III.A.5 Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation

P. Sofronis (Primary Contact), I. M. Robertson, D. D. Johnson
University of Illinois at Urbana-Champaign
Department of Materials Science and Engineering
1304 West Green Street
Urbana, IL 61801
Phone: (217) 333-2636; Fax: (217) 244-6534
E-mail: sofronis@uiuc.edu

DOE Technology Development Manager: Mark Paster
Phone: (202) 586-2821; Fax: (202) 586-9811
E-mail: Mark.Paster@ee.doe.gov

DOE Project Officer: Jill Gruber
Phone: (303) 275-4961; Fax: (303) 275-4753
E-mail: Jill.Gruber@go.doe.gov

Contract Number: To be determined

Start Date: May 1, 2005
Projected End Date: March 4, 2009

Objectives

- Develop mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise a fracture criterion for safe and reliable pipeline operation under hydrogen pressures of at least 7 MPa and loading conditions both static and cyclic (due to in-line compressors).
- 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, and/or coatings, or other materials to provide safe and reliable hydrogen transport and 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 (3.2.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines
(F) Hydrogen Delivery Infrastructure Storage Costs
(H) Storage Tank Materials and Cost
(I) Hydrogen Leakage
(J) Safety, Codes and Standards, Permitting and Sensors

Technical Targets

This project is conducting fundamental studies of hydrogen embrittlement of materials. Based on the understanding of the degradation mechanism, 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. protective coatings) to remediate hydrogen-induced degradation. These studies meet the following DOE 2010 hydrogen storage targets as mentioned in Table 3.2.2 of the March 2005 version of the HFCIT Program Multi-Year RD&D Plan:

- Pipelines Transmission and Distribution: Reliability relative to hydrogen embrittlement concerns and integrity. The project's goal is to develop a fracture criterion against hydrogen-induced degradation.
- Pipelines Transmission: Total capital cost will be optimized through pipeline engineering design based on failure criteria with predictive capabilities.
- Pipelines Distribution: Same cost optimization as above.

Accomplishments

- Developed a finite element code for the study of transient stress-driven hydrogen transport coupled with large strain material elastoplastic deformation.
- Designed a hydrogen permeation measurement system.
- Measured the macroscopic flow characteristics of three new, possibly compatible material microstructures.
- Validated ab-initio calculation code for decohesion energy calculations for the study of the effect of hydrogen on material interfacial cohesion.

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 this 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 in the new hydrogen economy and of the susceptibility of new alloys tailored for use in hydrogen related applications.

A hydrogen permeation rig has been built and the system is ready for permeation measurements to be carried out as a function of temperature. The hydrogen diffusion coefficient is an important parameter needed for the hydrogen transport analysis. Assuming a diffusion coefficient typical for pipeline steels, we carried out finite element calculations of transient hydrogen transport under plane strain conditions ahead of a crack tip simulating hydrogen uptake and transport in the interior surface of a pipeline. With regard to first-principles calculations for the study of hydrogen effects on internal material cohesion, we carried out several necessary validation "computer experiments" on the binding energies for H in Fe grain boundaries and free surfaces.

Approach

Our approach integrates mechanical property testing at the microscale, microstructural analyses and transmission electron microscopy 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.

In order to come up with a fracture criterion for safe pipeline operation under hydrogen pressures of at least 7.0 MPa we investigate the interaction of hydrogen transient transport kinetics with material elastoplastic deformation ahead of a crack tip. Understanding of this interaction requires the determination of the elastic and flow characteristics of pipeline materials in the presence of hydrogen, and the measurement in both pipeline steels and protective coatings of the hydrogen adsorption, permeability, and bulk diffusion characteristics, such as the nature and strength of microstructural trapping sites for hydrogen. These experimental data are used in finite element simulations of the hydrogen distribution ahead of a crack tip in an effort to understand the transient and steady state hydrogen population profiles. These profiles in conjunction with information from static fracture toughness, fatigue, and subcritical crack growth experiments will help to establish the regime of critical hydrogen concentrations and critical elapsed time for a crack to remain stable under high hydrogen pressure.

First-principles calculations and a thermodynamics methodology are used to calculate the reversible work of separation at precipitate/matrix or second phase/matrix interfaces as a function of the hydrogen concentration because such interfaces are expected to constitute potential fracture initiation sites. Such first-principles calculation results and thermodynamics-based cohesive criteria provide hydrogen-dependent traction-separation laws which in conjunction with the finite element simulation of the hydrogen concentration profiles ahead of a crack tip will allow for the development of engineering criteria in terms of macroscopic parameters for reliable pipeline and weld material operation in the presence of hydrogen.

