III.12 Hydrogen Embrittlement of Structural Steels

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Objectives

(1) Demonstrate reliability/integrity of steel hydrogen pipelines under cyclic pressure conditions:
   - Measure fatigue crack growth rates and fracture thresholds of line pipe steels in high-pressure hydrogen gas.
   - Evaluate performance of steel pipelines by applying a code-based structural integrity model coupled with steel properties measured in hydrogen gas.
   - Optimize materials test methods in hydrogen pipeline design codes.

(2) Enable development of micromechanics models of hydrogen embrittlement in pipeline steels:
   - Establish physical models of hydrogen embrittlement in line pipe steels using evidence from analytical techniques such as electron microscopy.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

(K) Safety, Codes and Standards, Permitting

Technical Targets

The principal target addressed by this project is the following (from Table 3.2.2):

- Pipeline Reliability/Integrity

The salient reliability/integrity issue for steel hydrogen pipelines is hydrogen embrittlement. One particular unresolved issue is the performance of steel hydrogen pipelines that are subjected to extensive pressure cycling. One of the objectives of this project is to enable safety assessments of steel hydrogen pipelines subjected to pressure cycling through the use of code-based structural integrity models. This structural integrity analysis can determine limits on design and operating parameters such as the allowable number of pressure cycles and pipeline wall thickness. Efficiently specifying pipeline dimensions such as wall thickness also affects pipeline cost through the quantity of material required in the design.

Accomplishments

Fracture properties for X52 line pipe steel were measured in high-pressure hydrogen gas to provide data for evaluating the reliability/integrity of steel hydrogen pipelines and to illuminate a pathway for optimizing materials test methods:

- Measured fatigue crack growth laws in high-pressure hydrogen gas.
- Established dependence of hydrogen-assisted fatigue crack growth rates on load-cycle frequency.
- Measured fracture thresholds as a function of loading rate.

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Introduction

Carbon-manganese steels are candidates for the structural materials in hydrogen gas pipelines, however it is well known that these steels are susceptible to hydrogen embrittlement. Decades of research and industrial experience have established that hydrogen embrittlement compromises the structural integrity of steel components. This experience has also helped identify the failure modes that can operate in hydrogen containment structures. As a result, there are tangible ideas for managing hydrogen embrittement in steels and quantifying safety margins for steel hydrogen containment structures. For example, fatigue crack growth aided by hydrogen embrittlement is a well-established failure mode for steel hydrogen containment structures subjected to pressure cycling. This pressure cycling represents one of the key differences in operating conditions between current hydrogen pipelines and those anticipated in a hydrogen fuel distribution infrastructure. Applying code-based structural integrity models coupled with measurement of relevant material properties allows quantification of the reliability/integrity of steel hydrogen pipelines subjected to pressure cycling. Furthermore, application of these structural integrity models is aided by the development of micromechanics models, which provide important insights such as the hydrogen distribution near defects in steel structures.

Approach

The principal objective of this project is to enable the application and optimization of structural integrity codes for steel hydrogen pipelines. The new ASME B31.12 design code for hydrogen pipelines includes a fracture mechanics-based design option, which requires material property inputs such as the fracture threshold and fatigue crack growth rate under cyclic loading. Thus, one focus of this project is to measure the fracture thresholds and fatigue crack growth rates of technologically relevant line pipe steels in high-pressure hydrogen gas. These properties must be measured for the base materials but more importantly for the welds, which are likely to be most vulnerable to hydrogen embrittlement. These data can be used to evaluate the reliability/integrity of steel hydrogen pipelines and to establish pathways for optimizing materials test methods in the design code.

A second objective of this project is to enable development of micromechanics models of hydrogen embrittlement in pipeline steels. The focus of this effort is to establish physical models of hydrogen embrittlement in line pipe steels using evidence from analytical techniques such as electron microscopy. These physical models then serve as the framework for developing sophisticated finite-element models, which can provide quantitative insight into the micromechanical state near defects. Understanding the micromechanics of defects can ensure that structural integrity models are applied accurately and conservatively.

Results

Efforts during Fiscal Year (FY) 2010 focused on measuring fatigue crack growth rates and fracture thresholds of X52 line pipe steel in hydrogen gas. The fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) relationship and the fracture threshold are necessary material-property inputs into code-based structural models that allow the reliability/integrity of steel hydrogen pipelines to be quantified. One such reliability/integrity methodology was recently published in the ASME B31.12 code.

The X52 line pipe steel was selected for this activity because of its recognized technological relevance for hydrogen pipelines. We decided to test the X52 steel from the round-robin tensile property study (FY 2008) for the following reasons: 1) some characterization of the material was already provided from the round-robin study, 2) ample quantities of material were still available from Concurrent Technologies Corporation, one of the participants in the Pipeline Working Group, and 3) the X52 steel was in the form of finished pipe, which is the most relevant product form and also allows samples to be extracted from the seam weld.

