III.10 Hydrogen Embrittlement of Pipeline Steels: Fundamentals, Experiments, Modeling

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Objectives

- Mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise fracture criteria for safe and reliable pipeline operation under hydrogen pressures of at least 15 MPa and loading conditions both static and cyclic.
- Explore methods of mitigation of hydrogen-induced failures through inhibiting species (e.g., water vapor) or regenerative coatings (e.g., surface oxidation).
- Explore suitable steel microstructures to provide safe and reliable hydrogen transport at reduced capital cost.
- Assess hydrogen compatibility of the existing natural gas pipeline system for transporting hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Delivery section (3.2.4) of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (FCT Multi-Year RD&D Plan):

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

(G) Storage Tank Materials and Costs

(K) Safety, Codes and Standards, Permitting

Technical Targets

This project is conducting fundamental studies of hydrogen embrittlement of materials using both numerical simulations and experimental observations of the degradation mechanisms. Based on the understanding of the degradation mechanisms the project's goal is to assess the reliability of the existing natural gas pipeline infrastructure when used for hydrogen transport, suggest possible new hydrogen-compatible material microstructures for hydrogen delivery, and propose technologies (e.g. regenerative coatings) to remediate hydrogen-induced degradation. These studies meet the following DOE technical targets for Hydrogen Delivery as mentioned in Table 3.2.2 of the FCT Multi-Year RD&D Plan:

- Pipelines: Transmission–Total capital investment will be optimized through pipeline engineering design that avoids conservatism. This requires the development of failure criteria to address the hydrogen effect on material degradation (2012 target).
- Pipelines: Distribution–Same cost optimization as above (2012 target).
- Pipelines: Transmission and Distribution–Reliability relative to H_2 embrittlement concerns and integrity, third party damage, or other issues causing cracks or failures. The project's goal is to develop fracture criteria with predictive capabilities against hydrogen-induced degradation (2017 target). It is emphasized that hydrogen pipelines currently in service operate in the absence of design criteria against hydrogen-induced failure.
- Off-Board Gaseous Hydrogen Storage Tanks (Tank cost and volumetric capacity)–Same cost optimization as in *Pipelines: Transmission* above. Current pressure vessel design criteria are overly conservative by applying conservative safety factors on the applied stress to address subcritical cracking. Design criteria addressing the hydrogen effect on material safety and reliability will allow for higher storage pressures to be considered (2015 target).

Accomplishments

- Discovered the nature and characteristics of the hydrogen degradation mechanisms of two promising microalloyed, low-carbon steel microstructures designated as B[1] and D[2] hereafter. The samples were provided by the DGS *Metallurgical Solutions, Inc*. The mechanisms of fracture were identified by using focused ion beam (FIB) machining to lift-out sections from fracture surfaces along with transmission electron microscopy (TEM) analysis of the extracted thin foils.

- Characterized the microstructure of pipelines steels through optical analysis, scanning electron microscopy (SEM), and TEM, and identified particle composition through energy dispersive spectroscopy for: a) laboratory specimens from Air Liquide, Air Products, and Kinder-Morgan industrial pipelines; b) new microalloyed, low-carbon steels from Oregon Steel Mills provided by DGS Metallurgical Solutions, Inc.
- Developed a thermodynamic theory of hydrogen-induced decohesion that was used to model and simulate hydrogen-induced subcritical cracking in high strength steels.
- Augmented our modeling and simulation capabilities of transient hydrogen transport to account for the mechanical deformation and hydrogen-induced grain boundary decohesion in high strength steels. Predictions have been made of threshold stress intensities associated with subcritical crack growth.
- Demonstrated environmental similitude between the single edge notch specimen (SENT) and a pipeline with an axial crack on the inner diameter surface. Hence, the SENT specimen can be used as a laboratory specimen to reliably estimate the fracture resistance of a pipeline steel in the presence of hydrogen.

