACC-S8-033-2019) Multi-Component Carbosilane Systems for the Modular Production and Printing of Polymer-Derived Ceramics (Invited)

M. B. Dickerson*[1]; L. Baldwin[1]; L. M. Rueschhoff[1]; C. Wyckoff[1]; M. Cinibulk[1]; H. Koerner[1]; M. Dalton[1]

1. Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Preceramic polymers (PCPs), a class of soluble semi-organic macromolecules that can be converted to refractory materials via pyrolysis, are essential for the development of additively manufactured ceramics and composites used in high temperature aerospace applications. In this talk, we will discuss our approach to synthesizing convenient, modular PCP systems with high ceramic yield. Through a one-step procedure, we have synthesized hyperbranched PCPs with low polydispersity, tailorable properties, and optimized processability. These hyperbranched PCPs are paired with reactive small molecule cross-linkers specifically selected and optimized for additive manufacturing. Effects of polymer chemistry and rheology on printability, ceramic composition, and high-temperature performance of printed ceramic will be detailed.

2:00 PM

(ICACC-S8-034-2019) Experimental Studies on Joinability of Zircaloy and SiC/SiC Composite with Titanium Powder

H. Serizawa*[1]; N. Nakazato[2]; Y. Sato[1]; M. Tsukamoto[1]; J. Park[2]; H. Kishimoto[2]

1. Osaka University, Joining and Welding Research Institute, Japan
2. Muroran Institute of Technology, Japan

As for the fuel cladding in the light-water reactor, silicon carbide fiber reinforced silicon carbide composite (SiC/SiC composite) is one of the promising candidates as a replacement of Zircaloy due to many superiorities, where it is necessary to develop the end-cap seal of SiC/SiC composite cladding. According to our previous researches, SiC/SiC composite and Zircaloy tubes were joined by employing the laser irradiation based on the caulking method. Zircaloy tube partially overlaps with SiC/SiC composite tube where the outer surface of SiC/SiC composite tube was circumferentially silted and titanium powder was inserted in the slit. Then, the laser irradiation was circumferentially applied on the outer surface of Zircaloy tube. In this research, in order to examine the joinability of Zircaloy and SiC/SiC composite precisely, Zircaloy plate is overlapped on SiC/SiC composite plate where the narrow slit is manufactured and titanium powder is inserted in the slit, and then the laser irradiation is applied on the surface of Zircaloy plate. Through the variety of laser irradiation conditions, the generation process of all proportional solid solution between titanium and zirconium is revealed.

2:20 PM

(ICACC-S8-035-2019) TEM Analysis of Interfaces in Diffusion-Bonded SiC Fiber-Bonded Ceramics Using metal Interlayers

T. Ozaki*[1]; Y. Hasegawa[1]; H. Tsuda[2]; S. Mori[2]; M. C. Halbig[3]; R. Asthana[4]; M. Singh[5]

1. Osaka Research Institute of Industrial Science and Technology, Japan
2. Osaka Prefecture University, Japan
3. NASA Glenn Research Center, USA
4. University of Wisconsin-Stout, USA
5. Ohio Aerospace Institute, USA

SiC-based fiber bonded ceramics are promising materials for a wide variety of aerospace and ground based thermo-structural and thermal management applications. Robust joining and integration technologies are indispensable for this material system in order to fabricate large size and complex shape components with desired functionalities. Active metal brazing and diffusion bonding techniques using metallic interlayers have been developed for integration of fiber bonded ceramics for intermediate temperature applications. Recently, robust joints of SiC fiber-bonded ceramics (SA-Tyrannohex: SA-THX) were obtained by diffusion bonding with metal interlayers. In that report, from the result of Knoop hardness measurement, when Ti/Mo foil was used, there was the difference in strength due to fiber direction of SA-THX and indenter position of the joint. On the other hand, when Ti/Cu foil is used, the variation of the Knoop hardness value was small, and the dependence on indenter position was not observed. These results indicate the effect of fiber structure derived from SA-THX and insert metal on the joint structure is closely related to the bonding quality. Therefore, in order to investigate the influence of fiber structure on the SA-THX joints fabricated using diffusion-bonding with metal interlayers, we carefully observed the microstructure of the interface using TEM /STEM.

2:40 PM

(ICACC-S8-036-2019) Novel Applications and Improved Processing of Commercial Pre-Ceramic Polymers (PCPs)

Z. D. Apostolov*[1]; E. Heckman[2]; T. Key[3]; M. Cinibulk[1]

1. Air Force Research Laboratory, USA
2. Wright State University, USA
3. UES, Inc., USA

While commercially available polymeric precursors can be an excellent source for the manufacturing of basic ceramic components, they are generally designed for a single processing method and fixed ceramic chemistry. Additionally, as products of large-scale synthesis, their Molecular Weight Distributions (MWDs) can be rather wide, and the variability in long-chain branching quite large. This makes their response to processing treatments somewhat unpredictable, and leads to difficulties in implementing a precise manufacturing schedule. In order to address some of these shortcomings, and allow for more flexibility in the polymers' utilization, while still taking advantage of their wide availability, efforts have been made to modify a number of the processing properties of representative PCPs. This work will present some of the effects of these modifications on the rheology, MWD, cure behavior, and ceramic yield of commercial polycarbosilane and polysilazane, with fiber spinning and improved ceramic matrix composites processing being among the targeted applications.

3:20 PM

(ICACC-S8-037-2019) Preceramic Polymer Routes to Silicon Oxycarbide-Based Ceramics (Invited)

E. Ionescu*[1]

1. Technical University Darmstadt, Materials Science, Germany

Silicon oxycarbides (SiOCs) can be considered as being carbon-containing silicates consisting of glass networks in which oxygen and carbon share bonds with silicon. The carbon-for-oxygen

substitution in silicate glass networks has been shown to induce significant changes in the network connectivity and consequently strong improvements in the properties of the silicate glass network. Thus, SiOC glasses exhibit E moduli, hardness values, glass transition and crystallization temperatures, which are superior to those of vitreous silica. Also, the SiOC glass network exhibits unique structural features such as reduced mass fractal dimension and nano-heterogeneity, which significantly affect and/or dictate its properties and behavior. In the present talk, a consideration of the current state of the art concerning the synthesis, processing and various structural and functional properties of SiOC-based materials is done. The synthesis of silicon oxycarbides starting from macromolecular precursors such as polysiloxanes or alkoxysilanes-based sol-gel systems as well as current advances related to their processing will be critically reviewed. Additionally, various structural and functional properties of silicon oxycarbides are presented. Specific emphasis will be put on the intimate correlation between the molecular architecture of the precursors and the structural features and properties of the resulting SiOCs.

3:50 PM

(ICACC-S8-038-2019) On the role of wetting and interfacial reactions in joining of ceramics by brazing alloys (Invited)

F. Hodaj*[1]

1. Grenoble Institute of Technology, Materials Science, France

Interfacial interactions between liquid metals and ceramics are of technological importance in many fields of materials engineering such as joining of ceramics by brazing alloys, manufacturing of metal/ceramic composites, casting of metals, etc. In non-reactive metal/ceramic systems, where non-wetting is usually observed, wetting can be significantly improved by certain alloying elements which form continuous layers of compounds at the interface, by reaction with the ceramic substrate. Such reactions are used in practice to promote wetting, especially for joining of ceramics by brazing alloys. In this presentation, after a short review of the fundamental equations of wetting, the contact angles of non-reactive liquid metals and molten oxides on different types of solids will be given and interpreted. Then, the main features and mechanisms of the reactive wetting are described and illustrated and the factors that govern the reactivity at the triple line and behind the triple line are also discussed. Finally, some particular cases of brazing in non-reactive and reactive systems are presented and discussed in order to show how wetting and reactivity can affect brazeability. All these points will be illustrated by analysis of results obtained in wetting and brazing experiments in metal/ceramic and glass/ceramic systems.

4:20 PM

(ICACC-S8-039-2019) Impact of resin-fibre interaction on macro-level impregnation pattern in resin transfer moulding

M. Nasr Esfahani*[1]; M. Jabbari[2]

1. University of Warwick, WMG, United Kingdom
2. University of Manchester, School of Mechanical, Aerospace and Civil Engineering, United Kingdom

In liquid composite moulding (LCM) processes permeability of preform is directly influenced by the fibre volume fraction (v_f), fibre size and fibre orientation. The variation of resin injection pressure changes the local fibre volume fraction at micro level by displacing the fibre location (geometrically), and hence, alters the permeability at macro level. In this study, we investigate the influence of resin injection pressure and fibre size on local permeability of unidirectional fibres. A benchmark study is carried out by coupling fluid flow analysis of resin impregnation with structural analysis of fibres through fluid-solid interaction (FSI). The preliminary results show that the resin injection pressure has a significant impact on the local permeability compared to fibre size.

4:40 PM

(ICACC-S8-040-2019) Fabricating Energy Absorbing Silicon Carbide Ceramic Nanostructures via Block-Copolymer Soft Templates

L. M. Rueschhoff*[1]; L. Baldwin[1]; R. Wheeler[1]; J. D. Berrigan[1]; M. Dalton[1]; H. Koerner[1]; M. Cinibulk[1]; M. B. Dickerson[1]

1. Air Force Research Lab, Materials and Manufacturing Directorate, USA

Ceramics and ceramic composites architected at the nanoscale can exhibit extraordinary mechanical properties, including elastic deformation and high toughness, but are difficult to fabricate using scalable production methods. The ability to control bottom-up templates for preceramic polymers (PCPs) allows for the production of hierarchical ceramic components with desired mechanical properties. The combination of block copolymers (BCPs) and PCPs allows for the templating of the PCPs as a result of the self-assembly of the BCPs. Subsequent pyrolysis of the material converts the PCP into a structural ceramic material while removing the self-assembled BCP fugitive template. Using this method we have created novel silicon carbide structures with nanoscale features and porosity. Insight into the relationship between polymer chemistry and structure in thin films of a novel and relatively inexpensive BCP/PCP system, as well as mechanical behavior of final porous ceramics, will be presented.

S9: Porous Ceramics: Novel Developments and Applications

High SSA Ceramics

Room: Coquina Salon E

Session Chairs: Paolo Colombo, University of Padova; Alberto Ortona, SUPSI

1:30 PM

(ICACC-S9-001-2019) Tuning Microporous Ceramic Membranes (Invited)

L. Winnubst*[1]

1. University of Twente, Inorganic Membranes, Netherlands

Membranes, based on ceramic materials, are interesting because of their robustness and can therefore be applied under several demanding conditions, like H_2 recovery from syngas, 'sweetening' of natural gas (CO_2/CH_4 separation) or organic solvents recovery. Not only robustness is important but also tuning pore size and membrane affinity is important to obtain membranes with the required separation properties. Fabrication, microstructure and transport properties will be discussed of membranes, having pore sizes of a few nanometers down to less than one nanometer: First solgel-derived ceramic membranes will be discussed and secondly polymer-functionalized ceramic membranes for solvent nanofiltration To obtain solgel-derived ceramic membranes with the desired separation properties in-depth knowledge is necessary on the whole fabrication process, from sol synthesis, via applying a gel-type coating on a porous support to temperature treatments in order to obtain a separation layer with the desired microstructure. For organic solvent nanofiltration (OSN) state-of-the art polymeric or ceramic membranes do not always meet stability and/or selectivity demands at process-relevant conditions. We developed a new type of OSN membrane by grafting small polymer chains into the pores of a 5 nm γ-alumina ceramic membrane. In this way the best of both was achieved, meaning the robustness of ceramic membranes and the selectivity of polymeric membranes.

2:00 PM

(ICACC-S9-002-2019) Resilient Ceramic Aerogel (Invited)

H. Wang*[1]; L. Su[1]

1. Xi'an Jiaotong University, China

Ceramic aerogel are well known for their low density, high porosity, large surface area, and excellent thermal and chemical stability, showing promising potential to be used as high-temperature thermal insulators, catalyst supports, filters, lightweight structural materials, and hosts for functional materials for various applications. However, conventional ceramic aerogels are usually constructed by oxide ceramic (e.g., silica) nanoparticles, and their practical applications have always been limited by the brittle nature of ceramics and volume shrinkage at elevated temperature (e.g., 600 °C for silica aerogels). As is known, the brittleness of ceramics is caused by their strong ionic-covalent bonds which bring them crack susceptibility. To solve the above problems, one dimensional nanoscale building blocks with mechanical flexibility, such as SiC nanowires and Si3N4 nanobelts, were used here to construct ultralight and resilient ceramic aerogels via a facile chemical vapordeposition (CVD) method. The macroscopic-assembled ceramic aerogels exhibits integrated properties of ultralow density, large strain recoverable compressibility, energy dissipation performance, refractory performance, high-temperature oxidation and heat resistance, thermal insulation performance and other functions, all originating from the well-interconnected highly porous 3D architecture and superior mechanical and chemical and physical of the building blocks.

2:30 PM

(ICACC-S9-003-2019) Ultralight and Resilient SiC Aerogel

L. Su*[1]; H. Wang[1]; M. Niu[1]; X. Fan[1]

1. Xi'an Jiaotong University, China

Ceramics aerogels are well known for their low density, high porosity, large surface area and excellent thermal and chemical stability, showing promising potential to be used as thermal insulator, catalyst support, filter, lightweight structural materials and hosts for functional materials for various applications. However, the practicle applications of conventional ceramic aerogels are usually limited by the brittle nature of ceramics and volume shrinkage at high temperature. SiC nanowire offers the integrated properties of flexibility and superior thermal and chemical stability, which makes it a promising building block for compressible ceramic nanowire aerogel (NWA). Here, we report the fabrication and properties of a highly porous SiC NWA assembled by a large number of interweaving 3C-SiC nanowires. The SiC NWA possess ultralow density (~5 mg cm^{-3}), excellent mechanical properties of large recoverable compression strain (>70 %) and fatigue resistance, refractory property, oxidation and high temperature resistance, and thermal insulating property. When used as absorbents, the SiC NWA exhibits an adsorption selectivity of low viscosity organic solvents with high absorption capacity. The successful fabrication of such an attractive material may provide new perspective to the design and development of other compressible and multifunctional ceramic NWAs.

2:50 PM

(ICACC-S9-004-2019) Polymer-Derived Ceramics with engineered mesoporosity: From design to application in catalysis

S. Bernard*[1]

1. CNRS IRCER, France

The scientific and technological challenges of energy-related fields are mainly associated with the emergence of new, advanced knowledge and fundamental understanding of materials. In the different categories of materials, ceramics offer a unique combination of physical and chemical properties making them key contributors for energy production/conversion and storage applications. The Polymer-Derived Ceramics (PDC) route enables the synthesis of such materials with an excellent control of the porosity at mesoscopic length offering potentialities as support materials to anchor and disperse active metals or for a direct use as catalysts. In this talk, a particular focus is made on the forming methods which have been associated with the PDCs route to engineer the mesoporosity of ceramics derived from preceramic polymers. Then, we describe the preparation of monolith-type PDCs with tailored mesoporosity using the exo-templating approach and their use as supports for the deposition of metal nanoparticles. Their recent application in various catalyst-assisted reactions is then discussed. Additionally, we outline the current challenges on the field of mesoporous PDCs and provide perspectives on the need for further advances in mesoporous PDCs.

Innovations in Processing Methods and Synthesis of Porous Ceramics I

Room: Coquina Salon E

Session Chairs: Louis Winnubst, University of Twente; Hongjie Wang, Xi'an Jiaotong University

3:30 PM

(ICACC-S9-005-2019) Strategies for Strength Enhancement of Reticulated Porous Ceramics (RPCs) Using Infiltration-Based Strut Functionalization Techniques (Invited)

U. Betke*[1]; M. Scheunemann[1]; M. Scheffler[1]

1. Otto-von-Guericke-University Magdeburg, Institute for Materials and Joining Technology, Germany

Ceramic Foams, as made by the polymer replication technique (Schwartzwalder process), are characterized by different classes of porosity. Besides the actual foam cells, hollow strut cavities and microstructural porosity in the ceramic strut material are found. The mechanical strength of these cellular ceramics is essentially limited by the hollow struts and longitudinal strut cracks. Strategies for strength enhancement in RPCs are usually based on mending these longitudinal strut cracks by applying a ceramic coating onto the strut surface or filling of the hollow strut cavities with a second ceramic phase. Within this talk these strength enhancement techniques are presented for alumina RPCs. In addition, a new approach for introducing a transformation toughening phase into the microstructure of strut-infiltrated alumina foams is described. This is based on a simple metal salt loading of the microstructural porosity subsequent to the hollow strut infiltratraton with a ceramic slurry. The effect of the transformation toughening is monitored as a function of the process parameters like the number of subsequent salt loading cycles or the properties of the respective solvent. As a result the compressive strength of the as processed alumina foams is improved by 30% to 60% in comparision to an alumina foam without a transformation toughening phase.

4:00 PM

(ICACC-S9-006-2019) Design and Additive Manufacturing of Porous Ceramic Structures (Invited)

A. Ortona*[1]

1. SUPSI, MEMTi, Switzerland

Porous ceramics are attracting hybrid material because of their outstanding effective properties. Albeit ceramic foams are already widely employed, they show scattered properties and severe limitations in their engineering. This work shows how periodic cellular ceramics can be designed and then, through to additive manufacturing (AM), transformed into ceramic objects. We developed an original method in which polymeric lattices templates are produced by 3D printing and further coated by replica. The advantage of this technique is its flexibility. Practically any ceramic material already produced in bulk form can be realized. A limitation of the above

mentioned technique is its resolution and the pores' size. For more detailed porous structures we are studying 3D printing by digital light processing (DLP) of ceramic pastes: we show how viscosity, wettability and printing strategy affect the final structure's properties. Finally several examples of ceramic components are presented.

4:30 PM

(ICACC-S9-007-2019) Direct Ink Writing of Three Dimensional Porous Ti_2AlC structures

H. Elsayed[1]; A. Chmielarz[3]; M. Potoczek[3]; T. Fey[2]; P. Colombo*[1]

1. University of Padova, Industrial Engineering, Italy
2. University of Erlangen-Nürnberg, Department of Materials Science (Glass and Ceramics), Germany
3. Rzeszow University of Technology, Faculty of Chemistry, Poland

MAX-phase (Ti_2AlC) porous scaffolds were 3D printed using Direct Ink Writing. Inks with suitable rheological properties were developed and characterized. Optimized firing conditions were investigated, to limit the decomposition of the MAX phase. The resulting scaffolds were characterized in terms of morphology and mechanical properties. Structural characterization of macro- and microstructure was carried out by CT-measurements of 3D-printed structures. Based on the real structure model data, numerical simulations for permeability and mechanical stress were performed.

4:50 PM

(ICACC-S9-008-2019) Scaling properties of woven-fiber preforms densified by chemical vapor infiltration

D. Liliedahl*[1]; C. Cha[1]; V. Ramanuj[2]; R. Sankaran[2]

1. Rolls-Royce Corporation, USA
2. Oak Ridge National Laboratory, USA

Massively parallel simulations of continuous fiber (5HS) preforms have been performed using a level-set model for the chemical vapor infiltration (CVI). The well-established level-set approach allows the complex, evolving topology in this problem to be efficiently described. In advancing the previous level-set CVI applications, the present approach includes finite-rate transport effects such that finite Thiele modulus effects can be studied. The numerical studies include the ultimate achievable porosity with Thiele modulus, as well as porosity scaling of structural functions like the surface-to-volume ratio. The scaling of infiltration properties (permeability and effective diffusivity) are also computed for the dry and partially-densified states.

S10: Ceramics Modeling, Genome and Informatics

Functional Ceramics I

Room: Coquina Salon G

Session Chairs: Rajeev Ahuja, Uppsala University; Valentino Cooper, Oak Ridge National Laboratory

8:30 AM

(ICACC-S10-001-2019) Thermoelectric thin film chromium- and scandium-based nitrides studied by an integrated theoretical-experimental approach (Invited)

P. Eklund*[1]

1. Linkoping University, Dept. of Physics, Chemistry, and Biology, Sweden

Thermoelectric devices directly convert heat into electricity or vice versa. Here, we present results from our experimental and theoretical investigations of CrN- and ScN-based thin film systems. ScN thin films exhibit an anomalously high thermoelectric power factor. However, ScN has high thermal conductivity, thus its thermoelectric figure of merit and corresponding efficiency is modest. To reduce thermal conductivity, potential strategies are nanostructuring, alloying or nanoinclusions. We have modeled the thermal conductivity in pure ScN as a function of grain size using time-dependent effective potentials (TDEP), correlating the ideal thermal conductivity of an infinite ideal crystal with the thermal conductivity reduction of grain-size effects, and alloying trends in mixing thermodynamics of ScN-based solid solutions. Pure CrN exhibits n-type conduction with a high power factor enabled by a high electron concentration thermally activated from N vacancies. We have demonstrated that it can be rendered p-type by Al alloying in combination with N superstoichometry. Further, the trends in mixing thermodynamics and densities-of-states of rocksalt-$Cr_{1-x}Sc_xN$ solid solutions were investigated by first-principles calculations, and $Cr_{1-x}Sc_xN$ thin films synthesized by magnetron sputtering.

8:55 AM

(ICACC-S10-002-2019) Atomic-Scale Modeling in Materials Design and Discovery (Invited)

S. Sinnott*[1]

1. Pennsylvania State University, Dept. of Materials Science and Engineering and Dept. of Chemistry, USA

The discovery and design of new materials is the limiting factor to improve many existing technologies or to enable new applications. Material modeling methods across length scales are now widely applied and show promise for fulfilling the ultimate goal contained within the phrase "materials by design". This presentation will review the evolution of reactive empirical potentials that are used in atomistic simulations and their integration with first principles approaches and experimental methods. Illustrative applications will be discussed within the context of novel two-dimensional materials and nanostructured porous systems. A future outlook of materials modeling within the context of material design and discovery will also be provided.

9:20 AM

(ICACC-S10-003-2019) Physics-Informed Machine Learning for Rapid Screening of Potential Inorganic Scintillator Chemistries (Invited)

G. Pilania[1]; C. Stanek[1]; K. Mcclellan[1]; B. P. Uberuaga*[1]

1. Los Alamos National Laboratory, Materials Science and Technology Division, USA

Applications of inorganic scintillators—activated with lanthanide dopants, such as Ce—are found in diverse fields. As a strict requirement to exhibit scintillation, the 4f ground state and $5d_1$ lowest excited state levels induced by the activator must lie within the host bandgap. This talk will discuss a new machine learning (ML) based screening strategy that relies on a high throughput prediction of the lanthanide dopants' 4f and $5d_1$ energy levels with respect to the host valance and conduction band edges for efficient chemical space exploration to discover novel scintillators. Building upon well-known physics-based chemical trends and available experimental data, the ML model can rapidly and reliably estimate the relative positions of the activator's energy levels relative to the band edges of any given host chemistry. Using a set of perovskites and elpasolites as examples, we demonstrate that the developed approach is able to (i) capture systematic chemical trends across host chemistries and (ii) effectively screen promising compounds in a high-throughput manner. While a number of other application-specific performance requirements need to be considered for a viable scintillator, the present scheme can be a practically useful tool to systematically down-select the most promising candidate materials in a first line of screening for a subsequent in-depth investigation.

9:45 AM

(ICACC-S10-004-2019) Stability and Transport Properties of Oxygen Vacancy in Perovskite Oxides Superlattice (Invited)

H. Xu*[1]

1. Oak Ridge National Lab, Materials Science and Technology Division, USA

This study presents the formation energies and migration energy barriers of an oxygen vacancy in prototypical perovskite oxide superlattices consisting of SrTiO3 and PbTiO3 using density functional theory (DFT) in combination with kinetic Monte Carlo (KMC) simulations. The effects of octahedral rotation, polar mode, charge state, and interface on the oxygen vacancy formation energies will be discussed. The defect trajectories obtained from KMC simulations reveal that oxygen vacancies are confined within certain layers of the superlattices, essentially resulting in a two-dimensional planar diffusion in some of the superlattices. The KMC simulations also show that the dominant vacancy position may vary in the superlattices, depending on the superlattice structure and stacking period, contradicting the common assumption that point defects reside at interfaces. Considering the variety of cations that can be accommodated in perovskite superlattices, this paper identifies a pathway to control defect properties and behavior for technological applications.

Functional Ceramics II

Room: Coquina Salon G

Session Chairs: Per Eklund, Linkoping University; Susan Sinnott, Pennsylvania State University

10:25 AM

(ICACC-S10-005-2019) Role of Catalysts and Nano Structuring in Hydrogen Storage Materials (Invited)

R. Ahuja*[1]

1. Uppsala University, Physics and Astronomy, Sweden

The purpose of this talk is to provide an overview of the most recent theoretical studies undertaken by us in the field of hydrogen storage materials research. On selected examples, the application of our computational tool of choice, density functional theory, will be illustrated to show how ab initio calculations can be of use in the effort to reach a better understanding of hydrogen storage materials and to occasionally also guide the search for new promising approaches. A deeper theoretical understanding of the catalytic mechanism involved in kinetic enhancement should be a very valuable guide in the design of new catalysts. Systems to be discussed include complex metal hydrides. Catalysis play an important role in many hydrogen desorption processes. We found (through a combination of experiment and theory) that carbon nanostructures, in particular nanotubes and fullerenes, can be used as catalyzing agents for hydrogen uptake and release in complex metal hydrides (such as sodium alanate, $NaAlH_4$) and provide a model which could explain the mechanism of the catalytic effects.

10:50 AM

(ICACC-S10-006-2019) An open-source python library to generate periodic grain boundary structures (Invited)

K. Yang*[1]

1. University of California San Diego, Department of NanoEngineering, USA

Studying the effects of grain boundaries on the materials properties has been an important research subject in materials science. In this talk, I am going to introduce an open-source python library framework for building periodic grain boundary models in a universal fashion. The software framework aims to generate tilt and twist grain boundaries from an input cubic or non-cubic crystal structure for ab-initio and classical atomistic simulation. It can output a coincidence site lattice (CSL) grain boundary for a cubic input structure and a non-CSL grain boundary for a non-cubic input structure. The developed algorithm in the open-source python library is expected to facilitate studies of grain boundary in materials science. The software framework is available on the website: aimsgb.org.

11:15 AM

(ICACC-S10-007-2019) First principles-based design of energy relevant materials at finite temperature (Invited)

V. R. Cooper*[1]; K. Pitike[1]; S. F. Yuk[2]; Y. Li[3]

1. Oak Ridge National Laboratory, Materials Science and Technology Division, USA
2. Pacific Northwest National Lab, Basic & Applied Molecular Foundations, USA
3. Oak Ridge National Lab, National Center for Computational Sciences, USA

Computational materials design requires knowledge of material performance under device relevant conditions. This entails an understanding of responses in specific temperature ranges; i.e. beyond 0 K groundstate density functional theory (DFT) calculations. However, evaluating finite-temperature behavior often requires Monte Carlo or molecular dynamics simulations employing DFT-trained models. These methods often deviate from experiments due to uncertainties in the phenomenological models and the DFT functionals used to parameterize them. I will discuss our efforts to examine the limits of DFT functionals with an eye to designing more robust, efficient approaches for studying finite-temperature, materials properties of ceramics. I will focus on temperature-dependent phase transitions in ferroelectric oxides; employing stochastic methods to access finite-temperature properties. This work illuminates the dependence of these results on the underlying DFT exchange-correlation functional. This combined approach provides a path forward for truly first-principles design of functional materials properties under device relevant conditions. Supported by the U.S. D.O.E., Office of Science, BES, MSED through the Office of Science Early Career Research Program (first principles) and the LDRD Program of ORNL (simulations), managed by UT-Battelle, LLC, for the U. S. DOE using resources at NERSC and OLCF.

11:40 AM

(ICACC-S10-008-2019) Efficiency improvement of synchrotron radiation powder X-ray diffraction and XAFS measurement

K. Fujimoto*[1]; A. Aimi[1]; S. Maruyama[2]

1. Tokyo University of Science, Japan
2. Tohoku University, Japan

Material prediction by machine learning in recent years requires huge data, and in many cases it is supplemented by text mining and computational chemical simulation. I think that development of high-throughput experimental tools should also be continued in order to interpolate diversity in data and to construct a new database. In case of high-throughput materials preparation and evaluation, we treat about several hundred samples in one day. As an example, in conventional method for synchrotron powder X-ray diffraction, we have to fill fine capillaries (c.a. 0.2 mmΦ) with well-grounded powder. We need at least 10 hours for only sample filling when we measure 100 sample in one day. In this study, we made a prototype for effective and high-throughput evaluation in synchrotron X-ray powder (XRD) diffraction and X-ray absorption fine structure (XAFS) measurements. Tools made with 3D printers made it possible to continuously measure powder libraries transferred to tape. The sample setting also allowed XAFS measurement without BN pellet creation. Furthermore, a method for efficiently refining the obtained powder X-ray diffraction data was also studied. Acknowledgements: These XRD and XAFS experiments were conducted at the BL5S1 and BL5S2 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Approval No.2017P0202).

Structural Ceramics I

Room: Coquina Salon G
Session Chairs: Katsuyuki Matsunaga, Nagoya University; Ghatu Subhash, University of Florida

1:30 PM

(ICACC-S10-009-2019) Computing Grain Boundary Diagrams: From Earlier Studies to a Recent Example of Au-doped Si and Beyond (Invited)

C. Hu[1]; J. Luo*[1]

1. University of California, San Diego, USA

We will first review our earlier efforts of developing several phenomenological and statistical interfacial thermodynamic models to construct grain boundray (GB) "phase" (complexion) diagrams briefly. Subsequently, our most recent atomistic simulation studies will be discussed in detail. Specifically, we are conducting hybrid molecular dynamics and Monte Carlo (hybrid MD/MC) simulations in semi-grand canonical ensembles. Our first atomistic-simulation-derived GB diagram example was constructed for Ni-doped Mo, where we also found the occurrence of first-order grain boundary transformation led to the break of mirror symmetry of a symmetric tilt boundary [Yang et al., Phys. Rev. Lett. 120: 085702 (2018)]. This talk will be then focused on our more recent on-going studies. For example, recent hybrid MC/MD simulations reveal the occurrence of first-order phase-like adsorption transformations in Au-doped Si twist GB at low temperatures, which become continuous at high temperatures above a GB critical point. The predicted first-order GB transformations from nominally "clean" GBs to bilayer adsorption of Au is supported by a prior experiment. The hexagonal Au adsorption pattern predicted by the hybrid MC/MD simulation is further verified by first-principles calculations. A GB diagram is computed for Au-Si. On-going studies of other systems will also be presented and discussed.

2:00 PM

(ICACC-S10-010-2019) Coupled Effects of Electronic and Nuclear Energy Loss on Damage Production in Ceramics (Invited)

W. J. Weber*[1]; E. Zarkadoula[2]; Y. Zhang[2]

1. University of Tennessee, Materials Science & Engineering, USA
2. Oak Ridge National Laboratory, USA

Ion-solid interactions result in energy loss to atomic nuclei and electrons. Using computational and experimental approaches, we have investigated the separate and combined effects of nuclear and electronic energy loss on the response of ceramics to ion irradiation. The loss of energy to electrons results in significant ionization and formation of hot electrons that create a local thermal spike via electron-phonon coupling. Using molecular dynamics (MD) simulations and the inelastic thermal spike model, the coupled effects of the nuclear and electronic energy loss have been investigated. Amorphous tracks are readily produced with high energy ions in many ceramic oxides above a threshold in electronic energy loss. We have discovered that, in some complex oxides, amorphous tracks can be produced below this threshold due to a synergy between the electronic energy dissipation processes and pre-existing defects; while in other materials, we find both additive and competitive effects of the electronic and nuclear energy loss. These results provide new insights into the complex processes involved in the coupling of electronic and atomic dynamics. Work supported by the U.S. DOE, BES, MSED.

2:30 PM

(ICACC-S10-011-2019) CALPHAD modeling of the Si-C-N-H system and combined computational-experimental analysis of polysilazane-derived Si-C-N ceramics (Invited)

H. J. Seifert*[1]; I. J. Markel[1]; M. Steinbrück[1]

1. Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

Si-C-N precursor-derived ceramics can be successfully synthesized by pyrolysis of different types of polysilazanes. Such materials are the base for production of ceramic matrix composites (CMC) by polymer infiltration and pyrolysis (PIP) process. Thereby a fiber preform is infiltrated with the liquid polymer, which is then thermally cured/crosslinked and pyrolyzed, transforming the polymer into a solid Si-C-N ceramic. Since the polymer is saturated with hydrogen, hydrogen-containing gas species are emitted to the surrounding atmosphere during pyrolysis. CALPHAD-type modeling (Computer coupling of phase diagrams and thermochemistry) was used to calculate pyrolysis products and high-temperature phase stabilities. Influences of the pyrolysis temperature and nitrogen partial pressure on the high-temperature stability and phase reactions were analyzed. Thermodynamic modeling of the quaternary Si-C-N-H system was performed for calculation of various types of phase diagrams (potential diagrams, isothermal sections, isopleths), property diagrams (phase fraction diagrams), phase composition diagrams and thermodynamic data, respectively. The materials were then investigated by STA, XRD and SEM/EDX. Gaseous products were analyzed by on-line mass spectrometry. Experimental findings are quantitatively confirmed and explained by CALPHAD approach.

Structural Ceramics II

Room: Coquina Salon G
Session Chair: Hans Seifert, Karlsruhe Institute of Technology

3:20 PM

(ICACC-S10-012-2019) Bonding Structure and Deformation Mechanism in Ultrahard Icosahedral Ceramics (Invited)

G. Subhash*[1]; A. Awasthi[1]

1. University of Florida, Mechanical and Aerospace Engineering, USA

The hardest know materials for engineering applications include diamond (HV>100 GPa), cubic-boron nitride (HV=60-75 GPa), boron carbide (HV=35-40 GPa), and boron suboxide (HV=30-40 GPa). While the former two materials have diamond structure and a density of around 3.5 g/cm^3, the latter two have icosahedral structure with a density of around 2.5 g/cm^3. These icosahedral solids also exhibit compressive strength in excess of 5 GPa. These properties favors them in applications including protective armor, abrasives and wear resistant materials, and machine tool bits. However, these boron-rich solids undergo a deleterious mechanism referred to as 'amorphization' when subjected to high pressures such as those encountered in ballistic impact. This mechanism has been attributed to reduced hardness and nonrealization of the intrinsic hardness of the crystalline phase. In this research, we utilize a range of novel experimental methods, TEM, Raman spectroscopy, density functional theory (DFT), density functional perturbation theory (DFPT) and molecular dynamic (MD)to probe into material deformation mechanism and explore novel avenues to mitigate amorphization and increase incidence of new strengthening mechanisms such as nanotwinning. These approaches show significant promise towards development of even harder ultrahard ceramics.

3:45 PM

(ICACC-S10-013-2019) The use of ab-initio and classical molecular dynamics modeling to design and synthesize complex disordered solid structures (Invited)

R. Sakidja*[1]; N. Baishnab[1]; R. Khadka[1]; P. Rulis[2]; J. Wu[3]

1. Missouri State University, Physics, Astronomy and Materials Science, USA
2. UMKC, Dept. of Physics & Astronomy, USA
3. The University of Kansas, Physics and Astronomy, USA

The combination of ab-initio and classical molecular dynamics simulations can be used as a powerful tool to design and synthesize a wide range of disordered structures. These modeling techniques allow us to provide a much deeper understanding on the clustering formation and networking mechanisms within the disordered solids. Two distinct examples are presented. One example is the use of atomistic modeling to refine the structures of amorphous boron carbide synthesized through a low temperature deposition process by means of organic precursors. Another example is the application of these simulation tools to examine the mechanisms of interfacial reactions and the formation of sub-nm amorphous alumina layer manufactured through Atomic Layer Deposition (ALD) process as a part of an ultra-thin tunnel barrier fabrication. Due to the inherent time constraints and the limit in spatial configurations for these simulations however, these approaches must certainly be utilized in conjunction with or as an integral part of other modeling methodologies so as to fully elucidate the internal structures and to aid the synthesis processing effectively. We are grateful for the supports from NSF through the DMREF (Award No. 1729176) and the EPMD (Award No. 1809284) programs.

4:10 PM

(ICACC-S10-014-2019) Electronic Mechanism of Room-Temperature Large Plasticity of Inorganic Compounds (Invited)

K. Matsunaga*[1]

1. Nagoya University, JFCC, Japan

Most of crystalline inorganic compounds tend to fail in a brittle manner at low temperatures. This has been generally considered to be mainly due to their complicated crystal structures and strong ionic/covalent bonds. In this study, however, it was found that zinc sulfide single crystals having the zinc blend structure can undergo significantly large plastic deformation even at room temperature in complete darkness (Oshima, Nakamura, and Matsunaga, Science (2018)). In normal light or ultraviolet light environments, zinc sulfide single crystals exhibit deformation twinning and then immediately fracture in a brittle manner after a few percent of plastic strain. In contrast, the single crystals show plastic deformation up to a strain of more than 40% in compression when they are deformed in darkness. A high density of glide dislocations on the {111} planes are introduced in the samples deformed in darkness, so that the large room-temperature deformation is caused by glide and multiplication of the dislocations. DFT calculations indicate specific electronic structures localized around the dislocations cores. A plausible mechanism is that stability and mobility of the dislocations may be controlled by electrons or holes produced via interband transition due to external light. Further details will be discussed in terms of experimental and theoretical data.

4:35 PM

(ICACC-S10-015-2019) Discovery of new promising substrate materials for high-power electronic devices: Cubic Si_3N_4 and Ge_3N_4 (Invited)

H. Xiang*[1]; Y. Zhou[1]

1. Aerospace Research Insitute of Materials and Processing Technology, China

Ceramic substrates play key roles in power electronic device technology through dissipating heat, wherein both high thermal conductivity and mechanical strength are required. The increased power of new devices has led to the replacement of Al_2O_3 by high thermal conducting AlN and further β-Si_3N_4 based substrates. However, the low mechanical strength and/or anisotropic mechanical/thermal properties are still the bottlenecks for the practical applications of these materials in high power electronic devices. Herein, using a combination of density functional theory and modified Debye-Callaway model, two new promising substrate materials γ-Si_3N_4 and γ-Ge_3N_4 are predicted. Our results demonstrate for the first time that both compounds exhibit higher room temperature thermal conductivity but less anisotropy in expansion and heat conduction compared to β-Si_3N_4. The mechanism underpins the high RT k is identified as relatively small anharmonicity, high phonon velocity and frequency.

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Carbide Properties and Oxidation II

Room: St. Johns

Session Chair: Miladin Radovic, Texas A&M University

8:30 AM

(ICACC-S12-029-2019) Oxidation Behavior of Hafnium Diboride-50 vol% Hafnium Carbide Composite System

C. M. Young*[1]; C. Zhang[1]; A. Loganathan[1]; B. Boesl[1]; A. Agarwal[1]

1. Florida International University, Mechanical and Materials Engineering, USA

The oxidation behavior of hafnium diboride 50 vol.% hafnium carbide (HfB_2-HfC) composite system are investigated in this study. Testing was conducted by exposing sintered pellets to high energy plasma-jet with a temperature reaching up to 2900°C. Isothermal oxidation behavior was also studied via thermogravimetric analysis (TGA) up to 1400°C. Both methods exhibit that HfB_2-HfC composite has a superior oxidation resistance as compared to pure HfC and HfB_2. The improved oxidation resistance is attributed to the high density of the HfB_2-HfC compact, as well as the formation of a glassy protective layer, filling in pores in the HfO_2 skeleton created by the escaping of gases during oxidation. TGA of the each sample further supports the proposed mechanism of oxidation of HfB_2-HfC. HfC and HfB_2 both have sharp increase in weight gain during oxidation, however, the HfB_2-HfC composite weight gain is gradual. The oxidation mechanisms of both HfB_2 and HfC impede one another, thus slowing the rate of oxidation of the composite sample, creating a superior material for ultra-high temperature applications for extreme environments.

8:50 AM

(ICACC-S12-030-2019) Densification, microstructure and mechanical properties of ZrC-SiC ceramics

L. Feng*[1]; W. Fahrenholtz[1]; G. Hilmas[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

ZrC/SiC ceramics were fabricated by high-energy ball milling (HEBM) and reactive hot pressing (RHP) of ZrH_2, carbon black and SiC. The ceramics were composed of nominally pure ZrC containing 0 to 30 vol% of SiC particles. The relative density increased as SiC content increased, from 96.8% for nominally pure ZrC to 99.3% for ZrC-30 vol% SiC. Young's modulus increased from 408 to 420 GPa and Vickers' hardness increased from 19.7 to 23.0 GPa as the SiC content increased from 10 to 30 vol%, due to a combination of the higher relative density of ceramics with higher SiC contents and higher young's modulus and hardness of SiC. Flexure strength was 308 MPa for a SiC content of 10 vol%, but increased to 576 MPa for a SiC content of 30 vol%. Fracture toughness did not vary significantly with composition and values were in the range of

2.3 MPa•$m^{1/2}$ to 2.6 MPa•$m^{1/2}$. Effects of SiC content on the densification, microstructure and mechanical properties of ZrC-SiC ceramics were systematically investigated in the present work.

High Entropy UHTCs

Room: St. Johns
Session Chairs: Xingang Luan, Northwestern Polytechical University; Carolina Tallon, Virginia Tech

9:10 AM

(ICACC-S12-031-2019) High-Entropy Metal Diborides (Invited)

J. Luo*[1]; J. Gild[1]; T. Harrington[1]; K. Vecchio[1]; C. Toher[2]; P. Sarker[2]; S. Curtarolo[2]; J. L. Braun[3]; L. Backman[3]; P. Hopkins[3]; E. J. Opila[3]; S. Daigle[4]; D. Brenner[4]; J. Maria[5]

1. University of California, San Diego, USA
2. Duke University, USA
3. University of Virginia, USA
4. North Carolina State University, USA
5. Pennsylvania State University, USA

Several equimolar, five-component, single-phase, metal diborides [e.g., $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$; Scientific Reports 6:37946 (2016)] were fabricated, representing a new type of ultra-high temperature ceramic (UHTC) as well as a new class of high-entropy materials that possess a non-cubic (hexagonal AlB_2 structure) and layered (quasi-2D) crystal structure. A density functional theory (DFT) based partial occupation method was implemented within the AFLOW to calculate energy distributions that were used to construct a descriptor to predict the formation and stability of these high-entropy materials. DFT based modeling of charge disorder and lattice distortions have also been conducted. Results from the most recent on-going studies of processing optimization, mechanical testing, and oxidation measurements will also be presented and discussed.

9:40 AM

(ICACC-S12-032-2019) High Entropy Ultra High Temperature Ceramics (Invited)

E. Castle*[1]; E. C. Schwind[4]; T. Csanadi[2]; X. Han[9]; G. Wickliffe[6]; S. A. Humphry-Baker[8]; R. Sedlak[2]; R. Zhang[1]; K. Chen[1]; M. Radovic[7]; P. Svec[3]; I. Abrahams[1]; C. Weber[5]; N. Bonini[5]; C. Zhang[9]; N. Orlovskaya[6]; J. Dusza[2]; W. Fahrenholtz[4]; M. Reece[1]

1. Queen Mary University of London, School of Engineering and Materials Science, United Kingdom
2. Institute of Materials Research, Slovak Academy of Sciences, Slovakia
3. Department of Metal Physics, Slovak Academy of Sciences, Slovakia
4. Missouri University of Science & Technology, USA
5. Kings College London, Theory & Simulation of Condensed Matter, United Kingdom
6. University of Central Florida, USA
7. Texas A&M University, USA
8. Imperial College, United Kingdom
9. Northwestern Polytechical University, China

A new class of materials, broadly named "High Entropy Compounds" (HECs), has recently emerged; revealing a vast new compositional space for the exploration of new ceramic materials. This has attracted significant attention from the Ultra High Temperature Ceramics (UHTCs) community, where the known compositional space for materials with melting temperatures >3000 °C is significantly limited. A "High Entropy" material may be generally defined as a single-phase material, into which equi- or near-equiatomic amounts of multiple atomic species are arranged randomly into at least one of the sub-lattices/atomic sites. Due to the incorporation of different atomic species (with differing atomic sizes, bonding preferences etc…) into the same lattice/sub-lattice/atomic site, there can be localised lattice strains, potential energy fluctuations and variations in chemical environment; all of which may significantly influence dislocation motion, chemical and vacancy diffusion, and thermal and electrical transport. The physical and mechanical properties of the HECs can therefore differ significantly with respect to that which would be expected from a rule of mixtures calculation from the systems components. We report on our investigations into the fabrication of UHTC HECs; including an assessment of their micro/nanostructural and crystallographic characteristics, and an evaluation of their physical and mechanical behaviour.

10:20 AM

(ICACC-S12-033-2019) Synthesis of fine powders for high entropy carbide, boride, and nitride ceramics

J. Xing[1]; P. Foroughi[1]; Z. Cheng*[1]

1. Florida International University, Mechanical & Materials Engineering, USA

Direct synthesis of fine powders for single-phase, multi-principle metal element or high-entropy metal carbide, boride, and nitride ceramics with a facile, low-cost method is of great interest since the materials could offer large compositional design space in tuning their chemical and physical properties and may find applications in aerospace and other critical areas. However, with the well-known synthesis route based on carbothermal reduction (CTR) of oxides by carbon, it is often difficult to obtain single phase solid solutions for the high-entropy carbide, boride, and nitride materials due to the limited solubility of the different oxides with each other and the large difference in the reactivity of the oxides with carbon in CTR reactions. In this study, alternative methods based on direct reactions between mixed metal chlorides and certain reactive agents (e.g., sodium borohydride, urea, or elemental boron) that avoid oxides formation have been explored for the synthesis of powders of those high-entropy ceramics, and the products are characterized using different techniques. XRD and SEM results revealed the formation of fine ceramic powders such as $(Hf_{0.25}Nb_{0.25}Ta_{0.25}Zr_{0.25})C$, $(Hf_{0.2}Nb_{0.2}Ta_{0.2}V_{0.2}Zr_{0.2})B_2$ and $(Hf_{0.2}Nb_{0.2}Ta_{0.2}V_{0.2}Zr_{0.2})N$, which illustrate the advantage of the synthesis technique. The directions for future research will also be pointed out.

10:40 AM

(ICACC-S12-034-2019) Microstructural Development of High Entropy, Ultra High Temperature Carbide Thin Films

T. M. Borman*[1]; M. Hossain[1]; C. M. Rost[2]; P. E. Hopkins[2]; D. Brenner[3]; J. Maria[1]

1. Pennsylvania State University, Materials Science and Engineering, USA
2. University of Virginia, Mechanical and Aerospace Engineering, USA
3. North Carolina State University, Materials Science and Engineering, USA

The authors describe the reactive sputtering of metallic alloy targets in order to fabricate high entropy carbide films. This technique enables the investigation of carbide films with a broad range of carbon stoichiometries ranging from near metallic to carbide-carbon nanocomposites containing more than 50% excess carbon. Sputtering allows for deposition of high density films across broad compositional ranges at significantly lower temperatures than bulk processing. Furthermore, the energetics and non-equilibrium nature of the sputtering process enable the room temperature study of metastable structures which prove challenging via bulk processing techniques. For instance, elements such as W and Mo can be readily incorporated into a metastable rocksalt structure by sputtering at temperatures as low as room temperature. In this work, the microstructural development of high entropy carbides sputtered over a broad range of carbon compositional space will be described. When deposited at modest temperatures (~650 °C) on c-plane sapphire, a broad range of microstructures can be observed: from rounded metallic grains and triangular pyramidal carbide grains to a nano-grained carbide / amorphous carbon nanocomposite structure. This large range of microstructures exhibits a diverse range of mechanical and thermal properties which will be discussed by collaborators.

11:00 AM

(ICACC-S12-035-2019) Oxidation Kinetics of High Entropy Carbide and Boride UHTCs

L. Backman*[1]; E. J. Opila[1]

1. University of Virginia, Materials Science and Engineering, USA

Bulk samples of high entropy ultra-high temperature ceramics (UHTCs) of the composition (HfNbTaTiZr)C and (HfNbTaTiZr)B_2 were fabricated via high energy ball milling and spark plasma sintering. Oxidation behavior of this new class of UHTCs was tested at 1500°C, 1700°C, and 1800°C using a resistive heating apparatus in 1 atmosphere 0.1%, 0.5% and 1% PO_2 oxygen/argon gas mixtures for times up to 30 minutes. Oxidation kinetics were determined from the variation of material consumption vs. time, and compared to ZrC and ZrB_2. Rapid oxidation rates were observed for both multicomponent carbides and borides at all temperatures. Oxide composition and morphology of the multicomponent ceramics were characterized using XRD, SEM, TEM and EDS. Surface layers consisting of multiphase complex oxides, subsurface layers showing evidence of internal and selective grain boundary oxidation, and selective depletion of Group IV elements were all observed. This work serves to further elucidate the oxidation behavior of a new class of ceramics that are proposed for ultra-high temperature applications where oxidation properties are of key importance.

11:20 AM

(ICACC-S12-036-2019) Mechanical Properties of High Entropy Carbides: Experiment and Theory

M. Hossain*[1]; T. M. Borman[1]; C. M. Rost[2]; P. Hopkins[2]; D. Brenner[3]; J. Maria[1]

1. Pennsylvania State University, Materials Science and Engineering, USA
2. University of Virginia, Mechanical and Aerospace Engineering, USA
3. North Carolina State University, Materials Science and Engineering, USA

In the present study we report the mechanical properties of high entropy carbides (HEC) as a function of C content. The HEC compositions contain five distinct elements from groups IVB, VB, VIB. Thin films are deposited using reactive sputtering from an alloy target with the partial pressure of CH_4 regulating the amount of C in the films. The types of C (bonded to metal and excess) and relative quantities are analyzed using X-ray photoelectron spectroscopy (XPS). The microhardness measurement data shows hardness increases with increasing C content up to certain percentage and then decreases rapidly. Correlation with XPS data reveals that the strengthening trends are related to the increasing quantity of carbon-metal bonds which gradually transforms the structure from a predominately metallic nature towards a stoichiometric carbide. The sharp drop in hardness is due to the excess C at the grain boundary where grains slide easily. Electronic structure evaluation using DFT calculations exhibits strong covalent bonds between C2p-Metal d orbital. However, deficiency in the bonded C introduces new energy states below the fermi level which are metallic in nature. By increasing the bonded C in the high entropy carbide, the materials change from a metallic towards a covalent nature, by filling covalent states. As these strongly bonded covalent states fill, the predicted hardness increases accordingly.

11:40 AM

(ICACC-S12-037-2019) High-Entropy Carbide Ceramics for Extreme Environments

F. Wang*[1]; X. Yan[1]; L. Constantin[1]; Y. Lu[1]; J. Francois[2]; M. Nastasi[1]; B. Cui[1]

1. University of Nebraska-Lincoln, USA
2. Institut de Chimie de la Matière Condensée de Bordeaux, France

A novel high-entropy carbide ceramic, $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ has been developed as a candidate material for high-temperature and irradiation extreme environments. X-ray diffraction suggests that it has a single-phase rock salt structure, in which the five metal elements likely share the cation position while the C element occupies the anion sublattice. This material is thermally stable after annealing to up to 1700°C in Ar atmosphere without phase transformation or decomposition. It inherits the high elastic modulus and hardness of the binary carbide ceramics. It exhibits a much lower thermal diffusivity and conductivity than the binary carbides, which may result from the significant phonon scattering at its distorted anion sublattice. Irradiation damage has been evaluated by conducting helium irradiation experiments. The microstructure changes, including the phase transformation and defect formation, have been characterized using transmission electron microscopy. This high entropy ceramic shows no amorphization after irradiation to 5 displacement-per-atom (dpa) at room temperature. Small helium bubbles with a diameter of one nanometer and dislocation loops with a diameter of several nanometers formed by irradiation.

Structure and Bonding in MAX Phases

Room: St. Johns

Session Chair: William Fahrenholtz, Missouri University of Science & Technology

1:30 PM

(ICACC-S12-038-2019) Electronic structure of MAX phases studied by angle-resolved photoemission spectroscopy (Invited)

T. Ito*[1]; M. Ikemoto[2]; D. Pinek[3]; M. Nakatake[4]; S. Ideta[5]; K. Tanaka[5]; T. Ouisse[3]

1. Nagoya University, Nagoya University Synchrotron Radiation research Center, Japan
2. Nagoya University, Japan
3. Université Grenoble-Alpes, CNRS, LMGP, France
4. Aichi Synchrotron Research Center, Japan
5. UVSOR Facility, Institute for Molecular Science, Japan

MAX phases have recently attracted much attention due to their possible application to the production of a new class of two-dimensional (2D) systems called MXenes. However, the bulk electronic structure of MAX phases has been studied mostly through ab initio, DFT calculations, mainly due to a lack of single crystalline samples. We have performed angle-resolved photoemission spectroscopy (ARPES) on several MAX phase single crystals to directly investigate the electronic structure of these systems. For Cr_2AlC, we find quasi-2D electron and hole like Fermi surfaces around the ΓA and ML lines, and we obtain a good agreement between ARPES and DFT. On the other hand, we find significant differences between the effective mass values extracted from ARPES and DFT, and kink dispersive features. Our results suggest that strong renormalization effects and electron-phonon coupling dominate the electronic structure near the Fermi level of Cr_2AlC. For V_2AlC, we did not find any band narrowing, while anomalous discontinuity of dispersive features has been observed around the 'Dirac'-like band crossing point expected by DFT. Furthermore, the existence of surface band dispersion around the M point has also been observed. These results illustrate the similarities but also the differences which may exist between various MAX phases, ranging from electron correlations to specific surface properties.

2:00 PM

(ICACC-S12-039-2019) Structure and Bonding in MXenes and MAX phases Investigated by X-ray Diffraction and Spectroscopy (Invited)

M. Magnuson*[1]

1. Linkoping University, Department of Physics, Chemistry and Biology, Sweden

The crystal and electronic structures as well as the chemical bonding in the 2D ceramic materials MXenes and MAX-phases are investigated by X-ray diffraction and X-ray spectroscopy compared to ab initio electronic structure calculations. Wide-angle X-ray diffraction studies using synchrotron radiation reveals how the structures

react to increasing temperature. Calculated spectra using density-functional theory (DFT) including core-to-valence dipole matrix elements are found to yield consistent spectral functions of experimental data. By varying the constituting elements and structures in MXenes and MAX-phases, a change of the electron population cause a change of covalent bonding between the laminated layers, which enables control of the macroscopic properties of the materials. For MXenes, the role of functional –OH, –O and –F temination groups at the interfaces and their local symmetries at different adsorption sites are discussed. Synchrotron radiation techniques such as bulk-sensitive soft X-ray absorption and emission spectroscopy are shown to be particularly useful for detecting detailed symmetry in the electronic structure that yield anisotropic information about internal monolayers and termination groups at the interfaces. Angle- and polarization-resolved measurements are shown to reveal differences in orbital occupation across and along the laminate basal plane.

2:30 PM

(ICACC-S12-040-2019) Are MAX phases elastically anisotropic (Invited)

W. Ching*[1]

1. University of Missouri-Kansas City, USA

We reoprt the calculation of the universal elastic anisotropy index (A^U) for 665 possible MAX ($M_{n+1}AX_n$) phases and found A^U to be very low in contrast to conventional notion. Detailed analysis shows A^U has no correlation with axial anisotropy (C_{33}/C_{11}) and the shear anisotropy (C_{66}/C_{44}), and A^U does not depend on the layer index n nor on the elements of critical layer A. We found that MAX nitrides have larger A^U than MAX carbides. By restricting our anlysis of A^U to 70 confirmed MAX phases, we conclude that MAX phases are isotropic in general. This is supported by the reasonable correlation of A^U with the total bond order desity (TBOD), a single quantum mechanical metric describing the internal cohesion based on electronic structure and interatomic bonding. Thus crystalline elastic anisotropy in MAX phases depends on the fundamental electronic structure, not their lattice contants.

Novel Applications and Device Fabrication III

Room: St. Johns

Session Chairs: Wai-Yim Ching, University of Missouri-Kansas City; Jesus Gonzalez-Julian, Forschungszentrum Juelich

3:20 PM

(ICACC-S12-041-2019) Accelerated development of MAX phase coatings for accident-tolerant fuel cladding materials

K. Lambrinou*[1]; T. Lapauw[2]; B. Tunca[2]; J. Vleugels[2]; P. Persson[3]; J. A. Hinks[4]

1. SCK-CEN, NMS, Belgium
2. KU Leuven, Materials Engineering, Belgium
3. Linkoping University, Physics, Sweden
4. University of Huddersfield, Electron Microscopy and Materials Analysis, United Kingdom

Material development in the nuclear sector involves many successive cycles of production, neutron irradiation and post-irradiation examination (PIE), until material performance complies with the stringent requirements of nuclear safety authorities. Such approach is time-consuming and costly, preventing industrial investments in innovative materials. The nuclear sector could benefit from an accelerated material development approach, which ensures the constant communication between material design, production and performance assessment. Successfully implementing this approach relies on high-throughput screening tools that can reliably assess material performance prior to its demonstration in the reactor; an example is the use of ion/proton irradiation to assess material radiation tolerance. This work illustrates the challenges involved in the accelerated development of Zr-based MAX phase coatings for accident-tolerant fuel cladding materials of Gen-II/III LWRs. Special focus is put on two aspects: phase purity and radiation behavior. Phase-pure $(Zr,Nb/Ti)_2(Al,Sn)C$ MAX phase ceramics were made based on a crystal structure design approach considering the distortion of the M_6A trigonal prism in the 211 lattice. The radiation behavior of phase-pure $(Zr,Ti)_2(Al,Sn)C$ MAX phases was studied by TEM during (a) in-situ irradiations (350-1000°C, 6 keV He^+, 3-5×10^{13} ions/cm^2s) and (b) a detailed PIE.

3:40 PM

(ICACC-S12-042-2019) Lightweight Ti,Nb-Al-C MAX-Phases - Based Materials: Structure and Heat-Resistance in Oxidizing and Hydrogen Atmosphere

T. Prikhna*[1]; V. Romaka[2]; T. Serbenyuk[1]; O. Ostash[3]; V. Podhurska[3]; B. Vasyliv[3]; V. Sverdun[1]; V. Moshchil[1]; M. Karpets[1]; S. Ponomarov[4]; A. Starostina[1]

1. Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
2. Lviv Polytechnic National University, Ukraine
3. Karpenko Physical-Mechanical Institute of the National Academy of Sciences of Ukraine, Ukraine
4. Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine, Ukraine

The experimental study shows that the dense MAX-phases-based materials of Ti,Nb–Al–C systems of 211 and 312 structural types are stable in hydrogen (40 h) and oxidizing environments (1000 h) at 600°C and they are about twice lighter and more stable in air than Cr-containing Crofer steels. The most resistant in air at 600 °C among the studied materials turned out to be Ti_2AlC-based and somewhat less stable Ti_3AlC_2 – based with Nb, while the bending strength of the last one increased for 10% after being kept in hydrogen and oxygen atmosphere and the thickness of the dense oxide film was the thinnest. The structure of Nb-contained ceramics was modeled and discussed. The thermocycling at 600 °C and 1200 °C has been performed which demonstrated practically no destruction of MAX phases structures. The most stable during thermocycling up to 1200 °C occurred to be MAX phases of 312 structural type. The characteristics of the developed materials make them promising for application, for example, as materials for interconnects of hydrogen fuel cells, in electrical transport (for pantographs) and aviation, etc.

4:00 PM

(ICACC-S12-043-2019) Intrinsic cleavage and shear behavior of MAX phases: Ceramic or metallic?

A. Srivastava*[1]; W. Son[1]; A. Talapatra[1]; T. Duong[1]; R. Arroyave[1]; M. Radovic[1]

1. Texas A&M University, Materials Science and Engineering, USA

A family of ternary carbides and nitrides, commonly referred to as MAX phases, possess unusual, and often unique set of properties that combine some of the best attributes pf ceramics and metals. These are light, stiff, thermodynamically stable and refractory, like other typical ceramics, but damage tolerant, pseudo-ductile at high temperatures and readily machinable like metals. In addition, the experimental observations suggest that the MAX phases exhibit a wide range of deformation and failure mechanisms. Intuitively, the onset of these deformation and failure modes depends on the mechanical properties of the strongly bonded layers and the interlayer bonds, mechanical constraints and loading conditions. In this work we investigate the cleavage and shear behavior of a MAX phase, Ti2AlC, in comparisons to TiC, Ti, and graphite using first-principle density-functional theory calculations. In particular, the cleavage stress, shear stress-strain response and the unstable stacking fault energy of all the materials are characterized and compared. Our results shed new lights on the competition of ceramic-like and metal-like deformation mechanisms in MAX phases.

4:20 PM

(ICACC-S12-044-2019) On the Synthesis and Characterization of Novel Ni-MAX Composite Systems

M. Dey*[1]; S. Javaid[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

$M_{n+1}AX_n$ (MAX) phases are candidates for novel materials for different types of structural applications due to their combination of interesting properties, for example, these solids are highly damage tolerant, thermal shock resistant, readily machinable, and soft for transition metal carbides and nitrides (hardness of 2-8 GPa) As a background, $M_{n+1}AX_n$ has a unique chemistry where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element, and X is C or N. Recently, we showed that the metal matrix reinforced with MAX phases shows promising tribological properties. In this paper, we will report the synthesis and characterization of novel Ni-MAX composite systems where the composition of MAX phases will be varied, for example, Ti_3SiC_2, Cr_2AlC, and Ti_3AlC_2. These results will be also compared with Ni-MoAlB composites.

4:40 PM

(ICACC-S12-045-2019) Synthesis and characterization of $(Ti_{1-x}, Zr_x)_{n+1}AlC_n$ MAX phases through magnetron sputtering and ex-situ annealing

C. Azina*[1]; A. Petruhins[1]; J. Rosen[1]; P. Eklund[1]

1. Linköping University, Department of Physics, Chemistry and Biology (IFM), Sweden

Among possible applications for MAX phases, their use as new fuel cladding materials for nuclear applications has gained recent attention. In fact, Zr-containing MAX phases would be suitable candidates for thermally stable, oxidation resistant and irradiation resistant coatings. In addition to the pure ternary phases, there are numerous isostructural solid solutions of MAX phases which, by tuning the composition, can have tunable physical properties. Here, we investigate the possibility of synthesizing $(Ti_{1-x},Zr_x)_{n+1}AlC_n$ MAX phase thin films using magnetron sputtering (n = 1, 2) from elemental, metal-alloy (Ti/Zr) and compound targets. XRD analyses have shown the formation of both the 312 and 211 phases. Microstructural analyses have confirmed the random orientation of the MAX phase crystals, while chemical analyses show uniform distribution of Al within the films. Ex-situ annealing was adopted to promote the transition towards a pure MAX phase. The films were systematically analyzed to track the evolution of the thin films and identify the resulting phases.

5:00 PM

(ICACC-S12-046-2019) High-throughput investigation of vacancy energetics in pure 211 MAX phases

A. Talapatra*[1]; T. Duong[1]; M. Radovic[1]; R. Arroyave[1]

1. Texas A&M University, USA

MAX phases have excellent oxidation resistance and good thermal stability at elevated temperatures. In Ti2AlC for example, the high diffusivity and activity of Al results in selective oxidation of Al and enhances the formation of a continuous and protective Al2O3 layer while still maintaining structural stability. It is thus essential to investigate the phase stability and diffusion mechanisms of M/A element defective MAX phases, to aid design of novel MAX phases with requisite oxidation resistance as well as predict the diffusion mechanisms in them. To this end, as a first step, high-throughput, first-principles based Nudged Elastic Band (NEB) calculations are used to estimate phase stability of M/A element defective phases and migration energies of M and A atoms in and across M and A layers for the conventional class of 211 MAX phases.

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Corrosion of Nuclear Ceramics

Room: Coquina Salon H

Session Chair: Peng Xu, Westinghouse Electric Company

8:30 AM

(ICACC-S13-028-2019) Corrosion Behavior of Arc Welded Ceramic Joints

D. King*[1]; J. Jarman[2]; J. Watts[2]; W. Fahrenholtz[2]; G. Hilmas[2]

1. UES, Inc., USA
2. Missouri University of Science & Technology, USA

Arc welding has been demonstrated as a potential joining technique for high temperature ceramics. Arc welding of the base material results in a joint that is the same composition as the base material, potentially alleviating concerns regarding differing joint compositions, i.e. brazes. To date, several studies have focused on SiC, ZrB_2, TiB_2, and ZrC based ceramics, where the ceramic composed at least 50 vol% of the material. It is known that SiC dissociates, rather than melts, under standard temperature and pressure conditions; instead, SiC can be melted into solutions, such as eutectics, with other constituents. Previous work on this topic has demonstrated that during solidification, in binary and ternary melts, the primary crystalizing phase tends to grow large anisotropic grains. Even when arc welding parameters are controlled to limit grain growth, large textured regions can form as the melt solidifies. Therefore, the corrosion behavior of the base ceramic and melted/resolidified joint regions may be different. The purpose of the present study is to investigate the corrosion response of parent material and arc welded joints in oxygen/air, steam, and molten salts.

8:50 AM

(ICACC-S13-029-2019) Irradiation-Corrosion of Coated Silicon Carbide for Accident Tolerant Fuel Cladding

S. S. Raiman*[2]; P. J. Doyle[1]; T. Koyanagi[2]; C. K. Ang[1]; D. Carpenter[3]; K. Terrani[2]; Y. Katoh[2]

1. University of Tennessee, USA
2. Oak Ridge National Laboratory, USA
3. Massachusetts Institute of Technology, USA

Since the Fukushima incident in 2011, the nuclear industry has sought to replace Zircaloy fuel cladding with a material which will better withstand a beyond-design-basis incident. SiC/SiC ceramic matrix composite (CMC) materials are an attractive accident tolerant fuel (ATF) cladding candidate. However, the high dissolution rate of SiC/SiC CMCs in light water reactor (LWR) coolant indicates a need for environmental barrier coatings. For this work, SiC and SiC/SiC composite materials were prepared with several candidate coatings including TiN, Cr, and CrN. Coated and uncoated samples were irradiated in the MIT reactor for 66 days in ~300°C water with 150 ppb H_2 and B+Li additions. Samples were placed in the core of the reactor where they were exposed to the radiolyzed reactor coolant plus a neutron flux (4.8×10^{24} n/m^2). Samples were also positioned above the core where they were exposed to radiolyzed water with no neutron fluence, and out of the core, where they were exposed to the coolant water alone without effects of radiation. After exposure, samples were characterized with optical microscopy, SEM, TEM, XRD, and Raman to determine corrosion properties, radiation tolerance, and coating adherence. This talk will report on the irradiation-corrosion performance of SiC and SiC with Cr, CrN, and TiN coatings for use as ATF cladding.

9:10 AM

(ICACC-S13-030-2019) Research Activities on Hydrothermal Corrosion of SiC Ceramics for LWR Fuel Cladding Application

W. Kim*[1]; J. Shin[1]; D. Kim[1]; H. Lee[1]; J. Park[1]

1. Korea Atomic Energy Research Institute, Republic of Korea

SiC fiber-reinforced SiC matrix (SiC_f/SiC) composites have potential applications in advanced nuclear reactors from advanced fission to fusion reactors because of their attractive properties such as excellent high-temperature mechanical properties, chemical stability, and irradiation tolerance. In recent years, there have also been efforts on applying the SiC_f/SiC composites to nuclear fuel claddings and fuel components of light water reactors (LWRs) owing to excellent safety features under severe accident conditions. However, hydrothermal corrosion of SiC under normal operating condition is one of the most critical feasibility issues for LWR fuel cladding application because it can affect the integrity of fuel cladding and alter the chemistry of coolant water as well. It has been reported that the corrosion of SiC is largely dependent on the microstructure of SiC ceramics as well as the water chemistry. In this study, we carried out corrosion tests on various grades of CVD SiC ceramics to elucidate how the microstructural features affect the corrosion behavior of SiC. We also applied various metallic and non-metallic coatings in order to mitigate the hydrothermal corrosion of SiC ceramics and the corrosion test results are presented.

9:30 AM

(ICACC-S13-031-2019) Corrosion and Irradiation Studies of Silicon Carbide as a Nuclear Fuel Cladding

L. Czerniak*[1]; J. Lyons[1]; R. Jacko[1]; P. Xu[1]; J. Partezana[1]; C. Gasparro[1]; M. Ruffner[1]

1. Westinhouse Electric Company, Research and Technology, USA

In response to the nuclear industry's desire for longer coping times following the Fukushima accident in Japan in 2011, accident tolerant fuel (ATF) solutions are being developed to allow the fuel within a nuclear reactor to tolerate the loss of active cooling for longer periods. Development of a silicon carbide (SiC) cladding that will improve the effectiveness of fuel cladding during a loss of active cooling is a focal point of study. SiC samples are being tested both at the Westinghouse Churchill Facility and Massachusetts Institute of Technology (MIT) to provide corrosion and combined irradiation data, respectively. The corrosion studies being carried out at Westinghouse occur in an autoclave where the SiC samples are exposed to a chemistry environment typical of a mid-cycle pressurized water reactor (PWR). Corrosion rates of composite samples are compared to alpha SiC and zirconium alloy controls. In parallel, MIT is conducting irradiation tests of SiC samples in their research reactor. The irradiation tests allow the SiC samples to receive a neutron dose to determine the mechanical properties and corrosion rates in a radiative environment. This paper will present autoclave and in-reactor corrosion results.

Material Technologies for Enhanced Accident Tolerance LWR Fuels

Room: Coquina Salon H
Session Chair: Weon-Ju Kim, Korea Atomic Energy Research Institute

10:10 AM

(ICACC-S13-032-2019) Exploratory Testing for Westinghouse EnCore SiC/SiC Composite Cladding

P. Xu*[1]; E. J. Lahoda[1]; K. Steger[1]; M. Conner[1]; P. Evans[1]; R. Lu[1]; R. Oelrich[1]; C. Deck[2]

1. Westinghouse Electric Company, USA
2. General Atomics, USA

SiC/SiC composite cladding is a game-changing accident tolerant fuel (ATF) technology and a key component of Westinghouse's new EnCore fuel. The lead test assembly (LTA) for EnCore® SiC/SiC composite cladding is planned for 2022. To meet this aggressive schedule, significant progress was made to advance the SiC technology, and various developmental activities will be reported here. Exploratory tests were performed to evaluate the compatibility of SiC cladding with the current fuel assembly design, including rod loading test, bend test, grid-to-rod fretting wear test, ultra-high temperature test, and etc. The effect of surface roughness and process conditions on the performance of SiC cladding will be discussed. The exploratory test results will be used as the basis to finalize the SiC tubing specification.

10:30 AM

(ICACC-S13-033-2019) Hermeticity evaluation of neutron-irradiated SiC tubes for LWR cladding application

X. Hu*[1]; T. Koyanagi[1]; C. Petrie[1]; C. K. Ang[2]; C. Deck[3]; Y. Katoh[1]

1. Oak Ridge National Lab, USA
2. University of Tennessee, USA
3. General Atomics, USA

The continuous SiC fiber-reinforced SiC matrix ceramic (SiC/SiC) composites have been perceived as one of the leading candidate materials for accident tolerant fuel cladding in light water reactors. Evaluation of the hermeticity of SiC/SiC composite cladding before and after neutron exposure is critically important. This presentation describes the development of a permeation testing station and its application to measure the helium and deuterium leak rates of SiC tubes at room temperature. The studied materials included CVD SiC tubes and SiC/SiC composite tubes with various coated materials before and after neutron irradiation at 300~500°C to 2 dpa in the High Flux Isotope Reactor. Results indicate that the developed permeation testing station has a high detection resolution of $8.07x10^{-12}$atm-cc/s and $2.83x10^{-12}$atm-cc/s for helium and deuterium, respectively. Permeation testing showed that the hermeticity of coated SiC/SiC composite tubes is strongly dependent on the coating materials and the preparation of the substrate SiC/SiC composite tubes. The CVD SiC and CrN-coated SiC/SiC composite tubes maintained gas tightness following neutron irradiation. Additionally, helium and deuterium leaking rate as a function of pressure were determined for the non-hermetic samples.

10:50 AM

(ICACC-S13-034-2019) Post-Irradiation Examination of SiC/SiC composite Cladding

A. Seshadri*[1]; K. Shirvan[1]; G. Jacobsen[2]; C. Deck[2]

1. Massachusetts Institute Of Technology, Nuclear Science and Engineering, USA
2. General Atomics, Nuclear Technologies and Materials Division, USA

This work investigates the post-irradiation examination (PIE) of performance of SiC/SiC composite specimens. SiC/SiC composite specimen fabricated at General Atomics (GA) were exposed to neutron irradiation in a PWR flowing water loop at the MITR. Mechanical and surface characterization was performed on the irradiated open tube samples and samples with one end sealed with an end plug. For the same architecture, the hoop strength and the microstrain at failure were in the similar range for both the unirradiated and irradiated test specimen. The endplug joint showed that nearly all the samples failed at the joint, often times with visible corrosion to the transient eutectic phase fabricated endplugs, suggesting these endplugs should be replaced with more corrosion resistant CVD SiC endplugs. Wettability, roughness and SEM analysis was also performed on the irradiated specimen. The SEM analysis combined with Energy dispersive X-ray spectroscopy revealed no presence of oxygen within the fibers or the overcoat. With no detection of oxygen, the SiC smooth outer surface did become rougher upon exposure to high temperature water which indicates corrosion likely occurred, but the silica was quickly dissolved off the surface. While the contact angle for SiC was found to be similar to Zricaloy-4,

the increase in hydrophilicity from gamma radiation was found to be more rapid compared to Zircaloy-4.

