III.6 FY 2008 SRNL Hydrogen Delivery Project—Hydrogen Permeability and Pipeline Integrity/Fiber Reinforced Composite Pipeline

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Project End Date: October 1, 2012

Objectives

Hydrogen Permeability & Pipeline Integrity

- Investigate the influence of weld fabrication microstructure (especially weld heat affected zones [HAZ]) on hydrogen compatibility.
- Measure hydrogen transport (diffusivity) in HAZ materials.
- Determine HAZ material susceptibility to hydrogen embrittlement.

Fiber Reinforced Polymer (FRP) Pipeline

- Focused evaluation of fiber reinforced composite piping for hydrogen service applications.
- Assessment of the structural integrity of the FRP piping and leakage of existing commercial available FRP joint designs and joint components.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section 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
(I) Hydrogen Leakage and Sensors
(K) Safety, Codes and Standards, Permitting

Technical Targets

This project is focused on the evaluation of FRP piping for hydrogen service applications. Assessment of the structural integrity of the FRP piping and the individual manufacturing components in hydrogen will be performed. Insights gained will support qualifications of these materials for hydrogen service including the DOE 2012 delivery targets:

- Pipeline Transmission and Distribution Cost: \$0.6 M/mile and 0.27 M/mile, respectively
- Hydrogen Leakage: to be determined, <0.5% by 2017

Accomplishments

- Developed E-Weld Predictor® simulations for weld HAZ microstructures.
- Fabricated and treated 20 GLEEBLE–HAZ simulation samples–controlling/tailoring microstructures allows for development of fundamental relationship between structure and properties.
- Characterized weld HAZ simulation microstructures–initial characterization completed.
- Measured hydrogen transport properties–diffusivity, solubility, and permeability–for weld HAZ microstructures.
- Completed 9-month hydrogen exposures for FRP pipe sections, compression samples, tensile and dynamic mechanical analysis (DMA) samples.
- Initiated commercial FRP joint leakage testing–established leak testing protocols and defined relevant testing conditions.

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Introduction

Hydrogen Permeability and Pipeline Integrity

The uniqueness of the microstructural features caused by the thermal influence of the welding processes in the HAZ often manifests in vast property changes. For example, in irradiated materials the fracture toughness of the HAZ has been demonstrated to be significantly lower than the corresponding base metal. With respect to HAZ performance in hydrogen similarly increased deleterious effects may be anticipated. The current research is focused on the evaluation of HAZ materials for hydrogen pipeline materials and attempts to correlate microstructural features–such as, grain size, volume fraction of phase constituents, etc.–with hydrogen transport and mechanical behavior.

FRP Pipeline

The use of FRP materials for hydrogen service will rely on the demonstrated compatibility of these materials for pipeline service environments and operating conditions. The ability of the polymer piping to withstand degradation while in service, the fiber strength wrapping to resist hydrogen attack, and the fiber-resin interface to remain intact are all critical to the successful implementation of these materials for hydrogen pipeline. The goal of the overall project is to successfully adapt spoolable FRP from oil and natural gas use to high-pressure hydrogen use. As such, the current research effort has been focused on two aspects: 1) long-term exposures of FRP piping sections and materials to gaseous hydrogen for subsequent materials property testing, and 2) evaluation of leakage behavior of existing commercially available FRP joints and joint components.

Approach

Hydrogen Permeability and Pipeline Integrity

The connection between hydrogen permeation and weld and weld HAZ s has been evaluated using low pressure hydrogen permeation tests to measure hydrogen permeation through weld and weld HAZs – both from actual welds and from GLEEBLE simulations – for representative hydrogen pipeline alloys. All of the permeation testing conducted under this task has been performed at pressures up to approximately 700 Torr and temperatures of 80°C and 150°C.

FRP Pipeline

SRNL has performed environmental exposure testing under accelerated conditions to simulate aging effects on FRP piping materials. This testing involves exposures of short piping sections to pure hydrogen environments at both ambient and non-ambient temperatures (140°F) and pressures of approximately 1,000 psig in order to evaluate hydrogen compatibility.