Results

Experiment

Three micro-alloyed steel microstructures, termed A, B, and C hereafter, have been identified as promising for hydrogen compatibility. The flow-stress characteristics of these systems have been measured in the absence of hydrogen and the experimental results are shown in Figure 1. A hydrogen permeation rig has been built and the system is ready for permeation measurements to be carried out as a function of temperature. Specimens from steels A, B, and C, either as received or annealed, have been cut and prepared for the permeation experiments.

Micro- and Macro-Modeling, and Simulation

Finite element calculations of transient hydrogen transport have been carried under plane strain conditions ahead of a crack tip simulating hydrogen uptake and transport ahead of a crack tip in the interior surface of a pipeline (Figure 2). Hydrogen transport was simulated to initiate after the specimen was loaded

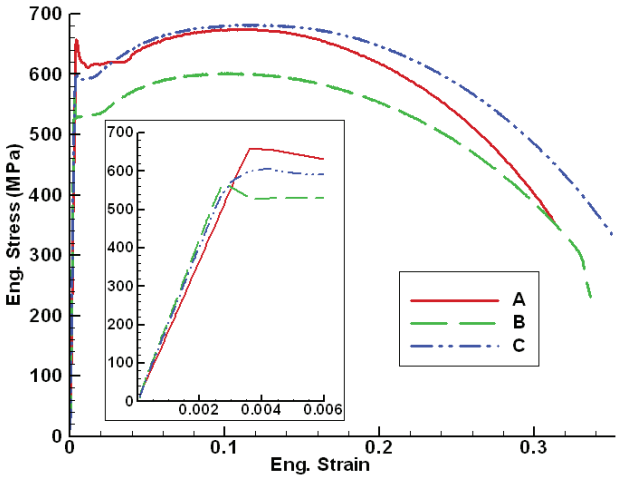

FIGURE 1. Stress-Strain Curves for Microalloy Steels A, B, and C

under small scale yielding conditions to an applied stress intensity factor of 55 MPa $m^{1/2}$. This type of transport environment simulates closely the conditions prevailing in subcritical crack growth experiments after a propagating crack has stopped when the applied stress intensity reached the threshold level. The numerical simulations were carried out for the C steel whose stress-plastic strain curve in uniaxial tension was modeled by a power law relationship. Figure 3 shows the comparison of the model curve with the experimental data as were extracted from Figure 1.

The simulations model transient hydrogen transport driven by hydrostatic stress and account for trapping of hydrogen at microstructural defects (dislocations) whose density increases with plastic straining. Hydrogen resides either at normal interstitial lattice sites (NILS) or reversible trapping sites at microstructural defects generated by plastic deformation. The two populations are always in equilibrium according to Oriani's theory. The governing equation for transient hydrogen diffusion accounting for trapping and hydrostatic-stress drift can be found in the work by Liang and Sofronis [1]. The material elastoplastic constitutive law in the presence of hydrogen accounts for the hydrogen lattice induced dilatation. It is evident that the hydrogen diffusion initial/boundary-value problem and the elastic-plastic boundary problem are fully coupled. Therefore, the problem of calculating the velocity field and the local distribution of hydrogen is coupled in a non-linear sense and the solution procedure involves iteration [1]. In the calculations, the hydrogen diffusion coefficient through the NILS at 300K was assumed to be 2.0 x 10^{-11} m^2/s. This value will be re-considered following the permeation measurements we plan in the experimental component of our project. It is noted though, that the assumed diffusion value reflects the nature of the ferritic microstructure in pipeline steels. The interstitial hydrogen expands the lattice isotropically and its partial molar volume in solution is 2.0 x 10^{-6} m^3/mole. It was considered that there is one trapping site per trap and the maximum NILS concentration is one hydrogen atom per solvent lattice atom. The trap density was assumed to increase with plastic straining according to the experimental results of Kumnick and Johnson [2] and the trap binding energy was 60 kJ/mole. As in the case of the diffusion coefficient, the nature and density of trapping sites will also be re-adjusted according to the anticipated experimental results from our permeation measurements and transmission electron microscopy (TEM) microstructural characterization. Uniform hydrogen concentration C_0 in the unstressed lattice in equilibrium with the hydrogen gas pressure was used as a boundary condition on the crack faces. For example, C_0=2.46 x 10^{-8} hydrogen atoms per solvent atom in the case of hydrogen gas at one atmosphere. A hydrogen-free lattice was assumed as an initial condition throughout the simulation domain just before diffusion initiated.

