III.E.1 Hydrogen Embrittlement of Pipelines: 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 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 Hydrogen Delivery Technical Challenges Section of the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan (MYPP):

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs
(I) Hydrogen Leakage and Sensors
(J) Other Refueling Site/Terminal Operations
(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. protective 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 April 27, 2007 version of the HFCIT MYPP:

- **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 H₂ embrittlement concerns and integrity. 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 absolute absence of any 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 as they do not account for the hydrogen effect on material fracture toughness. Design criteria addressing the hydrogen effect on material safety and reliability will allow for higher storage pressures to be considered (2010 target).
Accomplishments

- Characterized the microstructure of pipeline steels (laboratory specimens of industrial pipelines) using transmission electron microscopy (TEM) and identified carbide composition through energy dispersive spectroscopy (EDS).
- Measured the macroscopic flow characteristics of three new, possibly hydrogen compatible, material microstructures.
- Designed a hydrogen permeation device and permeability measurements of the microstructures above have been made.
- Developed and validated a finite element code for the study of transient stress-driven hydrogen transport coupled with large strain material elastoplastic deformation. The code has been used to simulate hydrogen uptake at the crack tip of an axial crack along the pipeline internal surface.
- Determined through finite element simulations the intensity of the hydrostatic constraint ahead of an axial wall-crack (T-stress approximately equal to -0.3 times the yield stress of the material) and demonstrated that constraint fracture mechanics is needed to describe the fracture processes.
- Validated ab-initio calculations 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.

Through our hydrogen permeation rig, we measured the permeability of a steel provided by Oregon Steel Mills (OSM), a possibly hydrogen compatible steel. We continue our measurements of solubility and diffusivity of three other OSM samples and hydrogen-pipeline samples provided by Air Liquide. Using TEM and EDS, we characterized the microstructure of the OSM and Air Liquide steels. Microstructural characterization is important for the identification of potential hydrogen trapping sites in the material. We carried out finite element calculations of transient hydrogen transport under plane strain conditions ahead of a crack tip simulating hydrogen uptake and transport through the interior surface of a pipeline with an axial crack on the wall. We demonstrated that small scale yielding conditions are appropriate to analyze crack tip response for hydrogen pressures as high as 15.0 MPa and that constraint fracture mechanics is a promising approach toward avoiding conservatism in the design of the pipelines. 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 an axial crack either on the internal or the external wall-surface of a pipeline. 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

Permeation Measurements

A hydrogen permeation rig has been built (Figure 1) and the system is being currently used to carry out permeation measurements as a function of temperature and hydrogen pressure. The materials tested are steel types A, B, and C provided by OSM (see last year’s annual progress report for details) and sample specimens taken from hydrogen pipelines operated by Air Liquide. Steel C is a typical low carbon (0.04% by wt.) Mn-Si-single microralloy API/Grade X70/X80 capable of producing a ferrite/acidicular microstructure. Such an alloy design and microstructure is typical for high strength natural gas pipelines. Preliminary permeability results for steel type C are shown in Figure 2. In this figure, the product of the steady-state flux \( J \) with the membrane thickness \( L \) is plotted against the square root of the hydrogen pressure at room temperature. The slope of this curve which is equal to \( 6.26 \times 10^{12} \text{Hatoms/} \sqrt{\text{MPa.m.s}} \) is the hydrogen permeability \( \Phi \) through the material. Currently, permeability measurements of extremely high purity iron for which data are available in the open literature are carried out in order to assess the accuracy of our preliminary measurements. The integral over time of the hydrogen flux \( J \) through the membrane when plotted as a function of time provides the time lag \( t_\tau = L^2/6D_\text{eff} \) which represents the time required for hydrogen to diffuse through the membrane under steady-state conditions, that is, after the trapping microstructural defects have been filled out by hydrogen. The parameter \( D_\text{eff} = D/(1 + \partial C_T / \partial C_L) \) (denotes the effective diffusion coefficient which accounts for trapping, \( D \) is the lattice diffusion constant, and \( C_T \) and \( C_L \) are respectively the lattice and trapping cite concentrations. It is noted that in the absence of trapping the time lag is given by \( t_\tau = L^2/6D \). From the measured time lag values \( t_\tau \) one can calculate the effective diffusion coefficient \( D_\text{eff} \). Matching the calculated values of the effective diffusion coefficient with corresponding finite element simulation predictions yields the lattice diffusion coefficient \( D \) as a function of temperature. These studies are currently under way.

