III.1 Hydrogen Embrittlement of Structural Steels

Jay Keller (Primary Contact), Brian Somerday, Chris San Marchi
Sandia National Laboratories
P.O. Box 969
Livermore, CA 94550
Phone: (925) 294-3316
E-mail: jokelle@sandia.gov

DOE Manager
HQ: Scott Weil
Phone: (202) 586-1758
E-mail: Kenneth.Weil@ee.doe.gov

Project Start Date: January 2007
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 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, emphasizing welds.
   - Evaluate performance of steel pipelines by applying code-based structural integrity model coupled with steel properties measured in hydrogen gas.
   - Quantify effects of gas impurities (e.g., O_2) in mitigating hydrogen-accelerated fatigue crack growth.

(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 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.

FY 2011 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:

- Conducted replicate measurements of fatigue crack growth relationships for X52 base metal and seam weld in high-pressure hydrogen gas.
- Compared fatigue crack growth relationships for X52 base metal and seam weld, revealing that the reliability/integrity of steel hydrogen pipelines is not limited by the seam weld.

✧ ✧ ✧ ✧ ✧

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 embrittlement 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 delivery 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 of code-based structural integrity models for evaluating the reliability/integrity of steel hydrogen pipelines. The new American Society of Mechanical Engineers (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.

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

The principal activity during FY 2011 was measuring the fatigue crack growth relationships for the base metal and electric resistance weld (ERW) from X52 line pipe steel in hydrogen gas. The fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) relationship is a necessary material-property input into structural models that enable engineering analysis of the design life of steel hydrogen pipelines. One such design life methodology for steel hydrogen pipelines was recently published in the ASME B31.12 code. The measurements of subcritical cracking thresholds and fatigue crack growth relationships in this task thus support the objective of establishing the reliability/integrity of steel hydrogen pipelines.

The X52 line pipe steel was selected for this task because of its recognized technological relevance for hydrogen pipelines. The X52 steel from the round robin tensile property study (FY 2008) was tested 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, 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 ERW seam.

The hydrogen-affected fatigue crack growth relationship (da/dN vs. ΔK) for the structural steel is the basic element in pipeline reliability/integrity models. The ASME B31.12 code requires measurement of the fatigue crack growth relationship for pipeline steels at the hydrogen gas operating pressure. Initial measurements of the fatigue crack growth relationship for X52 steel base metal were conducted in 21 MPa hydrogen gas (the upper limit specified for hydrogen pipelines in the ASME B31.12 code) at a load-cycle frequency of 1 Hz (Figure 1). This load-cycle frequency was selected to balance test effectiveness and test efficiency, since fatigue crack growth rates can be enhanced at lower test frequency but the test duration can become prohibitively protracted. Even at this relatively high load-cycle frequency, measurement of the fatigue crack growth relationship over the relevant range of ΔK could require several days. For example, the duration of the test conducted at a load ratio of 0.5 was 6 days. (Load ratio, R, is the ratio of minimum applied load to maximum applied load.)

Although the accepted trend is that increasing load-cycle frequency leads to lower (i.e., non-conservative) fatigue crack growth rates in hydrogen gas, this trend is predominantly based on fatigue crack growth rates measured for steels at relatively high ΔK, e.g., greater than 15 MPa $m^{1/2}$. The possibility of effectively measuring fatigue crack growth rates at high load-cycle frequency in the lower (and technologically relevant) range of ΔK was explored for the X52 steel in 21 MPa hydrogen gas. Fatigue crack growth rate relationships were measured at 10 Hz for two R ratios (0.1 and 0.5), and the results are compared to the fatigue crack growth relationships measured at 1 Hz in Figure 1. Although the fatigue crack growth relationships at 1 Hz and 10 Hz are not exactly coincident, there are only moderate differences in the fatigue crack growth rates over the ΔK range investigated. These preliminary results suggest that reliable fatigue crack growth relationships may be measured at high load-cycle frequency, which would allow the testing to be conducted more efficiently.

The fatigue crack growth relationship for the X52 ERW was also measured in 21 MPa hydrogen gas. Since steel microstructures in welds are not easily controlled, these weld microstructures can be inhomogeneous. Consequently, it is important to conduct replicate fatigue crack growth tests on welds to characterize potential variability in the data. Figure 2 shows the fatigue crack growth relationships measured for the X52 ERW from replicate tests. These tests were conducted at R=0.1 and 1 Hz so that the results could be directly compared to those for the X52 base metal. The following details are notable in Figure 2: 1) the da/dN vs. ΔK relationships for the X52 ERW exhibit significant variability,

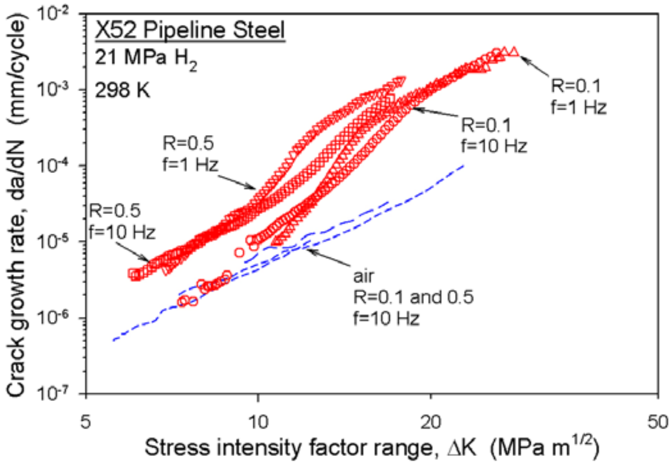

FIGURE 1. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) plots for X52 steel base metal in hydrogen gas and air.