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Introduction

Hydrogen is a ubiquitous element that enters materials from many different sources. It almost always has a deleterious effect on material properties. The goal of the project is to develop and verify a lifetime prediction methodology for failure of materials used in pipeline systems and welds exposed to high-pressure gaseous environments. Development and validation of such predictive capability and strategies to avoid material degradation is of paramount importance to the rapid assessment of the suitability of using the current pipeline distribution system for hydrogen transport and of the susceptibility of new alloys tailored for use in hydrogen related applications.

Last year we focused our attention on identifying and characterizing the mechanisms by which hydrogen induces fracture in microalloy steels B and D. We used FIB machining to lift out sections underneath the fracture surfaces in order to examine whether hydrogen-induced fracture follows a crystallographic cleavage plane or a slip plane. We carried out finite element calculations of transient hydrogen transport simulating hydrogen uptake and transport through an axial crack on the inner diameter surface of a pipeline, and determined through constraint fracture mechanics that the SENT specimen is the appropriate laboratory specimen for the study of the fracture resistance of a pipeline.

Approach

Our approach integrates mechanical property testing at the microscale, microstructural analyses and TEM observations of the deformation processes of materials at the micro- and nano-scale, first principle calculations of interfacial cohesion at the atomic scale, and finite element modeling and simulation at the micro- and macro-level.

To understand the hydrogen-induced fracture processes, we use high resolution SEM with three-dimensional (3-D) visualization and TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining. In order to come up with fracture criteria for safe pipeline operation under hydrogen pressures of at least 15.0 MPa, we investigate the interaction of hydrogen transient transport kinetics with material elastoplastic deformation ahead of an axial crack either on the inside diameter or the outer diameter surface of a pipeline. Using finite element simulations of the hydrogen transport in the neighborhood of the crack tip, we explore the transient and steady-state hydrogen population profiles and how their development influences the fracture processes/events.

To quantitatively describe the hydrogen effect on internal material cohesion as a function of the hydrogen concentration under transient hydrogen conditions, we devised a thermodynamic theory of decohesion at internal material interfaces such as grain boundaries, precipitate/matrix, and second-phase/matrix interfaces. We used first-principles calculations of the hydrogen effect on these interfaces, which constitute potential fracture initiation sites, to calibrate the parameters of the thermodynamic theory such as the ratio of the reversible work of separation in the presence of hydrogen to that in the absence of hydrogen. The information for the fracture mechanisms from the experiments and the hydrogen concentration profiles from the

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[1] Steel B is a typical low carbon (0.05% by wt) Mn-Si-single microalloy API/Grade X70/X80 capable of producing a ferrite/acicular microstructure. The alloy was found to perform well in sour natural gas service.

[2] Steel D is a typical low carbon (0.03% by wt) Mn-Si-single microalloy API/Grade X60, a predominantly ferrite microstructure with some pearlite. The alloy was found to perform very well in sour natural gas service.

simulations help to establish the regime of critical hydrogen concentrations and critical elapsed time for a crack to remain stable under high hydrogen pressure. Quantitatively this is assessed through the development of engineering fracture criteria in terms of macroscopic parameters.

Results

Identification and Characterization of the Fracture Mechanisms

The study of the fractured surfaces of our compact tension specimens using optical and SEM analyses revealed that hydrogen-induced fractures are distinctly different from the overload fractures in the absence of hydrogen. Figure 1 shows the SEM images of B and D type steels where the direction of the cracks was from bottom to top. In the fracture of these materials, the ductile fracture features such as microvoid nucleation, growth, and coalescence process expected for low and medium strength pipeline steels are not clearly identifiable.

In order to understand the fracture processes, we use high resolution SEM with 3-D visualization and TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining (see 2009 annual progress report). This technique can identify microstructural features such as grain boundaries and secondary phases such as carbides immediately below the fracture surface.

Examination of the fracture surfaces reveals several distinct morphologies such as precipitate nucleated failure, feathery region, ductile ridges, and flat fracture features. It is concluded that except for the precipitate nucleated failure, these features are not due to any compositional variation. The high-resolution SEM image (Figure 2b) of the feathery morphology (Figure 2a) reveals the presence of “saw-teeth” on top of the ridges and no evidence of precipitates at the ridges. These ridges are reminiscent of “saw-teeth” formed on final separation of thin sections as can be seen in Figure 2c for Cu-3%Co alloy deformed in situ in TEM. The presence of such ridges (Figure 2b) suggests plastic processes [1].