11:10 AM

(ICACC-S13-035-2019) Thermal diffusivity of neutron-irradiated SiC composite tubes measured by laser flash method

T. Koyanagi*[1]; Y. Katoh[1]; H. Wang[1]; C. Petrie[1]; C. Deck[2]; K. Terrani[1]

1. Oak Ridge National Laboratory, USA
2. General Atomics, USA

Thermal diffusivity is one of the most important physical properties for assessing the performance of silicon carbide (SiC) based fuel cladding of nuclear reactors. It is used to calculate thermal conductivity along with density and specific heat. However, there is a significant lack of data for tube materials because measurement is challenging owing to the specimen geometry. This is in contrast to plate materials, which have been systematically investigated. This study investigated the thermal diffusivity of coupons with a curvature, machined from SiC/SiC composite tubes with and without neutron irradiation. The measurement was conducted using a conventional laser flash apparatus. First, the effect of the specimen geometry on thermal diffusivity was investigated using a glass ceramic with known thermal diffusivity. The results showed insignificant impact of the specimen geometry on the thermal diffusivity in the case of a curvature radius of ~4 mm. Subsequently, nonirradiated and neutron-irradiated SiC/SiC composite coupons with the same geometry as the glass ceramic specimen were evaluated. It was found that irradiation significantly reduced the thermal diffusivity, and the magnitude of the reduction was the same level as the reported value for plate specimens. This study was supported by the US DOE, Office of Nuclear Energy.

11:30 AM

(ICACC-S13-036-2019) Kinetics of irradiation defect annealing and thermal conductivity recovery in silicon carbide and potential impact on advanced reactor safety characteristics

N. R. Brown*[1]; T. Koyanagi[2]; C. Lu[1]; Y. Katoh[2]

1. Pennsylvania State University, Mechanical and Nuclear Engineering, USA
2. Oak Ridge National Lab, USA

We are conducting experiments to enhance understanding of the annealing of irradiation induced defects in high purity and sintered SiC samples. Under neutron irradiation the thermal conductivity of SiC degrades significantly, and within a certain temperature range (<900°C) saturates at a nearly constant temperature-dependent value. This phenomenon has been consistently observed for both high purity variants (e.g. chemical vapor deposition SiC) and lower purity sintered variants, though to different extents. We used irradiated samples (1 DPA) of both high purity CVD SiC and lower purity sintered NITE SiC. This ongoing work will quantify the kinetics of defect annealing in the temperature range 300-500°C. This talk also includes example calculations showing the impact of the thermal conductivity recovery kinetics on reactor safety. The SiC-based peak cladding temperature is sensitive to the thermal conductivity during the high temperature phase of a super prompt reactivity-initiated accident. Another example is a loss-of-forced cooling in a high temperature gas-cooled reactor, where irradiation induced defects in SiC-based materials will anneal out during this slow heat up process and the thermal conductivity improves. The Nuclear Science User Facilities Program Rapid Turnaround Experiment is acknowledged for the experiment.

Radiation Damage, Defect Production, Evolutions, and Interactions I

Room: Coquina Salon H

Session Chair: Phil Edmondson, Oak Ridge National Lab

1:30 PM

(ICACC-S13-037-2019) Order and amorphization in complex oxides (Invited)

B. P. Uberuaga*[1]

1. Los Alamos National Laboratory, Materials Science and Technology Division, USA

Complex oxides have numerous applications in nuclear energy systems and thus understanding their response to irradiation is critical for predicting performance and developing new materials. Significant work has been devoted to the amorphization of pyrochlores, a potential nuclear waste form. Previous work has suggested a correlation between the amorphization resistance of pyrochlores and the ability of the cations to disorder in chemically different pyrochlores. Here, using transmission electron microscopy and x-ray diffraction, we show that the opposite behavior is observed in spinels, where amorphization resistance is inversely correlated to the ability of the cation sublattice to disorder. Using density functional theory and accelerated molecular dynamics, we attribute the different response in these materials to structural cation vacancies in spinel that facilitate kinetic relaxation and do not exist in pyrochlore. Using machine learning approaches, we then revisit the correlation between amorphization and disordering in pyrochlores, finding that, while disordering is indeed a correlating factor for predicting amorphization in these materials, it is not sufficient, and accounting for the amorphization energy itself is important for improving predictions. Together, these studies provide a more generalized view of amorphization in complex oxides.

2:00 PM

(ICACC-S13-038-2019) Microstructural Evolution of Ion-Irradiated Zirconium Carbide

R. Florez*[1]; J. Graham[1]; W. Fahrenholtz[2]; G. Hilmas[2]

1. Missouri University of Science & Technology, Nuclear Engineering, USA
2. Missouri University of Science & Technology, Material Science and Engineering, USA

The microstructural evolution of stoichiometric ZrC irradiated with Au^{3+} ions at 800^0C was investigated in the present work. Samples were irradiated to equivalent doses of 0.5, 1, 2.5, 5, 10, 20 and 30 dpa. Morphological, microstructural and compositional changes induced by the irradiation were characterized by electron microscopy (SEM and (S)TEM), Grazing Incidence X-ray diffraction (GIXRD) and Raman Spectroscopy. Surface nanostructuring due to contaminant uptake was observed in the near-surface area of the irradiated samples. The morphology, microstructure, and composition of the nanoislands formed at the surface were analyzed using High-Resolution Transmission Electron Microscopy (HRTEM), Electron Energy Loss Spectroscopy (ELLS) and Raman spectroscopy. Defect evolution as a function of irradiation dose was characterized using conventional dark and bright field diffraction imaging. Changes in lattice parameter and microstrain were also analyzed using GIXRD.

2:20 PM

(ICACC-S13-039-2019) Defect ordering in yttria stabilized zirconia under 45 MeV ion irradiation

N. J. Madden*[1]; K. Hattar[2]; J. A. Krogstad[1]

1. University of Illinois at Urbana-Champaign, Material Science and Engineering, USA
2. Sandia National Laboratories, USA

Yttria stabilized zirconia (YSZ) has been shown to be very resistant to phase transitions or amorphization under ion irradiation. Most of these studies have either focused on low ion energies below 4 MeV

or very high ion energies. Naturally, these different ion energies produce different effects within the material. Low energies interact more directly with the nuclei of the material, whereas the very high energies first interact with the electrons of the material. The intermediate or medium ion energy range has been largely overlooked. The convergence of known damage mechanisms from high and lower energy or the potential for unique interactions may be possible in this medium energy range. This work aims to further develop the fundamental science of ion beam material interactions and develop new processing routes for a new class of material by exploiting intermediate ion energies. Preliminary observations via electron diffraction in TEM have shown sublattice vacancy ordering in cubic YSZ under 45 MeV gold ion irradiation. This ordering effect is a function of the damage depth profile, corresponding to the decline in the electronic stopping power. This study will explore the relationship between ion energy, dosage and the likelihood of sublattice ordering, as well as the overall thermal stability of the ordered structure and preliminary efforts to correlate ordering with functional transport properties.

2:40 PM

(ICACC-S13-040-2019) Room Temperature Sintering of Yttria Stabilized Zirconia and Ceria Nanoparticles via Ion Irradiation

N. J. Madden*[1]; S. A. Briggs[2]; C. A. Taylor[3]; P. M. Price[3]; T. J. Boyle[3]; B. R. Muntifering[3]; K. Hattar[3]; J. A. Krogstad[1]

1. University of Illinois at Urbana-Champaign, Material Science and Engineering, USA
2. Oregon State University, School of Nuclear Science and Engineering, USA
3. Sandia National Laboratories, USA

In order to incorporate advanced ceramics into future nuclear applications, the fundamental mechanisms of materials evolution in these environments need to be understood. One way to elucidate the roles of morphology and size effects in advanced nuclear ceramics is to study ceramic nanoparticles (NPs) because the shape and size can be controlled independently. Here, ceramic systems isomorphic with many nuclear fuels were studied, specifically yttria stabilized zirconia and ceria. Morphology and size evolution of these particles where observed using in-situ ion irradiation TEM (I^3TEM) at Sandia National Laboratories. These experiments demonstrated strong evidence of irradiation-induced sintering in both NP systems, despite efforts to mitigate thermal effects on the material behavior through low flux ion irradiation with 2.8 MeV and 1.7 MeV gold ions. From these initial observations, there is a strong implication that the sintering or densification occurs through radiation-enhanced diffusion (RED) in both NP systems. This RED at room temperature is surprising because the RED regimes were only observed at high temperatures for bulk materials, indicating that there may be a size effect or surface diffusion effect. More studies are needed to fully understand how nanoparticle size, shape and irradiation temperature impact the radiation induced densification.

Radiation Damage, Defect Production, Evolutions, and Interactions II

Room: Coquina Salon H

Session Chair: Blas Uberuaga, Los Alamos National Laboratory

3:20 PM

(ICACC-S13-041-2019) Advanced characterization of high burnup urania towards understanding mechanism of restructuring

K. Terrani*[1]

1. Oak Ridge National Lab, USA

Urania irradiated to burnups >60 MWd/kgU in light water reactors fuel pins has been examined using advanced electron microscopy and nano-indentation techniques. The purpose of these characterization activities is to elucidate the mechanism of restructuring in urania. Given the burnup and temperature profile across the pin diameter, the microstructure may be selectively examined. This allows for capturing the microstructural features and structural properties at the onset of restructuring as well as once it has fully progressed. The results indicate that there is a clear link between fission gas bubble formation and restructuring in urania.

3:40 PM

(ICACC-S13-042-2019) Annealing of Radiation Damage in Ti-based MAX Phase Alloys

P. Edmondson*[1]; M. B. Pagan[2]; M. Tunes[3]

1. Oak Ridge National Lab, USA
2. University of Tennessee, USA
3. University of Huddersfield, United Kingdom

The so-called MAX phases (general formulation $M_{n-1}AX_n$, where M is an early transition metal, a group A element, and X is either C or N) have been proposed for use in future nuclear reactor concepts due to their excellent physical properties and purported tolerance to radiation damage. In order to develop a mechanistic understanding for the tolerance to radiation damage, it is critical to evaluate the damage formation and recovery at an atomistic scale. In this work, Ti_3SiC_2 and Ti_2AlC MAX phases have been neutron irradiated to 2 and 10 displacements per atom at a temperature of ~200 C. Post irradiation characterization and annealing up to 600 C has been conducted in situ of a transmission electron microscope (TEM) using a high stability, high temperature stage. This talk will summarize the observed result on defect stability, focusing on the stability of dislocation loops and lines, and stacking faults.

4:00 PM

(ICACC-S13-043-2019) High Temperature Radiation Response of Ti-based M_nAX_{n-1} Phases

M. Tunes*[1]; A. Mir[1]; G. Greaves[1]; P. E. Donnelly[1]; P. Edmondson[2]

1. University of Huddersfield, SCE, United Kingdom
2. Oak Ridge National Lab, USA

M_nAX_{n-1} (MAX) phases have a distinctive stochiometric formation rule involving the mixing of an early transition metal (M), a group A element, and C or N (X). Due to their reported strong stiffness, good thermal properties, high resistance to corrosion and high thermodynamic phase stability at high temperatures, MAX phases have been proposed for use in future nuclear reactor concepts. Therefore, the mechanisms of radiation damage and radiation-induced degradation of their microstructures need to be evaluated. Here, the neutron and ion irradiation response of Ti-based MAX phases are examined. Ti_3SiC_2 and Ti_2AlC have been subjected to neutron irradiations up to 2 and 10 dpa at 1273 K in the High-Flux Isotope Reactor (HFIR) and with 700 keV Kr^{+2} up to 7 dpa at 1008 K in situ within a Transmission Electron Microscope (TEM) at the MIAMI Facility. Post-irradiation electron microscopy characterisation reveals an intricate network of irradiation-induced defects in the neutron-irradiated specimens including voids, black-dots, dislocation loops, lines and stacking faults; in situ TEM with heavy ion irradiation experiments showed little damage under the studied conditions. The differences in the results between neutron and ion irradiations along with the future challenges in the application of such MAX phases within nuclear technology will be discussed.

4:20 PM

(ICACC-S13-044-2019) Relating Microstructure and Stored Energy in Irradiated Silicon Carbide

L. Snead*[2]; Y. Katoh[1]; T. Koyanagi[1]

1. ORNL, USA
2. Stony Brook University, USA

The high stored energy (>1390 J/g) recently found to exist in neutron-irradiated silicon carbide (SiC) has generated interest regarding its technological implications to light water reactor

systems. For such applications, as the energy release exceeds SiC specific heat the possibility of an autocatalytic temperature rise exists. However, that original stored energy work was based on materials irradiated in the amorphization regime (60°C) compared to the relevant LWR application temperature (300-350°C.) In the paper the implications of storing energy in SiC in the amorphization regime and the point defect regime (>200°C) will be contrasted and discussed. This comparison is supported by investigating the microstructure of SiC irradiated in both regimes using raman spectroscopy, TEM, and XRD utilizing the powder diffraction station at the NSLS-2. Of specific interest will be the nucleation of highly disordered pockets and carbon clusters as the amophization threshold dose is approached. This phenomenon along with the relative production of higher energy defects, such as antisite defects, for low temperature irradiation will discussed to suggest the differences in stored energy within the two irradiation temperature regimes.

4:40 PM

(ICACC-S13-045-2019) In-situ Ion Irradiation Response of a Silicon Carbide-Carbon Coated Nanostructured Ferritic Alloy Composite

K. K. Bawane*[1]; K. Lu[1]; J. Hu[2]; M. Li[2]

1. Virginia Tech, Materials Science and Engineering, USA
2. Argonne National Lab, Nuclear Engineering Division, USA

A composite of silicon carbide and carbon coated nanostructured ferritic alloy (25 vol% SiC-C@NFA) was densified using spark plasma sintering at 950ºC. In this work, the composite was irradiated with Kr^{++} ions at 1 MeV energy up to 10 dpa at 300ºC and 450ºC. Microstructures and defect evolution were recorded in-situ using the IVEM facility at Argonne National Laboratory. The effect of ion irradiation on various phases such as α-ferrite (NFA) matrix, $(Fe,Cr)_7C_3$ and (Ti,W)C precipitates was evaluated. α-ferrite grains showed continuous increase in dislocation density along with the formation of spatial ordering (or loop string) of dislocations above 5 dpa dose. The size of dislocation loops at 450ºC was higher than that at 300ºC. The nucleation and growth of new (Ti,W)C type precipitates with increasing dose level at 450ºC was observed throughout α-ferrite grains. SRIM simulations were carried out to theoretically estimate dpa damage. ThermoCalc/PRISMA calculations were performed to explain the precipitation behaviors.

S15: 3rd International Symposium on Additive Manufacturing and 3-D Printing Technologies

Characterization Tools I

Room: Coquina Salon B

Session Chair: Uwe Scheithauer, Fraunhofer IKTS

8:30 AM

(ICACC-S15-030-2019) Analysis of Multi-scale Mechanical Properties of Ceramic Trusses Prepared from Preceramic Polymers

J. E. Schmidt[2]; N. R. Brodnik*[1]; P. Colombo[2]; K. Faber[1]

1. California Institute of Technology, Materials Science, USA
2. University of Padova, Industrial Engineering, Italy

Recently, additive manufacturing of preceramic photopolymer systems has shown promise as a tool for producing net-shape ceramics of complex structure at low cost. The preceramic polymer is converted to ceramic through pyrolysis, which produces a dramatic size change. This study investigates the mechanical properties of trusses with different deformation modes, specifically bending and stretching. Trusses are tested in uniaxial compression to characterize the stiffness and strength of the entire structure. Constituent beam elements are further tested using 3-point bending to characterize their strength. Additionally, the relative shrinkage from pyrolysis is measured for both individual beam elements as well as the truss structure as a whole. This multi-scale characterization provides insight into how the conversion from polymer to ceramic affects sample geometry and resultant mechanical properties, which both scale non-uniformly between the truss structure and individual beams. Understanding these relationships will help better inform the design of parts with complex geometries for load-bearing applications.

8:50 AM

(ICACC-S15-031-2019) Mechanical properties of ceramic processed by stereolithography: Effect of surface polishing

D. Hautcoeur*[1]; C. Ott[1]; E. Juste[1]; F. Petit[1]

1. Belgian Ceramic Research Centre, Belgium

It is well known that the mechanical properties of alumina, silica and zirconia are strongly depended on the finish surface. The mechanical properties are determined on cut and polished samples while the final products are usually not. In the case of components obtained though additive manufacturing (especially Stereolithography-SLA), post-processing and finishing is a highly challenging task which cannot be usually carried out for very complex parts. The aim of this work is to determine whether or not the finish surface of raw parts obtained using SLA has an influence on the mechanical properties. SLA specimens have been prepared, sintered and further characterized by 3 points bending tests. A comparison of the mechanical properties has been performed between raw and polished samples. Moreover, mechanical strength of specimens processed by a classical shaping route (powder pressing) has been determined as well for completeness. The European Regional Development Fund (ERDF) and Wallonia, are gratefully acknowledged for their financial support to these research projects CERAMTOP and CERAMPLUS "Iawatha" in the frame of the "Transition programme."

9:10 AM

(ICACC-S15-032-2019) Study of the stiffness of ceramic parts using a numerical simulation model of the stereolithography process

J. Tarabeux*[1]; T. Chartier[2]; V. Pateloup[2]; P. Michaud[2]

1. University Limoges, France
2. IRCER, France

The control of the mechanical properties of green parts produced by stereolithography is an important aspect to take into account in the manufacturing process. In fact, stiffness has to be monitored in order to properly manufacture and clean parts. This study aims to use numerical simulation of photosensible ceramic system curing to predict the Young's Modulus of green parts. This model is validated by experimental Young's Modulus measurements by coupling a tensile test with a Digital Image Correlation technique. This experimental approach is conducted on a commercial photopolymerizable Al_2O_3 paste and by using a design of experiments to reduce the number of experiments. Therefore, the influence of manufacturing parameters on the stiffness of the parts is investigated. The simulation model enables to predict the Young's Modulus for each experiment with a maximum error of 6.1%, which makes it valid. Moreover, it allows to highlight that Young's Modulus measurements of green parts using an optical method is highly effective. The simulation model also provides visualization of the exposure distribution and the scattering phenomenon, which has to be considered, notably for ceramic systems.

9:30 AM

(ICACC-S15-033-2019) Quality and Testing of Ceramics by Lithography-based Ceramic Manufacturing

S. M. Allan*[1]

1. Lithoz America, LLC, USA

Additive manufacturing (AM) is providing design engineers with unprecedented access to prototyping and production of high performance ceramics, thanks to the elimination of tooling. The properties of ceramics produced by lithography-based ceramic manufacturing (LCM) are comparable with parts made by other more conventional forming processes. The relationship of properties and design contribute to the performance of ceramics produced by AM. Design for ceramic additive manufacturing (DfCAM) involves reducing stress risers, optimizing part orientation, and developing support structures for printing to best utilize the LCM process parameters. DfCAM must also consider stresses during binder burnout and sintering, particularly in components with varied wall thickness. The design of the part can mitigate or exacerbate the defects found in the ceramic inherent to processing. It is therefore important to consider both the properties and design when addressing ceramic AM challenges.

Characterization Tools II

Room: Coquina Salon B
Session Chair: Tyrone Jones, US Army Research Laboratory

10:10 AM

(ICACC-S15-034-2019) Additive Manufacturing of Ceramics and Composites for High Temperature Aerospace Applications

C. Smith*[1]; M. Singh[2]; M. C. Halbig[1]

1. NASA Glenn Research Center, USA
2. Ohio Aerospace Institute, USA

Ceramics, such as silicon carbide (SiC), have the potential to be used for aerospace thermal management systems. However, thin features and complex channels can be difficult to produce with conventional manufacturing. Additive manufacturing methods make it possible to produce complex geometries that cannot be made by conventional means. This talk will cover the approaches being explored at NASA Glenn Research Center for additive manufacturing of SiC-based advanced ceramics and SiC fiber-reinforced SiC composites (SiC/SiC). The effect of different powders and reinforcements on the microstructural and mechanical properties will be discussed. Various technical challenges and opportunities for additive manufacturing of ceramics and ceramic composites will be presented.

10:30 AM

(ICACC-S15-035-2019) Characterization method for real mechanical behavior of ceramic AM components

U. Scheithauer*[1]; P. Neumeister[1]; S. Roszeitis[1]; J. Abel[1]; E. Schwarzer[1]; S. Weingarten[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Shaping, Germany

Additive Manufacturing (AM) technologies are tool-free production processes which increase the freedom for the component design and allow designing and constructing oriented to function instead to fabrication. Certainly, these new technologies create new challenges, e.g. concerning the mechanical characterization of filigree structure components, which could not be manufactured before. Another challenge is the consideration of AM-specific properties like the cascading surfaces resulting from the layer-wise manufacturing process. Starting from this challenges we developed a new characterization method which bases on a single-sided fixed bending bar with varied cross section to secure a constant maximum bending stress. The effort to manufacture and to characterize a huge number of test samples could be decrease significantly. Furthermore differences in the surface quality resulting from different orientations of the components in the building volume can be simulated and considered. To demonstrate this characterization method we additively manufactured ceramic test components using the Lithography-based Ceramic Manufacturing (LCM) – technology and a device (CeraFab 7500) of Lithoz, Vienna. The geometry and the orientation of the bars were varied and the results differed for more than 30 %. The presentation will describe the developed characterization method as well as the achieved results in detail.

10:50 AM

(ICACC-S15-036-2019) A Novel Method for Characterizing the Dispersion of Additive Manufacturing Ceramic Suspensions

M. K. Alazzawi*[1]; B. Beyoglu[1]; R. A. Haber[1]

1. Rutgers University, Materials Science and Engineering, USA

Additive Manufacturing provides high capabilities in the fabrication of complex structures. The final product quality and properties are strongly influenced by the microstructure of the ceramic suspensions. A novel rigorous method will be presented that characterized the degree of dispersion of alumina photocurable suspension microstructures. Alumina slurries with varying degrees of dispersion were 3D printed using a digital light processing technology. The 3D printed objects were thermally decomposed and sintered. The porosity distribution and shrinkage were characterized and compared. A correlation between the final product properties and the microstructure of the slurries will be detailed.

11:10 AM

(ICACC-S15-037-2019) Prospects and measurement challenges for additive manufacturing of cement and concrete components

A. J. Allen*[1]; S. Jones[2]; F. Zhang[2]; J. Richards[3]

1. NIST, Materials Measurement Science Division, USA
2. NIST, USA
3. Northwestern University, USA

The advance of the digital age across all industrial sectors is spurring the introduction of additive manufacturing (AM) concepts to an increasingly broad range of fabricated products and components. While AM has spread well beyond its origins in polymer-based 3D printing, and various digitally-based prototyping exercises for materials-by-design, to include the wholesale AM fabrication of metal and alloy components and, more recently, emerging AM processes for ceramic components, it has not been exploited significantly, up to now, in the manufacture of cement and concrete components for the construction industry. The introduction of AM methods for cement and concrete construction components offers significant advantages in exploitation of the world's most used industrial material. However, to realize these opportunities, it is critical to optimize the development of cement properties during the hydration process for their use either as de facto 3D printing "inks" or as AM templates. This implies the carefully tuned addition of accelerators (e.g., aluminum sulfate) and retarders (e.g., sucrose) to optimize the hydration process. Accurate measurement of the effects on cement rheology, microstructure and strength evolution during hydration are key to realizing the AM potential of cements. Recent research at NIST focused on these objectives will be presented and discussed.

11:30 AM

(ICACC-S15-038-2019) Microstructural Evaluation of SLA Printed Alumina

B. Beyoglu*[1]; M. K. Alazzawi[1]; R. Haber[1]

1. Rutgers University, Material Science and Engineering, USA

Additive manufacturing (AM) is a revolutionary technology in production of a wide range of advance materials. In this study, a digital light processing (SLA) technology was used to 3D print alumina slurries having different degree of dispersion. Microstructural analysis was performed on final ceramic product to evaluate microstructural uniformity, porosity, and lamination

cracks correlated to the degree of dispersion of the slurries. Applying these findings, effectiveness of controlling the degree of dispersion of slurries in improving uniformity and preventing the formation of defects in 3D-printed ceramic parts will be discussed.

Emerging Technologies

Room: Coquina Salon B
Session Chair: Michael Halbig, NASA Glenn Research Center

1:30 PM

(ICACC-S15-039-2019) Ceramics Additive Manufacturing (Invited)

A. Michaelis*[1]

1. Fraunhofer IKTS, Germany

Additive manufacturing with ceramic materials is particularly challenging due to the needed pre- and post shaping processes such as ceramic paste or ink preparation and thermal post treatment (sintering). In the case of multi-material application the thermal expansion behavior of the materials have to be carefully adjusted for the co-sintering process. Know How from established 2,5 D multilayer ceramic technologies such as LTCC (low temperature co-fired ceramics) or multi-component injection moulding can be employed to address these issues. An important issue for all AM technologies is the improvement of reliability and performance of the manufactured components. Due to the time-consuming manufacturing processes and the layer-wise building process it is necessary to control the quality of each layer in order to repair a defective layer or to stop the building process to avoid waste of time and expensive material loss. Therefore, it is important to access the quality of the printed parts as early as possible. This requires in-operando non-destructive evaluation methods. For this, new optical methods such as speckle laser spectroscopy and optical coherence tomography can be applied. For a further functionalization of the AM parts, 2D printing technologies are applied. We present first results on this combination of 3D and 2D printing.

2:00 PM

(ICACC-S15-040-2019) Ballistic Evaluation and Damage Characterization of 3-D Printed, Alumina-based Ceramics for Light Armor Applications

T. Jones*[1]; L. Vargas[1]; C. Meredith[1]

1. US Army Research Laboratory, USA

The goal of this work is to present results of mechanical characterization and ballistic investigation of 3-D printed alumina-based armor plates. The 8mm thick plates were manufactured using two different additive manufacturing-based methods: tape cast and direct ink write (DIW). The DIW Al_2O_3 plates exhibited superior hardness, flexural strength, and density compared to the tape cast plates. Plates (90 mm × 90 mm × 8 mm) of these composition were manufactured for ballistic analysis in accordance with established ballistic characterization procedures, using a 50.8 mm thick Aluminum 6061 plate as backing and witness plates in the case of penetration or deformation. Six alumina plates were examined ballisitically (one shot per plate) against the 12.7 mm APM2 projectile (45.9 g) at an impact velocity of 840 m/s. The plates that were manufactured using the DIW method provided a higher impact resistance than the tape cast method.

2:20 PM

(ICACC-S15-041-2019) Process optimisation for selective laser melting of soda lime silica glass

K. Datsiou*[1]; I. Ashcroft[1]; R. Goodridge[1]; E. Saleh[1]; F. Spirrett[1]

1. University of Nottingham, Department of Engineering, United Kingdom

Selective laser melting (SLM), an additive manufacturing technology involving the fusing of metallic powders by selective laser heating, has become increasingly popular over the last few decades for the manufacture of bespoke parts. There is limited research to date on SLM of glass. However, if successful this could open new opportunities for a range of applications including electronics, flow chemistry, decorative glass and eventually for large scale applications in the automotive, aerospace and architectural industries. Glass is an attractive material for many applications due to its transparency, chemical durability and aesthetic appeal, as well as interesting thermal and electrical properties, however it is also a brittle material when solid and susceptible to thermal cracking, which is a challenge for SLM. In this study, SLM of a soda lime silica glass is investigated. Optimisation of the set-up including feedstock, substrate materials and laser focus position is initially undertaken. The optimised set-up is then used to populate process maps and identify laser processing parameters for the formation of monolayer single tracks and multilayer thin walls. It is found that by careful selection of feedstock material and the fine tuning of processing parameters, it is possible to manufacture crack-free amorphous glass parts.

2:40 PM

(ICACC-S15-042-2019) Dimensional Modulations of Alumina Components by Stereolithographic Additive Manufacturing

S. Kirihara*[1]; X. Wang[1]; T. Shimizu[1]; Y. Fujita[1]

1. Osaka University, Joining and Welding Research Institute, Japan

In stereolithographic additive manufacturing, 2D cross sectional patterns were created through photo polymerization by ultra violet laser drawing on spread resin paste including ceramic nanoparticles, and 3D composite models were sterically printed by layer lamination though chemical bonding. The stereolithography system has been developed to obtain bulky ceramic and metal components with functionally geometric structures. An automatic collimeter was newly equipped with the laser scanner to adjust beam diameter. Fine or coarse beams could realize high resolution or wide area drawings, respectively. Nanometer sized ceramic particles were dispersed in to photo sensitive liquid resins from 40 to 60 % in volume fraction. The paste was spread on a glass substrate at 10μm in layer thickness. An ultraviolet laser beam of 355 nm in wavelength was adjusted from 10 to 300 μm in variable diameter and scanned on the pasted resin surface. Irradiation power was changed automatically from 10 to 200 mW. The created precursor was dewaxed and sintered in an air atmosphere to obtain full metal or ceramic components. Through the computer aided design, manufacturing and evaluation, ordered porous structures of aluminium heat exchangers and alumina electromagnetic crystals were successfully fabricated.

Discussion Panel: Opportunities & Challenges in Ceramics Additive Manufacturing

Room: Coquina Salon B
Session Chairs: Andrew Allen, NIST; Igor Levin, NIST

3:20 PM

(ICACC-S15-043-2019) Issues in Additive Manufacturing of Ceramics (Invited)

T. Ohji*[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

AM (additive manufacturing) has several advantages including; (1) Realizing complex-shaped or integral-structured bodies which are never attainable conventionally, (2) Saving production time and cost due to a mold-less process, and (3) Actualizing unique material structures including compositionally or functionally gradient layer textures. However, there are also several issues for using AM as an industrial manufacturing tool (particularly when applying it into ceramics), including; (1) Melting and solidification, which are allowed in metals and polymers, are not usable in ceramics. Currently producing green bodies by AM, which are to be post-fired

in a conventional furnace, (2) Some restrictions apply in starting powder in terms of flowability, (3) Can AM products give us the same properties as conventional ones?, (4) Limited facilities adjustable to ceramics manufacture in powder bed fusion (mostly for polymer and metals), (5) Profitable only for large variety-small amount products, and (6) Facilities sometimes can be very expensive, requiring large initial costs. The talk will address and discuss these issues. A part of this work was conducted as a part of "High-value added ceramic products manufacturing technologies project" supported by CSTI, SIP, "Innovative design/manufacturing technologies (managed by NEDO)"

3:35 PM

(ICACC-S15-044-2019) Decarbonising ceramic manufacturing using energy efficient sintering technologies (Invited)

I. M. Reaney*[1]; L. Koh[2]; T. Ibn-Mohammed[2]

1. University of Sheffield, Materials Science and Engineering, United Kingdom
2. University of Sheffield, Management School, United Kingdom

This paper presents a critical review and analysis of a number of sintering techniques and compares them with the recently developed cold sintering process (CSP), including mode of operation, sintering mechanism, typical heating rates, duration of sintering, energy consumption profile and energy saving potential, limitations, key challenges for further development and current research efforts. By using a figure of merit, pounds per tonne of CO_2 saved (£/tCO_2-eq), which links initial capital investment with energy savings, within a framework derived from ranking principles such as marginal abatement cost curves and Pareto optimisation, we have demonstrated that under the scenarios considered for 3 separate functional oxides ZnO, PZT and $BaTiO_3$, CSP is the most economically attractive sintering option, indicating lower capital costs and best return on investment as well as considerable energy and emission savings. Although the current work establishes the viability of CSP as a competitive and sustainable alternative to other sintering techniques, the transition from laboratory to industry of CSP will require hugely different facilities and instrumentation as well as relevant property/performance validation to realise its full potential.

3:50 PM

(ICACC-S15-045-2019) Ceramic Additive Manufacturing in Healthcare (Invited)

S. M. Allan*[1]

1. Lithoz America, LLC, USA

Additive manufacturing of technical ceramics offers significant opportunities in healthcare for a wide range of materials for personalized implants, surgical tools, medical devices, and research devices. Ceramic AM components must meet the same physical and biocompatibility standards as parts produced by other forming methods. The layerwise forming processes of AM and the resulting characteristic flaw populations indicate the need to consider standards for directional property and performance measurement.

4:05 PM

(ICACC-S15-046-2019) Opportunities & Challenges in Ceramics Additive Manufacturing: Energy & Sustainability (Invited)

B. L. Armstrong*[1]

1. Oak Ridge National Lab, Material Science & Technology Division, USA

Opportunities & Challenges in Ceramics Additive Manufacturing: Energy & Sustainability Although there has been an increasing interest in ceramics additive manufacturing (AM), the research has lagged behind metal and polymeric materials work predominantly due to the secondary processing that is still required. This lag affords potential research and commercialization topics to be investigated. One category of interest is in energy & sustainability arena. A discussion of the challenges and opportunities within this market sector will be presented.

4:20 PM

(ICACC-S15-047-2019) Additive Manufacturing & 3D Printing Technologies: Air Force & Aerospace Applications (Invited)

M. B. Dickerson*[1]; L. M. Rueschhoff[1]

1. Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Aerospace applications present a multitude of opportunities and challenges for additive manufacturing (AM). Advancements in AM systems, materials processing, and component design have enabled the insertion of a limited number of 3D printed components into service. The nascent use of AM for metallic components as well as trends in high-temperature aerospace materials indicate a possible future for ceramic AM. In this presentation, trends, gaps, and challenges in ceramic AM for aerospace applications will be discussed.

S16: Geopolymers, Inorganic Polymers and Sustainable Materials

Synthesis, Processing and Microstructure

Room: Ponce de Leon

Session Chair: Waltraud Kriven, University of Illinois at Urbana-Champaign

8:30 AM

(ICACC-S16-001-2019) Synthesis of Aluminosilicate Nanoaggregates from Geopolymerization (Invited)

D. Seo*[1]; S. Chen[1]

1. Arizona State University, School of Molecular Sciences, USA

Nanoaggregates such as precipitated silica and carbon blacks are some of the most important inorganic nanomaterials used in modern technologies. We report detailed synthetic conditions for preparation of such nanoaggregates from geopolymerization process. Given the massive production and application of the latter materials in the range of millions of tonnes per year, the advent of the new geopolymer material type has a huge implication in novel large-scale applications of geopolymer. We discuss the key features of the synthetic conditions and the relationship between the synthetic parameters (the concentrations of the precursors, reaction time and temperatures) and the morphologies of the geopolymeric nanoaggregates in terms of surface areas, porosity, aggregate size, and zeolitic crystallinity.

9:00 AM

(ICACC-S16-002-2019) Geopolymer oil composite: Droplet structure and connectivity by X-ray microtomography (Invited)

C. Davy[2]; B. Planel[1]; G. Hauss[4]; D. Lambertin*[3]

1. CEA,DAM,DMA,SDAT,LGDA, France
2. Centrale Lille and UCCS UMR CNRS 8181, France
3. CEA DEN, DE2D, SEAD, LCBC, France
4. Plateforme d'imagerie par rayons X ISIS4D, France

Geopolymer cements are investigated in a number of domains, owing to their low environmental impact and to their performance in civil engineering, for radioactive waste immobilization, and in the synthesis of novel materials. Recently, composite materials made of geopolymer cement and liquid oil have been proposed for the synthesis of porosity-controlled media, e.g. as thermal insulating foams or filtration supports, for the management of radioactive organic liquid waste, and as phase change materials (PCM). In this study, by using X-Ray microtomography with a voxel size of 1 µm, we quantify the 3D distribution of oil droplets emulsified in a geopolymer (from 5 to 60% Vol.), after its solidification. The oil droplet size and distance distributions are evaluated in 3D, and the connectivity of the oil emulsion is assessed from the skeleton of the oil droplet network.

This research has shown that 3D X-Ray microtomography image analysis of geopolymer/oil composites provides useful insights into the spatial distribution of oil droplets emulsified in a fresh geopolymer paste. In particular, for 30 vol% of oil and more, the oil volume has a significantly greater connectivity than for 5, 10 or 20 vol% oil. This transition is useful to design disconnected oil/geopolymer composites (PCM or radioactive waste encapsulation), or to propose connected macroporous foams.

9:30 AM

(ICACC-S16-003-2019) Effect of silica and lignocellulosic additives on the formation and distribution of meso and macropores in metakaolin-based geopolymer foams for filtration

M. Youmoue*[1]; R. T. Tene Fongang[3]; A. Gharzouni[1]; E. Kamseu[3]; V. M. Sglavo[4]; I. K. Tonle[2]; B. Nait-Ali[1]; S. Rossignol[1]

1. Université de Limoges, Institut de Recherche sur les Céramiques, France
2. University of Dschang, Noxious Chemistry and Environmental Engineering Research Unit, Cameroon
3. Local Material Promotion Authority, Cameroon
4. University of Trento, Department of Materials Engineering and Industrial Technologies, Italy

This work investigates the effect of silica (from rice husk ash RHA2 and calcined sand Sa) and lignocellulosic sawdust (S) additives on the formation and the distribution of meso and macropores in metakaolin/silica fume - based geopolymers. Geopolymer foams were obtained by curing the paste at 70°C during 24 h. Samples were characterized through XRD, SEM and Mercury intrusion porosimetry (MIP). Results reveal sponge-like microstructure and some micro-cracks in geopolymer structure. The total cumulative intrusion volume of geopolymers (TCIV) is lower without any additives (131 $mm^3.g^{-1}$) and higher with fired sand (502 $mm^3.g^{-1}$). MIP analysis also shows that these geopolymer are constituted with meso, macro and coarse pores. Reference geopolymer is dominated by macropores (81% of TCIV). Meso and macropores constitute respectively 29% and 59% of TCIV with RHA2, 47% and 37 % of TCIV with fired sand addition. In sawdust geopolymer, coarse pores represented 60% of TCIV. Geopolymers are more stable with sawdust addition. Previous results show that elaborated geopolymers are suitable for wastewater filtration.

10:10 AM

(ICACC-S16-004-2019) Characterization of coal fly ash with potential use in the manufacture of geopolymers to solidify/stabilize heavy metals

P. M. Fonseca Alfonso*[1]; E. Murillo Ruiz[2]; M. Díaz Lagos[1]

1. Universidad Pedagógica y Tecnológica de Colombia, Colombia
2. Universidad Francisco de Paula Santander, Colombia

In this study, fly ash was obtained from thermal station Termopaipa IV, in the State of Boyacá, Colombia and the physicochemical properties investigated. The fly ash was characterized by X-ray fluorescence, X-ray diffraction, Fourier-transform infrared spectroscopy, inductively coupled plasma mass spectrometry and laser diffraction. It is noticeable that the ashes are made up of aluminum and silicon compounds. Besides, iron phases in low content such as hematite and limonite were also found. Highly toxic metals As, Sb, Cd, Cr, Hg and Pb as well as metals that are essential to health in trace amounts were also present were also measured. According to the features found in this study, it was determined that fly ash can be used in the manufacture of geopolymers with potential application in the solification/stabilization of heavy metals.

10:30 AM

(ICACC-S16-005-2019) Structure-property relation of portland cement paste blended with steel slag

H. Colorado*[1]; S. S. Sulekar[2]; J. C. Nino[2]

1. Universidad de Antioquia, Colombia
2. University of Florida, USA

This paper presents Portland cement mortar blended with different contents of steel slag. Steel slag is hazardous waste of constant concern in the world. The main goal of this research is to use this slag with cement in order to explore potential applications, from structural to electronics. Utilization of this waste is very beneficial to the environment not only because these materials typically contain hazardous metals, but also because our process is entirely conducted at room temperature. Up to 80wt% of steel slag was added to cement by mechanical mixing. Samples microstructure was analyzed with scanning electron microscopy (SEM) and x-ray diffraction (XRD). Dielectric and thermal diffusivity was evaluated as well. It was found that compressive strengh decreased as waste loading increased and strength values ranged from 73 to 7MPa.

3-D Printing

Room: Ponce de Leon

Session Chair: Kaushik Sankar, University of Illinois at Urbana-Champaign

11:00 AM

(ICACC-S16-006-2019) 3D Printing of Geopolymers: The path to Innovative Ceramic Composites (Invited)

P. Scanferla*[1]; G. Franchin[1]; P. Colombo[1]

1. University of Padova, Industrial Engineering, Italy

Geopolymers are inorganic materials generally obtained by the reaction of alumino-silicate powder in an alkaline solution. They can consolidate at low or even room temperatures and possess good mechanical properties, weather and heat resistance, which make them suitable for a wide range of applications, such as structural materials, thermal insulation, and so on. Our group developed mixtures based on geopolymer for additive manufacturing of porous components via direct ink writing (DIW). We optimized the rheological properties in order to obtain suitable inks for the production of highly porous lattices. It should be noted that, as geopolymer mixtures are subjected to ongoing poly-condensation reactions, their viscosity changes with time in what can be seen as a 4D printing process. Different materials were added to the mixture, such as fibers and micro particles, to produce innovative 3D printed geopolymeric composites.

11:30 AM

(ICACC-S16-007-2019) Geopolymer for ceramics formation, 3D printing and Cs^+/Sr^{2+} sealing (Invited)

P. He*[1]; D. Jia[2]

1. Harbin Institute of Technology, Institute for Advanced Ceramics, School of Materials Science and Engineering, China
2. Harbin Institute of Technology, Key Laboratory of Advanced Structural-Functional Integration Materials & Green Manufacturing Technology, China

Geopolymers are inorganic material with three-dimensional non-crystalline frameworks. Beyond being considered as alternative candidate for cement materials, geopolymer also provides a novel way to prepare advanced ceramics such as leucite, pollucite, BAS, SiC among others. The viscosity of geopolymer slurry can also be well controlled and curing rate can be tuned through the temperature adjustment, and therefore it can be 3D printed like organic materials. Meanwhile, the zeolite-like composition and structure make geopolymer a promising sealing material for nuclear wastes ions such as Cs^+ and Sr^{2+}. This presentation will show the research progress in ceramics formation, 3D printing and nuclear waste treatment through geopolymer in our group.

Composites

Room: Ponce de Leon
Session Chair: Nishant Garg, Princeton University

1:30 PM

(ICACC-S16-008-2019) On the Mechanical Behavior of K-based Geopolymer Reinforced with Chopped Basalt Fibers Manufactured for Cement Versus Epoxy-based Applications (Invited)

A. C. Trindade*[1]; W. M. Kriven[2]; F. d. Silva[1]

1. Pontifical Catholic University of Rio de Janeiro, Civil and Environmental Engineering, Brazil
2. University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, USA

In this study a K-based geopolymer was produced through the combination of MK and an alkaline solution (water-glass), in a final composition of $K_2O.Al_2O_3.4SiO_2.11H_2O$. A particulate reinforcement system was evaluated, incorporating chamotte in 25% by weight, resulting in a strength increase of 50%. Two types of ½ inch length basalt fibers (manufactured for cement and epoxy-based applications) were used, and compared, in 10% by weight content, using equal processing conditions. Their efficiency was analyzed through mechanical evaluations: compression and flexural tests. Similar average responses, in the range of 30.1 to 32 MPa, were found for both reinforcements in flexural evaluations. Pull-out and direct tensile tests were also performed. The effect of the addition of superplasticizer in varying weight % was examined through flow table and marsh funnel tests. 0.5% by weight was stablished as an adequate amount to improve the geopolymer workability, providing no mechanical interference, allowing a greater incorporation of both fibers into the mixture (20%). The basalt fibers manufactured for epoxy applications presented a greater compatibility, reaching 35 MPa in flexural tests. A Weibull analysis was performed, and it was possible to observe more reliable results for materials reinforced with greater amounts of fibers.

2:00 PM

(ICACC-S16-009-2019) Basalt Fibers and Minibars as Geopolymer Reinforcements

A. J. Steveson*[1]; D. W. Blake[1]; J. R. Davis[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Materials Science and Engineering, USA

The incorporation of basalt fibers has been shown to drastically improve the mechanical performance of geopolymers across several key material properties. In this work, we compare the performance of 1-inch chopped fibers with a new reinforcement geometry, ¾-inch Minibars (ReforceTech, Inc.), that demonstrate strength and toughness improvements over chopped fibers. We detail synthetic considerations for working with these reinforcements, report Weibull statistics for compression, flexure, fracture toughness, and shear testing results with comparison to previously reported data on related materials, and include macro- and microscopic observations to elucidate failure mechanisms and key differences between chopped fiber- and Minibar-reinforced geopolymer composites.

2:20 PM

(ICACC-S16-010-2019) Alkali-Resistant Glass Fibers as a Geopolymer Reinforcement

D. W. Blake*[1]; J. R. Davis[1]; A. J. Steveson[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, USA

Geopolymer composites show higher strength and toughness than do pure geopolymers. The purpose of this work was to document the mechanical properties of geopolymer reinforced with alkali-resistant-glass (AR glass) Minibars® (Cem-Fil MiniBarsTM (ReforceTech, Inc.))and compare their cost effectiveness to basalt fiber Minibars® (ReforceTech, Inc) reinforcements. Samples were made by first synthesizing geopolymer, using lab-made, alkali-silicate solution high shear mixed with Metamax metakaolin clay. Then chamotte powder (Mulcoa M70 from Imerys Refractory Minerals USA, Inc.) was added as a thickener, and finally mixing in the minibars. We report Weibull statistics of compressive, flexural, SENB fracture, and shear strength of this composite and compare with other similarly reinforced geopolymers, in particular, basalt minibars. We include microscopic observations to elucidate failure mechanisms and compare the failure mechanisms to those of other analogous composites.

2:40 PM

(ICACC-S16-011-2019) Mechanical Properties of Flax and Hemp Felt Geopolymer Composites

P. F. Keane*[2]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, USA
2. Construction Engineering Research Laboratory (CERL), USA

Two types of felt samples were received from Fibres Recherche Developpment® in France, via Mr. Ralph Davidovits. Continuous, non-woven mats of flax and hemp of dimensions 3 m^2 wide and weighing 300 g/m^2 were received. The flax mat was 100% flax while the hemp was composed of 80% hemp and 20% polyester threads in the form of very fine, white threads. The organic polyester was not expected to react with the geopolymer. The hemp and fiber felt were dispersed in potassium metakaolin-based, geopolymer reinforced with 50 mm size, mullite particulate reinforcements in the form of chamotte. The low viscosity of the KGP liquid was able to penetrate the felt upon the application of some pressure. Upon curing at ambient temperatures, for each type of reinforcement, ten bend bars of dimensions 1′″ x 1″ x 6″ were broken in 3-point flexure, and the data was analyzed by Weibull statistics. The microstructure and microchemistry of the fracture surfaces were examined by SEM and EDS.

3:30 PM

(ICACC-S16-012-2019) The Effect of Fibers Inclusion on The Properties of Geopolymer Composites: An Experimental Overview (Invited)

M. Al-Mashhadani*[1]

1. Yildiz Technical University, Turkey

The worldwide increasing need for cementitious binders has raised the trend of greenhouse gases. The emissions co_2 which are resulted from cement production represent a serious issue. Geopolymers, as green alternatives, have been recently become the main field for many researchers due to the remarkable results that could be achieved in terms of sustainability, strength, and other properties. The geopolymeric matrix has been observed as a compact and a durable matrix which makes its application more convenient in places where special properties are required such as resistance to chemical attacks, resistance to elevated temperatures and high strength properties. Nevertheless, using fibers to enhance some of the properties of the fabricated geopolymeric matrix was noticed as a beneficial procedure, flexural properties, abrasion resistance, and drying shrinkage could be enhanced when fibers are included. In this investigation, fly ash and metakaolin based geopolymer composites were reinforced with fibers of various types and various contents. Abrasion resistance, flexural properties, drying shrinkage and tensile strength properties were investigated. In general, an acceptable percentage of improvement was observed for the fibrous samples.

Sustainable Materials

Room: Ponce de Leon
Session Chair: Ghassan Al-Chaar, U.S. Army Corps of Engineers

4:00 PM

(ICACC-S16-013-2019) Amazonian Lateritic Soil-Based Geopolymer Reinforced with Granite-Marble Particulates (Invited)

M. G. Sá Ribeiro[1]; M. G. Sá Ribeiro[2]; W. M. Kriven[3]; R. A. Sa Ribeiro*[1]

1. INPA-National Institute for Amazonian Research, LTEE-Structural Engineering Laboratory, Brazil
2. Architect and Urban Planner, Brazil
3. University of Illinois at Urbana-Champaign, USA

This is part of an ongoing research program on Amazonian geopolymer (GP) composites for use in sustainable construction. The Amazonian GP composites are intended to be an alternative to conventional cements and concretes. This project uses Amazonian orange metakaolin (MKAO) obtained from calcined Amazonian lateritic soil (orange kaolin - KAO) and granite-marble particulate (GMP) industrial residues. While fly ash-based GPs are now an established technology, metakaolin-based cements and concretes still need to be developed and optimized based on the knowledge of the specific characteristics and properties of local resources. As part of this preliminary research, KAO, MKAO and GMP were characterized by thermal graphics analysis (TGA), scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray fluorescence (XRF), and energy dispersive XRF (EDXRF). In addition, MKAO GP and MKAO-GMP GP were tested for water resistance and for compressive strength. XRD and EDXRF were used to investigate the microstructure of the composite materials. XRD confirmed the formation of geopolymer. The preliminary results indicate that MKAO and MKAO-GMP GPs could be used as sustainable construction materials.

4:30 PM

(ICACC-S16-014-2019) Geopolymer-based beads for adsorption purposes (Invited)

E. Papa*[1]; V. Medri[1]; E. Landi[1]

1. ISTEC-CNR, Italy

Adsorption is considered as one of the most easy and effective techniques for different aims and alternative and low cost adsorbents, obtained by simple processes, are always researched. Beads and spheres have lately received attention for their potential use as adsorbents, thanks to the good mobility, high packing density, ease of separation and reuse after regeneration. Therefore, geopolymer-based spheres were produced exploiting spherification processes in order to obtain millimeter-size porous beads useful for adsorption purposes. The processes were established on the formulation of different geopolymer slurries based on the mixing of metakaolin with a potassium alkaline activating solution, and making use of an injection-solidification method in different mediums, i.e. polyethylene glycol or liquid nitrogen, to produce the beads. Furthermore, geopolymer slurries were mixed with a solution of sodium alginate and then dropped off in a hot $CaCl_2$ solution to obtain beads by means of a ionotropic gelation. An hybridization of the material (inorganic+organic), able to improve the adsorption properties, was obtained. The production process parameters were deeply investigated and the most performing spheres were selected and characterized in term of morphology, macro- and microstructure, composition-stoichiometry, porosity distribution and specific surface area together with the adsorption properties towards, for example, organic dyes.

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Multi-functional Materials I

Room: Halifax A/B
Session Chairs: Aycan Yurtsever, Institut national de la recherche scientifique (INRS); Graziella Malandrino, Universita' degli Studi di Catania

8:30 AM

(ICACC-S17-022-2019) From Supercapacitors to Water Filtering and More with the Same Material: Multifunctional Titania by Inorganic Surface Modification (Invited)

M. Epifani*[1]

1. CNR-IMM, Italy

Titanium dioxide is not widely known in water purification or as a versatile supercapacitor. It is possible to activate TiO_2 nanocrystals toward such and other seemingly unrelated applications by suitable surface chemical modification with another oxide. Currently, development of this strategy is being pursued by solvothermal processing of anatase nanocrystals. The example featured in the present work will be the deposition of vanadium pentoxide layers. It is not the surface V_2O_5 explicating the new functionalities, but it is the result of synergistic cooperation between the two constituent oxides. Actually, the newly formed nanocrystals most probably feature surface-graded electronic properties that are responsible for the enhanced surface response. In this paper it will be shown, after short introduction about the synthesis approach, that the initially designed strategy is successful since surface modified TiO_2 nanocrystals are: powerful sensors of such reducing gases like acetone and ethanol; very efficient adsorbents of methylene blue and other contaminants; stable supercapacitors retaining both the advantages of pure V_2O_5 and pure TiO_2; selective blockers of visible light in electrochromic windows. The synthesis perspectives will be discussed, related to the possibility of setting-up a whole class of materials architectures.

9:00 AM

(ICACC-S17-023-2019) Formation of Nanostructured Titania Layers on Ceramic-Metal Composites and Their Photochemical Functions (Invited)

S. Shi[1]; T. Goto[1]; S. Chou[1]; S. Lee[2]; T. Sekino*[1]

1. Osaka University, The Institute of Scientific and Industrial Research, Japan
2. Sun Moon University, Department of Environmental and Bio-Chemical Engineering, Republic of Korea

Nanostructured oxides exhibit significant photochemical and photelectrochemical performance due to synergy of their semiconductive properties and nanostructures. In this study, nanostructured titania was created on the ceramic-based composites. The composites consisted of alumina (Al_2O_3) matrix and fine titanium (Ti) dispersion were fabricated by controlled powder-metallurgical and hot-press sintering methods. Obtained materials exhibited enhanced mechanical properties with good electrical conductivity due to the percolation of dispersed Ti particles above 15 vol% in Al_2O_3. The composites were subjected to heat treated at elevated temperature. It was confirmed the nanostructured titania (TiO_2) such as nanorods were formed. On the other hand, when the pristine Al_2O_3/Ti composites were chemically modified in alkaline solution, nano-porous titanate network layers were successfully be formed on the composite surface. Further heat-treatment converted the nano-porous titania to the nanoparticles and nanorods on the composites. These surface nanostructured titania exhibited photocatalytic properties. Because the base ceramic-based composites have balanced mechanical and electrical properties, formation of nanostructured oxides on the surface is considered to add further multifunctions as for photocatalytic, electrochemical and photoelectrical applications.

9:30 AM

(ICACC-S17-024-2019) Superhydrophilic TiO_2 thin films produced by atmospheric plasma dielectric barrier discharge (Invited)

Z. Matouk[1]; B. Torriss[1]; R. Rincon[1]; M. Chaker*[1]

1. INRS, Energie materiaux télécommunications, Canada

The synthesis of TiO_2 thin films made by injecting an aerosol suspension of nanocolloidal suspension of TiO_2 (size of about 20 nm) in isopropanol (IPA) into a dielectric barrier discharge generated in N_2/N_2O at atmospheric pressure (AP-DBD) was investigated. The technology based on AP-DBD is industrially relevant due to its capability of performing low-temperature treatment on large surfaces. On the other hand, TiO_2 thin films show a major interest for many applications including photocatalysis, devices for energy production and storage, and more recently self-cleaning. In this work, the focus is put on the influence of the voltage (3-8 kV) applied to the AP-DBD operated at 4 kHz on the wettability of the as-deposited TiO_2 thin films. The TiO_2 films exhibit a significant change in their wetting property contact angle (WCA) when the voltage is increased. Indeed, the WCA drastically reduces from 70° for the reference TiO_2 powder (without plasma) to 5° for the 8 kV plasma deposited films. It is demonstrated that the hydrophilicity of the TiO_2 films mainly depends on surface roughness and/or chemical composition. Scanning electron microscopy (SEM) measurements indicate that the roughness increases with the voltage. In addition, XPS measurements show an increase of the hydroxyl group (-OH) density at the surface, which contributes to the better hydrophilicity of the films.

10:20 AM

(ICACC-S17-025-2019) Carbonaceous materials as enhancers of functional performances in nanostructured metal oxides: A critical overview (Invited)

I. Concina*[1]

1. Luleå Tekniska Universitet, Sweden

The use of carbonaceous materials, like graphene and its derivatives and carbon nanotubes, as enhancers of functional performances for nanostructured semiconducting metal oxides (MOx), has received a significant attention over the past ten years. These hybrid composites have found application in several fields, spanning from catalysis, to solar energy converting devices and photoelectrochemical water splitting. Researchers claim that improved performances in terms of electrical transport and catalytic activity can be obtained by the dispersion of carbonaceous materials in MOx such as TiO_2, ZnO and SnO_2. It is also claimed that the presence of these materials during the synthesis of nanostructured MOx has the potential to address the final aspect ratio of the nanostructures, thus also affecting their main functional features (including light management, electrical transport and number and nature of surface catalytic sites). This lecture presents a critical overview of the functional performances of these hybrid materials, including experimental results posing doubts on the real effects exerted by carbonaceous material, aimed at deepening the discussion in the field and investigating the potential offered by this multi-material approach.

10:50 AM

(ICACC-S17-026-2019) Rare Earth Doped Nanoparticles With Controlled Architectures (Invited)

F. Vetrone*[1]

1. Institut National de la Recherche Scientifique, Université du Québec, Centre Énergie, Matériaux et Télécommunications, Canada

Rare earth doped nanoparticles (RENPs) possess fascinating optical properties due to the multitude of long lived 4f electronic energy states. As a result, they can be excited as well as emit light at wavelengths spanning the UV to the near-infrared. Over the last few years advancements in our understanding of the synthetic techniques has allowed for the development of RENPs with architectures that permit for precise and selective doping of the rare earth ions in different components of the architecture. Such controlled doping has resulted the unprecedented ability to manipulate the optical properties of the RENPs potentially charting a course leading to new applications in diverse fields such as energy, environment and health. Here, we will give an overview of RENPs as well as present a perspective on the role of the nanoarchitecture on their optical properties and subsequently in different applications.

11:20 AM

(ICACC-S17-027-2019) Carbon-based composite materials with applications in Supercapacitors, Fuel Cells and Batteries (Invited)

D. Chua*[1]

1. National University of Singapore, Materials Science & Engineering, Singapore

Carbon materials have attracted much attention due to their unique properties, ranging from low dimensional effects, good structural integrity, high electrical and thermal conductivity, and chemical stability. Increasingly, carbon-based materials have progressed from thin films to the nanoscale dimensioned carbon nanotubes and graphene. In this aspect, one area of interest lies in whether carbon is useful as a catalyst support with direct applications in clean energy, specifically supercapacitors. In this talk, we will extend the design and engineering of various 1D and 2D carbon-based materials and apply it to other applications such as fuel cells and batteries. We will further show and compare the fuel cell properties when other 2D materials are integrated with the carbon-based materials as catalyst support. A series of in-situ tests are also performed which includes accelerated degradation test and electrochemical impedance spectroscopy to validate the effectiveness and robustness of these materials. We will mention briefly other applications for these carbon based materials.

11:50 AM

(ICACC-S17-028-2019) Performance Enhancement of Lithium Ion Battery with Magnetically Aligned Graphene Electrode

F. Lin*[1]; G. Yang[2]; H. Fang[3]; Z. Wang[1]; J. Bao[2]

1. University of Electronic Science and Technology of China, Institute of Fundamental and Frontier Sciences, China
2. University of Houston, USA
3. Sam Houston State University, USA

Improving the specific capacity of conventional graphite anodes of Li-ion battery remains the key challenge for large-scale applications. Graphene nanoflakes with high crystallinity, small lateral size, and high electron mobility, have displayed promising performance as anode material. Orientation control and alignment of graphene flake have been achieved with a weak magnetic field. In this work, we aligned graphene flakes vertically and horizontally using small commercial magnets. Non-aligned graphene and graphite electrode were also prepared. The electrochemical performance of various graphene/graphite electordes were investigated as anode in a full battery.

Multi-functional Materials II

Room: Halifax A/B

Session Chairs: Isabella Concina, CNR-IDASC SENSOR Laboratory & Brescia University; Fiorenzo Vetrone, Institut National de la Recherche Scientifique, Université du Québec

1:30 PM

(ICACC-S17-029-2019) On the Influence of Elemental Composition on the Optical and Mechanical Properties of SiC_xN_y Thin Films (Invited)

Z. Khatami[1]; P. Mascher*[1]

1. McMaster University, Engineering Physics and CEDT, Canada

In order for Si-based materials to be used in silicon photonics schemes it is necessary to have good control of the optical emission from these materials. This can be accomplished through careful design of the composition of multi-element thin film structures. After a brief review of the latest developments in the field, this talk will focus on the luminescence of undoped silicon nitrides, and carbides. Silicon carbonitrides (SiC_xN_y) in particular, have attracted interest for the manufacturing of materials with robust mechanical properties and promising optical features, suitable for applications in high-performance optoelectronics and harsh environments. This is a consequence of their unique properties inherited from the combined properties of binary substructures, silicon carbide (SiC), silicon nitride (SiN), and carbonitride (CN). We will show that the visible photoluminescence emission from SiC_xN_y films fabricated by plasma enhanced chemical vapour deposition (PECVD) is stronger than that of SiC and SiN materials and that the optical properties (band gap, transmittance, index of refraction, and light emission) can be controlled by adjusting the process parameters and the carbon content.

2:00 PM

(ICACC-S17-030-2019) Are solar-cell antiferromagnetic nickel oxide transparent electrodes antiferromagnetic? (Invited)

G. Fanchini*[1]

1. University of Western Ontario, Physics and Astronomy, Canada

Transparent conducting oxides (TCOs) are widely investigated due to their relevance in devices such as solar cells and flat panel displays. There is strong interest in NiO as a TCO because no heteroatoms are required to "dope" it at acceptable levels of transparency. A critical difference between NiO and commonly utilized TCOs is that ideal NiO crystals are antiferromagnetic. It has been speculated that vacancies compensated by Ni^{3+} or O^- centres are responsible for the electrical ctransport in otherwise insulating NiO, but data are limited to a few studies. Here we review the use of electron spin resonance (ESR) as a tool to gain insight into the intricate paramagnetism of nanostructured NiO electrodes. We identify two types of ESR-active centers in NiO, and, respectively, assign them to a) point defects, and b) to extended bulk states (above the Neel temperature, when NiO is paramagnetic) and to extended surface states (below the Neel temperature, when NiO is an antiferromagnet, but some ferromagnetic surfaces still exist). We observe a linear relationship between the electrical conductivity and intensity of signal A, which shows that electrical conductivity can be assigned to paramagnetic point defects in the NiO bulk, while surface states control the work function. Implications of such effects towards the use of NiO as a transparent electrode in thin-film solar cells are discussed.

2:30 PM

(ICACC-S17-031-2019) Upconversion and Downshifting: Lanthanide-based Optical Materials and their Potential Applications (Invited)

E. Hemmer*[1]

1. University of Ottawa, Chemistry and Biomolecular Sciences, Canada

Lanthanides are well known for their outstanding optical properties that are based on the electronic configuration of the trivalent lanthanide ions (Ln^{3+}), which is characterized by an incompletely filled 4f shell, located inside the complete $5s^2$ and $5p^6$ shells. Consequently, when doped in appropriate host materials, the influence of the host lattice on the optical transitions within the 4f configuration is small, and narrow optical absorption and emission bands as well as long lifetimes of the excited electronic states of the Ln^{3+} are obtained. Following a stepwise excitation with near-infrared (NIR, typically 980 nm) light, Ln^{3+}-doped nanostructures show upconversion (ultraviolet, visible and NIR light) emission. In addition, due to a downshifting process, NIR light of longer wavelengths (> 1000 nm) can be emitted under excitation with NIR light when appropriate Ln^{3+} dopants are chosen (e.g. Er^{3+} or Ho^{3+}). Alternatively, Ln^{3+} ions such as Eu^{3+}, Tb^{3+} or Dy^{3+} are suitable downshifting candidates leading to the emission of visible light under UV excitation. Based on their upconverting and downshifting properties, Ln^{3+}-doped materials and molecules have been suggested for a whole gamut of applications including the field of biomedicine, frequency conversion, and photocatalysis, a selection of which will be discussed in this presentation.

3:20 PM

(ICACC-S17-032-2019) 50 years of glass integrated optics (Invited)

G. C. Righini*[1]; S. Berneschi[2]; M. Ferrari[3]; G. Nunzi Conti[2]; S. Pelli[2]

1. Enrico Fermi Center, Italy
2. IFAC CNR, Italy
3. IFN CNR, Italy

The term integrated optics appeared for the first time in the seminal paper by S.E. Miller in 1968. Since then, a bunch of articles have been published: according to Clarivate Analytics Web of Science, almost 16,000 papers refer to integrated optic and glass topics. They covered developments in design, modeling, materials, fabrication technologies and devices, which have taken advantage of the concurrent development of micro- and nanophotonics. Focusing on the glass material, scientific breakthroughs happened, for instance, with IR-transmitting glasses, photoluminescent glasses, and glass ceramics. Improved or innovative characterization techniques have been developed. Several glass devices such as directional couplers, arrayed waveguide gratings (AWG), wavelength multiplexers, optical amplifiers and lasers are now commercial. A broad application range, varying from astronomy and microfluidics to telecommunications and sensing, makes glass integrated optics a mature and attractive technology. Compatibility with Si microfabrication techniques opens the prospect of further developments. A brief review of some among the most interesting achievements in this field will be presented.

3:50 PM

(ICACC-S17-033-2019) Laser-assisted anatase crystallization and micropatterning of amorphous TiO_2 films

J. A. Benavides*[1]

1. L'École de technologie supérieure, Génie électrique, Canada

We report on a route to controllably engineer laser-assited nanocrystalline films of anatase at room temperature. Based on sol-gel chemistry and surface defects our approach starts from an amorphous film to create a spatially-controlled anatase area, excelling in precision, reproducibility and control, avoiding costly high-temperature, ion metal-assisted or specific atmospheric processes that

undermine the integration of TiO2 in hybrid platforms. TiO2 is a material that possesses ubiquitous properties that are advantageous in several fields from water cleaning, production and transformation of energy and surfaces modification. From research to industrial applications, the ability to include thin layers of crystalline TiO2 without involving high temperature or additional chemical processes is a pivotal point to expand the market of this material. We test optical properties of the patterned film to confirm presence of anatase by Raman and laser scanning microscopy. The synthesis and thermodynamics involved in the process, also the factors underlying this laser-assisted and spatially-resolved transformation process were followed by TEM and AFM. We believe this level of control and the ability to engineer the TiO2 anatase at the microscopic scale will allow the design and fabrication of novel high-performance TiO2 devices for energy conversion and environmental applications.

4:10 PM

(ICACC-S17-034-2019) Novel W/WO_3/MoS_2 Electrode

J. Ting*[1]; B. Sie[1]

1. National Cheng Kung University, Materials Science and Engineering, Taiwan

In this study, tungsten filament was used as a cost-effective and flexible current collector. A dip-coating process followed by thermal oxidation was used to deposit WO_3 on the W. The effect of WO_3 precursor concentration on the characteristics of the resulting WO_3 was studied. Afterwards, MoS_2 was further grown on the WO_3 using a hydrothermal method to form WO_3/MoS_2. The effect of hydrothermal temperature and time on the characteristics of the formation of MoS_2 was studied. The obtained W/WO_3/MoS_2 nanocomposites were evaluated for use as an electrode in supercapacitor. The relationship between the material characteristics and the supercapacitor performance is addressed.

Poster Session B

Room: Ocean Center

5:00 PM

(ICACC-FS2-P068-2019) Using AE Energy and Frequency Analysis to Characterize Damage in SiC/SiC Minicomposites

A. J. Gorven*[1]; A. S. Almansour[2]; J. D. Kiser[2]

1. Boise State University, Mechanical Engineering, USA
2. NASA Glenn Research Center, Ceramic and Polymer Composites Branch, USA

Silicon carbide/silicon carbide (SiC/SiC) ceramic matrix minicomposites serve as an idealized model of a full-scale SiC/SiC ceramic matrix composite and provide a much more efficient means of obtaining damage evolution information by allowing for a robust experimental data set to be produced quickly. It is theorized that the sound waveforms emitted by damage events in ceramic matrix minicomposites will contain characteristic features that can be used to distinguish between various damage modes within the composite. In this work, acoustic emission (AE) damage monitoring and analysis were performed on both uncoated and EBC (environmental barrier coating) slurry-coated Hi-Nicalon Type S Fiber-reinforced chemically vapor infiltrated (CVI) SiC/SiC minicomposites that were tested to failure under room-temperature monotonic tensile loading. Analysis was performed in order to track damage energy, evolution and location. Additionally, frequency centroids were calculated from damage events' frequency spectra that were generated from near the ultimate composite failure surface in order to recognize specific patterns of event energies and frequencies. Minicomposite Characterization and frequency characterization results will be discussed.

(ICACC-FS4-P069-2019) High temperature shear tests on "RM-Wrap" joined C/SiC

P. Gianchandani*[1]; V. Casalegno[1]; M. Salvo[1]; M. Ferraris[1]; I. Dlouhý[2]

1. Politecnico di Torino, DISAT-Department of Applied Science and Technology, Italy
2. Institute of Physics of Materials CAS – Brno, Czech Republic, Czechia

A novel joining technique "RM-wrap" (RM = Mo, Nb, Ta) has been successfully applied to join C/SiC composites in this work. Optimized joining treatment consisted of heating to 1450 °C with heating rate of 1000 °C / hour followed by a dwell time of 5 minutes in a non-reactive environment of Argon flow. The joints were characterized by morphological analysis, microhardness and lap shear tests at room temperature 1000 °C. The joining material formed is in situ composite made of Si matrix reinforced by disilicides ($MoSi_2$, $NbSi_2$, $TaSi_2$). The joint morphology (interphase and interface) and elemental composition of the joining material were investigated in detail using FESEM and EDX which showed uniform, continuous and crack free joints. A test system with vacuum and/or inert gas atmosphere chamber (Zwick/Roell-Messphysik-Maytec) was used to measure the lap shear tests at room and elevated temperature.

(ICACC-S1-P070-2019) Microcantilever beam testing of single crystal silicon and diamond

H. Yamaguchi*[1]; J. Tatami[1]; M. Iijima[1]; T. Takahashi[2]; T. Yahagi[2]; H. Nakano[3]; T. Kondo[2]

1. Yokohama National University, Japan
2. Kanagawa Institute of Industrial Science and Technology, Japan
3. Toyohashi University of Technology, Japan

Micro electro mechanical systems (MEMS) are used in various fields, which are developed by semiconductor microfabrication technology using various materials including single crystal silicon and diamond. In order to ensure the mechanical reliability of the MEMS devices, the mechanical properties have to be evaluated in the same scale as the devices. In this study, the mechanical properties of single crystal silicon and diamond were evaluated using microcantilever beam specimens. The microcantilever beam specimens with various size were prepared on the surface of single crystal silicon and diamond by focused ion beam technique, followed by fracture test by loading using nano-indenter. In the initial stage of the stress-strain curve, the stress linearly increased with an increase in the strain. Young's modulus calculated from the slope of the stress-strain curve in this region was agreed with that obtained from ab initio calculation. When higher stress was applied, the relationship between stress and strain became nonlinear, which means that plastic deformation occurred in the bending test. Peierls stress calculated from the yield stress agreed with that estimated by the compression test. The smaller microcantilever beam specimens showed the higher bending strength. The bending strength of single crystal diamond showed much higher than that of single crystal silicon, which is similar value to the ideal strength.

(ICACC-S1-P071-2019) Solid Particle Erosion of Ceramic Matrix Composites

M. J. Presby*[1]; R. Panakarajupally[1]; G. N. Morscher[1]

1. University of Akron, Mechanical Engineering, USA

Damage due to the impingement of small, solid particles, termed erosion, is a common phenomenon observed in aero engine components. Erosion damage results in subsequent material loss leading to deteriorating effects of component properties and engine performance. As such, a key property for materials used in aero engines is resistance to solid erosive particles. While ceramic matrix composites (CMCs) are considered an enabling propulsion material system due to their high temperature capability and high strength-to-weight ratio little systematic work has been performed on the erosion of CMCs. Thus, the aim of the present study is to investigate and characterize the solid particle erosion behavior of gas-turbine grade CMCs at both ambient and elevated temperatures.

(ICACC-S1-P072-2019) International Standards for Properties and Performance of Advanced Ceramics – Thirty-three Years of High-Quality and Rigorous ASTM Standards

M. G. Jenkins*[1]; J. Salem[2]; G. D. Quinn[3]; J. Helfinstine[4]; S. T. Gonczy[5]

1. Bothell Engineering and Science Technologies, USA
2. NASA Glenn Research Center, USA
3. Consultant, USA
4. Consultant, USA
5. Gateway Materials Technology, USA

Mechanical and physical properties/performance of brittle bodies (e.g., advanced ceramics and glasses) are challenging to measure accurately and precisely unless the proper techniques are used. Now in its 33rd year of effort, ASTM Committee C28 on Advanced Ceramics, has developed numerous full-consensus standards (e.g., test methods, practices, guides, terminology) to measure various properties and performance of monolithic ceramics, composite ceramics and coatings that may be applicable to some glasses. These standards provide big and little picture details for determining many mechanical, physical, and thermal properties/performance, as well as characteristics for processing, thereby providing accurate, reliable, repeatable and complete data. Users, producers, researchers, designers, and academicians involved in ASTM Committee C28 write, update, and validate through round robin test programmes the over 50 standards under the jurisdiction of the Committee since its inception in 1986. This poster includes a pictogram of ASTM Committee C28 standards and how to obtain them as either individual copies or a complete collection of standards. Also included is a listing of other related ASTM committees. Finally, some examples of the tangible benefits of standards for advanced ceramics demonstrate their practical application are provided.

(ICACC-S1-P073-2019) Effect of Alkali-Silane Treatment on the Water Absorption of Kenaf Fibre Reinforced Polypropylene Composites

R. Paskaramoorthy*[1]; O. Asumani[1]

1. University of the Witwatersrand, Mechanical Engineering, South Africa

Due to the low density of natural fibres the specific properties of composites made using these fibres can match or even exceed those of glass fibre reinforced plastics. In spite of this, applications of natural fibre composites have been limited due to two primary challenges. The first one is the poor bonding between the kenaf fibre and the composite resin. Various surface modification techniques exist in the literature to address this problem. The second challenge is the excessive water abosrption in natural fibre composites. The present paper deals with the latter problem. Specifically, the effects of a combined alkali-silane treatment on the moisture absorption of kenaf fibre reinforced polypropylene composites are investigated. Composite plates fabricated by compression moulding using the film-stacking technique were subjected to long-term moisture diffusion tests. Untreated, alkali treated and alkali-silane treated kenaf fibres were considered. Scanning electron microscopy was used to analyse changes to the surface morphology of kenaf fibres caused by chemical treatments and moisture absorption. Results indicate that the alkali-silane treatment reduces the saturation water content in the composites by as much as 45%. This reduction was the consequence of improved interfacial adhesion between the fibre and matrix.

(ICACC-S1-P074-2019) Synthesis of zirconia toughened alumina fibers by sol-gel with centrifugal spinning

T. Natarajan*[1]

1. Indian Institute of Technology Bombay, Metallurgical Engineering and Materials Science, India

In the present work, we report the synthesis of zirconia toughened alumina by sol-gel with centrifugal spinning. Alumina-zirconia precursor sol (AZPS) was prepared, concentrated to achieve spinnable viscosity and spun in an in-house centrifugal spinning machine. Two approaches were tried to add grain growth controlling aid. In the first method, zirconia powder was added directly to alumina precursor sol to form composite sol. In the second method, zirconia precursor sol was prepared from nitrate source and added to alumina precursor to form composite sol. Results of the above studies indicated that uniform dispersion of the grain growth inhibitor (GGI) would be better achieved with use of precursor sol of the material. Average grain size (~ 4 μm) of monolithic alumina fibres got reduced to ~ 1.4 μm and the average zirconia size (for 5-20 wt. %) was in the range of 0.5 μm-0.7 μm. A20-3YSZ fibres heat treated to 1600°C for 24 hours did not show any exaggerated growth of grains.