Additionally, a testing program has been initiated to evaluate current existing metallic joint components for FRP piping. Commercially available joint types are being leak tested and leakage rates recorded. The leak rate data for the joints will be applied to determine the acceptability of existing metal joints available for FRP pipe and will also aid in the development of new joint materials and designs if necessary for hydrogen service.

Results

Hydrogen Permeability and Pipeline Integrity

A critical issue to understanding the susceptibility of metallic pipeline materials to hydrogen embrittlement is related to the development of a fundamental understanding of the link between microstructrural features and hydrogen transport within the materials. Elucidation of the impact of surface structure, micrsotructure scale, the role of various phases within a multi-phase structure and the impact of traps both reversible and irreversible on the transport of hydrogen in theses carbon-steel materials is paramount. As a result, hydrogen transport experiments have been conducted using a common pipeline material A106 Grade B. In an attempt to develop a more fundamental understanding of the impact of the varied microstructural features typical of a weld HAZ, weld simulation samples were prepared using a GLEEBLE thermal exposure system to produce weld HAZ samples simulating 0, 3, and 5 pass welds. Hydrogen transport testing was initiated using the 5-pass weld simulations sample. Characterization of the microstructures of this sample has shown that the 5-pass weld simulation microstructure is comprised of primary ferrite, acicular ferrite and small pearlite colonies (see Figure1).

Hydrogen transport testing to determine the diffusivity of hydrogen in this 5-pass weld sample microstructure using the SRNL permeation test rig was performed at 400 Torr and 700 Torr and temperature of 80°C and 150°C. Typical results from this testing are provided in Figure 2.

Based on the data in Figure 2, the diffusivity (D) was estimated by calculating the slope and the intercept of the linear region using a least squares method. These two variables were then used to determine the lag time (tl), i.e., the time at which the line crossed the y-axis at

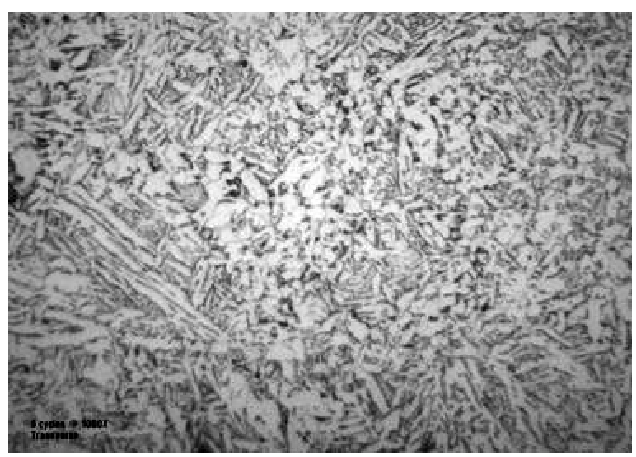

FIGURE 1. Photomicrograph of the Microstructure for a 5-Weld Pass GLEEBLE Simulation Sample

