ANALYSIS OF ELECTROCHEMCIAL EXPERIMENTS FOR EVALUATION OF SUSCEPTIBILITY TO EMBRITTLEMENT BY HYDROGEN GAS

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I. Introduction

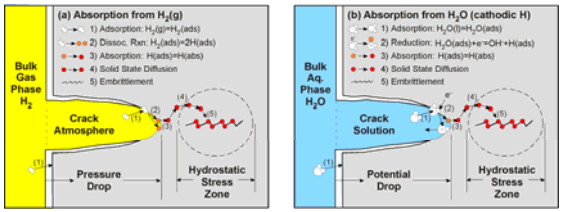
Innovation and growth in the emerging hydrogen economy will be facilitated by advances in two categories of testing methods:

(i) Qualification methods - to obtain design level data for codes and standards or qualifying materials and technologies

(ii) Research screening methods - to enable innovation and guide the development of hydrogen resistant materials and technologies.

The NIST Materials Reliability and Metallurgy Divisions are collaborating on a program that is addressing both of these areas of need.

A. Assumptions



(1) Hydrogen will cause embrittlement in fuel systems by a mechanism as illustrated above where embrittlement actually occurs in the hydrostatically stressed region of the plastic zone ahead of the crack tip.

(2) The properties of the material and the concentration or activity of hydrogen in the hydrostatic zone determines the extent of embrittlement.

Therefore, the surface reactions can only influence embrittlement through hydrogen concentration or activity and equivalent concentrations will produce essentially identical behavior regardless of the hydrogen source.

B. Fundamental Relationships

Reaction in acidic solutions

$$H^+ + e^- \rightarrow H(ads) \rightarrow (\tfrac{1}{2})H_2(g)$$

In neutral and basic solutions

$$H_2O + e^- \rightarrow (\tfrac{1}{2})H_2(g) + OH^-$$

Equilibrium Constant

$$K_{eq} = \frac{[H_2]^{0.5}}{[H^+]}$$

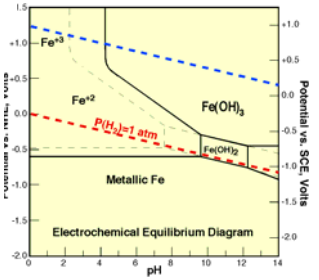
Potential and Free Energy

$$\Delta G = -nFE$$

Nernst Equation

$$E_{eq} = E^0 - \left(\frac{RT}{nF}\right)\ln(K_{eq})$$

$$E_{eq} = E^0 - (0.0296)\log[P(H_2)] - (0.059)pH$$



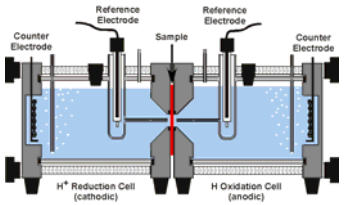
Hydrogen activity increases an order of magnitude for every 30 mV that the potential goes below the red line above.

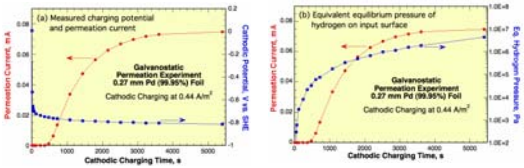
II. Diffusion and Solubility Measurements

Electrochemical methods can be used to measure:

1) hydrogen diffusion rates
2) hydrogen solubility
3) hydrogen absorption from service environments
4) the influence of metallurgical variables on these factors

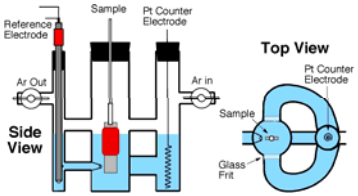
A. Electrochemical Permeation - Devanathan and Stachurski (1962) and ASTM G148

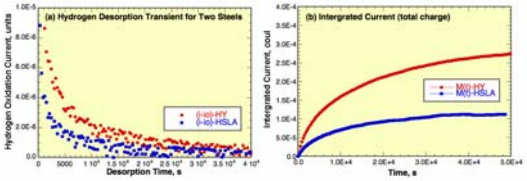




Constant current charging produces a constantly increasing hydrogen fugacity.

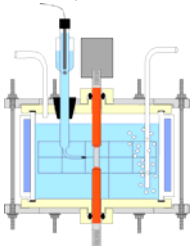
B. Electrochemical Absorption/Desorption



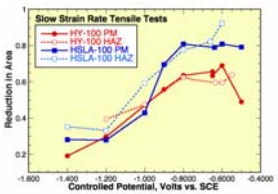


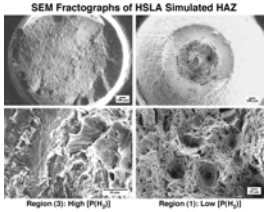
III. Mechanical Properties

A. Slow Strain Rate Tensile Tests - Controlled cathodic potentials for varying hydrogen activity

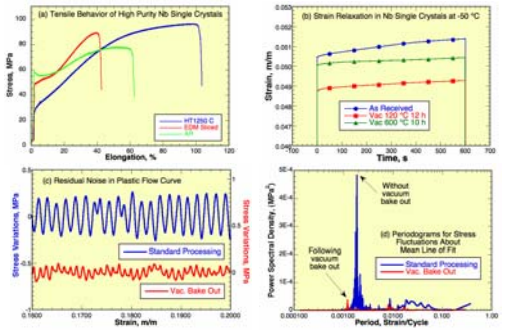


B. Hypothesis Testing - Guiding R&D into variables such as composition, microstructure, and heat treatments





C. Advanced Analytical Methods - Understanding interactions



IV. Conclusion

Electrochemical reactions are a convenient method for introducing hydrogen into metals for studying hydrogen embrittlement, testing hypotheses, or guiding innovation. In addition, electrochemistry can be used to directly control or measure hydrogen activity (potential) or flux (current) in these studies.