(ICACC-S1-P075-2019) Woven Kevlar Fiber Composite based Personal Thermal Management with Cu-Ni Core-shell Nanowires

A. Hazarika[1]; B. K. Deka[1]; D. Kim[1]; Y. Park[1]; H. Park*[1]

1. Ulsan National Institute of Science and Technology, Republic of Korea

A woven Kevlar fiber (WKF)-based personal thermal management device was fabricated by directly growing vertical copper-nickel (Cu-Ni) nanowires (NWs) on the WKF surface using a hydrothermal method. The treated WKF was combined with reduced graphene oxide (rGO) dispersed in polydimethylsiloxane (PDMS) to form composites using vacuum-assisted resin transfer molding (VARTM). This WKF-based personal thermal management system contained a conductive network of metallic NWs and rGO that promoted effective Joule heating and reflected back the infrared (IR) radiation emitted by the human body. It thus behaved as a type of thermal insulation. The Cu-Ni NWs were synthesized with a tunable Ni layer on Cu core NWs to enhance the oxidation resistance of the Cu NWs. The combined effect of the NW networks and rGO enabled a surface temperature of 70°C to be attained on application of 1.5 V to the composites. The Cu_3Ni_1-WKF/PDMS provided 43% more thermal insulation and higher IR reflectance than bare WKF/PDMS. The absorbed impact energy and tensile strength was highest for the Cu_1Ni_3- and rGO-integrated WKF/PDMS samples. Those Cu-Ni NWs having higher Ni contents displayed better mechanical properties and those with higher Cu contents showed higher Joule heating performance and IR reflectivity at a given rGO loading. The composite shows sufficient breathability and very high durability.

(ICACC-S1-P076-2019) Rotational Flexural Strength Testing of Brittle Material Cylinders

A. Wereszczak*[1]; R. Wiles[1]; E. Steiner[2]; B. Kuwik[2]; O. Jadaan[3]

1. Oak Ridge National Lab, USA
2. Oak Ridge Associated Universities, USA
3. University of North Florida, USA

A disadvantage of conventional, static flexural strength testing of entire brittle-material cylinders and tubes is only a small fraction of their entire surface area and volume are subjected to the maximum uniaxial tensile stress. The likelihood is therefore low that the largest strength-limiting flaw on, or within, the cylinder or tube is located in the vicinity of that applied maximum tensile stress, and the resulting measured tensile failure stress could be misleadingly large. The prospect of concurrently subjecting cylinders or tubes to rotation while they are being uniaxially flexed increases the likelihood that the largest flaw limits the measured failure stress. Toward that, a fixture was developed that rotates a cylinder or tube while it is positioned within a universal test frame. Glass rods were subjected to uniaxial 3-pt-bending while being rotated, and their rotational flexural strength distribution is compared with that of their static 3-pt-flexural strength distribution. Effective area and effective volume are analytically determined and are examined in context to the difference of those two measured strength distributions. A description of the text fixture, the test method, the effective area and effective volume, and test results are presented. This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

(ICACC-S4-P077-2019) Indentation Response of Vitreous Silicates as a Function of Poisson's Ratio

A. Wereszczak*[1]; B. Kuwik[3]; E. Steiner[3]; B. Hackett[2]

1. Oak Ridge National Lab, USA
2. University of Tennessee, USA
3. Oak Ridge Associated Universities, USA

Spherical and pyramidal-based indentation responses were examined of several vitreous silicates that have Poisson's ratios ranging from 0.18 to 0.30. The testing was motivated by work where the influence of Poisson's ratio on densification and fracture toughness responses (Rouxelet al.) and on contact-damage-behavior (Wilantewicz) were examined. For those studies though, dissimilar inorganic glasses (e.g., bulk metallic, chalcogenides, etc.) tended to be used to cover their explored range of Poisson's ratio. For the present study, more similar crown and flint vitreous silicates were examined. Their elastic moduli and Poisson's ratios were measured using resonance ultrasound spectroscopy. They were then subjected to spherical indentation testing to estimate the apparent yield stress and Knoop and Vickers indentation to estimate hardness. The habit of the indentation-induced damage was examined using optical microscopy and scanning electron microscopy. A description of the vitreous silicates and the test methods are described, and the apparent yield stress and hardness results (and the qualitative nature of indentation-induced damage) as a function of Poisson's ratio are presented. This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

(ICACC-S1-P078-2019) Joining of oxide/oxide (Nextel™610/alumina-zirconia) ceramic composites to Ti_6Al_4V

M. Akram*[1]; V. Casalegno[1]; M. Ferraris[1]; G. Puchas[2]; W. Krenkel[2]

1. Politecnico di Torino, DISAT, Italy
2. University of Bayreuth, Ceramic Materials Engineering, Germany

Nextel™610/alumina-zirconia oxide fiber composites were successfully joined to Ti_6Al_4V by using a novel glass-ceramic. Dilatometry measurements were carried out to tailor the coefficient of thermal expansion while sintering and crystallization behaviours were investigated by hot stage microscopy and differential thermal analysis, respectively. Scanning electron microscopy (SEM) was used to investigate the joint interfaces while X-ray diffraction (XRD) was used to identify the formation of different phases in the glass-ceramic. Lap off-set shear tests were performed at room temperature to check the mechanical strength of the joints.

(ICACC-S1-P079-2019) Advantages of adding diamond to reaction bonded ceramics for wear

A. Marshall*[1]

1. M Cubed Technologies, Inc., USA

Herein, the advantages of adding diamond to reaction bonded ceramics are discussed with relation to wear properties. Typical reaction bonded ceramics do not perform as well as tungsten carbide with low percentages of cobalt. By adding diamond at various loadings, comparisons are drawn between the wear properties of tungsten carbide cobalt and reaction bonded ceramics with diamond. The ASTM B611 and ASTM G65 wear tests are utilized to compare these new reaction bonded ceramics. SEM of the wear scars are also examined to present the mechanism in which the varying materials are eroded. Diamond loadings up to 70% by volume are presented.

(ICACC-S1-P081-2019) Densification of $CaCO_3$-Li_2MoO_4 Nanoparticle Composites Using the Cold Sintering Process

D. L. Rennie*[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

Additions of lithium molybdenum oxide, Li_2MoO_4, were added to $CaCO_3$ using the cold sintering process (CSP) significantly enhancing the density, microstructure, and mechanical properties. Optimized properties of $CaCO_3$- Li_2MoO_4 were obtained from pressures of 350 MPa around 200°C eliminating the usual high temperatures and CO_2 emissions that are problematic from a sustainability perspective for brick fabrication. Theoretical densities of >90% were achieved at Li_2MoO_4 volume percent's above 20. Large surface-volume ratios were obtained through ball milling $CaCO_3$ with Li_2MoO_4 achieving grain size less than 1 μm. Further improvement of the densification process was realized when a precursor of < 2MAA was chosen.

(ICACC-S1-P082-2019) Novel fabrication of magnesium phosphate cements doped with graphene

N. Lu*[1]; G. He[1]; J. Li[1]; J. Li[1]

1. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, China

Magnesium phosphate cements (MPC) doped with graphene were fabricated by combustion synthesis and acid-base reaction. MgO/graphene mixture powders were obtained by the combustion reaction between Mg powders and CO_2 gas. The composite cements were prepared by mixing MgO/graphene mixture powders with potassium dihydrogen phosphate (KH_2PO_4) using borax as retarder. The effect of graphene content on mechanical and functional properties of the prepared MPC/graphene cements was investigated. The results show that this MPC/graphene cements mainly consisted of MgO and $KMgPO_4$ $6H_2O$. With incorporating small amount of graphene into MPC, the flexural strength, spectral absorptivity and electrical conductivity of the composite were improved. In virtue of short processing time and homogeneous distribution of graphene, the novel fabrication provides a new method for preparing graphene-cement based composites, which are expected to use in civil engineering for the rapid repair of roads.

(ICACC-S3-P083-2019) Sealing-glass for SOFCs: Properties and stability in relevant conditions

I. Ritucci*[1]; R. Kiebach[1]; H. L. Frandsen[1]

1. DTU, Energy, Denmark

Glass-ceramics are commonly used as seals in solid oxide fuel cells (SOFCs) due to their ability to provide gas tight joints between the different stack components and the versatility in terms of processing. The Ba-free glass presented here has a promising CTE of 12.8 x 10^{-6} K^{-1} matching the CTE of the remaining materials and its glass transition temperature is 630°C which is below the SOC working temperature. Several processing approaches have been tested in order to reach a good adherence of the material. Moreover, some components that normally interface the sealant in an SOFC stack were used in representative samples, which were sintered in order to evaluate the compatibility of those with the glass. The stability of the glass for 250 hours at 750°C was studied by means of scanning electron microscopy and energy dispersive X-ray spectroscopy to evaluate possible interactions between the glass and the interconnect over time. Moreover, the crystallization was evaluated after ageing (via X-ray diffraction) without large variations recorder between the amorphous and crystalline phases, and the CTE of the glass ceramic remained stable.

(ICACC-S5-P084-2019) Development of high strength boron nitride nanoplate-calcium hydroxyapatite (BNNP-HAp) composite by cold sintering

M. ul Hassan*[1]; H. Ryu[1]

1. Korea Advanced Institute of Science and Technology (KAIST), NQE-NFML, Republic of Korea

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) is a phosphate-based mineral with well-known biocompatibility and use in medical industry. The undesirable decomposition and grain growth at elevated temperatures hamper the desired strength and bioactivity. A number of different sintering techniques have been reported to enhance mechanical properties of sintered $Ca_{10}(PO_4)_6OH_2$ in pure

and composite form. However; control of grain growth and decomposition still remain a challenge. In this study, we have applied the cold sintering technique for sintering of synthesized dried composite of boron nitride nanoplate-calcium hydroxyapatite (BNNP-HAp). The sintering was carried out at 200 °C, 500 MPa uniaxial load, for 10 min of dwell time. The sintering was carried out under an air environment. The sintered composite was composed of nano-grains (10-20nm) with compressive strength > 150 MPa, Young's modulus of 65 GPa and a hardness value of 3.5 GPa measured by nanoindentation. The sintering parameters showed no effect on chemical composition of the starting material and carbonated substitutions remained intact. Further studies are being carried out to investigate the role of BNNP in improving the hardness during cold sintering and the biodegradation of the cold sintered nanocomposite.

(ICACC-S5-P085-2019) The Critical Role of Electrical Conductivity on the Animal Modeling of HA-$CaTiO_3$ Composite for Biomedical Application

P. K. Mallik*[1]; B. Basu[2]; K. Balani[3]

1. Indira Gandi Institute of Technology Sarang, Metallurgical and Materials Engineering, India
2. Indian Institute of Science, Materials Research Centre, India
3. Indian Institute of Technology, Materials Science and Engineering, India

In view of the fact that bone healing can be enhanced due to external electric field application, it is important to assess the influence of the implant conductivity on the bone regeneration in vivo. In order to address this issue, the present study reports the in vivo biocompatibility property of multistage spark plasma sintered Hydroxyapatite (HA)-80 wt. % calcium titanate ($CaTiO_3$) composites and monolithic HA, which have widely different conductivity property (14 orders of magnitude difference). The ability of bone regeneration was assessed by implantation in cylindrical femoral bone defects of rabbit animal model for varying time period of 1, 4, and 12 weeks. The overall assessment of the histology results suggests that the progressive healing of bone defects around HA-80 wt.% $CaTiO_3$ is associated with a better efficacy w.r.t early stage neobone formation, which is histomorphometrically around 140% higher than monolithic HA. Overall, the present study demonstrates that the in vivo biocompatibility property of HA-80 wt.% $CaTiO_3$ with respect to local effects after 12 weeks of implantation is not compromised both qualitatively and quantitatively and a comparison with control implant (HA) points towards the critical role of electrical conductivity on better early stage bone regeneration.

(ICACC-S5-P086-2019) Hybrid nanoplatforms for magnetic and photothermal therapy

C. Multari*[1]; M. Miola[1]; R. Gerbaldo[1]; F. Laviano[1]; G. Pezzotti[2]; D. Debellis[3]; E. Verné[1]

1. Politecnico di Torino, DISAT, Italy
2. Kyoto Institute of Technology, Japan
3. IIT, Electron Microscopy Facility, Italy

Nano-sized particles have been deeply studied as new therapeutic and diagnosis tool for cancer treatment. Particularly, hybrid nanoplatforms (HNPs), composed by superparamagnetic iron oxide nanoparticles and gold nanoparticles or silver nanoparticles, are of great interest because they possess magnetic, plasmonic and antibacterial properties. This work concerns the development of a reproducible and innovative synthesis method to obtain HNPs and their chemical, physical, magnetic and optical characterization to verify their morphology, composition, superparamagnetic and plasmonic behaviors. A cytotoxicity study is performed on healthy and cancer cells exposed to HNPs by using a laser source in order to evaluate the ability of plasmonic nanoparticles to convert absorbed light into thermal energy. Cell tests confirm that HNPs cause an important damage of cancer cells while is not resulting dangerous in normal cells. This indicate that the HNPs allow to convert the received light into thermal energy, which in turn destroy cancer cells due to their high heat sensitivity. These HNPs are a new approach to cancer therapy because they can easily reach the tumor site, they can be used as drug delivery system, contrast agent and contemporaneously as photosensitizer for photothermal therapy.

(ICACC-S5-P087-2019) Palygorskite Sheets Produced by Aqueous Tape Casting Process

W. Acchar*[1]; F. Anna Karla[2]; S. Pergher[2]

1. Federal University of Rio Grande do Norte, Physics, Brazil
2. Federal University of Rio Grande do Norte, Materials Engineering, Brazil

Nanocomposites form a new class of materials composed of polymers filled with particles. Palygorskite is a clay which has been used in the pharmaceutical industry. The antibiotic neomycin is an amino-glycoside effective against a broad spectrum of bacteria gram-negative and gram-positive, and is widely used in topical medications such as creams, eye drops, among others. Polyvinyl alcohol [PVA] is commonly used in biomedical devices because of its excellent biocompatibility and biodegradability properties. Nanocomposites sheets based on palygorskite and polyvinylalcohol were produced by the aqueous tape casting method with the objective of increasing the applicability of the palygorskite. The stability of the suspension was investigated and the tapes were characterized by thermal analysis (TGA and DTA), X-ray diffraction (XRD) and field emission scanning electron microscopy (SEM). The antimicrobial activity was analyzed in order to test the applicability of the use of palygorskite incorporating neomycin to a new modified drug release system. Preliminary results showed that the palygorskite film via the tape casting method may be considered promising for pharmaceutical applications.

(ICACC-S5-P088-2019) Fabrication and Performance of Nanofibrous Cell- and Growth Factor-incorporated Tissue Engineering Scaffolds

L. Guo[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Nanofibrous tissue engineering scaffolds have distinctive advantages for regenerating human body tissues and electrospinning is a popular technique for making nanofibrous scaffolds. To overcome limitations of electronspun scaffolds, live cells should be incorporated in the scaffolds. Growth factors can also be encapsulated in scaffolds and their controlled release will enhance tissue regeneration. Thus we have developed versatile concurrent electrospinning and co-axial electrospray technologies for making cell- and growth factor-incorporated nanofibrous scaffolds. In this work, for technology demonstration and for gastrointestinal tract regeneration application, rat gastric smooth muscle cells (rGSMCs) and basic fibroblast growth factor (bFGF) were used to produce scaffolds for the targeted application. bFGF encapsulation was achieved through emulsion electrospinning; and rGSMCs were contained in core-shell structured hydrogel microspheres which were made by co-axial electrospray and placed randomly in nanofibrous bFGF-encapsulated scaffolds. Through in vitro biological studies, it was shown that rGSMCs were released from microspheres into scaffolds and had high viability and that bFGF was also released from scaffolds in a controlled manner. The released bFGF could enhance the proliferation and cytoskeleton development of the released rGSMCs inside the scaffolds.

(ICACC-S6-P089-2019) Preparation and Characterization of Cation-Substituted Na_3SbS_4 Electrolyte with Na^+ Ion Conductivity

N. Masuzawa*[1]; S. Yubuchi[1]; A. Sakuda[1]; A. Hayashi[1]; M. Tatsumisago[1]

1. Osaka Prefecture University, Applied Chemistry, Japan

All-solid-state batteries are attracting attention in a safety viewpoint because they use inorganic solid electrolytes instead of conventional organic liquid electrolytes. Among them, all-solid sodium ion batteries are expected as post lithium ion batteries due to abundant resources and low cost. We have developed cubic Na_3PS_4 electrolyte

with the conductivity of over 10^{-4} S cm^{-1} at 25ºC, and it has a favorable ductility, which is effective in making a good solid-solid contact with electrode active materials. Recently, Na_3SbS_4 with a higher conductivity of over 10^{-3} S cm^{-1} has been reported. To increase conductivity of Na_3SbS_4, partial substitution of alternative cations for Sb in Na_3SbS_4 has been done in this study. Cation-substituted Na_3SbS_4 was prepared via mechanochemistry, followed by heat-treatment to enhance their crystallinity. For example, $Na_{3+x}Sb_{1-x}Si_xS_4$, in which a part of Sb was replaced by Si, was prepared and their conductivities as a function of the Si content were evaluated. The substitution of a small amount of Si decreased the conductivity. Furthermore, a similar result was obtained by substituting Sn for Sb in Na_3SbS_4. It is suggested that the increase in the number of Na^+ ions was not effective for increasing the conductivity of Na_3SbS_4.

(ICACC-S6-P090-2019) Effect of annealing temperature on the phase transition and thermoelectric properties of Cu_2SnSe_3

M. Siyar[1]; J. Cho*[1]; W. Jin[1]; Y. Youn[1]; S. Han[1]; J. Kim[2]; C. Park[1]

1. Seoul National University, Materials Science And Engineering, Republic of Korea
2. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea

The effect of annealing temperature on the phase transition of Cu_2SnSe_3 was investigated in order to study the thermoelectric (TE) properties of the various Cu_2SnSe_3 phases. Rietveld refinement was used to calculate the amount of monoclinic and cubic phases for each sample. XRD analyses reveal that the samples annealed at 720 and 820 K have mostly monoclinic phase along with small amount of cubic phase. The Cu_2SnSe_3 annealed at 960 K was mostly cubic. TE properties of the cubic phase Cu_2SnSe_3 was studied for the first time, and it was found that it has much higher ZT (~0.09) than the monoclinic phase at 600 K. Better TE performance of the cubic phase can be attributed to the smaller band gap (~0.92 eV) compared to that of monoclinic Cu_2SnSe_3 (~1.0 eV) at room temperature. First principle calculations further confirmed the conductive metallic nature of the cubic phase Cu_2SnSe_3. Small polymorphic modification with increasing annealing temperature results in compositionally similar but different crystallographic phases, which is one of the possible reasons for nearly similar thermal conductivities of the two phases. The electrical conductivity of the cubic phase which is larger than that of the monoclinic phase and similar thermal conductivities of the two phases lead to the better thermoelectric performance (ZT) of the cubic Cu_2SnSe_3

(ICACC-S6-P091-2019) Mechanochemical synthesis of Na-Sb alloy negative electrode for all-solid-state sodium batteries with Na_3PS_4 glass-ceramic electrolyte

T. Ando*[1]; S. Yubuchi[1]; A. Sakuda[1]; A. Hayashi[1]; M. Tatsumisago[1]

1. Osaka Prefecture University, Applyed Chemistry, Japan

All-solid-state sodium batteries have been expected as post lithium-ion batteries with high safety and low cost. Negative electrode materials for the all-solid-state batteries have not been much studied so far. Although sodium metal has the lowest electrochemical potential in the sodium system, there is the risk of short circuiting because of the sodium dendrite growth. Thus, development of novel negative electrode materials with higher safety has been required. Here we have focused on antimony alloy negative electrodes that have high reversible capacities. These materials also have relatively high operating voltages, and thus it is expected to suppress decomposition of the solid electrolyte at a lower voltage. In this study, Na-Sb alloy was synthesized by a mechanochemical technique. The composite electrodes prepared by hand-grinding the Na-Sb active material and the Na_3PS_4 solid electrolyte showed the ionic conductivity of 3.4×10^{-5} S cm^{-1} at 25ºC. An all-solid-state symmetric cell using the composite electrode with the Na-Sb alloy exhibited a good performance at room temperature. In addition, a cell using TiS_2 as a positive electrode was also fabricated. The cell showed a reversible capacity of 200 mAh (g of TiS_2)$^{-1}$ with 98% capacity retention and almost 100% coulombic efficiency for 50 cycles.

(ICACC-S6-P092-2019) Structure, sinterability and Ionic Conductivity of $Li_{6.25}Ga_{0.25}La_{3-x}Sr_xZr_2O_{12}$ with garnet-type structure

D. Mori*[1]; K. Sugimoto[1]; K. Ohmori[1]; Y. Matsuda[2]; S. Taminato[1]; Y. Takeda[1]; N. Imanishi[1]

1. Mie University, Department of Chemistry for Materials, Japan
2. Osaka Institute Technology, Department of Applied Chemistry, Japan

Garnet-type lithium ionic conductor $Li_{6.25}M_{0.25}La_3Zr_2O_{12}$(M = Al, Ga) is known to be stable to Li metal and exhibit relatively high ionic conductivity. In previous study, we demonstrated that $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$(LLZ-Ga) showed better sinterability and higher ionic conductivity. In this study, in order to further improve sinterability and ionic conductivity, Sr substitution for LLZ-Ga was examined. Li_2CO_3, Ga_2O_3, $La(OH)_3$, $ZrO_2$and $Sr(NO_3)_2$was used as starting materials. $Li_{6.25}Ga_{0.25}La_{3-x}Sr_xZr_2O_{12}$(LLZ-GaSr) was synthesized at 800-1000 °C and then quenched from above 400 °C to avoid the reaction with H_2O and CO_2. Phase identification was carried out by XRD measurements. The sinterability and composition were examined by SEM-EDX. The ionic conductivity was evaluated by AC impedance measurements. The XRD measurements confirmed that cubic and tetragonal garnet phase was formed in x = 0-0.2 and 0.3-0.5 in LLZ-GaSr, respectively. The lattice parameter aincreased linearly as Sr content increased up to x= 0.1. The sintered density of the sample in x≤ 0.2 attained above 90%. The sample in x= 0.1 exhibited lithium ionic conductivity of 1.3 x 10^{-3}Scm^{-1}at 25 °C. Sr substitution for LLZ-Ga was effective to enhance sinterability and lithium ionic conductivity.

(ICACC-S7-P093-2019) Si-Doped Titania Oxide Nanotubes for Photoelectochemical Water Splitting

Z. Dong[1]; D. Ding*[1]; T. Li[1]; C. Ning[2]

1. Shanghai Jiao Tong University, School of Materials Science and Engineering, China
2. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Photoelectrochemical (PEC) water splitting based on one-dimensional titanium dioxide (TiO_2) nanostructures provides an efficient way for hydrogen generation. Here we successfully fabricated Si-doped TiO_2 (Ti-Si-O) nanotube arrays through anodizing Ti-Si alloys with different Si content. The PEC water splitting properties of the Ti-Si-O nanotube arrays fabricated on Ti-5 wt.% Si alloy demonstrated higher PEC activity with a photocurrent density of 0.83 mA/cm^2 at 0 V vs. Ag/AgCl. The maximum photoconversion efficiency was 0.54%, which was 2.7 times that of the undoped TiO_2 nanotube arrays.

(ICACC-S7-P094-2019) Application of Al-doped MicNo®-Zinc Oxide Particles as Conductive Fillers in Polymer Matrix Composites

P. Sengun*[1]; M. Kesim[2]; M. Caglar[3]; U. Savaci[1]; S. Turan[1]; I. Sahin[1]; E. Suvaci[1]

1. Eskisehir Technical University, Material Science and Engineering, Turkey
2. Entekno Materials, Turkey
3. Eskisehir Technical University, Department of Physics, Turkey

Conductive fillers which are mostly used in conductive polymer composites (CPCs) materials to build up conductive path into the polymer matrix phase. CPCs are utilized for protecting sensitive electronic components by preventing electrostatic discharge events (ESD). Generally, carbon-based materials and metal nanoparticles used as conductive filler in CPCs. In addition, zinc oxide (ZnO) can be used for this purpose. Pure ZnO has relatively high electrical resistivity (≈10^4 ohm) and doping is one of the widely applied methods to enhance the electrical conductivity. To date Al doped ZnO nanoparticles have been used in CPCs as conductive fillers.

However, agglomeration of nano filler particles in polymer matrix is a critical problem which may lead to isolation of fillers. Therefore, there is a need for new alternative materials with better percolation behavior and low electrical resistivities. MicNo® particles which are platelet shaped micron particles, composed of strong chemically bonded nano-sized primary particles exhibit both micron and nano size characteristics. Accordingly, we developed micron sized platelets of Al-doped ZnO particles (MicNo®-AZO) that exhibits ≈40 KΩ. cm bulk resistivity and addition of 10 wt% MicNo®-AZO into epoxy resin reduces the resistivity from ≈ 6 MΩ.cm to ≈ 1,7 MΩ.cm. The results show that MicNo®-AZO are suitable for utilization in CPCs.

(ICACC-S7-P095-2019) Systematic evaluation of $Mn_xCo_{3-x}O_4$ spinels as oxygen evolution catalysts for alkaline electrolyzers

K. Cysewska[1]; S. Molin*[1]

1. Gdansk University of Technology, Laboratory of Functional Materials, Faculty of Electronics, Telecommunications and Informatics, Denmark

Alkaline electrolyzers are relatively simple devices to convert water into gaseous hydrogen and oxygen. Electrolyzer efficiency is limited by the oxygen evolution reaction (OER), thus new highly active materials are sought. Mn-Co spinels with a general formula $Mn_xCo_{3-x}O_4$ (with x typically in the range of 1 to 2) are very versatile materials that have been already tested in supercapacitors, alkaline electrolyzers and even high-temperature solid oxide fuel cells. The properties of these materials can be altered either by a change in composition (Mn:Co ratio) or by substitution with new element (e.g. Fe, Cu). In this work $MnCo_2O_4$, Mn_2CoO_4 and $Mn_{1.5}Co_{1.5}O_4$ spinels are evaluated as electrode materials in alkaline electrolyzer cells. Thin spinel layers are deposited on conductive glass substrates by low-temperature spray pyrolysis method. Fabricated films are subjected to different heat treatments (400 °C – 800 °C) which results in materials with different grain sizes (~10 nm to 2000 nm). Compositional and microstructural effects of the electrode materials are evaluated electrochemically. Acknowledgment: This project is supported by FirstTeam project "Nanocrystalline ceramic materials for efficient electrochemical energy conversion" funded by the Foundation for Polish Science.

(ICACC-S7-P096-2019) Investigation of Optical and Photochemical Properties of Designed Co and Fe-Doped ZnO (MicNo®CZO-MicNo®FZO) Particles

B. Alkan*[1]; O. S. Ates[3]; E. Suvaci[2]

1. Hitit University, Metallurgical and Materials Enginnering, Turkey
2. Eskisehir Technical University, Material Science and Engineering, Turkey
3. ENTEKNO Corp., Turkey

ZnO is a wide band gap semiconductor that has been extensively studied due to its intrinsic properties and suitable for uses in broad range applications including transparent conductive films, varistors, photodetectors, gas sensors, dye, cosmetic products and photocatalysis. Although photocatalysis is of great use for many applications such as water splitting, organic pollutant scavenging, photocatalysis is a serious disadvantage in the use of ZnO as UV filter. In order to achieve high surface coverage while maintaining transparent characteristics in the visible regime, our group with the sponsorship of Entekno Materials (www.enteknomaterials.com) recently developed designed micron-sized, hexagonal ZnO platelets (MicNo®-ZnO) which are composed of nano primary particles. In some applications, pure ZnO can be too photoreactive such that it can result in degradation of the matrix via free radical formation. Co and Fe doping into ZnO is widely utilized approach to tailor the photoreactivity. In this presentation, optical properties as well as photochemical reactivity of Co or Fe-doped MicNo®-ZnO particles as a function of Co and Fe-dopant concentration will be discussed in detail.

(ICACC-S7-P097-2019) Effect of polar and non-polar solvents on the production of Graphene by attrition milling

S. Mancillas*[1]; E. Lopez-Honorato[1]

1. Center of Investigation and Advanced Studies of the National Politechnical Institute, Ceramic Engineering, Mexico

One of the main challenges in the exploitation of graphene is its production in large volumes. One possibility is the production of graphene by attrition milling, due to its simplicity and scalability. In this work we study the effect of polar (acetone, methanol and ethanol) and non-polar (hexane, toluene and xylene) solvents on the production of graphene, without the use of any other additive. Average particle size changed between 33, 50 and 22 μm for methanol, ethanol and acetone, respectively, whereas 51, 56 and 51 μm were obtained for hexane, toluene and xylene, respectively. Smaller particle sizes were obtained with polar solvents, despite having a lower wettability. Scanning electron microscopy revealed that polar solvents showed a better delamination of graphite sheets resulting in the production of graphene, particularly for acetone and methanol. X-ray diffraction analysis revealed that polar solvents introduced a lower concentration of defects into graphene than non-polar solvents as observed by selected area electron diffraction patterns. Raman spectroscopy showed a symmetrical 2D band of the graphene produced suggesting the formation of a few layer graphene; corroborated by TEM. The effect of these solvents was attributed to the physical of chemical properties of solvents.

(ICACC-S7-P098-2019) Effect of Interface on dielectric and energy storage properties of $SrTiO_3/BiFeO_3$ thin film capcacitors

C. Diao[1]; H. Liu*[1]; H. Hao[1]; Z. Yao[1]; M. Cao[1]

1. Wuhan University of Technology, China

In recent years, dielectric capacitors have attracted much attention for energy storage applications owing to high power density and fast charging/discharging speed. But their applications are limited for low energy density. In this study, $SrTiO_3$(STO)/$BiFeO_3$(BFO) hetrostructures were designed to improve the energy density and the effect of interface was investigated. The simple trilayered STO/BFO/STO thin film is marked as STO/BFO and the sample with more STO/BFO interfaces is labeled as STO/BFO*. The thickness of total STO layer and total BFO layer in STO/BFO* film is the same with that of STO/BFO film. The two samples show excellent frequency stability of dielectric constant within the measured frequency, while STO/BFO* film has higher dielectric constant which is probably attributed to the space charge between STO/BFO interface since the electrical properties of STO and BFO are different. The recoverable energy storage density of STO/BFO* thin film is much higher than that of STO/BFO thin film, which is probably due to that the STO/BFO interface inhibits the electrical tree and enhances the breakdown strength. Furthermore, The STO/BFO thin films were deposited on Pt and $LaNiO_3$ substrates, respectively. The energy density of both films is similar. In this system, interface is beneficial for energy storage and $LaNiO_3$ can be used as a cost-effective bottom material.

(ICACC-S7-P099-2019) Ionic conduction based ideal room-temperature gas sensors using highly porous SnO_2 nanorods

C. Kang*[1]; Y. Song[1]; S. Yi[1]; G. Kim[1]

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea

Over the past decade, there are various approaches to enhance the sensing performance at room-temperature using metal additives or heterojunctions and two-dimensional materials. Despite these extensive efforts, there remain challenging including poor response and incomplete recovery because electronic conduction based sensing mechanism is limited by insufficient reaction energy between the analytical molecule and sensing material at room-temperature. Herein, we suggest a new strategy for a room temperature gas sensor

using the ionic conduction based gas sensing mechanism. Glancing angle deposition (GLAD) method was used to fabricate highly porous SnO_2 nanorods. The ionic conduction induced by humidity was confirmed using impedance spectroscopy, I-V characteristic and XPS analysis. The relation between the sensing properties and relative humidity was systematically investigated. Our experimental results show that the response of SnO_2 nanorods to 5 ppm NO_2 has a maximum response over 1400 at RH 20%. Also, it is observed that the response rate and recovery rate are accelerated as relative humidity increases. The gas sensing mechanism can be demonstrated based on the principle of the ionic conduction, humidity sensor, and water splitting. We believe that the ionic conduction based SnO_2 nanorods open a new direction for developing the room temperature gas sensor.

(ICACC-S7-P100-2019) Spectrally matched ceramic nanoparticles as X-Ray fluorescence bioimaging contrast agent

Y. Li*[1]; V. Carmen[1]; K. S. Doodran[1]; J. Larsson[1]; H. Hertz[1]; M. S. Toprak[1]

1. KTH Royal Institute of Technology, Dept. of Applied Physics, Sweden

Nanoparticles (NPs) have been used as contrast agents for in-vivo bio-imaging, including MRI, near-IR fluorescence and CT techniques. Present macroscopic biomedical imaging methods provide either morphology with high spatial resolution (e.g., CT) or functional information with lower resolution (e.g., PET). X-ray fluorescence (XRF) can provide sensitive and quantitative detection of NPs. Up to now XRF using metal NPs (e.g. Au) as contrast agents showed low sensitivity and low spatial resolution, despite long exposure times and high dose. With spectrally matched molybdenum oxide NPs as contrast agents we demonstrated earlier in a laboratory XRF system that XRF tomography could achieve 200 μm spatial resolutions in mice, exceeding the spatial resolution of other imaging techniques. Here we present on the synthesis, characterization and evaluation of a series/library of ceramic NPs that are spectrally matched to the X-ray laboratory source. Their potential as XRF contrast agents is demonstrated successfully in small animal-sized phantoms confirming the theoretical modeling results.

(ICACC-S7-P101-2019) Effect of Substrate on Dy^{3+}-doped Strontium Molybdate Thin Film Luminescent Properties

R. Mazin Latini[1]; A. d. Marques*[1]

1. Federal University of Sao Paulo, Brazil

To produce light in LED devices, materials denominated phosphors are added to their design, which absorb the energy provided by the LED chip and converts it into a specific color. Molybdates, a class of $AMoO_4$ materials with scheelite-type tetragonal structure, are interesting for phosphor applications, and doping with rare earth ions can modify the emitted color. Dy^{3+}-doped strontium molybdate thin films were produced by the Complex Polymerization Method with posterior spin-coating on silicon and quartz substrates. XRD spectra showed the formation of a single scheelite phase. Raman spectra presents the characteristic active vibrational modes, corresponding to vibrations within the $[MoO_4]^{-2}$ group and Sr^{2+}/Dy^{3+} cations. PL spectra shows emission in the yellow region of the spectrum, with highest emission around 575 nm. Through UV-Vis reflectivity spectra, band gap was estimated for all samples, in a range of 4.07-4.30 eV. Further investigations include the optimization of preparation conditions for a higher yellow emission, SEM and AFM for textural and surface properties. Results demonstrated CPM was successful in the production of molybdates and yellow emission was achieved through dysprosium doping.

(ICACC-S8-P102-2019) In-situ observation of dewaxing process of ceramic powder compacts by optical coherence tomography

M. Kato*[1]; J. Tatami[1]; T. Takahashi[2]; M. Iijima[1]

1. Yokohama National University, Japan
2. Kanagawa Institute of Industrial Science and Technology, Japan

Internal structure of ceramics controls their properties and they changes during the fabrication process. In the dewaxing process, added organic compounds are decomposed and/or oxidized, resulting in deformation or failure of the powder compact in some cases. Therefore, observation of the internal structure is important to understand and control the development of the ceramic internal structure. Optical Coherence Tomography (OCT) is a new technique to observe inside of opaque substance based on the interference of light. In this study, the observation of the internal structure of the powder compact during dewaxing process was carried out by OCT. Al_2O_3 powder compacts were prepared using various kinds and quantity of binders. They were set into the furnace of infrared collect heating furnace. The sample was heated up to 600^{O}C in 1.0L/min air flow. The internal structure of the powder compact was observed from outside of the furnace using OCT. The weight of the powder compact was also measured with heating. As a result, internal structure was clearly observed in spite of the elevated temperatures. The internal structure gradually changed to be inhomogeneous with the decrease in the weight because of melting, evaporation and decomposition of the added binder. It was also shown that the change in the internal structure depended on the amount and kinds of the added binder.

(ICACC-S8-P103-2019) Enhancement of rare earth elements dissolution from weathered residual rare earth ore by mechanochemical activation and construction of new kinetic model

T. Kato*[1]; G. Granata[2]; Y. Tsunazawa[3]; C. Tokoro[2]

1. Waseda University, Graduate School of Creative Science and Engineering, Japan
2. Waseda University, Faculty of Science and Engineering, Japan
3. National Institute of Advanced Industrial Science and Technology, Japan

The weathered residual rare earth ore obtained from Republic of South Africa exhibits higher concentrations of heavy rare earth elements and lower concentration of thorium compared to other rare earth ores. Although this ore is widely distributed in the areas, it is not exploted as a source of rare earth elements due to the lack of an economical processing technology. If a suitable technology was developed, this ore could become a new supply source for rare earth elements. The objective of this study is to enhance rare earth elements dissolution and construct new kinetic model. To achive this purpose, ore was ground by planetary ball mill with and without solid sodium hydroxide. The rare earth elements targeted in this study were cerium and yttrium since they exhibited the highest concentrations among the rare earth elements. In the case of planetary ball milling without solid sodium hydrixide, only cerium dissolution was enhanced. On the other hand, in the case of planetary ball milling with solid sodium hydroxide, both cerium and yttrium dissolution were enhanced. XAFS anlaysis revealed a portion of tetravalent cerium reduced to trivalent cerium. Adding solid sodium hydroxide resulted in the partial conversion of yttrium phosphate to yttrium hydroxide. Based on experimental results, new kinetic model was constructed.

(ICACC-S8-P104-2019) Study of Mechanochemical Activation of Copper Minerals by Experiments and DEM Simulations

M. Minagawa*[1]; T. Kato[1]; G. Granata[2]; C. Tokoro[2]

1. Waseda University, Graduate School of Creative Science and Engineering, Japan
2. Waseda University, Faculty of Science and Engineering, Japan

Mechanochemical activation was reported as an efficient method to enhance Cu leaching from refractory sulfide minerals. However, further research is still required to identify the activation mechanism. This work elucidated the influence of different physical and chemical phenomena on the mechanochemical activation of refractory Cu sulfide minerals. Grinding experiments were performed by planetary ball milling under different grinding conditions. Discrete element method simulations were performed to calculate the collision energy from grinding experiments. Leaching experiments were carried out to assess rate parameters. Intensifying grinding conditions resulted into a progressive amorphization of Cu minerals, larger surface areas and larger collision energies. Leaching results suggested the occurrence of two dissolution reactions, one fast and one slow, contributing to the total Cu dissolution. The correlation between rate constants and collision energies revealed a progressive increase of the slow reaction rate with collision energy. This phenomenon was regarded as physical activation due to generation of surface area. In contrast, the rate constant of the fast reaction increased only beyond a threshold value of collision energy. This phenomenon was considered as mechanochemical reaction. The threshold energy was defined as mechanochemical reaction activation energy.

(ICACC-S8-P105-2019) Investigation of the HPGR Effect on Copper Liberation by Using DEM with Breakage Model

Y. Nagata*[4]; Y. Sawamura[4]; M. Minagawa[4]; G. Granata[5]; K. Tsukada[1]; Y. Yaguchi[2]; Y. Ebisu[3]; K. Mitsuhashi[3]; C. Tokoro[5]

1. Furukawa Industrial Machinery Systems Co. Ltd., Design Department Industrial Machinery Section, Japan
2. Furukawa Co., Ltd., Technology Division, Japan
3. Nittetsu Mining Co., Ltd., Research & Development Department, Japan
4. Waseda University, Graduate School of Creative Science and Engineering, Japan
5. Waseda University, Faculty of Science and Engineering, Japan

High Pressure Grinding Roll (HPGR) is a promising grinding method to enhance the mineral liberation from ores with high energy efficiency. Since the effectiveness of HPGR depends upon the specific sample, grinding conditions must be optimized through experiments. However, because the amount of sample required to run HPGR tests is very high, it is not always possible to perform an exhaustive experimental HPGR campaign. Discrete Element Method (DEM) simulations are a powerful tool to analyze the behavior of particles without experiments. In this work, DEM simulations were coupled with T10 breakage model to estimate the effect of HPGR on copper liberation from a copper ore. The parameters of the T10 model were initially determined by performing laboratory piston tests on two types of copper ores. Following this step, DEM simulations were performed changing four operating variables: pressing force per mm^2, roll rotational speed, initial roll gap and height of the feed. The resulting contact force within the HPGR was then calculated and correlated to the experimentally observed copper liberation. Results revealed a good correlation between contact force and copper liberation. Results also highlighted that increasing the applied force up to an optimal value determined an increase of copper liberation. Increasing further the applied force produced a decrease of copper liberation.

(ICACC-S8-P106-2019) Suppression of Cracking in Metakaoline Potassium Based Geopolymer and its Hardness

D. T. Le*[1]; I. Kudo[2]; T. Nakayama[1]; K. Niihara[1]; H. Suematsu[1]

1. Nagaoka University of Technology, Extreme Energy - Density Institute, Japan
2. ADVAN ENG. Co., Ltd., Japan

In Fukushima Daiichi Nuclear Power Station, after the waste treatment process, the secondary waste is generated and stored in a used cesium absorption tower. These secondary wastes generate hydrogen and may cause a hydrogen explosion. Therefore, hydrogen recombination catalyst has been required to prevent this accident and meet the requirement such as mass production, inexpensive and chemical stability to store in the long time period. Dense geopolymer as a hydrogen combination catalyst carrier has been developed because of its advantages such as high strength owing to compactness, high yield ratio, no clopping with water. In this report, we aim to suppress the crack in metakaoline potassium based geopolymer. In order to reduce the crack-induced in geopolymer samples, the changing the molar ratio and synthesis condition were carried out. Powders of metakaoline and microsilica were mixed and dissolved in a K_2SiO_3 and KOH solution. This slurry has the molar ratio of Si/Al, K/Al, and H_2O/K being 3-2, 2-1 and 12-8. Finally, the solution was poured into a mold sealed with a cap and dried at R.T. – 70^0C for 7 days. The sample cracking was suppressed by decreasing the water content and capping the mold. However, the Vickers hardness was decreased with decreasing the water content. The best synthesis conditions were of Si/Al=2, K/Al=1, and H_2O/K=8, curing at 40^0C for 2 days, with capping in 5 days.

(ICACC-S8-P107-2019) Residual stress free joining of liquid-phase sintered SiC ceramics using a SiC tape

Y. Kim*[1]; Y. Kim[1]

1. University of Seoul, Department of Materials Sceince & Engineering, Republic of Korea

This work reports the joining of liquid-phase sintered SiC ceramics using a thin SiC tape with the same composition with SiC base material. The base SiC ceramics was fabricated by hot pressing submicron SiC powders with Al_2O_3-Y_2O_3-MgO additives. The base SiC ceramics were joined by hot pressing at 1800-1900°C under a pressure of 10 or 20 MPa in an argon atmosphere. Flexural strength of the joined SiC ceramics, which was joined at 1850°C under 20 MPa, were 343 ± 53 MPa, which was higher than that of base SiC material (289 ± 53 MPa). All specimens were fractured at the base material rather than the joining interface. The joined SiC ceramics showed no residual stress built up near joining layer, which was evidenced by indentation cracks with almost same lengths in four directions, which were generated by a Vickers indentation on a joint.

(ICACC-S8-P108-2019) Ceramic Carbide powders: Specialized development for sintering applications

T. Schmidt*[1]; S. E. Vogel[2]

1. H.C. Starck Surface Technology and Ceramic Powders GmbH, Applied Technology, Germany
2. North American Höganäs LLC, Sales, USA

Due to unique properties metal carbides have found place in many technical applications and became high tech materials of industrial importance. They are known for hardness and show high resistance against chemical attack. Tungsten-based cemented carbides (hardmetals) are preferred in tooling and machining, wherein transition metal carbides serve as additive in complex formulations to improve certain desired properties. An increasing request for purer and finer qualities demands for continuous process improvement to ensure the best lot to lot consistency. Today's powder manufacturers face a multitude of challenges to satisfy customers' requirements for higher quality. H.C. Starck STC – Germany, now part of the Höganäs group, is a renowned producer of non-oxide ceramic powders, among them

many special carbides like TiC, VC, ZrC, Cr3C2, Mo2C, etc. which are added to cemented carbides. They increase hardness or heat resistance (TiC) or help to control the final morphology in sintered parts by limiting exaggerated grain growth (VC, ZrC, Cr3C2). The distinct grades reveal purity improvements due to a combination of various preparation and purification techniques available through our versatile technology platform. We will discuss the results of chemical and physical powder characterization, with emphasis on the quality improvements achieved and their potential impact and benefits for the use of the powders.

(ICACC-S8-P109-2019) Examination of micro- and nanosized milled h-BN addition on sintered Si_3N_4/h-BN ceramic composites

K. Balazsi[1]; M. Furko[1]; Z. Fogarassy[1]; C. Balazsi*[1]

1. HAS Centre for Energy Research, Hungary

Silicon nitride ceramics containing 1 and 5 wt% of hexagonal boron nitride (h-BN) were prepared by attrition milling and hot-isostatic pressing. Thorough morphological characterizations have been carried out to reveal the influence of the milling parameters on the size of the h-BN additives. The results confirmed significant decrease in h-BN particle size by increasing milling time. The transmission electron microscopy (TEM) measurements revealed that the h-BN particles were incorporated into the ceramic matrix. The results showed that the increase of the h-BN content decreased significantly the hardness of materials. Moreover, the hardness values were higher when the size of h-BN was larger. The same tendency was observed in the case of Young's modulus.

(ICACC-S8-P110-2019) Effect of attritor milling on grain size and distribution of carbon nanotubes in YSZ/MWCNT composites

K. Balazsi*[1]; S. Lamnini[1]; C. Balazsi[1]

1. Centre for Energy Research HAS, Thin Film Physics, Hungary

Several energetical applications are known where yttria-stabilized zirconia (YSZ) and zirconia/multiwall carbon nanotube (MWCNT) composites were used as parts of solid oxide fuel cells (SOFC), photovoltaic solar cells, supercapacitor or hydrogen storage materials. The Ni – YSZ cermets are widely accepted as anodic materials in SOFCs with high catalitic activity and electrical conductivity. Some research works showed the drawbacks in hydrocarbon fuels as carbon build-up, sulfur poisoning or low tolerance to redox cycling. These irreversible processes damage the microstructure of anodes and reduce the cell performance, therefore Ni-free anode materials are continously researched and developed to overcome these problems. In this work, the design of milled YSZ / MWCNT composites was studied. The effect of attritor milling on structure of 8 mol.% yttria-stabilized zirconia (8YSZ) composites with 1wt.%, 5 wt.% and 10 wt.% MWCNT. The detailed structural investigations confirmed the MWCNT clusters in all cases, while the best homogenization was obtained in the case of YSZ / 1 wt.% MWCNT composite. The Raman measurements showed unanimously results with structural observations. The apparition of the G and D bands for all the composites at 1589cm^{-1} and 1356 cm^{-1}confirmed the structural integrity of MWCNT after the milling process.

(ICACC-S8-P111-2019) Silicon nitride dispersion strengthened sintered stainless steel

C. Balazsi*[1]; H. Ben Zine[1]; K. Balazsi[1]; A. Horvath[1]; V. Ryukhtin[4]; L. Almasy[2]; H. Murakami[3]; S. Kobayashi[3]

1. HAS Centre for Energy Research, Hungary
2. Wigner Research Centre, Hungary
3. Iwate University, Japan
4. Nuclear Physics Institute CAS, Czechia

The role of the submicrometer-sized silicon nitride addition on the morphological and structural properties of the ceramic dispersion strengthened (CDS) 316L stainless steels prepared by powder technology has been studied. Two composites were prepared: 316L/0.33 wt. % Si_3N_4 and 316L/1 wt. % Si_3N_4. Spark plasma sintering (SPS) was used for fast compacting of milled composites. The intensive milling assured an optimal coverage of 316L stainless grains with Si_3N_4 submicrometer-sized particles in both cases as demonstrated by energy dispersive spectroscopy (EDS) and TEM. On the other hand, the 316L phase has been maintained during and after the milling and sintering. The partial phase transformation of α-Si3N4 to SiOx was observed by EDS. The structure of CDS steels after thermal aging has been evaluated with magnetic measurements, electron back-scatter diffraction (EBSD) and small angle neutron scattering (SANS).

(ICACC-S8-P112-2019) Electronics ceramics microstructure Minkowski hull analysis

V. Mitic*[1]; G. Lazovic[3]; L. Kocic[2]; V. Paunovic[2]; S. Veljkovic[2]; B. Vlahovic[4]

1. Serbian Academy of Sciences, Institute of Technical Sciences, Serbia
2. University of Nis, Faculty of Electronic Engineering, Serbia
3. University of Belgrade, Faculty of Mechanical Engineering, Serbia
4. North Carolina Central University, USA

Technological parameters and different additives can be used to control BaTiO3 based materials structure. In this paper, Yb2O3 doped BaTiO3, sintered from 1320 to 1380 °C, microstructure (by using SEM/EDS and quantitative metallography) and dielectric properties have been investigated. Correlation between microstructure and dielectric properties, based on fractal geometry and micro-contact surfaces, has been developed. Using the fractal descriptors of the grains contact surface, a reconstruction of microstructure configurations (grains shapes, intergranular contacts), has been successfully done. Obtained results indicated that fractal analysis of different shapes contact surfaces, are important for BaTiO3-ceramics microstructure and dielectric properties prognosis. The ceramics grain's morphology pointed out developing new structure analytical methods validity. Model based on Minkowski hull is presented as new tool for structure research. Materials properties prognosis is determined by correlations synthesis–structure–property. The fractal BaTiO3-ceramic grains investigation, concerning the relationship between temperature and contact surface area is also introduced.

(ICACC-S9-P113-2019) Preparation of self-reinforcement of porous mullite through in situ synthesis of mullite whisker with HF in the precursor

H. Zhang*[1]; J. Tang[1]

1. Xi'an Aeronautical University, China

Mullite has the ability to form elongated grains along [001] direction and forms whiskers or needle-shaped grains, which help to form an interlocked microstructure. This ability of mullite crystals is very useful for making porous supports having higher strength. This self-reinforcement porous mullite can be grown from Si-Al-O system precursor powders by a vapour phase reaction in presence of SiF_4 gas, which can be formed in-situ by adding fluoride into the precursors. In this article, porous mullite with interlocked needle shape microstructure was developed from silica sol, aluminium chlorohydrate and hydrofluoric acid as the precursor. The effects of parameters like sintering temperature, and the amount of HF on the phase evolution, microstructure and porosity have been studied. The role of HF in mechanism of mullite formation was investigated using X-ray diffraction. Porous mullite ceramics with 82% open porosity and 15MPa compressive strength have been prepared at a relatively lower temperature of 1400 °C. The results show that a mixture of topaz and mullite is formed around 1200 °C at the intermediate stage of sintering and then followed by complete mullitisation. The F ion in hydrofluoric acid did play a crucial role as the form of fluorine-substituted silicic acid ($Si(OH)_{4-x}F_x$) in the diaphasic mullite gel decomposes on heating to $(SiF3)^+$.

(ICACC-S9-P115-2019) Effect of sintering temperature on thermal conductivity of porous nano-SiC ceramics

Y. Kim*[1]; Y. Kim[1]

1. University of Seoul, Department of Materials Sceince & Engineering, Republic of Korea

Highly porous nano-SiC cearamics with extremely low thermal conductivity were fabricated by partial sintering using SiC nano-powder and sacrificial templates. The effect of sintering temperature on the porosity, thermal conductivity, and compressive strength of the porous nano-SiC ceramics was investigated. The porosity decreased from 63% to 37% with increasing sintering temperature from 600°C to 1200°C, whereas the compressive strength increased from 9.5 MPa to 40 MPa with increasing sintering temperature from 600°C to 1200°C. The thermal conductivity increased from 0.209 W/mK to 0.406 W/mK with increasing sintering temperature from 600°C to 1200°C. By adding 30 wt% template into the nano-SiC, the porosity increased from 63% to 76% when sintered at 600°C. In contrast, the compressive strength and thermal conductivity decreased from 9.5 MPa and 0.209 W/mK to 1.6 MPa and 0.047 W/mK, respectively, when sintered at 600°C. Typical porosity, compressive strength, and thermal conductivity of a porous nano-SiC ceramic at 1000°C were 71%, 4.3 MPa, and 0.049 W/mK, respectively.

(ICACC-S9-P116-2019) Fibrous Si_3N_4 Ceramic with High Porosity Fabricated through Gas-Solid Reaction of CNT and SiO

J. Yang*[1]; Q. Zhi[1]

1. Xi'an Jiaotong University, China

In this work, a delicate strategy that carbothermal reduction-nitridation (CRN) reaction carried out by carbon nanotube and SiO vapor, combined with low temperature liquid-phase sintering, was rationally designed for direct fabrication of fibrous nano-sized β-Si_3N_4 structured porous ceramic, with average diameter of grain of approximately 200nm, and average aspect ratio of higher than 20. More strikingly, its porosity was up to 73%, while the ceramic possessed a superior mechanical properties, The bending and compressive strength reached up to 62 and 80 MPa respectively, and particularly, it exhibited a large strain to failure and 'pseudo-plastic' deformation behavior during the compressive test. More significantly, the underlying growth mechanism of the high aspect ratio nano-sized β-Si_3N_4 grain synthesized via this method was comprehensively analyzed and tentatively put forward.

(ICACC-S9-P117-2019) Porous Alumina ceramics by gel casting: Effect of type of sacrifical template

F. Akhtar*[1]; J. Nordin[2]

1. Luleå University of Technology, Division of Materials Science, Sweden
2. AkzoNobel AB, Sweden

Sacrificial template technique is widely used in producing porous ceramic with controlled morphologies and properties. The sacrificial templating takes advantage of the broad range of templates to tailor structure and properties of porous ceramics. In this study, we report processing of macroporous alumina ceramics with controlled pore size and good mechanical properties using expandable polymer microspheres and glassy carbon as sacrificial template. The influence of the choice of the organic sacrificial templates, glassy carbon and expandable microspheres, is studied in detail using SEM, TGA-GC-MS and compression test. A comparison of the effect of type of scarificial template on the ceramic processing, strength of green bodies, debinding process and mechanical properties of green bodies and sintered alumina ceramics have been presented.

(ICACC-S9-P118-2019) Combustion Synthesis of porous Si_3N_4 ceramics with high porosity and strength

G. He*[1]; L. Wang[1]; J. Li[1]

1. Technical Institute of Physics and Chemistry, Chinese Academy of Science, China

Porous Si_3N_4 ceramics were prepared by combustion synthesis method using low-cost Si powder as raw material. The results show that porous Si_3N_4 ceramics with porosity of 50% and bending strength over 100 MPa can be prepared by combustion synthesis of Si, α-Si_3N_4 and Y_2O_3 in high pressure nitrogen. Phase composition and microstructure results indicate that the main phase of the porous Si_3N_4 ceramics is β-Si_3N_4, and its microstructure is well-developed hexagonal prism single crystal. The reaction mechanism for maintain the size and shape of the porous structure during the combustion process was discussed under two combustion synthesis modes of "chemical oven" and "direct ignition". The effects of additions of Y_2O_3 and NH_4Cl on the structure and properties of prepared porous Si_3N_4 ceramics were investigated. Further attempts were made to synthesize porous Si_3N_4 ceramics having complex shapes (tubes, rings). With low cost Si powder as raw material and no energy consumption in combustion synthesis process, porous Si_3N_4 ceramics is expected to play an important role in high temperature filtration and water treatment due to its outstanding cost-effective advantages.

(ICACC-S10-P119-2019) Effect of the Al_2O_3 Film on Stress Corrosion Cracking of the Ni-Al Alloy in High Temperature and Pressure Water Analyzed by Molecular Dynamics Simulation

H. Yanagisawa*[1]; Q. Chen[1]; N. Miyazaki[1]; Y. Ootani[1]; N. Ozawa[1]; M. Kubo[1]

1. Institute for Materials Research, Tohoku University, Japan

The Ni-Al alloy composed of the Ni_3Al and Ni phases has excellent corrosion resistance by forming Al_2O_3 on the surface. Therefore, it is used as a structural material at high temperature and pressure part in a steam turbine, which causes corrosion. However, steam in the turbine is supercritical water, and the Ni-Al alloy degrades due to stress corrosion cracking by the supercritical water. In this study, to obtain design principles to prevent stress corrosion cracking, the corrosion process at Ni/Ni_3Al coherent interface in water under tensile stress, high temperature, and high pressure was investigated by molecular dynamics method using reactive force field. For the model, we constructed the Ni/Ni_3Al coherent interface with water molecules, and applied the strain to the model under the temperature of 900 K and pressure of 25 MPa. As the strain increases, Ni and water interacted on the surface, and Ni atoms were dissolved in water. Furthermore, the Ni-Al-O amorphous film was formed on the surface of the Ni_3Al phase, and H^+ dissociated from the water invaded into the Ni phase from the stress concentrated part. On the other hand, invasion of H^+ into the Ni_3Al phase was almost not observed. Thus, we found that the Ni-Al-O amorphous film can suppress invasion of H^+ and prevent the propagation of the stress corrosion cracking.

(ICACC-S10-P120-2019) Molecular Dynamics Simulation of Li Behavior in All-Solid-State Lithium Battery Anode

K. Nagai*[1]; N. Miyazaki[1]; Y. Ootani[1]; N. Ozawa[1]; M. Kubo[1]

1. Institute for Materials Research, Tohoku University, Japan

Compared with a conventional Li ion batteries with liquid electrolyte, an all-solid-state lithium battery has a potential for greater safety and higher energy densities. For the practical use of the all-solid-state lithium battery, the charging characteristics should be improved. For the anode, porous materials consisting of graphite as active materials and Li_2S/P_2S_5 as electrolytes are used. The all-solid-state lithium battery charges by intercalating of Li into the graphite layers. For improving charging capacity, the behavior of Li in the anode should be clarified. However, it is difficult to observe the behavior of Li by experimental methods. In this study, the behavior of Li in the

composite of the graphite layers and Li_2S particles are firstly investigated by molecular dynamics simulation using reactive force field. The simulation model is a porous structure of Li_2S particles joined with graphite layers. To elucidate the behavior of Li in the model, we investigate the change in the density of Li. The density reduction of Li near the interface is observed. The density of Li increases near the voids in the Li_2S porous structure. Therefore, we suggest that intercalated Li in the graphite layers near the interface moves and concentrates on the voids in the Li_2S porous structure.

(ICACC-S10-P121-2019) Effects of Chemical Reactions on Fracture of SiO_2-Composite Microelectromechanical Systems under Water Condition: Reactive Molecular Dynamics Simulation Analysis

S. Yamashita*[1]; N. Miyazaki[1]; Y. Ootani[1]; N. Ozawa[1]; M. Kubo[1]

1. Institute for Materials Research, Tohoku University, Japan

To measure extremely accurate flow rate, the microelectromechanical systems (MEMS) flow sensor has been developed. As the fluid channel of this MEMS flow sensor, the microtube made with sintered silica glass powder is used. However this silica micro tube would be fracture by cyclic-vibrational load due to shear flow caused by nano-pump and cyclic-thermal load caused by heat-generating electronic parts. One of the triggers of fracture of silica micro tube is considered as a decrease in yield strength due to the chemical reaction of the silica glass with water, while the specific mechanism has not been clarified. Thus, the detailed atomic scale insights into fracture mechanisms of silica glass are great importance to improve the durability of MEMS devices. Therefore, in this work, we analyzed the effects of water on the fracture mechanism of silica glass by means of molecular dynamics method. We used reactive force field which can take chemical reaction into consideration with low computational costs. The model of silica glass surface of MEMS's channel were modeled with amorphous SiO_2. For this model, we applied shear deformation tests in both of water and vacuum environment. In this presentation, we will present the effect of chemical reaction of silica glass with water on fracture strength.

(ICACC-S10-P122-2019) Molecular Dynamics Simulations on Chemical Mechanical Polishing Process of Nitride Substrate with Nanobubble

S. Kimura*[1]; N. Miyazaki[1]; Y. Ootani[1]; N. Ozawa[1]; M. Kubo[1]

1. Institute for Materials Research, Tohoku University, Japan

Since a nitride semiconductor such as AlN and GaN has a wide band gap and high saturated electron velocity, it is desirable for a high voltage and frequency power semiconductor materials. In order to improve the performance of the device, it is essential to develop a non-defective and atomically planarized substrate. For planarization of the nitride semiconductor substrate on atomic scale, chemical mechanical polishing (CMP) is used. However, since the nitride semiconductor substrate is a processing resistant material due to its high hardness and chemical stability, the polishing rate is remarkably low. In order to achieve more efficient CMP process, we focused on a nanobubble. When the nanobubble collapses, the liquid around the bubble forms a jet, which causes a water hammer shock. In order to reveal the effects of the nanobubble collapse on CMP of an AlN (0001) substrate, we performed nanobubble collapse simulation by molecular dynamics method using reactive force field. First, we prepared the nanobubble by removing solvent molecules spherically. Next, we applied water hammer shock to the AlN (0001) substrate by nanobubble collapse. We found that the terminated OH groups on the surface were pushed into the AlN (0001) substrate by the jet and Al-OH-Al bond was generated. It indicates that the oxidation of AlN (0001) is induced by the collapse of nanobubble.

(ICACC-S10-P123-2019) DFT Study of Silicon and Rare Earth Adsorption on Oxygen Terminated (0001) Boron suboxide Surface

J. S. Dunn*[1]; K. D. Behler[1]; J. LaSalvia[1]; C. Marvel[2]; M. P. Harmer[2]

1. U.S. Army Research Laboratory, USA
2. Lehigh University, Materials Science and Engineering, USA

In this paper, we develop a first principles Density Functional Theory (DFT) model of an oxygen terminated (0001) boron suboxide (B_6O) surface and study the structural and electronic reconstructions that result from the adsorption of silicon, lutetium, lanthanum and yttrium. To determine the effect of these different surface reconstructions on the chemistry and bonding behavior at the surface, we perform a qualitative analysis of the electron localization function (ELF), electron density difference (EDD), band structure, and partial density of states (PDOS). Finally, to validate the model, we compare model predictions to aberration-corrected Scanning Transmission Electron Microscopy (AC-STEM) with High-Angle Annular Dark Field (STEM-HAADF) measurements of the atomic positions for the surface adsorbed silicon and rare earths along B_6O grain boundaries.

(ICACC-S12-P124-2019) Synthesis, densification, microstructure and mechanical properties of samarium hexaboride ceramic

L. Feng*[1]; W. Fahrenholtz[1]; G. Hilmas[1]; Y. Hor[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

Samarium hexaboride (SmB_6) powders were synthesized by boro/carbothermal reduction of Sm_2O_3 with B_4C. Nominally pure SmB_6 powder had a mean particle size of about 400 nm and an oxygen content of 0.12 wt%. $SmBO_3$ formed as an intermediate phase during the synthesis. The synthesized powder was hot pressed at 1950°C to produce SmB_6 ceramics with relative densities>99.6% and a mean grain size of 4.4 μm. Vickers' hardness was 20.1±0.7 GPa. Young's modulus measured by bending and ultrasonic methods were 271 and 244 GPa, respectively. The flexure strength was 253±79 MPaand fracture toughness was 2.1±0.1 $MPa{\cdot}m^{1/2}$. These are the first reported results of the microstructure and bulk mechanical behavior of SmB_6 ceramics.

(ICACC-S12-P125-2019) Thermal and Mechanical Properties of a High Entropy Carbide

E. C. Schwind*[1]; G. Hilmas[1]; W. Fahrenholtz[1]; E. Castle[2]; M. Reece[2]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA
2. Queen Mary University of London, United Kingdom

Equimolar amounts of ZrC, TaC, HfC and NbC were mixed and reactively hot pressed at 2300°C and 40 MPa into billets of a high entropy carbide. X-ray diffraction analysis indicated that the four carbides formed a single phase solid solution. These billets were used to measure mechanical and thermal properties. Flexure strength was measured from room temperature up to 2000°C and fracture toughness was measured at room temperature. Thermal diffusivity was measured up to 2000°C and heat capacity was measured up to 1500°C. The values for the high entropy carbide were compared to the values obtained for nominally pure HfC and TaC, which were constituents of the HEC.

(ICACC-S12-P126-2019) Intrinsic Mechanical Properties of Zirconium Carbide Ceramics

N. Korklan*[1]; G. Hilmas[1]; W. Fahrenholtz[1]

1. Missouri University of Science & Technology, Material Science and Engineering, USA

Zirconium carbide (ZrC) was synthesized by carbothermally reducing zirconia and carbon black in an effort to prepare phase pure ZrC and determine its intrinsic properties. The prepared ZrC had a low hafnium content, 0.01 to 0.04 at%, with known oxygen and nitrogen impurities determined by inert gas fusion analysis. X-ray diffraction indicated that the reacted power was nominally phase

pure and Raman spectroscopy identified the ZrC as sub-stoichiometric. Powders were prepared with varying carbon stoichiometry and then hot pressed at a temperature of 2200°C at a 40 MPa applied pressure. A difference in density after hot pressing was found with varying carbon stoichiometry. ZrC compositions having a relative density of at least 95% were machined to produce specimens for mechanical property measurements. Mechanical properties were measured including Vickers hardness, elastic modulus, and fracture toughness at room temperature, along with flexural strength from room temperature to 2000°C. The effects of carbon stoichiometry and relative density on properties will be discussed.

(ICACC-S12-P127-2019) Structural and Physical Properties of $Ti_2(Al,Bi)C$

E. Prehn*[1]; Z. Tan[1]; A. Talapatra[1]; T. Duong[1]; R. Arroyave[1]; M. Radovic[1]; A. Poznyak[2]

1. Texas A&M University, MSEN, USA
2. National University of Sciences and Technology, Department of Nanofunctional Systems and High-Temperature Materials, Russian Federation

The list of MAX phases, a family of ternary carbides and nitrides where M is an early transition metal, A is a post-transition metal element, and X is either carbon or nitrogen, is ever-expanding. The ability to form solid solutions, with the M, A, and/or X sublattice comprising of two or more elements, allows for further tailoring of their unique properties. Herein we report on the synthesis of the recently-discovered MAX phase solid solution $Ti_2(Al,Bi)C$, which exhibits a highly anisotropic lattice stretching due to substitution of aluminum atoms in Ti2AlC with significantly larger bismuth atoms. The present work describes the effect of bismuth addition on phase stability and anisotropic lattice stretching in $Ti_2(Al,Bi)C$. Mechanical, thermal, and electrical properties of series of $Ti_2(Al,Bi)C$ solid solutions, containing from 0% to 38.4% Bi on Al-sublattice, were determined using different techniques (such as Nanoindentation, Resonant Ultrasound Spectroscopy, Differential Scanning Calorimetry, and Hall and hot-disc measurements) and discussed.

(ICACC-S12-P128-2019) Heterogeneously dispersed ceramic matrix composites for harsh environments

B. A. Baker*[1]; J. Binner[1]

1. University of Birmingham, School of Metallurgy and Materials, United Kingdom

Ultra-high temperature ceramic matrix composites (UHTCMCs) are the most plausible material solution for extreme environments, where aggressively oxidising atmospheres and high thermomechanical loads prohibit the use of superalloys and C/C or SiC/SiC alone. Work in this area honing the anti-ablation and high-temperature post-oxidation structural performance is both well established and on-going. However, reports concerning functionally graded materials, as would be both expected and demanded in application for adequate performance per unit cost, are currently sparse. Presented here is a demonstration of the fabrication, testing and analysis of functionally graded C/C-HfB_2-ZrB_2 composites with the goal of minimising the high material fabrication cost of pure HfB_2 composites, while retaining sufficient anti-oxidation and structural performance. 2.5D composites of ZrB_2/HfB_2 were produced and analysed, and an update of results to date will be presented.

(ICACC-S13-P129-2019) Flexural Strength of CMC Tubes Used as Components in Nuclear Applications: ASTM Draft Standard Using Transverse Loading for Flexure Stress

M. G. Jenkins*[1]; J. E. Gallego[1]

1. Bothell Engineering and Science Technologies, USA

Plans are afoot by US DOE to use advanced materials for core and reactor-unit components in various advanced reactor concepts. Ceramic matrix composites (CMC), specifically SiC fibre-SiC matrix composites, could greatly expand the design window for various components in terms of operating temperatures, application stresses, and service lives, as compared to heat-resistant metallic alloys, while significantly improving accident tolerance and safety margins. Examples of CMC tubular components include fuel rods, control rod sleeves, and control rod joints. Possible failure modes for these components include axial and hoop tension, axial flexure, axial and diametral compression, and axial shear. A draft ASTM standard test method has been developed and submitted for full-consensus ballot to determine the flexural strength of ceramic matrix composite tubes subjected to bending moments produced by transverse loading. Empirical tests of composite tubes provided validation of the parameters specified in the test method. The draft standard test method addresses the following experimental issues -- test specimen geometries/preparation, test fixtures, test equipment, interferences, testing modes/procedures, data collection, calculations, reporting requirements, precision/bias.

(ICACC-S13-P130-2019) Compressive Strength of CMC Tubes Used as Components in Nuclear Applications: ASTM Draft Standard Using Axial Compression Loading

M. G. Jenkins*[1]; J. E. Gallego[1]

1. Bothell Engineering and Science Technologies, USA

US DOE has plans to use advanced materials for the core and the reactor unit components in various advanced reactor concepts. Ceramic matrix composites (CMCs), in particular silicon carbide (SiC) fiber SiC-matrix (SiC-SiC) composites, could greatly expand the design window for various components in terms of operating temperatures, applicable stresses, and service lives, compared to heat-resistant metallic alloys, while significantly improving accident tolerance and safety margins. Potential CMC tubular components include fuel rods, control rod sleeves, and control rod joints. Possible failure modes for these components include axial and hoop tension, axial flexure, axial and diametral compression, and axial shear. A draft ASTM standard test method has been developed and submitted for full-consensus ballot to determine the longitudinal compressive strength of ceramic matrix composite tubes subjected to axial compression. Modeling and empirical tests of composite tubes provided validation of the parameters specified in the test method. The draft standard test method addresses the following experimental issues -- test specimen geometries/preparation, test fixtures, test equipment, interferences, testing modes/procedures, data collection, calculations, reporting requirements, precision/bias.

(ICACC-S13-P131-2019) Effect of deposition conditions on the production of ZrO_2 coatings produced by PE-CVD as environmental barrier coatings for the Molten Salt Reactor

L. J. Espinoza Perez*[1]; E. Lopez-Honorato[1]

1. CINVESTAV, Metallurgical and Ceramic Engineering, Mexico

An important challenge in the progress of the Molten Salt Reactor is the development of structural materials capable of resisting the harsh corrosion environment that results from the use of fluoride molten salts as fuels and the reduction on mechanical strength at temperatures above 700°C. In this work, we report the development of ZrO_2 coatings produced by plasma-enhanced chemical vapor deposition (PE-CVD) as environmental barrier coatings. We studied the feasibility of using zirconium (IV) acetyl acetonate [$Zr(acac)_4$] as precursor and the effect of temperature and oxygen concentration on the deposition of ZrO_2. $Zr(acac)_4$ was evaporated at 200°C using a deposition temperature between 500-800°C, with an oxygen concentration between 20-60% and a plasma power fixed at 250 watts. Due to the decomposition of $Zr(acac)_4$, carbon can be co-deposited along with ZrO_2. At low temperatures (500-600°C), the carbon content was between 20-24 at%. At higher temperatures (700-800°C) and oxygen content (20-60%), the amount of carbon decreased to 16-20 at% and 16-18 at%, respectively. All the coatings showed a granular morphology in the surface and a mix of monoclinic and tetragonal ZrO_2 phases were identified by SEM and XRD, respectively.

(ICACC-S13-P132-2019) Advanced Metallic-SiC Composite Claddings for Improved Damage Tolerance

J. S. O'Dell*[1]; L. Snead[2]; K. Shirvan[3]

1. Plasma Processes, LLC, USA
2. Stony Brook University, USA
3. Massachusetts Institute of Technology, USA

SiC/SiC composites have been identified as a leading candidate for nuclear fuel claddings. However, the retention of fission products within a SiC-based cladding may be an issue. Some clad designs seek to overcome this issue through a CVD SiC coating. However, the community has recently raised concerns regarding hydrothermal corrosion of SiC. Therefore, an alternative concept to the fully-ceramic SiC/SiC clad is needed. One such design is a hybrid clad, where a thin metallic coating on the exterior of the composite is used. This coating could provide fission product retention under normal operating conditions and the required environmental barrier coating (EBC) against corrosion. During this effort, an innovative coating technique has been developed for producing the metallic EBC, i.e., Vacuum Plasma Spray–Thin Film (VPS-TF). The process enables the production of dense, thin film coatings at lower pressures with higher plasma power than conventional VPS processing. As a result, the feedstock material is evaporated or partially evaporated resulting in a very fine coating microstructure of splats and columnar growth, which possess improved strain tolerance. Using this process, corrosion resistant metallic coatings were successfully deposited on SiC/SiC tubes. Preliminary testing at MIT has produced very encouraging results including improved hydrothermal corrosion resistance as compared to uncoated SiC/SiC.

