Ni-Si alloys for Hydrogen Generation by the Sulfur-Iodine Cycle

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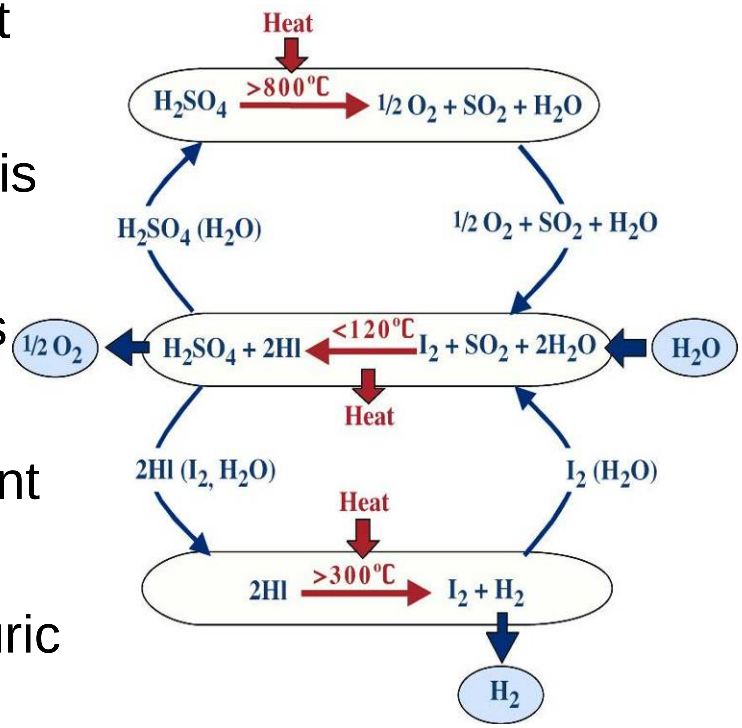
Introduction

- Sulfur Iodine (S-I) cycle offers significant advantages in hydrogen production
- Direct heat exchanger is desirable for this cycle
- High temperatures and hence pressures also desired
- No standard structural alloys are resistant enough to be used
- Alloy based on Ni_3Si developed for sulfuric acid recycling offers promise of meeting requirements
- Hydrogen Initiative project to further develop alloy for this application



Project goals

Develop alloy for use in vessels to contain hot, pressurized sulfuric acid

- Determine mechanism for protective nature of alloy
    - Passivation reaction
    - Stability of protective film under corrosion-erosion
    - Cause of Ti degradation and possible solution
- Evaluate performance under service conditions and improve where possible
    - Testing in hot, pressurized sulfuric
    - Erosion testing in closed loop
- Develop wrought analog to cast alloy, including characterization of high temperature properties
    - Alloys cold rolled and annealed
    - Hot deformation evaluated
    - Mechanical properties measured
- Fabricate vessels for testing

Outline of Talk

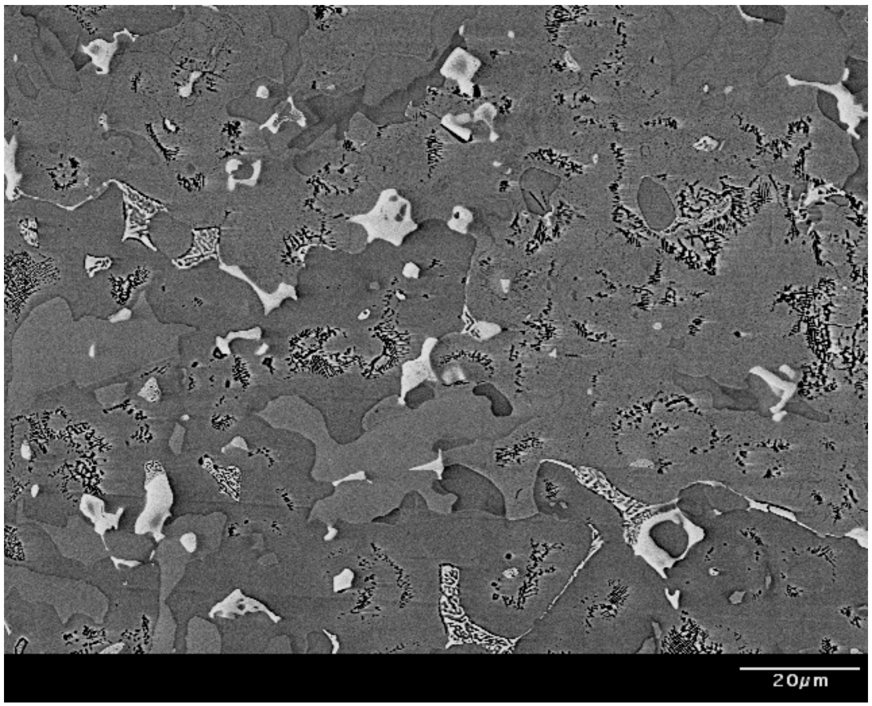
- Alloy property development & characterization
- Corrosion resistance development
- Fabrication development
- Conclusions