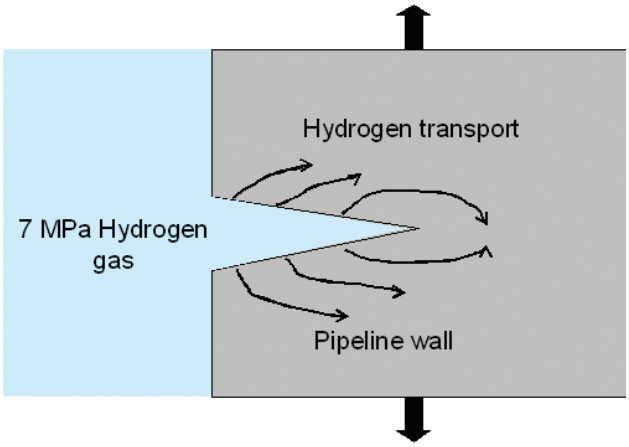

FIGURE 2. Schematic of Hydrogen Uptake through the Faces of a Crack in a Pipeline Wall

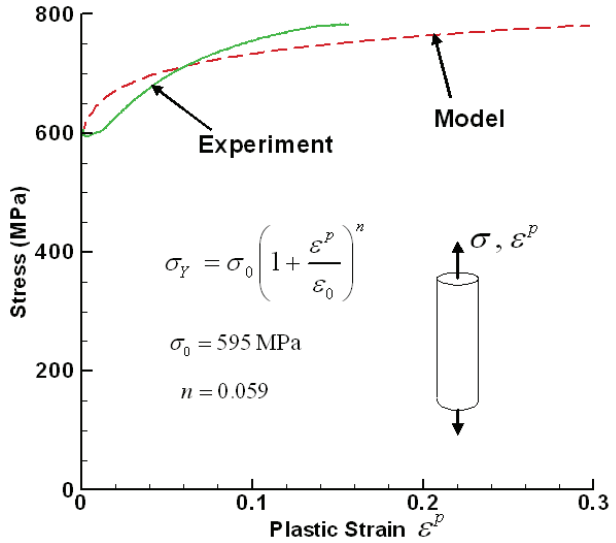

FIGURE 3. Stress-Strain Curve For Microalloy Steel C and the Material Properties used in the Simulation

Figure 4 shows the time evolution of the normalized NILS hydrogen concentration ahead of the crack tip as a function of the normalized distance R/b from the tip [3]. The parameter b=18.13 microns is the crack opening displacement associated with the applied load of 55 MPa $m^{1/2}$. The calculations show that a steady-state is reached after about 100 days from the initiation of hydrogen diffusion in the system. At this time, the maximum of the NILS profile coincides with the maximum of the hydrostatic stress peak location ahead of the crack tip. The contour plots of the normalized NILS hydrogen concentration near the crack tip at various times as the system evolves toward steady-state are shown in Figure 5. It can be considered, within a

good approximation, that the maximum concentration at the hydrostatic stress-peak location reaches its steady-state value in 20 days rather than 100 days as the difference in the corresponding concentrations is less than 2% (Figure 4). Notably, after 100 days, diffusing hydrogen solutes reach the outer boundary of the simulation domain – the size of the region in which the crack is embedded – located at 10 mm away from the crack tip whereas after 20 days they do not. In general, the exact time toward steady-state for the entire system does depend on the size of the simulation domain. The time to steady-state is of engineering significance as it sets an upper bound on the time period during which hydrogen embrittlement phenomena may take place after hydrogen absorption in the highly strained volume ahead of a crack tip.

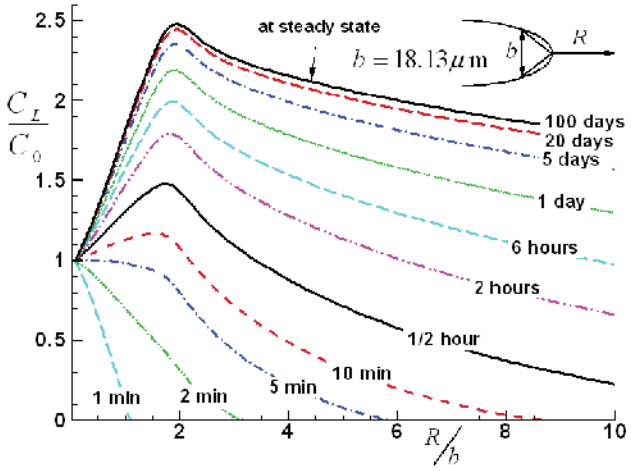

FIGURE 4. Plot of the normalized hydrogen concentration at NILS ahead of the crack tip as a function of the normalized distance from the tip at various times after hydrogen is adsorbed on the crack faces and begins to diffuse in the material. The normalizing concentration C_0 is the hydrogen concentration at the crack face in equilibrium with hydrogen gas.

