# III.12 A Combined Materials Science/Mechanics Approach to the Study of Hydrogen Embrittlement of Pipeline Steels

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## Fiscal Year (FY) 2011 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 (due to in-line compressors).
- 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (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 and suggest possible new hydrogen-compatible material microstructures for hydrogen delivery. These studies meet the following DOE technical targets for Hydrogen Delivery as mentioned in Table 3.2.2 of the 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).

## FY 2011 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.

[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.

- Identified the microstructure of pipelines steels through optical analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and identified particle composition through energy dispersive spectroscopy (EDS) 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 model for predicting hydrogen-induced fracture on the basis of the fracture mechanism acting at the microscale.
- Investigated the mechanism of fatigue fracture of 304 and 316 stainless steel in a hydrogen environment through FIB/TEM analysis. Unique localized martensitic lath bands were identified underneath the fracture surface.
- 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.

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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.

We focused our effort on analyzing the fracture mechanisms of two promising steel microstructures (microalloy steels B and D) with large fracture resistance to hydrogen degradation. We also advanced our studies of the fracture mechanisms of 304 and 316 stainless steel samples fatigued in a hydrogen environment. Accounting for the identified hydrogen-induced fracture mechanisms, void growth at slip band intersection, we employ a tested model of the hydrogen-deformation interactions to develop a simulation tool for pipeline crack behavior with predictive capabilities.

## 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. We investigate the interaction of hydrogen transient transport kinetics with material elastoplastic deformation ahead of an axial crack either on the internal diameter (ID) or outer diameter (OD) 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.

## Results

### Identification and Characterization of the Fracture Mechanisms

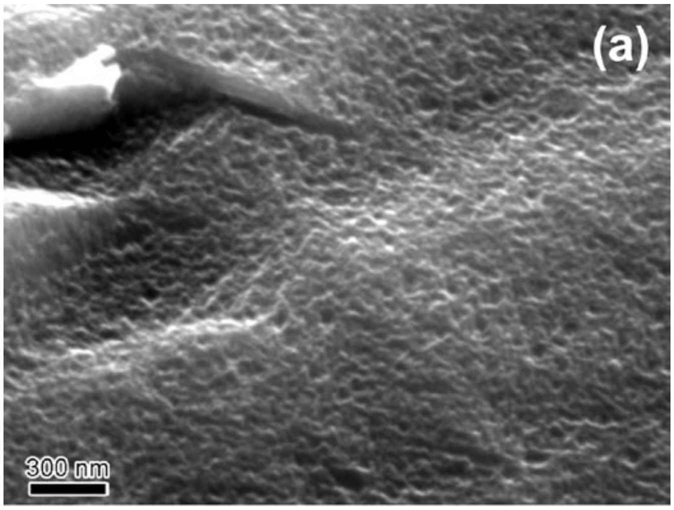
The study of the fractured surfaces of our compact tension specimens of B and D type steels revealed several distinct morphologies (such as feathery region, ductile ridges, and featureless flat areas) which were not observed in the overload fracture of compact tension specimens in the absence of hydrogen. The feathery region and ductile ridges were analyzed (see 2010 annual progress report) using high resolution SEM, 3-D visualization, and TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining. The analysis suggested that hydrogen-induced fracture mechanism is governed by dislocation slip activity [1].

In order to understand the fracture processes, we further studied the featureless flat regions of the fractured surfaces. The 3-D visualization demonstrated that the featureless surfaces are not really flat but are undulating. Figure 1a shows the high resolution SEM image of the flat surfaces. The micrograph reveals that those undulations are covered with very small rounded mounds. The roughness of the surfaces is confirmed by atomic force microscopy measurements. Our TEM analysis of the lift-out sections beneath the featureless flat regions shows enormously high dislocation densities (Figure 1b). These observations demonstrably confirm that severe plastic processes control the fracture of these pipeline steels in a hydrogen environment [2].

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

### Identification and Characterization of Fatigue Mechanisms

Along with the characterization of specimens fractured under monotonic or static loading, similar analysis was carried out for 304 and 316 stainless steel samples fatigued