(ICACC-S13-P133-2019) Characterization of SiC_f/SiC Woven Tubular Composites

J. Nance*[1]; G. Subhash[2]; C. Deck[3]

1. University of Florida, Material Science Engineering, USA
2. University of Florida, Mechanical and Aerospace Engineering, USA
3. General Atomics, USA

In the nuclear power industry, fuel-pellet swelling and pellet-cladding interactions induce complex stress states in the cladding material. While Zircaloy® has been the preferred cladding material, in recent years ceramic composite cladding tubes have been proposed due to their superior ability to withstand this load, better radiation resistance, as well as its high modulus, strength and thermal resistance. In the current work woven, tubular cladding with continuous silicon carbide fibers and a high-purity stoichiometric silicon-carbide matrix (i.e., SiC_f/SiC) has been studied for its mechanical integrity using a variety of mechanical testing methods such as Charpy-impact, split-Hopkinson pressure bar (SHPB), indentation and custom designed dynamic flexure. The goal is to establish failure envelopes at multiple strain rates and quantify uncertainty in these envelopes as a function of porosity and microstructural variability (variations in matrix thickness, weave architecture, tube thickness, etc.). The woven SiC_f/SiC tubes were analyzed in comparison to monolithic SiC using the aforementioned tests, and the performance of the woven material is established.

Thursday, January 31, 2019

FS1: Bio-inspired Processing of Advanced Materials

Mechanical Properties of Natural and Bioinspired Materials

Room: Coquina Salon F
Session Chair: Joaquin Ramirez-Rico, Universidad de Sevilla

8:30 AM

(ICACC-FS1-001-2019) Strong and tough ceramic inspired by nature (Invited)

F. Bouville*[1]

1. Imperial College London, Department of Materials, United Kingdom

Heterogeneous composites with intricate microstructures are widely spread in the natural world where they are needed to fulfil the specific functional demands imposed by the environment. Our ability to make structure using natural materials design principles is still a challenge due to the lack of adequate processing tools. We introduced a technology, called Magnetically-Assisted Slip Casting (M.A.S.C.) that combines an aqueous-based slip casting process with magnetically-directed particle assembly to create programmed microstructural designs using anisotropic stiff platelets in a ceramic, metal or polymer functional matrix. This process opened a new and easy way to produce completely mineral nacre-inspired brick-and-mortar structure, with a high degree of control on the grain orientation and the inter-granular phase chemistry. Using this approach and pressure-assisted sintering, we were able to design a variety of nacre like ceramic that are at the same time strong, with strengths up to 672 MPa, and tough, with toughness up to 7.4 MPa. $m^{1/2}$ for alumina based ceramics. Because of the interplay between the mortar and the brick strengths, these samples also present slow crack propagation, making them even more damage tolerant and this at temperature up to 1200°C.

9:00 AM

(ICACC-FS1-002-2019) Tailoring architecture and microstructure to design bio-inspired layered ceramics with enhanced damage tolerance (Invited)

R. Bermejo*[1]; A. Hofer[1]; R. Walton[2]; G. L. Messing[2]

1. Montanuniversitaet Leoben, Institut fuer Struktur- und Funktionskeramik, Austria
2. Pennsylvania State University, Materials science and Engineering, USA

The design of "bio-inspired" layered ceramic composites with weak or strong interfaces can significantly increase failure resistance of the material and, in some cases, hinder, or even arrest, the propagation of cracks. In this work, novel concepts are presented which combine different approaches used in layered architectural design to obtain highly reliable ceramic materials with enhanced fracture resistance. The use of tailored residual stresses in embedded layers within the structure is demonstrated to act as an effective barrier to the propagation of cracks from surface flaws, providing the material with a minimum design strength, below which no failure occurs. Moreover, texturing of the microstructure in embedded layers is utilized to provide preferential paths for conducting propagating cracks, thus protecting the underlying structure. A combination of experiments and modelling is presented, showing the potential of layered architectures in the design of future ceramic components with enhanced damage tolerance.

9:30 AM

(ICACC-FS1-003-2019) Biomorphic transformations give nature-inspired 3-D ceramics with enhanced functional and mechanical performance (Invited)

S. Sprio*[1]; A. Tampieri[1]; A. Ruffini[1]; S. Panseri[1]; M. Montesi[1]

1. National Research Council of Italy, Institute of Science and Technology for Ceramics, Italy

The achievement of 3-D ceramics retaining functionally-active chemistry is a highly desired goal, but so far largely prevented by the need of sintering for structural consolidation, which transforms metastable phases into stoichiometric and less active phases. A clear example is given by the biomedical field where ion-doped hydroxyapatite, considered as the elective phases for bone regeneration, cannot be obtained as 3-D scaffolds and this prevented substantial success in regeneration of load-bearing bone, so far. The present study describes a new chemical approach for 3-D ceramic development consisting in nucleation and growth of bioactive phases directly in the 3-D state, thanks to the use of a bone-mimicking natural template acting as a structural guide for the whole process. Heterogeneous chemistry at controlled temperature and pressure in supercritical conditions allows to obtain nanocrystalline 3-D ceramics with highly bioactive composition and multi-scale pore structure inherited by the original natural template, giving high strength and damage-tolerant behavior similar to natural bone. These features open to frontier applications in medicine. In a wider perspective, this new concept of fabrication can pave the way for the development of innovative functional ceramics, today unabled by chemical and structural degradation inherent to conventional processing.

10:20 AM

(ICACC-FS1-004-2019) Biomimetic Composites Derived from an Impact Resistant Crustacean (Invited)

N. Yaraghi[1]; L. Grunenfelder[1]; N. D. Suksangpanya[2]; D. Restrepo Arango[2]; P. Zavattieri[2]; D. Kisailus*[1]

1. University of California, Materials Science and Engineering, USA
2. Purdue University, USA

Nature has evolved efficient strategies to synthesize complex mineralized structures that exhibit exceptional damage tolerance. One such example is found in the hyper-mineralized hammer-like dactyl clubs of the stomatopods, a group of highly aggressive marine crustaceans. We have revealed that the dactyl club is a multi-phase composite of oriented crystalline hydroxyapatite and amorphous calcium phosphate, in conjunction with a highly expanded helicoidal organization of the fibrillar chitinous organic matrix. We describe each region, including a recently uncovered a novel and previously unobserved architectural design, called the "herringbone structure", which consists of a compacted and pitch-graded sinusoidal arrangement of helicoidally arranged alpha-chitin/hydroxyapatite fibers. This exhibits a notable departure from the traditional helicoidal (Bouligand) structure found within most crustacean exoskeletons, including the innermost energy absorbing region of the club. This structure, in combination with an outer dense particulate apatite layer, enhances stress redistribution under compressive loading and yields a tough and impact-resistant structure capable of delivering high-energy strikes without failure. The findings presented herein can provide inspiration and ongoing design guidelines for the fabrication of next-generation impact-resistant composite materials.

10:50 AM

(ICACC-FS1-005-2019) Clever mechanisms and impact resistance strategies found in the architecture of some naturally occurring materials (Invited)

N. D. Suksangpanya[1]; N. D. Guarin-Zapata[1]; D. D. Wang[1]; N. Yaraghi[2]; D. Kisailus[2]; P. Zavattieri*[1]

1. Purdue University, USA
2. University of California, Riverside, USA

The focus of this talks is to discuss some interesting mechanics problems that we encountered as we studied the extraordinary damage tolerance of Bouligand Structures, a naturally-occurring architecture typically found in arthropods such as the smashing Mantis Shrimp. We carry out a combined analytical, computational and experimental investigation of the structure-function relationship of these structures Bouligand structure. Our results revealed different mechanisms that could be incorporated in the design of new impact resistant biomimetic composites at different scales. Our discussion will be focused on the material capability to delocalize damage, modulate mechanical properties and filter stress waves.

11:20 AM

(ICACC-FS1-006-2019) Geologically-Inspired Ceramics – Understanding the mechanism behind room temperature cold sintering

M. Haug*[1]; F. Bouville[1]; A. Studart[1]

1. ETH Zurich, Materials, Switzerland

In Earth's upper crust, dense ceramic material can be formed at mild pressures and nearly ambient temperature. This means a tremendous reduction in energy used for densification compared to technical ceramic processing, in which temperatures above 1'000 °C are needed to produce dense structures. Inspired from this geological phenomenon, we demonstrated a new method called room-temperature cold sintering. With the addition of small amounts of water and the application of pressures up to 500 MPa, calcium carbonates can be compacted into structures reaching 85 % relative density within only 30 min. In geological carbonates, this process is presumably based on dissolution – precipitation of the inorganic material and the diffusion through the thin water film present on the surface of the particles. However, in synthetic systems this room-temperature method is still limited to only a handful of materials and the underlying processes are not yet fully understood. We present different strategies to investigate this phenomenon and their results. We studied the effect of pressure, bulk solubility on the densification kinetics of the carbonates in order to shed light on the main factors that drive the room temperature cold sintering process.

Processing of Biomorphic and Biomimetic Materials

Room: Coquina Salon F

Session Chairs: Florian Bouville, ETH Zürich; Pablo Zavattieri, Purdue University

1:30 PM

(ICACC-FS1-007-2019) New advances in ice-templating technique: From architectural control to biomimetic functional materials (Invited)

H. Bai*[1]

1. Zhejiang University, College of Chemical and Biological Engineering, China

Natural materials, such as bone, shells and bamboo, exhibit outstanding properties despite being porous and made of weak constituents. Frequently, they represent a source of inspiration to design strong, tough, lightweight, self-healing (i.e., multifunctional) materials. Ice-templating (e.g., freeze casting) has been widely applied in making biomimetic porous materials. Recently, we have advanced this technique to achieve a higher level of control over materials' architectures and therefore functionalities. Bidirectional

freezing and freeze-spinning technique have been developed to make biomimetic porous and composite materials with multiscale architecture and multifunctionality. The plant-inspired graphene aerogel is both high strength and resilience, holding great promise for flexible electronics. By mimicking the architecture of polar bear hair, the freeze-spun polymer fiber is highly thermal insulating for personal thermal management.

2:00 PM

(ICACC-FS1-008-2019) Colloidal Processing Enabling Microstructure Control and Manufacturing of Bio-inspired Ceramics (Invited)

C. Tallon*[1]

1. Virginia Tech, Materials Science and Engineering, USA

The unique microstructures and functionalities we find in nature have captured the imagination of materials scientists and engineers seeking to develop new type of materials. As ceramics researchers aiming to mimic such bio-inspired features, we need a toolbox that allows an exhaustive control of the different building blocks (particles, solvents, molecules, polymers, bubbles and micelles) to create those exceptional microstructures. Colloidal processing offers versatility to assemble the building blocks into bio-inspired materials, but also offers other advantages to be taken into consideration if we are to translate those features into real life applications: reliability; complex shape; scale-up, and design for manufacturing. This talk will showcase the power of colloidal processing to create bio-inspired multi-scale microstructures at the nano- and micron-size level that are made into large complex shapes without compromising those microstructural features. A case study using multi-scale hierarchical porous ceramic structures will be discussed from fundamental particle-particle interactions, processing method selection, microstructural and properties characterization, large scale production and predictive-performance modelling. Bringing together colloidal ceramic processing, design for manufacturing and bio-inspired materials will ensure the next-generation of ceramic materials.

2:30 PM

(ICACC-FS1-009-2019) Robocasting of zirconia scaffolds with multi-scale porous networks

L. Tabard*[1]; E. Prud'Homme[1]; L. Gremillard[1]; V. Garnier[1]

1. INSA Lyon, MATEIS, France

The aim of this work is to fabricate porous zirconia at various scales of porosity to optimize flow distribution in a complex structure through different interconnected channels. Additive manufacturing with robocasting was chosen to fabricate a scaffold-like structure. Robocasting allows the control of macro-channels in a range of 50 to 500 μm by zirconia paste extrusion. Focusing on the filament scale of the scaffold, partial sintering and addition of porogen in the printing paste were combined to create interconnected networks of porosity at different levels. Wheat starch was chosen as porogen thanks to its globular shape and its gelatinization ability when hydrated, faciliting post-process drying. Scaffolds with varying amount of porogen were printed in order to create the most porous scaffold possible while keeping mechanical resistance. Mercury porosimetry was used to measure channel size and pore content at filament scale, revealing the presence of two different pore network: 0.1 μm; 1 to 50 μm. SEM and local x-ray tomography revealed interconnection of porosity created by wheat starch. Mechanical compression is currently investigated, showing resistance up to 2 MPa for scaffolds up to 80% of total porosity. This tree-like structure maximizes flows distribution and is based on constructal idea. Such structure with different pore networks are close to those of wood, lung or bone.

3:10 PM

(ICACC-FS1-010-2019) Bioprocess-Inspired Synthesis of Advanced Materials: The Design and Implementation (Invited)

H. Xie*[1]; H. Ping[1]; Z. Fu[1]

1. Wuhan University of Technology, China

In nature, it is vital for living organisms to produce biomaterials with elegant structures as well as unique functions and properties through bioprocesses. A bioprocess usually consists of sequential biochemical reactions that rely on functional proteins or enzymes. Important characteristics of bioprocesses are environmentally friendly, reasonable efficiency, self driving, spatial confinement and temporal ordering. Learning from bioprocesses, one can modify and construct bioprocesses by taking advantages of genetically modified functional proteins. Hence, we explored the synthesis of advanced materials through deliberately designed bioprocesses. Several recombinant proteins were constructed by combing and reorganizing functional protein domains to optimize and integrate bioprocesses such as biomineralization for producing advanced materials with elegant structures and/or improved functions. It was observed that these recombinant proteins did affect or induce the formation of various unique materials in confined environments (such as on bacterial surface or inside collagen fibrils). The structure, morphology, and function of as prepared materials were evaluated. These studies demonstrate the protein/enzyme-based integration of bioprocesses for producing advanced materials.

3:40 PM

(ICACC-FS1-011-2019) Processing Novel Materials to Engineer Bioinspired Ceramic Composites (Invited)

V. Garcia Rocha*[1]; G. Menendez[1]; S. Evans[1]; G. Min[1]

1. Cardiff University, School of Engineering, United Kingdom

Engineering advanced composites is a challenging field and graphene, one atom thick carbon layer with extraordinary electrical, mechanical and thermal properties, could certainly play an important role in developing novel ceramic composites. Pure Graphene is an extraordinary material in terms of properties due to its extreme lightness and thickness but for composites manufacturing it is not the most useful one. If we start from Graphite instead and reach and intermediate called Graphene Oxide, via its chemical exfoliation we will find novel ways of processing composites. GO is a highly hydrophilic that can be suspended in water and easily processed and graphene properties can be restored by thermal annealing. Examples of automotive, aerospace and biomedical ceramics are SiC, Si_3N_4, Al_2O_3 and ZrO_2. However, its lack of toughness is the major challenge they face. Using water based suspensions of graphene oxide to design novel graphene-ceramic composites with weak interfaces, and excellent damage tolerance, electric and sensing properties, has recently been demonstrated by mimicking the hierarchical architectures present in nature. In this talk I will briefly recall a successful bioinspired composite in which graphene weak interfaces in a glass-ceramic matrix allowed self monitoring capabilities combined with high toughness and will draft the results towards bioinspired alumina composites using graphene.

4:10 PM

(ICACC-FS1-012-2019) Electrosprayed bioactive calcium phosphate layers starting from biogenic raw materials

C. Balazsi*[1]; K. Balazsi[1]

1. HAS Centre for Energy Research, Hungary

The materials used for artificial implants by default are TiAl6V4, Ti alloy and ceramics. Despite application of different biocompatible materials with properties of native joints has not been found to date. Biomaterials used for implant should possess some important properties in order to long term usage in the body without rejection and should be made with properties as excellent biocompatibility, superior corrosion resistance and non-toxic. Ceramic structures at

the nanometre range have been proven to have improved properties and characteristics that differ from their bulk, allowing for opportunities in novel technological applications. Ceramic layers with some advantages, including a very high surface-to-volume and aspect ratio can be processed by cheap and quick method, that is electrospraying. This presentation reviews results on the electrospinning and electrospraying of various bioceramic layers and their potential applications in the biomedical field.

4:30 PM

(ICACC-FS1-013-2019) Developing bioinspired graphene/ceramic composites

G. Menendez*[1]; G. Min[1]; S. Evans[1]; V. Garcia Rocha[1]

1. Cardiff University, Cardiff School of Engineering, United Kingdom

Graphene is currently the benchmark of two-dimensional materials. However, a decade after its rise in popularity, scalability issues and costliness are still limiting its spread into commercial applications. Graphene-reinforced composites appear a promising vehicle to spread graphene throughout the industry. In this work, we plan to develop novel graphene/ceramic composites by using freeze-casting and wet chemistry processing. Through this strategy, the hierarchy of cast materials can be maintained across many length scales, resembling structures found in natural composites. Graphene oxide (GO) and aluminium lactate and chloride have been selected as the composite precursors. Freeze-cast GO foams were obtained by shifting freezing rates, additives and solid concentration. The standard foams were frozen under 5 °C/min rates and annealed at 900 °C for 1h, leading to reduced aerogels of 5 mg/cm^3 for slurries with 3 – 5 mg/ml GO concentration. Alignment of the network was confirmed, with average pore diameters of 10 – 20 μm. The current stage is focused on doping GO slurries with alumina nanoparticles in graphene/alumina ratios ranging from 1:1 to 9:1. Stability and castability should be preserved, aiming for a subsequent alumina infiltration in the scaffolds. This approach will show whether graphene networks can be successfully implemented in advanced ceramics, leading to stronger composites with additional functionalities.

FS2: Image based Characterization and Modelling of Ceramics by Non-destructive Examination Techniques

Characterization NDE Technologies for Sintering Analysis, Stress, Void and Distribution I

Room: Coquina Salon A

Session Chair: Amjad Almansour, NASA Glenn Research Center

1:30 PM

(ICACC-FS2-001-2019) Three dimensional microstructure analysis with X-ray microscopy (Invited)

C. Thieme*[1]; R. B. Wehrspohn[1]

1. Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Germany

Today, materials development without the usage of modern high resolution imaging techniques is almost impossible. Electron microscopy is often the first choice to take a look at the microstructure of a material. However, failure diagnostics with this technique can be complicated because of the effect of sample preparation and the limited information depth. Especially in the case of the characterization of micro cracks and the localization of their origin, a three dimensional information depth is necessary. This problem can be overcome by 3D imaging techniques. Not so long ago, this was only possible by using synchrotron radiation, but now X-ray microscopy has become available. This technique allows the 3D characterization on a laboratory scale with a resolution down to below 100 nm. Together with a large sample volume of up to around 50 μm x 50 μm x 50 μm, this method is suitable for the characterization of bulk materials, which are not affected by the sample preparation. This paper will give an overview on X-ray microscopy as a new high throughput method for failure diagnostics and materials development. This technique will be compared with conventional analysis techniques using examples from recent material developments.

2:00 PM

(ICACC-FS2-002-2019) Non-Destructive Electrical Characterization of Ceramic Microstructures: Outside and Inside the Furnace

M. C. Golt*[1]; E. Hernandez-Rivera[1]; K. Strawhecker[1]; S. Kilczewski[1]

1. U.S. Army Research Laboratory, USA

Measurements of electrical properties can be fast, non-destructive, volumetric, and relatively easy to perform in-situ. Since these measurements involve the measure of the interactions of traveling electrons with the microstructure, they provide atomic resolution-a necessary capability when measuring grain boundary properties. Frequency-dependent impedance measurements provide distinction between the contributions of the grains from the grain boundaries. Analytical and numerical modeling can then be used to reconstruct entire microstructures, providing knowledge of the largest features in the microstructure, the grain size distribution, all the way down to the number of defect atoms at the grain boundary. What's more, we show that these measurements can be performed in real-time on the evolving microstructure during sintering, providing valuable insights into the dynamics of the sintering process. We will discuss how we have used electrical measurements to characterize ceramic microstructures, non-destructively, on large specimens, over a variety of compositions. We show how bulk electrical measurements compare with conductive-AFM measurements and how to relate processing with structure and performance. Finally, we detail how these experiments validate numerical models that help to visualize, understand, and predict the relationship between the measurement and the structure.

2:20 PM

(ICACC-FS2-003-2019) Designing High Performance Advanced Ceramics using Advanced Microscopy Characterization, Modelling and Machine Learning Image Segmentation

A. Stratulat*[1]

1. Carl Zeiss Microscopy Limited, United Kingdom

Ceramics have become the material of choice for a wide range of high performance applications thanks to the ability to design their macroscopic properties and combine these with modern processing techniques. To drive innovation, a material's microstructure and its interaction with environment must be characterized in situ, in multi dimensions and using different modalities, taking advantage of modern microscopy solutions, combined with software packages for simulations and image segmentation. ZEISS ZEN Intellesis provides and additional tool for industrial ceramics researchers interested in getting more insights from their data: data-agnostic machine learning system that can be used alone or in conjunction with other software platforms. This presentation will overview the advantages of using non-destructive 3D and 4D analysis to model real structures, to identify defects and investigate failures with example applications on solid oxide fuel cells, in situ nanomechanical testing in dentin, multi-scale and multi-modal analysis investigation of fiber reinforced composites, study the multiple layers of thermal barrier coatings, as well as non-destructive crack analysis in 3D and 4D study under environmental conditions in building materials.

2:40 PM

(ICACC-FS2-004-2019) Strain field measurements for tensile-loaded carbon/carbon composites by DIC method at elevated temperatures

H. Sato*[1]; T. Aoki[2]; R. Kitamura[3]; S. Ogihara[3]

1. Tokyo University of Science, Department of Mechanical engineering, Graduate School of Science and Technology, Japan
2. Japan Aerospace Exploration Agency, Aeronautical Technology Directorate, Japan
3. Tokyo University of Science, Department of Mechanical Engineering, Faculty of Science and Technology, Japan

Digital image correlation (DIC) is a non-contact strain measurement that can be used for the mechanical testing of CMCs at elevated temperatures. However, DIC measurements at elevated temperatures often suffer from the issues that cause measurement errors. In this study, a series of experiments was conducted to improve the accuracy of the measurements at elevated temperatures. Heat haze outside the furnace resulted in substantial image distortions. Hence, the window of furnace used for observations was narrowed to minimize radiative heat flux from the furnace. It was also found that thermal radiation from the test specimen altered the contrast of the speckle pattern at temperatures exceeding 1000°C, and introduced significant errors even at non-stressed state. Therefore, an optical filter was used to eliminate radiative light from the specimen. These experimental measures improved the accuracy of the measurements. As a result, the measurement accuracy at elevated temperatures became comparable to that at room temperature. Monotonic tensile tests of a plain-woven carbon/carbon composite were performed at 1200°C under vacuum environment. The averaged strains determined by DIC technique agreed well with those obtained by a contacting-type extensometer. The strain distribution reflecting the woven fiber structures was successfully obtained by the present DIC measurements.

Characterization NDE Technologies for Sintering Analysis, Stress, Void and Distribution II

Room: Coquina Salon A

Session Chair: Benoit Rousseau, LTN UMR CNRS 6607

3:20 PM

(ICACC-FS2-005-2019) Influence of µCT resolution on structural parameters determining the minimal Volume-of-Interest (VOI)

T. Fey*[1]

1. Friedrich-Alexander University Erlangen-Nürnberg, Department Material Science and Engineering, Germany

At present micro computer tomography is a sophisticating method for non-destructive testing of materials and getting an in-sight view of the internal microstructure. Based on the 3D-volume or 2D-slice data structural parameters as cell size or strut thickness distribution, tortuosity, porosity, interface density and Jeffrey number can be calculated. Main influence on the validness, precision and error deviation of these parameters were caused by a) scanning resolution and b) defined volume-of-interest (VOI). Based on 30, 45 and 80 ppi alumina foams (dimension 20x20x60 mm) were scanned at three different resolution (6.7, 13.2 and 27.1 µm/pixel). After reconstruction of the sinograms calculation of structural parameters were performed on the whole scanned volume. In addition smaller sub-volume down to 1/20 of the complete sample volume were computed with random starting coordinates inside the sample volume from the reconstructed data followed by calculation of the structural parameters. Based on the results a minimum VOI for a given resolution can be defined.

3:40 PM

(ICACC-FS2-006-2019) Observations of Anti-thermal Grain Growth of Strontium Titanate with Non-Destructive 3D X-ray Diffraction

A. R. Krause*[1]; M. Wang[3]; A. Roti Roti[2]; M. P. Harmer[2]; C. Krill[3]

1. University of Florida, Materials Science and Engineering, USA
2. Lehigh University, Materials Science and Engineering, USA
3. Ulm University, Germany

Strontium titanate ($SrTiO_3$) exhibits anti-thermal grain growth, where the grain growth constant appears to decrease as the temperature increases from 1350 °C to 1425 °C. This non-Arrhenius growth behavior is desirable for high temperature applications and processing methods to retain or achieve small grains, but the mechanism remains elusive. Previously, the change in growth behavior has been correlated with changes in the grain boundary character distribution and grain boundary energy. However, the contribution of grain boundaries of different character, and their associated mobilities, to overall grain growth remains unknown. Therefore, we employed a non-destructive characterization method, 3D-x-ray diffraction microscopy, to track individual grains and grain boundaries of $SrTiO_3$ at multiple timesteps during grain growth at two different temperatures. Here, we will discuss initial observations comparing growth at the two temperatures measured. Furthermore, the technique's opportunities and challenges for studying anti-thermal grain growth will be discussed.

4:00 PM

(ICACC-FS2-007-2019) Design of Novel Porous Foams by Pyrolyzing Lignin

S. Gupta*[1]; M. Dey[1]; K. Hall[1]; C. Matzke[1]; G. Ellis[1]; S. Javaid[1]; Y. Ji[2]

1. University of North Dakota, Mechanical Engineering, USA
2. University of North Dakota, Chemical Engineering, USA

In this paper, we will report the synthesis and characterization of novel porous structures by pyrolyzing lignin at different temperatures. We will report the microstructure and mechanical behavior of these interesting materials. X-ray tomography has been performed to study the intricate cellular structure of these porous foams. SEM studies have performed to further confirm the X-ray tomography findings. The mechanical behavior of these solids will be compared with different types of porous Carbon based foams. It is expected that these materials can be used for different applications.

Influence of Inhomogenity

Room: Coquina Salon A

Session Chairs: Ashley Hilmas, University of Michigan; Christian Thieme, Fraunhofer Institute for Microstructure of Materials and Systems IMWS

4:20 PM

(ICACC-FS2-008-2019) Properties relied on Internal Structure of Ceramics from 3D View of X-ray tomography

S. Wang*[1]; L. Zhang[1]

1. Institute of Metal Research, Shenyang National laboratory of Materials Science, China

X-ray tomography (XRT) is a unique tool for ceramic characterization with 3D global view of the internal structure in a nondestructive way. This method facilitates the research of some specified properties related to the ceramic internal structures, such as the porosity and the composites. Highly porous ceramic was quantitatively characterized for the morphological parameters within the 3D volume. The size, shape of the pores as well as their distribution and connectivity, can be evaluated for the property of thermal insulation with the supplementary of modeling and analysis. As a bio-inspirited material, sea urchin spine is composed of bio ceramic and organic substance with a hierarchical structure. The complex 3D volume of

a sampled structure was digitalized with the XRT techniques. The meshed 3D volume can be input Finite Element Analyses (FEA) for mechanical test with the 3D global scale. Compression of the real structure model revealed that the stress concentrates along the dense growth rings and dissipates through the strut structures. It implied that the rationally constructed hierarchical structure in nature play an important role in high strength-to-weight property. Its mechanical property might be optimized for potential applications of bone defect repair.

4:40 PM

(ICACC-FS2-009-2019) Contact-free imaging of the thermal conductivity of ceramic thin films at the nanoscale

S. Kazemian[1]; S. Ezugwu[1]; G. Fanchini*[1]

1. University of Western Ontario, Physics and Astronomy, Canada

Virtually any technique used so far to image the thermal properties of ceramic thin films at the nanoscale require to position the sample in contact with voluminous atomic-force microscopy (AFM) probes acting as undesirable thermal sinks. Thermoreflectivity, an optical technique in which thermal transport properties are measured by contactlessly probing the heat-induced changes in reflectivity at the air-sample interface, has been utilized to investigate the thermal properties of solids at the macroscopic and microscopic level, but, so far, has been diffraction-limited in its applicability at the nanoscale. Here, we present near-field scanning thermoreflectance imaging (NeSTRI), a new scanning probe technique derived from near-field scanning optical microscopy (NSOM). An aperture-type AFM/NSOM in non-contact mode is used to determine the thermoreflectance of 2D ceramic materials at sub-wavelength resolution. While the order of magnitude of the thermal conductivity measured is consistent with the corresponding macroscopic measurements, NeSTRI is capable of imaging the local effects on the thermal conductivity of edges and wrinkles in graphene and 2D ceramic domains. Our technique is uniquely suited to investigate the thermal properties in a large class of nanoscale 2D materials.

5:00 PM

(ICACC-FS2-010-2019) Contribution of μ-tomography X to the understanding of thermal radiative transfer in cellular materials

B. Rousseau*[1]

1. LTeN UMR6607, France

Knowledge of thermal radiative properties (TRPs) of cellular materials is mandatory for engineering systems and processes where the energy contribution of thermal radiation is significant. A first group of TRPs can be directly measured (reflectance, transmittance, emittance) trough experimental facilities until homogenous conditions of heating are ensured. Another second group (absorption and scattering coefficient, scattering phase function) is needed to solve the Radiative Transfer Equation (RTE) that is unavoidable to solve the generalized heat equation when radiation exchanges occur. Properties of the second group can be deduced from the first one by applying some inverse processes involving (i) an optical bench based often based on spectrometer and (ii) a direct model based on the RTE. Nevertheless, the exact resolution of the RTE is tricky making that simplification of the absorbing/scattering behavior of studied porous compound must be realized. This approximation ignores the real texture of the material The introduction of X-ray μ-tomography has opened new doors (i) to compute all the TRPs (ii) to understand the main length scales which govern the TRPs on real samples (iii) to validate material generation algorithms. Key results will be recalled and new challenges will be given especially when textural information is passed over by X-ray μ-tomography.

FS4: Green Technologies and Joining of Ceramics

Future Directions of Materials Innovation and Joining Technology

Room: Tomoka C

Session Chairs: Federico Smeacetto, Politecnico di Torino; Jonathan Ligda, US Army Research Laboratory

8:30 AM

(ICACC-FS4-016-2019) Laser supported heating: An efficient technology for the joining of ceramics (Invited)

M. Herrmann*[1]; M. Graffé[1]; W. Lippmann[1]; A. Hurtado[1]

1. Technische Universität Dresden, Institute of Power Engineering, Germany

Advanced ceramics like silicon carbide (SiC), alumina (Al_2O_3) and zirconia (ZrO_2) play an important role in the field of high temperature engineering. Many applications require thermal resistant, mechanical strong and gas-tight joints or seals of ceramic components. At TU Dresden was developed a technology using laser beam as heating source in the joining process. Important for that kind of heating are optical properties like absorptivity and reflectivity as well as thermo-physical properties (heat conductivity, coefficient of thermal expansion). The above-mentioned ceramics are varying in their properties what leads to different laser-material-interactions and as a result in different heating behavior. The laser supported joining by glass and glass-ceramic interlayers on samples of the mentioned ceramics will be demonstrated. The microstructural characterization as well as the measurement of mechanical strength and gas-tightness will show that the short-time (1-3 minutes) laser process lead to results comparable with furnace joining. This illustrates the energy efficiency of the laser supported joining process. Furthermore, will be shown examples where this technology is the only way for the manufacturing for ceramic components.

9:00 AM

(ICACC-FS4-017-2019) Fabrication of Interconnects on ceramic substrates using active brazing materials

M. Rohde*[1]; H. J. Seifert[1]; V. Schulze[2]; E. Götze[2]; T. Stoll[3]; J. Franke[3]

1. Karlsruhe Institute of Technology, Institute for Applied Materials, Germany
2. Karlsruhe Institute of Technology, Germany
3. Friedrich-Alexander Universität Erlangen-Nuernberg, Germany

Within this work, we have studied an alternative fabrication process for the deposition of electrical conducting lines onto ceramic substrates. In order to apply these power lines in a one-step process we used active brazing materials, which were designed to join metals to ceramics within one heating cycle. The brazing materials was selected from the ternary alloy system Ag-Cu-Ti which is commercially available as a paste, but we also extended our studies to alloys Ag-Ti, Cu-Ti and Sn-Ag-Ti with specifically designed compositions. For the ceramics, we used thin AlN and Al_2O_3 substrates (Ceramtec AG, Germany) with a thickness of 0.6 mm as well as alumina, which was produced with a 3D-printing process (Cerafab7500, Lithoz, Austria) with a subsequent sintering procedure. With the results of our studies, we could demonstrate the ability of this alternative process for the fabrication of power lines on ceramic surfaces. Due to the good wetting behaviour, the conducting lines are mechanically and thermally very stable. The electrical resistance varies with the fraction of the activating element Ti but also with the complexity of the alloy. Compared to pure Cu, the resistance increase in the eutectic Ag-Cu-Ti is only 20%.

9:20 AM

(ICACC-FS4-018-2019) Joining of ceramics using electric field induced current across the interface

H. Charalambous*[1]; S. K. Jha[1]; Q. Yang[1]; R. T. Lay[1]; T. Tsakalakos[1]

1. Rutgers University, Materials Science and Engineering, USA

The flow of current through ceramic green compacts under applied electrical field has been demonstrated to dramatically enhance the interdiffusion in oxide ceramics. This technique can be further applied to the joining of ceramic components, demonstrated in the current study for the test case of a ZnO-TiO_2 diffusion couple. Conventional heating to 1300°C under moderate contact pressure of 10 MPa is found to be insufficient to join the two components. However, a >10 μm thick Zn_2TiO_4 interface is formed, which welds the ZnO and TiO_2 bulk ceramics, when sintered under electrical field. Elemental, orientational, and phase analysis across the interface is performed using EDS, EBSD, and Raman Spectroscopy. Flash joining offers a new route to joining of ceramic-ceramic components.

9:40 AM

(ICACC-FS4-019-2019) Enhancement in electron transfer properties in $BaTiO_3$ based embedded flexible electro-active sensors towards development of wearable energy harvesting textiles

W. Tuff*[1]; J. Lor[1]; S. Ahmed[2]; S. Banerjee[1]

1. California State University, Fresno, Mechanical Engineering, USA
2. SUNY Buffalo State, Mechanical Engineering, USA

Piezoelectric energy harvesters convert waste energy from the moving components of a system into useful electrical energy. This energy can then be utilized to enhance the system's performance or can be used to power supplementary systems. Therefore, wearable energy harvesting textiles are a potential tool that can be used to collect the waste energy from the movements of people in their everyday lives. Lead-free, barium titanate-based composite textiles were fabricated with the volume fraction of barium titanate varying from 0.10 to 0.70, and the moles of barium titanate per unit volume of sol-gel was kept constant. The conductance of the textile was modified using multiple techniques (application of copper tape, incorporation of metallic fibers, and sputtering of a metallic layer). The dipoles of the composite were aligned using a corona plasma technique. The piezoelectric strain coefficients (d33 and d31) were measured using a piezometer, and the electrical properties (impedance, conductance, capacitance, and phase angle) were measured with an impedance analyzer. The surface morphology and particle distribution were analyzed using a scanning electron microscope.

10:00 AM

(ICACC-FS4-020-2019) Small Molecule Adsorption on the Semiconductor/Ionic-Liquid Interface and Application to Green Sensing and Conversion (Invited)

Z. Wang*[1]; K. Riley[1]

1. Xavier University of Louisiana, Chemistry Dept., USA

This project entails both theoretical and experimental studies aimed at investigating the structures of semiconductor/ionic liquid (SC/IL) interfaces, effective selective adsorption on these interfaces, effects of adsorption on adsorbant bond strength, and understanding of the molecular mechanisms involved therein. This fundamental study will have strong implications for any future projects involving miniaturized sensors, gas separation, or high-performance green catalytic conversion utilizing ILs and/or SCs. ILs generate a very unique solid-like interface; consequently, they can generate extremely high electric fields and induce exceptionally large charge densities at the solid/liquid interface. The electric double layer (EDL) charge density can be much higher than traditional field-effects and allows for new levels of electrostatic modulation to be accessible. The pure ionic structure of IL itself also brings an electrostatic environment, which can potentially be manipulated for facilitating certain small molecule activation. However, electrified IL/electrode interfaces, especially SC's, with adsorbed gas molecules have not been either theoretically or experimentally studied.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Design, Life Prediction and Tribological Performance

Room: Coquina Salon D

Session Chairs: Mathias Woydt, BAM Federal Institute for Materials Research and Testing; Amjad Almansour, NASA Glenn Research Center

8:30 AM

(ICACC-S1-046-2019) The potential of NbC-TiC_7N_3 cermets as cutting tools and for wear protection

M. Woydt*[1]; H. Mohrbacher[2]; E. Cannizza[3]; J. Vleugels[4]; S. Huang[4]

1. BAM Federal Institute for Materials Research and Testing, Germany
2. Niobelcon bvba, Belgium
3. EHT-Engineering Consulting Ltd., Brazil
4. K.U. Leuven, MTM, Belgium

The present paper illuminates the functional profile of nickel bonded NbC-TiC_7N_3-xMeC for machining and wear protection. The tribological profile of rotating disks made in NbC-yNi-TiC_7N_3-xMeC mated against stationary toroids in alumina (99.7%) were determined under unidirectional sliding tests (0.1 m/s to 8.0 m/s; 22°C and 400°C) under unlubricated (dry) conditions. In addition, the microstructure and mechanical properties (4-point bending, K_{IC} notch) were determined as well, including the elastic modulus and hot hardness up to 1.200°C and compared to Ni-bonded NbC and Co-bonded WC. The hardness-toughness profile of NbC-TiC_7N_3 grades match those of WC grades. Apart from the aforementioned parameters, the properties depend from the powder processing and sintering conditions. Abrasive wear (G65) as well as hard turning under emulsion and dry semi-finishing turning of different alloys (C45E (1045), 42CrMo4 Q&T and AlSi9Cu4Mg) will be compared to commercially available WC-co grades.

8:50 AM

(ICACC-S1-047-2019) Wear resistance and surface changes of $MgAl_2O_4$ spinel ceramic after abrasion and scratch exposure

S. von Helden*[1]; J. Malzbender[1]; M. Krüger[1]

1. Forschungszentrum Juelich, Institute of Energy and Climate Research (IEK-2), Germany

Transparent ceramics and in particular spinel have high potential for use as armor ceramics and also for sensor application. For this type of application, the optical and the mechanical properties are highly important. In the current work a transparent spinel ceramic is compared to different types of glasses as well as a polymer in terms of their optical and mechanical properties. In addition, a laminate system consisting of a thin top layer of the spinel glued on a transparent substrate is investigated. This combines the benefits of the ceramic with a lighter and cheaper glass or polymer to achieve a good cost-performance ratio. The mechanical behavior of the materials are compared on the basis of various depth-sensitive indentations and ring-on-ring bending tests, deriving representative load dependent hardness, elastic modulus and fracture stress values. The specimens have been analyzed after certain exposure times of sand blasting and different loads during scratch tests via balance, confocal laser scanning and optical microscopes to define the wear resistance in the form of surface roughness, mass loss, critical loads and initial damage.

9:10 AM

(ICACC-S1-048-2019) Evaluation of hydration free energy of glass by electric potential change during chemical mechanical polishing

S. Suda*[1]; R. Fukuzaki[1]; K. Kawahara[2]

1. Shizuoka University, Engineering, Japan
2. Japan Fine Ceramics Center, Japan

Chemical mechanical polishing (CMP) is an essential planarization technique of glass. We claim that the chemical process of CMP would be charge transfer reactions of both abrasives and glasses, and it would result in hydration layer on the surface of glasses. If the chemical process is followed by our suggestion, the charge transfer reactions of CMP process could be clarified with electric potential change. We then set up a novel CMP model system using lanthanum-doped cerium oxide (LDC) dense plate and soda-lime glass to measure electrical potential during polishing. The electric potential between LDC plate and water solution were continuously measured by changing the rotation of LDC plate under a constant load. The potential was decreased by inducing the rotation reversibly, and the change in potential was slightly decreased with increasing rotation rate. LDC abrasive works as mechanical polishing as well as chemical polishing. The strength of mechanical polishing is proportional to rotation rate by Preston's law. Therefore, potential change value extrapolated to the rotation rate of zero would correspond to Gibbs free-energy of the chemical process. The free-energy would almost coincide with hydration free-energy.

9:30 AM

(ICACC-S1-049-2019) The Effect of Combined Cyclic Loading on Conductance of Resistive Switching Material HfO_2: A Molecular Dynamics Study

M. Kayser*[1]; A. Adnan[1]

1. University of Texas, Arlington, Mechanical, USA

Because of the less power consumption, excellent scalability, high endurance life, Hafnium dioxide (HfO_2) is considered one of the most promising materials to be used for memristor. Memristors are two terminal devices able to change their conductance from a High Conductance State (HCS) to a Low Conductance State (LCS) to mimic the activity of biological synapse in the brain. Although the fatigue behavior of HfO_2 was reported for electrical loading, the combined thermal and electrical effect has not been studied yet. In this work, Molecular Dynamics simulation has been carried out to investigate the mechanical behavior of HfO_2 thin films under simultaneous electrical and thermal cyclic loading. The vacancy creation that is related with the conductance of HfO_2 is observed due to the combined loading. In order to obtain a fundamental understanding of this material behavior, several MD simulations are carried out by varying key parameters such as film thickness and temperature.

10:10 AM

(ICACC-S1-050-2019) Slow crack growth of boron nitride for electric propulsion

J. Salem*[1]; J. Mackey[2]; H. Kamhawi[2]

1. NASA Glenn Research Center, Materials and Structures, USA
2. NASA Glenn Research Center, Electric Propulsion Systems, USA

The Deep Space Gateway requires thruster systems to maintain spatial position. One control system being considered involves Hall thrusters. Historically, Hall thruster discharge channels have used several grades of hot pressed hexagonal boron nitride. This study compliments data presented at ICACC 2018 and investigates the fracture toughness and slow crack growth parameters of several commercially available boron nitride grades including HP, M, M26, and Shapal Hi-M. The prior work revealed that some grades of BN absorb water and change strength thus presenting a philosophical conundrum on crack growth test methods. Advantages of different test methods will be discussed. The grades selected for this study are of interest because their available billet size is sufficient for Hall thruster discharge channels, or because they have heritage in Hall thruster applications. Ultimately, the data will be used to perform material selection, system design and reliability analyses.

10:30 AM

(ICACC-S1-051-2019) Effect of microcrack propagation on the creep deformation behavior of an orthogonal 3-D woven SiC fiber/SiC matrix composite under tensile loading at elevated temperatures

Y. Ikarashi*[1]; T. Aoki[2]; Y. Asakura[1]; T. Ogasawara[1]

1. Tokyo University of Agriculture and Technology, Japan
2. Japan Aerospace Exploration Agency, Japan

This study examined monotonic tensile and creep deformation behaviors of an orthogonal 3-D woven SiC fiber (Tyranno ZMI) / BN interphase/ SiC matrix (CVI+PIP-SiC) composite under tensile load at 1200°C in vacuum. The matrix crack propagation in transverse (90°) layers was evaluated using the digital image correlation (DIC) method. Non-linear viscoelastic behavior was observed above the proportional limit stress (80 MPa). The experimental results implied that the transverse cracks significantly affected the non-linear viscoelastic behavior of the composite. A creep deformation model was proposed by incorporating the microscopic damage propagation model into the shear-lag model. The predicted creep deformation agreed well with the experimentally obtained results.

10:50 AM

(ICACC-S1-052-2019) Thermomechanical fatigue damage evolution and lifetime prediction of fiber-reinforced ceramic-matrix composites

L. Li*[1]

1. Nanjing University of Aeronautics and Astronautics, College of Civil Aviation, China

The thermomechanical fatigue damage evolution and lifetime prediction of fiber-reinforced ceramic-matrix composites (CMCs) are investigated using the micromechanical approach. The multiple damage mechanisms of matrix multicracking, fiber/matrix interface debonding/sliding/wear, and interface oxidation under thermomechanical fatigue loading are considered. The relationships between the damage mechanisms, damage models and thermomechanical fatigue lifetime are established. The experimental thermomechanical fatigue damage evolution and lifetime are predicted.

11:10 AM

(ICACC-S1-053-2019) Effect of Graphene Addition on Crack Propagation Resistance in Glass Fibre Reinforced Polymer Matrix Composite

B. Shanmugavel*[1]; R. Paskaramoorthy[2]; G. Vigneshwaran[1]

1. Anna University, Mechanical Engineering, India
2. University of the Witwatersrand, Johannesburg, School of Mechanical, Industrial & Aeronautical Engineering, South Africa

The effect of graphene nanoplatelets (GNPs) on enhancing the interlaminar fracture toughness of glass fiber/epoxy composites was investigated. The GnPs were physically deposited on the fiber surface by the dip coating technique. The composites were fabricated by hand layup technique followed by the compression molding process. Mode-I fracture test was conducted on the composite specimens. Crack propagation was studied by the digital image correlation (DIC) technique. Mode-I fracture toughness for composites loaded with 0.5 wt.% GnPs showed improvement by an average of 60% when compared to the pristine composites. It is concluded that the addition of GnPs produces a strong fiber/matrix interface bonding which effectively limits the crack propagation.

11:30 AM

(ICACC-S1-054-2019) Static and Dynamic Compression Strength of Ceramics

J. Swab*[1]; C. Meredith[1]

1. Army Research Laboratory, USA

The intrinsic compression strength of ceramics can be very difficult to determine. The specimen geometry and fixture used to apply the load, if not properly designed, can result in the generation of tensile stresses that lead to premature fracture and misleadingly low strength values. Often the compression strength is inferred from hardness values but this is not appropriate for ceramic materials. Since compression strength is an input parameter in numerous modeling and simulation packages used to predict performance in some applications it is imperative that the compressive strength of the ceramics be properly and accurately measured. Candidate armor ceramics such as hot-pressed boron carbide and alumina as well as sintered and hot-pressed versions of silicon carbide were machined into dumbbell-shaped specimens that were designed to induce fracture from within the gage section while minimizing the stress concentrations that can lead to the undesirable tensile stresses. Quasi-static experiments were performed using a screw-driven load frame and the fracture process was recorded with a high speed camera. Dynamic experiments were performed using a split-Hopkinson pressure bar setup with bars having the same diameter as the specimen and an ultra-high speed camera to record the fracture process. This presentation will summarize the results to date and identifies if a change in strain rate influences the compression strength value

Mechanics, Characterization Techniques, and Equipment

Room: Coquina Salon D
Session Chairs: Raul Bermejo, Montanuniversitaet Leoben; Matthew Appleby, The University of Akron

1:30 PM

(ICACC-S1-055-2019) Characterization of crack propagation in ceramic matrix composites at high temperature

E. Maillet*[1]; M. Schuster[1]; V. Gupta[1]; A. Singhal[1]; G. Zorn[1]; D. Dunn[1]

1. GE Global Research, USA

Understanding the durability of ceramic matrix composites (CMCs) requires a thorough understanding of damage initiation and propagation as a function of microstructure, stress, temperature, and environment. The present paper discusses recent efforts in testing and characterization of crack propagation in CMCs at high temperature, and how these techniques help quantify the contribution of mechanical and environmental degradation to damage progression.

1:50 PM

(ICACC-S1-056-2019) Mode II Interlaminar Fracture of a SiC/SiC Ceramic Matrix Composite (CMC) using the End-Notched Flexure (ENF) Test

M. J. Presby*[1]; M. Kannan[1]; G. N. Morscher[1]; C. Godines[2]; A. Eftekharian[2]; J. Ahmad[2]; F. Abdi[2]; S. R. Choi[3]

1. University of Akron, Mechanical Engineering, USA
2. AlphaSTAR Corporation, USA
3. Naval Air Systems Command, USA

Delamination is a common failure mode observed in ceramic matrix composites (CMCs) and occurs as a result of applied interlaminar tensile and shear stresses exceeding the interlaminar strength. As CMCs are further implemented into aerospace applications the need to understand their interlaminar failure becomes increasingly important. While significant contributions have been made toward understanding the mode I fracture toughness of CMCs, limited work exists on mode II. This work investigates the mode II fracture toughness of a melt-infiltrated SiC/SiC CMC at ambient temperature using the end-notched flexure (ENF) test. Acoustic emission (AE), electrical resistance (ER), and digital image correlation (DIC) are used to monitor crack initiation and propagation. Preliminary results obtained from multi-scale modeling will also be presented along with a discussion on the extension of mode II testing to elevated temperature.

2:10 PM

(ICACC-S1-057-2019) Study of direct current spreading in ceramic matrix composites

Y. P. Singh*[1]; R. Panakarajupally[1]; R. Mansour[2]; D. Koch[3]; G. N. Morscher[1]

1. The University of Akron, Mechanical Engineering, USA
2. Teledyne Scientific Company, USA
3. Institute of Structures and Design, Germany

We propose a simple electrical model based on a ladder-network of resistors to study the spreading of direct current in ceramic matrix composite materials. The results of simulations are compared with the experimentally measured data on different rectangular pieces of laminates and woven-fiber composites. Good agreement between the two data set is found in case of laminate composites and some deviations are observed in case of woven fiber composites. The proposed mechanism of current flow helps in estimating the through thickness resistivity of CMC materials from a known in-plane resistivity. The estimated values are verified by comparing with the measured through thickness resistivities using an in-house built copper disc electrode device which works on 4-probe principle of measuring resistivities.

2:30 PM

(ICACC-S1-058-2019) Modeling of the electrical resistivity of melt-infiltrated ceramic matrix composite laminates: Effects of microstructure and transverse matrix cracking

M. P. Appleby*[2]; E. Maillet[1]; G. N. Morscher[3]

1. GE Global Research, USA
2. NASA Glenn Research Center, USA
3. University of Akron, USA

Electrical resistivity (ER) measurements show promise for assessing the health of ceramic matrix composite (CMC) components. To realize the full potential of ER as an inspection and monitoring technique for CMCs, it is important (1) to understand the effects of microstructure and constituents on the composite's ER, and (2) to be able to accurately predict the electrical response of a CMC to damage. In the present paper, current flow in an as-produced CMC was modeled in order to quantify the effects of microstructure and constituent properties on the electrical resistivity of CMC laminates. A combined mechanical/electrical micromechanics-based model was then developed to predict the ER response of CMC laminates to transverse matrix cracking.

3:10 PM

(ICACC-S1-059-2019) In situ Stable Fracture of Ceramic Interfaces Tested under Environmental Conditions

F. Giuliani*[1]; G. Sernicola[1]

1. Imperial College London, United Kingdom

The fracture toughness of ceramics is often dominated by the structure of their grain boundaries. Our capacity to improve the performance of ceramic components depends on our ability to investigate the properties of individual grain boundaries. To measure the fracture energy of individual interfaces we have used a double cantilever geometry to obtain stable crack growth and we calculate the fracture energy under a constant wedging displacement. Our tests have proved it is possible to initiate and stably grow a crack in a controlled manner in ceramic materials for several

microns. This approach has been validated on SiC where it gives a good approximation of the surface energy and then extended to SiC bi-crystals along with Ni-Al2O3 interfaces where crack blunting and bridging mechanism can be observed and measured. Finally we will show the effect of moisture on the fracture energy of a individual oxide interface.

3:30 PM

(ICACC-S1-060-2019) Effect of surface flaws and their orientation on the mechanical strength of brittle single crystals for microelectronic applications

M. Gruber*[1]; I. Kraleva[2]; P. Supancic[1]; D. Kiener[1]; A. Leitner[1]; R. Bermejo[1]

1. Montanuniversitaet Leoben, Austria
2. Materials Center Leoben, Austria

Brittle single crystalline materials are widely used in microelectronic systems due to their exceptional electrical and optical properties. In this context, $LiNbO_3$ and $LiTaO_3$ single crystals have found an important application as Surface Acoustic Wave (SAW) filters for mobile devices. Even though they are used because of their functionality, structural integrity is often a limiting factor especially when a certain surface roughness is required for an enhanced performance. To investigate onset and effect of irreversible deformations, which occur in the grinding and polishing processes, nanoindentation and nanoscratch experiments were performed on mirror-polished $LiNbO_3$ and $LiTaO_3$ single crystalline specimens. Plastic deformation and cracks were found along certain crystallographic directions, which lead to a significant reduction in biaxial strength. The alignment of these introduced artificial defects with respect to crystallographic planes has thereby also an influence on the mechanical performance. To explain the observed anisotropic fracture behaviour, in-situ micromechanical tests of notched micro-cantilevers were performed together with DFT simulations.

3:50 PM

(ICACC-S1-061-2019) On Crack Branching Angles

G. D. Quinn*[1]

1. NIST, Materials Measurement Sciences Div, USA

Cracks branch when they run at high velocities. The branch angle is directly related to the stress state at fracture. Observations of crack branching angles are useful in fractographic analysis since they can be used to estimate the stress state in a part when it breaks. Uniaxial loading causes branch angles of 30 to 45 degrees, although scatter can be large. Biaxial loading causes larger branching angles. Various authors have examined the angles over the years. For example, Roy Rice discussed them in on six pages in his 1984 fractography review paper at an ASTM conference on Fractography of Ceramics and Metals. The first quantitative trend of crack branching angle with stress state was shown by Frank Preston in his two-page paper in the Journal of the American Ceramic Society in 1935. It now appears that the branching angle trend he showed is in error. Over the decades many researchers including Dr. Janet Quinn have obtained smaller angles than those shown by Preston. A critical (but not widely known) paper by J. Kalthoff at the Fraunhofer Institute in 1973, analyzed the crack branching angle for the uniaxial stress state. His results, plus data from dozens of new tests that I have done, using a variety of loading configurations, indicate that Preston's 1935 trend must be corrected.

4:10 PM

(ICACC-S1-062-2019) Prediction of fracture in brittle solids and components using a stress-energy coupled criterion

R. Bermejo*[1]; O. Sevecek[2]; E. Martin[3]; D. Leguillon[4]

1. Montanuniversitaet Leoben, Institut fuer Struktur- und Funktionskeramik, Austria
2. Brno University of Technology, Institute of Solid Mechanics, Mechatronics and Biomechanics, Czechia
3. Université de Bordeaux, Laboratoire des Composites Thermo-Structuraux, France
4. Sorbonne Université, Institut Jean Le Rond ∂'Alembert, France

Linear Elastic Fracture Mechanics (LEFM) describes the conditions for crack propagation, assuming that an initial crack exists in the material. To predict the onset of cracks in brittle solids another theory must be considered, i.e. the Finite Fracture Mechanics (FFM) approach. FFM considers that the crack originates/extends by a jump of a finite length. A widely used criterion within FFM for fracture prediction is the stress-energy coupled criterion (CC). According to this criterion a crack initiates with a "finite" length increment if two conditions (i.e. stress and energy conditions) are fulfilled simultaneously – namely $\sigma(a) \geq \sigma_c$ and $G_{inc}(a) \geq G_c$, where s is the stress along the prospective crack path, G_{inc} is the incremental energy release rate for finite crack increments, and σ_c and G_c are material properties. Several examples are shown where the CC has been applied to predict edge cracking in ceramic laminates and the onset of cracks in ceramic-metal architectures. The effect of residual stress, geometry and material properties is analyzed and compared with experiments. The use of the CC in predicting crack formation in ceramic systems is currently used in thin films structures as well as in bulk ceramics under different loading configurations.

4:30 PM

(ICACC-S1-063-2019) Quasi-plastic zone characterization of regular and Si-doped boron carbide

S. Xiang[1]; K. Y. Xie*[1]; B. Yang[2]; C. Hwang[2]; R. Haber[2]

1. Texas A&M University, Materials Science and Engineering, USA
2. Rutgers University, USA

Boron carbide (B_4C) is a hard and lightweight material, which has many engineering applications. However, B_4C loses its strength and toughness when subjected to high shear stresses. To improve its mechanical properties, the previous computation work has suggested micro-alloying B_4C with Si. Very limited understanding of the failure mechanism of boron carbide, both Si-free and Si-doped, under high shear stress conditions is due to the lack of direct experimental observation at the relevant length scale for damage zone. Here we investigate the local deformation microstructure of regular and Si-doped boron carbide under indents, using a novel precession electron diffraction technique and high-resolution transmission electron microscopy. We observed that Si-doped boron carbide displays dispensed micro-cracks, while Si-free boron carbide exhibits major local cracks and low interfaces.

S3: 16th International Symposium on Solid Oxide Cells (SOC): Materials, Science and Technology

Air Electrode Performance

Room: Crystal
Session Chair: Narottam Bansal, NASA Glenn Research Center

8:30 AM

(ICACC-S3-042-2019) Computational Design of Solid Oxide Fuel Cell Cathodes from First-Principles (Invited)

R. Jacobs*[1]; D. Morgan[1]

1. University of Wisconsin - Madison, Materials Science and Engineering, USA

Perovskites are typically used as cathodes in solid oxide fuel cells (SOFCs), and enable practical electrocatalysis of O_2 gas to O^{2-} in the solid state. However, these cathodes typically require higher temperatures than desirable, generating strong interest in the development of more catalytically active cathode materials that can operate efficiently at lower temperatures. Both the discovery of new electrode compounds and enhancement of current commercial materials, coupled with enhanced fundamental understanding of the factors governing the catalytic activity and oxygen transport properties of these materials will help enable their widespread use. Density Functional Theory (DFT) methods can provide insights into the bulk, surface, and catalytic properties of perovskite oxides for SOFCs, helping interpret experimental observations and providing guidance for cathode materials design. In this talk, we discuss how one can use DFT methods to screen for new SOFC electrode materials and understand factors governing the bulk stability, defect chemistry, and oxygen transport through these materials using electronic structure descriptors. Materials design principles to simultaneously maximize the stability and catalytic activity of a perovskite will be discussed, as well as the effect of strain on the catalytic activity, defect formation and oxygen transport in thin film perovskite SOFC cathodes.

9:00 AM

(ICACC-S3-043-2019) SOFC Cathodes Operated under Aggressive Conditions: AC Impedance, Durability Testing, and Microstructural Analysis

C. Deng*[1]; M. McAllister[1]; A. Cai[1]; M. R. De Guire[1]; A. H. Heuer[1]

1. Case Western Reserve University, Materials Science and Engineering, USA

Area specific resistance (ASR) of solid oxide fuel cells (SOFC) typically increases during operation. Rate of ASR change over time provides a primary measure of cell degradation rate. ASR may be measured from the DC cell output voltage at constant current density (DC ASR), and from electrochemical impedance spectroscopy (EIS) measurements during operation. Whereas DC ASR is the more direct and relevant indicator of cell performance, ASR from EIS may give insights into mechanisms and locations of cell degradation. Button cells with cathodes of lanthanum-strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm z}$) with excess manganese (Mn/(La+Sr) = 1+w, where w= 2%, 5%, or 11%) underwent 200–600 hours of operation under conventional or aggressive conditions (high temperature, high current density, and/or low oxygen activity) with periodic linear sweep voltammetry (LSV) and EIS measurements. Post-test microstructural analysis consisted of transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS), focused ion-beam scanning electron microscopy (FIB/SEM) and 3D reconstruction. This presentation discusses relationships between the EIS analyses and previously reported microstructure-performance correlations. In particular, we explore whether the EIS findings reflect observed changes in cathode microstructure of the various LSM compositions.

9:20 AM

(ICACC-S3-044-2019) The electrochemical performance of LSM with A-site non-stoichiometry under cathodic polarization

J. Liu*[2]; T. Yang[1]; Y. Yu[2]; H. O. Finklea[3]; H. Abernathy[2]; T. L. Kalapos[2]; G. Hackett[1]; P. Ohodnicki[1]

1. NETL, USA
2. AECOM, USA
3. West Virginia University, Eugene Bennett Department of Chemistry, USA

The activation behavior of a LSM based-cathode in a SOFC is characterized by a rapid reduction in the electrode polarization resistance after cathodic current passage treatment. Due to the sensitivity of the activation process to the operation history, a comprehensive study was carried out to reveal the relationship between the activation conditions, the steady state cathode performance and the long term stability. The effects of current density and overpotentials on the activation behavior of a LSM based electrode were investigated. The impacts of temperature and oxygen partial pressure to the activation process and final performance are also discussed. Studies on LSM electrodes with different A site cation deficiency suggested that the defect chemistry of LSM plays a significant role in the activation process. The final performance of the LSM cathode, on the other hand, was mostly determined by the activation process and the working condition. The A site non-stoichiometry only shows minor impact. Numerical simulation of the LSM-based cathode was conducted with a multi-step oxygen reduction reaction (ORR) mechanism for a better understanding of the nature of the activation process. The results are of great relevance as the electrode performance depends on not only the fabrication but also on the initial break-in procedure.

9:40 AM

(ICACC-S3-045-2019) DC and AC single electrode studies of composite LSM/YSZ on a thick YSZ electrolyte over a range of oxygen partial pressures

A. Szendrei*[1]; T. D. Sparks[1]; A. V. Virkar[1]

1. University of Utah, Materials Science and Engineering, USA

Electrochemical impedance spectroscopy (EIS) is a ubiquitously used technique to characterize the behavior from both electrodes. Symmetric electrodes are often applied to an electrolyte and an implicit assumption of equivalent electrochemical behavior from both electrodes is utilized in the analysis. Individual electrode measurements are often desired; however, it is difficult to get accurate three-probe EIS measurements for thin electrolyte cells. Composite electrodes composed of 50 wt% Sr-doped $LaMnO_3$- yttria stabilized zirconia (LSM-YSZ) was applied to both sides of a thick cylindrical YSZ electrolyte. The sample was exposed to a range of oxygen partial pressures at a temperature of 611°C. For each atmospheric composition investigated the electrode polarizations were calculated from 4-point DC measurements using Kirchhoff's voltage law. Three-probe EIS was also performed on the sample. The DC and AC measurements compared well to each other. The electrode polarization resistance increased with decreasing O_2 partial pressure as expected. A large variation in the electrode polarization resistance was observed from the two electrodes despite the same application method.

Air Electrode: Powders, Fabrication, Contacting

Room: Crystal
Session Chair: Jason Nicholas, Michigan State University

10:20 AM

(ICACC-S3-046-2019) Development of New Materials to Improve the SOFC Supply Chain (Invited)

N. J. Kidner*[1]; C. Corwin[1]; N. Cooley[1]; M. Seabaugh[1]; S. L. Swartz[1]

1. Nexceris, LLC, USA

The accelerated electrification of large sectors of the economy such as transport and heating, and the intensified deployment of renewable energy sources provides enormous opportunities for advanced energy devices such as fuel cells and batteries. With increased demand, competition for key raw materials is likely to intensify, leading to a greater focus on new material formulations to meet future performance requirements while offsetting price volatility and decreasing supply chain risk. For example, the emergence of electric mobility has led to speculation over a future global shortage of cobalt, resulting in a rapid increase in cobalt prices. Supply chain management and raw materials security are therefore critical issues for SOFC developers. Nexceris is working with its partners to understand future material challenges and mitigate potential risks through the development of alternative formulations and manufacturing processes. This talk will highlight several examples including the development of cobalt-free electrode and coating formulations and the use of functional coatings to reduce material usage.

10:50 AM

(ICACC-S3-047-2019) Performance degradation by room temperature ageing of (La,Sr)(Co,Fe)O_3 cathodes in solid oxide fuel cells

Y. Xu*[2]; D. C. Cronauer[1]; V. Maroni[1]; L. Ge[1]; B. J. Ingram[1]; A. S. Hock[2]

1. Argonne National Lab, CSE, USA
2. Illinois Institute of Technology, Chemistry, USA

Porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) electrodes fabricated from LSCF powders from three different vendors were aged at room temperature under a humidified CO_2 atmosphere for 5 days. Electrochemical performance of both fresh and aged cells supported on YSZ electrolyte was measured by Electrochemical Impedance Spectroscopy (EIS). The performance of cells was found to decrease as a result of this accelerated aging protocol. Analysis of surface $SrCO_3$ was performed using Fourier-transform infrared spectroscopy (FTIR) and the amount of surface $SrCO_3$ was associated with granularity of powder and correlated with conductance of cells. Addition of Sr by infiltration of LSCF powders was also used to study Sr segregation and showed lower performance than the artificially aged cells. Raman spectroscopy revealed the existence of a spinel phase on surface of LSCF and high-resolution X-ray diffraction (HR-XRD) was used to show several other secondary phases exist, such as $SrCO_3$, M_3O_4 (M=Fe, Co), and La_2O_3, depending on the source and thermal history of the materials. The overall impacts of particle size, phase segregation, aging studies will be discussed.

11:10 AM

(ICACC-S3-048-2019) Optimised composite cathodes for SOFC

A. B. Richter[1]; G. Syvertsen-Wiig[1]; S. Labonnote-Weber*[1]; K. Wiik[2]; M. Angeltveit[2]

1. Cerpotech, Norway
2. NTNU, Materials Science and Engineering, Norway

Solid oxide cells run at high temperatures, which cause degradation and limit the lifetime of the device. In order to reduce the operating temperature new materials that allow a low area specific resistance (ASR) at low temperatures need to be developed. Two composite materials of the same composition but different synthesis routes have been investigated for cathode performance, both consisting of 70 wt% $Ce_{0.9}Gd_{0.1}O_2$ (CGO) and 30 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF). Composite A was prepared by spray pyrolysis at Cerpotech AS, consisting of a well-dispersed mixture of the two phases and thus a potential high density of reaction sites. Composite B was prepared as a conventional composite by mechanical mixing using pure LSCF and CGO. Cathode layers were deposited onto dense CGO pellets and heat treated at 650-1150°C. Symmetrical cells were tested for cathode performance by impedance spectroscopy at 600°C, 700°C and 800°C in dry air. The area specific resistance (ASR) at each operating temperature and the activation energy was calculated. Composite A showed lower ASR at all operating temperatures and the difference in ASR between the two composites, heat treated at 950°C, was significant. Compared with data reported for pure LSCF, composite A showed significantly lower ASR at 600°C. The improved properties of composite A were attributed to the synthesis method, giving a fine grained composite with a high density of triple phase boundaries.

11:30 AM

(ICACC-S3-049-2019) Thermal and Electrical Properties of LSCo-Mullite Composite Contact Material for Solid Oxide Fuel Cells

Y. Chou*[1]; N. L. Canfield[1]; J. F. Bonnett[1]; J. W. Stevenson[1]

1. Pacific Northwest National Lab, Materials, USA

Lanthanum strontium cobaltite (LSCo) is considered a major candidate for the cathode contact material because of its high electrical conductivity. Direct use of LSCo as a cathode contact material, however, often results in poor thermal cycle stability since LSCo has a much higher coefficient of thermal expansion (CTE) than the cell and interconnect materials. To solve this problem, we have proposed a composite approach by mixing LSCo with a potentially inert material of low CTE to match the composite's CTE with mating materials. In this work, mullite will be mixed with LSCo at volume fractions from 0.1, 0.2, 0.3, and 0.4, and sintered at typical stack firing temperatures. CTE will be measured in both the as-sintered and aged (500h) states. XRD will be used to determine chemical compatibility between mullite and LSCo. In addition, electrical conductivity will be measured at elevated temperatures and contact strength will also be measured by tensile testing of joined bilayers before and after thermal cycling.

11:50 AM

(ICACC-S3-050-2019) Interactions between magnesium silicate support substrate and state-of-the-art cathodes during co-sintering of an all-ceramic SOFC

S. J. Harboe*[1]; N. H. Menzler[1]; O. Guillon[1]; F. Grimm[1]; P. Lupetin[2]

1. Forschungszentrum Juelich, Institute of Energy and Climate Research, Germany
2. Robert Bosch, Applied Research 1 - Advanced Functional and Sintered Materials - Ceramic Materials and Processing (CR/ARM2), Germany

A novel, cost-efficient, all-ceramic Solid Oxide fuel Cell (SOFC) is investigated. The design includes a low-cost mechanical support material; a porous membrane made of a doped magnesium silicate, on the cathode (air) side of the cell. The manufacturing route involves a single step co-firing process at <1300°C of the support and all functional layers. This is significantly lower than the maximal temperature applied in the usual SOFC manufacturing sequence, but higher than the usual sintering temperature of the cathodes. So far, the effects of the use of magnesium silicate as support material and the co-firing production route on performance and lifetime of this SOFC concept are scarcely examined. Thus, the present investigations are analyzing the interactions between the support material and candidate cathode materials occurring during the high temperature sintering step. Various cathode materials are investigated. Inter-diffusion and secondary phase formations between the layers are characterized by means of energy dispersive X-ray spectroscopy and X-ray crystallography. The effect of chemical interactions on electrochemical performance is investigated with electrochemical

impedance spectroscopy. As well, the outcomes of the co-firing on the macro scale geometry and the microstructural properties of selected cathode materials are evaluated.

Proton Conducting Fuel Cells I

Room: Crystal
Session Chair: Kiho Bae, Korea University

1:30 PM

(ICACC-S3-051-2019) Reversible Electrochemical Cells for Fuel to and from Electricity (Invited)

S. M. Haile*[1]; S. Choi[1]

1. Northwestern University, Materials Science and Engineering, USA

Over the past decade, the availability of electricity from sustainable energy sources has risen dramatically while the cost has fallen steeply. These factors have driven a surge in activity in the development of energy storage technologies. While much of this effort has been directed towards photocatalytically generated solar fuels and grid-scale batteries, reversible hydrogen electrochemical cells offer untapped opportunities. In particular, electrochemical cells based on proton conducting ceramic oxides are attractive candidates for interconversion between hydrogen and electricity. However, despite high conductivity in protonic ceramic oxides, electrochemical performance has remained low. Moreover, the most commonly pursued electrolyte compositions suffer from poor chemical stability. We describe here recent progress achieved using a combination of three advances: a new electrolyte composition, a new air electrode, and processing methods to decrease the contact resistance between these two components. The resulting cells display exceptional power densities in fuel cell mode. In electrolysis mode, the electricity-to-hydrogen conversion efficiency is limited by electronic leakage across the cell, but is nevertheless attractive. In addition, the cells are extremely stable over hundreds of hours of operation and dozens of cycles.

2:00 PM

(ICACC-S3-052-2019) A Novel Triple Conducting Electrode for Fast Hydrogen Production in Protonic Ceramic Electrochemical Cells

H. Ding*[1]; W. Wu[1]; C. Jiang[1]; T. He[1]; D. Ding[1]

1. Idaho National Lab, USA

Solid oxide electrolysis cell is an attractive electrochemical technology to store renewable energies by producing hydrogen which is a clean and effective energy carrier. Recently the development of protonic ceramic electrochemical cells has shown the potential of reducing operating temperature down to 500 °C, which is promising to mitigate relevant tehnical problems involved in material system, stack operation and manufacturing cost. For fast hydrogen production at intermediate temperatures, steam electrode is critical to water splitting reaction which requires triple phase conducting material to extend the catalysis throughout the entire electrode. However, there are few material candidates proved to show proton, electron and oxygen ion conductivity simultaneously. In this week, we present a novel perovskite matieral that shows substantial hydration in wet condition and low proton migration energy in experiment and calculation. The electrochemical cells show remarkable hydrogen production rate at low temperatures, and demonstrate stable reversible operation, which provides great promise to develop next-generation electrotrolysis cells in temperature range (400~500 °C).

2:20 PM

(ICACC-S3-053-2019) Highly Performing Triple-Conductive $Pr_2NiO_{4+\delta}$ Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell

W. Li*[1]; B. Guan[1]; L. Ma[2]; S. Hu[1]; N. Zhang[1]; X. Liu[1]

1. West Virginia University, Mechanical and Aerospace Engineering, USA
2. Hebei University of Engineering, School of Materials Science and Engineering, China

The development of proton-conducting solid oxide electrolysis cells for the intermediate-temperature range application is largely hindered by the limited choices of adequate anode materials. In this study, $Pr_2NiO_{4+\delta}$ (PNO) is investigated as anode for the electrolysis cell. The introduction of protons into PNO lattice is confirmed through an insertion-induced conductivity variation measurement. Good chemical compatibility is verified between PNO and $Ba(ZrCeY)O_{3-\delta}$ (BZCY) proton-conducting electrolyte. Excellent catalytic activity towards water splitting is observed for PNO anode, 0.52 Ωcm^2 for 550°C, 0.057 Ωcm^2 for 700°C. The water-splitting process is disclosed by the impedance spectroscopy. The performance of the PNO anode is determined by two charge transfer processes whose kinetics is governed the electrolyzing potential. Cathode-supported Ni-BZCY//BZCY//PNO-BZCY single cells are fabricated and characterized. ~95% current efficiency is confirmed. At 700°C, a current density of 977 mA/cm^2 is achieved at a 1.3 V electrolyzing potential, e.g. 0.37 V overpotential, which is one of the best performances of the proton-conducting steam electrolysis cells so far. The PNO anode accounts only for 16% of the overall polarization resistance at 700°C. These findings prove that the triple-conductive PNO is a promising anode material for proton-based steam electrolysis cells.

2:40 PM

(ICACC-S3-054-2019) Catalyst performance of Yttrium doped Barium Zirconate (BZY) in the water gas shift (WGS) reaction

D. Jennings*[1]; I. Reimanis[1]; C. Karakaya[2]

1. Colorado School of Mines, Materials and Metallurgical Engineering, USA
2. Colorado School of Mines, Mechanical Engineering, USA

Yttrium doped barium zirconate (BZY) is a promising material for use in proton conducting fuel cells, but its catalytic performance is not well understood. In this work, the catalytic performance of BZY as a catalyst support material is tested in the water gas shift (WGS) reaction, and bifunctionality of BZY as a catalyst support is demonstrated. To optimize performance of this catalyst material it is critical to understand the structure of Ni containing BZY in its operating environments, and how that structure evolves over time. Transmission electron microscopy reveals that under reducing conditions nickel nanoparticles exsolve. Their formation and stability at elevated temperature determine the overall catalyst performance.