Certainly, our research so far points away from the traditional and vague designation of the fracture processes as quasi-cleavage – this is the designation frequently used when the fracture surface appearance is neither clearly ductile nor clearly cleavage and the underlying fracture mechanism is not understood. In fact, the 3-D visualization of the fracture topography (January-March 2010 trimester report) demonstrates clearly the absence of cleavage characteristics and confirms the ridge formation. Feature height

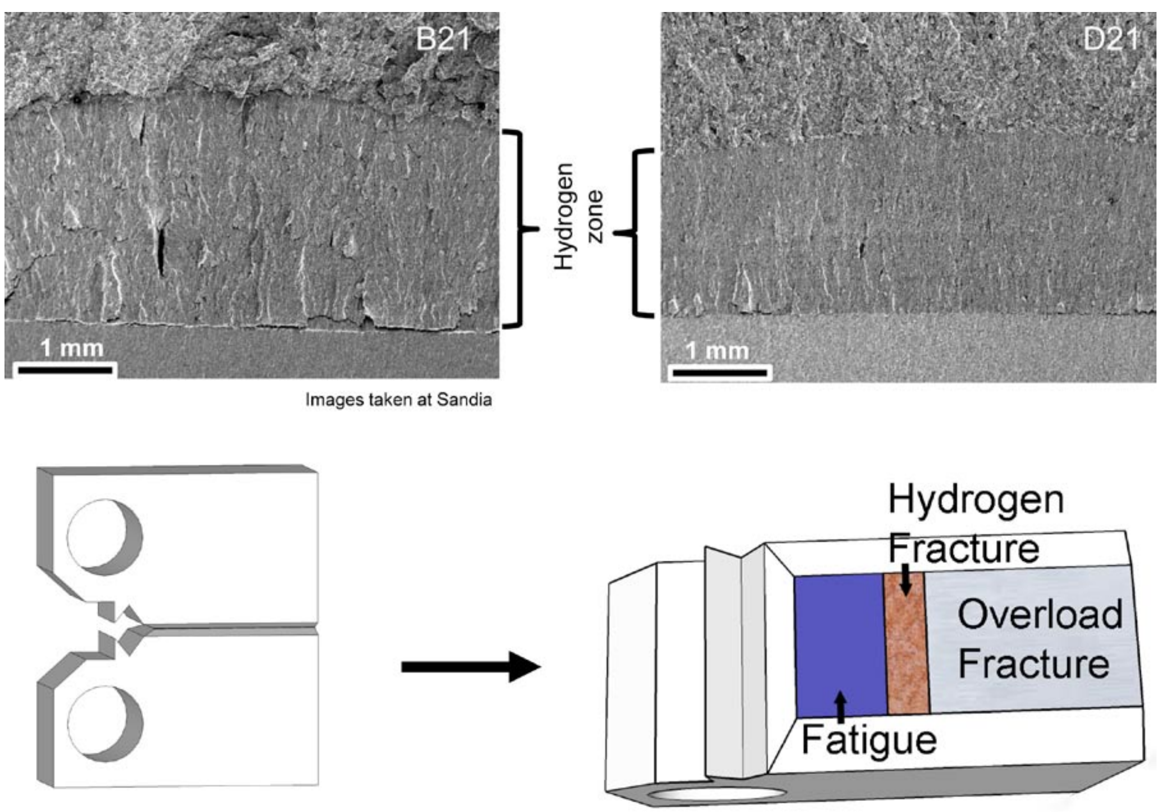

FIGURE 1. Wide-view SEM of compact tension specimens made from B and D type steel samples and fractured in 3 ksi hydrogen gas.