Development of Ni_3Si Alloys

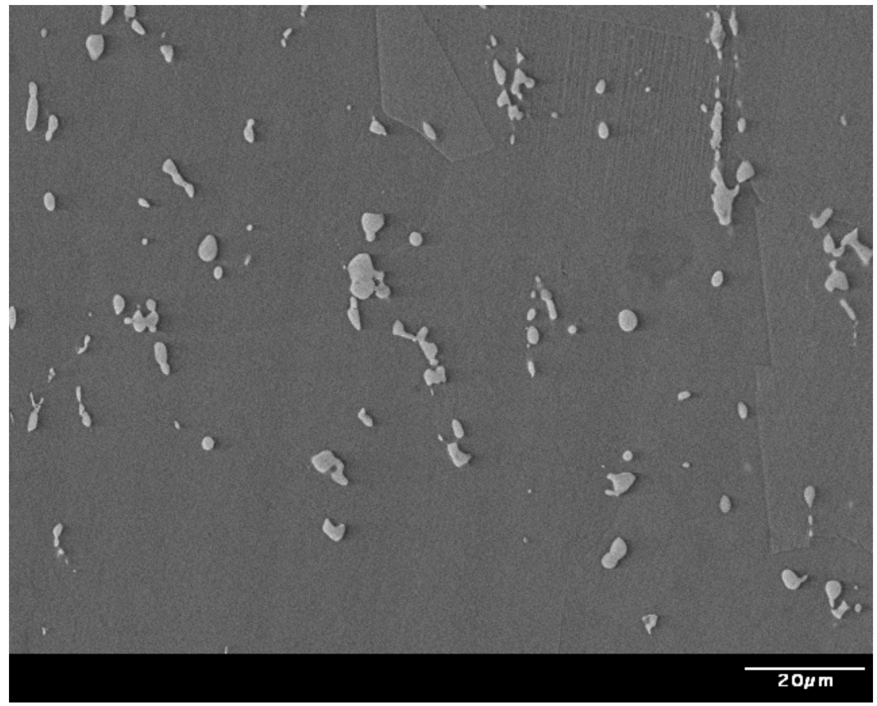
- Mechanical Properties
  - Silicides are mostly brittle but there is one that is not, Ni_3Si
  - B or C doping reduces environmental embrittlement
  - Ti, Hf, and Nb enhance ductility with Ti having the most benefit
- Corrosion Resistance
  - Ni_3Si would be expected to form an adherent SiO_2 film
  - Titanium hurts corrosion resistance in sulfuric
  - Nb has positive effect on both mechanical properties and corrosion
  - However, Nb is limited in solubility (~2%)

G. Welsch, et al., *Oxidation and Corrosion of Intermetallic Alloys*, pp.121-264 (1996).

Microstructural Issues



•As-Cast
•Four phases form during solidification



•Homogenized 4 days at 980C
•Cold rolled 12 times for total of 60% reduction
•Ni_3Si + G-phase

Effect of Nb on Properties

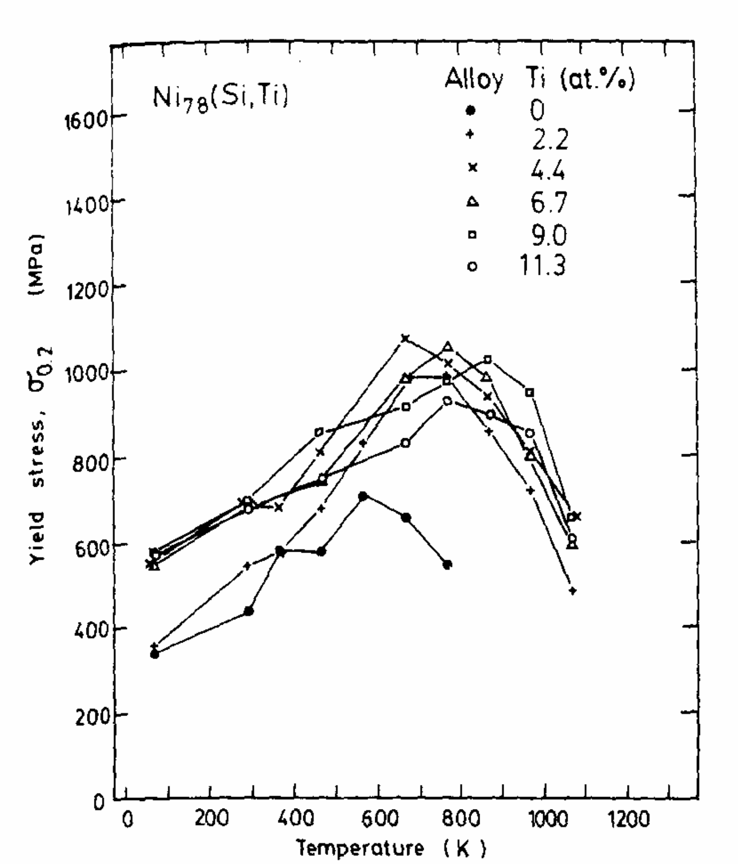
Alloy	Heat Treatment	UTS ksi	Elongation %	Note
$NiSi_{20}Nb_3B_{0.5}$	900°C for 1 day	*	<0.9	2" gage, 0.5" D
	950°C for 4 days	127±2.5	3.6±1.6	1" gage, 0.25" D
	1050°C for 8 hours	87±3	<2	1" gage, 0.25" D
$NiSi_{19}Nb_3B_{0.5}$*	950°C for 1 days	110	2.9	2" gage, 0.5" D
	950°C for 2 days	97	2.4	2" gage, 0.5" D
	980°C for 1 days	93	2.1	2" gage, 0.5" D