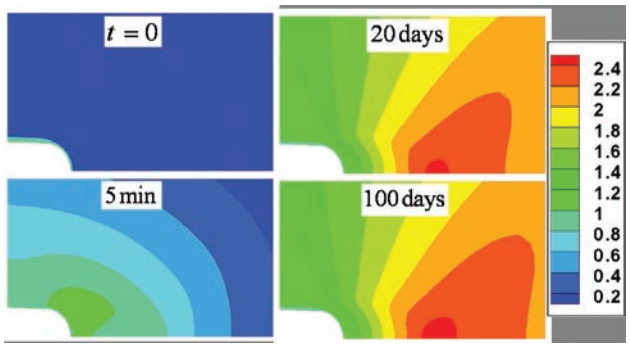

FIGURE 5. Contour plots of the normalized hydrogen concentration in normal interstitial lattice sites near the crack tip. The normalizing concentration is the hydrogen concentration at the crack face in equilibrium with hydrogen gas.

Figure 6 shows a contour plot of the normalized hydrogen concentration at trapping sites as they develop during the diffusion process toward steady-state. There is an intensification of trapped hydrogen populations at the crack tip due to the presence of a large number of trapping sites (dislocations) associated with the severe plastic straining at the root of the notch.

First-Principles Assessment of Hydrogen Effects on Interfacial Cohesion

First-principles (density-functional-theory) calculations, despite some drawbacks (e.g., small numbers of atoms and time intervals) can reveal unexpected phenomena and mechanisms, as well as quantitative trends. Central to the hydrogen embrittlement problem for existing pipeline steels is the decohesion (work to break surfaces apart) for the Fe/MnS precipitate interface as a function of hydrogen concentration, providing the H-dependent traction-separation law needed for the finite element modeling of the fracture initiation mechanism in the simulations described in the section above and revealing the effect of hydrogen on the interfaces during shearing.

We have completed several necessary validation "computer experiments" on the binding energies for H in Fe grain boundary and free surface using a pseudopotential based plane-wave method via projected-augmented wave basis functions, as implemented in the Vienna *ab initio* Simulation Package. A subset of our validation results provides unrelaxed binding energies for H in Fe for GB/FS equal to -3.23/-3.57 eV, and the binding energies difference of the GB and FS equal to +0.34 eV, in good agreement with values in literature [4].

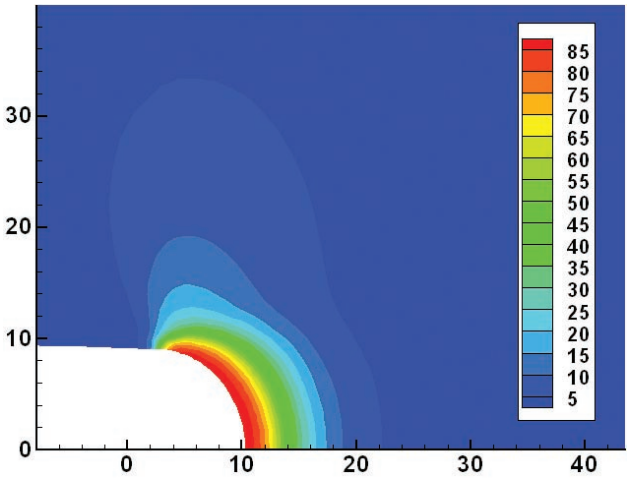

FIGURE 6. Contour plot of the normalized hydrogen concentration at trapping dislocation sites ahead of the crack tip at steady-state. The dimensions are in microns.