The hydrogen-affected fatigue crack growth law (da/dN vs. ΔK) for the structural steel is the basic element in pipeline reliability/integrity models. Results from the technical literature indicate that the da/dN vs. ΔK trends for steels in hydrogen gas exhibit several transitions, and these transitions can depend on variables such as the R ratio (i.e., ratio of minimum applied load to maximum applied load). Consequently, it is important to measure the da/dN vs. ΔK relationship over a wide enough range in ΔK to capture the transitions. The da/dN vs. ΔK relationships were measured for the X52 steel at two R ratios (0.1 and 0.5) to establish baseline trends. These tests were conducted in 21 MPa (3,000 psi) hydrogen gas and a load-cycle frequency of 1 Hz. The pressure represents the upper limit specified for hydrogen pipelines in the ASME B31.12 code. The load-cycle frequency was selected to balance test effectiveness and test efficiency, since fatigue crack growth rates are enhanced at lower test frequency but the test duration can become prohibitively protracted. The measured da/dN vs. ΔK data are plotted in Figure 1.

The data in Figure 1 illustrate the expected transitions in the da/dN vs. ΔK trend measured in hydrogen gas. In particular, data for the test conducted at R=0.1 show that crack growth rates are similar to those measured in air until a critical K level is reached. At this point, the crack growth rates accelerate and the da/dN vs. ΔK relationship has a characteristic slope in the log-log plot. As ΔK continues to increase, another transition is observed in which the slope of the da/dN vs. ΔK trend abruptly decreases.

The da/dN vs. ΔK relationships in Figure 1 were measured at a load-cycle frequency of 1 Hz. This frequency was selected to enhance the efficiency of measuring the baseline da/dN vs. ΔK relationships. However, fatigue crack growth rates are known to depend on the load-cycle frequency, and it is important to ensure that the da/dN vs. ΔK relationships represent

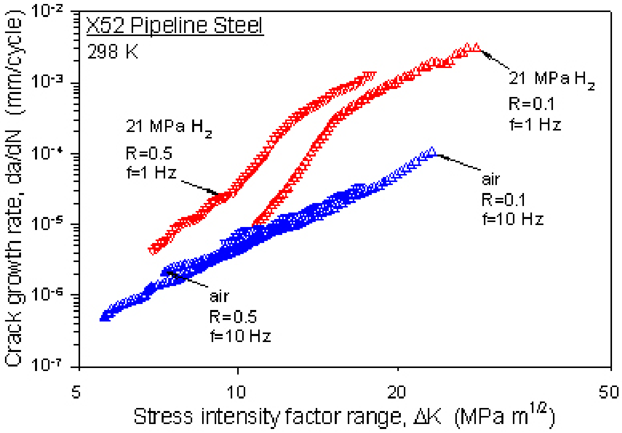

FIGURE 1. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) plots for X52 steel in hydrogen gas and air.

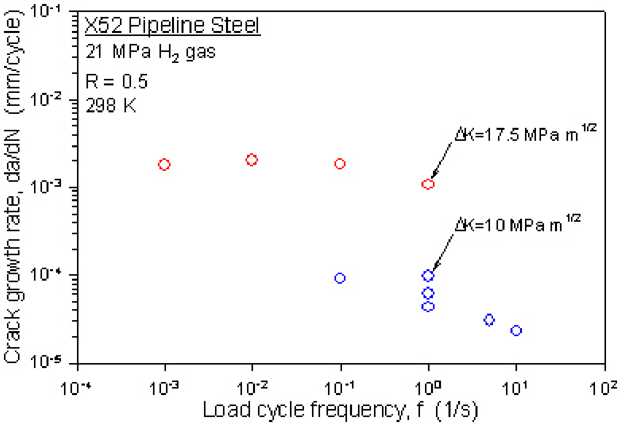

FIGURE 2. Fatigue crack growth rate (da/dN) vs. load-cycle frequency (f) plots for X52 steel in hydrogen gas.

conservative data for reliability/integrity calculations. This dependence of crack growth rate on frequency is related to the kinetic steps necessary for hydrogen transport from the gas into the steel. To address the limiting test frequency for producing conservative da/dN vs. ΔK data, the fatigue crack growth rates for X52 steel were measured at a fixed ΔK and R ratio (0.5) over a range of frequencies. The fixed ΔK levels were selected as 10.0 and 17.5 MPa $m^{1/2}$, since the crack growth rates at these ΔK levels are high (Figure 1). Establishing the limiting test frequency at a high fatigue crack growth rate ensures that this test frequency will yield reliable data at lower crack growth rates as well, since the limiting test frequency for conservative crack growth rates increases as the growth rate decreases. The da/dN vs. load-cycle frequency data measured for X52 in 21 MPa hydrogen gas are summarized in Figure 2.