***200 lb Commercial Sand Casting**

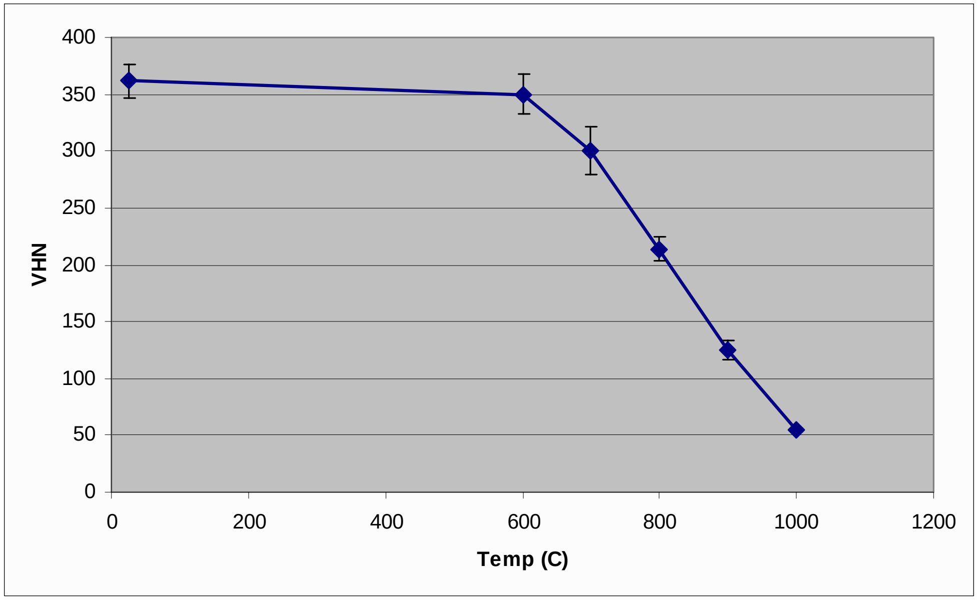
Alloy	HT	Corrosion rate (mils/year), Boiling Solutions								
		60 % H_2SO_4		70 % H_2SO_4		80 % H_2SO_4		90 %	96 %	98 %
		1st	2nd	1st	2nd	1st	2nd	1st	1st	1st
$NiSi_{22}Nb_2B_{0.5}$	900°C, 1d									
	950°C, 4d	79±6	0±0.4	10±1	0±0.4					
$NiSi_{20}Nb_3B_{0.5}$	900°C, 1d	67 ±5	50±4	75±21	2±0.5	6±1	0.7±0.4	3.5±1.5	4.0±1.5	3.0±1.0
	950°C, 4d	53±4	18±2	75±5	0.6±0.4					
	1050°C, 8h	439±29		83±6	0.3±0.4					

- **Good strength and ductility in cast form**
- **Slightly lower strength, but greater ductility in wrought form**
- **Weldable & Machinable**
- **Passivation occurs during sulfuric exposure**

High Temperature Properties of Ni_3Si Alloys



Hot hardness results on baseline alloy (Data from ARL-DOE)