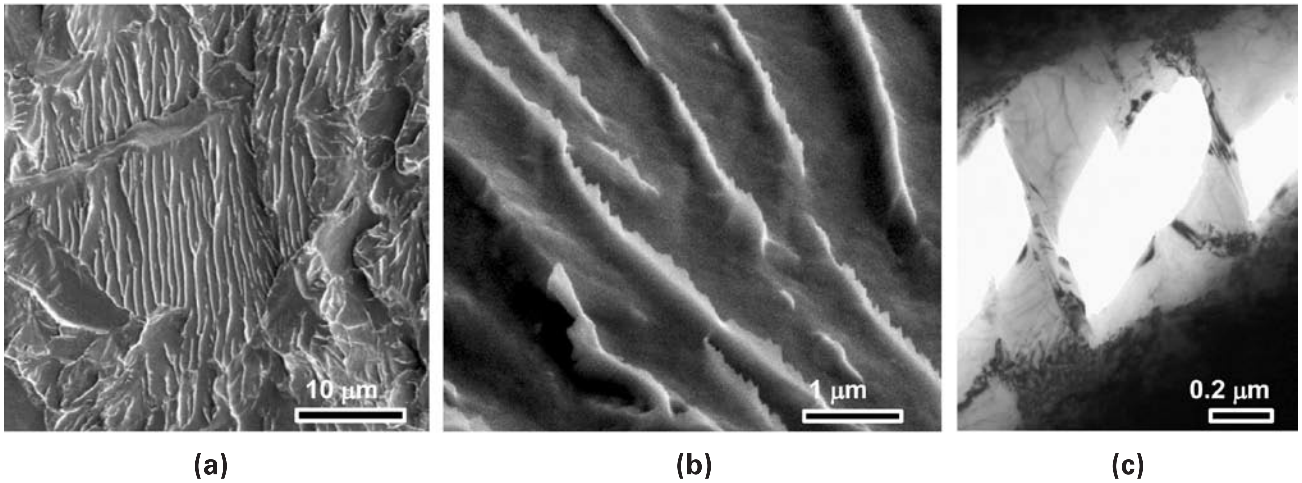

FIGURE 2. a) Select area of a fracture surface showing the features typical of a quasi-cleavage surface; b) high resolution SEM image showing the "saw-teeth" on top of the ridges. These are reminiscent of "saw-teeth" formed on final separation of thin sections in the transmission electron microscope; c) TEM image of in situ fractured Cu-3%Co alloy revealing saw-teeth due to final tearing (image c courtesy of G.C. Liu).

measurement shows that ridges are protrusions of approximately 400 nm. In particular, TEM analysis of the lift-out section beneath the fracture surface (Figure 3) shows slip bands parallel to ridge edges, suggesting a fracture mechanism completely governed by dislocation slip. In fact, enhanced and confined slip activity is consistent with the hydrogen enhanced local plasticity mechanism [2]. This year's discovery requires the development and introduction of a new component in our model of the hydrogen-deformation interaction which is the subject of ongoing work.

The identification and characterization of the precise mechanism of hydrogen-induced fracture in pipeline steel materials serves all objectives of the project.

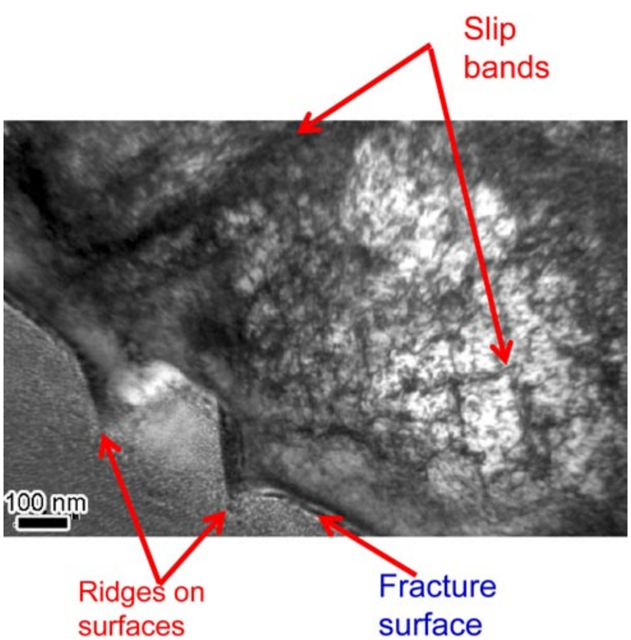

FIGURE 3. Electron micrograph showing the microstructure immediately beneath the ridges on the fracture surface. Two ridges on the fracture surface are evident. Image shows slip bands parallel to ridge edges, suggesting that quasi-cleavage is not a cleavage like process but is related to dislocation slip.

