Objectives

- Quantify the effects of welding and joining on the resistance to hydrogen embrittlement (HE) of high-strength pipeline and other structural steels under high-pressure hydrogen.
- Determine the hydrogen transport behavior (absorption, diffusion, trapping, etc.) in steels.
- Develop the technical basis and guidelines to manage hydrogen, stress and microstructure in the weld region to ensure structural integrity and safety of hydrogen delivery systems.
- Develop welding/joining technology that greatly reduces the capital cost and eliminate HE concerns in constructing new pipelines and converting existing pipelines for high-pressure hydrogen delivery.
- Develop risk assessment-based approach to manage the integrity and safety of hydrogen pipelines including weld joints.

Technical Barriers

This project addresses the following technical barriers from the 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
(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs
(K) Safety, Codes and Standards, Permitting

Introduction

The hydrogen energy delivery infrastructure will require extensive use of steels and other cost-effective structural and functional materials under high-pressure gaseous hydrogen (H₂) exposure. For example, high pressure (up to 3,000 psi) hydrogen pipelines are presently considered to be one of the most cost-effective and energy-efficient means to transport very large amounts of hydrogen to much of the market as is done currently for natural gas [1]. Under high hydrogen pressures, there are concerns about HE of steel pipelines and its potential catastrophic consequences [2]. Concerns regarding HE are not limited to steel pipelines; according to a recent DOE Basic Energy Science Office report [3], HE needs to be addressed for a variety of
hydrogen storage and delivery system parts made of metallic materials that are exposed to hydrogen.

As in the case of natural gas and other energy carrier transmission pipelines, welding will be used to construct steel pipelines for high-pressure hydrogen delivery. Welding will be also widely used in fabrication of other system components for hydrogen production, storage, and delivery. However, welds in pipeline steels and other engineering materials are often the most susceptible regions to HE due to the formation of unfavorable microstructures and high tensile residual stresses. Indeed, recent studies [4] on pipeline steels have shown that the焊 region exhibits delayed cracking (signature of HE) when exposed to high-pressure hydrogen gas. Furthermore, the weld region typically has substantially lower resistance to hydrogen crack initiation and higher crack growth rates, when compared to the baseline pipeline steel (base metal). In this regard, the weld region can be the weakest link for the structural integrity and safety of hydrogen pipelines and hydrogen delivery infrastructure. A systematic approach to deal with weld property degradation under high-pressure hydrogen gas is critical to ensure the safe, cost-effective operation and long-term reliability of the hydrogen delivery infrastructure.

Approach

While there have been extensive studies in the past on hydrogen embrittlement and hydrogen induced material property degradation of pipeline steels, the high-pressure hydrogen delivery pipeline presents some unique issues that are seldom addressed in the past. At the center of these issues is the hydrogen transport behavior in metal – the absorption, diffusion, and trapping of hydrogen in metal. At the present time, very limited knowledge is available about the rate of diffusion and amount of hydrogen in steel under high-pressure gaseous environment relevant to the hydrogen delivery infrastructure. Therefore, the first major effort in this project is directed toward high-pressure H₂ permeation and mechanical performance tests to systematically study the hydrogen permeation behavior and to evaluate the tolerance level to hydrogen of different steels before considerable mechanical property degradation would occur.

The weld joint in steel pipeline is expected to be a critical region mostly susceptible to HE due to the formation of unfavorable microstructure and the high residual stresses. The second major activity of this project focuses on developing new welding technology and/or improve existing welding technology to optimize weld microstructure and proactively control the weld residual stress for H₂ pipeline construction and repair. In addition, special testing methods need to be developed to quantify the degradation of mechanical properties in the weld region with complex microstructure and HE resistance gradients. Finally, risk assessment-based approach will be developed to manage the integrity and safety of hydrogen pipelines including the weld joints.

Results

Hydrogen Transport Study: The specially designed high-pressure hydrogen permeation measurement device was systematically calibrated with pure Pt and Pd, demonstrating that the system has the required repeatability and accuracy for hydrogen permeation and diffusion measurements. Baseline hydrogen diffusion and permeation measurement in high purity iron was completed. Initial results on hydrogen diffusion and permeation in steels and their welds under high hydrogen pressure (up to 2,000 psi) have been obtained for A106 steel and X52 pipeline steels. The effects of weld microstructure on hydrogen trapping, diffusion and permeation have been studied for these steels using a combined experimental and computational modeling approach. The effects of hydrogen pressure (up to 2,000 psi) and temperature (from 25 to 150°C) on the diffusivity, concentration and permeation of hydrogen were obtained. The permeation rate shows square root dependency on hydrogen pressure.