The design of the permeation experimental apparatus and the related hydrogen permeation measurements meet all objectives of the project.

Microstructural Characterization

Figure 3 shows a TEM micrograph of the type C steel microstructure. Particles and high dislocation densities are observed along with irregular grain boundaries, indicative of a microstructure that has not been fully recrystallized and recovered. Figure 4 shows results from EDS performed on the sample. The fine particles inside the ferrite grains have been identified as precipitates composed of Ti and Nb. Figure 5 shows an EDS study of the Air Liquide pipeline sample. Clearly, large intergranular cementite particles are characteristic of this microstructure. It is emphasized that such particles constitute potential trapping sites and the determination of their density and hydrogen binding energy is a critical input to the finite element simulation of the hydrogen transport through the material. These microstructural characterization results meet all objectives stated above.

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 in the neighborhood ahead of an axial crack on the interior surface of a pipeline (see Figure 2 in last year’s annual progress report). Hydrogen transport was simulated to initiate after the specimen was loaded under small scale yielding (SSY) conditions to a specified applied stress intensity factor characteristic of real world axial cracks in pipeline walls. 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 is reported in the 2006 annual progress report.

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 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] and Dadfarnia et al. [2]. The material elastoplastic constitutive law in the presence of hydrogen accounts for the hydrogen-induced lattice dilatation. The problem of simulating material deformation and local hydrogen distributions is coupled in a non-linear sense and the solution procedure involves iteration [1]. In the calculations, the hydrogen diffusion coefficient through NILS at 300 K was assumed to be $2 \times 10^{-11}$ m$^2$/s. This value will be reconsidered 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 $2.0 \times 10^{-6}$ 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
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FIGURE 5. Energy Dispersive Spectroscopy for Particle Composition in the Air Liquide Hydrogen Pipeline Sample

to the experimental results of Kumnick and Johnson [3] 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 TEM microstructural characterization. Uniform hydrogen concentration \( C_0 \) in equilibrium with the hydrogen gas pressure inside the pipeline as dictated by Sievert’s law was used as a boundary condition on the crack faces. A hydrogen-free lattice was considered as an initial condition throughout the SSY simulation domain just before diffusion was switched on in the simulations.

An effective time parameter \( t_{ss} \) has been introduced to denote the time at which the hydrogen concentration at the highly stressed elements of volume ahead of the crack tip reaches 98% of the final steady state value. Figure 6 shows the normalized effective time \( t_{ss} = D t_{ss}/b^2 \) plotted as a function of the normalized domain size \( L/b \), where \( L \) is the distance from the crack tip of the outer boundary on which a zero hydrogen concentration is assigned [2] and \( b \) is the crack tip opening displacement which is a function of the applied stress intensity factor. Although increasing pressure reduces the time to steady-state, we found that the peak values of the normalized hydrogen concentration in NILS at the effective time to steady-state \( t_{ss} \) do not vary with pressure and they level to a value less than 2.7. We note that the normalizing hydrogen concentration is \( C_0 \) which is a function of the hydrogen gas pressure. Attention should be drawn to the fact that these results are independent of the applied stress intensity factor. The effect of the stress intensity factor is implicit through the crack tip opening displacement \( b \).

The results shown in Figure 6 demonstrate that there exists a scaling between the time required for hydrogen to reach steady-state and the material, geometric, and loading parameters of the system such as specimen size, diffusion constant, and applied stress intensity factor. Therefore, the present simulation results have established an analytical tool for predicting a possible upper bound on the time hydrogen solute atoms take to degrade the fracture resistance of pipeline steels.