Micro- and Macro-Modeling and Simulation

We used our hydrogen-transport/material-deformation simulation tool (see 2009 annual progress report) to investigate for the first time issues of environmental similitude which is a key requirement for the transferability of fracture toughness results from laboratory specimens to a real-life pipeline.

We solved the initial/boundary-value problem for transient hydrogen diffusion coupled with material elastoplasticity in an SENT specimen embedded in a hydrogen atmosphere with a shallow crack under tension load. The dimensions of the specimen and the applied tension load were chosen such that the cracks in the SENT specimen and pipeline were subjected to the same stress intensity factor K_I and T-stress for a given hydrogen pressure which is the hydrogen transport pressure.

The stress and deformation fields close to the crack tip for the SENT specimen and the pipeline structure are shown in Figure 4. In view of the fact that the stress intensity factor and T-stress for the SENT specimen and the pipeline are the same, the associated stress and deformation fields near the crack tips are almost identical. This ensures mechanical transferability of the fracture resistance results obtained from the SENT specimen. Superposed on Figure 4 are the normalized normal interstitial lattice sites (NILS) hydrogen concentrations C_L/C_0 ahead of the crack tip from the hydrogen transport solutions for the SENT specimen and pipeline for two different boundary conditions respectively on the remote boundaries and outer diameter surface: zero flux and zero NILS hydrogen concentration. One can clearly see that the hydrogen concentration profiles for the two solutions (SENT specimen and pipeline) are extremely close with a deviation of only about 2% between the two solutions at the location of the peak NILS hydrogen concentration. Hence, one can state that environmental transferability is also warranted [3].

We are continuing on with the modeling and simulation of the rising load fracture toughness tests performed at the Sandia National Laboratories on steel types B and D. In this test, the load on the fracture specimen which is embedded in a hydrogen environment is increased at a constant stress intensity factor rate. The test is used to determine the "initiation threshold", a very important parameter which denotes the critical stress intensity factor for the onset of crack propagation in hydrogen containing vessel.

The simulations described in this section are meeting all objectives of our project.

Conclusions and Future Directions

- In collaboration with Sandia National Laboratories, we carried out fracture testing of promising micro-alloyed, low-carbon steel microstructures. Using FIB machining, high-resolution SEM, and TEM studies, we discovered that the hydrogen-induced failure mechanism in these steels is hydrogen induced localized plasticity. In particular, we found that the fracture process is governed by intense slip activity despite the fact that the fracture surfaces have the appearance of what is known to be quasi-cleavage type of fracture. In fact, our research establishes that quasi-cleavage is a mode of fracture fully controlled by ductile processes.
- We will model the discovered mechanism of failure and implement the result in our finite element codes to simulate and predict onset of crack propagation under gaseous hydrogen transport at fixed pressure (static conditions). The predictions will be compared with results from rising load fracture toughness testing. This will lead to the development of a fracture criterion for pipeline safe operation in terms of the hydrogen pressure, geometric, and material characteristics of the pipeline. Next, we will carry out fatigue fracture testing and modeling for damage tolerance assessment under cyclic pressure conditions.
- Carrying out hydrogen transport simulations coupled with material deformation, we demonstrated that the fields in the SENT specimen exhibit mechanical and environmental similitude to those ahead of an axial crack in a pipeline. Therefore the SENT specimen can be used to reliably assess the fracture resistance of pipeline steels.
- We continue our collaboration with the Hydrogen National Institute for Use and Storage (HYDROGENIUS) of Japan. We participate in the annual meetings of automobile Industry of Japan (Toyota, Honda, Nissan) on Hydrogen Technology Standards.