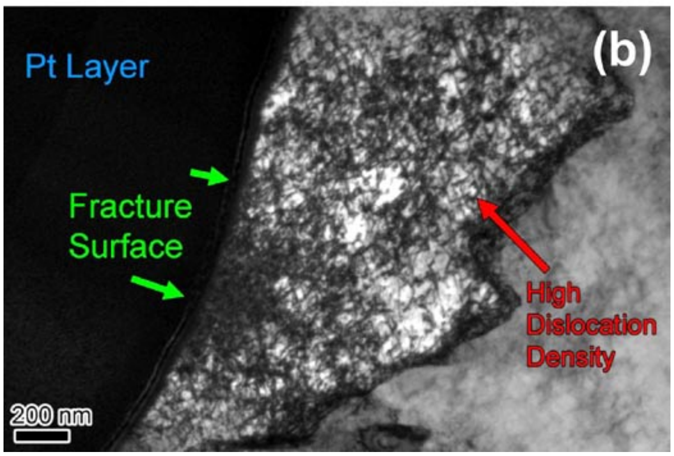




**FIGURE 1.** a) High-magnification SEM image of flat feature which shows that the flat surface in actuality is heavily dimpled. b) TEM micrograph showing the microstructure immediately beneath the flat features on the fracture surface. Image shows a high dislocation density suggesting that the fracture process is related to dislocation slip. The grains below the one shown have similar dislocation densities suggesting plasticity occurred not just immediately below the fracture surface.

in a hydrogen environment. Figure 2 shows the striations on the fractured surface which mark the progression of the fatigue crack with cycling. TEM analysis of sample extracted perpendicular to striations shows three sets of intersecting deformation bands (Figure 3). A large amount of plastic deformation, both in the bands and in the matrix, is visible. It appears that the bands intersect the surface at the striations, but further analysis is needed to confirm this. Diffraction analysis suggests that these bands are martensite laths which are localized closer to the crack tip with increasing hydrogen. This would suggest that with increasing hydrogen, martensite formation is localized closer to crack tip and produced in finer laths, which would be less visible to techniques such as electron backscatter diffraction. This is in agreement with the results of Mine et al. [3] who

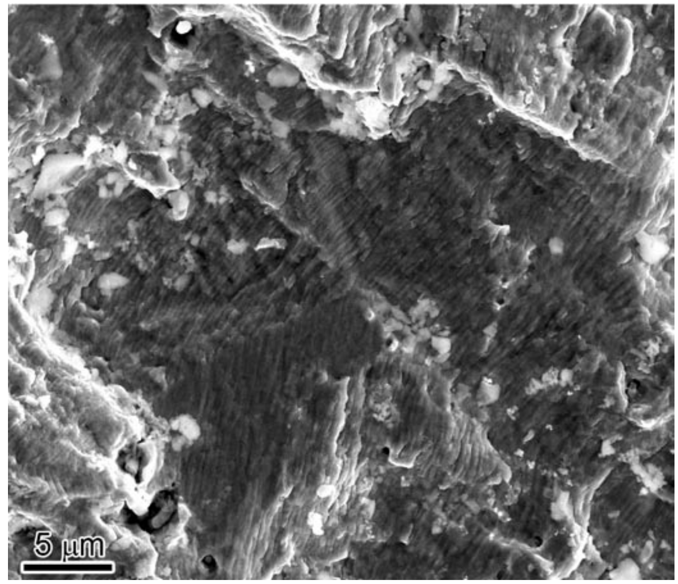



**FIGURE 2.** SEM image showing striations, a typical feature on fatigue surfaces, on the fracture surface of a 304 stainless steel sample fatigued under hydrogen atmosphere. A sample was extracted perpendicular to the marking and examined in the TEM.

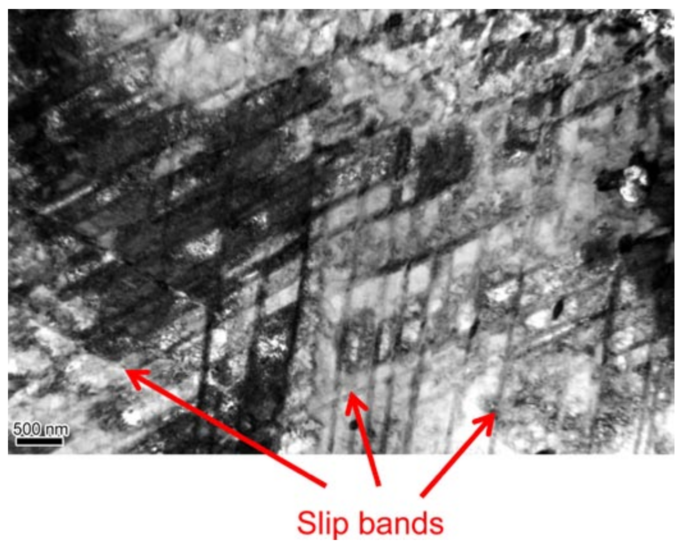



**FIGURE 3.** TEM micrograph showing the microstructure immediately beneath the fatigue fracture surface. The intersecting sets of deformation bands are visible. These features continue for several microns below the fracture surface.

observed the decrease in deformation induced martensite with increasing hydrogen saturation.

To further understand this phenomenon, we are investigating samples extracted by the FIB in a different way. From fatigued but unfractured specimens of the 304 and 316 steels, samples were extracted perpendicular to the polished surface and perpendicular to the crack in locations identified to likely be similar to the striations observed on the fracture surface. This method will enable the observation of the microstructure directly ahead of the crack tip and possibly confirm that the microstructure is universal.