Several features are notable in the da/dN vs. load-cycle frequency plots in Figure 2. First, the fatigue crack growth rates are consistent with the growth rates in the da/dN vs. ΔK plot from Figure 1 at ΔK levels equal to 10.0 and 17.5 MPa $m^{1/2}$, respectively. Second, the growth rates appear to be essentially constant below a limiting frequency, i.e., 1 Hz and 0.1 Hz for ΔK equal to 10.0 and 17.5 MPa $m^{1/2}$, respectively. These trends suggest that the da/dN vs. ΔK results in Figure 1 do not represent conservative data in the higher range of crack growth rates. In addition, the limiting test frequency for conservative crack growth rates depends on the absolute crack growth rate. Further testing is planned to determine limiting test frequencies for lower crack growth rates.

It must be noted that the results in both Figures 1 and 2 represent tests that have rather extended durations. For example, the test in Figure 1 at R=0.5 required almost 6 days to complete. In addition, the data point at $f=10^{-3}$ Hz in Figure 2 represents 5 days of testing time. These results demonstrate that reducing test duration by developing more efficient test methods is one pathway for optimizing pipeline structural integrity codes.

Fracture threshold measurements were conducted on the X52 steel under rising-displacement loading conditions in hydrogen gas. Recent results from the Materials Compatibility task in the Safety, Codes and Standards project at Sandia indicate that fracture threshold measurements under rising-displacement loading may yield more conservative values compared to measurements under static-displacement loading. As such, the fracture thresholds for X52 were measured under rising-displacement loading at rates of approximately 0.0051 and 0.051 mm/min. Similar to the issue with load-cycle frequency in fatigue crack growth rate testing in hydrogen gas, the limiting displacement rate for measuring lower-bound fracture thresholds must be established. The crack growth resistance curves in Figure 3 indicate that the fracture thresholds (indicated by the intersection of the dashed "blunting line" with the resistance curve) for X52 steel are not sensitive to loading rate over the range explored.

Conclusions and Future Directions

- Measured fatigue crack growth laws allow evaluation of reliability/integrity of steel hydrogen pipelines under cyclic pressure conditions. Hydrogen embrittlement can be accommodated by measuring fracture properties in hydrogen following ASME B31.12 pipeline design standard.
- Measurements show that fatigue crack growth rates in hydrogen depend on load-cycle frequency. These results can help optimize test methods in pipeline codes, i.e., enhancing test efficiency without compromising data reliability.

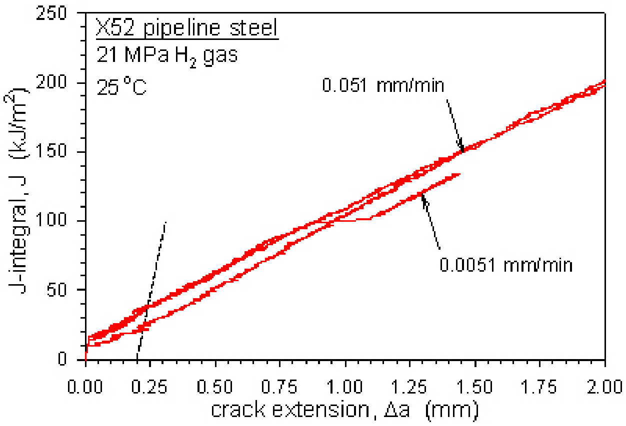

FIGURE 3. Crack-growth resistance curves measured for X52 steel in 21 MPa hydrogen gas at two rising-displacement rates. The fracture thresholds are indicated by the intersection of the dashed "blunting line" with the crack-growth resistance curves.

- (future work) Complete measurements of da/dN vs. frequency for X52 steel in hydrogen at lower fatigue crack growth rates.
- (future work) Complete fracture threshold measurements for X52 steel in hydrogen as a function of displacement rate.
- (future work) Measure fatigue crack growth laws for X52 steel seam welds and girth welds in hydrogen.

FY 2010 Publications/Presentations

1. (invited presentation) "Hydrogen-Assisted Fracture: Mechanisms and Technological Implications", B. Somerday, Gordon Research Conference on Hydrogen-Metal Systems, Barga, Italy, July 2009.

2. "Fracture Control of Hydrogen Containment Components", B. Somerday, C. San Marchi, and K. Nibur, 3rd International Conference on Hydrogen Safety, Ajaccio, Corsica, France, Sept. 2009.

3. (invited presentation) "Design Qualification for Hydrogen Containment Components", B. Somerday, International Hydrogen Energy Development Forum 2010, Fukuoka, Japan, Feb. 2010.

4. "Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen", C. San Marchi, B. Somerday, K. Nibur, D. Stalheim, T. Boggess, and S. Jansto, Proceedings of the ASME 2010 Pressure Vessels & Piping Division / K-PVP Conference, Bellevue, WA, July 18–22, 2010.