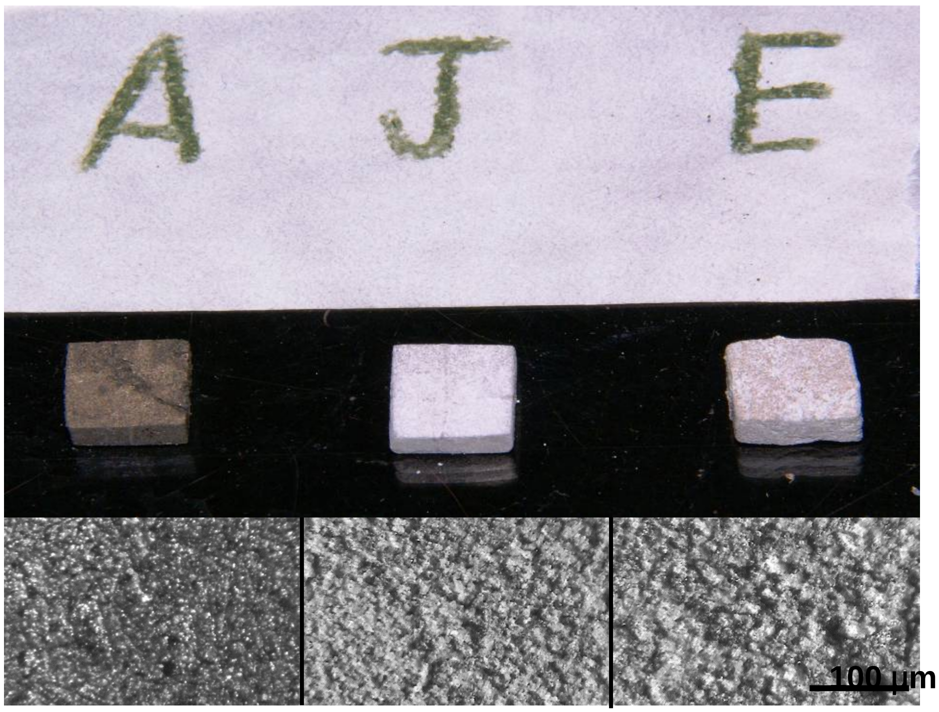
Rupture life significantly better than D-205 at 650C and 410 MPa

J.H. Zhu and C.T. Liu, *Intermetallics,* 10, 309-316 (2002).