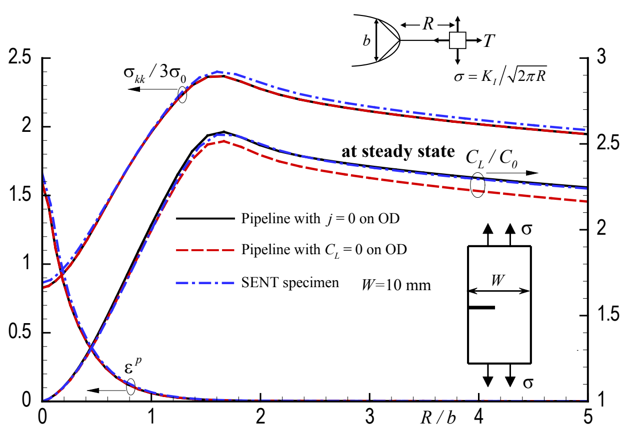

FIGURE 4. Comparison between the SENT specimen solution and the full-field pipeline solution along the axis of symmetry ahead of the crack tip for the normalized hydrostatic stress $\sigma_{kk}/3\sigma_0$, plastic strain ε^p, and the normalized hydrogen concentrations C_L/C_0 under equilibrium conditions of hydrogen transport in the SENT specimen and impermeable or outgassing outer diameter surface in the pipeline. The parameter b which equals 7.13 μm for the pipeline and 7.08 μm for the SENT specimen denotes the crack tip opening displacement.

Special Recognitions & Awards/Patents Issued

1. P. Sofronis visited Japan from June 9 to June 25, 2006 as a fellow of the Japan Society for the Promotion of Science (JSPS) to collaborate on research related to hydrogen/material compatibility.
2. P. Sofronis and I. Robertson were invited speakers at the *International Hydrogen Energy Development Fora* organized by HYDROGENIUS at Fukuoka, Japan on January 31 - February 1, 2007, February 4-8, 2008, February 4-6, 2009, and February 3-4, 2010.
3. Sofronis was elected a fellow of the American Society of Mechanical Engineers (ASME) for his contributions to the field of hydrogen embrittlement.

FY 2010 Publications/Presentations

Publications

1. (invited) Robertson, I.M., Sofronis, P., and Birnbaum, H.K. (2009) "Hydrogen effects on plasticity," In J.P. Hirth and L. Kubin, Editors: "Dislocations in Solids," Vol. 15, pp. 249-293, Elsevier, The Netherlands: North Holland.

2. (invited) Dadfarnia, M., Somerday, B.P., Sofronis, P., Robertson, I.M., Stalheim, D. (2009) "Interaction of Hydrogen Transport and Material Elastoplasticity in Pipeline Steels," Journal of Pressure Vessel and Technology, 131, 041404.

3. Dadfarnia, M., P., Sofronis, B. Somerday, I, Robertson (2009) Effect of remote hydrogen boundary conditions on the near crack-tip hydrogen concentration profiles in a cracked pipeline, In: Materials Innovations in an Emerging Hydrogen Economy, G.G. Wicks and J. Simon, editors, The American Ceramic Society, Ceramic Transactions, Volume 202, pp. 187-199.

4. Sofronis, P., M. Dadfarnia, P. Novak, R. Yuan, B. Somerday, I.M. Robertson, R.O. Ritchie, T. Kanezaki, and Y. Murakami (2009) "A Combined Applied Mechanics/Materials Science Approach Toward Quantifying the Role of Hydrogen on Material Degradation," Proceedings of the 12th Intl. Conf. on Fracture, Ottawa, Canada, 2009.

5. Sobotka, J.C., Dodds, R. Jr., and Sofronis, P. (2009) "Effect of Hydrogen on Steady, Ductile Crack Growth: Computational Studies," International Journal of Solids and Structures, 46, 4095-4106.

6. Dadfarnia, M., Novak, P., Ahn, D.C., Liu, J.B., Sofronis, P., Johnson, D.D., and Robertson, I.M. (2010). "Recent Advances in the Study of Structural Materials Compatibility with Hydrogen," Advanced Materials, v. 22, 1128-1135.

7. Robertson, I.M., Fenske, J., Martin, M., Bricena, M., Dadfarnia, M., Novak, P., Ahn, D.C., Sofronis, P., Liu, J.B., Johnson, D.D. (2010) "Understanding How Hydrogen Influences the Mechanical Properties of Iron and Steel." In Proceedings of the 2nd International Symposium on Steel Science.