Proton Conducting Fuel Cells II

Room: Crystal
Session Chair: Sossina Haile, Northwestern University

3:20 PM

(ICACC-S3-055-2019) Fabrication of High Performance Protonic Ceramic Fuel Cells with Thin-Film Electrolytes and Multi-scale Structures (Invited)

K. Bae*[1]; H. Choi[2]; D. Kim[2]; J. Son[3]; J. Shim[2]

1. Stanford University, USA
2. Korea University, Republic of Korea
3. Korea Institute of Science and Technology, Republic of Korea

Fast thermal degradation and bulky insulating package sizes due to high temperature operation has been pointed out as the main challenges of conventional ceramic fuel cells. Protonic ceramics

(PCs) allow those problem improve with high ionic conductivity at temperatures under 600 °C. Recent experiments with protonic ceramic fuel cells (PCFCs) have demonstrated the long-term stable operation overcoming the poor chemical stability of PCs. Despite the development of these materials, however, PCFCs still suffer from low power outputs with large cell resistances. The state-of-art technologies for PCFCs requires that the consideration of an optimal structure design is essential to achieve high performance, not only the development of new materials. In this study, we show record-high power outputs from PCFCs with greatly reduced ohmic resistance at the temperatures less than 650 °C. A multi-scale anode structure was used, which facilitates growth of single-grain columnar electrolytes without blocking the grain-boundary in proton-conducting pathways. The high performance was repeatedly confirmed in the PCFCs satisfying optimal geometric configurations, indicating good reproducibility. The fabricated PCFCs were composed of typical materials, and further improvement is expected through the use of high-performance materials in the future.

3:50 PM

(ICACC-S3-056-2019) Enhancing Conductivity Through In Situ Cu Exsolution from $Ba_{0.95}Ce_{0.5}Zr_{0.3}Y_{0.16}Cu_{0.04}O_{3-\delta}$

M. Wang*[1]; C. Savaniu[1]; J. Hui[1]; D. Miller[1]; J. T. Irvine[1]

1. University of St Andrews, School of Chemistry, United Kingdom

Doped barium cerate possesses high proton conductivity in the intermediate temperature range. However, for a given electrolyte, electrochemical performance is largely determined by electrode process, which requires the electrode with not only high proton conductivity, but also good electronic conductivity.and catalytic property. Rencently, in situ exsolution method was proposed to introduce nano-catalysts on perovskite surface by simply reducing the perovskite doped with the certain element on the B-site. After reduction, both electronic conductivity and catalytic property of electrode can be greatly improved. Here, barium cerate zirconate based proton conductor, $BaCe_{0.5}Zr_{0.3}Y_{0.16}Cu_{0.04}O_{3-\delta}$ (denoted as BCZYC), was prepared by solid state method. Then, nano-catalyst, Cu, was obtained by reducing the as-prepared BCZYC oxide in 5% H_2/Ar at 500-900 °C for 12 h. Scanning electron microscopy images showed that different size range of particles were achieved not only on the native surface but also the inner surface due to the high mobility of Cu. Moreover, the conductivity of the sample increased dramatically to 43.4 S/cm at 600 °C after exsolution. Most interestingly, the material transferred from a semiconductor property to a metallic behaviour after reduction. Therefore, in situ exsolution of Cu from BCZYC provided a quite effective and promising method to improve the electrode properties.

4:10 PM

(ICACC-S3-057-2019) In-depth study of the poisoning effects of carbon dioxide on the anode for proton conducting SOFC

S. Sun[1]; Z. Cheng*[1]

1. Florida International University, Mechanical and Materials Engineering, USA

Carbon dioxide (CO_2) is often not regarded as a poison for conventional oxide-ion conducting solid oxide fuel cells (SOFC). However, our previous studies have revealed that the anode of proton conducting SOFC based on $BaZe_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte and Ni-BZCYYb cermet anode appears to get poisoned by CO_2 at the low percentage level. In this study, an in-depth investigation on the effects of CO_2 on the anode for proton conducting SOFC is conducted using different cell structures including electrolyte-supported full cells, anode-supported full cells as well as anode symmetrical cells. To help understand the effect of CO_2 adsorption vs. bulk reaction, both BZCYYb and the more stable $BaZe_{0.8}Y_{0.2}O_{3-\delta}$ (BZY) are used as the proton conducting electrolyte. The electrochemical responses for the cells are recorded in the temperature range of 750 to 450°C. In addition, the samples including Ni-proton conducting electrolyte composite pellets are characterized using different techniques including in situ Raman microspectroscopy at ~450°C to understand the mechanism of the displayed CO_2 poisoning behaviors. The experimental results will be presented and their implications on the roles of proton conducting oxides in the anode reaction for proton conducting SOFCs will be discussed.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics and Biocomposites I

Room: Coquina Salon B

Session Chairs: Leena Hupa, Åbo Akademi University; Fiorenzo Vetrone, Institut National de la Recherche Scientifique, Université du Québec

8:30 AM

(ICACC-S5-001-2019) Suspension Flame Sprayed Metal Doped Calcium Phosphate Coatings with Antibacterial Properties for Infection Prophylaxis (Invited)

R. Gadow*[1]; P. Krieg[2]; A. Killinger[2]; A. Bernstein[3]

1. University of Stuttgart, Graduate School of Excellence Advanced Manufacturing Engineering (GSaME), Germany
2. University of Stuttgart, Institute for Manufacturing Technologies of Ceramic Components and Composites, Germany
3. University of Freiburg, Musculoskeletal Research Lab, Clinics of Orthopedics and Trauma Surgery, Germany

High Velocity Suspension Flame Spraying (HVSFS) has been successfully employed to produce a wide variety of bioceramic coatings for prosthetic devices and bone implants. The HVSFS process has proven to be capable to process biomaterials resulting in dense and well adherent coatings on various types of metal and ceramic substrates. Degradable bioceramic coatings offer a faster osseointegration of endoprosthetic structures. A common problem that occurs after the application of all types of implants is the risk of infection due to the presence of bacteria which can result in severe post operative inflammation reactions associated with a high risk of losing the implant. In a novel approach, metals with known antibacterial properties are incorporated into the coating as a nanosize dispersion dopant to reduce the risk of inflammation. Metal doped coatings based on bioceramics were suspension flame sprayed using modified suspensions containing additional metals or metal salt based precursors. These coatings were evaluated regarding their microstructure and phase composition, as well as their in-vitro behavior. The presence of metal and metal oxide particles in the coating were characterized using micro-Raman and SEM. To evaluate the biocompatibility, a live/dead-assay study based on MG-63 cells was performed. Results showed no evidence for any cytotoxic reaction.

9:00 AM

(ICACC-S5-002-2019) 3D Printing of Bioceramics for Bone Regeneration Applications

S. Esslinger*[1]; R. Gadow[1]; A. Bernstein[2]

1. University of Stuttgart, Graduate School of Excellence Advanced Manufacturing Engineering (GSaME), Germany
2. University of Freiburg, Musculoskeletal Research Lab, Clinics of Orthopedics and Trauma Surgery, Germany

The use of bioceramics like calcium phosphates or bioactive glasses for the regeneration of critical bone defects, as they can occur for example after serious injury or diseases is intensively researched worldwide. The advantages of the additive manufacturing technology make it possible to process these ceramics into customized patient-specific implants, so called scaffolds. In this work the process chain of powder-based inkjet-3D-printing is presented. This

includes the production of bioceramic suspensions from bioglass, calcium phosphates and composites and spray granulation to obtain flowable granulates. 3D-printing is performed from CAD-modeling to postprocessing of the printed structures. Printed components are sintered and characterized with respect to mechanical properties and in vitro biocompatibility. After sintering the scaffolds show high porosity (about 70 %) and high surface roughness (Ra about 25 µm, Rz up to 200 µm) which is beneficial for the colonization of bone cells. The compressive strength was lower than 1 MPa for every scaffold, what makes them inappropriate for load bearing applications. In vitro tests using MG-63 cells showed the growth of cells on the outer and inner surface of the scaffolds and the formation of hydroxyapatite crystals.

9:20 AM

(ICACC-S5-003-2019) Defined open-porous tricalcium phosphate scaffolds produced by additive manufacturing (Invited)

M. Schwentenwein*[1]; D. Bomze[1]; J. Homa[1]

1. Lithoz GmbH, Austria

Scaffolds from bioresorbable such as tricalcium phosphate (TCP), hydroxyapatite (HA) or blends thereof providing defined and open porosity are challenging to produce. With lithography-based ceramic manufacturing (LCM) it is possible to produce very complex scaffolds of adjustable pore geometry and size in highly reproducible manner. LCM is a slurry-based additive manufacturing technique that relies on the selective curing of photosensitive ceramic suspensions. Scaffolds with defined pore sizes were produced and the pore and strut sizes were measured by light and scanning electron microscopy as well as computer tomography. Using this data, nominal-actual comparisons were performed and the reproducibility of pore geometry could be determined. High resolution and reproducibility show that the proposed approach is a suitable technique for the production of biomimetic scaffolds of bioresorbable ceramics. It could be shown that highly porous scaffolds could be produced with a minimum feature resolution around 150 µm for struts and pores as well as with a relative standard deviation of well below 3% even for small features. In addition, basic mechanical and biological testing was performed and the obtained results underline the good suitability for the usage if such structures as scaffolds in non-load bearing applications.

10:10 AM

(ICACC-S5-004-2019) Rare Earth Doped Nanoparticles for Theranostics (Invited)

F. Vetrone*[1]

1. Institut National de la Recherche Scientifique, Université du Québec, Centre Énergie, Matériaux et Télécommunications, Canada

Exciting light-emitting inorganic nanoparticles with near-infrared (NIR) light has made possible their use in theranostics where the therapeutic and diagnosticmodalities are delivered at the same time. The use of NIR light for excitation overcomes the drawbacks associated with high-energy light (UV or blue) excitation, for example, little to no background autofluorescence from the specimen under investigation as well as no incurred photodamage. Moreover, one of the biggest limitations is of course, that of penetration. As such, NIR light can penetrate tissues much better than high-energy light especially when these wavelengths lie within the three biological windows. Significant strides in the synthesis of rare earth doped nanoparticles (RENPs) coupled with their versatile optical properties has placed them at the forefront of theranostics. In this presentation, we discuss and demonstrate their potential for such applications.

10:40 AM

(ICACC-S5-005-2019) Structure / property relationships in Biomaterials at the nanoscale (Invited)

F. Rosei*[1]

1. INRS, Canada

Nanostructuring materials allows to optimize their properties, by exploiting size effects. We created nanopatterns that act as surface cues, affecting cell behavior. Chemical oxidation creates nanoscale topographies, that improve biocompatibility. Our treatment provides a differential signal, selectively inhibiting fibroblast proliferation while promoting osteoblast growth in vitro. Improving antibacterial properties using laser/plasma strategies and growing graphene oxide coatings will be discussed. Finally, sensing and therapeutic approaches can be harnessed by exploiting optical properties of nanocrystals, including Quantum Dots and upconverting nanoparticles.

11:10 AM

(ICACC-S5-006-2019) Differentiation behavior of osteogenic cell on surface potential-controlled TiO_2 scale formed by oxynitridation of Ti (Invited)

M. Hashimoto*[1]; T. Ogawa[1]; S. Kitaoka[1]; M. Furuya[2]; H. Kanetaka[2]; S. Muto[3]; M. Abe[4]; H. Yamashita[4]

1. Japan Fine Ceramics Center, Japan
2. Tohoku University, Japan
3. Nagoya University, Japan
4. Osaka University, Japan

The difference of the osteogenesis on surface potential-controlled rutile-type TiO_2 scale was examined by differentiation of osteogenic cell (MC3T3-E1). The surface potentials of rutile-type TiO_2 scales formed on Ti were controlled by varying the Ti heat treatment conditions in a N_2 atmosphere containing a trace amount of O_2. The zeta potentials of the samples heated at 873 and 973 K for 1 h developed large negative and positive charges, respectively, while MC3T3-E1 cell differentiation on the surface was enhanced in the both treatments (14 days incubation). In the case of untreated Ti, the cell showed low differentiation and the zeta potential was close to zero. In the initial stage of osteogenesis, protein such as fibronectin (FN) that was detected by the immunogold-labeling technique was adsorbed on the surfaces of the all samples irrespective of presence or absence of the surface treatments. However, Ca and P species, which were detected by time-of-flight secondary ion mass spectrometry, were simultaneously adsorbed only on the treated surfaces. Enhancement of adsorption of the inorganic species in addition to the protein adsorption was probably responsible for promoting osteogenesis.

11:40 AM

(ICACC-S5-007-2019) Novel Applications of Hydroxyapatite/ Collagen Bone-Like Nanocomposite as Coating on Ti and Self-Setting Bone Paste (Invited)

M. Kikuchi*[1]; T. Sato[2]; Y. Shirosaki[3]; M. Aizawa[2]; K. Kadowaki[4]; M. Uezono[4]; K. Moriyama[4]; T. Uchikoshi[5]

1. National Institute for Materials Science (NIMS), Bioceramics Group, Japan
2. Meiji University, Japan
3. Kyushu Institute of Technology, Japan
4. Tokyo Medical and Dental University, Japan
5. National Institute for Materials Science (NIMS), Fine Particles Engineering Group, Japan

Hydroxyapatite (HAp) ceramics was considered as non-bioresorbable materials even bone HAp is resorbed by osteoclasts. In 2001, we introduced a novel composite, hydroxyapatite/collagen bone-like nanocomposite (HAp/Col) having bone-like nanostructure and chemical composition, and the HAp/Col is completely incorporated into bone remodeling process in the same time-frame as transplanted autologous bone. After that, osteoclastic resorption of

ceramics having higher solubility product than HAp, β-tricalcium phosphate and carbonated apatite ceramics were reported but the time-frames were far longer than that of the HAp/Col. These results suggested that crystallite size of calcium phosphate could be much important than solubility product. Anyway, the HAp/Col has a possibility to show unique biological properties when it applied to medical prostheses other than bone void fillers. In fact, dip-coated HAp/Col on Ti realized three-times faster osseointegration due to its incorporation into bone remodeling process. The dip coating is easy and simple way but not suit for mass production because it has difficulty in control thickness of coating layer as well as low adhesive strength to its substrate. In the present lecture, modified electrophoretic deposition technique applied to the HAp/Col and preparation of self-setting bone paste of the HAp/Col will be delivered.

Bioceramics and Biocomposites II

Room: Coquina Salon B

Session Chair: Enrico Bernardo, University of Padova

1:30 PM

(ICACC-S5-008-2019) Bioactive glasses in vitro and in vivo vs. clinical observations (Invited)

L. Hupa*[1]

1. Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Finland

Bioactive glasses are clinically used mainly as bone fillers. The ion release from the typical commercial products, i.e., glass particles, not only stimulates osteogenesis but ideally also creates a local bacteriostatic environment around the dissolving glass. Over the years, various buffered solutions and experimental conditions have been used to assess the capability of different glass compositions to form the bone apatite-like surface layer characteristic for bioactivity. In this presentation, the pros and cons of different experimental set-ups and buffered solutions used to predict in vivo bioactivity are compared. Finally, the most important findings are verified with the published clinical results of using the bioactive glass S53P4 (BonAlive) in the treatment of bone defects and trauma. The overall goal is to compare how the in vitro tests are to be performed for them to simulate as well as possible the multitude of conditions and criteria in the clinical application. Traditional static in vitro tests using so-called simulated body fluid are suitable for assessing the overall bioactivity. Furthermore, in vitro tests in a controlled continuous fluid flow could be useful for certain applications of bioactive glasses.

2:00 PM

(ICACC-S5-009-2019) Polymorphism in Metal Oxides and Gas-Selectivity-Building the medical diagnostic tools of the future (Invited)

P. Gouma*[1]

1. The Ohio State University, MSE, USA

This work presents a crystallo-chemical approach to selective chemosensing. By addressing the effects of processing on the phase selection for a given metal oxide system, either a binary or a ternary one, it is shown that certain crystal structures show affinity to specific gases or classes of gaseous compounds. The nature of the chemo-selection process varies for the different crystal structures, spanning reaction, adsorption, or ferroelectric poling mechanisms. The importance of this finding is that breath and skin gas detector are being developed which detect and discriminate among signaling metabolites controlling human health and well-being.

2:30 PM

(ICACC-S5-010-2019) Multi-Functional Biomaterial Systems Designed by Guided Biofabrication (Invited)

C. Tamerler*[1]

1. University of Kansas, Mechanical Eng & BioEngineering, USA

Non-covalent biomolecular self-assembly has become a prominent strategy in biofabrication for multi-functional materials and systems with a wide range of applications, ranging from reparative and regenerative medicine to biotechnology. Nature provides bioinspired design strategies to develop innovative materials that simultaneously self-assemble and self-organize, two design characteristics that are essential to man-made purely synthetic systems. Proteins play an essential role in fabrication of biological materials owning to their functional range, from structural to biochemical. Our group has focused on mimiking protein's abilities in the design of functional materials and devices that are self-guided and undergo co-assembled through engineered biomolecular building blocks. This presentation will provide an overview on the guided co-assembly design approaches demonstrated to repair defective tissue interfaces, create antimicrobial coatings, target diseased cells, as well as enhance biocatalytic performance of enzyme catalysts as novel sensing modalities.

3:20 PM

(ICACC-S5-011-2019) Continuous Wet Spinning and Dug-loaded Wet-spun Fibers

J. Wu[1]; H. Sun[1]; L. Guo[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Wet spinning is a simple technique and may be used to produce fibrous biomedical products. However, continuous wet spinning to make structures with aligned fibers is not easy and requires detailed investigations. In wet spinning itself, several parameters (polymer, polymer solution concentration, spinneret inner diameter, fiber drawing speed, coagulation bath, etc.) have major influences on the fibrous products. For biomedical applications, wet-spun fibers may serve as delivery vehicles for biomolecules such as drugs. In the current work, an apparatus was designed and constructed for the continuous wet spinning of biomedical polymers such as sodium alginate (SA). Working without fiber drawing by simple injecting a polymer solution into the coagulation bath, non-woven fibers could be obtained; working at a sufficient drawing speed, aligned fibers could be made and collected on a mandrel. For investigating wet spinning of drug-loaded fibers, SA and fluorouracil (5-FU, an anticancer drug) were used in the current study. SA solutions of different concentrations and also different drug concentrations were used to make wet-spun fibers. Subsequently, in vitro release tests were conducted to study drug release from fibers. It was shown that the SA solution concentration had significant effects on the morphology and diameter of wet-spun SA fibers and consequently the release behavior of 5-FU from these fibers.

3:40 PM

(ICACC-S5-012-2019) Hierarchically Porous 3D-printed Akermanite Scaffolds from Silicones and Engineered Fillers (Invited)

A. Dasan[2]; H. Elsayed[1]; E. Bernardo*[1]

1. University of Padova, Department of Industrial Engineering, Italy
2. Alexander Dubcek University of Trencin, FunGlass – Centre for Functional and Surface Functionalized Glass, Slovakia

Silicones mixed with CaO and MgO are known to yield bioactive akermanite (Ca2MgSi2O7) foams. In fact, a liquid silicone may be foamed by water vapour release, at 300-350 °C, from the decomposition of Mg(OH)2 and hydrated borate salts, as extra fillers, before firing at 1100 °C. High phase purity is achieved with the help of the liquid phase provided by the borate (3 wt% of the total ceramic). The present investigation recovers the concept of akermanite ceramics as

developed by direct reaction between silica, from the oxidation of a commercial silicone resin, and oxide fillers, for the manufacturing of reticulated three-dimensional scaffolds, processed by means of direct ink writing of silicone-based pastes. Despite the change of starting silicone, an excellent phase purity was obtained again, with the help of the liquid phase provided by anhydrous sodium borate ($Na_2B_4O_7$), upon firing. Crack-free scaffolds, with dense and regular struts, were due to the use of $CaCO_3$ and MgO nano-particles as reactive fillers. The structure of the scaffolds, finally, was successfully modified by using Mg(OH)2 and hydrated sodium borate: besides macro-porosity from direct ink writing, the new scaffolds exhibited homogenous 'spongy' struts (owing to water vapour release in the heating step), with no crack. Both type of scaffolds (with dense or porous struts) exhibited remarkable strength-to-density ratios.

4:10 PM

(ICACC-S5-013-2019) Incorporation, Release and Functioning of Theranostics from Multifunctional Tissue Engineering Scaffolds (Invited)

M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Cancer patients can have specific needs for medical treatments. After surgery, new tissues need to be formed at the original tumor site to recover body functions. Human tissue regeneration can be greatly enhanced by using cell-laden nanofibrous tissue engineering scaffolds encapsulated with growth factors. Also, embedding theranostics in scaffolds and controlling their release will enable the detection and treatment of recurring cancer for post-operative patients. We have developed novel technologies to fabricate such advanced scaffolds. This lecture presents our designs and investigations of Au-based theranostics-embedded, rGSMC-laden and bFGF-incorporated multifunctional scaffolds. The theranostics are contained in polymer microspheres and deposited in nanofibrous scaffolds randomly during scaffold fabrication. Systematic investigations show that theranostics can be gradually released in scaffolds due to microsphere biodegradation and they accumulate at cancer cells via active targeting. Cellular uptake of theranostics occurs through FR-mediated endocytosis. In vitro biological experiments demonstrate successful cancer cell detection and imaging and photothermal therapy. In the meantime, with these scaffolds, enhanced rGSMC proliferation and migration for tissue regeneration are observed. All these results show the great potential of novel scaffolds for cancer patients.

4:40 PM

(ICACC-S5-014-2019) The study of internal stresses and ageing behavior of zirconia inclusions in biomedical grade ZTA composites

C. Wei*[1]; L. Gremillard[2]

1. Northwestern Polytechnical University, School of Mechanics, Civil Engineering and Architecture, China
2. INSA Lyon, MATEIS, France

Zirconia based bio-ceramics are often used in orthopaedic and dental implants. The low temperature degradation behaviour of zirconia under water environments is an important factor affecting the lifetime of zirconia-based biomaterials. ZTA (Zirconia-toughened alumina) composite is a representative of these materials. In this work, the ZTA composites of zirconia inclusion particles with different sizes were obtained by different milling procedures, and the internal stress state and ageing behaviour of zirconia inclusions in the composites were studied by Raman analysis and XRD analysis. The results show that the zirconia particles are tensile in the composite, and that the tensile stress increases almost linearly with the local alumina rate around the inclusions. The polishing causes a slight transformation towards the monoclinic phase, reduces on average the residual stresses but causes a widening of their distribution, making it more likely the presence of zones under strong stresses. Moreover, the maximum fraction of monoclinic phase after ageing seems to decrease when the internal stress increases. Finally, the incidence of cracking increases with the size of the zirconia inclusions.

5:00 PM

(ICACC-S5-015-2019) In situ luminescence analysis of coordination sensors (ILACS): New light on monitoring the formation of bioceramics

H. Terraschke*[1]

1. Christian-Albrechts-Universität zu Kiel, Institute of Inorganic Chemistry, Germany

Efficiently monitoring the events occurring during the formation of solids in solutions including nucleation, crystal growth, formation of reaction intermediates and phase transitions culminating in the crystallization of the final product require the application of in situ characterization techniques. Within the in situ luminescence analysis of coordination sensors (ILACS) approach, lanthanide ions are incorporated into the investigated materials during synthesis as local coordination sensors. Due to the sensitivity of their spectroscopic properties assigned to 5d → 4f or 4f → 4f electronic transitions to the coordination environment, changes in the coordination of the cation sites can be detected by measuring in situ luminescence measurements applying fast detectors under real reaction conditions. Bioceramics are important for constituting endo and exoskeleton of several species, being also widely used for producing medical implants and prosthesis. Therefore, this work shows the application of the ILACS technique for monitoring the intensively discussed formation and phase transitions of calcium phosphates and carbonates, which are important for better comprehending the transitions between healthy and diseased tissue as well as for predicting and preventing the degradation of implants and prosthesis in our bodies.

5:20 PM

(ICACC-S5-016-2019) Synthesis of porous bio-ceramic(Silicon and Calcium silicate) implants by selective laser melting for local delivery of Vancomycin

N. K. Kamboj*[1]; I. Hussainova[1]; M. A. Rodríguez Barbero[2]; S. Rodrigo[2]; P. K. Gokuldoss[1]

1. Tallinn University of Technology, Mechanical and Industrial Engineering, Estonia
2. Institute of Ceramics and Glasses, Spain

Although direct additive manufacturing technology has various advantages, it is not commonly applied for fabrication of bio-ceramic implants. One main reason can be the low absorption of laser beam energy and the poor thermal shock resistance of bio-ceramics. The research aims to produce advanced bio-ceramic implants by direct Additive Manufacturing technology (AM), in particular by selective laser melting process. The work also aims for the novel feedstock for the 3D printer and preparation of the silicon and calcium silicate implants with controlled structure and interconnected porosity by employing selective laser melting technology. The scaffolds produced are highly bioactive and tends to shows better biodegradability. The selective laser melted scaffolds tend to shows various multifunctional applications like bone repair properties and local drug delivery (Vancomycin). The bio-scaffolds produced does not require any post-processing techniques like sintering which act as a huge disadvantage in traditional ceramic producing approaches. The scientific objectives are: 1. to develop general and customized bio-scaffolds easily tailored in size and shape to the diseased or injured area by selective laser melting at the reduced cost 2. to produce bio-scaffolds with significant mechanical competence/ compliance by selective laser melting

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Li-O2 and Li-S I

Room: Tomoka A

Session Chair: Hiroaki Kobayashi, Tohoku University

8:30 AM

(ICACC-S6-039-2019) Rational Approach for Dense $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ Ceramics by Pressureless Sintering for All-solid-state Lithium-ion Batteries

D. Kim*[1]; J. Yun[1]; D. Kim[1]

1. Korea Advanced Institute of Science and Engineering (KAIST), Department of Materials Science and Engineering, Republic of Korea

Use of flammable organic liquid electrolytes that have low ignition point and low thermal stability can cause explosion accidents. To resolve the safety issues, solid electrolytes become an excellent candidate. LATP ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) is one of promising solid electrolyte due to its good ionic conductivity and chemical stability against water but it suffers from low density of sintered body. Most of previous works have adopted hot press sintering and spark plasma sintering to alleviate the density issue, although those processes are not cost-effective. In this work, we introduced a single step pressureless sintering to anneal the LATP ceramics with a good density and ionic conductivity in a simple process. To improve the density, we prepared the LATP powders using different phase of TiO_2 precursors (rutile and anatase) with an investigation of densification aspect. Replacing Ti^{4+} ions with trivalent ions and lithium ions is also explored to achieve an excellent electrochemical performance. This study will open new avenues for the sintering of dense LATP solid electrolytes.

8:50 AM

(ICACC-S6-040-2019) The novel low-temperature synthesis route of garnet-type solid electrolyte using precursor oxides

N. Hamao*[1]; Y. Yamaguchi[1]; K. Hamamoto[1]; Y. Fujishiro[1]; J. Akimoto[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

All-solid-state Li-ion batteries are considered to be high energy density and safer than lithium secondary batteries due to using non-flammable solid electrolyte. In order to improve the performance of All-solid-state Li-ion batteries, a solid-state electrolyte is required a high Li-ion conductivity and a wide electrochemical window. Among of Li-ion conductivity oxide, we have focused attention on the garnet-type $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZT). However, LLZT has been attracted attention as solid electrolyte due to their high Li-ion conductivity, the LLZT is difficult to synthesize single phase sample due to high reaction temperature. Recently, low-temperature synthesis of $Li_7La_3Zr_2O_{12}$ using $La_2Zr_2O_7$ as precursor has been reported. In this work, we attempted to prepare the garnet-type electrolyte at a relatively low-temperature using pyrochlore-type $La_2Zr_2O_7$ and weberite-type La_3TaO_7, also examined the sintering condition and the conductive properties. To investigate the conductive property, the Li-ion conductivity was measured by the AC impedance method.

9:10 AM

(ICACC-S6-041-2019) Al-doped $Li_7La_3Zr_2O_{12}$ – PEO_{18}LiTFSI as an Electrolyte for All-Solid-State Batteries

R. Scipioni*[1]; S. Barnett[1]

1. Northwestern University, Materials Science & Engineering, USA

Organic liquid electrolytes in rechargeable Li-ion batteries are one of the major safety issues because of their flammability and, with the development of large-scale batteries, the risk of fire and explosion has become a serious problem. Replacing the liquid electrolyte with an inorganic solid electrolyte is a possible solution to the safety issues and recent improvements in fast ion-conducting oxides are making all-solid-state batteries more attractive. $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising candidate to be used in solid state batteries and it exhibits a very high conductivity ($2.1x10^{-4}$ Scm^{-1}) when the cubic phase is stabilized with Al-doping. However, LLZO had the possibility of brittle fracture, and the lack of flexibility limits cell geometries. In this work, a composite electrolyte slurry is prepared by mixing Al-doped LLZO ($Li_{7-3x}Al_xLa_3Zr_2O_{12}$) with PEO_{18}LiTFSI and poly(ethylene glycol) dimethyl ether (PEGDME) as plasticizer. The thin electrolyte layer is cast on a conventional $LiFePO_4$ electrode modified by the addition of Al-doped LLZO and PEGDME to improve the electrode-electrolyte contact. Various electrolytes with different Al-doping contents are investigated and tested in a full battery using lithium metal as the negative electrode. The addition of PEGDME confers flexibility to the solid electrolyte, making it suitable for cylindrical cell and possible wearable device applications.

9:30 AM

(ICACC-S6-042-2019) Exploring Lithium-Based Ionic Liquid and Highly Concentrated Electrolyte Systems for Air and Sulfur Batteries (Invited)

M. L. Thomas*[1]; K. Ueno[1]; K. Dokko[1]; M. Watanabe[1]

1. Yokohama National University, Japan

The development of "beyond lithium-ion" technologies, including lithium air and lithium sulfur systems, requires development of robust and task-specific cell components. We have been studying ionic liquids and highly concentrated solutions as novel, low-volatility electrolytes, and in this presentation we will elaborate on the specific physico-chemical characteristics (including solvation phenomena and transport properties) of such media making them attractive for such applications. We will highlight how the decreased solubility of conversion intermediates (including superoxide and polysulfides) opens new avenues for exploiting alternative pathways for cell operation, and we will further comment on how the mechanisms for ion transport in solution in the concentrated regime likewise offer novel approaches to improve device performance. We will also highlight the importance of developing understanding of how these novel systems interact with solid-state electrode materials, and on recent developments on hybrid electrolyte materials.

Li-O2 and Li-S II

Room: Tomoka A

Session Chair: Palani Balaya, National University of Singapore

10:20 AM

(ICACC-S6-043-2019) Li_2O-Based Cathode Materials Using Redox of Peroxide/Oxide Ions in Solids (Invited)

H. Kobayashi*[1]

1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, Japan

Using reactions not involving redox of heavy transition metal ions is an effective method for remarkably improving the energy density of Li-ion batteries. Recently, we developed Li_2O-based cathode materials using redox of peroxide/oxide ions in solids. The Li-ion battery system combined with Li_2O cathode and Li metal anode is expressed as $Li_2O_2 + 2Li \rightarrow 2Li_2O$, and potentially delivers a high theoretical specific capacity and an energy density of 897 mAh $g^{-1}$and 2570 Wh kg^{-1}, respectively. We demonstrated the redox of peroxide/oxide ions with transition metal-doped Li_2O cathodes, such as Co-, Fe-, and Cu-doped Li_2O. In these material, the transition metal ions were substitutionally doped into the Li-sites of antifluorite-type Li_2O. These materials exhibited the specific capacity more than 200 mAh g^{-1}, indicating that more than one electron reaction per doped transition metal (ca. 100 mAh g^{-1}) proceeded. Especially, Co-doped Li_2O exhibited the specific capacity of 450 mAh g^{-1} for more than 30 cycles.

10:50 AM

(ICACC-S6-044-2019) Exploring Conduction Mechanisms in Argyrodite Li6PS5X Solid Electrolytes with Molecular Dynamics Simulations (Invited)

B. Morgan*[1]

1. University of Bath, Chemistry, United Kingdom

Halide-substituted lithium-argyrodites, Li6PS5X (X=Cl, Br, I) are a promising family of lithium-ion solid electrolytes, with potential applications in all-solid-state batteries. Changing X from I to Cl produces a strong increase in lithium-ion conductivity, which has been attributed to increased crystallographic disorder for X and S ions across 4a and 4c sites. A previous molecular dynamics study has predicted that long-ranged Li-ion transport is only achieved for X/S disordered systems. A microscopic explanation for this change in lithium-ion dynamics, however, is lacking. We have performed a series of ab initio molecular dynamics simulations of ordered and disordered Li6PS5X (X=Cl, I) to disentangle the effect of changing structure and changing composition on the distribution of lithium ions, and on their atomic-scale conduction mechanisms. We find that lithium preferentially coordinates sulphur anions, but the preferred Li6S octahedral coordination is disrupted by anion disordering, resulting in a large increase in local lithium disorder, and a large enhancement in ionic conductivity.

11:20 AM

(ICACC-S6-045-2019) Nanostructural Design of Porous Matrix by Interwoven Carbon Nanofibers for High-Areal-Capacity Li-S Batteries

J. Yun*[1]; J. Kim[1]; H. Lee[2]; D. Kim[1]

1. Korea Advanced Institute of Science and Engineering (KAIST), Materials Science and Engineering, Republic of Korea
2. UNIST, Republic of Korea

The development of high performance rechargeable batteries beyond the state-of-the-art Li-ion batteries is always desirable to satisfy the energy requirement for grid energy storage system and EVs. In such scenario, Lithium-sulfur (Li-S) battery has been regarded as a promising battery system owing to high theoretical capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}). Despite the merits of Li-S, electrically insulating sulfur and dissolved lithium polysulfide impede the commercialization of Li-S. Physical encapsulation of sulfur through nanostructural design not only ameliorate those issues, but also realize a high sulfur loading which is essential to practical use. In this regard, we introduce an electrospun carbon nanofiber (CNF) matrix to confine sulfur in the cathode. This simple unwoven structure elevates the sulfur loading up to 10.5 mg cm^{-2} with a high areal capapcity of ~ 8 mAh cm^{-2} and an excellent cycle stability, which is associated with the excellent electrical conductivity of interwoven 1-D structure. Moreover, we have observed that the reacted active materials adhere to the junction of the CNF network as concave quadrangles, indicating that the viscous polysulfides are trapped between the narrow gaps in the CNF web during cycling. The results of this study pave the way for the nanostructural design of high-areal-capacity Li–S batteries

11:40 AM

(ICACC-S6-046-2019) Beyond the Theoretical Capacity of GeS_2 Conversion-Alloying Hybrid Anode by Electrochemical Amorphization

J. Kim[1]; J. Yun[1]; D. Kim*[1]

1. Korea Advanced Institute of Science and Engineering (KAIST), Dept. of Mater Sci & Eng, Republic of Korea

Sodium ion batteries (NIBs) are a promising next generation energy storage, alternating the predominant lithium ion batteries. High-performance anode materials has become essential to satisfy the demand for NIBs. This work is the first report on GeS_2 nanocomposites uniformly distributed on reduced graphene oxide (rGO) as promising anode materials for NIBs prepared via a facile hydrothermal synthesis and a unique carbothermal annealing. The GeS_2/rGO hybrid anode delivers a high reversible capacity of 805 mA h g^{-1} beyond the theoretical capacity, a great rate capability of 616 mA h g^{-1} at 5 A g^{-1}, and a cycle retention of 89.4% after 100 cycles. The ex situ characterizations through X-ray absorption near edge structure (XANES) measurement, Raman spectroscopy, TEM images reveal that the electrochemically driven amorphization plays a key role in achieving efficient sodium storage by accommodating excess sodium ions in the electrode materials. This study paves the way for understanding the sequential conversion-alloying reaction mechanism of anode materials for NIBs.

12:00 PM

(ICACC-S6-047-2019) Polycrystalline 1-D TiN based freestanding composite electrode for better performance Li-polysulfide cell

E. Heo*[1]; A. Beyene[1]; J. Yun[1]; D. Kim[1]

1. Korea Advanced Institute of Science and Engineering (KAIST), Republic of Korea

Li-sulfur battery is expected to transform the electrochemical energy storage technology to the next level as it holds the possibility to get two to three times higher energy density than the state of the art Li-ion battery. However, the poor electrical conductivity of sulfur, and the high diffusivity of the intermediate lithium polysulfides create various problems, which limited the utilization of its full potential. Polar conductive sulfur hosts, such as titanium nitride (TiN), make it possible to get remarkable improvements in active material utilization and capacity retention for long term cycling. However, it has not been possible to use these polar, conductive, ceramic materials for higher active material loading (> 2mg/cm^2) due to their low flexibility compared to carbonaceous materials. Here we have demonstrated the possibility of designing three dimensional freestanding electrode using polycrystalline 1-D TiN for a relatively higher sulfur loading of 2.5mg/cm^2. The electrochemical performance of this 1-D TiN based electrode is compared with 1-D TiO_2 (the starting material for TiN synthesis) based electrode and it was possible to witness catalytic effect of TiN by virtue of its endowed conductivity which results in remarkable capacity retention and better active material utilization at high C-rates compared to TiO_2 based electrode.

S7: 13th International Symposium on Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental, and Health Applications

Nanomaterials for Energy Conversion and Storage and Catalysis

Room: Coquina Salon C

Session Chair: Yakup Gönüllü, University of Cologne

8:30 AM

(ICACC-S7-008-2019) Multifunctional materials for emerging technologies (Invited)

F. Rosei*[1]

1. INRS, Canada

As the age of fossil fuels is coming to an end, now more than ever there is the need for more efficient and sustainable renewable energy technologies. This presentation will give an overview on recent developments in solar technologies that aim to address the energy challenge. In particular, nanostructured materials synthesized via the bottom–up approach present an opportunity for future generation low cost manufacturing of devices. We demonstrate various multifunctional materials, namely materials that exhibit more than

one functionality, and structure/property relationships in such systems, including new strategies for the synthesis of multifunctional nanoscale materials to be used for applications in photovoltaics, solar hydrogen production, luminescent solar concentrators and other emerging optoelectronic technologies.

9:00 AM

(ICACC-S7-009-2019) Thermoelectric Enhancement and Thermal Stability of Nano $Cu_{1.8}Se$, Cu_2Se and solid solution of Nano Cu_2Se-$Fe_{3.25}Co_{0.75}Sb_{12}$ (Invited)

S. Ballikaya*[1]; B. Hamawandi[2]; T. Temel[3]; T. Bailey[4]; B. Ozkal[3]; C. Uher[4]; M. S. Toprak[2]

1. Istanbul University, Elec. Engineering Dept., Turkey
2. KTH Royal Institute of Technology, Applied Physics Department, Sweden
3. Istanbul Technical University, Material Science and Engineering, Turkey
4. University of Michigan, Physics, USA

Recently, copper chalgonedies have attracted great attention due to their potential application for mid-temperature power generation. In this work, we report the thermoelectric and thermal stability properties of nanostructured $Cu_{1.8}Se$, Cu_2Se, and solid solution of 2% and 5% of nano $Fe_{3.25}Co_{0.75}Sb_{12}$ included nano Cu_2Se compounds. $Cu_{1.8}Se$, Cu_2Se All samples were prepared by a rapid microwave assisted solution synthesis method while nano $Fe_{3.25}Co_{0.75}Sb_{12}$ was prepared by organometallic chemical processing followed by spark plasma sintering method. High temperature transport properties were assessed by Seebeck coefficient, electrical conductivity and thermal conductivity measurements. Structural properties were performed by powder x-ray diffraction (PXRD) and SEM-EDX analysis while thermal stability of samples were examined via hot stage microscope. The sign of Seebeck coefficient sign indicates that holes are main carriers in all samples. Maximum electrical conductivity value of ~2000 S/cm obtained for $Cu_{1.8}Se$ due to copper deficiency in this compound. It is seen that thermal conductivity decreases and thermal stability of compounds increases with nano $Fe_{3.25}Co_{0.75}Sb_{12}$ inclusion. The maximum ZT value reached ~2.1 at 900 K in nano $Cu_{1.8}Se$ likely due to high power factor of this compound.

9:20 AM

(ICACC-S7-010-2019) Composite ceramic nanostructures for high-efficiency Sunlight conversion (Invited)

A. Vomiero*[1]

1. Lulea University of Technology, Engineering Sciences & Mathematics, Sweden

Composite ceramic nanostructures can be efficiently applied for Sunlight detection and conversion. In most of the applied systems, like photodetectors, excitonic solar cells and photoelectrochemical cells to produce solar fuels, nanomaterials can play a critical role in boosting photoconversion efficiency by ameliorating the processes of charge photogeneration, exciton dissociation and charge transport. Several strategies can be pursued, including broadening of light absorbance to reduce solar light losses, fastening exciton dissociation and charge injection from the photoactive medium to the charge transporting materials, reducing charge recombination during charge transport and collection at the electrodes. In this lecture, a few examples of application of nanocomposites will be thoroughly discussed, highlighting the role of interface engineering to improve the efficiency of energy conversion from Sunlight to electric power and/or chemical fuels.

9:40 AM

(ICACC-S7-011-2019) Carbothermal nitridation ZrN:(Eu/La) particles; from gel to nano-phase powders

S. Naim Katea*[1]; G. Westin[1]

1. Uppsala University, Chemistry-Ångström, Sweden

Zirconium nitride ceramics are used, or considered for a wide range of applications including, optical, solar hydrogen, energy storage and as matrix for nuclear fuels where La simulates Ac and Am. Often nano-particles are required for these applications, either for their large surface area, or as starting powders for sintering into high density compacts for use as e.g. nuclear fuels. In this work, carbothermal nitridation of La/Eu-Zr-carbon-gels to La/Eu-doped ZrN nano-phase powders is presented. Traditional powder based carbothermal processes give poor mixing of the constituent compounds which results in high synthesis temperatures and long annealing times, yielding large and extensively agglomerated powders. A solution chemical based method using sucrose-Zr-La-alkoxide and sucrose-Zr-Eu-alkoxide as precursors is described in detail, using TG-DTA, IR, XRD, Raman, XPS, SEM-EDS, TEM-EDS. It was found that the phase evolution differed when the redox stable La^{3+} was used compared to the redox active Eu^{3+}, where the latter formed $EuZrO_3$ and the former $La_2Zr_2O_7$ as intermediate phases. Both systems ended with cubic Ln-doped ZrN at 1495°C, which could also contain some O and or C, mixed with carbon.

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures III

Room: Coquina Salon C
Session Chair: Eva Hemmer, University of Ottawa

10:20 AM

(ICACC-S7-012-2019) From molecules to materials: Lanthanide-based structures for biomedical and optical applications (Invited)

R. Marin[1]; I. Halimi[1]; N. Liu[1]; N. Panov[1]; E. Hemmer*[1]

1. University of Ottawa, Chemistry and Biomolecular Sciences, Canada

Based on their outstanding optical properties, Ln^{3+}-based compounds have been suggested for a wide range of applications including the field of biomedicine, optoelectronics and solar energy conversion. For instance, the capability of Ln^{3+}-based materials to emit visible and near-infrared (NIR) light under NIR excitation is highly sought after when aiming for biomedical applications. This is due to the fact that NIR light penetrates deeper into biological tissue when compared to UV or visible light. Fluorides, such as $NaGdF_4$, are commonly considered as suitable host materials for upconverting and NIR emitting Ln^{3+} ions (e.g. Er^{3+}) and their preparation via the thermal decomposition process has been widely studied. The microwave-assisted approach offers a promising alternative for the synthesis of Ln^{3+}-nanoparticles of controlled size and crystalline phase. Besides Ln^{3+}-doped materials, Ln^{3+}-based molecular compounds attract attention due to their optical properties, and they have been suggested for application in opto-electronic devices or to reduce efficiency loss in solar cells. In this context, Ln^{3+} ions such as Eu^{3+}, Tb^{3+} or Dy^{3+} are suitable candidates emitting visible light under UV excitation. This presentation will shine a light on the versatile landscape of photoluminescent lanthanide-based materials and molecules as well as their hybrids.

10:50 AM

(ICACC-S7-013-2019) Formation of Anisotropic Nanostructures in Magnetic Field Assisted Chemical Vapor Deposition and Their Transformation to Catalysts for Renewable Energy Harvesting

D. Stadler*[2]; T. Brede[1]; D. Bialuschewski[2]; A. Moellmann[2]; T. Fischer[2]; C. A. Volkert[1]; S. Mathur[2]

1. Georg-August-University, Germany
2. University of Cologne, Insitute of Inorganic Chemistry, Germany

Processing and manufacturing of nanomaterials and -coatings is a key challenge to overcome pressing issues, like biomedical applicability, computer chip design, as well as green energy harvesting and transformation. For the latter, photoelectrochemical water splitting (PEC) demonstrated great potential during the last years. Caused by its non-toxicity, abundancy, and suitable bandgap, hematite demonstrated a special ecological potential for this method. Nevertheless, the material suffers from short recombination length, charge

accumulation at grain boundaries and decent absorption coefficients. It has been shown that the formation of onedimensional (1D) nanostructures leads to increased water splitting kinetics. However, the formation of 1D hematite nanostructures through chemical vapor deposition (CVD) usually requires pre-structured surfaces and thus is not applicable to polycrystalline surfaces, such as F:SnO_2 (FTO). In this work, we would like to demonstrate the anisotropic structure formation of iron nanostructures in magnetic field assisted CVD (mfCVD) and the successful transformation to 1D hematite nanostructures on FTO. The role of the substrate, field orientation and strength will be presented. Furthermore, a field dependent increase in catalytic PEC performance is discussed.

11:10 AM

(ICACC-S7-014-2019) Nano-probes for X-ray Fluorescence Bio-imaging (Invited)

M. S. Toprak*[1]

1. KTH Royal Institute of Technology, Dept. of Applied Physics, Sweden

Nanoparticles have been used as contrast agents for in-vivo bio-imaging, including MRI, near-IR fluorescence and CT techniques. Present macroscopic biomedical imaging methods provide either morphology with high spatial resolution (e.g., CT) or functional/molecular information with lower resolution (e.g., PET). X-ray fluorescence (XRF) from targeted nanoparticles allows molecular or functional imaging but sensitivity has so far been insufficient resulting in low spatial resolution, despite long exposure times and high dose. In the present paper, we show that laboratory XRF tomography with spectrally matched transition metal oxide nanoparticles provides a path to functional biomedical imaging with ~100-μm resolution in living rodents. The method is demonstrated on mice for 3D tumor imaging via passive targeting (EPR effect) of fabricated molybdenum oxide NPs.

11:30 AM

(ICACC-S7-015-2019) Broadband and efficient enhancement of rare-earth-ion photoluminescence in optical materials by semiconductor or metal nanoaggregates (Invited)

F. Enrichi*[1]

1. Centro Studi e Ricerche E. Fermi (Italy) and Luleå University of Technology (Sweden), Italy

The spectroscopic properties of rare-earth-ions (RE^{3+}), characterized by specific narrow photoluminescence emissions and long luminescence lifetimes, make them suitable for many optical applications. Their use is well established in phosphors for lighting and light-emitting devices, light amplifiers, lasers, spectral up- and down-conversion layers, and optical biomarkers. However, major limitations are related to their small excitation cross section and absorption spectral bandwidth, which reduce their effective implementation and use. This presentation will be focused on the sensitization process of rare earth ions by semiconductor or metal nanoaggregates. As examples, I will illustrate the role of silicon or silver nanoaggregates for broadband enhanced PL excitation in different rare earth doped materials, with potential applications in optical amplifiers, photovoltaic solar cells and lighting.

11:50 AM

(ICACC-S7-016-2019) Probing the stability and dissolution of nano-MoO_x X-Ray fluorescence bioimaging contrast agent

V. Carmen*[1]; Y. Li[1]; E. Yilmaz[2]; M. S. Toprak[1]

1. KTH Royal Institute of Technology, Applied Physics, Sweden
2. National Nanotechnology Research Center (UNAM) Bilkent University, Turkey

Contrast media based on nanoparticles (NPs) are used in various biomedical imaging techniques. X-ray fluorescence (XRF) can provide sensitive and quantitative detection of NPs. Recently we showed in a laboratory XRF system that XRF tomography could use spectrally matched molybdenum oxide (MoOx) based NPs as contrast agents to achieve 200 μm spatial resolutions in mice, beyond what can be achieved with other imaging techniques (PET, SPECT, MRI). Understanding the behavior and fate of NPs in biological systems is still a challenge. NPs will have a biodistribution and uptake in-vivo, driven mainly by their size and surface properties. Moreover, the NPs will suffer critical modification in biological media, mostly via protein adsorption and the formation of a protein corona. Studying the in-vitro stability and dissolution of the NPs in physiological mimicking media is relevant to the in-vivo behavior of the nanoparticles. We investigated the stability of MoOx NPs using dialysis as membrane barrier model and UV-Vis, DLS, FTIR, ICP, TEM and XPS as the characterization techniques. Our results show that after initial agglomeration of the NPs in the presence of the proteins the particles will dissolve at the physiological pH and will probably be excreted in the form of ions. The obtained results will be discussed in detail, suggesting a plausible mechanism of dissolution/interaction.

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures IV

Room: Coquina Salon C

Session Chair: Muhammet Toprak, KTH Royal Institute of Technology

1:30 PM

(ICACC-S7-017-2019) Nanocomposite Electrospun Membranes Designed for Water Treatment (Invited)

A. Uheida*[1]

1. KTH Royal Institute of Technology, Applied Physics, Sweden

Rapid industrialization and societal development have led to elevated releases of toxic substances into the environment. These substances seriously influence the metabolism of living organisms and cause permanent threats; therefore they represent a potential hazard to the ecosystem. High environmental standards have made the removal of contaminates such as heavy metals (arsenic, chromium) and other toxic substances from water bodies an important problem for environmental engineering. Therefore, there is a need for the development of efficient and effective process for the treatment of discharge streams and recovery of valuable components. This presentation aims at providing a brief overview on the design and development of surface engineered nanomaterials including surface functionalized electrospun nanofibers, nanofiber/nanoparticles composites to be implemented in environmental clean-up including wastewater treatment and specifically the treatment of industrial effluents. Specifically, we present results obtained from surface engineered nanocomposite membranes such as PAN/TiO_2-NH_2, PAN-CNT/TiO_2-NH_2, PAN/SiO_2-PEI-Fe^{+3}, and PAN/ZnO NRs, respectively. The results demonstrate that due to their relatively high adsorption and photocatalytic capabilities, nanocomposite electrospun membranes have the potential to be utilized for the removal of heavy metals and destruction of toxic organic compounds from water.

2:00 PM

(ICACC-S7-018-2019) Au nanoparticle decorated rGO/MoS_2 Sandwich Photoanode

J. Ting[1]; P. Lin*[1]

1. National Cheng Kung University, Materials Science and Engineering, Taiwan

As an effort to combat the global warming, human beings are looking for clean, sustainable, and even low cost energy sources. Undoubtedly, hydrogen is one of the promising alternative energy sources to replace fossil fuels, such as coal, petroleum, and natural gas. Hydrogen generation through, for example, water splitting reaction, is therefore being intensively investigated. One of the key issues in water splitting technique resides on the catalyst that is used as the photoanode. In the study, we have investigated a novel catalyst for

use as the photoanode. The material is a novel visible light response Au nanoparticle decorated rGO/MoS_2 photocatalyst. The synthesis of such photocatalyst involves the use of a supercritical fluid carbon dioxide process. The processing conditions were studied to obtained desired characteristics of the photocatalyst. Photoanodes were then made form selected photocatalyst. The hydrogen generation was evaluated using a water splitting cell having such photoanodes.

2:20 PM

(ICACC-S7-019-2019) Synthesis of $BaTiO_3$ nanoparticles by hydrothermal method using electrospun TiO_2 nanofibers

S. Teber[1]; O. Küçük[1]; I. Kaya[1]; V. Kalem*[1]; H. Akyildiz[1]

1. Konya Technical University, Metallurgical and Materials Engineering, Turkey

Synthesis of barium titanate nanoparticles was achieved via two consecutive methods. In the first step, titania nanofibers were obtained via the electrospinning method. Then, these nanofibers were used as the Ti-source in the hydrothermal synthesis of nano-scale barium titanate particles. Formation of barium titanate particles and their final properties are directly affected by the shape, size, and chemistry of Ti-precursor. Thus, microstructural and compositional analyses were conducted for both the titania nanofibers and the barium titanate nanoparticles. Phase-structure analyses revealed that cubic symmetry was dominant in the nanoparticles, whereas Raman spectroscopy results indicated the coexistence of cubic and tetragonal symmetries. The average diameter of titania nanofibers was measured as ~153 nm, and the average size of barium titanate nanoparticles was ~110 nm. Photocatalytic activities of the nanoparticles were determined via the decomposition of methylene blue dye aqueous solutions under UV-A and visible light irradiations. Degradation efficiencies after 1 h for UV-A and visible light reached 38.6% and 28.1%, respectively. Dielectric characterization was conducted on sintered and electroded disc-shaped samples. Among the employed temperatures for sintering, 1250 °C led to the highest relative density (90 %) and the highest dielectric constant value (2165 at 1 MHz).

2:40 PM

(ICACC-S7-020-2019) Hydrothermal synthesis of MoS_2/CdS heterostructures on montmorillonite nanosheets for enhanced photocatalytic activity

K. Peng*[1]; H. Wang[1]

1. Xi'an Jiaotong University, China

Montmorillonite@MoS_2/CdS composite materials (MMT@MoS_2/CdS) were successfully prepared through one-step hydrothermal growth of MoS_2 nanosheets/CdS nanoparticles heterostructures on surface of montmorillonite. The photocatalytic activity of samples was evaluated by degradation of organic dye Rhodamine B, and the ratio of MoS_2 and CdS was optimized. The microstructure and morphology characterization indicates that MoS_2 nanosheets and CdS nanoparticles are assembled on the surface of montmorillonite with the interface interaction, which have smaller size and higher dispersibility in composites. MMT@MoS_2/CdS composites have large special surface area, high visible light absorption and low recombination rate of photogenerated electron-hole pairs. MMT@MoS_2/CdS-7 exhibits the highest adsorption rate and photocatalytic activity, and the overall decoloration rate of RhB was up to 98.8% after visible light irradiation for 45 min. The special structure of montmorillonite and MoS_2/CdS heterostructures could enhance visible light photocatalytic activity of composites through a synergistic effect, and the possible photocatalytic reaction mechanism was explored. The MMT@MoS_2/CdS composites show prospective application for photocatalytic degradation of organic dye in wastewater under visible light irradiation.

Synthesis, Functionalization and Assembly of Inorganic and Hybrid Nanostructures V

Room: Coquina Salon C

Session Chair: Daniel Stadler, University of Cologne

3:20 PM

(ICACC-S7-021-2019) Again on TiO_2. Fundamental Studies and Applications of Colloidal TiO_2 and Complex Nanocrystals (Invited)

M. Epifani*[1]

1. CNR-IMM, Italy

Titanium dioxide has become a very popular material displaying a plethora of different properties and applications. The synthesis of TiO_2 nanocrystals with controlled shape, size and phase is now well established by a variety of techniques. Nevertheless, still there is room for learning more about the fundamental properties of such materials. In the present work the solvothermal crystallization to anatase of small (size <5 nm) amorphous TiO_2 nanoparticles will be summarized, evidencing the importance of surface composition in crystallization phenomena in such size regime. Hints about the shape control by oriented attachment will be provided. Finally, it will be shown that the involved sol-gel chemistry allows the tailoring of the surface composition of titania nanocrystals and, hence, of the surface properties and reactivity. In particular, the deposition of layers of another oxide such as MoO_3, Fe_2O_3, V_2O_5 will be illustrated. The resulting applications in scattered fields such as chemical sensors, supercapacitors and water filtering will be briefly discussed, as demonstration of the effectiveness of the surface modification and of the range of properties achievable by using the same TiO_2 base material.

3:50 PM

(ICACC-S7-022-2019) Development of graphene oxide based materials for the adsorption of arsenic in water

C. Reynosa[1]; G. Navarro[1]; E. Lopez-Honorato*[1]

1. CINVESTAV, Mexico

The contamination of water wells by arsenic is an important challenge that affects millions of people worldwide. Although nanomaterials are capable of adsorbing arsenic with high efficiencies in laboratory tests, when tested in natural waters their efficiency generally drops due to interference of secondary salts such as sulfates, phosphates or carbonates. In this work we show the synthesis of graphene oxide with different degrees of oxidation (maximum adsorption capacity of 288 mg/g) functionalized with different thiol based molecules (cysteamine, SO3H, sulfanilic acid) and calixarenes, with the aim of producing an adsorbent material with selectivity towards arsenic. We compare the effect of pH and secondary salts (phosphates, sulphates and carbonates) on the maximum adsorption capacities for As(III). We show that it is possible to maintain adsorption capacity regardless of pH value and reduce the effect of secondary molecules by controlling the functionalization of graphene oxide.

4:10 PM

(ICACC-S7-023-2019) Economical materials design and processing guided by DFT-thermodynamics calculations

H. Choi*[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Finding new functional materials and accurate quality control of commercial materials are of great research interests both in academy and industry. Phase transition, defect formation, nanostructure geometry change are all important in materials manufacturing, and also are the results of thermodynamic equilibrium in given fabrication conditions. Good understanding and accurate predictions of phase equilibria and property changes are always wanted, but frequently encounter the difficulties in obtaining thermodynamic

parameter. Density functional theory (DFT) calculations are capable of giving exact energy parameters, which can be important building blocks of prediction of phase equilibria and materials properties (magnetic, optical, electrical, mechanical, etc). In this talk, I will present my recent successful stories about fast and 1) economical new materials discovery for memory device, 2) guiding one-step solution synthesis of highly active photocatalytic material, and 3) quality control of commercial photocatalytic materials using DFT-thermodynamics simulations.

4:30 PM

(ICACC-S7-024-2019) Photocatalytic performance of rGO/$Mo_xW_{1-x}S_2$ nanocomposite and its application for photoelectrochemical water splitting

J. Ting[1]; M. Li*[1]

1. National Cheng Kung University, Materials Science and Engineering, Taiwan

Hydrogen generation is one of the most important renewable energy technologies in these days, because its high energy density and environmental friendliness. In this study, we have synthesized a novel material, namely, reduced graphene oxide (rGO)/$Mo_xW_{1-x}S_2$ nanocomposites and demonstrated its use as a light-driven photocatalytic water splitting. The $Mo_xW_{1-x}S_2$ was first alloyed using a one-step microwave-assisted hydrothermal (MHT) method. Different ratios of the Transition metal dichalcogenides (TMDs) precursors were used in order to obtain $Mo_xW_{1-x}S_2$ having various characteristics. rGO was then added using either the MHT method or a supercritical fluid technique. The rGO was added to enhance the electron transfer so that the electron-hole pair recombination is reduced or eliminated. Effects of the synthesis condition on the characteristics of the $Mo_xW_{1-x}S_2$ and rGO/$Mo_xW_{1-x}S_2$ nanocomposite were investigated. The hydrogen generation performance is discussed.

4:50 PM

(ICACC-S7-025-2019) ZnO nanorod gas sensors deposited by atomic layer deposition

C. R. Foschini*[1]; A. Simões[1]; C. A. Fortulan[2]; E. Longo[3]; K. Zhang[4]; H. Baumgart[4]

1. São Paulo State University - UNESP, Mechanical Engineering, Brazil
2. University of São Paulo, Mechanical Engineering, Brazil
3. Federal University of Sao Carlos, Chemistry, Brazil
4. Old Dominion University, Electrical and Computer Engineering, USA

Zinc oxide (ZnO) is an important multifunctional material with versatile applications in gas and biological sensors, solar cells, catalysts, electronics, piezoelectric devices and high-efficiency short-wavelength optoelectronic nanodevices owing to their wide band-gap (3.37 eV), high mechanical and thermal stabilities, and good electrical conductivity while being piezoelectric and optically transparent. Gas sensors based on ZnO nanostructures can be used to detect the concentration of ethanol vapor, and carbon monoxide. Especially, due to their high surface-to-volume ratio, ZnO nanorods are commonly introduced into gas sensors in many applications. In this work, we report on hydrothermal growth of well-aligned ZnO nanorod arrays perpendicularly oriented on ZnO seed layers which were prepared on the substrate by atomic layer deposition (ALD). The ZnO nanorods were growth by hydrothermal method with zinc nitrate hexahydrate, hexamethylenetetramine, and DI water. Very fine grained ZnO seed layers were deposited by ALD and dense ZnO nanorod arrays were grown by hydrothermal process. The crystal structure of ZnO was analyzed by X-ray diffraction (XRD). ZnO nanorods morphology was inspected using a field emission scanning electron microscopy (FE-SEM) and ZnO seed layer was investigated by atomic force microscopy (AFM). The sensing performance of ZnO nanorod samples were investigated using a sensor testing system.

S8: 13th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT13)

Functional Materials and Composites

Room: Coquina Salon A

Session Chairs: Fiqiri Hodaj, Grenoble Institute of Technology; Emanuel Ionescu, Technical University Darmstadt

8:30 AM

(ICACC-S8-041-2019) In-situ Catalytic Preparation of High Performance Ceramic Nanofibers and Reinforced Composites (Invited)

S. Zhang*[1]

1. University of Exeter, United Kingdom

In-situ catalytic formation technique exhibits several advantages, including: 1) low formation temperature and high product yield, 2) in-situ formation, 3) use of less-expensive precursors, and 4) high performance of product nanofibers and composites. Consequently, it has attracted a great deal of interest. In this talk, the recent work at Exeter on using this technique to synthesize novel ceramic nanofibers and reinforced composites will be reviewed. The presentation starts with a brief background introduction, which is followed by a detailed description of the techniques developed for nanocatalyst preparation. The third part focuses on in-situ formation of some representative types of ceramic nanofibers such as high aspect ratio carbon nanofibers/tubes, Si_3N_4 nanofibers/belts and SiC nanofibers. The effects of various catalysts on their formation will be discussed, based on which, and the first-principles density-functional theory calculations, the corresponding catalytic formation mechanisms will be clarified. In the fourth part, the work on in-situ nanofiber reinforced ceramic composites, e.g., carbon nanofiber reinforced alumina composites, Si_3N_4 nanofiber reinforced SiC composites, and SiC nanofiber self-reinforced SiC composites will be presented. Finally, future work on using this in-situ technique to synthesize other types of novel ceramic materials will be suggested.

9:00 AM

(ICACC-S8-042-2019) Bioinspired materials templates by nature species

D. Zhang*[1]; J. Gu[1]; Z. Li[1]; W. Zhang[1]; Q. Liu[1]; D. Xiong[1]; Y. Li[1]

1. Shanghai Jiao Tong University, China

Biological materials naturally display an astonishing variety of sophisticated nanostructures that are difficult to obtain even with the most technologically advanced synthetic methodologies. Inspired from nature materials with hierarchical structures, many functional materials are developed based on the templating synthesis method. We change their original components into our desired materials with original morphologies faithfully kept. Properties of the obtained materials are studied in details. Based on these results, we discuss the possibility of using these materials in photonic control, solar cells, electromagnetic shielding, energy harvesting, and gas sensitive devices, et al. In addition, the fabrication method could be applied to other nature substrate template and inorganic systems that could eventually lead to the production of optical, magnetic, electric devices or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems. These bioinspired functional materials with improved performance characteristics are becoming increasing important, which will have great values on the development on structural function materials in the near future.

9:20 AM

(ICACC-S8-043-2019) Formation of Tungsten Carbide Nanoparticles by Wire Explosion Process

P. Ranjan*[1]; T. Kurosaki[2]; H. Suematsu[2]; R. Jayaganthan[3]; R. Sarathi[1]

1. Indian Institute of Technology Madras, Department of Electrical Engineering, India
2. Nagaoka University of Technology, Extreme Energy-Density Research Institute, Japan
3. Indian Institute of Technology Madras, Department of Engineering Design, India

Wire explosion process (WEP) or pulsed wire discharge is a single step and economic method to produce metal and its compound (oxide, nitride, carbide and intermetallic etc.) nanoparticles (NPs). Here, a metal wire is subjected to pulsed current of high magnitude to sublimate it, the ambient fluid works as reacting as well as cooling medium for the formation of NPs of required size and phase content. In WEP, morphology and phase of NPs are controlled using different levels of energy ratio, K (ratio of energy supplied to wire and sublimation energy of wire), type and pressure, P of ambience. Tungsten carbide finds various applications and the conventional preparation processes are cumbersome and time consuming. Thus in the present study, the formation of tungsten carbide (WC_{1-X}) in a single step by WEP using methane and argon-acetylene mixture as carburizing medium, is detailed. XRD and TEM were used to observe the phase and morphology of the produced NPs. High purity WC_{1-X} NPs was synthesized in methane ambience with a high K (=19) and a high P (270 kPa). A thorough study has been made to understand the impact of type of carburising medium. Methane-acetylene mixture gave two phases of carbides. Argon-acetylene ambience provided complete carburization in specific cases. In general, the formed NPs are spherical in shape. Formation mechanism of tungsten carbide NPs is detailed in the work

9:40 AM

(ICACC-S8-044-2019) Demonstration of lead-free piezoceramic components

S. Labonnote-Weber*[1]; M. Christensen[1]; G. Syvertsen-Wiig[1]; A. B. Richter[1]

1. Ceramic Powder Technology AS, Norway

Today, more than 98% of the piezoceramic components are based on lead-containing materials (PZT). The state-of-the art process used to produce PZT materials, solid-state synthesis, is not suitable for lead-free piezoceramics, mainly due to evaporation of volatile species and poor sinterability. Therefore, substantial effort is needed to develop and modify production- and processing technologies to qualify lead-free piezoceramic materials, components and devices. Proven reliability and consistency over time - of both materials and components - are key technological barriers to overcome in order to commercialize lead-free piezoelectric devices. Here we present a modular synthesis route, spray pyrolysis, capable of producing lead-free piezoceramic materials at industrial scale. The process yields homogeneous materials, gives very good stoichiometric control and produces submicron powders with excellent sinterability. Despite the beneficial properties and quality offered by spray pyrolysis, protocols developed for solid-state powders cannot be directly used with spray pyrolysed materials to produce components. Cerpotech and partners are developing components using spray pyrolysed powders and existing industrial manufacturing platforms to validate the performance and consistency of materials and components for competitive products.

10:20 AM

(ICACC-S8-045-2019) Nanoporous Nitrides for Energy and Catalysis (Invited)

A. Vinu*[1]

1. University of Newcastle, Global Innovative Center for Advanced Nanomaterials, Australia

Our group has been actively researching on the design of new mesoporous materials including carbons, nitrides, fullerenes, polymers and biomolecules. A new family of mesoporous materials such as mesoporous CN, BN, BCN and carbides with different structures, morphology, and pore diameters which have unique basic and electronic properties has been discovered. Here, I will discuss about the synthesis of novel mesoporous BN and BCN materials with hexagonal and cage type porous structure and spherical morphology using mesoporous carbon or carbon nanocages with 3D porous structure as a template via an elemental substitution method at a low synthesis temperature. The obtained materials exhibit a large specific pore volume with uniform pore size distribution and the specific surface area. I will also show the application of these materials for field emission. I will discuss about the preparation techniques, basics and the mechanism behind the synthesis of various nanoporous nitride materials with different pore structure and textural parameters. One of the important features of the materials is that they have inbuilt basic sites in the form of NH2 or NH and can be used as a metal free basic catalyst. I will also demonstrate their applications in energy storage and catalysis.

10:50 AM

(ICACC-S8-046-2019) Bioinspired 3D Superhydrophobic Porous Ceramics for Oil-water Separation (Invited)

H. Zhang*[1]

1. Wuhan University of Science and Technology, State Key Laboratory of Refractories and Metallurgy, China

Oil/water separation is a global challenge. Hydrophobic and oleophilic sorbents play an important role in the remediation processes of oil spills. Herein, lotus seedpod bioinspired 3D superhydrophobic diatomite and sepiolite porous ceramics with good mechanical strength and thermal stability were fabricated using graphene/carbon nanobelts as modifier. The carbon nanobelts were in-situ formed using polyethylene as carbon precursor. The as-prepared porous ceramics demonstrated 3-30 times higher adsorption capacity of oil/water separation than conventional inorganic sorbent materials, and their compressive strength is about 70-270 times higher than that sponge/graphene based sorbent materials. More importantly, the as-prepared porous ceramics can continuously separate oil from oil/water mixture. Meanwhile, this work may offer a new strategy for the treatment/recycling of the so-called "White Pollution" of waste plastics.

11:20 AM

(ICACC-S8-047-2019) Electronic Ceramics Science, Solar Energy and Fractal Nature

V. Mitic*[1]; G. Lazovic[3]; V. Paunovic[2]; S. Shaikh[4]; S. Veljkovic[2]; B. Vlahovic[5]

1. Serbian Academy of Sciences, Institute of Technical Sciences, Serbia
2. University of Nis, Faculty of Electronic Engineering, Serbia
3. University of Belgrade, Faculty of Mechanical Engineering, Serbia
4. Pune University, India
5. North Carolina Central University, USA

The advance material science faces the lack of energy, incline towards new energy sources. The BaTiO3 as a perovskite, has fractal configuration based on three different phenomena: grains have fractal shape as a contour in cross section or as a surface, so-called "negative space" made of pores (important role in micro-capacity, microelectronics, PTCR and other), and Brownian micro-particles fractal motion inside the material (ions, atoms and electrons). These triple factors are basic effects for complex fractal correction.

The stress is set on inter-granular super micro-capacitors and overall impedances distribution in function of energy harvesting and storage. Fractal nature recognize micro-capacitors with fractal electrodes. Inter-granular permeability is taken as fundamental thermodynamic parameter temperature function. In this paper, for the first time we are successfully involving the fractal correction in electrical current Butler-Volmer equation. This is the new approach within the alternative energy sources by fractal nature corrections.

S9: Porous Ceramics: Novel Developments and Applications

Modeling and Mechanical Properties of Porous Ceramics

Room: Coquina Salon E

Session Chair: Tobias Fey, Friedrich-Alexander University Erlangen-Nürnberg

8:20 AM

(ICACC-S9-009-2019) Structural Modeling of Cellular (porous) Ceramics (Invited)

M. Ravichandran*[1]

1. Corning Research and Development Corporation, USA

Cellular porous ceramics have a significant position in automotive applications for environmental protection due to their high surface to volume ratio. Understanding their structural response in use as well as during manufacturing is important for maintaining a sustainable value proposition. There are several challenges in structural modeling of cellular ceramics – some obvious and others non-intuitive. Structural modeling with these materials typically needs discretization to feed the problem to commercial or home-grown simulation software. The obvious challenge of over-discretizing is circumvented by using "effective" or continuum properties. Determining "correct" continuum properties is not always trivial particularly when the in-situ behavior differs substantially from constituent components, e.g. plugs in particulate filters. Gathering such inputs for "in process" structural modeling poses problems of a different kind due to path dependence, lack of stability of intermediates etc. Challenges with the drivers of structural response, mainly temperature distributions or related quantities/derivatives, are more conventional, i.e. not necessarily due to the cellular structure. Finally, extracting usable assessments from modeled responses needs some finesse in post-processing. This talk will outline the challenges and mitigation strategies that can help enhance the quality of the modeled responses towards credible assessments.

8:50 AM

(ICACC-S9-010-2019) Computational Micromechanical Modeling of Compressive Behavior for Freeze-Casted Porous Ceramic (Invited)

O. Kravchenko*[1]; S. Sattar[1]; D. Ghosh[1]

1. Old Dominion University, Mechanical and Aerospace Engineering, USA

The computational micromechanical model to understand the structure-property behavior of ice-templated ceramic is proposed. The developed framework allows to determine how various parameters such as the porosity, wall thickness and bridge density control the effective mechanical behavior of porous anisotropic ceramic under various loading conditions. In order to capture complex deformation behavior, an efficient computational scheme is established, which captures the hierarchical multi-scale nature of ice-templated morphology. Specifically, in-plane assembly of regions, orthogonal to the ice crystal growth direction, represent the transversely isotropic meso-scale of the material. The micro-scale is captured by the aligned lamella walls and bridges, giving rise to anisotropic hierarchical morphology effective to resisting compressive deformation, which strongly depends on the porosity. The proposed computational framework is instrumental in understanding the microscopic deformation mechanisms and competing failure modes that originate in this material system. The model provides a quantitative method of predicting the effective mechanical properties and is valuable for formulating ice-templated structures with targeted mechanical properties for various applications.

9:20 AM

(ICACC-S9-011-2019) A systematic mechanical study on ceramic triply periodic minimal surfaces: Design, FEM analysis, stereo lithography, sintering and compression testing

M. Pelanconi[1]; O. Al-Ketan[2]; O. Santoliquido[1]; R. Abu Al-Rub[2]; A. Ortona*[1]

1. SUPSI, MEMTi, Switzerland
2. Khalifa University of Science and Technology, Mechanical Engineering Department, Masdar Institute, United Arab Emirates

Triply periodic minimal surfaces (TPMS) are bio inspired porous structures which present outstanding effective mechanical properties because of the optimal spatial disposition of their solid phase. These structures are emerging in these days because it is now possible to physically realize them, thanks to additive manufacturing (AM). In this work, we present a systematic framework to create ceramic TPMS. We start with mathematically creating the minimal surface using level-set approximation equations, then the minimal surfaces are either thickened to create sheet-based structures, or solidified to create strut-based structures. The considered TPMS are CLP-sheet, Gyroid-sheet, Gyroid-strut, Primitive-sheet and Primitive-struts. After the design process, CAD files were exported and samples were 3D printed using the photo-polymerization additive manufacturing technique, then ceramized via thermal treatments. Mechanical properties were obtained by compression tests. Their behaviour was deeply studied thanks to a parallel computational work with by finite element analysis.

9:40 AM

(ICACC-S9-012-2019) Mechanical properties of porous ceramics with tailored microstructure

B. Wang*[1]; J. Yang[1]

1. Xi'an Jiaotong Universitty, State Key Laboratory for Mechanical Behavior of Materials, China

Porous ceramics with ultra-low density are of great interest as potential engineering material at high temperature environment. However, high porosity of ceramics leads to low mechanical properties. For improving the specific mechanical properties of porous ceramics, three methods (i) implanting pressurized gas in the closed pores, (ii) decreasing the grain size to nano-scale, and (iii) tailoring the necking area between grains were proposed. The results were shown that high enclosed gas pressure in porous Pyrex glass led to high collapse stress of closed pores, consequently contributing to high strength. The strength of porous silicon nitride with porosity of 73% could reach to 70 MPa, due to its low diameter of rod-like β-Si3N4 grains ~200 nm. Higher value of d/d0 (the diameter of necking area size/ the diameter of SiC,) led to higher flexural strength of porous SiC ceramics.