T. Takasugi, M. Nagashima, and O. Izumi, Acta Metall. Mater. 38 (1990)

Sulfuric Acid testing @ 1 Atm

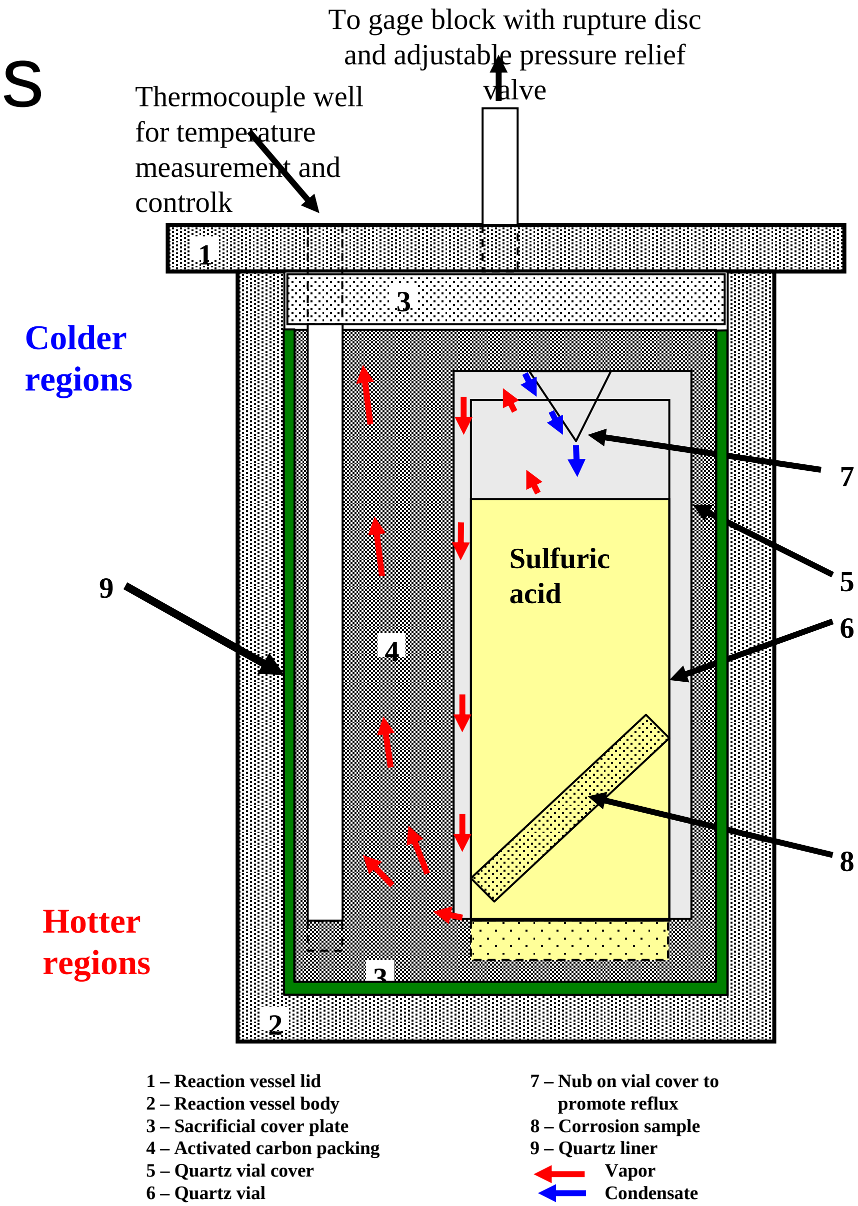
3%Nb 3%Nb+1%Ti 3%Ti



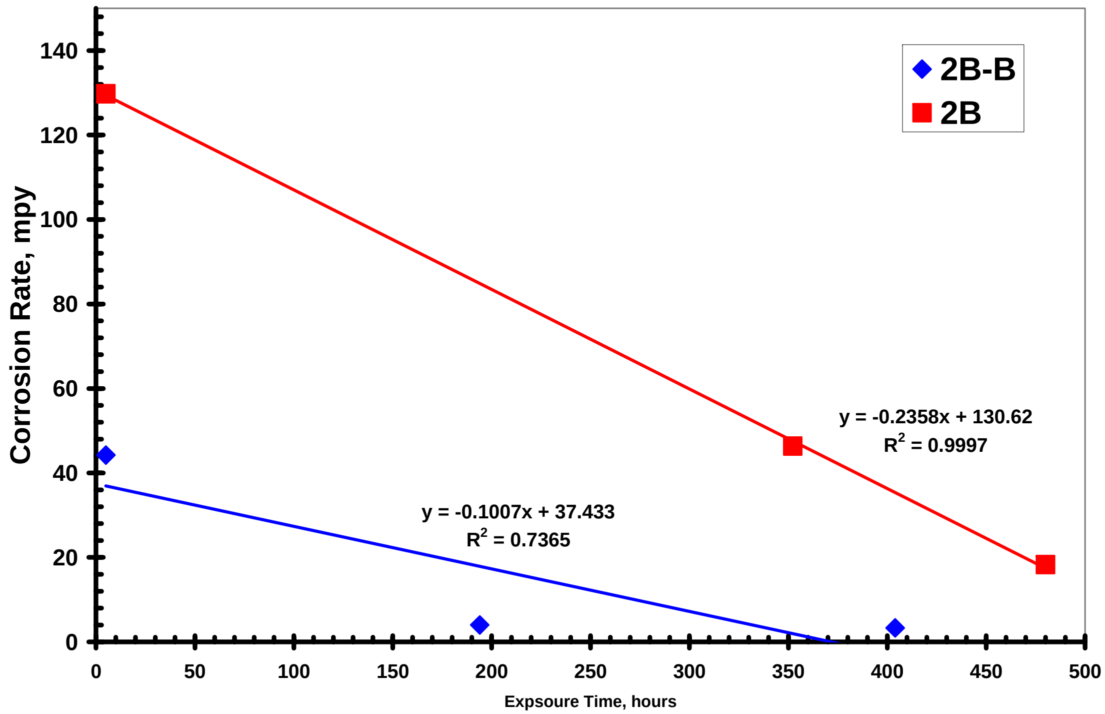
- 3 days in boiling 70% sulfuric causes weight loss
- Alloys containing Nb, but no Ti form a clear coating (glass?)
- Alloys containing Ti or Ti and Nb form an opaque loose layer of reaction product

INL Test Apparatus

- Sealed, pressurized testing at temperature
- Rectangular sample spends many days in environment
- Only one sample at a time
- No provision for stirring acid
- Sample weighed periodically to determine corrosion rate



High Pressure, Temp. Static Testing



- Homogenized alloy passivates quickly
- Rate after passivation <5 mpy
- Considered adequate for the application
- Flowing sulfuric testing needed

Condition	Sulfuric %	Temp (C)	Pressure (psi)
$NiSi_{20}Nb_3B_{0.5}$ As-cast	96	375	500
$NiSi_{20}Nb_3B_{0.5}$ 950C, 4d	96	375	500