8. Stalheim, D., Boggess, T., San Marci, C., Jansto, S., Somerday, B., Muralidharan, G., Sofronis, P. (2010) Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen, Proceedings of IPC 2010 8th International Pipeline Conference, September 27 – October 1, 2010, Calgary, Alberta, Canada.

9. Martin, M., Fenske, J., Sofronis, P., Robertson, I.M. (2010), On the Formation and Nature of Quasi-Cleavage Fracture Surfaces in Hydrogen Embrittled Steels, Acta Materialia, to be submitted.

Presentations

1. Sofronis, P. (invited) "Materials for the Hydrogen Economy: Embrittlement and Remediation," 45th Annual Technical Meeting, Society of Engineering Science, Urbana, Illinois, October 13–15, 2009.

2. Dadfarnia, M. "A Methodology for Studying Hydrogen Embrittlement in a Steel Pipeline ," 45th Annual Technical Meeting, Society of Engineering Science, Urbana, Illinois, October 13–15, 2009.

3. Sofronis, P. (invited) "On the Design of Steel Pipelines against Hydrogen Embrittlement," Third International Hydrogen Energy Development Forum, Hotel Okura, Fukuoka, Japan, Feb. 4, 2009.

4. Ritchie, R.O. and Sofronis, P. (invited) "Micro-Mechanical Modeling of Hydrogen-Induced Brittle Fracture," Third International Hydrogen Energy Development Forum, Hotel Okura, Fukuoka, Japan, Feb. 4, 2009.

5. Sofronis, P. (invited) "Assessing the Hydrogen Effect on Fracture: valid Fracture Testing," International HYDROGENIUS Symposium on Hydrogen-Materials-Interaction, Kyushu University, Fukuoka, Japan, Feb. 5, 2009.

6. Robertson, I.M. (invited) "Hydrogen and Grain Boundaries," International HYDROGENIUS Symposium on Hydrogen-Materials-Interaction, Kyushu University, Fukuoka, Japan, Feb. 5, 2009.

7. Sofronis, P. (invited) "Hydrogen-induced fracture: modeling and simulation." BP Company, Houston, TX, June 5, 2009.

8. Sofronis, P. (invited) "A Combined Applied Mechanics/Materials Science Approach toward Quantifying the Role of Hydrogen on Material Degradation." University of Pennsylvania, Department of Mechanical Engineering and Applied Mechanics, June 11, 2009.

9. Sofronis, P. (invited) "A Combined Applied Mechanics/Materials Science Approach toward Quantifying the Role of Hydrogen on Material Degradation." Brown University, Providence, RI, November 2, 2009.

10. Sofronis, P. (invited) "Hydrogen concentrations at crack tips: Implications for fracture." International HYDROGENIUS Symposium on Hydrogen-Materials-Interaction, Kyushu University, Fukuoka, Japan, Feb. 4, 2010.

12. Sofronis, P. (invited) "Application of Vitek's relationship between the plastic dissipation and the work expended on brittle decohesion to the understanding of hydrogen-induced intergranular cracking" The Vasek Vitek Honorary Symposium on Crystal Defects, Computational Materials Science and Applications: Mechanical Properties" 139th TMS Meeting and Exhibition, Seattle, Washington, Feb. 16, 2010.

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1. Martin, M., Fenske, J., Sofronis, P., Robertson, I.M. (2010), On the Formation and Nature of Quasi-Cleavage Fracture Surfaces in Hydrogen Embrittled Steels, Acta Materialia, to be submitted.

2. Robertson, I.M. (2001) "The effect of hydrogen on dislocation dynamics," Engineering Fracture Mechanics, 68(6), pp. 671-692.

3. Dadfarnia, M., Sofronis, P., Somerday, B.P., Balch, D.K., Schembri, P., Melcher, R.J. (2010) On the Environmental Similitude for Fracture in the SENT Specimen and a Cracked Hydrogen Gas Pipeline, Engineering Fracture Mechanics, Under review.