Innovations in Processing Methods and Synthesis of Porous Ceramics II

Room: Coquina Salon E

Session Chairs: Manivannan Ravichandran, Corning Research and Development Corporation; Oleksandr Kravchenko, Case Western Reserve University

10:20 AM

(ICACC-S9-013-2019) Porous silicon nitride: A material for the bioactive composite implants (Invited)

P. Sajgalik*[1]

1. Instute of Inorganic Chemistry, Slovak Academy of Sciences, Ceramics Department, Slovakia

Silicon nitride-based ceramics are characterized especially by high chemical resistance, superior combination of fracture toughness, hardness, and thermal shock and wear resistance. On the other side silicon nitride attracts interest also for bio-applications in the human body as bio inert material. In this work porous or dense silicon nitride based substrate in the form of bulk or granules/microspheres were prepared and subsequently covered by the hydroxyapatite/ calcium phosphate phase thin layer in order to change the substrate from bio-inert to bio-active. Four different silicon nitride based bio-active materials will be presented with the aim to show a potential of silicon nitride in bio applications: 1.) Porous silicon nitride with bone-like pore structure prepared by replica method and 2.) Porous spheres of size about one millimeter (or more) on average prepared by water silicon nitride suspension by freeze drying. 3.) Surface modification of dense silicon nitride body using an oxyacetylene torch at high temperatures and the formation of a thin (2-5 mm) and porous bioactive layer based on the grain boundary composition with chemical adhesion to substrate. 4.) Porous silicon nitride microspheres of size about 10-100mm prepared by flame synthesis.

10:50 AM

(ICACC-S9-014-2019) Novel modular ceramic building blocks / polymer composites based on a near net shape process: Manufacturing, characterisation and application (Invited)

J. Biggemann[1]; M. Stumpf[1]; B. Diepold[1]; M. Pezoldt[1]; P. Greil[1]; T. Fey*[1]

1. Friedrich-Alexander University Erlangen-Nürnberg, Department Material Science and Engineering, Germany

Modular composites with a 3D periodic structure, consisting of a brittle inorganic phase (building-blocks) and a viscoelastic organic matrix, offer great potentials for improved fracture toughness and failure probability. Ceramic building blocks were assembled by a placing system equipped for 3D periodic structures as cubic, monoclinic and triclinic unit cells in a near-net-shape approach. Afterwards infiltration with a epoxy resin to fabricate epoxy-alumina composites follows. The brick-and-mortar like building block exhibited improved bending strength, fracture toughness and failure probability compared to monolithic epoxy. Based on these basic structures modular ceramic arteriovenous loops (AV-loops) with a hierarchical porosity approach were designed to ensure rapid vascularization for bone ingrowth. Bioactive building blocks with dimensions of 1.5 – 3.0 mm were assembled to complex AV-loop scaffolds using a biocompatible adhesive. The modular AV-loop scaffolds provide a hierarchical interconnected pore network (P = 58.8 %) for optimum vascularization and complete bone ingrowth. The modular building block approach allows to design patient individualized scaffolds with complex hierarchical pore networks where volume, size and can be tuned by changing the dimensions, shape and placing gap of the bioactive building blocks.

11:20 AM

(ICACC-S9-015-2019) A process to control the microstructure of porous alumina using spherical porous powder (Invited)

S. Takahashi*[1]; S. Suehiro[1]; H. Okawa[1]; T. Kimura[1]

1. Japan Fine Ceramics Center, Materials Research and Development Laboratory, Japan

Porous ceramics are utilized for many applications like thermal insulation, separation membrane and catalyst support. In this study, porous alumina was synthesized using spherical porous powder. The spherical powder was synthesized by splay pyrolysis method with ultrasonic nebulizer. Aluminum nitrate, citric acid and ammonia water were dissolved in deionized water and the solution was sprayed in the apparatus. Green disks were prepared by CIP at 245MPa after uniaxial pressing at 49MPa, and were sintered at 1400°C for 2 hours in air. Sintered discs showed the high porosity and the sharp pore size distribution. For example, an open porosity of a disk was 55.9%, the average pore diameter was 0.60μm and a ratio of D10/D90 was 1.4. By conventional process, it was not able to achieve a porous alumina with high porosity, pore size of submicron and sharp pore size distribution simultaneously. There is some possibility of controlling such a microstructure of porous alumina in this process.

11:50 AM

(ICACC-S9-016-2019) MAX-phase (Ti_2AlC) foams by gelcasting

T. Fey*[1]; M. Stumpf[1]; A. Chmielarz[2]; P. Colombo[3]; P. Greil[1]; M. Potoczek[2]

1. Friedrich-Alexander University Erlangen-Nürnberg, Department Material Science and Engineering, Germany
2. Faculty of Chemistry, Rzeszow University of Technology, Poland
3. Dipartimento di Ingegneria Industriale, Università di Padova, Italy

Ceramic MAX-phase (Ti_2AlC) foams were manufactured by gel-casting. As gelling agent agarose was used. The microstructural, mechanical and thermal properties were investigated. SEM-analysis was used for microstructural determinations and compared with X-ray micro tomography measurements. Impulse excitation technique was used for Young's Modulus of Ti_2AlC foams determination. The experimental data was correlated with the Gibson-Ashby, Spriggs and Cross-property relation models. Laser-Flash analysis were used to determine thermal conductivity up to 900°C. These measurements were correlated to the pore network in the Ti_2AlC foam structure derived from μCT measurement. FEM-simulations of the mechanical behaviour were carried out on real structure models to determine a strut wise stress distribution under load.

Innovations in Processing Methods and Synthesis of Porous Ceramics III

Room: Coquina Salon E

Session Chair: Valentina Medri, National Research Council of Italy

1:30 PM

(ICACC-S9-017-2019) Pore Tunability and Composite Strategies for Reliable Porous Ceramics (Invited)

K. Faber*[1]; N. Arai[1]; C. Kuo[1]; C. Keck[1]

1. California Institute of Technology, USA

Porous ceramics are often limited by their mechanical strength, despite their desirable flow, transport and high surface area characteristics. Solution-based directional freeze casting of preceramic polymers has been particularly fitting for tunability of pore networks and walls and for creating hierarchical porous microstructures. A number of strategies are reported here for both pore and pore wall design for enhanced mechanical behavior of porous Si-based ceramics. Firstly, the viscosity of polymethylsiloxane preceramic polymer is shown to influence bridge formation between lamellar SiOC walls, and consequently mechanical robustness. Secondly,

wall-to-wall bridges are also created using a two-stage freeze casting method. Thirdly, reinforcing fillers are incorporated into the freeze-casting process to created composite wall structures. Multiwall carbon nanotubes or SiC whiskers are dispersed in casting solutions, and are retained through pyrolyzation. The carbon nanotubes are preserved within SiOC walls, while the SiC whiskers both reinforce walls and form bridges. For each of the strategies explored, permeability, compressive strength, and microstructure are assessed to verify the efficacy of these approaches.

2:00 PM

(ICACC-S9-018-2019) Macroporous alumina ceramics using pre-expanded polymer microspheres as sacrificial templates

M. Ciurans Oset[1]; J. Nordin[2]; F. Akhtar*[1]

1. Luleå University of Technology, Division of Materials Science, Sweden
2. AkzoNobel Performance Chemicals AB, Expancel, Sweden

In this study, macroporous alumina ceramic foams were fabricated by gel-casting using pre-expanded polymeric microspheres of diameters of 40 μm, 20 μm and 12 μm as sacrificial templates. The gel-casting method, as well as the drying, debinding and sintering conditions were investigated and optimized to process mechanically strong and highly porous alumina ceramics. Furthermore, a reliable model relating the amount of pre-expanded polymeric microspheres and the total porosity of the sintered foams was developed and validated by mercury intrusion porosimetry measurements. The electron microscopy investigation of the sintered foams revealed that the size distribution and the shape of the pores could be tailored by controlling the particle size distribution and the shape of the expanded microspheres. Highly uniform and mechanically stable alumina foams with compressive strengths ranging from 3.3 to 36.7 MPa were processed with 61.6 to 80.2 vol. % bimodal porosity. Given the relatively open pore structure, the pore size distribution, the mechanical strength and the high porosity achieved, alumina foams produced could potentially be used as support structures for separation, catalytic and filtration applications.

2:20 PM

(ICACC-S9-019-2019) Aligning and Engulfment of High-Aspect Ratio Fillers in Freeze Casting

C. Kuo*[1]; K. Faber[1]

1. California Institute of Technology, Material Science, USA

As high-aspect ratio fillers are used more often in freeze casting nowadays for their ability to achieve mechanical reinforcement, high conductivity and magnetic alignment, understanding the interaction between the solidification front and high-aspect ratio fillers becomes increasingly important for processing and material-designing. In our research, SiC whisker-SiOC porous composites were produced by dispersing silicon carbide whiskers in a polysiloxane preceramic polymer solution, followed by freeze-casting and pyrolysis. The resulting porous solids demonstrate both microstructural wall reinforcement by whiskers and interlamellar whisker bridges, produced by whisker engulfment by the freezing front during freeze casting. To define conditions for whisker engulfment, we model various freezing front-whisker configurations. We found that the respective position of high-aspect fillers to the freeze-cast walls (in-wall or between-wall) can theoretically be controlled by changing the attractive and repulsive forces at play during solidification, and hence, change the structure of freeze-cast materials. The results from the engulfment models were compared with the experimental values. The effect of bridges formed by aligned fillers on strength and permeability in freeze-cast structures were also investigated experimentally.

2:40 PM

(ICACC-S9-020-2019) Synthesis of a Highly Porous Nano Fibrous Si_3N_4 Ceramic through Gas-Solid Reaction of CNT and SiO Combined with Liquid-Phase Sintering

Q. Zhi*[1]; B. Wang[1]; Y. Deng[1]; N. Zhang[1]; J. Yang[1]

1. State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, China

In this work, a delicate strategy that carbothermal reduction-nitridation (CRN) reaction carried out by carbon nanotube and SiO vapor, combined with low temperature liquid-phase sintering, was rationally designed for direct fabrication of fibrous nano-sized β-Si_3N_4 structured porous ceramic, with average diameter of grain of approximately 200nm, and average aspect ratio of higher than 20. More strikingly, its porosity was up to 73%, while the ceramic possessed a superior mechanical properties, The bending and compressive strength reached up to 62 and 80 MPa respectively, and particularly, it exhibited a large strain to failure and 'pseudo-plastic' deformation behavior during the compressive test. More significantly, the underlying growth mechanism of the high aspect ratio nano-sized β-Si_3N_4 grain synthesized via this method was comprehensively analyzed and tentatively put forward.

Properties of Porous Ceramics

Room: Coquina Salon E

Session Chairs: Katherine Faber, California Institute of Technology; Seiji Takahashi, Japan Fine Ceramics Center

3:20 PM

(ICACC-S9-021-2019) Preparation and hydrogen peroxide decomposition behavior of layered double hydroxides (LDHs) composed of various transition metals (Invited)

Y. Kameshima*[1]; S. Nishimoto[1]; M. Miyake[1]

1. Okayama University, Japan

Layered double hydroxides (LDHs) have been investigated for many years as host materials for anion exchange intercalation reactions. They have been used extensively as ion-exchange materials, catalysts, sorbents and halogen scavengers. LDHs composed of various transition metals are also known as precursors of metal oxide catalysts and photocatalysts. On the other hand, we have already found the phenomenon that Mg-Fe type layered double hydroxides (LDHs) decomposed $H_2O_2$by oxidation - reduction reaction of iron ions in LDH host layer. In this paper, LDHs composed of various transition metals were prepared and hydrogen peroxide decomposition behavior of these LDHs were investigated. The LDHs were prepared by co-precipitation method. The obtained LDHs were characterized by XRD, FT-IR and SEM-EDS. The obtained LDH was dispersed in hydrogen peroxide solution having a predetermined concentration and the amount of oxygen generated and the concentration of hydrogen peroxide in the solution were analyzed. It was suggested that the hydrogen peroxide decomposition behavior varied depending on the transition metal contained in LDH.

3:50 PM

(ICACC-S9-022-2019) Geopolymers Composites for CO_2 Adsorption (Invited)

V. Medri*[1]; E. Papa[1]; E. Landi[1]; P. Benito[2]; A. Vaccari[2]; M. Minelli[2]

1. National Research Council of Italy, ISTEC, Italy
2. University of Bologna, Italy

Geopolymers can be regarded as the amorphous counterpart or precursor of crystalline zeolites. Moreover geopolymers have a quite good CO_2 adsorption capacity and an excellent CO_2/N_2 and CO_2/CH_4 capacity selectivity. The addition of zeolites or hydrotalcites as fillers can further improve the adsorption capacity and composites can be designed and produced in forms of monoliths to be used as solid adsorbents for low and intermediate temperature

CO_2 capture applications. Concerning geopolymer-zeolite composites, Na-based geopolymer composite revealed a synergistic effect, as the CO_2 capacity at low temperature was approximately 20% larger that the value expected. This effect is attributed to the large interaction among the phases obtained by the effective chemical mixing achieved during the geopolymerization reaction. As well different types of hydrotalcites with different Mg/Al ratio can be used as fillers in geopolymer matrices. Upon calcination, the structure of hydrotalcite changes, with loss of interlayered anions and water. The final structure is a mixed oxide metaphase, which presents a large surface area and great affinity for CO_2. At the end of each cycle of calcination/CO_2 adsorption /desorption the composite regains the initial structure thanks to the memory effect.

4:20 PM

(ICACC-S9-023-2019) Porous Foam Glass Insulator Properties Understanding through Microscopy Characterization

A. Stratulat*[1]

1. Carl Zeiss Microscopy Limited, United Kingdom

The development of new advanced foam glass insulators for industrial applications (cavity walls, roofs, piping, etc.) relies on the understanding of the material structure (porosity), material properties (thermal conductivity) and process optimization. In order to solve some of the industrial challenges (achieve homogeneity of pore size distribution, minimize defects, lower thermal conductivity), advanced characterization techniques are required to better understand the performance of these materials. 3D X-Ray Microscopy (XRM) provides methods for imaging and analysis of ceramics such as porosity measurement throughout the volume of interest, identification and segmentation of different phases and non-destructive observations of internal defects or voids. In addition, real 3D structures are generated that can be imported into simulation models to predict thermal properties. This presentation will overview the advantages of coupling XRM with simulations to better understand and improve the materials properties of foam glass insulators.

4:40 PM

(ICACC-S9-024-2019) Pore Morphologies Tailored for Flow and Filtration

N. Arai*[1]; O. Bateman[2]; J. A. Kornfield[2]; K. Faber[1]

1. California Institute of Technology, Materials Science, USA
2. California Institute of Technology, Chemistry and Chemical Engineering, USA

Freeze casting is a ceramic processing method that can tailor the orientation, size and morphology of the pores by changing freezing front velocity, solvent, or solute/particle concentration. However, fundamental understanding is lacking to guide selection of the temperature gradient to provide a desired degree of undercooling and, hence, pore structure. Here, solution-based freeze casting of a preceramic polymer is used as a model system, and the temperature of the freezing solution is controlled from the top and bottom to precisely control the temperature gradient. The effects of the temperature gradient on the resulting freezing front velocity and pore morphology are examined. Mercury intrusion porosimetry reveals the size distribution for both primary pores and secondary dendritic pores. Furthermore, a transition from dendritic to cellular pores is explored by further tuning temperature gradient, freezing front velocity and preceramic polymer concentration. Dendritic pore geometries open new opportunities for filtration: primary pores set a cutoff size for particles entering and secondary pores offer slow recirculation in the "side arms" to delay particles that are small enough to enter them. Performance of freeze-cast SiOC membranes with different pore size distributions will be presented, including the effectiveness of dendritic side arms to retain small particles.

5:00 PM

(ICACC-S9-025-2019) Adsorption of Hydrogen on Polymer Derived Porous Silicon Oxycarbide Ceramics

P. K. Chauhan*[1]; S. Ravindran[1]; P. Rajagopalan[1]

1. Birla Institute of Technology and Science, Hyderabad Campus, Mechanical Engineering, India

Hydrogen as a fuel has huge role to play in future world economy and hence there have been efforts to use it as a fuel. But given its molecular weight, it has been difficult to store and transfer it. Researchers have tried capturing it as hydride, on carbonaceous materials and also on porous Si-O-C. Porous Si-O-C being thermally stable offers a bright prospect. Therefore, we have synthesized porous Si-O-C with aligned porosity and average pore size 2-4 nm. We intend to use this Si-O-C for the hydrogen adsorption studies to be done in custom designed equipment called Sievert's Apparatus. We would be focusing on establishing the nature of the adsorbent surface by relating it to a suitable adsorption model after conducting the studies. We also look forward towards arriving at a clear idea on factors affecting the adsorption, like pore morphology. We also intend to study the isentropic heat of adsorption in detail and relate it to the amount of adsorption and its relevance to formation of a multilayer during the adsorption. This work therefore, aims to establish the various factors affecting adsorption, their co-relation and finally optimization of these variables.

5:20 PM

(ICACC-S9-026-2019) Bulk Cellular SiC with submicron pores: A Study of Processing Temperature's Effect on Microstructure and Mechanical Properties

C. Kassner*[1]

1. University of Virginia, Materials Science and Engineering, USA

Cellular structures have been shown to offer low density alternatives to bulk materials whilst exhibiting relatively high strength and toughness. Specifically, high temperature porous ceramics have extended the possibilities of filtration, light weight structural materials, sensors, etc. In particular, nanoporous structures are a lightweight alternative to bulk materials. Additionally, due to their mesostructure, they possess unique properties due to their ligament size and high surface area. However, scalability has been an issue for most techniques. Submicron cellular SiC, with pore diameters of 500-600nm, have been fabricated using a polycarbosilane preceramic polymer, β-SiC nanopowder, and PMMA powder. The resulting structures were approximately 2cm in length and 1cm in diameter. The samples were then heat treated at temperatures ranging from 1200-1500°C resulting in densities ranging from 950 – 1,150 kg/m3. The compressive strength was measured and values exceeding 100MPa were achieved. It is shown that the addition of β-SiC nanopowder increases the strength of the samples. However, the strength of the samples degrade at processing temperatures above 1300°C. By understanding these processes, we will be able to reduce defect populations on the macro, meso, and nano scale leading to high strength low density ceramics.

S10: Ceramics Modeling, Genome and Informatics

Structural Ceramics III

Room: Coquina Salon G
Session Chairs: Paul Rulis, University of Missouri - Kansas City; David Poerschke, University of Minnesota

8:30 AM

(ICACC-S10-016-2019) Electronic structure and mechanical properties of Ni-based superalloys: Haynes282 and Inconel740 (Invited)

W. Ching*[1]

1. University of Missouri-Kansas City, USA

The electronic structure and interatomic bonding of two solid solution models of Ni-based super-alloys each having 864 atoms with 11 elements are calculated by using ab initio density functional theory methods. The alloys are Haynes282 ($Ni_{444}Cr_{202}Co_{79}Al_{56}Ti_{25}Mo_{25}Fe_{12}Mn_3Si_5C_{12}B$) and Inconel740 ($Ni_{373}Cr_{246}Co_{153}Al_{33}Ti_{21}Nb_6MoFe_6Mn_3Si_{17}C_5$). These complex multi-component alloys have very complicated electronic structure, bonding and partial charge distributions depending on the composition and strength of local bonding. The calculated total bond order density (TBOD) and its partial components (PBOD) is controlled by delicate balance between the propensity of metallic bonding between Ni, Cr and Co atoms, and the very strong bonds with C, Al and other minor elements. Inconel740 has a slightly stronger mechanical properties than Haynes282. Extension of these studies to other high entropy alloys and the effect of precipitates and temperature will be discussed.

9:00 AM

(ICACC-S10-017-2019) A double kinetic equation solver for conducto-radiative heat transfer in porous ceramics (Invited)

B. Dubroca[3]; R. Turpault[2]; G. L. Vignoles*[1]

1. University of Bordeaux, LCTS - Lab for ThermoStructural Composites, France
2. Bordeaux INP, IMB - Maths Institute of Bordeaux, France
3. CEA - LCTS, Lab. for ThermoStructural Composites, France

High-temperature porous ceramics are used for thermal management applications in several contexts: thermal protection systems for atmospheric re-entry of space objects, concentrated solar power plants, porous burners and heat exchangers in industrial facilities, … In all these cases, their heat transfer performances are central to their optimal design and use; so, heat transfer modeling in porous media is an essential tool for them. The difficulty being that radiative and conductive heat transfer occur simultaneously, few efficient numerical solutions have been developed so far. We propose here a new model based on the simultaneous solution of two kinetic equations, one related to conductive heat of the solid phases and the other to the radiative heat. An asymptotic-preserving reduced scheme accounting only for the first moments of the kinetic distributions is set up. Numerical tests of the method are performed to validate it and to assess its performances; applications to realistic 3D images of cellular ceramics in various cases of transient or steady-state heat transfer conditions are discussed.

9:30 AM

(ICACC-S10-018-2019) Theoretical prediction on elevated temperature elastic and thermodynamic properties of transition metal diborides (Invited)

Y. Zhou*[1]; H. Xiang[1]

1. Aerospace Research Institute of Materials & Processing Technology, China

Transition-metal diborides based UHTCs are regarded as the materials of choice for wing leading edges, nose cones of hypersonic vehicles due to their high melting point, chemical inertness, high thermal and electrical conductivity. The service environments are extremely harsh such that selecting and designing materials with suitable high-temperature properties are crucial. Thus, understanding the HT properties is one of the main concerns for UHTCs. However, evaluating HT properties of UHTCs is quite a challenge since few facilities are capable of enduring the harsh testing conditions. Therefore, developing theoretical models to accurately predict HT properties of UHTCs is necessary and a promising solution to the difficulty of evaluating HT properties. In this presentation, thermodynamic and mechanical properties of ZrB_2 and HfB_2 from 0 K to 2000 K obtained from a combination of first principles calculations and quasi-harmonic approximations will be introduced. The calculated ground-state properties, including lattice parameters, elastic constants, phonon dispersion, and mode-Grüneisen parameters will be presented first. Then the theoretical thermal expansion, elastic and thermodynamic properties at elevated temperatures will be shown. Finally, the thermal conducting behavior will be discussed.

Structural Ceramics IV

Room: Coquina Salon G
Session Chairs: Wai-Yim Ching, University of Missouri-Kansas City; Gerard Vignoles, University Bordeaux

10:20 AM

(ICACC-S10-019-2019) Utilizing interface mechanics with the extended finite element method to predict crack growth in ZrB_2-carbon based composites

L. Jarvis*[1]; G. Hilmas[1]; W. Fahrenholtz[1]; M. A. Zaeem[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

Engineered architectures of ZrB_2-carbon based systems have been shown to increase fracture toughness by promoting crack deflection. While different architectures have been studied experimentally, accurate computational modeling of these systems could allow for the design of new and novel architectures in a shorter timeframe. The goal of this research is to predict the crack path in multi-material architectures by utilizing the extended finite element method (XFEM). Typical XFEM implementation has been designed for single material systems. To facilitate accurate prediction of crack growth in these multi-material architectures, a FORTRAN code that incorporates He and Hutchinson's criterion for crack deflection was developed for use in ABAQUS 6.14. These user subroutines were benchmarked by comparing the stress intensity factors to closed-form solutions of cracks in different loading conditions. Preliminary benchmarking showed simulated stress intensity factors within 95 to 97 % of the closed-form solutions for Mode I and Mixed Mode loading conditions. Crack propagation in laminates and fibrous monolithic architectures was then simulated and compared to experimental results. With proper validation, new architectures can be designed to increase the fracture toughness without significantly decreasing the strength.

10:40 AM

(ICACC-S10-020-2019) First-Principles Study on Impurity Tolerance of Pt/Metal-Oxide Catalyst in Anode of Polymer Electrolyte Fuel Cell

N. Ozawa*[1]; K. Kuranari[1]; M. Kubo[1]

1. Tohoku University, Institute for Materials Research, Japan

Polymer electrolyte fuel cell (PEFC) needs anode materials with high tolerance to poisoning by impurities such as CO, which degrades the PEFC performance. Here, Pt/WO_3 catalyst is effective for CO removal by oxidation. For theoretical design of anode materials with high tolerance to impurity poisoning, the mechanism of the CO oxidation on Pt/WO_3 should be revealed. In this study, we investigated CO oxidation processes on a Pt cluster/WO_3(001) by first-principles calculation. To investigate the adsorption states of CO, we calculated the adsorption energy of CO on Pt/WO_3(001). For a Pt/WO_3(001) model, a Pt_{20} cluster is put on WO_3(001). To discuss the role of WO_3, the adsorption energy of CO on an isolated Pt_{20} cluster is also calculated. The adsorption energies on the Pt/WO_3(001) and Pt cluster are 36.40 and 38.24 kcal/mol, respectively. This shows that WO_3 decreases the adsorption energy of CO on the Pt cluster. Next, we discuss CO oxidation on Pt/WO_3(001). The CO oxidation by H_2O proceeds as follows; (i) $H_2O \rightarrow OH + H$ and (ii) $CO + OH \rightarrow CO_2 + H$. Here, we firstly investigated H_2O dissociation on Pt/WO_3(001). The activation energy for the H_2O dissociation is 19.87 kcal/mol, which is lower than that on pure Pt(111) (23.70 kcal/mol). Thus, we suggest that WO_3(001) decreases an adsorption energy of CO and activation energy for H_2O dissociation on Pt during CO oxidation.

11:00 AM

(ICACC-S10-021-2019) Workflow for High-Throughput Atomistic Models of Silicon Carbide Grain Boundaries

M. Guziewski*[1]; C. Carlin[1]; S. P. Coleman[1]

1. US Army Research Laboratory, USA

High throughput atomistic models are used to probe the uncertainty in the structure and mechanical response of ceramics at grain boundaries. In this work, the boundaries formed between silicon carbide grains, as well as those between silicon carbide and diamond, are studied using both molecular statics and molecular dynamics models. These models seek to capture the variance in structure and energy as a function of the five macroscopic degrees of freedom that describe the boundary geometry and connect these properties to the mechanical response. This presentation shows the workflow that was developed to automate both the structural and mechanical testing, and how the NIST Materials Data Curation System can be utilized to store the high-throughput simulation data. This database of grain boundary structures and properties will serve as the platform for advanced analysis, enabling higher fidelity mesoscale modeling.

11:20 AM

(ICACC-S10-022-2019) Damage Modeling of a 3D Carbon/Carbon Composite - Behavior at Room Temperature

A. Este*[1]; B. Toson[1]; J. El Yagoubi[2]; J. Saliba[2]; E. Martin[3]; S. Morel[2]

1. CEA, France
2. University Bordeaux, France
3. LCTS - CNRS, France

3D C/C composites are commonly employed in aerospace industry due to their outstanding mechanical properties at high temperatures. In order to ensure the integrity of structures, knowledge of the composite mechanical behaviour and fracture mechanisms is crucial. For this purpose, damage modeling of a 3D C/C composite, at room temperature, is proposed in which a meso-scale approach is considered. At this description scale, 3D C/C composites are made of two materials: carbon fibers yarns and carbon matrix. Each material behavior is modeled by an elastic damage law (isotropic for matrix, orthotropic for yarns) with a limited number of parameters. The parameters identification process is based on experimental data obtained from previous work and from an experimental campaign carried out through this work. This campaign aimed to a greater understanding of the material mechanical behavior at mesoscopic scale. Furthermore, experimental tests were carried out to validate the composite modeling. It is shown that experimental responses obtained from four-point and three-point bending tests are particularly well described from the proposed mesoscopic model.

11:40 AM

(ICACC-S10-023-2019) Predicting Effective Fracture Toughness of ZrB_2-Based Ultra-High Temperature Composite Ceramics by Multi-Phase-Field Modeling

A. Emdadi*[1]; W. Fahrenholtz[1]; G. Hilmas[1]; M. A. Zaeem[2]

1. Missouri Univ of Science and Tech, Materials Science and Engineering, USA
2. Colorado School of Mines, Mechanical Engineering, USA

A modified phase-field model based on Griffith's theory was used to quantitatively evaluate the effective fracture toughness of ZrB_2-based composite ceramics with different engineered microarchitectures. The modified phase-field model for crack propagation considers the effect of material strength on crack nucleation and propagation independent of the regularization parameter. The model also equates the maximum stress in front of the crack tip to the stress predicted by classical fracture mechanics. The critical crack surface energy was initially calculated for monolithic ZrB_2, then the effective fracture toughness was predicted for different percentages of C in ZrB_2–C fibrous monoliths (FM) and the results compared with the experimental data. FM with 10%, and 30% C had the same effective fracture toughness. Increasing the C content to 50% significantly decreased the effective fracture toughness, in agreement with the experimental data. The numerical results show that replacing the ZrB_2 hexagon–cell with the circle–cell of the same surface area make the effective toughness of the FM more sensitive to the C volume percentage. Predicting the effective fracture toughness of engineered composite ceramics having phases with different material properties and microarchitectures can be used to guide design of composites with enhanced damage tolerance.

Structural Ceramics V

Room: Coquina Salon G

Session Chair: Martin Magnuson, Linkoping University

1:30 PM

(ICACC-S10-024-2019) Thermodynamic calculations and modeling for ceramics (Invited)

O. Rapaud*[1]

1. University of Limoges, IRCER, France

Thermodynamic calculations are usually the starting point for materials design or synthesis process in materials science. They allow to predict phases at equilibrium under specific conditions, to plot property diagrams, and of course to compute phase diagrams. These calculations are achieved using a database, where the thermodynamic data are gathered using a specific formalism and various models. The accuracy of the calculations depends on the quality of the thermodynamic data. Since ceramics exhibit a wide range of properties (phase transitions, range of stoichiometry, high temperature, nature of bonds, ordering…), it's then of importance to take care of the selected models and to critically select the thermodynamic data. DFT calculations are increasingly used to extend or supplant experimental data. We will depict here the models that we may use for ceramics modeling, and the problematic of thermodynamic data acquisition at high temperature. Different cases will be presented for different applications (nuclear materials, aeronautics and aerospace), mostly in harsh environment. Until now, the thermodynamic data were assessed from 298K up to high temperature,

and lower temperature values were extrapolated, violating the third law of thermodynamics. More recently, researchers started the design the third generation of database, from 0K up to high temperature, coupling DFT calculations, new models, and experimental data.

1:55 PM

(ICACC-S10-025-2019) Microstructure based modeling of in-reactor behavior of oxide nuclear fuels (Invited)

Y. Zhang*[1]

1. Idaho National Lab, Fuel Modeling and Simulation, USA

During operation, the chemistry of fuels changes due to the fissile events, and their microstructure evolves due to the evolution of radiation produced defects, segregation and precipitation of fission products, and mechanical deformation, leading to degradation of fuel properties that directly impacting fuel performance and safety. Accurate prediction of the transient fuel properties is critical for engineering scale fuel performance modeling, which is a powerful tool for fuel development and qualification. Conventionally, the degradations of fuel properties are usually empirically correlated with temperature and burnup. Albeit their usefulness for light water reactor fuels, the empirical nature strongly limit their usage for new fuels and reactors. In this talk, the microstructure-based fuel performance modeling approach adopted by the DOE Nuclear Energy Advanced Modeling and Simulation program is presented. A few examples will be given including grain size evolution, swelling, and thermal conductivity degradation. This new approach tracks the evolution of state variables, which represent the transient fuel microstructure and define the properties, based on the operation conditions. The explicit consideration of fuel microstructure allows for more accurate predictions of transient fuel microstructure and properties, and better transferability to new fuel types and operation conditions.

2:20 PM

(ICACC-S10-026-2019) Predictive Modeling of Complex Disordered Solids: Application to amorphous hydrogenated boron carbide (Invited)

P. Rulis*[1]; M. Paquette[1]; J. Hwang[2]

1. University of Missouri - Kansas City, Physics and Astronomy, USA
2. Ohio State University, Materials Science and Engineering, USA

Complex disordered solids may be produced from the use of molecular precursors as source ingredients in low-temperature and non-thermodynamic plasma enhanced chemical vapor deposition (PECVD) thin-film growth processes. Under the PECVD conditions the molecular precursor substructure is retained in the resultant amorphous thin film. Via control of the growth process, the resultant film may be tuned for performance in target applications. Unfortunately, optimizing the film for a target application is time consuming and expensive. Therefore, there is a significant need for the development of computational methods that can realistically model the possible resultant structures and enable the search for models with the desired properties. In this presentation progress on the development of such an approach will be presented. The application of atomic scale model generation to amorphous hydrogenated boron carbide will be shown. The retention of molecular substructure and the formation of medium range order are key components of the process. Comparison of the resultant models with variance data from fluctuation electron microscopy analysis of comparable growth samples will be used to help judge the product quality.

2:45 PM

(ICACC-S10-027-2019) Material informatics accelerates innovative design of multifunctional thermal environmental barrier coating materials (Invited)

J. Wang*[1]

1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics Division, China

SiC_f/SiC ceramic matrix composites (CMCs) are the key high temperature structural materials in next generation gas turbines. Multifunctional thermal environmental barrier coating (TEBC) is critically requested to protect CMC-components from severe high temperature oxidation and corrosion in extreme combustion environments. There are crucial challenges for the optimal choices of TEBC candidates due to their complex and tunable crystal chemistry and performances. Highly efficient screening of advanced TEBC materials would be promoted based on material informatics of diverse candidates. Strategic material-genome initiative would also prevail to disclose mechanisms of property diversity and to further adopt novel concepts for the design of robust TEBC for advanced SiC_f/SiC CMCs.

Structural Ceramics VI

Room: Coquina Salon G

Session Chair: Jingyang Wang, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences

3:25 PM

(ICACC-S10-028-2019) Chemical thermodynamic calculations for materials synthesis and reactivity: case of Si_3N_4/TiN composite (Invited)

J. Roger*[1]; Y. Le Petitcorps[1]; M. Dourges[1]; L. Nouvian[1]; L. Maillé[1]

1. Université de Bordeaux-CNRS, Laboratoire des Composites ThermoStructuraux, UMR 5801, France

The development and optimization of materials are generally time-consuming and costly operations, generally on a "trial-and error" basis. Thermochemical equilibrium calculations based on the Calphad method allow the simulation of many high-temperature processes. They are a powerful method: 1) to identify efficient chemical systems and parameters, 2) to predict the reactivity of materials with the environment and 3) to highlight limiting mechanisms leading to metastable equilibria. This methodology was applied to the synthesis of a ceramic based on the expansive formation of TiN and Si_3N_4 by nitridation of porous $TiSi_2$ compacts. This conversion reaction was found to be very sluggish because of unfavorable diffusion coefficients which limit nitridation of silicon atoms. An efficient process to achieve conversion was designed based on the formation of a transient liquid phase. According to thermodynamic computations, weak amounts of nickel powder to the $TiSi_2$ powder can generate a eutectic liquid which promotes atomic diffusion and nitrides growth. Experimental results confirmed the benefit of this approach: a complete and rapid nitridation of $TiSi_2$ compacts was obtained. The high-temperature-oxidation sensitivity of the obtained material was also estimated from calculations and compared to experiments.

3:50 PM

(ICACC-S10-029-2019) Atomistic Modeling of Anisotropic Grain Boundary Mobilities in Uranium Dioxide (Invited)

J. French[1]; X. Bai*[1]

1. Virginia Tech, Materials Science and Engineering, USA

Uranium dioxide (UO_2) is the primary nuclear fuel in light water reactors. Grain growth in UO_2 can significantly impact the fuel performance properties. Therefore, an accurately prediction of the

grain growth behavior is important for correctly model the microstructural evolution in UO_2 fuels. In mesoscale modeling of grain growth, typically an average or isotropic grain boundary mobility is used as an input parameter, regardless of the grain boundary character. In this work, molecular dynamics modeling is used to study the misorientation-dependent grain boundary mobilities. The grain boundary mobilities are calculated using the shrinkage of a circular grain method. Grain boundary mobilities for the three rotation axes <100>, <110>, and <111> are calculated and a strong anisotropy in the mobility exists. The atomic transfer mechanism across grain boundaries during grain growth is analyzed to explain the anisotropic behavior of the mobilities observed from the atomistic modeling. In addition, the impurity (e.g., Xe) trapping effects on grain boundary motion is also studied in this work.

4:15 PM

(ICACC-S10-030-2019) Structure Properties of Transition Metal Borides Investigated by X-ray Spectroscopy and Ab-Initio Electronic-Structure Calculations (Invited)

M. Magnuson*[1]

1. Linkoping University, Department of Physics, Chemistry and Biology, Sweden

Transition metal-borides are known to exhibit interesting materials properties from superhardness to superconductivity with high thermal and chemical stability. These materials have a potential to be used for the next generation of hard, wear- and corrosion-resistant coatings. In particular, this is the case for borides with an AlB_2 type of structure (Strukturbericht notation C32), where the B atoms form honeycombed, graphite-like sheets that are interleaved between hexagonal close packed Zr atoms. From a combination of ab-initio electronic structure calculations and analysis with XPS, XRD, XANES, and EXAFS, the local chemical bonding structure and structural properties with atomic distances are investigated in an epitaxial ZrB_2 film and compared to properties to those of the ZrB_2 compound target from which the film was synthesized as well as a bulk a-Zr reference. Epitaxial films are promising for property determination of borides and future exploration also of other material classes.

4:40 PM

(ICACC-S10-031-2019) Machine learning for phase selection in multi-principal element alloys (Invited)

H. Zhuang*[1]; N. Islam[1]; W. Huang[1]

1. Arizona State University, School for Engineering of Matter, Transport & Energy, USA

Multi-principal element alloys (MPEAs) especially high entropy alloys have attracted significant attention and resulted in a novel concept of designing metal alloys via exploring the wide composition space. Abundant experimental data of MPEAs are available to show connections between elemental properties and the resulting phases such as single-phase solid solution, amorphous, intermetallic compounds. To gain insights of designing MPEAs, here we employ neural network (NN) in the machine learning framework to recognize the underlying data pattern using an experimental dataset to classify the corresponding phase selection in MPEAs. For the full dataset, our trained NN model reaches an accuracy of over 99%, meaning that more than 99% of the phases in the MPEAs are correctly labeled. Furthermore, the trained NN parameters suggest that the valence electron concentration plays the most dominant role in determining the ensuing phases. For the cross-validation training and testing datasets, we obtain an average generalization accuracy of higher than 80%. Our trained NN model can be extended to classify different phases in numerous other MPEAs.

5:05 PM

(ICACC-S10-032-2019) Configuration-dependent corrections in the first-principles calculations of multiplet states of transition-metal ions and rare-earth ions in crystals (Invited)

K. Ogasawara*[1]; S. Takemura[1]

1. Kwansei Gakuin University, Department of Chemistry, Japan

The prediction of multiplet spectra of transition-metal (TM) ions and rare-earth (RE) ions in crystals is important for the theoretical design of novel optical materials such as solid state lasers and phosphors. In order to perform the first-principles calculations of multiplet states of TM ions and RE ions in crystals, we have developed a fully-relativistic many-electron calculation program based on the configuration-interaction (CI) approach, which we call the discrete variational multi-electron (DVME) program. However, energy separations between the barycenters of different electronic configurations tend to be overestimated by simple CI calculations presumably due to the underestimation of the electron correlation resulting from the finite number of the Slater determinants used as the basis functions. In order to improve the accuracy of the theoretical prediction, we introduced an efficient and effective correction method based on the consistency between the one-electron molecular orbital calculation and the many-electon CI calculation, which we call the configuration dependent correction (CDC). In this presentation, we will show some examples of the CDC in the first-principles calculations of multiplet states of TM ions and RE ions in crystals and summarize its effectiveness.

5:30 PM

(ICACC-S10-033-2019) Reliable prediction of lattice thermal conductivity of $La_2Zr_2O_7$ TBC material using modified two-channel model

Y. Luo*[1]; X. Yang[2]; J. Wang[1]; X. Ruan[2]

1. Institute of Metal Research, Chinese Academy of Sciences, China
2. School of Mechanical Engineering, Purdue University, USA

Reliable prediction of lattice thermal conductivity (κ_L) for low-κ_L complex oxide ceramics is a critical challenge in the searching and design of thermal barrier coating (TBC) materials. In this study for advanced TBC material $La_2Zr_2O_7$, we discover that considerable numbers of phonon modes have extremely small mean free path below the scale of minimum interatomic spacing. The physical mechanism is demonstrated to be low group velocity and/or high scattering rate of these modes, due to the structural complexity and atomic bonding heterogeneity. This raises concerns whether these modes can be properly treated using the conventional phonon Peierls-Boltzmann transport theory. Hence, we modify a previously proposed two-channel model to derive κ_L, through combining a phonon conduction channel as well as a hopping channel from short-mean-free-path vibrations, and avoiding double-counting of phonons. Our approach yields theoretical temperature dependence of κ_L in much better agreement with experimental measurement than the all-phonon theory and the original two-channel model, and hence may provide quantitative guideline for screening complex-structure oxide ceramics as TBC candidates.

S12: Advanced MAX/MXene Phases and UHTC Materials for Extreme and High Temperature Environment

Synthesis, Processing, and Densification

Room: St. Johns

Session Chairs: Ji Zou, University of Birmingham; Jie Zhang, Institute of metal research, Chinese Academy of sciences

8:30 AM

(ICACC-S12-047-2019) Design and Manufacturing of Multi-Scale Porous UHTCs for Passive and Active Cooling Components (Invited)

C. Tallon*[1]

1. Virginia Tech, Materials Science and Engineering, USA

Active and passive cooling elements for hypersonic vehicles can provide additional strategies to survive the severe conditions they endure: large heat fluxes, extreme temperatures, extensive thermal gradients, stagnation pressures and oxidative environments. These elements also need to show minimal material ablation, overall weight, while meeting complex shapes and tolerances for integration with other aircraft components. Multi-scale porous UHTCs with a suitable combination of microstructure (pore size, type and amount) and properties (thermal conductivity, pore network connectivity and thermomechanical response) may meet those requirements. However, deciding what that suitable combination of microstructure-properties is the real challenge. In this work, a dual approach for design and manufacturing of multi-scale porous UHTCs is presented. This approach consist of an integrated combination of predictive thermomechanical modelling of porous UHTCs with tailored processing routes to create porous structures to match the desired performance. The processing routes produce 50-90% porosity and pore sizes of 5-500 um, with controlled alignment to direct the flow of a second phase or divert the heat away by tailoring thermal conductivity. Computational approaches are validated by experimental characterization of actual samples, as a pathway to develop predictive capabilities.

8:50 AM

(ICACC-S12-048-2019) Manufacture of Designed Porosity for Transpiration Cooling

L. J. Vandeperre*[1]; R. Hedgecock[1]; C. Fradin[1]; D. Glymond[1]

1. Imperial College London, Materials, United Kingdom

Transpiration cooling is a modern cooling technology in which a fluid heats up by flowing through a finely distributed array of fine pores in the component, exits the component at the same temperature as the surface, and forms a film between the surface and the surrounding flow atmosphere thereby reducing heat transfer from the environment to the component. It has the potential to both enable UHTC components to be loaded with higher heat fluxes before being damaged as well as to reduce or eliminate oxidation even at temperatures well in excess of 1600 °C To benefit optimally from this technology, the porosity has to be designed with the aim to maintain the strength and thermal conductivity of the component as much as possible, while also ensuring good heat transfer from the solid to the fluid. Here we present the results of the development of a simple approach for generating designed porous microstructures in ZrB_2 and discuss how these influence the overall performance of the material by contrasting the results with results obtained by traditional methods for creating highly porous microstructures.

9:10 AM

(ICACC-S12-049-2019) High temperature adhesives derived from SiBCN precursors (Invited)

S. Chang[1]; J. Wang[1]; X. Luan*[1]; L. Cheng[1]

1. Northwestern Polytechical University, China

High temperature adhesive using in air is extremely important for ceramic components. A novel adhesive for joining Al_2O_3 ceramic was made using polyborosilazanes usually it was donated as PSNB. The ceramic joints were heat-treated at temperatures ranging from 1300 to 1500 °C in air surroundings. The bonding strength was tested at room temperature and high temperatures respectively. The best performance of bonding strength at room temperature was 15.73 MPa. The formation of $Al_2O_3 \bullet B_2O_3$ means the reaction of adhesive and adhesion, and result in improving the bonding strength apparently. Compared to the bonding strength at room temperature, the bonding strength at 800 °C was 12.91 MPa, only decreased 18%. To obtain an adhesive with high temperature bonding strength and low preparation temperature, polysilazane (PSNB) was modified by PBSZ, PSO, nano-Al_2O_3 as additives. Effects of the SiO_2 to B_2O_3 ratio and stick pressure on microstructure and high temperature strength of the modified adhesives has been investigated. The bond strength of the modified adhesive reaches up to 12.08 MPa at room temperature, what is more, the strength still has 6.65 MPa at 1000 °C which is 2 times higher than the unmodified one. It is found that a balance between the fluidity of the adhesive and the processing pressure must be controlled to obtain the highest bonding strength.

9:30 AM

(ICACC-S12-050-2019) Synthesis and ablation performance of c1-$Sm_{0.2}Zr_{0.8}O_{1.9}$ for hypersonic applications

A. Brenner*[1]; A. Payne[1]; R. Trice[1]

1. Purdue University, Materials Engineering, USA

Samarium-doped zirconium diboride/silicon carbide (Sm-ZBS) ceramics possess emissive properties of 0.9 at 1600°C and develop oxide scales that have excellent ablation performance. However, the porosity and glassy products formed by ZBS ceramics limits the use of the UHTC. One of the oxide scales formed during the ablation process is c1-$Sm_{0.2}Zr_{0.8}O_{1.9}$ which has a melting temperature exceeding 2500°C. In this study, c1-$Sm_{0.2}Zr_{0.8}O_{1.9}$ was formed via a furnace treatment from precursor oxides of Sm_2O_3 and ZrO_2. SEM/EDS and XRD analysis was performed on the resulting oxide before and after ablation to investigate the stability of the material and its potential for use in hypersonic applications. CTE and Vickers hardness measurements were also taken.

10:10 AM

(ICACC-S12-051-2019) Synthesis and Flash Sintering of $Ta_{0.5}Hf_{0.5}B_2$ Solid Solution Nanopowders

P. Foroughi[1]; A. Durygin[2]; Z. Cheng*[1]

1. Florida International University, Mechanical & Materials Engineering, USA
2. Florida International University, CeSMEC, USA

Densification of ultrahigh temperature ceramics (UHTCs) is challenging due to their high melting point, strong covalent bonding and low self-diffusivity. All these lead to very high sintering temperature and long dwell time resulting in more energy consumption and often excessive grain growth. Here, the authors first synthesized single-phase $Ta_{0.5}Hf_{0.5}B_2$ UHTC solid solution nanopowder via direct reaction between metal chlorides ($TaCl_5$ and $HfCl_4$) and sodium borohydride ($NaBH_4$) in inert atmosphere at elevated temperature. The synthesized powder was then consolidated using a modified flash sintering technique. The densification occurs within ~5 min as a result of joule heating caused by the application of a DC electric field over the power compact. Different from ionic conducting oxides such as yttria stabilized zirconia (YSZ), no preheating was required for flash sintering of $Ta_{0.5}Hf_{0.5}B_2$ due to its high electrical

conductivity allowing electric current to pass through even at room temperature. Meanwhile, the inter-particle contact was ensured by applying a relatively low pressure (~10 MPa) during the sintering process. The impacts of flash sintering parameters (e.g., current density, dwell time, sintering aid, and applied pressure) on microstructure and properties of sintered $Ta_{0.5}Hf_{0.5}B_2$ ceramics are studied and the directions for future research will also be pointed out.

10:30 AM

(ICACC-S12-052-2019) Hot Isostatic Pressing of Zirconium Diboride for Advanced Manufacturing of Near-Net-Shaped UHTCs components

C. T. Garza*[1]; C. Tallon[1]

1. Virginia Polytechnic Institute and State University, Materials Science & Engineering, USA

Hot isostatic pressing (HIP) allows the full densification of near-net-shaped ceramics, at lower temperatures with a controlled final grain growth and no porosity. It is widely used in industry and it is the perfect complementary post-processing step for advanced and additive manufacturing of a range of materials. To continue understanding densification of near-net-shaped Ultra-High Temperature Ceramics and the effect of manufacturing variables, such as processing and equipment conditions, zirconium diboride (ZrB_2) was subjected to and compared to three different sintering routes, to assess the use of HIP for their manufacturing: i) pressureless sintering (PS): ii) pressureless sintered and then HIP; and iii) direct HIP (with and without encapsulation). All the green bodies were prepared through colloidal processing techniques, using suspensions with solid concentrations between 50-54 vol%, with and without sintering aids (2 to 4 wt% of carbon or boron carbide). Sintered samples were characterized in terms of density, grain size, pore size, mechanical properties and oxyacetylene testing. Comparison of the different sintering routes, gives a key insight of the densification mechanisms achieved using hot isostatic pressing for ZrB_2 and how this sintering technique can enable advancing manufacturing of near-net-shaped UHTCs components for extreme applications.

Ultra-High Temperature Composites I

Room: St. Johns

Session Chair: Sea-Hoon Lee, Korea Institute of Materials Science

10:50 AM

(ICACC-S12-053-2019) Testing UHTCMCs at ultra-high temperature and harsh environment (Invited)

D. Sciti*[1]; L. Zoli[1]; L. Silvestroni[1]; F. Monteverde[1]; R. Savino[2]; J. Binner[3]; T. Reimer[4]

1. ISTEC-CNR, Italy
2. University of Naples, Federico II, Italy
3. University of Birmingham, United Kingdom
4. German Aerospace Center, Institute of Structures and Design, Germany

Reusable components for hypersonic flight, next generation rocket engines, and thermal protection systems require materials with high strength at temperatures above 2000°C, oxidation and wear resistance, and ability to withstand high heat fluxes and thermal shock. Ultra-high-temperature-ceramics are a class of materials characterized by melting points exceeding 3000°C, high thermal and electrical conductivities, and good ablation resistance. However, their low fracture toughness and poor thermal shock resistance pose major obstacles to their implementation. In the past few years, a new class of materials labelled UHTCMCs (ultra-high temperature ceramic matrix composites) has been developed. These materials consist of a UHTC rich matrix reinforced with carbon fibres. Fibre reinforcement has been shown to improve the damage tolerance at room temperature but testing in relevant environment is needed to assess the reliability of these new materials. Furthermore, relevant thermomechanical testing must be carried out at temperature >1500°C. In this talk we will show different variants of UHTCMCs based on ZrB_2 and Carbon fibres and their testing in oxyacetylene torch up to 2100°C, arc jet up to 2500°C, combustion chamber of rocket motors and free-jet. In addition, we will show relevant thermomechanical properties at high and ultra-high temperature.

11:10 AM

(ICACC-S12-054-2019) Anisotropic Thermal Conductivity in Flexible Woven Ceramic Fibers for Hypersonic Atmospheric Entry

R. Penide-Fernandez*[1]; F. Sansoz[1]

1. The University of Vermont, Department of Mechanical Engineering, USA

Flexible thermal protection materials from two-dimensional woven ceramics fibers are of significant interest for hypersonic inflatable aerodynamic decelerators being developed by NASA for future Mars missions. A key component of the thermal shield is a heat-resistant outer ceramic fabric that must withstand harsh aero-thermal atmospheric entry conditions. A predictive and basic understanding of heat conduction processes in complex woven-fiber ceramic materials, however, is currently lacking. This talk presents a combined experimental and computational study of thermal conductivity in flexible 5-harness-satin woven Nextel 440 fibers, using the hot-disk transient plane source method and advanced thermo-mechanical finite-element analysis. A focus of this study is to understand and predict the effect of deformation on anisotropic heat conduction in this type of flexible woven ceramics. The results show that thermal conductivity rises, as the transverse load increases, whereas the anisotropy between in-plane and through-plane conductivities is reduced significantly. Also, we show that our methodology could be applicable to more complex loading conditions and to different high-temperature ceramic fabric materials, such as Hi-Nicalon silicon-carbide fibers.

11:30 AM

(ICACC-S12-055-2019) Fabrication and performance of ultra-high temperature ceramic matrix composites through RF enhanced chemical vapour infiltration

V. Venkatachalam*[1]; V. Rubio[2]; J. Binner[1]

1. University of Birmingham, Department of Metallurgy and Materials, United Kingdom
2. National Composites Centre, United Kingdom

Ultra High Temperature Ceramic Matrix Composites (UHTCMCs) have proven to be excellent materials that can survive nearly 3000°C in highly oxidizing environments. This means that they have excellent potential for use in aerospace applications such as rocket nozzle throats and thermal protection systems (TPS). Due to the presence of the carbon fibres, UHTCMCs offer high strength and modulus combined with excellent thermal shock behaviour whilst the presence of the ultra-high temperature ceramic phase protects the carbon fibers at the application temperatures. In the present work, 2.5D and 3D carbon fibre preforms have been impregnated by ZrB_2 slurries to fill the inter-tow porosity between the different orientation plies of the preform and then infiltrated with a carbon matrix using a radio frequency (RF) enhanced CVI process. This fills both the intra-tow and residual inter-tow porosity porosity. The advantage of RF heating is that it creates an inverse temperature profile in the sample, which means that the infiltration starts from inside and progresses outwards. This allows the time needed for processing to be reduced significantly compared to the conventional CVI process. This presentation will report on the latest results from the research, which has been undertaken at the University of Birmingham within the European Horizon 2020 C^3HARME program.

11:50 AM

(ICACC-S12-056-2019) Fabrication and Testing of Ultra-High Temperature Ceramic Matrix Composites for Extreme Aerospace Applications

D. King*[1]; C. Carney[2]; M. Cinibulk[2]

1. UES, Inc., USA
2. Air Force Research Lab, USA

Supersonic flight envelopes are limited by the materials that can survive the extreme thermo-mechanical stresses and termperatures that develop. Due to the costs, risks, and infrequency of flight tests, ground tests are utilized to screen new materials, and models are relied upon to predict material performance. Unfortunately, no individual ground test can adequately simulate all flight regimes, so multiple tests are used in tandem to more thoroughly interrogate potential material response. In this talk, the fabrication and testing of ultra-high temperature ceramic matrix composites (UHTCMCs) will be discussed. Through the polymer infiltration and pyrolysis (PIP) process CMCs can be fabricated with matrices tailored for extreme environments. Topics such as development of low-temperature polymer processing and the fabrication of graded matrices will be discussed in terms of their ability to increase processing efficiency and improve oxidation resistance of the composite. The performance of the PIP UHTCMCs will be discussed. Testing methods will include, oxy-acetylene torch, laser, and laser testing coupled with an elevated Mach shear flow of air.

Ultra-High Temperature Composites II

Room: St. Johns

Session Chair: Diletta Sciti, ISTEC-CNR

1:30 PM

(ICACC-S12-057-2019) Ablation behavior of ultra-high temperature ceramics

S. Lee*[1]; J. Kim[1]; N. Quyet[1]; S. Hong[2]

1. Korea Institute of Materials Science, Republic of Korea
2. Chonbuk National University, High-enthalpy Plasma Research Center, Republic of Korea

HfC-SiC, HfB_2-SiC, ZrC-SiC, ZrB_2-SiC nano composites and C_f/HfC-SiC UHTCMC were prepared and their ablation behavior was tested using an oxy-acetylene torch and arc-jet plasma facility. The materials did not have strong recession after the testing using oxy-acetylene torch at 2700ºC for 30 min. in air. The thickness of the oxide layer on the surface of the HfC-SiC composites was less than 200mm, showing excellent oxidation resistance of the HfC-SiC nano composites. The oxidation of the carbon fibers in the C_f/HfC-SiC UHTCMC was successfully suppressed by the formation of the protective layer on the surface of the CMC. The recession rate of the HfC-SiC nano-composite was 5×10^{-4}mm/s at 2700ºC. Arc-jet testing was performed with changing the heat flux between 2 – 10MW/m^2 for 60 seconds. The ablation rate was 6×10^{-4}mm/s at 2000ºC when the heat flux was 2MW/m^2. The ablation rate of the HfC-SiC nano-composites was 5×10^{-2}mm/s at 2500ºC under the heat flux of 5MW/m^2. The material could not withstand the intensive heating when the heat flux increased to 10MW/m^2. The surface temperature exceeded 3,000ºC within 0.2 second after testing. Intensive crack formation was observed in the samples and the growth of SiC grains occurred in the cracks. The ablation behavior of HfB_2-SiC, ZrC-SiC and ZrB_2-SiC nano-composites was also analyzed.

1:50 PM

(ICACC-S12-058-2019) Oxidation resistance of carbon fibre reinforced ZrB_2/SiC composites at T>2000°C

A. Vinci*[1]; T. Reimer[2]; L. Zoli[1]; D. Sciti[1]; D. Koch[2]

1. ISTEC-CNR, DSCTM, Italy
2. DLR - German Aerospace Center, Germany

Ultra-High-Temperature-Ceramics (UHTCs) are refractory ceramics with melting points above 3000°C and high thermo-mechanical properties and are being investigated as candidates for the use in extreme environments where temperatures above 2000°C are reached. In particular, ZrB_2 composites have been extensively studied due to their low density and high thermal conductivity but their low oxidation resistance above 1000°C and low fracture toughness remain a major obstacle. The addition of carbon fibres was found to increase the damage tolerance, while the presence of silicon carbide provided oxidation resistance up to 1650°C. However, no characterization was carried out at extreme temperatures (T>2000°C). Moreover SiC undergoes active oxidation at low oxygen pressures with the evolution of volatile oxides (SiO). In the present work carbon fibre reinforced ZrB_2/SiC composites were fabricated by slurry infiltration and hot pressing. Oxidation tests were carried out at 2000 and 2200°C in air at pressures between 1 – 900 mbar. The resulting microstructures were analysed by SEM-EDS and X-ray diffraction analysis. All specimens experienced mass loss due to the evaporation of the outer silica layer and oxidation of fibres which was more pronounced at 900 mbar. The main oxidation product was ZrO_2 as ascertained by XRD and EDS. A model for the oxidation phenomena taking place is presented.

Novel Applications and Device Fabrication IV

Room: St. Johns

Session Chairs: Konstantina Lambrinou, SCK-CEN; Guobing Ying, Hohai University, China

2:10 PM

(ICACC-S12-059-2019) Elastic properties of Ti_2AlC and Ti_3SiC_2 MAX phase foams with controlled porosity and pore size produced by powder metallurgy

S. A. Tsipas*[1]; E. Tabares[1]; B. Velasco[1]; E. Gordo[1]; L. Hu[2]; M. Radovic[2]; A. Jimenez-Morales[1]

1. Universidad Carlos III de Madrid, Materials Science and Engineering, Spain
2. Texas A&M University, Materials Science and Engineering, USA

MAX phase foams have a great potential for various applications where tailored functional and mechanical properties are required, such as high electrical and thermal conductivity, high elastic stiffness and low thermal expansion coefficient. In this study, Ti_2AlC and Ti_3SiC_2 MAX phase foams with controlled porosity and pore size, where produced. The foams where produced from powders using crystalline carbohydrate as space holder. Consolidation was performed by cold isostatic pressing followed by complete dissolution of the water-leachable space-holder and pressureless vacuum sintering. Foams with porosity up to about 60 vol% and pore size distribution ranging from about 250 to1000 μm were successfully produced. The foams were characterized and the experimental porosity was compared to the theoretical one. The results show a bimodal porosity that can be customized by controlling the sintering and the space holder amount. Elastic moduli of the foams were measured by resonant ultrasound spectroscopy (RUS) and studied as a function of porosity and/or pore size. The results show that porosity and pore size control can be used to tailor elastic properties.

2:30 PM

(ICACC-S12-060-2019) HPPMS deposition from composite targets: Effect of two orders of magnitude target power density changes on the composition of Cr-Al-C thin films

H. Rueß*[1]; M. to Baben[2]; S. Mráz[1]; L. Shang[1]; P. Polcik[3]; S. Kolozsvári[3]; M. Hans[1]; D. Primetzhofer[4]; J. M. Schneider[1]

1. RWTH Aachen University, Materials Chemistry, Germany
2. GTT-Technologies, Germany
3. Plansee Composite Materials GmbH, Germany
4. Uppsala University, Department of Physics and Astronomy, Sweden

The effect of target power density, substrate bias potential and substrate temperature on the thin film composition was studied. A Cr-Al-C composite target was sputtered utilizing direct current (DCMS: 2.3 W/cm^2) and high power pulsed magnetron sputtering (HPPMS: 373 W/cm^2) generators. At floating potential, all Cr-Al-C thin films showed similar compositions, independently of the applied target power density. However, as substrate bias potential was increased to -400 V, aluminum deficiencies by a factor of up to 1.6 for DCMS and 4.1 for HPPMS were obtained. Based on the measured ion currents at the substrate, preferential re-sputtering of Al is suggested to cause the dramatic Al depletion. As the substrate temperature was increased to 560 °C, the Al concentration was reduced by a factor of up to 1.9 compared to the room temperature deposition. This additional reduction may be rationalized by thermally induced desorption being active in addition to re-sputtering.

2:50 PM

(ICACC-S12-061-2019) Understanding inhomogeneity in elastic properties within complex crystals using Raman scattering

J. Lyons*[1]; W. Clegg[2]; F. Giuliani[1]

1. Imperial College London, United Kingdom
2. University of Cambridge, United Kingdom

Recent work has predicted that variations in the elastic properties within a crystal structure can explain the large variations in critical resolved shear stress often observed in layered compounds such as MAX phases. In this work we show that variations in elastic properties can be measured using a combination of small scale mechanics and Raman scattering. Large grained polycrystalline Ti_3SiC_2 was deformed by wedge indentation within individual grains along specific directions and the resultant Raman shifts of the peaks associated with bonding in particular layers was mapped. Significantly increased compliance was observed by bonds associated with the A layers. These compliances will also be compared to DFT calculations of the structure.

3:30 PM

(ICACC-S12-062-2019) First-principles investigations of inherent cleavage and shear behaviors of M2AlC (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Hf, and Ta)

W. Son[1]; A. Talapatra[1]; T. Duong*[1]; A. Srivastava[1]; R. Arroyave[1]; M. Radovic[1]

1. Texas A&M University, Materials Science and Engineering, USA

First-principles calculations within the framework of density-functional study have been conducted to investigate the intrinsic cleavage and shear behaviors of 13 MAX phases including: Sc2AlC, Ti2AlC, V2AlC, Cr2AlC, Mn2AlC, Fe2AlC, Co2AlC, Ni2AlC, Y2AlC, Zr2AlC, Ta2AlC, Hf2AlC, and Ta2AlC. As the chemistry changes, it has been observed that the cleavage stresses and unstable stacking fault energies of the studied MAX phases exhibit similar trends. For the first transition-metal row, the cleavage stress and unstable stacking fault energy particularly reach their maximum values at Mn and V respectively. For the second and third transition-metal rows, it appears that the maximum cleavage stress and stacking fault energies also fall within the middle elements. This is likely owning to the higher numbers of valence electrons of these elements that can establish atomic bonding with Al and C. Along the studied columns, the inherent cleavage and shear behaviors exhibit minimums in the middle. This is thought to be the results of two opposite trends: the increase the bond strength as the charge transfer increases with increasing row number and the decrease in bond strength as the bond length increases as the atomic radius of M element increases with increasing row number.

3:50 PM

(ICACC-S12-063-2019) Novel processing of MAX Phase Ti_3SiC_2 by Powder Injection Molding

E. Tabares*[1]; S. A. Tsipas[1]; E. Gordo[1]; A. Jimenez-Morales[1]

1. Universidad Carlos III de Madrid, Materials Science and Engineering, Spain

MAX phase materials have caught the attention of researchers due to their unique combination of properties; their nanolaminated structure gives this family of materials the excellent attributes characteristic of both metal and ceramic compounds. In this work, Ti_3SiC_2 was synthesized from initial powder mixtures of Ti, SiC and C. The initial powders were compacted by Cold Isostatic Pressure (CIP) and sintered in a vacuum furnace. The MAX phase pellets obtained were milled in planetary ball mill to obtain the powders. High purity Ti_3SiC_2 MAX phase powders were processed by Powder Injection Molding technology (PIM). Ti_3SiC_2 powders were characterized to study the suitability of the morphology and particle size distribution for the injection process. In addition, thermal analysis were conducted to determine the behavior of the powders synthesized. A sustainable feedstock was produced studying the optimal powder load for the MAX phase powder using Polylactic Acid (PLA) as binder. Additionally, rheological properties of the feedstock were analyzed to adjust the different parameters during the injection. Green parts were obtained for posterior debinding and sintering processes.

Novel Processing of MXenes and Their Composites II

Room: St. Johns

Session Chair: Joseph Halim, Linkoping University

4:10 PM

(ICACC-S12-064-2019) On the Design of Metal Deficient MAX (MAXenes) and MAB (MABenes) Phases

S. Gupta*[1]

1. University of North Dakota, Mechanical Engineering, USA

Recently, MXenes and MBenes have emerged as a new class of 2D materials where A group elements are deintercalated from the MAX Phases. In this presentation, we will present some of the recent findings where A group elements have been selectively deintercalated to form A-deficient or etched surfaces. It is expected that these new avatar of MAX and MAB phases can be used for designing novel structures and composites for multifunctional applications. As a part of this presentation, I will also review some of the recent manufacturing methods of MXenes and MBenes as a comparison.

4:30 PM

(ICACC-S12-065-2019) Water adsorption on ion intercalated MXene studied with Ambient Pressure XPS

W. B. Zaman*[1]; M. Dixit[1]; F. Shen[1]; K. B. Hatzell[1]

1. Vanderbilt University, Department of Mechnanical Engineering, USA

The properties of water and ions, in a confined state, deviate significantly from bulk physical properties. In electrochemical systems, structural water is often present within the nanopores (carbon) or structural tunnels (inorganic materials). The presence of structural water can play a role in enabling large ion insertion/intercalation mechanisms without causing deformation in the layered crystal structure upon applying an electric field (variable charge). Previous reports have suggested that the crystal water can form a solvation shell which screens lattice-ion interactions for improved transport.

Understanding how the presences or cointercalation of structural water in an layered MXene materials impacts electronic interactions is of significant importance for tailoring materials for desired applications. Herein, we probe how the surface of MXene changes when exposed to different environmental conditions (humidities, temperature) using Ambient Pressure XPS. The results suggest that water adsorption properties are impacted by the presence of (or lack there of) inorganic interacalants.

4:50 PM

(ICACC-S12-066-2019) Tuning the surface properties of Ti_3C_2 MXene using different etching agents

M. Benchakar*[1]; C. Garnero[1]; C. Morais[1]; S. Morisset[1]; P. Chartier[2]; C. Canaff[1]; V. Mauchamp[2]; A. Habrioux[1]; S. Celerier[1]

1. Institut de Chimie des Milieux et Matériaux de Poitiers IC2MP UMR7285, France
2. Institut PPRIME, Physics, France

MXenes are among the newest and largest family of 2D materials with already demonstrated applications in diverse fields (e.g. energy storage and conversion or electromagnetic interference shielding). Beyond the possibility to tune the MXene compositions and related properties by changing the MAX phase precursor, the etching process is also a key step since it leads to the surface functionalization of the MXene sheets with different T terminal groups (F, OH or O): these groups also deeply alter the MXenes properties. Although crucial for many applications, controlling the MXenes functionalization is still in its infancy because of the limited number of etching processes and the need to establish characterization protocols allowing the accurate determination of the generated surface properties. The aim of this presentation is to highlight the role of different etching agents (HF, LiF/HCl and FeF_3/HCl) on the control of the surface properties of Ti_3C_2 MXenes. A complete set of characterizations (XRD, SEM, EDX, XPS, Raman, electrocatalysis) is performed to determine their surface properties with particular attention paid on their activity towards hydrogen evolution reaction (HER – electrolyser). The ultimate goal is to show how the etching agent can be selected toward one application and related properties and not suitable for another one and vice versa.

5:10 PM

(ICACC-S12-067-2019) Self-assembled $Ti_3C_2T_x$ electrodes with improved electrochemical performance for supercapacitor in a solution processing

G. Ying*[1]; L. Su[1]; F. Ma[1]; L. Liu[1]; K. Zhang[1]; C. Zhang[1]

1. Hohai University, China, Department of Materials Science and Engineering, China

Herein, we demonstrate the fabrication of $Ti_3C_2T_x$ electrodes using self-assembled solution processing. The two-dimensional (2D) nanometer $Ti_3C_2T_x$ flakes are self-assembled site aggregated on copper and nickel foam papers with a reconstituted three-dimensional (3D) structure consisted of overlapping and open-pore 2D flakes. When employed as electrochemical capacitor electrodes, the capacitances were comparable to literature values. Quantitative linear growth trend relationship between the capacitance and foam thicknesses is developed. Given the process scalability and the morphological control that is possible, these results bode well for a road map for convenient and economical supercapacitors.

S13: Development and Applications of Advanced Ceramics and Composites for Nuclear Fission and Fusion Energy Systems

Mechanical Properties and Test Methods

Room: Coquina Salon H

Session Chairs: Lance Snead, ORNL; Koroush Shirvan, Massachusetts Institute of Technology

8:30 AM

(ICACC-S13-046-2019) SiC-SiC CMCs and Graphite for Nuclear Applications: Update on Evolving Chapters in the ASME BPV Code Section III, Division 5, Working Group on Graphite and Composites

M. G. Jenkins*[1]; S. T. Gonczy[2]; Y. Katoh[3]

1. Bothell Engineering and Science Technologies, USA
2. Gateway Materials Technology, USA
3. Oak Ridge National Lab, USA

High-temperature reactors (HTRs) planned by US DOE use SiC-SiC CMCs and graphite to enhance fuel performance and improve accident tolerance because these materials are tolerant to the relevant irradiation and chemical environments. As nonconventional materials, SiC-SiC CMCs and graphite are of special concern because the mission of the US Nuclear Regulatory Commission (NRC) is to license and regulate the nation's civilian nuclear reactors, reactor designs and reactor materials. NRC is legally required to use consensus codes and standards as integral parts of the regulatory process. Therefore, the ASME Boiler and Pressure Vessel (BPV) Code Section III "Rules for Construction of Nuclear Components" (including accepted materials) is included in the NRC regulations. Division 5 on HTRs of Section III has supported a working group on graphite and ceramic composites for many years. For SiC-SiC CMCs to be incorporated into future HTRs, they must be included in ASME BPV Code as acceptable materials. A progress update (including recent balloting) is provided on the new portions of ASME BPV Code including design and qualification of SiC-SiC CMCs as well as appendices regarding the testing, classification, composition, structure, manufacture, and properties of SiC-SiC CMCs for nuclear applications.

8:50 AM

(ICACC-S13-047-2019) Mechanical Deformation and Damage of Nuclear Grade SiC/SiC Composite Tube under Flexure Loading

X. Huang*[1]; W. Bristow[1]; J. Bao[1]; D. McCleeary[1]; K. Shapovalov[2]; G. Jacobsen[2]

1. University of South Carolina, Mechanical Engineering, USA
2. General Atomics, USA

Silicon Carbide (SiC) fiber reinforced SiC matrix composite is an excellent material candidate for accident-tolerant fuel cladding. Flexure loading (bending) is a potential load on fuel cladding during handling and service. Experimental techniques have been developed to study the mechanical response and damage of the SiC composite tube under flexure loading. A modified four-point bend test was implemented to induce a pure bending moment in the gage section of a tubular sample. By avoiding excessive stress at the loading point, gage-section failure of SiC composite tube was obtained consistently. Local and distributed strain measurements and acoustic emission (AE) monitoring were utilized to analyze material deformation and damage behavior. Multiple AE sensors were used to calculate the location of the damage events. It was observed that flexure stress-strain behavior is very similar to that under uniaxial loading; however, the damage is non-uniformly distributed. The material under tensile stress develops much more damage than that under compression, as a result the neutral axis shifts during flexure loading. The effect of internal pressure on the bending response and the effect of bending-induced damage on the burst strength were also investigated.

9:10 AM

(ICACC-S13-048-2019) Mechanical testing of SiGA cladding under relevant off-normal operating conditions

K. Shapovalov*[1]; G. Jacobsen[1]; S. Gonderman[1]; C. Deck[1]

1. General Atomics, USA

General Atomics (GA) is developing a silicon carbide fiber silicon carbide matrix composite technology, SiGA™, as a cladding material for light water reactors (LWR). Regulatory licensing of this technology will require complete understanding of SiGA mechanical behavior for both normal and off normal operation. This includes high temperature mechanical behavior, pellet cladding mechanical interaction (PCMI), leak tightness, and more. In order to address these issues GA has designed and implemented custom test capabilities focused on understanding potential SiGA failure mechanisms. A variation on elastomeric insert testing was performed at temperatures up to 1500°C using metals and glasses as the insert have been performed. These tests simulate accident scenarios where high internal pressure or uniform pellet-cladding contact may occur. Additional testing has explored the use of more complex shaped plug inserts that apply more complex load distributions on the internal cladding wall. In this way, localized loading effects on SiGA cladding are explored as might be expected due to pellet fracture and relocation during both normal and off-normal conditions. Tests have been performed with digital image correlation (DIC) measurements to measure mechanical stress strain response and acoustic emission to analyze microcracking in SiGA cladding. Funding was provided by DOE contract DE-NE-0008222.

9:30 AM

(ICACC-S13-049-2019) Micro-Mechanical Modeling to Design Micro-Pillar Compression Tests for Interfacial Debond Strength Extraction

P. Prabhakar*[1]; T. Koyanagi[2]; J. Kabel[3]; M. Balooch[3]; P. Hosemann[3]; Y. Katoh[2]

1. University of Wisconsin, Civil and Environmental Engineering, USA
2. Oak Ridge National Lab, USA
3. University of California Berkeley, Nuclear Engineering, USA

A micro-mechanical modeling approach is presented hereto design test specimens for determination of interfacial mechanical properties of continuous ceramic fiber reinforced ceramics matrix composites, in particular, fiber/matrixinterfacial debond shear strength and internal friction coefficient. Virtual compression tests of micro-pillar specimens with fiber/matrix interface placed at an angle to the axial loading direction are conducted using the validated model developed in finite element method. A parametric study of the influence of various parameters, including but not limited to, PyC layer thickness and angle, number of PyC layers, location of fiber and matrix regions with respect to the indenter, weak interfaces, specimen geometry like taper angle along the length, is conducted using this computational model. Robust design of the micro-pillar specimens and verification of the test method will be enabled by adding damage mechanics to the model. The modeling results will be validated based on experiments of an in-situ micropillar compression test of chemical vapor infiltrated SiC-SiC composites with PyC coated Hi-Nicalon Type S and Tyranno SA3 SiC fibers using a flat-punch indentation system. The research was partially sponsored by the U.S. DOE, Office of Fusion Energy Sciences under contact DE-AC05-00OR22725 with ORNL managed by UT-Battelle, LLC.