Conclusions and Future Directions

- A finite element code for transient hydrogen transport analysis ahead of a crack tip on the inside wall of a pipeline has been developed. The simulation accounts for stress driven diffusion through interstitial lattice sites and trapping of hydrogen at microstructural defects. We will determine possible correlations between time for steady-state hydrogen transport, applied stress intensity, specimen size, and material diffusivity in order to come up with an estimate of an expected upper limit on the incubation time for embrittlement.
- A permeation measurement apparatus has been built for diffusion coefficient measurements. Identification of the diffusion characteristics of existing and new pipeline steel microstructures will be carried out.
- Validated ab-initio calculations code for decohesion energy calculations for the study of the effect of hydrogen on material interfacial cohesion. We will determine the stresses to fracture and surface energies as a function of hydrogen coverage at various particle/matrix interfaces, such as Fe_3C/alpha-Fe and MnS/alpha-Fe interfaces.
- We will carry out fracture toughness testing along with scanning electron microscopy and TEM studies to identify the failure mechanisms and associated microstructural features in the presence of hydrogen.
- We will couple the hydrogen transport kinetics with the initiation of a fracture event at a crack tip, e.g. void growth and coalescence to devise a fracture criterion in terms of macroscopic parameters.

Special Recognitions & Awards/Patents Issued

P. Sofronis, received a fellowship award from the Japan Society for the Promotion of Science (JSPS) and visited Japan from June 9 to June 25, 2006 for collaboration on research related to hydrogen material compatibility.

FY 2006 Publications/Presentations

Publications

1. Y. Liang, D. C. Ahn, P. Sofronis, R. Dodds, and D. Bammann, "Hydrogen Effects on Void Growth and Coalescence in Metals and Alloys," submitted to *Mechanics of Materials*, under review.

2. Sofronis, P. and Robertson, I. M., "Viable Mechanisms of Hydrogen Embrittlement-A Review" To be published in the proceedings of the International Symposium of Hydrogen in Matter (ISOHIM 2005) held at the Angstrom Laboratory, Uppsala University, Sweden, June 13-17, 2005.

3. M. Dadfarnia, P. Sofronis, I. Robertson, B. P. Somerday, G. Muralidharan, D. Stalheim, "Numerical Simulation of Hydrogen Transport at a Crack Tip in a Pipeline Steel," submitted for the proceedings of IPC2006, 6th International Pipeline Conference, September 25-26, 2006, Cargary, Alberta, Canada.

Presentations

4. Mechanisms and Models for Hydrogen Embrittlement," McMAT2005, Joint ASCE/ASME/SES Conference on Mechanics of Materials, Baton Rouge, LA, June 1-3, 2005.

5. Sofronis, P. invited *plenary speaker* on "Hydrogen embrittlement" at the International Symposium of Hydrogen in Matter (ISOHIM 2005), Angstrom Laboratory at Uppsala University, Sweden, June 13-17, 2005.

6. Sofronis, P. "On the Development of Fracture Criteria for Hydrogen Embrittlement of Pipeline Steels," Hydrogen Gas Embrittlement Workshop, ASTM Meeting, Dallas, TX, November 8, 2005.

7. Sofronis, P., (invited) "Materials for the Hydrogen Economy," Clean Power Systems: Applications, Corrosion, and Protection Symposium, 135th Annual Meeting of the TMS, San Antonio, TX, March 12-16, 2006.

8. Sofronis, P., (invited) "Materials for the New Hydrogen Economy: Embrittlement Problems and Remediation," Kyushu University, Japan, June 13, 2006.

9. Sofronis, P., (invited) "The New Hydrogen Economy: New Science and Technology Challenges for the 21st Century," Kyushu University, Fukuoka, Japan, June 19, 2006.

10. Sofronis, P., (invited) "Materials for the New Hydrogen Economy: Embrittlement Problems and Remediation," Nagoya University, Nagoya, Japan, June 21, 2006.

11. Sofronis, P., (invited) "Materials for the New Hydrogen Economy: Embrittlement Problems and Remediation," The Japan Gas Association, Tokyo, Japan, June 22, 2006.

References

1. Liang, Y. and Sofronis, P. (2003) Toward a phenomenological description of hydrogen-induced decohesion at particle/matrix interfaces. *J. Mech. Phys. Solids*, 51, 1509-1531 (2003).

2. Kumnick, A. J., and Johnson, H. H. (1980) Hydrogen transport through annealed and deformed iron. *Metall. Trans*, 1974, 5A, 1199-1206.

3. Dadfarnia, M., Sofronis, P., Robertson, I., M., Somerday, B. P., Muralidharan, G., Stalheim, D. (2006) "Numerical Simulation of Hydrogen Transport at a Crack Tip in a Pipeline Steel," submitted for publication in the proceedings of IPC2006, 6th International Pipeline Conference, September 25-26, 2006, Cargary, Alberta, Canada.

4. Zhong, L., Wu, R., Freeman, A. J., and Olson, G. B. (2000) Charge transfer mechanism of hydrogen-induced intergranular embrittlement of iron. *Phys. Rev. B*, **62**, 13938-41.