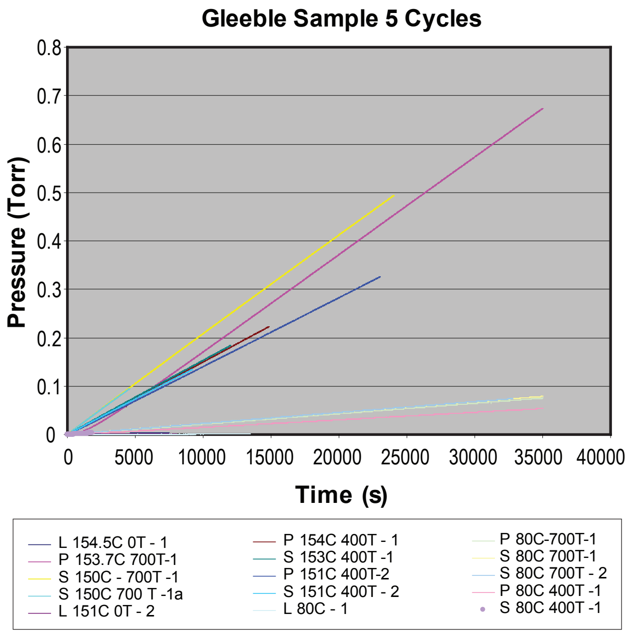

FIGURE 2. Typical Hydrogen Transport Results for 5-Pass Weld Simulation Sample

zero. Lag time, tl, was used in the equation: $tl = x^2/6D$ to determine D. From this approach, the diffusivity for hydrogen in the 5-pass weld microstructure was calculated to be in the range of $1.25 \times 10^{-6} - 3.0 \times 10^{-7}$ cm^2/s. This value for hydrogen diffusivity is comparable to previous measurement from SRNL on actual field welded A106 Grade B pipeline materials and also is in agreement with previously published lower temperature literature values. The results from this work in conjunction with previous literature results indicates that at the lower temperatures <200°C the most dominate materials feature affecting hydrogen diffusivity may be surface phenomenon–oxides, surface finish, etc.–and microstructural trap sites. For the microstructural trap sites a reduction in microstructural scale and phase shape–i.e., acicular ferrite–in the HAZ region can potentially result in increased trapping of hydrogen and subsequently lower apparent diffusivities in comparison to the bulk baseline microstructure. However, the role/impact of surface features cannot be ignored and at lower temperatures may play a more significant role in retarding the ingress of hydrogen into the materials.

FRP Pipeline

Testing of FRP materials in Fiscal Year 2008 has focused on two major areas: 1) environmental exposure of FRP pipe section and materials of construction to gaseous hydrogen, and 2) leak testing of commercial FRP joint components. SRNL has completed the 9-month environmental exposures in support of Oak Ridge National Laboratory (ORNL) FRP materials testing effort. Multiple 4-ft sections of 2.5" outside diameter (OD) FRP pipe and materials test samples–tensile dog-bones, compression rings, DMA test strips–have been exposed to 99.9995% hydrogen gas at nominally 140°F and 1,000 psig in the newly designed, fabricated, and installed SRNL FRP hydrogen exposure station (Figure 3).

Following exposure of these materials to gaseous hydrogen ORNL will work with a commercial FRP vendor to subject the 4-ft pipe sections to commercial standard product quality tests in addition to internally conducting materials evaluation testing on the exposed test samples.

In addition to the hydrogen exposure testing, leakage testing of commercially available FRP joint components has been initiated. Samples of 2.5" OD FRP piping with attached end fittings and joint fittings form two major FRP ping vendor Fiberspar and Polyflow have been procured (Figure 4). The Fiberspar technology makes use of an o-ring compression mechanical system to maintain seal integrity while the Polyflow uses a high pressure hydraulically crimped technology.

Leak testing for these typical joint/end-fitting components were conducted using two approaches. The first approach used conventional helium detection technology with a leak sensitivity of 1×10^{-9} cc/sec. Results from the helium leak rate determination for the Fiberspar o-ring compression system and the Polyflow hydraulically crimped system are as follows: 1) Fiberspar, $>1 \times 10^{-4}$ stdcc/sec at 1atm and room temperature and 2) Polyflow, $>1 \times 10^{-5}$ stdcc/sec at 1 atm and room temperature. Evaluation of these He leak rate values was higher than expected, however, from previous research effort it was known that He leakage rates can be higher than actual hydrogen leak rates due to the