9:50 AM

(ICACC-S13-050-2019) Small scale mechanical testing of dual-purpose barrier coatings on CVD SiC

J. Kabel*[1]; P. Hosemann[1]; T. Koyanagi[2]; Y. Katoh[2]

1. University of California, Berkeley, Nuclear Engineering, USA
2. Oak Ridge National Lab, Materials Science Division, USA

SiC/SiC composites have gained attention as accident tolerant fuel cladding for their high temperature mechanical properties and superior oxidation kinetics in accident scenarios. However, operational LWR coolant conditions causes issues regarding SiC matrix dissolution and fission product retention. A potential solution is application of a dual-purpose environmental barrier coating. Our research investigated the mechanical stability of two coating materials, Cr and CrN, that have shown exceptional corrosion resistance under LWR relevant chemistries. Micro-cantilever testing was applied to evaluate the dependence of coating type and irradiation on interface fracture stress. Using the flexural formula, the average fracture stress for the SiC/Cr and SiC/CrN interfaces were 385±53 MPa and 224±46 MPa respectively. Neutron irradiated SiC/Cr interfaces (~0.5dpa) showed fracture stress 248±41 MPa. The SiC/Cr interface appears to be stronger than both SiC/CrN irradiated SiC/Cr interface, though additional modelling of the true interface stress state will allow for definitive variation in strength. It was also found that SiC/CrN cantilevers always broke at the interface, whereas the SiC/Cr and SiC/Cr_irr did not. This may suggest a gradient of strength and be representative of a diffused interface. A TEM study has identified interface characteristics that are likely responsible for these observations.

10:10 AM

(ICACC-S13-051-2019) Modified Burst Test of SiC/SiC Tubes with Strain Rates Relevant to Reactivity-Initiated Accidents

M. N. Cinbiz*[1]; N. R. Brown[2]; T. Koyanagi[1]; Y. Katoh[1]; K. Terrani[1]

1. Oak Ridge National Lab, USA
2. The Pennsylvania State University, Mechanical and Nuclear Engineering, USA

Mechanical response of a silicon carbide fiber and silicon carbide matrix (SiC/SiC) composite was investigated under pellet-cladding mechanical interaction (PCMI) loading conditions at the strain-rates similar to that of a postulated reactivity-initiated accidents (RIAs). The strain-driven nature of the PCMI was simulated by a modified-burst test (MBT) to investigate the possible RIA events ranging from 100 to 13 milliseconds (ms). The evolution of the mechanical strains was determined from the speckle-painted outer surface of the samples using a digital image correlation technique. The failure strain of samples (1.1%) tested at slower-rates, 52 and 100 ms, showed a good agreement with the reported values of similar composites tested at low-strain rates in the literature, but the failure strain was calculated lower (0.6%) for the fast-rate tests (13 ms). The present results suggested that SiC/SiC composite tubes might be affected by the imposed strain-rate during a postulated RIA.

S16: Geopolymers, Inorganic Polymers and Sustainable Materials

Phosphates and Other Inorganic Materials

Room: Ponce de Leon
Session Chair: Dong-Kyun Seo, Arizona State University

8:30 AM

(ICACC-S16-015-2019) Acid-based geopolymers: Structural evolutions during consolidation and in temperature (Invited)

V. Mathivet*[1]; H. Celerier[1]; J. Jouin[1]; S. Rossignol[1]; M. Parlier[2]

1. Laboratoire IRCER, France
2. ONERA, France

For a use at intermediate temperatures, geopolymers can be selected as new matrices in ceramic composites. However, alkali-based binders are not suitable due to fibers degradation induced by remaining alkali ions. Consequently, acid-based geopolymers are a promising alternative with improved mechanical properties and formation of refractory phases as $AlPO_4$ with the increase of temperature. This study focuses on the understanding of the structural evolutions during consolidation and heat-treatment of acid-based geopolymers. The structural evolutions were characterized by Fourier Transform Infrared and Nuclear Magnetic Resonance spectroscopies, X-ray diffraction and thermal analyses. After the attack of the metakolin by the phosphoric acid, a major aluminophosphate network and a minor hydrated silicate network are formed during the consolidation at room temperature. During heat-treatment, various polymorphs of $AlPO_4$ are formed and for intermediate temperatures, hydrated $AlPO_4$ phases are present. This work highlights the formation of coexisting amorphous networks of different compositions during consolidation and the crystallization of $AlPO_4$ polymorphs with increasing temperatures.

9:00 AM

(ICACC-S16-016-2019) Al/P ratio variation of acid-based geopolymers: Structural investigation by NMR and XRD analyses (Invited)

H. Celerier*[1]; J. Jouin[1]; V. Mathivet[1]; N. Tessier-Doyen[1]; I. Sobrados[2]; A. Gharzouni[1]; S. Rossignol[1]

1. Laboratoire IRCER, France
2. Instituto de ciencia de materiales de Madrid, Spain

New interest leads to develop acid-based geopolymers for several applications. These materials are based on the reaction of aluminosilicate sources and phosphoric acid. They exhibit interesting final properties such as higher temperature resistance (up to 1450°C) and better mechanical properties compared to alkali-based geopolymers. Previous study has demonstrated that the chemical composition and synthesis parameters such as setting temperature control the different final properties (water and thermal resistance). The aim of this study is to determine the origin of these properties by structural investigation. Four samples with different properties and Al/P ratio were selected to realize NMR and XRD experiments. Consolidated geopolymers present different networks as Al-O-P, Si-O-P, vitreous silica and Si-O-Al (just for Al/P =4). The proportions of this networks in each sample are closely related to the different final properties of materials.

9:30 AM

(ICACC-S16-017-2019) Decision support framework for sustainable materials selection: A case study of mine tailings management (Invited)

M. Sarkkinen*[1]; K. Kujala[1]; A. Al-Natsheh[2]; A. Kuoppala[2]; S. Gehör[1]

1. KAMK University, Mechanical and Mining Engineering, Finland
2. KAMK/CBD, Finland

The amount of waste is growing, and the problems related to sustainable waste management are becoming more complex. Mine tailings are one of the major categories of industrial waste, the disposal of which is problematic from the sustainability viewpoint. Typically, the chosen material solutions emphasize low construction costs over environmental and technical criteria and for this reason, decision-making is challenging. The aim of the work was to develop a framework for the sustainable selection of alternative material options with multiple-criteria decision analysis (MCDA). The case study comprised 11 criteria and five different material options: moraine-based cover, biofuel fly ash - steel slag composite cover, stabilization with Portland cement or with alkali activated composite (AAC), and the use of an advanced hardpan cover liner (AHCL). The proposed approach evaluated the economic, technical and social-ecological implications of the options. Overall, the results from this study show that when considering total sustainability, the AHCL was preferred when the main technical, social-ecological and economic criteria were equally weighted (33%). The criteria weightings affected the final priority order. The higher weighting of social-ecological and technical criteria (50%) favored stabilization with AAC, while the higher weighting (50%) of costs favored moraine cover.

Alkali Activated Cements and Materials I

Room: Ponce de Leon
Session Chair: Cristina Leonelli, University of Modena and Reggio Emilia

10:30 AM

(ICACC-S16-018-2019) Alkali-activated materials and their formation mechanisms (Invited)

C. E. White*[1]; K. Gong[1]; K. Yang[1]

1. Princeton University, Civil and Environmental Engineering, USA

With the world facing a climate crisis due to increasing CO_2 emissions there is pressing need to develop and implement sustainable construction materials across the globe. Alkali-activated materials (AAMs) pose as one such sustainable alternative to conventional ordinary Portland cement (OPC) concrete, however, questions remain regarding the link between short-term formation mechanisms and long-term performance of AAMs. For instance, the pore structure development during early-age formation is known to influence the material's permeability. Here, key in situ neutron and synchrotron characterization methods are used, including quasi-elastic neutron scattering and X-ray pair distribution function analysis, to elucidate the short-term formation mechanisms of AAMs. The experimental findings will be discussed in the context of ongoing coarse-grained simulation efforts focused on modeling the evolution of the sub-micron pore network in these sustainable cements, with the aim of being able to computationally design pore structures in these materials with optimal transport properties (i.e., low permeability).

11:00 AM

(ICACC-S16-019-2019) Manipulating Reaction Kinetics of Alkali-activated Materials using Nano-sized Additives (Invited)

N. Garg*[2]; J. Gomez[1]; C. E. White[1]

1. Princeton University, USA
2. University of Illinois at Urbana-Champaign, USA

Alkali-activated materials (AAMs) are a class of sustainable cements that can help supplant the highly CO_2-intensive ordinary Portland cement (OPC). For traditional OPC there are numerous chemical additives available to manipulate its hydration and setting. However, for alternative cements like AAMs, the availability of suitable additives is severely limited. This scarcity is attributed to the differences in solution and surface chemistry between OPC and AAMs, where existing admixtures are either unstable in the alkaline solution or show mixed/limited efficacy. Here, for the alkali activation of blast furnace slag, we report two unique additives that can successfully manipulate the reaction mechanisms and associated kinetics. Specifically, using isothermal calorimetry and in situ X-ray pair distribution function analysis, we find that zinc oxide nanoparticles can effectively retard the reaction while calcium-silicate-hydrate based nanoseeds cause an acceleration.

11:30 AM

(ICACC-S16-020-2019) Quality of Precursors and Nanostructural Evolution of Binding Phases in Slag-Fly Ash-Metakaolin-based Binders (Invited)

K. Sankar*[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Material Science and Engineering, USA

Slag-fly ash and slag-metakaolin binders are two types of room temperature hardening binders that have excellent mechanical properties and significantly lower carbon footprint than OPC. C-N-A-S-H gel and geopolymer are the binding phases in these binders. The aim of this study was two-fold. The first aim was to evaluate the quality of precursors (slag, metakaolin, and fly ash) using MAS-NMR, FTIR, XRD, XRF, and laser diffraction. The second aim was to monitor the structural changes of the binding phases with increasing time, temperature, and slag/fly ash ratio. This was achieved by using selective chemical extractions and nuclear magnetic resonance (MAS-NMR). Using ^{27}Al MAS-NMR the proportion of four-, five- and six-coordinated Al in precursors was determined. The structure of C-N-A-S-H gel and geopolymer at various times, slag/fly ash ratios, and curing temperatures were determined using ^{29}Si MAS-NMR. A "soft gel" was formed during setting in slag-fly ash binders. The structure of this "soft gel" which had a solid percolating network but could not bear load was put forth. FTIR was used to corroborate the results of MAS-NMR.

Alkali Activated Cements and Materials II

Room: Ponce de Leon

Session Chair: Claire White, Princeton University

1:30 PM

(ICACC-S16-021-2019) Alkali activation of volcanic ash and "ghiara" from Mount Etna, Sicily, Italy (Invited)

C. Finocchiaro[2]; C. Sgarlata[1]; G. Barone[2]; I. Lancellotti[1]; P. Mazzoleni[2]; C. Leonelli*[1]

1. University of Modena and Reggio Emilia, Department of Engineering "Enzo Ferrari", Italy
2. University of Catania, Dipartimento di Scienze biologiche, geologiche e ambientali, Italy

Several volcanos all over the world have been erupting for years and their ashes have generated interesting deposits of partially devitrified aluminosilicates. Additionally, the ground in contact with the molten lava have been naturally decomposed by the high temperatures reached during eruptions. This ground in also a partially amorphised aluminosilicate, that in the region of Mount Etna, Sicily, Italy, is defined with the term "ghiara". In the past, volcanic ash and ghiara have been used to produce building materials for the inhabitants living on the sides of the volcano. At present, we propose the alkali activation as low cost consolidation technology to prepare shaped building materials for the territory in the proximity of the deposits of ashes and "ghiara". The first attemps to produce alkali activated materials, AAM, leading to success in the lab, were obtained treating the volcanic ash at 400 deg C, after fine grinding. For the "ghiara", the thermal treatment was necessary only after the alkali activation with a curing cycle at 100 deg C. The final products were tested after 28 days for mechanical and chemical perfomance.

2:00 PM

(ICACC-S16-022-2019) Investigating the shrinkage and strength properties of a self-compacting, Fe-rich, inorganic polymer grout

G. Beersaerts*[1]; Y. Pontikes[1]

1. KU Leuven, Materials Engineering, Belgium

Fe-rich inorganic polymers (IPs) can be produced by the alkali activation of an Fe-rich glassy precursor which originates from the Cu-industry. In the present work, an IP grout was developed by optimising the particle packing, workability and strength properties. Focus was placed on controlling the shrinkage, as this was one of the main challenges in order to avoid curling and the formation of cracks. Therefore, the autogenous and drying shrinkage behaviour was investigated by modifying the activating solution chemistry and curing conditions and by introducing reactive and non-reactive additives. The curing conditions were either high pressure and high temperature (autoclave), or high temperature or ambient conditions. Samples cured at ambient conditions resulted in high shrinkage (>4000 μm/m), while heat-cured samples had the least shrinkage (<3500 μm/m). Addition of sand and Ground Granulated Blast Furnace Slag (GGBFS) decreased shrinkage. The strength of the IPs increased significantly (>100 MPa) when GGBFS was introduced and when the samples were heat-cured or autoclaved.

2:20 PM

(ICACC-S16-023-2019) Open-cell porous inorganic polymers from industrial Fe-rich slags

R. Murillo Alarcón*[1]; T. Hertel[1]; Y. Pontikes[1]

1. KU Leuven, Department of Materials Engineering, Belgium

This work describes the synthesis of porous inorganic polymers (IP) after alkaline activation of an industrial Fe-rich slag and chemical foaming. These materials are of interest due to their potential use as thermal insulators and/or noise absorbers. The porous IP were synthetized from a four component blend: Fe-rich slag and different amounts of alkaline activator, surfactant and aluminum powder. The effect of processing parameters, such as alkaline activator to slag mass ratio (0.30 - 0.40), surfactant (0.015 - 0.045 wt%) and aluminum concentration (0.10 - 0.20 wt%), on the morphology and properties of the samples were assessed. It was observed that the L/S ratio as well as the surfactant concentration have a significant influence on the pore shape and size. The highest strength was obtained in samples with small spherical pores which were uniformly distributed. Furthermore, when the aluminum concentration was increased, the porosity also increased from 55 % to 85 %. The increased porosity resulted in a drop of thermal conductivity from 0.180 to 0.069 W/(m.K) and a decrease of the compressive strength from 5.5 to 0.5 MPa. This work is part of the first steps in the development of porous IP from iron rich slags, but further research needs to be done, in particular regarding to their durability.

2:40 PM

(ICACC-S16-024-2019) Investigating different commercial metakaolin sources and waste alkaline solutions for producing geopolymer

D. Samuel*[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Materials Science and Engineering, USA

Commercial development of geopolymer products is beginning, but progress can still be made in identifying source materials giving improved performance and lower cost. Metakaolin remains the best aluminosilicate source since the main alternative, fly ash and ground-granulated blast furnace slag, results primarily in the formation of non-geopolymer CSH and CASH binding phases. However, multiple metakaolins are available with different properties. Alternatively, waste alkaline solutions may be used to reduce cost, though the initial composition and impurities must be considered. In this work we compared geopolymer samples made with Argical M1200 S, MetaStar 501, MetaStar 501 HP (all from Imerys S.A., France), Powerpozz (Advanced Cement Tech., WA, USA), and Metamax® (BASF SE, Germany) metakaolin and reinforced with Nyad G wollastonite needles (NYCO Minerals, NY, USA) via 3-pt. bending and pull-off tests. We also used Metamax® to test the flexural and compressive strengths of geopolymer made using waste KOH solutions (Pall Corp., FL, USA). The resulting samples were comparable to standard potassium geopolymer. Finally, to represent a commercial product we made larger bars (40 mm×40 mm×160 mm) using Metamax®, waste-KOH waterglass, Cem-FIL MiniBars® (Owens Corning, OH, USA), and Mulcoa M70 chamotte (Imerys S.A.), and investigated the 3-pt. flexural and compressive properties.

Novel Applications

Room: Ponce de Leon

Session Chair: Minna Sarkkinen, KAMK University

3:30 PM

(ICACC-S16-025-2019) Potential medical applications of geopolymeric nanomaterials (Invited)

D. Seo*[1]

1. Arizona State University, School of Molecular Sciences, USA

Geopolymeric aluminosilicate nanomaterials are a new class of inorganic materials and may be listed among the few that can be produced conveniently in a large scale under ambient synthetic conditions. For example, by adjusting the geopolymer resin compositions with high alkali concentrations, geopolymerization process can be controlled to produce high-surface area and high-porosity nanomaterials. Given the massive production and application of the materials in the range of millions of tonnes per year, the advent of the new geopolymeric material type has a huge implication in novel large-scale applications of geopolymer. We will discuss promising applications of the geopolymeric nanomaterials in medical field particularly in killing or removing bacteria and/or biological toxins.

4:00 PM

(ICACC-S16-026-2019) Rehabilitation of Deteriorated Wood Railroad Ties using Alkali Activated, Slag Fly Ash Binders (Invited)

G. Al-Chaar*[2]; K. Sankar[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Material Science and Engineering, USA
2. Construction Engineering Research Laboratory, USA

Wood is the most commonly used material for railroad ties in the US because it has the right amount of stiffness, ability to be drilled for rail fastening systems, load-bearing capacity, favorable life-cycle economics and environmental friendliness. Wooden railroads have a finite useful life and undergo deterioration due to many factors such as rotting, insect infestation and other biological factors. Some of the current methods to rehabilitate wooden railroad tie life is the use of harsh and toxic chemicals like Creosote to kill the fungi and termites. In other cases, wooden ties need to be removed and replaced which costs a lot of time and money. In this study, new slag-fly ash binder mixtures and a method to apply them to rehabilitate a deteriorated railroad tie in place were created. It was found that the mixtures developed were easy to prepare on-site, cost-effective, had excellent flow, and excellent compressive and flexural strengths. Hence an effective material and method to rehabilitate railroad ties is proposed in this report.

4:30 PM

(ICACC-S16-027-2019) Amorphous, Self-Glazed (ASG-G) Geopolymer & (ASG-C) Ceramic Composites (Invited)

V. Chadha*[1]; W. M. Kriven[1]

1. University of Illinois at Urbana-Champaign, Materials Science and Engineering, USA

Basalt is the most common volcanic rock-type on earth. Potassium geopolymer in the stoichiometric composition $K_2O•Al_2O_3•4SiO_2•11H_2O$ was produced from fumed silica, deionized water, potassium hydroxide, (i.e. waterglass) and metakaolin. The geopolymer matrix was fabricated in an IKA® high shear mixer (Model RW20DZM, IKA, Germany) to which 15 wt. % glass frit was added. With the addition of 0.5 wt. % Sapetin® D20 superplasticizer(Wöllner, GmbH, Germany) as a dispersing agent, the maximum amount of ¼" chopped basalt fibers(Kameny Vek, Moscow, Russia) reinforcements was increased to 15 wt%. Both were then dispersed in the KGP using a Thinky ARE-250 planetary mixer(Intertronics, Oxfordshire, England) and the samples were allowed to set at ambient temperature for 1 day followed by 1 day at 50°C to complete the reaction. The glass frit(T_m = 825°C)(Uroboros Glass F1-424-96-8 Cobalt Blue) was added to produce self-glazing in a dehydrated, amorphous(GP) or crystallized ceramic composite(1100-1200°C) and to counteract excessive porosity left by the superplasticizer after high-temperature heat treatments. Samples were of 1″x1″x6″ in dimensions. The chopped basalt fibers melted after the KGP matrix crystallized into leucite providing a network/glass filling system in a ceramic(1200°C). The amorphous self-glazing effect of the glass frit significantly improved the flexure strength of the geopolymer and ceramic composites.

S17: Advanced Ceramic Materials and Processing for Photonics and Energy

Multi-functional Materials III

Room: Halifax A/B

Session Chair: Giovanni Fanchini, University of Western Ontario

8:30 AM

(ICACC-S17-035-2019) Enhanced dielectric and piezoelectric response in ferroic thin films for MEMS applications (Invited)

N. Bassiri-Gharb*[1]

1. Georgia Institute of Technology, Woodruff School of Mechanical Engineering, USA

This presentation discusses advancements in the processing of ferroelectric, relaxor-ferroelectric and antiferroelectric thin films for applications in microelectromechanical sensors, actuators and transducers. Specifically, approaches for enhanced crystallographic orientation in polycrystalline films on Si substrates, and alternative compositions to the prototypical lead zirconate titanate (PZT) are presented. Current state-of-the-art as well as future directions are discussed.

9:00 AM

(ICACC-S17-036-2019) Soft Processing for Direct Fabrication of Functionalized Graphenes, Their Hybrids and MoS2 Inks in Solution under Ambient Conditions (Invited)

M. Yoshimura*[1]

1. National Cheng Kung University, Mater. Sci. & Eng., Taiwan

We present Soft Processing for Direct Fabrication of Functionalized Graphene Inks via "Submerged Liquid Plasma [SLP]" and "Electrocemical Exfoliation [ECE] methods. SLP methods resulted the direct synthesis of Nitrogen functionalized Graphene Nanosheets from Graphene suspension and/or Graphite electrode in acetonitrile liquids. [Products contains few layers (< 5) Graphene nanosheets. Unsaturated or high energy functional group (e.g. C = C, C = N and C•N) have formed in the products. Reduction and functionalization of Graphene oxides and Synthesis of Graphene/Au Hybrids also realized by SLP. In the ECE, graphite anode is exfoliated electrochemically by H_2O_2-NaOH or Glycine-H_2SO_4 aqueous solutions under ambient temperature and pressure, for 5-30 min with +1-+5 volt, into 3-6 layers Graphene Nanosheets [GNs]. The GNs suspended in solutions can be transformed into N-FG, further into Au-Hybridized N-FG by the sonification. Those hybrids have excellent catalytic performances. It should be noted that Soft Processing can directly produce "Graphene Ink"; Graphenes dispersed in various liquids, under mild conditions. Other 2D materials like MoS_2 can also be dispersed in a Solution via Sonochemical and/or Electrochemical ways.

9:30 AM

(ICACC-S17-037-2019) Reversible Sodium and Lithium Insertion in Iron Fluorides (Invited)

N. Pinna*[1]

1. Humboldt-Universität zu Berlin, Department of Chemistry, Germany

3d-transition metal fluorides, such as FeF_3, have drawn attention as Na and Li-ion positive electrode material due to their ability to deliver high potential thanks to the high polarity of the metal-fluorine bond. However, the insulating character of these highly ionic materials in practice leads to high polarisation and slow insertion kinetics. Moreover, since the positive electrode in current LIBs and NIBs is the reservoir of alkali ions, metal fluorides are not applicable in alkali-ion technology against a carbonaceous anode without pre-lithiation/sodiation. In order to solve these issues, here we introduce a microwave-assisted solution synthesis of $NaFeF_3$ perovskite nanoparticles from pre-synthesized rutile FeF_2 colloidal particles, sodium ethoxide and ammonium fluoride. Our $NaFeF_3$ material shows a reversible electrochemical activity of 1Na or 1Li per iron with low polarisation and excellent capacity retention after 100 cycles. The unexpected reversible insertion of both sodium and lithium ions, studied through ex-situ and operando X-ray diffraction measurements, is attributed to a kinetic stabilization of corner-shared cubic A_xFeF_3 (A = Li, Na) frameworks along the cycles involving low volume change without high thermodynamic cost as supported by a polymorphism theoretical analysis.

10:20 AM

(ICACC-S17-038-2019) Triboelectric Nanogenerator for Energy Harvesting and Self-Powered Sensing (Invited)

X. Sun*[1]

1. Soochow University, Institute of Functional Nano & Soft Materials, China

Triboelectric nanogenerator (TENG), a recently emerging technology that is based on the combination of triboelectrication and electrostatic induction, has been found to be a promising solution to harvest large amounts of underutilized and low-frequency mechanical energy and convert them to electricity. Our recent research interest mainly focuses on the design and fabrication of high performance TENGs for energy harvesting and self-powered sensing. In this presentation, I will firstly introduce a couple of recent achievements regarding highly flexible and deformable TENGs based on different kinds of electrodes, including geometrically designed rigid electrode, liquid electrode and 3D printed compressible electrode, etc. Then, I would like to present the combination of TENGs with other functional devices, such as supercapacitor for self-charging powered package, solar cell or electromagnet generator for large-scale energy harvesting, as well as photoanodes for self-powered photoelectrochemical water splitting system. Lastly, I will illustrate two different concepts of TENG based self-powered sensing, including TENGs as self-powered sensors for actively detecting the static and dynamic processes arising from mechanical agitation, and impedance matching effect between TENGs and traditional sensors induced self-powered sensing process.

10:50 AM

(ICACC-S17-039-2019) Structure of ionic liquid-metal oxide electrical double layers in ion-gated transistors (Invited)

C. Santato*[1]; M. O. Orlandi[2]; M. Barbosa[2]

1. Ecole Polytechnque de Montreal, Canada
2. UNESP, Brazil

The structure and properties of the electrical double layer (EDL) in ionic liquids is of interest in a wide range of areas including energy storage, catalysis, lubrication, and many more. EG-TFTs are devices based on mixed electronic and ionic transport that can modulate the current that flows in a semiconductor channel using an electrolyte as the gating medium. The principle of operation of EG-FETs revolves around two main mechanisms: the electrostatic mechanism, where an EDL at the electrolyte/semiconductor interface causes the accumulation (or the depletion) of charge carriers in the channel; the electrochemical mechanism, where electrochemical processes are responsible for the charge carrier density modulation in the channel. One of the biggest challenges, in the study and optimization of EG-TFTs, is the comprehension of how the doping mechanism is affected by specific experimental conditions, in particular the physicochemical properties of the ionic liquid and the electrical bias applied. Here we report on the characteristics of the EDL formed during the operation of an EG-TFT where WO_3 is employed as the channel material and ionic liquids are employed as gating media by In situ Force Spectroscopy, an effective tool to detect ion ordering within the EDL of ionic liquids.

11:20 AM

(ICACC-S17-040-2019) Molecular/2D-Material Hybrid van der Waals Heterostructures (Invited)

E. Orgiu*[1]

1. Institut National de la Recherche Scientifique, Energy Materials Telecommunications, Canada

The rise of graphene and related 2D materials makes it possible to form heterostructures held together by weak interplanar van der Waals (vdW) interactions. The incorporation of organic molecules within these systems holds an immense potential. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities. In my talk I will talk about the very many possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, it is highlighted how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional. In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, periodic potentials naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of the individual 2D components within the stack and their

alignment, thus offering the possibility to build up hybrid and novel materials with novel properties.

11:50 AM

(ICACC-S17-041-2019) The potential of biomass for the synthesis of carbon dots (Invited)

C. Ouellet-Plamondon*[1]; D. Benetti[2]; A. Nkeumaleu[1]

1. ETS, Université du Québec, Construction, Canada
2. INRS - Institut National de la Recherche Scientifique Centre -, Energie Materiaux Telecommunications, Canada

Carbon dots are emerging nontoxic semiconductive nanomaterials, an alternative to quantum dots. They can be synthesized with non-harmful elements (C, N and O) in large quantity with simple solvothermal treatment. A number of natural precursors are potential candidates, they can turn low-cost materials into high value luminescent materials. In this study, the carbon dots are synthetized by microwave methods using ascorbic acid and urea as reference precursors, and with other biosourced materials. The emission spectra in fluorescence is measured as a function of excitation wavelength, time and temperature. The carbon dots have the potential to be incorporated in thin films and ceramics. As the quantum yield of the carbon dot increase, they can serve as solar concentrators to reduce the cost of photovoltaic (PV) materials by increasing the power generated per unit area.

Friday, February 1, 2019

FS1: Bio-inspired Processing of Advanced Materials

Bioinspired Materials for Functional Applications

Room: Coquina Salon F

Session Chairs: Simone Sprio, National Research Council of Italy; Hao Xie, Wuhan University of Technology

8:30 AM

(ICACC-FS1-014-2019) Hard carbon derived from olive stone as anode for sodium-ion batteries: Further insights into the microstructure on Na^+ storage mechanisms (Invited)

A. Gomez-Martin*[1]; J. Martinez-Fernandez[1]; M. Ruttert[2]; T. Placke[2]; J. Ramirez-Rico[1]

1. Universidad de Sevilla, Departamento Física de la Materia Condensada, Spain
2. University of Münster, MEET Battery Research Center, Germany

Growing energy demand and concerns related to the depletion of lithium resources are main driving forces to the search for affordable alternatives to current lithium-ion batteries. In this sense, sodium-ion batteries (SIBs) are receiving considerable attention due to the abundance of sodium metal in the Earth's crust and comparable electrochemical potential to that of Li. Owing to the high interplanar distances and available storage places arising from their disordered structures, hard carbons are the preferred anode material. From an economical and environmental point of view, there is a growing interest in developing hard carbons from biomass resources or industrial wastes. Despite the large number of publications in this area, the role of microstructure and crystallinity in the sodium insertion mechanism in hard carbons is not fully understood. In this work we report on the behavior of hard carbons from carbonization of olive stones at different temperatures as anodes for SIBs. Olive stone-derived carbon obtained at 1400°C delivered the highest reversible capacity reaching up to ≈280 mAh/g with a 1st cycle coulombic efficiency of 80%. Potential profiles and sloping and plateau capacities are evaluated as a function of treatment temperature, aiming at establishing a relationship between structural order and electrochemical behavior.

9:00 AM

(ICACC-FS1-015-2019) Porous graphene-like nanosheets from biomass resources as electrodes for energy storage applications

A. Gomez-Martin[1]; J. Martinez-Fernandez[1]; J. Ramirez-Rico*[1]

1. Universidad de Sevilla, Spain

Porous 3D carbon frameworks are promising materials as electrodes for electric-double layer capacitors, since their high and accessible surface area results in shorter ionic diffusion lengths and faster ionic transport access during electric double-layer formation. These features, along with the hierarchical microstructure, bring an improved electrochemical performance and rate capability. We report a low-cost and simple method for the synthesis of a three-dimensional porous graphene-like carbon framework from an environmentally friendly biomass resource, using an aqueous Ni solution to provide the graphitization catalyst. Impregnation promotes a self-propagating exothermic reaction during the pyrolysis-step at ≈150 °C, breaking down the original cell wall structure to form a complex three-dimensional network formed by the stacking of randomly and crumpled graphene-like nanosheets. The formed nickel nanoparticles induce the catalytic graphitization of the carbon structure simultaneously during pyrolysis at lower temperatures than previously reported. After acid etching, nickel particles are fully removed leaving in-plane nanopores into the wrinkled sheets. The thermal behavior during carbonization as well as the resulting microstructure's features and surface properties are evaluated with a view to their electrochemical performance as electrodes for supercapacitor devices.

9:20 AM

(ICACC-FS1-016-2019) Biomimetic patterned surfaces from sol-gel dewetting

E. Colusso*[1]; A. Martucci[1]; C. Neto[2]

1. University of Padova, Italy
2. University of Sydney, Australia

Inspired by examples found in nature, patterned surfaces able to collect water from the atmosphere have been proposed as sustainable approaches for addressing global water shortages. In this presentation, we report the fabrication of silica based surface micropatterns with wettability contrast, prepared through dewetting of sol-gel films. Dewetting is a spontaneous phenomenon that occurs when unstable thin liquid films break apart on a substrate, driven by unfavorable intermolecular forces at the interface. While film dewetting is well-studied in polymeric thin films to generate patterned surfaces, dewetting in sol-gel films is poorly understood. Thin layers were obtained by sequential deposition of sol-gel solutions by spin coating. Dewetting of the top film was promoted by exposing the xerogel to a saturated solvent vapor atmosphere. The key factors to control the process were identified and patterns with tunable size were fabricated. By changing the chemistry of the sol-gel, we realized patterns with chemical and topological contrast, consisting of hydrophilic bumps on a hydrophobic layer. These surfaces, inspired by the hexoskeleton of a desert beetle, will be investigated for their potential to collect atmospheric water.

9:40 AM

(ICACC-FS1-017-2019) Biological Crystallization of Ultrahard Teeth and Translation to Multi-Functional Materials

S. Herrera[1]; H. Tang[1]; R. Zhou[1]; M. Nemoto[2]; D. Kisailus*[1]

1. University of California, Materials Science and Engineering, USA
2. Okayama University, Japan

Natural systems have evolved efficient strategies to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and

hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials. Here, we discuss the formation of heavily crystallized radular teeth the chitons, a group of elongated mollusks that graze on hard substrates for algae. We investigate the synthesis of these incredibly hard and wear resistant teeth with highly controlled nanostructured components. All of this is controlled by precise release of mineral precursor nucleated on underlying organic-inorganic fibrous tissue. Specifically, From the investigation of synthesis-structure-property relationships in these unique organisms, we are now developing and fabricating multifunctional engineering materials for energy conversion and storage.

10:00 AM

(ICACC-FS1-018-2019) Protective Role of Sutures Bio-inspired by the Boxfish Carapace

M. Hosseini*[1]; S. Garner[3]; S. E. Naleway[2]; J. McKittrick[3]; P. Zavattieri[1]

1. Purdue University, Civil Engineering, USA
2. University of Utah, Mechanical Engineering, USA
3. University of California, San Diego, Mechanical Engineering, USA

The boxfish carapace (Lactoria cornuta) contains hexagonal dermal scutes, a combination of the brittle hexagonal plate (hydroxyapatite) and hyperplastic (collagen) materials to develop flexible armor and protect against the predation of other species. The mineralized plates are connected to each other through sutures. However, unlike other species in nature, these sutures are not connected by an intermediate compliant phase. Instead, the individual plates are connected only through the collagen base. As such, contact only takes place under compression and shear loading. In this work, we focus on the protective role of the boxfish carapace under shear loading conditions. The material properties of the boxfish scute are characterized through a combination of using in-situ tests and finite element models. Our numerical results reveal that the architecture of the sutures, together with the material mechanical property play a significant role in controlling the damage mechanisms of the carapace system. We present a parametric and systematic modeling analysis study that employs analytical and numerical tools to understand the role of different geometrical and material parameters of the system. As part of the experimental validation, we built bio-inspired specimens using brittle and soft materials.

FS2: Image based Characterization and Modelling of Ceramics by Non-destructive Examination Techniques

Use of NDE Techniques for Detection of Local Microstructural Changes and Damage Characteristics in Ceramic Matrix Composites I

Room: Coquina Salon A

Session Chair: Tobias Fey, Friedrich-Alexander University Erlangen-Nürnberg

8:00 AM

(ICACC-FS2-011-2019) Health Monitoring of Ceramic Matrix Composites using Acoustic Emission, Electrical Resistance, and Digital Image Correlation (Invited)

M. J. Presby*[1]; R. Panakarajupally[1]; Y. P. Singh[1]; M. Kannan[1]; G. N. Morscher[1]

1. University of Akron, Mechanical Engineering, USA

Successful modeling and simulation of the mechanical behavior in ceramic matrix composites (CMCs) is dependent upon characterizing and understanding the damage progression and failure modes under various modes of loading and environmental conditions. Acoustic emission (AE), electrical resistance (ER), and digital image correlation (DIC) are three techniques that have been shown to be successful in monitoring the onset and progression of damage in SiC-based CMCs. Results from the use of AE, ER, and DIC will be discussed for various loading scenarios at ambient and elevated temperatures. In addition, the effects of elevated temperatures on the use of these health monitoring techniques, particularly ER, will also be discussed.

8:30 AM

(ICACC-FS2-012-2019) Using X-Ray tomography techniques to study damage progression in SiC/SiC composites (Invited)

A. Hilmas*[1]; K. M. Sevener[1]; Y. Zhou[2]; A. Singhal[2]

1. University of Michigan, USA
2. GE Global Research Center, USA

Due to their high temperature capabilities, high toughness, and their light weight, SiC/SiC CMCs are currently being used in aerospace applications. X-ray tomography techniques have recently been utilized as a method to study these composite materials in order to better understand their mechanical properties. In this study, MI SiC/SiC CMCs were characterized through the use of synchrotron x-ray tomography at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory and a lab scale x-ray tomography using a Zeiss Xradia. SiC/SiC CMC specimens were imaged in order to better understand damage progression as it relates to microstructural features in the composite.

9:00 AM

(ICACC-FS2-013-2019) Discernment of Damage in Ceramic Matrix Composites Using Acoustic Emission (Invited)

G. N. Morscher*[1]

1. University of Akron, Mechanical Engineering Dept., USA

Ceramic matrix composite damage development is quite complex. Damage takes various crack formations dependent on stress state as well as fiber-breakage which leads to failure. However, the observance of damage and identification of damage with a given mechanical state is not always that straightforward. Initial cracking typically occurs at stresses below which noticeable differences in the nonlinearity of stress/strain behavior is observed. One technique that is quite versatile to the detection of damage and in some cases to the identification of damage is acoustic emission (AE). AE is the stress wave response caused by the pressure exerted on the material from a mechanical event. With proper sensor placement, two-dimensional location of damage can be discerned. It is the best technique to discern the lowest-stress damage. Also, it is a technique that can be used on complex shapes. In this work, some past and more recent research in the use of AE to monitor damage development via acoustic emission and identify damage sources in CMCs under a variety of fatigue conditions will be discussed.

9:30 AM

(ICACC-FS2-014-2019) Characterizing Early Damage Evolution in CMCs

B. Swaminathan*[1]; A. S. Almansour[2]; J. D. Kiser[2]; K. M. Sevener[3]; S. Daly[4]

1. University of California, Santa Barbara, Materials, USA
2. NASA Glenn Research Center, USA
3. University of Michigan, USA
4. University of California, Santa Barbara, Mechanical Engineering, USA

Silicon carbide / silicon carbide ceramic matrix composites (SiC/SiC CMCs) are structural ceramics that are well-suited for the extreme environment conditions of space and aerospace applications largely due to their low weight, creep resistance, damage tolerance, and high specific strength. In CMCs, the initiation and accumulation

of damage depends on characteristics of the constituent landscape including porosity, interfacial properties, and geometric distribution of CMC constituents. In order to accurately predict the lifetimes of these advanced composites, it is critical to understand the evolution of damage and to characterize which early damage mechanisms subsequently lead to crack coalescence and macroscopic failure. In this study, SiC/SiC minicomposites are characterized through an experimental approach combining acoustic emission (AE) with tensile testing in-SEM (scanning electron microscope), in order to examine early damage initiation (below the proportional limit) and its evolution at room temperature. The approach provides insight into the relative activity of early damage mechanisms in CMCs at both the surface and subsurface levels and sheds light on the impact of fabrication choices on the evolution of damage to final failure. The potential application of this combined approach towards the characterization of damage in SiC/SiC CMCs under more complex testing conditions will also be discussed.

9:50 AM

(ICACC-FS2-015-2019) Use of Digital Imaging and Acoustic Emission to Assess Damage in EBC-CMC Systems

A. S. Almansour*[1]; B. J. Harder[2]; J. D. Kiser[1]; K. Lee[2]; J. Setlock[3]; D. Gorican[4]; A. Gorven[5]; M. J. Presby[6]

1. NASA Glenn Research Center, Ceramic and Polymer Composites Branch, USA
2. NASA Glenn Research Center, Environmental Effects and Coatings Branch, USA
3. University of Toledo at NASA Glenn Research Center, Environmental Effects and Coatings Branch, USA
4. Vantage Partners, LLC at NASA Glenn Research Center, Ceramic and Polymer Composites Branch, USA
5. Boise State University, Mechanical Engineering, USA
6. University of Akron, Mechanical Engineering, USA

SiC fiber-reinforced SiC ceramic matrix composites (SiC_f/SiC) react with oxygen at high temperatures forming a protective silica layer. However, this silica layer reacts with water vapor to form volatile silicon hydroxide ($Si(OH)_4$) which degrades the composite. Therefore, environmental barrier coatings (EBCs) are needed for ceramic matrix composite (CMC) components that are being used in water vapor-rich jet engine environments in order to provide elevated temperature environmental stability and achieve protection against oxidation. In this work, several layers of oxide-based environmental barrier coatings were applied on Hi-Nicalon Type S SiC fiber-reinforced chemical vapor infiltrated (CVI) SiC minicomposites via a slurry-based infiltration approach. Minicomposites were then tested in monotonic tension at room temperature. Digital imaging and acoustic emission health monitoring techniques were used to assess surface and subsurface damage mechanisms in the EBC-CMC system, respectively. EBC/CMC damage onset, progression, and interaction through-thickness and at the matrix/coating interface were characterized and compared to that of the uncoated, pristine CMC.

10:10 AM

(ICACC-FS2-016-2019) Developing structure-property linkages for damage initiation/propagation in continuous ceramic fiber reinforced ceramics matrix composites (Invited)

D. Patel[1]; D. Rapking*[2]; T. A. Parthasarathy[1]; M. V. Braginsky[2]; C. P. Przybyla[3]

1. UES, Inc., USA
2. UDRI, USA
3. Air Force Research Lab, USA

Continuous fiber reinforced ceramic matrix composites (CMCs) exhibit hierarchical internal structure with rich details at multiple length scales of interest. To accelerate the rate of development and deployment of this class of structural materials, computationally efficient structure-property linkages are critical for characterizing their damage performance. In this work, a reduced-order, data-driven, predictive model to quantify damage initiation/propagation in CMCs at pertinent length scales is developed. A framework is described for predicting structure-property linkages in CMCs microstructures under transverse loading. Digital representations of the composite structure at the scale of the fibers has been constructed for micromechanical simulation of damage initiation and progression. The physics of crack initiation and propagation is captured via a discrete damage modeling approach. A parametric finite element model has been developed to assess and quantify the damage accumulation under transverse cracking of CMCs. Reduced order representations of microstructures using n-point spatial statistics are utilized to build computationally efficient relationships between each of the selected microstructures and their effective damage properties via a machine learning approach.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics and Biocomposites III

Room: Coquina Salon B
Session Chairs: Akiyoshi Osaka, Okayama University; Faleh Tamimi, McGill University

8:30 AM

(ICACC-S5-017-2019) Finite Element model calculation on osteoporosis modeling (Invited)

J. Liu[1]; J. Wang[1]; X. Chen[1]; G. Wang[1]; A. Osaka*[1]

1. Henan University of Science & Technology, Sch Mat Sci & Eng, China

Osteoporosis strongly reduces the quality of life of elderly people. Porous polymer bodies whose struts are coated with some bone-active layer seem superior to other types of substitutes, from the viewpoints of controllable stiffness and biological activity. We carried out Finite Element model (FEM) calculations for 1~3-dimensional (1~3-D) cube honeycombs as well as 1-D and 2-D planar grids, where the struts were made of Nylon®66 or polyethylene. The edge length of the honeycombs and grids remained constant at 0.9 mmm while their edge length of the components was varied from 0.1 mm to 0.4 mm. With removal of 1 to16 struts out of ~500, analyzed was the tendency of the change in the stress and strain (von Mises criterion) as well as Young's modulus. It waa discussed in terms of the number of removed struts, the mode of removing struts (random, parallel, cross-type), in addition to anisotropy effects.

9:00 AM

(ICACC-S5-018-2019) Porous Silica-Polymer Hybrid Gels for Oligo Delivery

D. Kapusuz*[1]

1. Gaziantep University, Metallurgical and Materials Engineering, Turkey

One of the most exciting developments in medicine was the recognition of the therapeutic potential of oligonucleotides by suppressing the genetic transcription of patient cells. Since naked oligonucleotides are quite fragile and rapidly degraded in the bloodstream, researchers developed nanoparticles that could deliver oligonucleotides to cells without degradation. In order to enable cellular uptake, oligonucleotides were first bonded on the particle surfaces by electrostatic attraction or covalently, then the surfaces were functionalized with polymers. Polyethylene glycol (PEG) and polyethylene imine (PEI) could protect oligonucleotides and provided cellular uptake. Distinctively, adsorbing oligonucleotides on surface pores of mesoporous silica has shown greater potential for oligo delivery, compared to liposomes, lipids or polymers which required cationic interactions with oligonucleotides resulting in increased toxicity and/or decreased release capability. In this study, for the first time, hybrid silica/PEG gel networks were formed by sol-gel

reaction and oligonucleotides were simultaneously entrapped inside the pores, which present not only on the surface but also inside the whole network. By this means, oligonucleotides were homogeneously distributed, protected from pre-release or degradation and higher number of active sites on the surfaces could be modified with PEI and antibodies for cell targeting.

9:20 AM

(ICACC-S5-019-2019) Tough and aging resistant zirconia composites for dental implants

E. Adolfsson*[1]; N. Courtois[2]; P. Palmero[3]; J. Chevalier[4]; T. Fuerderer[5]; R. Kohal[6]; H. Reveron[4]

1. Swerea IVF AB, Sweden
2. Anthogyr, France
3. Politecnico di Torino, Italy
4. INSA, France
5. DoCeram, Germany
6. UNIVERSITÄTSKLINIKUM, Germany

Most of the dental implants today are manufactured from yttria stabilized zirconia. These materials are known to be susceptible to aging and to obtain excellent mechanical properties when evaluated using well prepared surfaces. Such a surface is however less suitable for bone anchored implants where a rougher surface is desired in order to enhance osseointergration. Other materials are then needed in order to reduce the sensitivity to aging and the reduction of the strength that can occur due to an increased surface roughness. A solution to avoid these drawbacks was found to be ceria stabilized zirconia composites with alumina and strontium aluminates developed in the EU project LONGLIFE. The addition of fine grained alumina and strontium aluminates contributed to a reduced grain size of the ceria stabilized zirconia. This improved the strength compared to a pure ceria stabilized zirconia and the toughness compared to yttria stabilized zirconia. This allowed a high strength to be maintained even with coarser surface structures. An additional surface modification was also applied that enhanced the bone tissue response. These composites have been further developed within the EU project SISCERA.

10:00 AM

(ICACC-S5-020-2019) Selective Regulation of Brushite Bioceramics by Chiral Biomolecules (Invited)

W. Jiang[1]; H. Moussa[1]; A. Mansour[1]; A. Alsheghri[1]; J. Song[1]; M. McKee[1]; F. Tamimi*[1]

1. McGill University, Canada

In biomineralization, biomolecules are believed to be responsible for the formation and organization of otherwise brittle mineral phases to endow hierarchically organized structures with enhanced mechanical function. Interestingly, these functional biomolecules are homochiral, being composed exclusively of L-amino acids. Here, we show that a chiral form of tartaric acid can selectively improve the mechanical properties of a bone-like bioceramic (calcium-phosphate brushite) by regulating crystal structure. The compressive strength and fracture toughness of brushite bioceramic can be substantially improved by the simple addition of L-(+)-tartaric acid that decreases subunit crystal size, whereas the D-(-)-tartaric acid enantiomer has the opposite effect, reducing its mechanical properties. Characterization from the macro- to atomic-level reveals that this selective regulation is attributable to stereochemical matching between L-(+)-tartaric acid and dynamic chiral steps of brushite, which results in the inhibition of brushite crystallization. These findings provide insight into our understanding of the role of chiral L-biomolecules in biominerals, and provide guidance for the rational fabrication of bioceramics having controlled crystallographic structure providing enhanced mechanical properties.

10:30 AM

(ICACC-S5-021-2019) Enhanced tendon to bone healing by PLLA/CPS composite films prepared by a simple melt-pressing method

C. Ning*[1]; J. Guo[1]; J. Zhao[2]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China
2. Shanghai Jiao Tong University Affiliated Sixth People's Hospital, Department of Sports Medicine, China

The high failure rate of tendon to bone healing after surgery has always been a challenge in rotator cuff repair. Therefore, various biomaterials are developed to repair and regenerate the tendon to bone tissue. Considering the flexibility of PLLA and bioactivity of CPS ceramic, PLLA/CPS composite films were produced by melt-pressing technique and the physicochemical behavior of PLLA/CPS composite films were characterized and the biocompatibility and bioactivity were also investigated in vitro and in vivo. Compared to pure PLLA, PLLA/CPS composite films exhibited a decreased water contact angle, rougher and more positive charge surface. The degradation rate also increased with the increase of CPS content. The cytological evaluation showed that the addition of CPS enhanced the adhesion and proliferation of rBMSCS. The expression of ALP activity, extracellular matrix mineralization and collagen secretion were also improved by the addition of CPS. The in vivo results revealed that the PLLA/CPS composite film had good biocompatibility and biodegradability, which enhanced the formation of an engineered tendon to bone interface by improving the organization of collagen, the formation of cartilage and bone. It revealed that PLLA/CPS composite films would be promising biomaterials for tendon to bone healing.

10:50 AM

(ICACC-S5-022-2019) Development of novel zirconium containing bioactive glass fibers: Physical and mechanical properties

S. Mokhtari*[1]; A. W. Wren[1]

1. Alfred University, Materials Science and Engineering, USA

The primary goal of this study is to develop zirconium containing glass fibers that can be served as high-strength bioactive glass fibers for biomedical applications. A series of zirconium containing glasses were synthesized and incorporated into a SiO_2-CaO-Na_2O-P_2O_5 based glass system. Glass powders were prepared, melted and fibers were drawn from the melt at 1200°C in air. Initial characterization on the starting glass powders and subsequent glass fibers included X-ray diffraction (XRD) to determine the amorphicity/ crystallinity, and differential thermal analysis (DTA) to analyze thermal profile of each glass. To further investigate the effects of zirconium incorporation in the glass structure, X-ray photoelectron spectroscopy (XPS) and magic angle spinning nuclear magnetic (MAS-NMR) were conducted. Mechanical properties of the glass fibers were characterized by analyzing tensile strength (ASTMD3370-75) and flexural strength (ASTMC1161-02C). Ion release profile of the fibers were determined after 1, 10, 100, and 1000 hours incubation in DI water using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES). To evaluate in-vitro bioactivity, simulated body fluid (SBF) testing was conducted on the fibers incubated for 1000 hours, and the chemical and morphological changes were studied using scanning electron microscopy and energy-dispersive X-ray analysis (SEM/EDS).

11:10 AM

(ICACC-S5-023-2019) In Vitro Efficacy of Antimicrobial-releasing Mesoporous Ceramics for Load-bearing Implant Applications

C. D'Haeyer[1]; K. Thevissen[2]; A. Braem*[1]

1. KULeuven, Department of Materials Engineering, Belgium
2. KULeuven, Centre of Microbial and Plant Genetics, Belgium

Rough implant surfaces, used to achieve successful osseointegration, entail a high risk for colonization by microorganisms and subsequent development of biofilm associated infections, thereby burdening both patients and healthcare systems. Implants incorporating and locally releasing anti-infective molecules at their surface in a controlled manner are proposed as a possible antimicrobial strategy. Sol-gel derived mesoporous ceramics, e.g. silica or bioactive glass, are of interest as these materials exhibit tunable pore structures allowing adjusting the diffusion kinetics, and hence the release profile, of drug molecules through the pores. However, coating materials tend to be fragile and cannot be refilled risking premature depletion. Within this context, we developed a mesoporous diffusion barrier inside a high-strength porous Ti structure enabling a sustained drug release from an internal reservoir to the implant surface. A proof-of-concept was established for the continuous release of constant therapeutic concentrations of chlorhexidine, an antimicrobial agent commonly applied in mouthwashes, and this for a prolonged time. Efficacy of the released chlorhexidine against various pathogens was evaluated in a preventive as well as curative setting. We hypothesize that implants made out of such composite materials can take metal-based drug eluting systems to a clinical level.

S10: Ceramics Modeling, Genome and Informatics

Structural Ceramics VII

Room: Coquina Salon G

Session Chairs: Jérôme Roger, University of Bordeaux; Xianming Bai, Virginia Tech

8:30 AM

(ICACC-S10-034-2019) Large-scale DFT study of complex surfaces and interfaces with the CONQUEST code (Invited)

T. Miyazaki*[1]

1. National Institute for Materials Science (NIMS), International Center for Materials Nanoarchitectonics (WPI-MANA), Japan

I will present our density functional theory (DFT) study of complex surfaces and interfaces using our linear-scaling or O(N)code CONQUEST (Concurrent O(N) Quantum Electronic Structure Technique). The code uses local orbitaland O(N) methods, and is very efficient on massively parallel supercomputers. With the code, we can treat very large systems containing more than a million atoms. We can perform robust and accurate electronic structure calculations, including structure relaxations or molecular dynamics. So far, CONQUEST has been used mainly for complex semiconductor surfaces or nano-scale materials, but it can be also applied to ceramics. In the presentation, I will report our recent study of the atomic and electronic structures of Si/Ge core-shell nanowires and discuss the ability of the code. This work is done in collaboration with Dr. J. Lin (NIMS), and Prof. D. R. Bowler (UCL). The development of the CONQUEST code is performed jointly by the groups of University College London (Prof. D. R. Bowler), National Institute for Materials Science (First-principles simulation group), and the University of Bordeaux (Dr. L. Truflandier).

8:55 AM

(ICACC-S10-035-2019) Computationally-Guided Design of Multicomponent Thermal and Environmental Barrier Coatings for Improved Multifunctional Performance (Invited)

D. L. Poerschke*[1]

1. University of Minnesota, Chemical Engineering and Materials Science, USA

The design of next-generation thermal and environmental barrier coatings (T/EBC) seeks to increase the temperature capability and improve the coating resistance to degradation by molten silicate deposits while also maintaining good phase stability, thermal strain tolerance, and resistance to foreign-object damage. Simultaneously achieving each of these design requirements is likely to involve multi-component, multi-layer coating architectures tuned to optimize the properties of the individual constituents and overall coating architecture. A combined computational and experimental framework has been developed to accelerate the design of these new coating systems. The application of these tools will be demonstrated using case studies examining the reactions with RE-silicate EBC materials and RE-zirconate TBC materials, and then the focus will shift to efforts to develop new composite materials in order to precisely tune the coating coefficient of thermal expansion to manage thermal strains while also providing effective resistance to molten silicate attack over a wide range of operating conditions.

9:20 AM

(ICACC-S10-036-2019) Chemical Evolution of Ceramic Interfaces in Nuclear Reactor Environments (Invited)

J. Xi*[1]

1. University of Wisconsin-Madison, Materials Science and Engineering, USA

One of the essential requirements for ceramics in nuclear reactor applications is that they maintain chemical stability under extreme conditions, including exposure to radiation, high temperature, and harsh chemical environments. Properties of ceramic interfaces (e.g., grain boundaries and interphases) are particularly critical in this context because, depending on the circumstances, interfaces can lead to both improvement and degradation of materials performance under extreme conditions of nuclear reactors. In this talk, I will discuss results of theoretical studies of chemical evolution of interfaces in nuclear ceramics. In the first example, I will show predictions based on ab initio calculations of how grain boundaries in ceria (CeO_2) evolve due to segregation and diffusion of radiation-induced defects. In the second example, I will discuss evolution of silicon carbide (SiC) surfaces during corrosion in molten salts. Specifically, I will present ab initiobased thermodynamic model for SiC corrosion and discuss specific mechanisms underlying environmental degradation of this material.

9:45 AM

(ICACC-S10-037-2019) Role of Impurities on the Surface Properties of HfC

J. M. Rimsza*[1]; S. Foiles[1]; W. Mackie[2]; J. Michael[1]; K. Larson[1]

1. Sandia National Laboratories, USA
2. AP Tech, USA

HfC has shown promise as an improved material for field emission due to the low work function of the (100) surface and high melting point resulting in a stable structure in relatively extreme conditions. Under high fields and temperature, unexpected faceting causes increasing work function and failure of the tip, limiting the application space. We investigated the role of stabilized defects and impurities (Ta, N) on the surface properties, including the surface energy and work function, using density functional theory (DFT) simulations to predict which defects or impurities may allow for higher temperature service. Results suggest that impurities which increase the melting point may have minimal impact on the favorable work function, providing a viable pathway for improved surface conditions of HfC for field emission. Sandia National Laboratories

is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2018-9905 A

Structural Ceramics VIII

Room: Coquina Salon G

Session Chairs: Tsuyoshi Miyazaki, National Institute for Materials Science (NIMS); Jianqi Xi, University of Wisconsin-Madison

10:20 AM

(ICACC-S10-038-2019) Ab initio modeling of interfaces and defects in Ni (γ-phase) and Ni_3Al (γ'-phase)

S. San*[1]; W. Ching[1]

1. University of Missouri, Kansas City, Physics and Astronomy, USA

Using first-principles methods based on density functional theory, we explore the structural, electronic and mechanical properties of 7 interface and defect-containing models on Ni-based alloys. The alloy phase of γ(Ni) and γ' (Ni_3Al) are solid solution on FCC lattice. The 6×6×6 supercell models with 864 atoms each are carefully constructed and fully relaxed. We investigate the interface model between γ and γ′, and three models of inclusion of γ′ in γ as precipitate with different volumes. By removing the included γ′ precipitate and then fully relax the models again, we obtain three models with specific voids of different porosity. The electronic structure, partial charge distribution, interatomic bonding and mechanical properties of these 7 models are calculated. The results show that the defect models are more ductile than the pure alloy system. The average charge transfer is from Al to Ni at the interface and inclusion models.

10:40 AM

(ICACC-S10-039-2019) Molecular Dynamics Simulation Study on Synthesis and Characterization of Boron Carbide from Orthocarborane

N. Baishnab*[1]; R. Khadka[1]; P. Rulis[2]; R. Sakidja[1]

1. Missouri State University, Materials Science, USA
2. University of Missouri, Kansas City, Physics and Astronomy, USA

In this study, we modelled the amorphous structures of hydrogenated boron synthesized through a low-temperature deposition processing that utilizes orthocarborane precursors. To model the early stage of the synthesis processes which are initiated by the argon bombardment onto the orthocarborane precursors, we introduced orthocarborane fragments and free radicals into the structure model. We further created artificial chemically active sites within the orthocarboranes by removing some hydrogen atoms from the icosahedral structures so as to elucidate its role in establishing internal structural connections within the amorphous phase. We also modelled the argon bombardment onto an orthocarborane slab and analyzed the amorphorization processes. In addition, the effect of hydrogen content toward densification process and thermo-mechanical properties was assessed with the overarching goal in acquiring the capability to tune in the synthesis parameters such as the deposition temperature and pressure, as well as the chemistry of the precursors available initially. We gratefully acknowledged the financial support from NSF's DMREF grant (No. 1729176) and the DOE's NERSC for the computational support.

11:00 AM

(ICACC-S10-040-2019) The Structure of amorphous hydrogenated boron carbide (a-BC: H) studied using a Hybrid Reverse Monte Carlo algorithm (HRMC)

R. Khadka*[1]; N. Baishnab[1]; G. Opletal[2]; P. Rulis[3]; M. Paquette[3]; N. Oyler[3]; J. Hwang[4]; R. Sakidja[1]

1. Missouri State University, Physics, Astronomy and Material Science, USA
2. CSIRO, Molecular Materials Modelling, Australia
3. University of Missouri, Kansas City, Physics and Astronomy, USA
4. Ohio State University, Material Science and Engineering, USA

In this study, the Hybrid Reverse Monte Carlo (HRMC) technique has been used to explore the multi-stage and multi-constraint modelling with the goal of developing realistic models of amorphous hydrogenated boron carbide (a-BC: H). HRMC incorporates both the experimental and energy based constraints which describe the structure of amorphous solids. The original Stillinger-Weber parameters of a-BC: H that we further developed was used as an energy constraint in this work. The a-BC: H modelled from orthocarborane was used as a source of experimental constraints including Radial Distribution Function (RDF), structure factor (SF), Bond Types, Coordination Environments and Bond Angle Distribution to guide the initial configurations and simulations. The total energy and weighted error functions that incorporate these constraints were used as a basis to measure the quality of the structural model. The outcomes matched well with a reasonable accuracy. Also, we would like to acknowledge the support from NSF's DMREF grant (No. 1729176) and DOE's NERSC computational support.

11:20 AM

(ICACC-S10-041-2019) Generation of a classical interatomic potential for boron and its application to amorphous molecular solids containing boron icosahedra

P. Khanal*[1]; P. Rulis[1]

1. University of Missouri, Kansas City, Physics and Astronomy, USA

Various hard and super hard boron based ceramics are intensely studied due to their importance in modern science and technology. Boron exists in a wide variety of complex isomorphic forms, approximately 16 allotropes have been reported so far. Almost all known structures of boron contain icosahedral B_{12} clusters with metallic like three-center bonds within the icosahedra and covalent two- and three-center bonds between the icosahedra. The amorphous form of boron contains regular boron icosahedral (B_{12}) units that are randomly bonded to each other without long range order. In this presentation, I will discuss efforts to use density-functional-theory-based ab initio molecular dynamics (MD) simulations and the force matching method to generate a classical interatomic potential for modeling boron. Bond lengths, the bulk modulus, lattice constants, and the cohesive energy calculations as compared to values in the existing literature are used to illustrate verification of the classical potential. Application of the potential to the modeling of amorphous boron will be shown. The developed classical potential parameters for boron will be used as a guide to generate classical potential for boron based molecular solids such as boron carbide and amorphous hydrogenated boron carbide (a-B:CH). Those prospects will also be discussed.

Author Index

*** Denotes Presenter**

A

Abdi, F. 20, 182
Abdulrahman, M. 51, 97
Abe, M. 188
Abel, J. 91, 154
Abernathy, H. 99, 100, 124, 184
Abrahams, I. 146
Abu Al-Rub, R. 198
Abu Aldam, S.* 115
Acchar, W.* 165
Adamczyk, E. 132
Adams, M. 22
Adelung, R. 51
Adhikari, S. 97
Adlung, M.* 97
Adnan, A. 181
Adolfsson, E.* 39, 219
Agarwal, A. 145
Aghajanian, M. 67
Ahmad, J. 182
Ahmann, M.* 51, 97
Ahmed, S. 17, 180
Ahmed, S.* 115
Ahuja, R.* 143
Aimi, A. 143
Aizawa, M. 188
Akdogan, E. 74
Akhtar, F.* 171, 200
Akimoto, H.* 105
Akimoto, J. 191
Akimoto, M. 83
Akira, I. 107
Akram, M. 117
Akram, M.* 164
Akurati, S. 96
Akurati, S.* 17
Akyildiz, H. 195
Al-Chaar, G.* 214
Al-Ketan, O. 198
Al-Mashhadani, M.* 158
Al-Natsheh, A. 212
Alazzawi, M. K. 154
Alazzawi, M. K.* 154
Alex, A. 94
Alkan, B.* 167
Allan, S. M.* 154, 156
Allen, A. J.* 154
Almansour, A. S. 162, 217
Almansour, A. S.* 218
Almasy, L. 170
Alshaya, M. 51, 97
Alsheghri, A. 219
Altintas, Z. 109
Altun, A. 39
Amada, H. 87
Amaral, L. B. 108
Amorós, J. 91, 124
An, H. 82
An, H.* 64
Anazawa, T. 87
Andersen, K. 31
Andes, K.* 129
Ando, A.* 111
Ando, T.* 166
Ang, C. K. 35, 84, 149, 150
Ang, C. K.* 35, 81
Angeltveit, M. 185
Anna Karla, F. 165
Ansar, A. 63
Aoki, A. 138
Aoki, T. 19, 57, 58, 59, 178, 181
Aoki, T.* 59
Aoki, Y. 21
Aphale, A. 65, 127
Aphale, A.* 16
Apostolov, Z. D.* 139
Appleby, M. P.* 182
Arai, N. 199
Arai, N.* 201
Arai, Y.* 21, 60
Aratani, S. 75
Armand, M. 70
Armstrong, B. L.* 156
Arroyave, R. 32, 148, 149, 173, 209
Asai, K. 37, 104
Asaka, T. 43
Asakura, Y. 57, 181
Ashcroft, I. 91, 155
Ashida, Y. 137
Ashitaka, K. 75
Askin, C.* 106
Asthana, R. 139
Asumani, O. 163
Ates, O. S. 106, 167
Ates, O. S.* 105
Athanasiou, C. E.* 20
Atsumi, R. 127
Avci, A. 106
Avci, M. 105
Awasthi, A. 69, 144
Awasthi, A.* 69, 101
Aydelotte, B.* 24
Azina, C.* 149

B

Baba, S.* 138
Baba, T. 20
Bäcke, O. 52
Backman, L. 146
Backman, L.* 147
Bae, K.* 186
Baek, Y. 58
Bahri, M. 114
Bai, H.* 175
Bai, X.* 204
Bai, Y. 98
Bail, C. 33
Bailey, T. 193
Baishnab, N. 145, 221
Baishnab, N.* 221
Bakan, E. 60
Baker, B. A.* 173
Baker, C. R. 67
Balani, K. 165
Balaya, P.* 135
Balazsi, C. 98, 170
Balazsi, C.* 74, 170, 176
Balazsi, K. 74, 170, 176
Balazsi, K.* 16, 98, 170
Balci, O.* 109
Baldwin, L. 139, 140
Ballikaya, S.* 193
Balooch, M. 34, 211
Banda, M. 96, 101
Banda, M.* 17
Banerjee, D. 96
Banerjee, S. 115, 180
Banerjee, S.* 17
Bangash, M. 117
Bansal, N. P. 18, 49
Bao, J. 94, 160, 210
Barbosa, M. 215
Barnett, S. 128, 191
Barone, G. 213
Barroso, G. 123
Barsoum, M. 82
Barsoum, M.* 81
Barvitskyi, P. 25
Bassiri-Gharb, N.* 214
Basu, B. 165
Bateman, O. 201
Baumgart, H. 196
Bavdekar, S. 101
Bawane, K. K.* 153
Beersaerts, G.* 213
Begley, M. 18
Behler, K. D. 68, 103, 172
Behler, K. D.* 102, 132
Beidaghi, M.* 82
Belko, S. 16, 65
Belleville, P. 40
Ben Zine, H. 170
Benavides, J. A. 96
Benavides, J. A.* 161
Benchakar, M.* 210
Benetti, D. 216
Benetti, D.* 41, 49
Benito, P. 200
Bennesky, K. 81
Berens, S. 121
Beretta, A. 93, 107
Bergonzoni, M. 107
Bermejo, R. 183
Bermejo, R.* 174, 183
Bernard, S. 43, 114
Bernard, S.* 54, 141
Bernardo, E.* 28, 115, 117, 189
Berneschi, S. 161
Bernik, S.* 27
Bernstein, A. 187
Berrigan, J. D. 140
Berthelot, R.* 133
Betke, U.* 141
Bettotti, P. 114
Beyene, A. 192
Beyoglu, B. 154
Beyoglu, B.* 154
Bhattacharjee, A.* 128
Bhave, C. 86
Bialuschewski, D. 48, 193
Bialuschewski, D.* 97
Bianchi, G. 39
Bianchi, G.* 57
Bicer, H. 74
Bieler, T. R. 63
Biesuz, M. 114
Biggemann, J. 199
Bigotta, S. 28
Binner, J. 76, 79, 173, 207
Blackburn, S. 108
Blair, V. L.* 104
Blake, D. W. 158
Blake, D. W.* 158
Blangero, M. 72
Blasco, E. 91, 124
Bliem, P. 32
Blum, M. H.* 123
Boakye, E. E.* 56
Boccaccini, A. R. 112
Bodis, E.* 110
Boehmler, J. 28, 132
Boesl, B. 145
Boiko, V. 108

Boman, M.* 52
Bomze, D. 188
Bonini, N. 146
Bonnett, J. F. 185
Borgato, L. 36
Borgna, A. 90
Borman, T. M. 122, 147
Borman, T. M.* 146
Bortolotti, M. 114
Bosch, R. 33
Bose, S.* 47
Boussmen, M. 113
Bouville, F. 175
Bouville, F.* 174
Bouzidi, S. S.* 42
Boyle, T. J. 152
Braem, A. 109
Braem, A.* 220
Braginsky, M. V. 218
Brar, H. 17
Braun, J. L. 146
Brecher, C. 37
Brede, T. 48, 193
Brennan, R. E. 131
Brenner, A.* 80, 206
Brenner, D. 122, 146, 147
Brewster, G. 60
Briggs, S. A. 152
Brinckmann, S. A.* 40
Brisse, A. 127
Bristow, W. 210
Britt, D. 107
Brodnik, N. R.* 153
Brown, N. 86
Brown, N. R. 211
Brown, N. R.* 151
Brueck, B. 120
Buchmeiser, M. R. 119, 120
Buffolo, M. 36
Bui, P. P. 40
Burke, P.* 22
Burmistrov, I. 109
Burns, J. 86
Byung-Koog, J. 76

C

Cabana, J.* 72
Cabelguen, P. 72
Cabioch, T.* 33
Caglar, M. 166
Cai, A. 184
Caliari, F. R.* 133
Callaway, E. B.* 57
Campostrini, R. 114
Canaff, C. 210
Canfield, N. L. 99, 126, 185
Cannizza, E. 180
Cano, F. 85
Cao, M. 167
Caouette-Fritsch, H.* 122
Capobianco, J. A.* 43
Carlier, D. 72
Carlin, C. 203
Carmen, V. 168
Carmen, V.* 194
Carney, C. 208
Carpenter, D. 149
Carr, P. 96
Carrasco, J. 70
Casalegno, V. 117, 162, 164
Casalegno, V.* 84
Casas-Cabanas, M.* 70
Caspi, E. 33
Castle, E. 172
Castle, E.* 146
Celerier, H. 58, 212
Celerier, H.* 212
Celerier, S. 210
Celik, A. M. 102
Celik, A. M.* 102
Celik, I. B. 99
Cerrone, A. 120, 121
Cerrone, A.* 120
Cervesato, A. 93
Ceynowa, F. 51
Cha, C. 142
Chadha, V.* 214
Chaker, M.* 160
Chang, C. 22, 73, 89, 100
Chang, C.* 66
Chang, S. 206
Chapman, K. 72
Chaput, C. 63
Charalambous, H. 131
Charalambous, H.* 64, 105, 180
Chartier, D. 37
Chartier, P. 32, 33, 210
Chartier, T. 153
Chase, G. G. 19
Chauhan, P. K.* 201
Cheenady, A.* 69
Chen, C. 26, 134
Chen, J. 50, 81
Chen, J.* 72, 89
Chen, K. 134, 146
Chen, K.* 62
Chen, Q. 171
Chen, S. 156
Chen, X. 32, 86, 218
Chen, X.* 138
Chen, Y. 60, 124
Chen, Y.* 32
Cheng, L. 206
Cheng, T. 51
Cheng, Y. 22, 99
Cheng, Z.* 146, 187, 206
Chern Lin, J. 103
Chern Lin, J.* 79
Chernova, N. 72
Chevalier, J. 219
Chevalier, J.* 117
Chi, M.* 26
Ching, W. 221
Ching, W.* 148, 202
Chiou, S. 79
Chiu, Y. 55
Chmielarz, A. 142, 199
Cho, J.* 166
Cho, Y. 99
Choe, K. 78
Choi, H. 30, 186
Choi, H.* 31, 55, 195
Choi, J. 78, 126
Choi, S. 186
Choi, S. R. 182
Chou, S. 159
Chou, W. 73
Chou, Y.* 126, 185
Christensen, M. 197
Christian, K. H. 64
Christiansen, S.* 53
Chu, I. 72
Chua, D.* 137, 160
Chuang, W. 103
Chung, S.* 73
Cicchetti, N. 37
Cil, M.* 128
Cima, M.* 15
Cinbiz, M. N.* 211
Cinibulk, M. 56, 76, 139, 140, 208
Ciurans Oset, M. 200
Clauss, B. 120
Clegg, W. 209
Clemens, F. 90
Cloutier, S. G. 42, 96
Coati, A. 54
Cohen, S.* 37
Coleman, S. P. 203
Collier, V.* 18
Colombo, P. 72, 90, 93, 107, 153, 157, 199
Colombo, P.* 90, 142
Colorado, H.* 114, 115, 157
Colusso, E.* 216
Concina, I.* 160
Condorelli, G. G. 53
Conner, M. 150
Connor, P. 125
Constantin, L. 147
Cook, W. 122
Cooley, N. 185
Cooper, R. C. 121
Cooper, V. R.* 143
Cordero, Z. C.* 93
Cormier, J. 32
Corwin, C. 185
Costa, G.* 18
Costakis, W. J. 68, 107
Costakis, W. J.* 68
Courtois, N. 219
Coyle, C. A. 99
Coyle, T. W. 122, 123
Craft, N. 80
Cramer, C. L.* 129
Crawshaw, C. 63
Cronauer, D. C. 185
Csanadi, T. 146
Cuccato, R. 72
Cui, B. 147
Cui, B.* 102
Currie, B. J. 19
Curtarolo, S. 146
Cvetnić, M. 110
Cysewska, K. 167
Czerniak, L.* 150
Czympiel, L. 54

D

D'Angio, A. 76
D'Haeyer, C. 220
D'Haeyer, C.* 109
D'Isanto, F. 84
D'Isanto, F.* 134
Dai, F. 82
Dai, Z.* 108
Daigle, S. 122, 146
Daiko, Y. 43
Dalton, M. 139, 140
Daly, S. 217
Dambournet, D.* 134
Damodaran, V. 19
Dasan, A. 189
Datsiou, K. C. 91
Datsiou, K.* 155
Davis, J. R. 158
Davy, C. 156
de Beauvoir, T. H. 46
De Guire, M. R. 184
De La Pierre, S. 117
De La Pierre, S.* 64