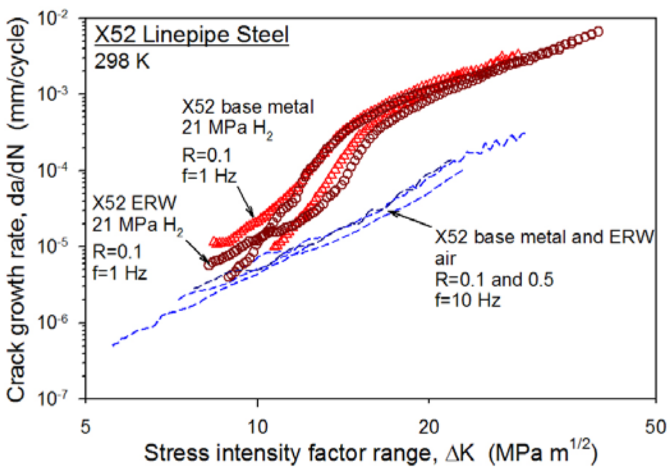

FIGURE 2. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) plots for X52 steel base metal and ERW seam in hydrogen gas and air. Unstable cleavage fracture was observed for the ERW tested in air at K_{max}>40 MPa $m^{1/2}$.

2) the da/dN vs. ΔK relationships for the X52 base metal also exhibit variability, and 3) despite the variability in the da/dN vs. ΔK relationships, it is apparent that the fatigue crack growth rates are similar for the base metal and the weld in hydrogen gas.

While microstructure is one salient variable that can contribute to variability in the da/dN vs. ΔK relationships for X52, other variables must be considered as well. For example, the hydrogen test gas was sampled at the conclusion of both tests conducted on the X52 ERW. The leak rates from the pressure vessel were unusually high, and such an abnormal operating condition prompted sampling of the test gas. The hydrogen test gas contained relatively high concentrations of oxygen (>10 vppm) for both tests. Since oxygen is known to inhibit hydrogen uptake into steels, it is possible that the high levels of oxygen in the test gas affected the results. Additional tests are in progress on the ERW material to clarify whether variability in the da/dN vs. ΔK relationships can be attributed to oxygen in the test gas.

A fatigue crack growth test was also conducted on the X52 ERW in air. Such data serves as a baseline for comparison to measurements on the ERW in hydrogen gas as well as for comparison to measurements on the base metal in air. Test conditions for the ERW in air included R=0.5 and a load-cycle frequency of 10 Hz. Figure 2 shows that the da/dN vs. ΔK relationship for the ERW measured in air is similar to the relationship measured for the base metal in air. However, the test on the ERW was unexpectedly terminated at K_{max} ~40 MPa $m^{1/2}$ by unstable crack extension associated with cleavage fracture. This result suggests that some region of the ERW microstructure has extremely low fracture toughness. The consequence of this inherently low fracture resistance on hydrogen-assisted subcritical cracking must be explored.

Conclusions and Future Directions

Conclusions

- Fatigue crack growth relationships for X52 steel measured in hydrogen gas enable evaluation of reliability/integrity of steel pipelines under cyclic pressure conditions. Hydrogen embrittlement can be accommodated by coupling structural design models and measured fracture properties following the ASME B31.12 pipeline standard.
- The measured fatigue crack growth relationships for X52 base metal and ERW seam are similar. This trend was evident despite variability in replicate data sets. These results demonstrate that reliability/integrity of steel hydrogen pipelines is not limited by the ERW seam.

Future Directions

- Determine the threshold level of oxygen impurity concentration required to mitigate accelerated fatigue crack growth of X52 steel in hydrogen at gas pressures up to 21 MPa.
- Complete measurements of fatigue crack growth relationships for low-strength pipeline steel girth welds in hydrogen gas.

FY 2011 Publications/Presentations

1. "Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen", D. Stalheim, T. Boggess, C. San Marchi, S. Jansto, B. Somerday, G. Muralidharan, and P. Sofronis, *Proceedings of IPC 2010 8th International Pipeline Conference*, Calgary, Alberta, 2010, Paper No. IPC2010-31301.

2. "Fracture Toughness and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen", C. San Marchi, B. Somerday, K. Nibur, D. Stalheim, T. Boggess, and S. Jansto, *Proceedings of the ASME 2011 Pressure Vessels & Piping Division / K-PVP Conference (PVP11)*, Baltimore, MD, 2011, Paper No. PVP2011-57684.

3. "Improving the Fatigue Resistance of Ferritic Steels in Hydrogen Gas" (invited presentation), B. Somerday, I^2CNER Kick-off Symposium, Fukuoka, Japan, Feb. 2011.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000