### Micro- and Macro-Modeling and Simulation

The hydrogen-induced fracture mechanism of B and D type of steel pipelines under rising load has been identified as void nucleation and growth at slip band intersections [1]. We use a continuum mechanics description of the dislocation slip bands to investigate the conditions for a microcrack and then a void to be formed at slip band intersections in the hydrogen environment ahead of a crack tip.

We model the process by simulating the pile-up formation and interaction as shown in Figure 4. The simulation involves hydrogen-induced increased dislocation activity and interaction of dislocations with the applied load. We assume that fracture occurs when the energy of the system with a void forming at the intersection of the pile-ups is less than the energy in the absence of the void. The insertion of a void is considered energetically expensive due to the surface energy creation. We designate the stress intensity factor at which void formation occurs as a descriptor of the fracture resistance of the material to hydrogen embrittlement. This is one of the main project objectives, that is, to come up with a fracture criterion for these steels that is predicated on the underlying fracture mechanism acting at the microscale. The predictions will be compared with results obtained at Sandia Laboratories from rising load fracture toughness testing with B and D steels.

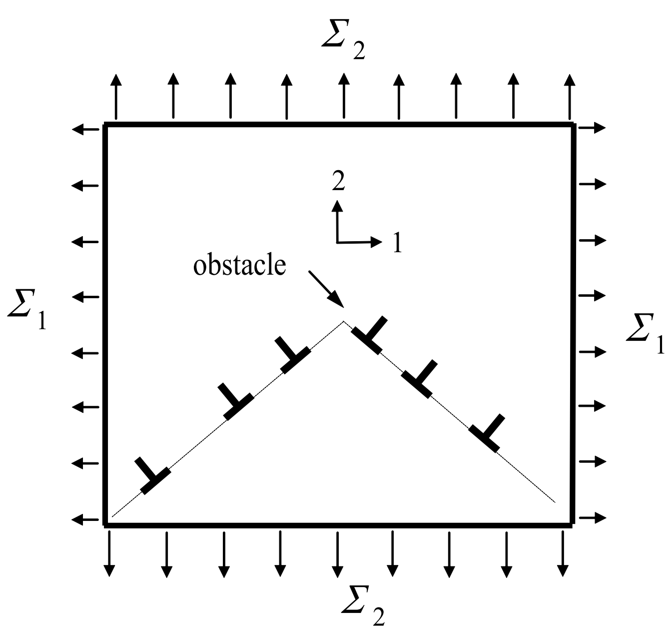



**FIGURE 4.** Schematic of the unit cell used for the modeling of the microcrack/void formation at the intersection of pile-ups. The cell is under applied macroscopic stress characteristic of the crack tip stress environment.

In order to understand the hydrogen/fatigue interactions, we developed a crystal plasticity constitutive model that accounts for the effect of hydrogen on the activation and operation of the slip systems. The face-centered cubic material version of the model has been implemented in the general purpose finite element code ABAQUS through a User Material subroutine. We are investigating the response of a crack whose tip is within a single grain to understand the material's response under cyclic loading. The development of a criterion for hydrogen-induced fatigue onset is also a central objective of our project.

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. Our TEM analysis of lift-out sections beneath the fracture surface shows slip bands parallel to ridge edges, suggesting a fracture mechanism completely governed by dislocation slip. Such enhanced and confined slip activity is consistent with the hydrogen-induced localized plasticity mechanism for hydrogen embrittlement. This discovery of intense hydrogen-induced slip band formation also leads to the recognition that the coining of the term "quasi-cleavage" is misleading as it denotes cleavage events for a fracture that is controlled clearly by dislocation processes.
- In collaboration with the International Institute for Carbon Neutral Energy Research and the Institute for Hydrogen Industrial Use and Storage of Japan, we performed fatigue testing of stainless steel specimens in hydrogen environment. We analyzed the microstructure beneath the fracture surface and identified localized martensitic lath bands. This fatigue fracture testing is used for the damage tolerance assessment under cyclic pressure conditions.
- We model the discovered mechanism of failure, void nucleation and growth at slip band intersections, 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 results have been used to develop a fracture criterion for pipeline safe operation in terms of the hydrogen pressure, geometric, and material characteristics of the pipeline.
- We continue our collaboration with the International Institute for Carbon Neutral Energy Research and the Institute for Hydrogen Industrial Use and Storage of Japan. We participate in the annual meetings of the automobile Industry of Japan (Toyota, Honda, Nissan) on hydrogen technology standards.

## Special Recognitions & Awards

**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. M. 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, February 3–4, 2010, February 2-3, 2011.