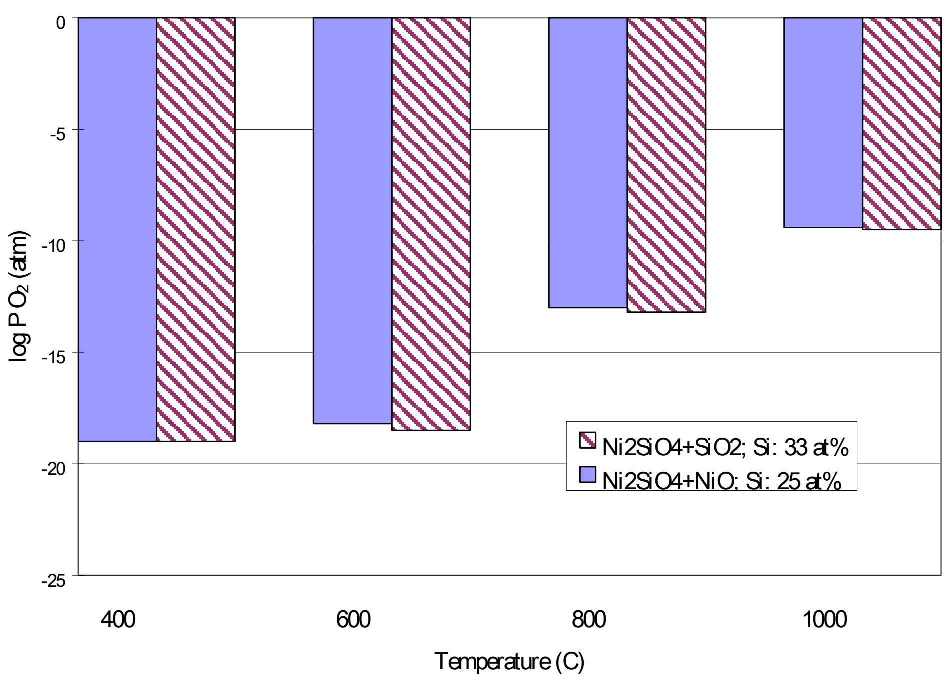
Corrosion Resistance Development

- SiO_2 forms during exposure to oxidizing levels of sulfuric acid
- Presence of Nb does not interfere with corrosion resistance, while Ti does
- Doping the alloys with silica modifiers may be possible
- However the mechanism for corrosion protection must be understood first
  - Thermodynamic modeling
  - Surface analysis

Thermodynamic Simulation

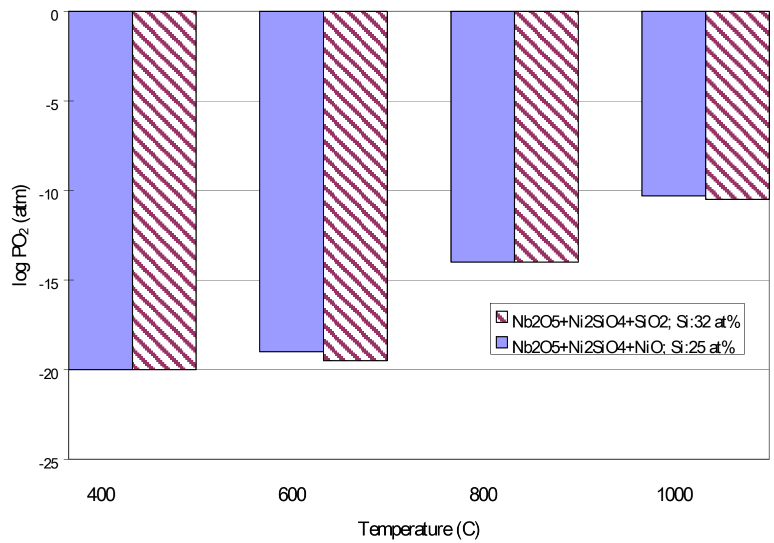
- Modeling of metal-gas systems
  - Ni-Si-B, Ni-Si-Nb, and Ni-Si-Ti
  - Gases – CO_2-O_2, H_2O-O_2, and SO_2-O_2
  - Temperatures from 400C to 1000C
- Modeling in liquid sulfuric and nitric acid to be done
- Factsage software used