Author Index

De Santi, C. . . . 36
Debellis, D. . . . 165
Deck, C. . . . 83, 84, 86, 150, 151, 174, 211
Deguchi, M. . . . 138
Deijkers, J.* . . . 61
Deka, B. K. . . . 163
Delaire, O.* . . . 70
Delmas, C. . . . 72
Delorme, F.* . . . 26
Delville, R. . . . 33
Demirel, R. . . . 136
Demkowicz, P. A.* . . . 34
Dendooven, J. . . . 54
Deng, C.* . . . 184
Deng, L. . . . 102
Deng, Y. . . . 200
Deng, Y.* . . . 118
Destino, J. . . . 129
Detavernier, C. . . . 54
Detwiler, K.* . . . 19
Devaraj, A. . . . 99
DeVries, L. K. . . . 58
DeVries, M. . . . 25, 69
DeVries, M.* . . . 69
Dey, M. . . . 18, 49, 115, 178
Dey, M.* . . . 149
Diao, C. . . . 167
Diau, E. . . . 41
Díaz Lagos, M. . . . 157
Dibiase, R. . . . 121
Dickerson, M. B. . . . 140
Dickerson, M. B.* . . . 139, 156
Dickey, E. C.* . . . 112
Diener, S. . . . 90, 92
Diepold, B. . . . 199
Dieraert, A.* . . . 40
DiGiovanni, A. A. . . . 67, 103
DiGiovanni, A. A.* . . . 66, 101
Ding, D. . . . 65, 186
Ding, D.* . . . 166
Ding, H.* . . . 186
Dixit, M. . . . 135, 209
Dlouhý, I. . . . 162
Do, T. . . . 30, 73
Do, T.* . . . 29
Do, V. . . . 29
Doeff, M.* . . . 71
Dogdibegovic, E. . . . 127
Dokko, K. . . . 191
Domnich, V. . . . 25, 67, 68, 102
Dong, D. V. . . . 73
Dong, Z. . . . 166
Donnelly, P. E. . . . 152
Doodran, K. S. . . . 168
Dorner, A. N.* . . . 80
Dougherty, P. R.* . . . 96
Dourges, M. . . . 204
Doyle, P. J. . . . 84, 149
Doyle, P. J.* . . . 84
Dravid, V. P.* . . . 46
Drouelle, E. . . . 32
Du, W. . . . 93
Dub, S. . . . 25
Dubois, S. . . . 32
Dubroca, B. . . . 202
Duclère, J. . . . 43
Dudukovic, N. . . . 129
Duffiet, M.* . . . 72
Dunn, D. . . . 120, 121, 182
Dunn, J. S. . . . 102
Dunn, J. S.* . . . 103, 172
Dunn, R. . . . 130
Duong, T. . . . 32, 148, 149, 173
Duong, T.* . . . 209
Durygin, A. . . . 206
Dusza, J. . . . 110, 146
Dylla-Spears, R. J.* . . . 129

E

Ebisu, Y. . . . 169
Eckel, Z. C. . . . 40
Edano, A. . . . 75
Edmondson, P. . . . 152
Edmondson, P.* . . . 152
Edwards, D. J. . . . 99
Eftekharian, A. . . . 20, 182
Egorov, I. . . . 122
Ek, M.* . . . 48
Eklund, P. . . . 82, 149
Eklund, P.* . . . 71, 142
El Yagoubi, J. . . . 203
Elangovan, S.* . . . 22
Eldridge, J. I.* . . . 61
Ellis, G. . . . 178
Ellis, G.* . . . 18
Elsayed, H. . . . 28, 117, 142, 189
Emdadi, A.* . . . 203
Enrichi, F.* . . . 44, 194
Epifani, M.* . . . 159, 195
Erb, D. . . . 116
Erdemir, A. . . . 78
Ersen, O. . . . 114
Eryilmaz, O. . . . 78
Espinoza Perez, L. J. . . . 85
Espinoza Perez, L. J.* . . . 173
Esposito, V. . . . 63
Esquivel, S. . . . 85
Esslinger, S.* . . . 187
Este, A.* . . . 203
Etzold, A. M. . . . 68
Evans, G. . . . 67
Evans, P. . . . 150
Evans, S. . . . 176, 177
Ezugwu, S. . . . 179

F

Faber, K. . . . 153, 200, 201
Faber, K.* . . . 199
Fahrenholtz, W. . . . 80, 81, 83, 85, 145, 146, 149, 151, 172, 202, 203
Fahrenholtz, W.* . . . 115
Failla, S.* . . . 131
Fan, X. . . . 97, 141
Fan, X.* . . . 124
Fan, Y.* . . . 124
Fanchini, G.* . . . 161, 179
Fang, H. . . . 160
Fears, T. . . . 129
Feldman, B. . . . 23
Fendt, S. . . . 65
Feng, F.* . . . 77
Feng, L.* . . . 145, 172
Ferrari, M. . . . 161
Ferraris, M. . . . 64, 84, 117, 162, 164
Ferraris, M.* . . . 117
Fertig, R. S. . . . 40
Fey, T. . . . 142
Fey, T.* . . . 178, 199
Finklea, H. O. . . . 184
Finocchiaro, C. . . . 213
Fiorese, A.* . . . 29
Firshtman, N.* . . . 130
Fischer, T. . . . 43, 48, 54, 95, 98, 193
Fischer, T.* . . . 53
Flores, O. . . . 114
Florez, R.* . . . 151
Fogarassy, Z. . . . 170
Foiles, S. . . . 220
Folgner, C. . . . 65, 126
Fonseca Alfonso, P. M.* . . . 157
Foroughi, P. . . . 146, 206
Forslund, A. . . . 52
Fortulan, C. A. . . . 196
Fortulan, C. A.* . . . 108
Foschini, C. R. . . . 108
Foschini, C. R.* . . . 196
Fourmont, P. . . . 42
Fradin, C. . . . 206
Frage, N. . . . 37, 130
Franchin, G. . . . 72, 90, 93, 107, 157
Franchin, G.* . . . 90
Franco, A. A.* . . . 70
Francois, J. . . . 147
Frandsen, H. L. . . . 64, 164
Frank, M. . . . 43
Frank, M.* . . . 54
Franke, J. . . . 179
French, C. . . . 37
French, J. . . . 204
Frick, C. . . . 40
Frohnhoven, R. . . . 98
Fu, C. . . . 66, 100
Fu, X. . . . 106
Fu, Z. . . . 16, 28, 74, 176
Fuerderer, T. . . . 219
Fujii, Y. . . . 38
Fujimaki, Y. . . . 127
Fujimoto, K.* . . . 143
Fujimoto, Y. . . . 37, 38, 104
Fujishiro, Y. . . . 127, 191
Fujita, Y. . . . 155
Fukahori, T. . . . 84
Fukuda, K. . . . 104
Fukuzaki, R. . . . 181
Furko, M. . . . 170
Furtat, P. . . . 114
Furuya, M. . . . 188

G

Gabaudan, V. . . . 133
Gadow, R. . . . 76, 123, 187
Gadow, R.* . . . 187
Gagnepain, M.* . . . 132
Gahlot, S. . . . 55
Gaignon, R.* . . . 38
Galceran, M. . . . 70
Gallego, J. E. . . . 173
Galusek, D. . . . 28
Gan, K.* . . . 73
Gao, H. A. . . . 82
Gao, H.* . . . 97
Garces, H. . . . 62
Garcia Granados, E.* . . . 21
Garcia Rocha, V. . . . 177
Garcia Rocha, V.* . . . 176
Garcia, V. . . . 45, 106
Garcia, V.* . . . 107
Garg, A. . . . 49
Garg, A.* . . . 34
Garg, N.* . . . 213
Garner, S. . . . 217
Garnero, C. . . . 210
Garnier, V. . . . 176
Garza, C. T.* . . . 207
Gasparro, C. . . . 150
Gaume, R. M. . . . 37
Gaume, R. M.* . . . 86
Gauthier-Brunet, V.* . . . 32
Ge, L. . . . 185

Gedamu, D. M.* 87
Gehör, S. 212
Geipel, C. 23
Geis, M. 65
Gell, M. 61
Geng, S. M. 92
Gerbaldo, R. 165
Gerdes, K. 124
Gerus, A. 108
Ghaffari, K.* 101
Gharzouni, A. 157, 212
Ghosh, D. 17, 96, 198
Ghosh, D.* 101
Gianchandani, P. 84, 117
Gianchandani, P.* 162
Gild, J. 146
Gildersleeve, E. J. 60
Gildersleeve, E. J.* 61
Giovannelli, F. 26
Giuliani, F. 209
Giuliani, F.* 182
Gjata, K. 80
Glodo, J. 37
Glymond, D. 206
Go, T. 32
Gobbin, F.* 93, 107
Godbole, E.* 121
Godines, C. 20, 182
Goduguchinta, R. K. 34
Gofuku, H. 134
Gokuldoss, P. K. 190
Goldsby, J.* 133
Goller, R.* 75
Golt, M. C. 29, 129
Golt, M. C.* 177
Gomez-Martin, A. 216
Gomez-Martin, A.* 216
Gomez, J. 213
Gonczy, S. T. 163, 210
Gonderman, S. 211
Gonderman, S.* 83
Gondolini, A. 63
Gong, K. 212
Gönüllü, Y. 98
Gonzalez-Julian, J.* 32
Goodridge, R. 91, 155
Gopalan, V.* 111
Gordo, E. 208, 209
Gorican, D. 218
Gorjan, L. 90
Gorton, J. 86
Gorven, A. 218
Gorven, A. J.* 162
Goto, T. 53, 159
Götze, E. 179
Gouma, P.* 47, 189
Grabowski, A. 96
Graffé, M. 83, 179
Graham-Brady, L. 128
Graham, J. 151
Granata, G. 168, 169
Granata, G.* 138
Grant, L. O. 93
Graule, T. 109
Greaves, G. 152
Green, M. J. 82
Greenwood, R. 108
Greil, P. 199
Gremillard, L. 176, 190
Gremillard, L.* 118
Grenier, A. 72
Grilo, J.* 110
Grimm, F. 185
Gronde, B. 59
Grosch, M.* 98
Gross, M. D.* 124
Grosse, M. 33
Gruber, M.* 183
Grunenfelder, L. 175
Gu, J. 120, 196
Guan, B. 186
Guarin-Zapata, N. D. 175
Guarriello, R.* 57
Gucci, F. 134
Guenster, J. 92
Guenster, J.* 89
Guillon, O. 21, 185
Guillon, O.* 65
Guilmeau, E. 27
Guilmeau, E.* 27
Guimbao, J. 63
Guo, J. 46, 219
Guo, L. 165, 189
Guo, X.* 96
Gupta, S. 18, 49, 51, 90, 96, 97, 115, 149
Gupta, S.* 178, 209
Gupta, V. 182
Gurevich, E. L. 97
Gurnani, L.* 58
Gutierrez, C. 118
Guziewski, M.* 203

H

Haber, R. 67, 68, 102, 132, 154, 183
Haber, R. A. 25, 67, 119, 154
Habib, T. 82
Habrioux, A. 210
Hackett, B. 164
Hackett, G. 99, 100, 124, 184
Hadermann, J. 33
Hafen, T. 22
Hagiwara, R. 71
Hahn, Y.* 51
Haile, S. M.* 186
Halbig, M. C. 92, 139, 154
Halbig, M. C.* 45, 92
Halim, J.* 82
Halimi, I. 193
Hall, K. 115, 178
Hall, K.* 90
Halvarsson, M. 52
Hamamoto, K. 191
Hamana, D. 43
Hamao, N.* 191
Hamawandi, B. 193
Han, H.* 30
Han, S. 125, 166
Han, X. 146
Hans, M. 209
Hao, H. 167
Hara, T. 21
Harada, S. 89
Harboe, S. J.* 185
Harder, B. J. 18, 20, 49, 218
Harder, B. J.* 21
Hardy, J. S.* 99
Harmer, M. P. 68, 102, 103, 132, 172, 178
Harrington, T. 146
Harris, J. 115
Harrison, G. T. 52
Harrison, S.* 34
Hart, A. 92
Hartvigsen, J. 22
Hase, M. 100
Hasegawa, Y. 139
Hashimoto, A. 137
Hashimoto, M.* 188
Hashimoto, S. 18
Hassani, E. 115
Hatta, H. 21, 60
Hattar, K. 151, 152
Hatzell, K. B. 135, 209
Hatzell, K. B.* 135
Haug, M.* 175
Haugen, A. B.* 31
Hauss, G. 156
Hautcoeur, D.* 153
Hay, R. 56
Hayakawa, H. 101
Hayakawa, T. 43
Hayama, N. 58
Hayama, N.* 59
Hayashi, A. 165, 166
Hayashi, A.* 45
Hazarika, A. 163
He, G. 164
He, G.* 171
He, P.* 157
He, Q. 28
He, T. 186
Heckman, E. 139
Hedgecock, R. 206
Heidenreich, B. 119, 120
Heki, H. 83
Helfinstine, J. 163
Hemker, K. 67
Hemmer, E. 44
Hemmer, E.* 161, 193
Hemrick, J. G.* 47
Hendriksen, P. 116
Heo, E.* 192
Heo, S. 16
Hermanutz, F. 120
Hermida-Merino, D. 54
Hernandez-Rivera, E. 177
Hernández, L. 63
Hernandez, P. 122
Herrera, S. 216
Herrmann, M. 66
Herrmann, M.* 83, 137, 179
Herrmann, S. 65
Hertel, T. 213
Hertz, H. 168
Heuer, A. H. 184
Hidalgo, M. 72
Hielscher, S. 23, 65
Higgs, C. F. 93
Hillebrecht, H.* 131
Hillman, W. 79
Hilmas, A.* 217
Hilmas, G. 80, 81, 83, 85, 145, 149, 151, 172, 202, 203
Hinks, J. A. 148
Hinoki, T. 75
Hinoki, T.* 137
Hirai, S. 136
Hirose, S. 112
Hochenauer, C. 65, 66
Hock, A. S. 185
Hodaj, F.* 140
Hoeppener, R.* 63
Hofer, A. 174
Hogan, J. D.* 24
Hokari, S. 137
Holgate, C. S.* 62
Hollenbach, J.* 29
Homa, J. 39, 188
Honda, S. 43
Hong, H.* 104

Author Index

Hong, J. . . . 16
Hong, S. . . . 208
Hong, W. . . . 22, 79
Hopkins, P. . . . 146, 147
Hopkins, P. E. . . . 122, 146
Hoppius, J. . . . 97
Hor, Y. . . . 172
Horcher, A. C.* . . . 123
Horn, S. . . . 119, 120
Hornés, A. . . . 63
Horvath, A. . . . 170
Hosemann, P. . . . 211
Hoshina, T. . . . 111
Hoshino, T.* . . . 30
Hossain, K. G.* . . . 116
Hossain, M. . . . 122, 146
Hossain, M.* . . . 147
Hosseini, M.* . . . 217
Hotta, Y. . . . 75
Houki, T.* . . . 38
Hreniak, D. . . . 108
Hsieh, P. . . . 55
Hsieh, T. . . . 73
Hsu, N. . . . 22
Hsu, Y.* . . . 55
Hu, B. . . . 16
Hu, B.* . . . 65
Hu, C. . . . 144
Hu, J. . . . 153
Hu, L. . . . 208
Hu, S. . . . 186
Hu, X. . . . 84
Hu, X.* . . . 150
Huang, D. . . . 20
Huang, S. . . . 73, 180
Huang, W. . . . 205
Huang, X.* . . . 210
Huang, Y. . . . 73
Hug, G. A.* . . . 32
Hui, J. . . . 187
Humbs, W.* . . . 56
Humphry-Baker, S. A. . . . 146
Humphry-Baker, S. A.* . . . 19, 85
Hundley, J. M. . . . 40
Hupa, L.* . . . 189
Hurley, R. . . . 128
Hurtado, A. . . . 83, 179
Hussainova, I. . . . 190
Hwang, C. . . . 67, 102, 132, 183
Hwang, C.* . . . 67
Hwang, J. . . . 204, 221
Hwang, K. . . . 127
Hyuga, H. . . . 18

I

Ibn-Mohammed, T. . . . 156
Ideta, S. . . . 147
Idriss, H.* . . . 52
Igawa, K. . . . 75
Iihama, J. . . . 43
Iijima, M. . . . 105, 111, 162, 168
Ikarashi, Y.* . . . 181
Ikeda, T. . . . 89
Ikemoto, M. . . . 33, 147
Imanaka, Y.* . . . 87, 112
Imanishi, N. . . . 166
Imanishi, N.* . . . 26
Ina, T. . . . 104
Inerbaev, T. . . . 109
Ingram, B. J. . . . 185
Inomata, D. . . . 107
Ionescu, E.* . . . 31, 112, 139
Irisawa, T.* . . . 77
Irvine, J. . . . 125
Irvine, J. T. . . . 187
Ishibashi, R.* . . . 84
Ishigaki, T.* . . . 88
Ishikawa, T. . . . 113
Ishikawa, T.* . . . 138
Ishiyama, T. . . . 127
Ishizu, T. . . . 89
Islam, N. . . . 205
Italiano, A. . . . 93, 107
Ito, A.* . . . 21
Ito, T. . . . 33
Ito, T.* . . . 147
Ivanković, H. . . . 110
Ivanković, M. . . . 110
Iwamoto, T. . . . 36
Iwamoto, Y.* . . . 43, 45
Iwasawa, H. . . . 77
Iwasawa, H.* . . . 77
Iwashita, Y. . . . 36
Iwazaki, Y.* . . . 88, 112

J

Jabbari, M. . . . 96, 140
Jacko, R. . . . 150
Jacobs, R.* . . . 184
Jacobsen, G. . . . 83, 150, 210, 211
Jadaan, O. . . . 163
James, C. M.* . . . 27
Jang, B.* . . . 121
Jankowiak, A. . . . 32
Jarman, J. . . . 149
Jarman, J.* . . . 83
Jarockyte, G. . . . 51
Jarvis, L.* . . . 202
Javaid, S. . . . 149, 178
Javaid, S.* . . . 49
Javed, H. . . . 64, 117, 126
Jayaganthan, R. . . . 197
Jenkins, M. G.* . . . 163, 173, 210
Jennings, D.* . . . 186
Jeong, H. . . . 65
Jha, S. K. . . . 64, 105, 180
Jhimi, K. . . . 50
Ji Hwoan, L.* . . . 76
Ji, H. . . . 64, 125
Ji, W. . . . 28
Ji, W.* . . . 16
Ji, Y. . . . 90, 115, 178
Jia, D. . . . 119, 157
Jiang, C. . . . 61, 186
Jiang, L. . . . 62
Jiang, W. . . . 219
Jiménez Martínez, M.* . . . 76
Jimenez-Morales, A. . . . 208, 209
Jin, W. . . . 166
Johansson, E. . . . 39
John, J. E. . . . 17, 101
Johnson, M. A. . . . 129
Jokar, E. . . . 41
Jolly, B. . . . 34, 85
Jolly, B.* . . . 84
Jones, E. L. . . . 18
Jones, E.* . . . 108
Jones, S. . . . 154
Jones, T.* . . . 155
Jordan, E. H. . . . 121
Jordan, E. H.* . . . 61
Jouin, J. . . . 58, 212
Ju, C. . . . 79
Ju, C.* . . . 103
Julian, M. . . . 37
Jun, B.* . . . 121
Jupalli, T. T. . . . 136
Juste, E. . . . 153

K

Kaabouch, N. . . . 49, 96
Kabel, J. . . . 211
Kabel, J.* . . . 211
Kadowaki, K. . . . 188
Kadyrov, A. . . . 122
Kagawa, Y. . . . 21, 60
Kailer, A. . . . 137
Kaiser, A. . . . 116
Kakihana, M. . . . 36, 55
Kalabukhov, S. . . . 37, 130
Kalantar-zadeh, K.* . . . 40
Kalapos, T. . . . 124
Kalapos, T. L. . . . 184
Kalem, V.* . . . 195
Kamboj, N. K.* . . . 190
Kameshima, Y.* . . . 200
Kamhawi, H. . . . 181
Kamiya, R. . . . 18
Kamoshida, K. . . . 75
Kamseu, E. . . . 157
Kanayama, T. . . . 75
Kanazawa, S. . . . 22, 57
Kanazawa, S.* . . . 56
Kandel, B. . . . 94
Kanetaka, H. . . . 188
Kang, C.* . . . 167
Kannan, M. . . . 19, 182, 217
Kao, W. . . . 99
Kaplan, W. D.* . . . 68
Kaps, S. . . . 51
Kapush, D. . . . 18, 51
Kapusuz, D.* . . . 218
Karabanovas, V. . . . 51
Karakaya, C. . . . 186
Karpets, M. . . . 25, 148
Karppinen, M.* . . . 52
Kartuzov, I. . . . 102
Kartuzov, I.* . . . 69
Kartuzov, V.* . . . 102
Kassner, C.* . . . 201
Katcho, N. . . . 70
Kato, A. . . . 75
Kato, H. . . . 55
Kato, M.* . . . 168
Kato, T. . . . 38, 106, 169
Kato, T.* . . . 120, 168
Katoh, Y. . . . 35, 84, 86, 149, 150, 151, 152, 210, 211
Katoh, Y.* . . . 84
Katsiev, K. . . . 52
Katsikis, N. . . . 90
Katsui, H.* . . . 53
Katz, A. . . . 28
Kawabata, Y.* . . . 22
Kawaguchi, N. . . . 37, 104, 105, 106
Kawaguchi, N.* . . . 38, 105, 106
Kawaguchi, T. . . . 136
Kawahara, K. . . . 181
Kawamura, G. . . . 137
Kawanishi, K. . . . 120
Kawasaki, K. . . . 137
Kawashima, N. . . . 60
Kaya, I. . . . 195
Kayali, E. . . . 82
Kayser, M.* . . . 181
Kazemian, S. . . . 179
Keane, P. F.* . . . 158

Keck, C. . . . 199
Kenttämaa, H. . . . 121
Kesim, M. . . . 166
Key, T. . . . 56, 139
Khadka, R. . . . 145, 221
Khadka, R.* . . . 221
Khalifa, H. . . . 83
Khan, A. U. . . . 67, 102, 132
Khan, A. U.* . . . 102
Khanal, P.* . . . 221
Khatami, Z. . . . 161
Khoshsima, S. . . . 109
Kidner, N. J.* . . . 185
Kiebach, R. . . . 116, 164
Kiener, D. . . . 183
Kikuchi, M.* . . . 188
Kilaz, G. . . . 121
Kilczewski, S. . . . 177
Killinger, A. . . . 123, 187
Kim, B. . . . 64
Kim, D. . . . 78, 150, 163, 186, 191, 192
Kim, D.* . . . 79, 97, 191, 192
Kim, G. . . . 167
Kim, H. . . . 21, 64, 121, 125, 127
Kim, H.* . . . 108
Kim, J. . . . 58, 166, 192, 208
Kim, M. . . . 104, 127
Kim, M.* . . . 78
Kim, S. . . . 121
Kim, S.* . . . 21
Kim, T. . . . 79
Kim, W.* . . . 150
Kim, Y. . . . 35, 76, 169, 171
Kim, Y.* . . . 35, 76, 103, 169, 171
Kimura, H.* . . . 106
Kimura, S.* . . . 172
Kimura, T. . . . 199
Kimura, T.* . . . 87
Kinemuchi, Y. . . . 70
King, D. . . . 83
King, D.* . . . 149, 208
King, M. K.* . . . 48, 96
Kirihara, S. . . . 38
Kirihara, S.* . . . 155
Kisailus, D. . . . 175
Kisailus, D.* . . . 175, 216
Kiser, J. D. . . . 162, 217, 218
Kishimoto, H. . . . 139
Kishimoto, H.* . . . 127
Kitajou, A. . . . 71
Kitamura, R. . . . 59, 178
Kitanaka, Y. . . . 106
Kitaoka, S. . . . 60, 188
Klemm, H. . . . 39, 56, 91
Klemm, H.* . . . 59, 91
Kobayashi, H.* . . . 191
Kobayashi, M.* . . . 55
Kobayashi, S. . . . 77, 170
Koch, B. . . . 24
Koch, D. . . . 60, 118, 120, 182, 208
Koch, D.* . . . 118, 119
Kocic, L. . . . 170
Koerner, H. . . . 139, 140
Koh, L. . . . 156
Kohal, R. . . . 219
Koindikar, P. . . . 67
Kolesnikov, E. . . . 109
Kolozsvári, S. . . . 209
Kondo, N. . . . 53
Kondo, T. . . . 84, 162
Kondo, Y. . . . 71
Konusov, F. . . . 122
Koparal, A. . . . 136
Korklan, N.* . . . 172
Kornecki, M. . . . 131
Kornfield, J. A. . . . 201
Kos, S.* . . . 78
Koshimizu, M. . . . 106
Koshimizu, M.* . . . 37, 104
Kosin, M. . . . 119
Koval, M. . . . 62
Kowalski, B. . . . 21
Koyanagi, T. . . . 83, 84, 149, 150, 151, 152, 211
Koyanagi, T.* . . . 151
Kozuma, M. . . . 89
Kraleva, I. . . . 183
Krause, A. R.* . . . 178
Kravchenko, O.* . . . 198
Kraxner, J. . . . 28
Krenkel, W. . . . 123, 164
Krenkel, W.* . . . 116
Krieg, P. . . . 187
Krill, C. . . . 178
Kriven, W. M. . . . 51, 158, 159, 213, 214
Krogstad, J. A. . . . 119, 151, 152
Krüger, M. . . . 180
Ku, N. . . . 90, 129
Ku, N.* . . . 130
Kubo, K. . . . 70
Kubo, M. . . . 171, 172, 203
Kubushiro, K. . . . 22, 56
Kubushiro, K.* . . . 57
Küçük, O. . . . 195
Kudo, I. . . . 30, 169
Kuetemeyer, M. . . . 118
Kujala, K. . . . 212
Kumar, R. . . . 61
Kumar, R.* . . . 54
Kumar, U. . . . 58
Kumari, N. . . . 34
Kunz, W. . . . 59
Kunze, S. . . . 137
Kunze, S.* . . . 66
Künzel, R. . . . 107
Kuo, C. . . . 199
Kuo, C.* . . . 200
Kuo, H.* . . . 99
Kuo, M. . . . 55
Kuoppala, A. . . . 212
Kuranari, K. . . . 203
Kurosaki, T. . . . 197
Kusnezoff, M. . . . 65
Kusnezoff, M.* . . . 126
Kuwabata, S. . . . 134
Kuwik, B. . . . 163, 164
Kuznetsov, D. . . . 109

L

La, M. . . . 78
Labonnote-Weber, S.* . . . 185, 197
Lafdi, K. . . . 56
Lagny, M. . . . 28
Lahoda, E. J. . . . 150
Lai, K. . . . 125
Lai, T. . . . 55
Lale, A. . . . 54
Lambertin, D.* . . . 156
Lambrinou, K. . . . 33
Lambrinou, K.* . . . 148
Lamnini, S. . . . 170
Lancellotti, I. . . . 213
Landi, E. . . . 159, 200
Lange, A. . . . 129
Lapauw, T. . . . 33, 148
Laredo, B. B. . . . 17, 101
Larsen, D. . . . 22
Larson, K. . . . 220
Larsson, H. . . . 52
Larsson, J. . . . 168
Larsson, T. . . . 52
LaSalvia, J. . . . 25, 68, 102, 103, 132, 172
LaSalvia, J.* . . . 103
Laviano, F. . . . 165
Lay, R. T. . . . 180
Lazovic, G. . . . 170, 197
Le Meillour, G. . . . 63
Le Petitcorps, Y. . . . 204
Le, D. T.* . . . 169
Leal-Quiros, E. . . . 17
Leduc, J. . . . 95
Leduc, J.* . . . 43
Lee, B. . . . 26
Lee, D.* . . . 31
Lee, G. . . . 130
Lee, H. . . . 21, 64, 78, 120, 133, 150, 192
Lee, H.* . . . 78
Lee, J. . . . 64, 79, 125
Lee, K. . . . 21, 103, 218
Lee, K. N. . . . 18
Lee, K. N.* . . . 20
Lee, M. J. . . . 26
Lee, R. . . . 22, 66, 99, 100
Lee, S. . . . 21, 35, 100, 124, 159
Lee, S.* . . . 26, 120, 123, 208
Lefevere, J. . . . 90
Leguillon, D. . . . 183
Lei, C.* . . . 135
Lei, Y.* . . . 33
Leitner, A. . . . 183
Lemonnier, S. . . . 28, 132
Lences, Z.* . . . 36
Leonard, H. S. . . . 92
Leonard, H. S.* . . . 92
Leonelli, C.* . . . 213
Leriche, A. L. . . . 132
Leriche, A. L.* . . . 28
Levassort, F. . . . 31
Levi, C. G. . . . 62
Levraut, B. . . . 32
Li, B. . . . 46
Li, C. . . . 79
Li, D. . . . 69
Li, G. . . . 27
Li, J. . . . 164, 171
Li, L.* . . . 181
Li, M. . . . 153
Li, M.* . . . 196
Li, T. . . . 166
Li, W. . . . 86, 100
Li, W.* . . . 186
Li, X. . . . 72
Li, Y. . . . 143, 194, 196
Li, Y.* . . . 138, 168
Li, Z. . . . 196
Lian, J. . . . 86
Lieftink, D. . . . 63
Lienenklaus, S. . . . 93
Liensdorf, T. . . . 116
Ligda, J.* . . . 25
Liliedahl, D.* . . . 142
Lim, K. . . . 35
Lim, M. . . . 122
Lima, P. . . . 92
Lin, C. . . . 79
Lin, F. . . . 94
Lin, F.* . . . 160
Lin, P.* . . . 194
Lin, T. . . . 22, 89, 99
Lin, Y. . . . 72

Lippmann, W. 83, 179
Lis, J.* 15
Litke, A. 63
Liu, C. 99
Liu, C.* 22
Liu, H.* 167
Liu, J. 100, 218
Liu, J.* 73, 184
Liu, L. 210
Liu, N. 193
Liu, Q. 128, 196
Liu, T. 26
Liu, X. 100, 186
Liu, Z. 74
Llanos, G. 39
Lo, C. 24
Loganathan, A. 145
Longato, A. 36
Longo, E. 196
Lopez-Ferber, D. 54
Lopez-Honorato, E. 167, 173
Lopez-Honorato, E.* 85, 122, 195
López, O. 58
Lor, J. 180
Lorgouilloux, Y. 28, 132
Lowden, R. A. 129
Lu, B. 60
Lu, C. 151
Lu, J. 82
Lu, K. 153
Lu, K.* 116
Lu, N.* 164
Lu, R. 150
Lu, Y. 73, 102, 147
Luan, X.* 206
Lüchtenborg, J. 92
Lundberg, P. 23
Luo, J. 29
Luo, J.* 144, 146
Luo, Y.* 205
Lupan, O. 51
Lupetin, P. 185
Lutkenhaus, J. L. 82
Lyons, J. 122, 150
Lyons, J.* 209

M

Ma, C.* 93
Ma, F. 210
Ma, L. 186
Ma, R. 116
Ma, Y. 63
Macairan, J. 94
Macedo, D. 110
MacGregor, M. 122
Mack, D. 32
Mackey, J. 181
Mackie, W. 220
Madden, N. J.* 151, 152
Maeda, M. 71
Magnuson, M.* 147, 205
Mahapatra, M. 48, 96
Mahapatra, M.* 117
Maher, I.* 119
Maillé, L. 204
Maillet, E. 120, 121, 182
Maillet, E.* 120, 182
Malandrino, G.* 53, 95
Mallick, S. 89
Mallik, P. K.* 89, 165
Malzbender, J. 64, 180
Manabe, T. 87
Mancillas, S.* 167
Manna, L. 84
Mansour, A. 219
Mansour, R. 182
Manthiram, A.* 125
Maria, J. 122, 146, 147
Marin, R. 193
Marin, R.* 44
Marina, O. 65
Marinkovic, B. 104
Markel, I. J. 144
Markowska, M. 108
Maroni, V. 185
Marques, A. d.* 107, 168
Marques, F. 110
Marshal, A. 33
Marshall, A.* 164
Marsico, C. A. 129, 130
Marsico, C. A.* 90
Martens, P. 63
Martin, E. 183, 203
Martinez-Fernandez, J. 216
Martins, J. P. 60
Martucci, A. 216
Martucci, A.* 36, 41
Maruyama, H. 31
Maruyama, H.* 64
Maruyama, S. 143
Marvel, C. 102, 103, 132, 172
Marvel, C. J.* 16
Marvel, C.* 68
Marzouki, A.* 99
Masai, H.* 36, 104
Mascher, P.* 161
Mason, J. H.* 99
Masuzawa, N.* 165
Mathivet, V. 212
Mathivet, V.* 58, 212
Mathur, S. 43, 48, 53, 54, 97, 98, 193
Mathur, S.* 42, 95
Matouk, Z. 160
Matsuda, A. 137
Matsuda, Y. 166
Matsudaira, T. 60
Matsumoto, H. 134
Matsumoto, K. 71
Matsumoto, Y. 29
Matsunaga, K.* 145
Matsuzaki, T. 89
Matsuzaki, Y. 22
Matthey, B. 66, 137
Mattner, A. 93
Matzke, C. 90, 178
Mauchamp, V. 210
Mauer, G. 32
Mazin Latini, R. 107, 168
Mazo, A. 114
Mazzoleni, P. 213
McAllister, M. 184
McCleeary, D. 210
Mcclellan, K. 142
McCormack, S. J.* 51
McIntyre, R. 60
McKee, M. 219
McKittrick, J. 217
McMeeking, R. M. 18
McMurray, J. W. 34
Mechnich, P.* 62
Medri, V. 159
Medri, V.* 200
Medvecka, V. 110
Medvedovski, E.* 28, 122
Megel, S. 23, 65
Meisel, C.* 107
Mellac, S. 32
Meneghini, M. 36
Menendez, G. 176
Menendez, G.* 177
Menzler, N. H. 65, 185
Mera, G. 112
Mera, G.* 113
Mercadelli, E. 63
Meredith, C. 155, 182
Messing, G. L. 174
Meyer, P. 120, 121
Meyers, M. A. 129
Mhin, S. 30
Mhin, S.* 30
Miao, G. 93
Miao, X.* 64
Michael, J. 220
Michaelis, A. 39, 56, 65, 66, 91, 126, 154
Michaelis, A.* 155
Michaud, P. 153
Michielsen, B. 90
Middelkoop, V. 90
Miele, P. 113
Mikami, M.* 70
Miles, A. 51, 97
Milisavljevic, I.* 38
Miller, D. 187
Min, G. 176, 177
Minagawa, M. 169
Minagawa, M.* 169
Minelli, M. 200
Mineshige, A. 101
Minhas, A. 51, 97
Minjauw, M. 54
Minor, S. 18
Mintken, M. 51
Miola, M. 165
Mir, A. 152
Mishra, S.* 55
Mishra, Y. K. 98
Mishra, Y. K.* 51
Misture, S. T.* 40, 133
Mitic, V.* 170, 197
Mitsuhashi, K. 169
Mittmann, F. 23
Miwa, N. 75
Miyake, M. 200
Miyashita, K. 96
Miyayama, M. 106
Miyazaki, H. 70
Miyazaki, N. 171, 172
Miyazaki, T. 104
Miyazaki, T.* 220
Mizoguchi, T. 104
Mochalin, V. N.* 82
Moellmann, A. 48, 193
Mogilevsky, P. 56
Mohd Pauzi, M. B. 75
Mohrbacher, H. 180
Mokhtari, S.* 219
Molin, S. 126
Molin, S.* 126, 167
Momai, M. 101
Monconduit, L. 133
Mondin, N. 90
Montesi, M. 175
Monteverde, F. 207
Montinaro, D.* 23
Moon, E. 82
Moon, K. 78
Moon, K.* 78
Morais, C. 210
Morata, A. 63

More, V.* . . . 108
Morel, S. . . . 203
Moreno, A.* . . . 91, 124
Morgan, B.* . . . 192
Morgan, D. . . . 184
Mori, D. . . . 26
Mori, D.* . . . 166
Mori, S. . . . 139
Morikawa, R.* . . . 100
Morinvil, A. . . . 51
Morisset, S. . . . 210
Moritz, T. . . . 39, 91
Moriya, K. . . . 75
Moriyama, K. . . . 188
Morscher, G. N. . . . 19, 20, 162, 182, 217
Morscher, G. N.* . . . 217
Moscinski, M. . . . 120
Moscinski, M.* . . . 120, 121
Moshchil, V. . . . 25, 148
Moshe, R. . . . 68
Mostaghimi, J. . . . 123
Motz, G. . . . 123
Motz, G.* . . . 114
Moussa, H. . . . 219
Mráz, S. . . . 209
Muccillo, E. N.* . . . 99
Mudra, E. . . . 110
Muecke, R. . . . 60
Mueller, K.* . . . 80
Mueller, W. E. . . . 27
Mueller, W. M.* . . . 120
Mühler, T. . . . 92
Muhoza, S. P. . . . 124
Mukasyan, A.* . . . 74
Mukherjee, S. . . . 72
Mukhopadhyay, A. . . . 58
Muller Costa, I. . . . 104
Multari, C.* . . . 165
Muntifering, B. R. . . . 152
Murakami, H. . . . 170
Muratov, V. . . . 25
Murgia, F. . . . 133
Murillo Alarcón, R.* . . . 213
Murillo Ruiz, E. . . . 157
Muroya, Y. . . . 37, 104
Murugesu, M. . . . 44
Musil, J. . . . 78, 122
Muto, H. . . . 137
Muto, S. . . . 120, 188

N

Nabat Al-Ajrash, S.* . . . 56
Naccache, R.* . . . 94
Nagai, K.* . . . 171
Nagao, N. . . . 77
Nagata, Y.* . . . 169
Naikade, M. K.* . . . 109
Naim Katea, S.* . . . 193
Nait-Ali, B. . . . 157
Nakajima, T. . . . 89
Nakamura, T. . . . 22, 56, 57
Nakano, H. . . . 162
Nakashima, Y.* . . . 18
Nakatake, M. . . . 147
Nakauchi, D. . . . 106
Nakayama, M. . . . 71
Nakayama, T. . . . 29, 30, 73, 75, 77, 169
Nakayama, T.* . . . 76, 111
Nakazato, N. . . . 139
Naleway, S. E. . . . 217
Nance, J.* . . . 174
Nanko, M. . . . 73
Narayan, R.* . . . 47
Nascimento, R. M. . . . 110
Nasr Esfahani, M.* . . . 96, 140
Nastasi, M. . . . 102, 147
Natarajan, T.* . . . 163
Navarro, G. . . . 195
Navarro, S. . . . 91
Navasa, M. . . . 64
Navrotsky, A. . . . 18, 51, 112
Navrotsky, A.* . . . 42
Nbelayim, P. S.* . . . 137
Ndayishimiye, A. . . . 46
Neal, C.* . . . 107
Nechache, R. . . . 42
Nechache, R.* . . . 41
Neeway, J. . . . 99
Nei, K. . . . 89
Nemoto, M. . . . 216
Neraj, J. . . . 119
Neto, C. . . . 216
Neumeister, P. . . . 154
Neupane, R. . . . 94
Nguyen-Tri, P. . . . 50
Nguyen, D. T. . . . 129
Nguyen, S. T. . . . 77
Nguyen, T.* . . . 75, 77
Ni, C.* . . . 67
Nicholas, J. D.* . . . 63
Nie, J.* . . . 29
Niederhaus, J. . . . 24
Nieto, A.* . . . 17
Niihara, K. . . . 73, 75, 77, 169
Ning, C. . . . 166
Ning, C.* . . . 219
Ning, X.* . . . 134
Nino, J. C. . . . 64, 157
Nino, J. C.* . . . 31
Nishimoto, S. . . . 200
Nishino, Y. . . . 70
Niu, M. . . . 124, 141
Nkeumaleu, A. . . . 216
Noguchi, Y. . . . 106
Nohira, T. . . . 71
Nomoto, J. . . . 89
Nordin, J. . . . 171, 200
Norsworthy, G. . . . 63
Noun, F. . . . 94
Nouvian, L. . . . 204
Nowicki, K. M.* . . . 125
Nunzi Conti, G. . . . 161

O

O'Dell, J. S.* . . . 174
O'Keefe, M. . . . 115
O'Masta, M. R. . . . 40
Oakmura, M. . . . 56
Odahara, J. . . . 36
Oelrich, R. . . . 150
Ogasawara, K.* . . . 205
Ogasawara, T. . . . 19, 57, 58, 59, 181
Ogawa, T. . . . 29, 30, 60, 188
Ogihara, S. . . . 59, 178
Ogitani, S.* . . . 75
Oh, M. . . . 127
Oh, T.* . . . 50, 115
Oh, Y. . . . 21, 121, 123
Ohashi, N. . . . 106
Ohashi, N.* . . . 112
Ohji, T.* . . . 155
Ohmori, K. . . . 166
Ohno, T. . . . 136
Ohodnicki, P. . . . 184
Ohsawa, T. . . . 112
Ohtaki, M.* . . . 133
Okada, G. . . . 38, 104
Okada, S. . . . 71
Okamoto, Y.* . . . 89
Okasinski, J. . . . 64, 131
Okawa, A. . . . 77
Okawa, A.* . . . 77
Okawa, H. . . . 199
Okuda, T. . . . 105
Okuizumi, S.* . . . 57
Okuno, E. . . . 107
Olchowka, J. . . . 93
Olevsky, E. A.* . . . 130
Omenya, F. . . . 72
Ong, S.* . . . 72
Ootani, Y. . . . 171, 172
Opeka, S. . . . 56
Opila, E. J. . . . 19, 20, 57, 59, 62, 80, 98, 146, 147
Opitz, A. K.* . . . 125
Opletal, G. . . . 221
Orangi, J. . . . 82
Orgiu, E.* . . . 215
Orlandi, M. O. . . . 215
Orlovskaya, N. . . . 146
Oropeza Gomez, D.* . . . 92
Ortiz, A. L. . . . 58
Ortona, A. . . . 39, 57, 109
Ortona, A.* . . . 141, 198
Osada, M.* . . . 88
Osaka, A.* . . . 218
Öst, T.* . . . 23
Ostash, O. . . . 148
Ott, C. . . . 153
Ou, J. . . . 40
Ouellet-Plamondon, C.* . . . 50, 216
Ouisse, T. . . . 33, 147
Ouyang, L. . . . 94
Oyler, N. . . . 221
Ozaki, T. . . . 50
Ozaki, T.* . . . 139
Ozawa, N. . . . 171, 172
Ozawa, N.* . . . 203
Ozkal, B. . . . 193

P

Padarti, J. K. . . . 136
Padture, N. P. . . . 58, 62
Padture, N. P.* . . . 44
Pagan, M. B. . . . 152
Palisaitis, J. . . . 82
Palmero, P. . . . 219
Panakarajupally, R. . . . 162, 182, 217
Panakarajupally, R.* . . . 19
Pandey, A. . . . 127
Pankov, V. . . . 62
Panov, N. . . . 193
Panseri, S. . . . 175
Papa, E. . . . 200
Papa, E.* . . . 159
Paquette, M. . . . 204, 221
Park, B. . . . 128
Park, B.* . . . 128
Park, C. . . . 166
Park, H. . . . 58
Park, H.* . . . 163
Park, J. . . . 139, 150
Park, J.* . . . 58, 125
Park, S. . . . 123
Park, Y. . . . 163
Parker, C. G.* . . . 20, 59
Parlier, M. . . . 58, 212
Partezana, J. . . . 150
Parthasarathy, T. A. . . . 56, 218
Pasaogullari, U. . . . 65

Author Index

Paschoa, J. L. . . . 108
Paskaramoorthy, R. . . . 181
Paskaramoorthy, R.* . . . 163
Patel, D. . . . 218
Pateloup, V. . . . 153
Patnaik, P. . . . 62
Patnaik, S. C. . . . 89
Paul, B. . . . 71
Paul, R. M.* . . . 49
Paulo, W. J. . . . 77
Paulose, M. . . . 94
Paulowicz, I. . . . 51
Paunovic, V. . . . 170, 197
Pavlov, S. . . . 122
Payne, A. . . . 206
Payne, H. E. . . . 132
Pazniak, H.* . . . 109
Peddamallu, N.* . . . 75
Pegna, J. . . . 34
Pei, Z. . . . 93
Pelanconi, M. . . . 198
Pellegrino, A. . . . 53, 95
Pelli, S. . . . 161
Pelz, J. . . . 130
Pelz, J.* . . . 129
Pena, A. A.* . . . 80
Peng, K.* . . . 195
Penide-Fernandez, R.* . . . 207
Perez-Maqueda, L. . . . 105
Pérez, J. . . . 91
Pergher, S. . . . 165
Pershin, L. . . . 123
Persson, P. . . . 82, 148
Petit, F. . . . 153
Petrie, C. . . . 83, 84, 150, 151
Petrie, C.* . . . 86
Petruhins, A. . . . 149
Pezoldt, M. . . . 199
Pezzotti, G. . . . 165
Picco, S. . . . 36
Picicco, M. . . . 28
Pierce, J. . . . 19
Pietras, J.* . . . 23
Pilania, G. . . . 142
Pineault, R. . . . 124
Pinek, D. . . . 147
Pinek, D.* . . . 33
Ping, H. . . . 176
Pinna, N.* . . . 136, 215
Pinnisi, D. . . . 80
Pint, B. A.* . . . 21
Pirou, S.* . . . 116
Pitike, K. . . . 143
Pittari, J. J.* . . . 24
Piven, K. . . . 32
Placke, T. . . . 216
Planel, B. . . . 156
Podhurska, V. . . . 148
Poerschke, D. L. . . . 62, 121
Poerschke, D. L.* . . . 220
Pohl, L. . . . 107
Polcik, P. . . . 209
Polyzois, I. . . . 24
Ponomarov, S. . . . 148
Pontikes, Y. . . . 213
Portale, G. . . . 54
Porter, K. A. . . . 40
Porter, M.* . . . 76
Post, E.* . . . 79
Poszdiech, O. . . . 23
Potoczek, M. . . . 142, 199
Povolny, S.* . . . 80
Poznyak, A. . . . 173
Prabhakar, P.* . . . 19, 211
Pradeep, K. . . . 33
Pralong, V.* . . . 132
Precner, M. . . . 82
Prehn, E.* . . . 173
Preininger, M. . . . 65
Preininger, M.* . . . 66
Presby, M. J. . . . 19, 218
Presby, M. J.* . . . 20, 162, 182, 217
Price, P. M. . . . 152
Prikhna, T.* . . . 25, 148
Primetzhofer, D. . . . 209
Prud'Homme, E. . . . 176
Przybyla, C. P. . . . 18, 218
Puchas, G. . . . 164
Puleo, B. J. . . . 20

Q

Qin, Z.* . . . 94
Quinn, G. D. . . . 24, 163
Quinn, G. D.* . . . 183
Quyet, N. . . . 208

R

Radovic, M. . . . 32, 146, 148, 149, 173, 208, 209
Radovic, M.* . . . 82
Radwan, M. . . . 36
Raftery, A. M.* . . . 34
Rai, A. K. . . . 61
Raiman, S. S. . . . 84
Raiman, S. S.* . . . 149
Rajagopalan, P. . . . 201
Rajan, K.* . . . 68
Raju, S.* . . . 131
Rak, Z. . . . 122
Ramachandran, R. K. . . . 54
Ramanuj, V. . . . 142
Ramanujam, S. . . . 75
Ramesh, K. . . . 25, 103, 129
Ramirez Velasco, J. H.* . . . 121
Ramirez-Rico, J. . . . 216
Ramirez-Rico, J.* . . . 216
Ramírez, C. . . . 20
Ramirez, G.* . . . 78
Ramos, F. . . . 63
Randall, C.* . . . 46
Rangon, G. . . . 93
Ranjan, P.* . . . 197
Rao, D. . . . 35
Rapaud, O.* . . . 203
Rapking, D.* . . . 218
Ratzker, B. . . . 37
Ravichandran, M.* . . . 198
Ravinder, D.* . . . 27
Ravindran, S. . . . 201
Reaney, I. M.* . . . 156
Rečnik, A. . . . 27
Reece, M. . . . 134, 146, 172
Reimanis, I. . . . 186
Reimer, T. . . . 207, 208
Reis, S. L. . . . 99
Reisert, M. . . . 16, 65
Reisert, M.* . . . 127
Remnev, G. . . . 78
Remnev, G.* . . . 122
Ren, L. . . . 74
Rennie, D. L.* . . . 164
Ressler, A.* . . . 110
Restrepo Arango, D. . . . 175
Reveron, H. . . . 219
Reverter, S. . . . 91
Reynaud, M. . . . 70
Reynosa, C. . . . 195
Ribeiro, L. . . . 114
Richards, J. . . . 154
Richter, A. B. . . . 185, 197
Ridley, M. J.* . . . 98
Riedel, R.* . . . 113
Riera, R. A.* . . . 25
Righini, G. C.* . . . 161
Riley, K. . . . 180
Rimsza, J. M.* . . . 220
Rincon, R. . . . 160
Ringgaard, E. . . . 31
Ritucci, I.* . . . 164
Rivera, S. . . . 118
Rodrigo, S. . . . 190
Rodríguez Barbero, M. A. . . . 190
Roger, J.* . . . 204
Rohde, M.* . . . 134, 179
Rohrer, G.* . . . 45
Rojo, T. . . . 70
Romaka, V. . . . 148
Rombouts, M.* . . . 90
Rosa, M. . . . 63
Rose, K. O. . . . 104
Rosei, F. . . . 41, 49
Rosei, F.* . . . 188, 192
Rosen, J. . . . 82, 149
Rossignol, S. . . . 58, 157, 212
Rost, C. M. . . . 146, 147
Rost, C. M.* . . . 122
Roszeitis, S. . . . 154
Rothe, S.* . . . 65
Rothmann, M. . . . 56
Roti Roti, A. . . . 178
Rotomskis, R. . . . 51
Rousseau, B.* . . . 179
Roy-Moisan, F. . . . 96
Ruan, X. . . . 205
Rubio, F. . . . 114
Rubio, J. . . . 114
Rubio, V. . . . 207
Rueschhoff, L. M. . . . 139, 156
Rueschhoff, L. M.* . . . 16, 140
Rueß, H.* . . . 209
Ruffini, A. . . . 175
Ruffner, M. . . . 150
Ruggles-Wrenn, M.* . . . 18
Rulis, P. . . . 145, 221
Rulis, P.* . . . 204
Ruttert, M. . . . 216
Ryu, H. . . . 35, 164
Ryukhtin, V. . . . 170

S

Sá Ribeiro, M. G. . . . 159
Sa Ribeiro, R. A.* . . . 159
Sabato, A. . . . 64, 117, 126
Sadia, Y.* . . . 71, 125
Sahin, I. . . . 166
Sahoo, J. K. . . . 89
Sajgalik, P. . . . 36
Sajgalik, P.* . . . 199
Sakamoto, F. . . . 111
Sakamoto, N. . . . 136
Sakidja, R. . . . 221
Sakidja, R.* . . . 145
Sakthivel, T. S. . . . 107
Sakuda, A. . . . 165, 166
Sakuma, H.* . . . 100
Saladino, M. L. . . . 108
Salameh, C.* . . . 113
Salamone, S.* . . . 67
Saleh, E. . . . 91, 155
Saleh, T. A. . . . 35

Salem, A. C. . . . 92
Salem, A. C.* . . . 92
Salem, J. . . . 163
Salem, J.* . . . 181
Saliba, J. . . . 203
Sallot, P. . . . 32
Salvo, M. . . . 84, 117, 134, 162
Salvo, M.* . . . 117
Sampath, S. . . . 21, 60, 61, 133
Samuel, D.* . . . 214
San, S.* . . . 221
Sanchez, C. . . . 40
Sankar, K. . . . 214
Sankar, K.* . . . 213
Sankaran, R. . . . 142
Sano, T. . . . 24
Sanson, A.* . . . 63
Sansoz, F. . . . 207
Santamaria-Pang, A. . . . 120
Santato, C.* . . . 215
Santoliquido, O. . . . 198
Santoliquido, O.* . . . 39
Sarathi, R. . . . 197
Sarker, P. . . . 146
Sarkkinen, M.* . . . 212
Sasaki, K. . . . 22
Sasaki, Y. . . . 28
Sasan, K. . . . 129
Sato, H. . . . 83
Sato, H.* . . . 178
Sato, M. . . . 60
Sato, T. . . . 188
Sato, Y. . . . 139
Sato, Y.* . . . 36
Sattar, S. . . . 198
Sauchuk, V. . . . 65, 126
Savaci, U. . . . 166
Savaniu, C. . . . 187
Savino, R. . . . 207
Savkliyildiz, I.* . . . 74
Sawamura, Y. . . . 169
Scanferla, P.* . . . 157
Schaedler, T.* . . . 40
Schaefer, M. C.* . . . 25
Schappel, D. . . . 34, 85, 86
Schauperl, R. . . . 66
Scheffler, M. . . . 141
Schefold, J.* . . . 127
Scheithauer, U.* . . . 39, 91, 154
Scheunemann, M. . . . 141
Schlup, A. . . . 68, 107
Schlup, A.* . . . 68
Schmidt, J. E. . . . 153
Schmidt, M. . . . 54
Schmidt, T.* . . . 169
Schmitt, M.* . . . 61
Schneck, T. K. . . . 120
Schneider, J. M. . . . 33, 209
Schneider, J. M.* . . . 32
Schneider, K. . . . 97
Schneiter, J. L. . . . 34
Schnetter, J. . . . 23
Schönfeld, K. . . . 59
Schulz, M. . . . 120
Schulze, V. . . . 179
Schülzgen, A.* . . . 37
Schumacher, A. . . . 84, 85
Schuster, B. . . . 25
Schuster, M. . . . 182
Schütt, F. . . . 51
Schwarzer, E. . . . 39, 154
Schwentenwein, M.* . . . 39, 188
Schwind, E. C. . . . 146
Schwind, E. C.* . . . 81, 172
Scipioni, R.* . . . 191
Sciti, D. . . . 118, 131, 208
Sciti, D.* . . . 207
Seabaugh, M. . . . 185
Seal, S. . . . 107
Sedlak, R. . . . 146
Seepalakottai, S. . . . 135
Seibert, R.* . . . 34
Seidel, G. . . . 80
Seifert, H. J. . . . 134, 179
Seifert, H. J.* . . . 69, 144
Seitz, M.* . . . 87
Seki, M. . . . 73
Sekino, T.* . . . 159
Sen, S. . . . 112
Sengun, P.* . . . 166
Seo, D.* . . . 156, 214
Seo, J. . . . 46
Serbenyuk, T. . . . 148
Serizawa, H.* . . . 139
Sernicola, G. . . . 182
Seshadri, A.* . . . 150
Setlock, J. . . . 20, 218
Sevecek, O. . . . 183
Sevener, K. M. . . . 217
Sgarlata, C. . . . 213
Sglavo, V. M. . . . 157
Shah, K. . . . 37
Shah, S. A. . . . 82
Shaikh, S. . . . 197
Shang, L. . . . 209
Shankar, K.* . . . 95
Shanmugavel, B.* . . . 181
Shapovalov, K. . . . 83, 210
Shapovalov, K.* . . . 211
Sharma, L. K.* . . . 47
Sheldon, B. . . . 20
Shen, F. . . . 135, 209
Shen, F.* . . . 135
Shepa, I.* . . . 110
Shi, S. . . . 159
Shi, Y. . . . 119
Shim, J. . . . 186
Shimada, H. . . . 127
Shimamoto, D. . . . 75
Shimamura, K. . . . 107
Shimamura, K.* . . . 45, 106
Shimizu, T. . . . 155
Shimoda, K. . . . 75, 137
Shin, D. . . . 64
Shin, J. . . . 79, 150
Shin, P. . . . 58
Shin, T.* . . . 127
Shinde, S. V.* . . . 60
Shinoda, F. . . . 137
Shirosaki, Y. . . . 188
Shirvan, K. . . . 150, 174
Shirvan, K.* . . . 86
Shirwadkar, U. . . . 37
Shivprasad, A. P.* . . . 35
Shoulders, T. . . . 101, 102, 103
Shoulders, T.* . . . 67
Shree, S. . . . 51
Sie, B. . . . 162
Siebert, L. . . . 51
Silva, F. d. . . . 158
Silvestroni, L. . . . 207
Simões, A. . . . 196
Singh, D.* . . . 15
Singh, G. . . . 35
Singh, G.* . . . 35, 72, 86
Singh, M. . . . 45, 91, 92, 139, 154
Singh, P. . . . 16, 65, 127
Singh, P.* . . . 46
Singh, Y. P. . . . 217
Singh, Y. P.* . . . 182
Singhal, A. . . . 182, 217
Sinnott, S.* . . . 142
Siyar, M. . . . 166
Skinner, S. . . . 125
Skripka, A.* . . . 51
Slagle, J. . . . 80
Smeacetto, F. . . . 64, 117, 134
Smeacetto, F.* . . . 126
Smith, C. S.* . . . 119
Smith, C.* . . . 154
Snead, L. . . . 35, 174
Snead, L.* . . . 152
Sobrados, I. . . . 212
Sohn, Y. . . . 21
Sokol, M. . . . 37
Solano, E.* . . . 54
Somer, M. . . . 109
Son, J. . . . 64, 125, 186
Son, W. . . . 148, 209
Song, E. . . . 83
Song, J. . . . 219
Song, K. . . . 72
Song, X. . . . 124
Song, Y. . . . 167
Sønsteby, H. H.* . . . 53
Soraru, G.* . . . 114
Sougrati, M. . . . 133
Sparks, T. D. . . . 135, 184
Speghini, A. . . . 53, 95
Speranza, G. . . . 114
Spirrett, F. . . . 155
Spirrett, F.* . . . 91
Sprio, S.* . . . 175
Sridharan, K. . . . 75
Srivastava, A. . . . 32, 209
Srivastava, A.* . . . 148
Stadler, D. . . . 98
Stadler, D.* . . . 48, 193
Stanek, C. . . . 142
Stanfield, A.* . . . 80
Starostina, A. . . . 148
Steger, K. . . . 150
Steinborn, C.* . . . 56
Steinbrück, M. . . . 144
Steiner, E. . . . 163, 164
Stelzer, B. . . . 32
Sternlicht, H. . . . 62
Stevenson, J. W. . . . 65, 99, 126, 185
Steveson, A. J. . . . 158
Steveson, A. J.* . . . 158
Stievano, L. . . . 133
Stocky, R.* . . . 132
Stoeckl, B. . . . 65, 66
Stokes, J. . . . 61
Stoll, T. . . . 179
Stratulat, A.* . . . 177, 201
Strawhecker, K. . . . 177
Strohbach, T. . . . 23
Studart, A. . . . 175
Stumpf, M. . . . 199
Su, L. . . . 97, 141, 210
Su, L.* . . . 141
Subhash, G. . . . 25, 69, 101, 174
Subhash, G.* . . . 144
Subotic, V. . . . 66
Subotic, V.* . . . 65
Suda, S. . . . 100
Suda, S.* . . . 181
Suehiro, S. . . . 87, 199

Author Index

Suematsu, H. 29, 75, 77, 169, 197
Suematsu, H.* 30, 73
Suess, M. 117
Suganuma, K.* 47
Sugimoto, K. 166
Sugimoto, Y.* 49, 75
Sugiya, K. 77
Suksangpanya, N. D. 175
Sulekar, S. S. 157
Sun, H. 189
Sun, S. 187
Sun, X.* 25, 215
Sun, Z. 50, 72
Sun, Z.* 81
Supancic, P. 183
Sutorius, A.* 98
Suvaci, E. 105, 106, 166, 167
Suvaci, E.* 136
Suyama, S.* 83
Suyama, T. 50
Suzuki, H.* 136
Suzuki, T. 73, 77
Svec, P. 146
Sverdun, V. 148
Swab, J. 24
Swab, J.* 24, 182
Swaminathan, B.* 217
Swartz, S. L. 185
Sweet, R. 85
Sysoev, V. 109
Syvertsen-Wiig, G. 185, 197
Szendrei, A.* 184
Szlufarska, I. 20

T

Tabard, L.* 176
Tabares, E. 208
Tabares, E.* 209
Taghaddos, E. 105
Taguchi, S. 75
Tahara, R. 96
Tajima, R. 89
Takagi, Y. 23
Takahashi, K. 89
Takahashi, S.* 199
Takahashi, T. 75, 105, 111, 162, 168
Takase, K. 30
Takata, M. 60
Takeda, H.* 111
Takeda, M. 56
Takeda, Y. 166
Takemura, S. 205
Takeuchi, T. 89
Talapatra, A. 32, 148, 173, 209
Talapatra, A.* 149
Talic, B. 126
Tallon, C. 80, 207
Tallon, C.* 176, 206
Tamayo, A.* 114
Tamerler, C.* 189
Tamimi, F.* 219
Taminato, S. 26, 166
Tampieri, A. 175
Tan, W. K. 137
Tan, Z. 173
Tanabe, Y. 77
Tanaka, K. 147
Tanaka, S. 138
Tanaka, S.* 74, 97
Tang, H. 216
Tang, J. 170
Tang, J.* 98
Tangermann-Gerk, K. 123
Tanibata, N.* 71
Tarabeux, J.* 153
Tarancón, A.* 63
Tarbokov, V. 122
Tatami, J. 105, 162, 168
Tatami, J.* 111
Tatsumisago, M. 165, 166
Taylor, C. A. 152
Teber, S. 195
Temel, T. 193
Tene Fongang, R. T. 157
Tennant, N. 17
Terrani, K. 34, 84, 85, 86, 149, 151, 211
Terrani, K.* 152
Terraschke, H.* 190
Terrones, D. A. 17, 101
Terrones, D. A.* 96
Tessier-Doyen, N. 212
Tetik, H. 106
Thevissen, K. 109, 220
Thieme, C.* 177
Thomas, M. L.* 191
Thompson, G. 81
Thornberg, j. 82
Thornton, G. 52
Tian, T. 27
Tian, W. 50, 72, 81
Ting, J. 194, 196
Ting, J.* 162
to Baben, M. 209
Toda, K.* 88
Toher, C. 146
Tokoi, Y. 75
Tokoro, C. 138, 168, 169
Tonello, R. 90
Tonge, A. 25, 103
Tonks, M. R.* 86
Tonle, I. K. 157
Toprak, M. S. 168, 193, 194
Toprak, M. S.* 194
Torresani, E. 130
Torriss, B. 160
Toson, B. 203
Toujinbara, K. 75
Toussaint, G.* 24
Trammell, M. 34, 84
Trammell, M.* 85
Tran, R. 72
Trice, R. 68, 80, 107, 121, 130, 206
Trindade, A. C.* 158
Trivellin, N. 36
Tsai, C. 66, 100
Tsakalakos, T. 64, 74, 105, 180
Tsakalakos, T.* 131
Tseng, K. 51
Tsipas, S. A. 209
Tsipas, S. A.* 208
Tsuchiya, T.* 89
Tsuda, H. 139
Tsuda, T.* 134
Tsujikura, K. 138
Tsukada, K. 169
Tsukamoto, M. 139
Tsunazawa, Y. 168
Tsunoura, T. 59
Tsunoura, T.* 19, 58, 96
Tsurui, N. 137
Tsurumi, T. 111
Tsurumi, T.* 44
Tucker, M. C. 127
Tuff, W.* 180
Tunca Altintas, B.* 33
Tunca, B. 33, 148
Tunes, M. 152
Tunes, M.* 152
Turan, S. 166
Turcer, L. R.* 62
Turpault, R. 202
Tutu, S. 90
Tyagi, S. 34

U

Uberuaga, B. P.* 142, 151
Uchikoshi, T. 188
Uchiyama, N. 70
Ueda, S. 112
Uemura, Y. 134
Ueno, K. 191
Uezono, M. 188
Uheida, A.* 194
Uher, C. 193
Ukai, M. 83
ul Hassan, M.* 35, 164
Umisedo, N. K. 107
Ursi, F. 108
Ushakov, S. 18, 51
Usukawa, R.* 113
Utsumi, T. 30
Uysal Sapanci, G.* 131
Uzawa, Y. 89

V

Vaaler, E. G. 34
Vaccari, A. 200
VahidMohammadi, A. 82
Van Hout, T. 109
Van Loo, K.* 33
Van Meerbeek, B. 39, 109
Van Nong, N. 31
Vandeperre, L. J. 19
Vandeperre, L. J.* 206
Varezhnikov, A. 109
Vargas, L. 67, 90, 101, 103, 129, 130, 132, 155
Vargas, L.* 129
Varghese, O. K.* 94
Vassen, R. 21, 32
Vassen, R.* 60
Vasyliv, B. 148
Vecchio, K. 146
Vela, J.* 42, 136
Velasco, B. 208
Veljkovic, S. 170, 197
Venkatachalam, V.* 207
Venneri, P. 81
Vergara, L. 114
Verné, E. 165
Vetrone, F. 51
Vetrone, F.* 137, 160, 188
Victoria, F. 94
Vigneshwaran, G. 181
Vignoles, G. L.* 202
Villechaise, P. 32
Vinci, A. 118
Vinci, A.* 118, 208
Vinnichenko, M. 126
Vinu, A.* 197
Virkar, A. V. 135, 184
Vlahovic, B. 170, 197
Vleugels, J. 33, 39, 109, 148, 180
Vodermayer, A. 57
Vogel, S. E. 169
Voiry, D. 113
Vojtko, M. 110
Volkert, C. A. 48, 193
Vomiero, A. 41, 49
Vomiero, A.* 193

von Fieandt, L. . . . 52
von Helden, S.* . . . 180
Voorhees, P. . . . 128
Vora, S. D. . . . 22

W

Wada, K.* . . . 56
Wada, M.* . . . 60
Wada, S.* . . . 46
Wadley, H. . . . 61
Wakiya, N. . . . 136
Walck, S. D. . . . 102, 103, 132
Walter, C.* . . . 23
Walton, R. . . . 174
Wang, A. . . . 28
Wang, B. . . . 118, 200
Wang, B.* . . . 198
Wang, D. . . . 72
Wang, D. D. . . . 175
Wang, D.* . . . 41
Wang, F. . . . 102
Wang, F.* . . . 147
Wang, G. . . . 218
Wang, H. . . . 28, 97, 124, 141, 151, 195
Wang, H.* . . . 74, 141
Wang, J. . . . 15, 33, 205, 206, 218
Wang, J.* . . . 204
Wang, K. . . . 46
Wang, L. . . . 116, 171
Wang, M. . . . 178
Wang, M.* . . . 165, 187, 189, 190
Wang, Q.* . . . 58
Wang, R.* . . . 127
Wang, S.* . . . 178
Wang, W. . . . 74
Wang, W.* . . . 28
Wang, X. . . . 155
Wang, Y. . . . 124
Wang, Y.* . . . 37
Wang, Z. . . . 72, 94, 160
Wang, Z.* . . . 180
Wassel, M. A. . . . 105
Watanabe, M. . . . 191
Watanabe, S. . . . 26
Watts, C. . . . 58, 62
Watts, J. . . . 83, 149
Weaver, E.* . . . 130
Weber, C. . . . 146
Weber, L. . . . 109
Weber, R. . . . 51
Weber, W. J.* . . . 144
Webster, R.* . . . 62
Wehrspohn, R. B. . . . 177
Wei, C. . . . 118
Wei, C.* . . . 190
Weinberger, C. R.* . . . 81
Weingarten, S. . . . 91, 154
Weiß, S. . . . 93
Wereszczak, A.* . . . 163, 164
Wermer, J. R. . . . 35
Westin, G. . . . 48, 193
Westin, G.* . . . 55, 93
Wheeler, R. . . . 140
White, C. E. . . . 213
White, C. E.* . . . 212
White, J. T. . . . 35
Whittingham, M. . . . 72
Wickleder, C. . . . 97
Wickleder, C.* . . . 93
Wickleder, M. S. . . . 27
Wickleder, M. S.* . . . 43
Wickliffe, G. . . . 146
Wiesner, U.* . . . 42
Wiesner, V. L. . . . 18
Wiesner, V. L.* . . . 49
Wiff, J. P. . . . 100
Wiik, K. . . . 185
Wiles, R. . . . 163
Wilhelmi, C. . . . 117
Willems, E.* . . . 39, 109
Williams, K. L. . . . 34
Winnubst, L.* . . . 140
Wirth, B. . . . 86
Wirth, B.* . . . 85
Wizner, A. . . . 70
Wolfe, D. E. . . . 61
Wong, L. H.* . . . 94
Wong, L. L. . . . 129
Woydt, M.* . . . 180
Wren, A. W. . . . 219
Wroblewski, A. C. . . . 61
Wu, J. . . . 145, 189
Wu, J.* . . . 52
Wu, S. . . . 22
Wu, W. . . . 186
Wu, X. . . . 86
Wu, Y. . . . 38, 87, 138
Wyckoff, C. . . . 139
Wynn, J. . . . 67
Wynn, M. . . . 54

X

Xi, J.* . . . 220
Xiang, H. . . . 82, 202
Xiang, H.* . . . 145
Xiang, S. . . . 67, 183
Xiao, D. . . . 72
Xiao, P.* . . . 60
Xie, H.* . . . 176
Xie, K. . . . 67
Xie, K. Y.* . . . 67, 183
Xing, J. . . . 146
Xiong, D. . . . 196
Xu, H. . . . 72
Xu, H.* . . . 143
Xu, J.* . . . 100
Xu, P. . . . 84, 150
Xu, P.* . . . 123, 150
Xu, W. . . . 18
Xu, Y.* . . . 185

Y

Yagi, S.* . . . 101
Yaguchi, Y. . . . 169
Yahagi, T. . . . 162
Yamada, S. . . . 71
Yamaguchi, H.* . . . 162
Yamaguchi, S.* . . . 50
Yamaguchi, T. . . . 127
Yamaguchi, Y. . . . 191
Yamaji, K. . . . 127
Yamamoto, H. . . . 37, 104
Yamamoto, T.* . . . 71
Yamaoka, K. . . . 75
Yamashita, H. . . . 188
Yamashita, S. . . . 37, 84, 104
Yamashita, S.* . . . 172
Yamazaki, N. . . . 56, 57
Yamazaki, N.* . . . 22
Yamazaki, S. . . . 89
Yamazaki, S.* . . . 15
Yan, X. . . . 102, 147
Yanagida, T. . . . 37, 38, 104, 105, 106
Yanagida, T.* . . . 37, 105
Yanagisawa, H.* . . . 171
Yang, B. . . . 67, 79, 119, 183
Yang, C. . . . 66, 100
Yang, G. . . . 160
Yang, J. . . . 73, 79, 118, 198, 200
Yang, J.* . . . 171
Yang, K. . . . 212
Yang, K.* . . . 143
Yang, L. . . . 50, 81
Yang, Q. . . . 67, 180
Yang, Q.* . . . 102
Yang, S. . . . 66
Yang, S.* . . . 100
Yang, T. . . . 184
Yang, T.* . . . 100
Yang, X. . . . 205
Yang, Z. . . . 119
Yano, T. . . . 19, 58, 96
Yao, J. . . . 40
Yao, Z. . . . 167
Yaraghi, N. . . . 175
Yarur, F. . . . 94
Yasuda, K. . . . 77
Yee, T. D. . . . 129
Yeh, C. . . . 99
Yi, S. . . . 167
Yilmaz, E. . . . 194
Ying, G.* . . . 210
Yokoe, D. . . . 60
Yokouchi, M. . . . 105
Yoon, D. . . . 125
Yoon, H. . . . 78
Yoon, K. . . . 64, 125
Yoshida, H.* . . . 28
Yoshida, K. . . . 19, 58, 59, 96
Yoshimura, E. M. . . . 107
Yoshimura, M.* . . . 46, 215
Youmoue, M.* . . . 157
Youn, Y. . . . 166
Young, C. M.* . . . 145
Youngblood, J. P. . . . 68, 107, 130
Yu, H. . . . 81
Yu, R. . . . 119
Yu, S.* . . . 87
Yu, Y. . . . 184
Yu, Z.* . . . 48, 113
Yubuchi, S. . . . 165, 166
Yue, S. . . . 94
Yue, X. . . . 125
Yuk, S. F. . . . 143
Yun, H.* . . . 38
Yun, J. . . . 191, 192
Yun, J.* . . . 192
Yurtsever, A.* . . . 95

Z

Zaeem, M. A. . . . 202, 203
Zagyva, T. . . . 98
Zaman, W. B.* . . . 209
Zanchi, E. . . . 126
Zarkadoula, E. . . . 144
Zavattieri, P. . . . 175, 217
Zavattieri, P.* . . . 175
Zavelani-Rossi, M.* . . . 94
Zecchini, A. . . . 93
Zeljkovic, S. . . . 31, 64
Zeng, Q.* . . . 103
Zeng, S. . . . 95
Zenkin, S. . . . 122
Zhan, Z. . . . 32
Zhang, C. . . . 102, 145, 146, 210
Zhang, D.* . . . 196
Zhang, F. . . . 39, 109, 154
Zhang, H. . . . 73, 74, 81, 82
Zhang, H.* . . . 170, 197

Author Index

Zhang, J. 33
Zhang, J.* 15
Zhang, K. 196, 210
Zhang, L.. 178
Zhang, N. 118, 186, 200
Zhang, P.. . . . . 50, 72, 81
Zhang, P.* 119
Zhang, Q. 26, 128
Zhang, Q.* 128
Zhang, R. 146
Zhang, S.* 196
Zhang, W.. . . . . 20, 50, 69, 72, 81, 196
Zhang, X. 73
Zhang, Y. 50, 67, 81, 86, 144
Zhang, Y.* 204
Zhang, Z.. 82
Zhao, H. 41, 49
Zhao, H.* 94
Zhao, J. 219
Zhao, X.. 46
Zheng, W.. 81
Zheng, W.* 50
Zheng, Y. 26
Zhi, Q.. 171
Zhi, Q.* 200
Zhong, Z. 74
Zhou, F.* 26
Zhou, G. 72
Zhou, J. 19
Zhou, Q. 63
Zhou, R. 216
Zhou, Y. 49, 145, 217
Zhou, Y.* 82, 85, 202
Zhuang, H.* 205
Zimmermann, L. 93
Zinkle, S. J. 81, 84
Zins, M.. 66
Zocca, A.. 89
Zocca, A.* 92
Zok, F. W.. . . . . 18, 57
Zoli, L.. . . . . 118, 131, 207, 208
Zong, X. 74
Zorn, G. 182
Zou, J.* 79
Zuccarini, C.* 48