The root cause of very slow “apparent” diffusion coefficients in steels in early low- and high-pressure hydrogen diffusion measurements at several projects sites including ORNL under gaseous hydrogen environments has been identified and traced to surface hydrogen dissociation and absorption phenomenon. Using a modified testing procedure (coating the samples with a nanometer thick Pd layer), the surface absorption effect was essentially eliminated. A multi-thickness testing procedure, combined with numerical modeling, was utilized to further separate the surface hydrogen dissociation/absorption from the diffusion of hydrogen.

As an example, Figure 1 presents the permeation testing data of a heat-affected zone (HAZ) sample of A106 Grade B pipeline steel from which the effective diffusivity of hydrogen and the amount of hydrogen in the irreversible traps were determined. The results of three repeated runs on the same sample are shown in the figure. The effects of irreversible traps on hydrogen diffusion are evident by comparing the permeation curves of the first and second run. The nearly identical second run and third run demonstrate that the measurement was highly repeatable and without the data scatter problem encountered in the previous measurements. The effective diffusivity, determined by the lag-time technique, of hydrogen in A106 Grade B steel are summarized in Figure 2. These results include both the base metal and the HAZ microstructures under different temperature and pressure levels. The effective diffusivity under the high-pressure gaseous hydrogen environment obtained in this project is at or below the
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Mechanical Property Measurement of Weld Region: Current standard methods for testing hydrogen-induced mechanical property degradation of base metal have shown to be inadequate for the weld metal region due to the highly inhomogeneous microstructure and property gradients of the weld region \[4\]. In this project, we designed and fabricated miniaturized and self-loading testing devices for in situ measurement of mechanical property degradation of weld metal in high-pressure gaseous hydrogen environment. Two types of the mechanical testing devices were devised. The first one was a special multiple-notched tensile test where the notch is precisely located in different regions of weld. This test is intended as a quick yet quantitative screening test of weld property changes under high-pressure hydrogen. The second type test was a novel fracture toughness test based on the spiral notch torsion test principle. The compact size and self-loading mechanisms employed in both testing devices make it possible that the entire loading assembly and the test specimen be placed inside a relatively small high-pressure chamber. This minimizes the capital cost of the testing system and allows for multiple testing devices to be operated in a single high-pressure vessel to cost-effectively study and quantify the effects of the weld microstructure on HE resistance of different steels. The effects of high-pressure hydrogen on the stability of load sensors immersed in hydrogen have been solved with a novel sensor design.

In Fiscal Year 2008, we focused on the development of the multiple notched tensile test. Figure 3 shows the miniature testing device and the multiple notch sample to measure the resistance to HE of different weld microstructures. The miniature self-loading device was evaluated for its applicability for hydrogen-induced embrittlement in the weld region of pipeline steels. Figure 4 shows the fracture surfaces of an AISI4340 steel with fully hardened microstructure tested with and without high-pressure hydrogen. The suitability of such test for HE resistance measurement has been demonstrated.

Welding Technology Development for Hydrogen Steel Pipelines: Friction stir welding is a novel solid-state material joining technology. It can potentially eliminate the coarse grain region in the HAZ and the use of “rich” weld metal chemistry for matching the base metal properties in the conventional arc welding processes – the two primary factors contributing to the hardened microstructures in weld region that reduce the resistance to HE. A section of friction stir welded X65 pipeline has been produced using a prototype portable friction stir welding system for field construction of...
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pipelines. Superior in-air mechanical properties (tensile strength and impact energy) have been obtained which suggests the possibility of improved weld hydrogen embrittlement resistance. Testing the friction stir welds under high-pressure hydrogen is planned in FY 2009 and beyond using the miniature weld test device being developed in this project.

Conclusions and Future Directions

This project focuses on the resistance of HE in the weld region of steels, the region regarded as the weakest link for the structural integrity and safety of hydrogen pipeline and hydrogen delivery infrastructure. We have accomplished the followings milestones in FY 2008:

- Initial work on friction stir welding on pipeline steels which showed considerable improvement of weld toughness and strength over the conventional arc welds.
- Development of a new testing method specific to quantify and rank the sensitivity of different microstructures in the weld region to HE.

The project plan for FY 2009 and beyond includes (1) develop the understanding and the relationship between hydrogen permeation and diffusion and various microstructures in pipeline steels, (2) continue on welding technology development to reduce the weld residual stress and manage the weld microstructure to improve the resistance to HE, and (3) complete the development of testing methods to quantify the HE resistance in the weld region under both static and cyclic loading conditions.

Special Recognitions & Awards/Patents Issued


FY 2008 Publications/Presentations


References