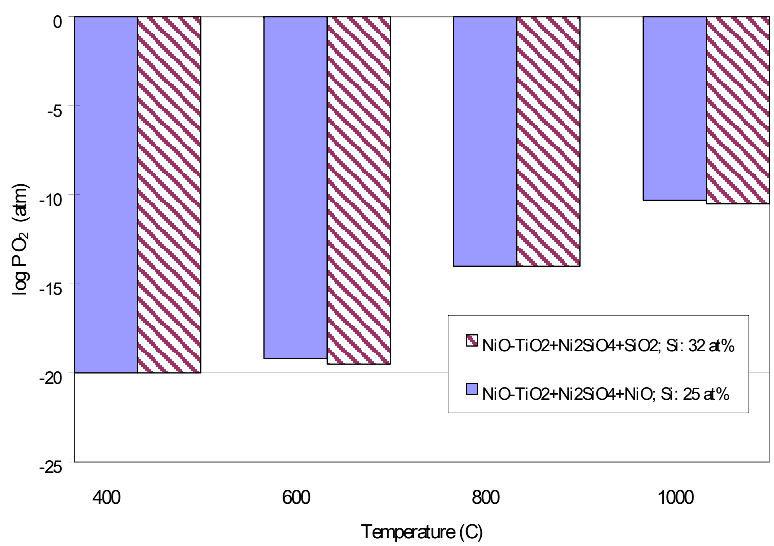
Ni-Si in H_2O-O_2



- At alloy Si level, SiO_2 not stable
- If Ni is leached out, SiO_2 becomes stable at 33 at.%
- NiO and Nickel Silicate stable in air

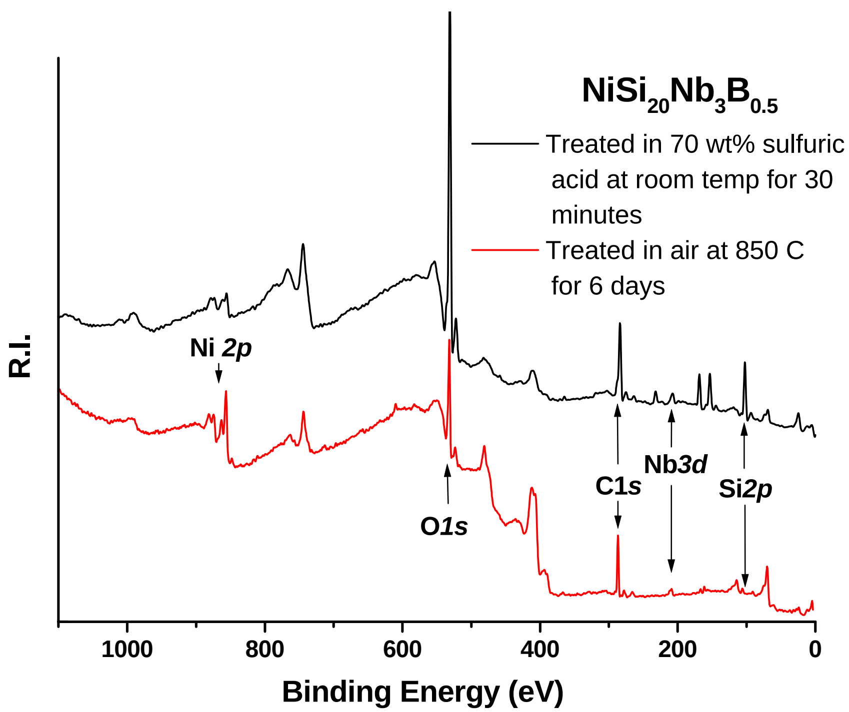
Ni-Si-Nb vs Ni-Si-Ti





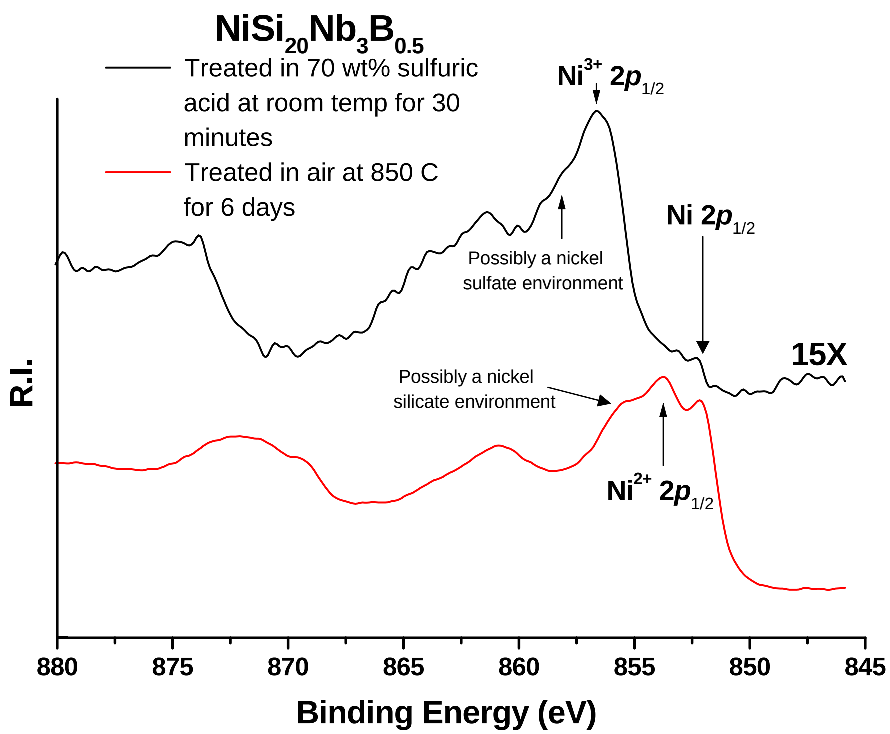
- Nb adds Nb_2O_5 to mix of compounds
- Ti adds NiO-TiO_2 to mix
- Reduced Ni (leaching) once again stabilizes SiO_2
- Modeling of SO_2 vs O_2 shows Ni_2SiO_4 replaced with $NiSO_4$