Calculations were also performed to explore whether the small scale yielding approach can be used to simulate hydrogen transport and material elastoplasticity ahead of a real-world axial crack on the interior wall-surface of a pipeline. Preliminary

FIGURE 6. Plot of normalized effective time for hydrogen to reach steady state \( t_{ss} = D t_{ss}/b^2 \) vs. normalized domain size \( L/b \) through a pipeline with an axial crack along the interior wall surface which is in equilibrium with hydrogen gas for the cases of hydrogen pressures of 1 atm and 15 MPa. The parameter \( D \) denotes the lattice diffusion coefficient, \( b \) the crack opening displacement, and \( L \) the pipeline wall thickness.
results from an analysis of transient hydrogen transport and material elastoplasticity performed for a typical pipeline geometry with an outer diameter of 40.64 cm (8”), wall thickness h = 9.52 mm (0.375”), and an axial crack of depth a = 1.9 mm (a / h = 0.2) on the internal wall-surface are shown in Figure 7. The hydrogen gas pressure was 15 MPa and was applied on the interior surface of the pipeline as well as on the crack faces. Figure 7 shows the solution for the hydrostatic stress ahead of the crack tip obtained through the modified boundary layer formulation superposed on the full-field solution by considering the full pipeline geometry. The modified boundary layer solution was obtained through the stress intensity factor \( K_I = 34.12 \text{MPa}\sqrt{a} \) and the \( T \)-stress equal to \(-0.316\sigma_y\) associated with the hydrogen gas pressure of 15 MPa. The parameter \( \sigma_y \) denotes the yield stress of the material and is equal to 595 MPa. It is noted that the \( T \)-stress is the second, non-singular constant term in the asymptotic mode I linear elastic crack-tip field expansion and represents a stress acting parallel to the crack plane. Clearly Figure 7 indicates that a modified boundary layer approach accounting for the \( T \)-stress effect is very appropriate to describe the hydrostatic tip constraint ahead of the crack tip in a pipeline. This is indeed a promising new result as it will allow for the exploration of a J-T fracture locus for a pipeline. This is indeed a promising new result as it will allow for the exploration of a J-T fracture locus approach. It is emphasized that such a constraint-based fracture mechanics approach eliminates the conservatism embedded in the J-based alone design of materials against fracture.

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

**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 \textit{ab-initio} Simulation Package. A subset of our validation results provides unrelaxed binding energies for \( H \) in Fe for grain boundary (GB)/free surface (FS) equal to \(-3.23\) to \(-3.57 \text{ eV}\), and the binding energies difference of the GB and FS equal to \(+0.34 \text{ eV}\), in good agreement with values in literature [4].

These first-principles calculations are required to establish a fracture criterion accounting for the hydrogen effect (objectives [i], [iii], and [iv]).

**Conclusions and Future Directions**

- A finite element simulation code for transient hydrogen transport analysis ahead of a crack tip on the inside or outside wall-surface of a pipeline has been developed and tested. The code can treat stress-driven diffusion through interstitial lattice sites and trapping of hydrogen at microstructural defects. We correlated the time to steady-state of hydrogen transport in terms of the material diffusivity, applied stress intensity, and specimen size.
- We will couple these simulations with hydrogen-induced material degradation. We will study the hydrogen transport kinetics concurrently 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.
- We demonstrated that the deformation conditions ahead of a crack tip in a pipeline can be described by a modified boundary layer formulation using the \( T \)-stress approach to characterize the hydrostatic constraint. We emphasize that such a constraint-based fracture mechanics approach eliminates the conservatism embedded in the J-based alone design of materials against fracture.
• The dependence of the T-stress effect on microstructural changes due to hydrogen effects on material deformation such as softening will be explored.

• A permeation measurement apparatus has been built for diffusion coefficient measurements. Identification of the diffusion characteristics (e.g. permeability, solubility, trap strength and density) of existing and new pipeline steel microstructures will be carried out with increasing membrane thickness to isolate and understand potential surface adsorption related effects. In particular, the effect of protective coatings on these characteristics will be studied.

• Our initial TEM and EDS studies revealed a high density of sizable carbide particles in existing hydrogen pipelines and in the C-type steel. We will perform additional TEM and EDS studies on all material microstructures (Air Liquide, Air Products, and OSM test-pieces) to find out whether large dislocation density populations can compete with carbide particles in trapping hydrogen.

• 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 Fe₃C/alpha-Fe and MnS/alpha-Fe interfaces.

• We will carry out fracture toughness testing along with SEM and TEM studies to identify the failure mechanisms and associated microstructural features in the presence of hydrogen.

• We will continue our collaboration with the Hydrogen National Institute for Use and Storage (HYDROGENIUS) of Japan and the NATURALHY project sponsored by the European Union.

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 Forum organized by HYDROGENIUS at Fukuoka, Japan on January 31 and February 1, 2007.

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References