**3.** P. Sofronis was elected to a fellow of the American Society of Mechanical Engineers (ASME) for his contributions to the field of hydrogen embrittlement.

**4.** P. Sofronis and I. M. Robertson received the 2011 Delivery Team Award from the Hydrogen and Fuel Cells Program of the U.S. Department of Energy.

## FY 2011 Publications/Presentations

### Publications

**1.** 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 2$^{nd}$ International Symposium on Steel Science.

**2.** 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 8$^{th}$ International Pipeline Conference, September 27 – October 1, 2010, Calgary, Alberta, Canada.

**3.** Martin, M., Fenske, J., Sofronis, P., Robertson, I.M. (2011), On the Formation and Nature of Quasi-Cleavage Fracture Surfaces in Hydrogen Embrittled Steels, Acta Materialia, 59 (4), 1601-1606.

**4.** Martin, M., Robertson, I.M., Sofronis, P. (2011) Interpreting Hydrogen-Induced Fracture Surfaces in Terms of Deformation Processes–A New Approach, Acta Materialia, 59 (9), 3680-3687.

**5.** Dadfarnia, M., Sofronis, P., Somerday, B.P., Balch, D.K., Schembri, P., and Melcher, R.J., (2011) On the Environmental Similitude for Fracture in the SENT Specimen and a Cracked Hydrogen Gas Pipeline, Engineering Fracture Mechanics, 78(12), 2429-2438.

**6.** Dadfarnia, M., Sofronis, P., Somerday, B.P., Balch, D.K., and Schembri, P. (2011) Degradation Models for Hydrogen Embrittlement. In: "Gaseous Hydrogen Embrittlement of High Performance Metals in Energy Systems." eds. R.P. Gangloff and B.P. Somerday.

### Presentations

**1.** Martin, M.L., Robertson, I.M., Somerday, B., San Marchi, C., and Sofronis, P. (2010) Multi-scale Investigation of Hydrogen-Assisted Failure of X60 Pipeline Steel, Platform Talk, Microscopy and Microanalysis 2010 Meeting, August 1–5, 2010, Portland, OR.

**2.** Dadfarnia, M., Sofronis, P., Somerday, B.P., Balch, D.K., and Schembri, P. (2010) On Modeling Hydrogen-Induced Sustained-Load Intergranular Cracking, 47$^{th}$ Annual Technical Meeting, Society of Engineering Science, Ames, Iowa, October 4–6, 2010.

**3.** Martin, M.L., Robertson, I.M., Somerday, B., San Marchi, C., and Sofronis, P. (2010) Multi-scale Investigation of the Hydrogen-Assisted Failure of X60 Pipeline Steel, Platform Talk, Materials Science and Technology 2010 Conference and Exhibition, October 17–21, Houston, TX.

**4.** Dadfarnia, M. and Sofronis, P. (2011) Understanding Brittle Fracture in the Presence of Plasticity, ExxonMobil Research and Engineering Company, January 25, Clinton, NJ.

**5.** Dadfarnia, M., Martin, M., Sofronis, P., Robertson, I.M., Somerday, B.P., Balch, D.K., and Schembri, P. (2011) Mechanisms and Models of Hydrogen-Induced Cracking, HYDROGENIUS and I$^2$CNER Research Symposium, Fukuoka, Japan, February 3, 2011.

**6.** Sofronis, P., Dadfarnia, M., Martin, M.L., Robertson, I.M. (2011) Micromechanics of Hydrogen-induced Fracture: from Experiments and Modeling to Prognosis, Invited presentation in the 2011 Hydrogen Metal Systems Gordon Research Conference, Stonehill College, Easton, Massachusetts, July 17–22.

**7.** Martin, M.L., Robertson, I.M., Sofronis, P., and Murakami, Y. (2011) A Microstructural Based Understanding of Hydrogen-Enhanced Fatigue of Stainless Steels, Platform Talk, Materials Science and Technology 2011 Conference and Exhibition, Accepted for presentation in October 16, Columbus, OH.

## References

**1.** Martin, M., Fenske, J., Sofronis, P., Robertson, I.M. (2011), On the Formation and Nature of Quasi-Cleavage Fracture Surfaces in Hydrogen Embrittled Steels, Acta Materialia, 59 (4), 1601-1606.

**2.** Martin, M., Robertson, I.M., Sofronis, P. (2011) Interpreting Hydrogen-Induced Fracture Surfaces in Terms of Deformation Processes–A New Approach, Acta Materialia, 59 (9), 3680-3687.

**3.** Mine, Y., Narazaki, C., Murakami, K., Matsuoka, S., Murakami, Y. (2009) Hydrogen Transport in Solution-Treated and Pre-strained Austenitic Stainless Steels and Its Role in Hydrogen-Enhanced Fatigue Crack Growth, International Journal of Hydrogen Energy, 34, 1097-1107.