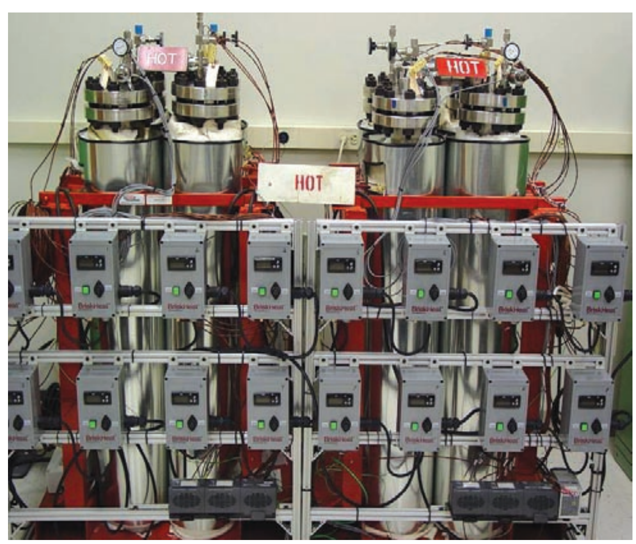

FIGURE 3. SRNL Large Chamber FRP Hydrogen Exposure Station

FIGURE 4. Typical Commercially Available FRP Joining and End-Fitting Components: (a) Fiberspar Joint Fitting and (b) Polyflow End-Fitting

He molecule being smaller than the diatomic hydrogen molecule.

As a result, pressure decay testing using gaseous hydrogen at 1,000 psig was initiated for both joint/end-fitting designs. Initial results from this testing have indicated leak rates on the order of >1 x 10^{-2} stdcc/sec for 1 hr durations. Again as a result of these results being higher than expected SRNL is working with colleagues at ORNL to evaluate test techniques and to define the appropriate test protocols for evaluating gaseous hydrogen leakage rates from commercial FRP joint/end-fitting components.

Conclusions and Future Directions

Conclusions

Hydrogen Permeability and Pipeline Integrity

- Effect of microstructure on diffusivity of hydrogen in pipeline steels is critical to aiding understanding hydrogen embrittlement–fundamental materials science link between structure-properties-processing–management of hydrogen embrittlement key to hydrogen pipeline structural integrity.
- Preliminary 5-pass weld HAZ microstructure (ferrite/acicular ferrite/sm. pearlite) diffusivity data comparative to previous measured actual field weld HAZ microstructure (ferrite/pearlite)–measurement of both dominated by ferrite (body centered cubic) permeation/diffusivity.
- Project eliminated March 2008.

FRP Pipeline

- Critical issue for demonstrating feasibility of FRP pipeline for hydrogen service is development of the technical basis to demonstrate structural integrity by defining FRP susceptibility to hydrogen embrittlement.
- Qualification of existing commercial FRP joint components with respect to leakage identified in DOT Gap Analysis Report as one of four major needs for demonstrating composite FRP piping feasibility.
- Initial leakage results indicate higher leak rates than anticipated–SRNL and ORNL meeting to review results and review leak testing protocols for FRP.

Future Work

- Initiate testing to assess impact of joint loading and flexure on commercial FRP joint/joint component leakage.
- Initiate testing to evaluate effect of pressure cycling on leakage of polyflow crimp-type joint/joint component leakage.
- Hydrogen absorption/solubility testing–evaluation of the long-term absorption/solvation of gaseous hydrogen in typical FRP liner materials.
- Structural integrity–hydrogen embrittlement susceptibility evaluation (ASTM G142) of metallic commercial FRP joint/joint component materials.

FY 2008 Publications/Presentations

1. SRNL Weld/HAZ Permeation & Embrittlement, Presentation to Hydrogen Delivery Pipeline Working Group, Savannah River National Laboratory, September 25, 2007.

2. SRNL Support for FRP Piping Project, Presentation to Hydrogen Delivery Pipeline Working Group, Savannah River National Laboratory, September 25, 2007.

3. Weld/HAZ Hydrogen Transport & Embrittlement Testing, Presentation to Hydrogen Delivery Pipeline Working Group, Sandia National Laboratory, February 21, 2008.

4. SRNL FRP Piping Project, Presentation to Hydrogen Delivery Pipeline Working Group, Sandia National Laboratory, February 21, 2008.

5. Affect of Microstructure on Hydrogen Permeation and Embrittlement in Pipeline Materials, Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, Feb. 25-27, 2008.

6. SRNL-MST-2007-00207, "Proposed Thermal Cycle for HAZ Simulated Samples Produced Using the Gleeble", Nov. 2007.

7. SRNL-MST-2008-00023, "SRNL Permeation Testing Conditions – Round Robin Tests", Jan. 2008.