Air vs Sulfuric Acid



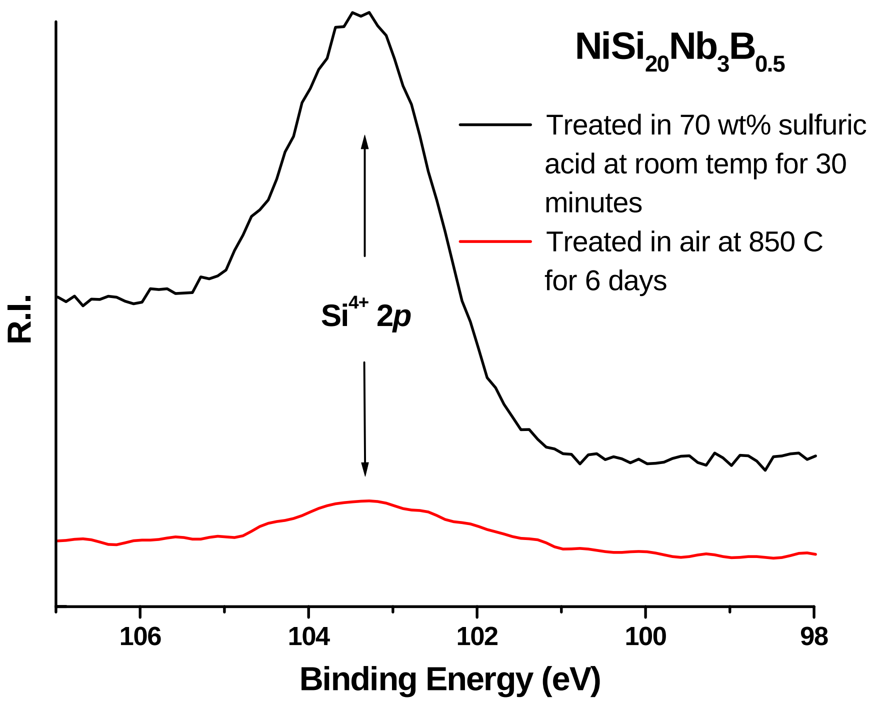
- XPS of surfaces exposed to hot air or boiling sulfuric
- Look for SiO_2 vs NiO
- Also Ni_2SiO_4 vs $NiSO_4$

Air vs Sulfuric Acid



- NiO seen after treatment in air
- Sample also turns bright green, indicating NiO
- Additional compound of Ni forms in air, possibly Ni_2SiO_4
- Less Ni found on surface treated with sulfuric (15X magnification)
- A different compound, possibly $NiSO_4$ forms

Air vs Sulfuric Acid



- SiO_2 forms in quantity on surface treated with sulfuric
- Si is depleted from surface treated in air
- Nb (not shown) is in form of Nb_2O_5 when treated in air
- Nb is in three different oxidation states in film formed during sulfuric treatment

Mechanism Summary

- Weight loss means metal is lost (Ni?)
- SiO_2 forms in boiling sulfuric, but not in air at 850C
- Nb does not fully oxidize
- Presumably silicon is enriched while Ni is depleted
- Thick adherent film forms oxidation barrier, stopping further corrosion
- Simulation shows that many modifiers are stable and will form naturally

Fabrication Development

- Casting alloy available and patented
- Welding demonstrated
- Machining developed
- Cold rolling demonstrated, but limited
- Hot rolling
  - High temperature properties being characterized with INL Gleeble
  - Hot rolling parameters will be optimized with Gleeble
  - Two rolling shops already agreed to roll large pieces

Conclusions

- An alloy is available with a good combination of mechanical properties and corrosion resistance
- High temperature mechanical properties look promising, but evaluation is still underway
- Early tests at high temperatures & pressures show acceptable corrosion resistance
- The corrosion mechanism is still being determined
- Better corrosion and erosion resistance may be able to be engineered
- Pipes could be fabricated by casting, but evaluation of the formability will be carried out.