III.11 Enabling Hydrogen Embrittlement Modeling of Structural Steels

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Project End Date: Project continuation and direction determined annually by DOE

Objectives

(1) Enable application of structural integrity models to steel hydrogen pipelines:
   - Measure fatigue crack growth rates and sustained-load cracking thresholds of line pipe steels in high-pressure hydrogen gas.
   - Apply structural integrity model coupled with steel properties measured in hydrogen gas to assess performance of steel pipeline.

(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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

(G) Storage Tank Materials and Costs

Technical Targets

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

- 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 structural integrity models.

Accomplishments

- Completed measurements of sustained-load cracking thresholds of X100 steel in hydrogen gas over a range of pressures.
- Gathered initial evidence for hydrogen-assisted fracture mode in X100 steel.
- Completed assembly of laboratory capability for conducting fatigue crack growth tests on materials in high-pressure hydrogen gas.

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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 key failure mode for steel hydrogen containment structures subjected to pressure cycling. Applying appropriate structural integrity models coupled with measurement of relevant material properties allows quantification of safety margins against fatigue crack growth in hydrogen containment structures. 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 application of structural integrity models to steel hydrogen pipelines. The new American Society of

Mechanical Engineers (ASME) B31.12 design code for hydrogen pipelines will include a fracture mechanics-based design option, which requires material property inputs such as the threshold for sustained-load cracking and fatigue crack growth rate under cyclic loading. Thus, one focus of this project is to measure the sustained-load cracking thresholds and fatigue crack growth rates of 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. The measured properties can be evaluated by predicting the performance of the pipeline using a relevant structural integrity model, such as that in ASME B31.12.

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

Fracture mechanics tests were conducted on X100 steel to measure crack growth kinetics and sustained-load cracking thresholds as a function of hydrogen gas pressure. Measurement of the sustained-load cracking threshold was assigned high priority since this property is integral to structural integrity analysis of hydrogen gas pipelines. Additionally, determining the crack growth kinetics as a function of gas pressure can provide insights into the mechanisms for hydrogen-assisted fracture. The X100 steel was selected for testing since inducing sustained-load cracking in carbon steels is more likely in high strength materials. Once reliable procedures are established for measuring the fracture mechanics properties of carbon steels in high-pressure hydrogen gas, testing will focus on more technologically relevant materials such as lower-strength X42 and X52.

Sustained-load cracking tests on X100 steel were conducted over a range of hydrogen gas pressures from 21 to 138 MPa. The sustained-load cracking thresholds were measured using the wedge-opening load (WOL) fracture mechanics specimen, where load is applied by opening the crack using a bolt. The bolt maintains a fixed displacement on the specimen and also reacts against a load cell, which provides continuous data on the applied load while the specimen is exposed to hydrogen gas. Figure 1 shows the measured sustained-load cracking threshold (K_{TH}) vs. gas pressure trend.

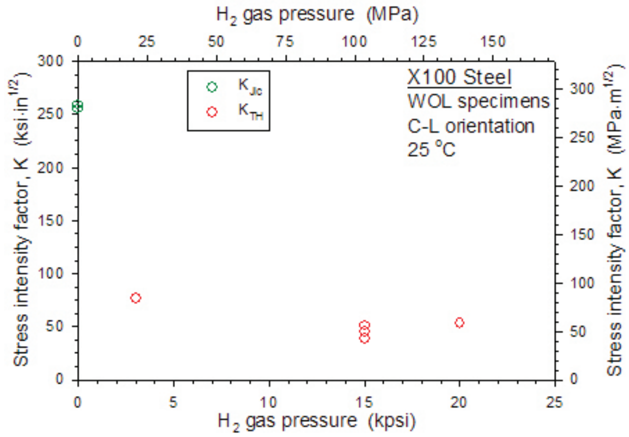

FIGURE 1. Threshold for Sustained-Load Cracking (K_{TH}) as a Function of Hydrogen Gas Pressure for X100 Steel

Consistent with trends for other steels tested in hydrogen gas, the K_{TH} for X100 decreases as the hydrogen gas pressure increases.

The measured sustained-load cracking thresholds can be used to assess the performance of a steel pipeline. Figure 1 shows that K_{TH} was measured at a gas pressure of 21 MPa, which is in the range of gas pressures where hydrogen pipelines could operate. The K_{TH} value at 21 MPa gas pressure (85 MPa-m$^{1/2}$) is a reasonably high value, particularly considering the high strength level of X100 steel. Assuming that an X100 pipeline was constructed with an inner diameter of 30 cm and a wall thickness of 1.3 cm, the pipeline could tolerate an axial defect on the inner surface with a depth equal to 0.6 cm (45% of the wall thickness). A crack of this depth could be easily detected with non-destructive examination techniques.

Microscopy techniques were applied to sustained-load cracking specimens of X100 steel to assess the hydrogen-assisted fracture mode. Figure 2 shows an image of the fracture profile of an X100 specimen tested in 100 MPa hydrogen gas. The image shows the region below the fracture surface, where the crack propagation direction was from right to left. There is clear evidence for the formation of transgranular microcracks in the ferrite phase. This information provides the first step in establishing the detailed physical model for hydrogen-assisted fracture in X100 steel.

A laboratory capability for measuring fatigue crack growth rates in high-pressure hydrogen gas is being developed. Once all of the essential hardware components were received and assembled (Figure 3), the next objective was to exercise the system and assess whether the system functioned according to expectations. This system testing revealed that the greatest challenge is the sliding seals. There are three Teflon U-cup sliding seals that are designed to minimize frictional forces and prevent leakage of hydrogen gas

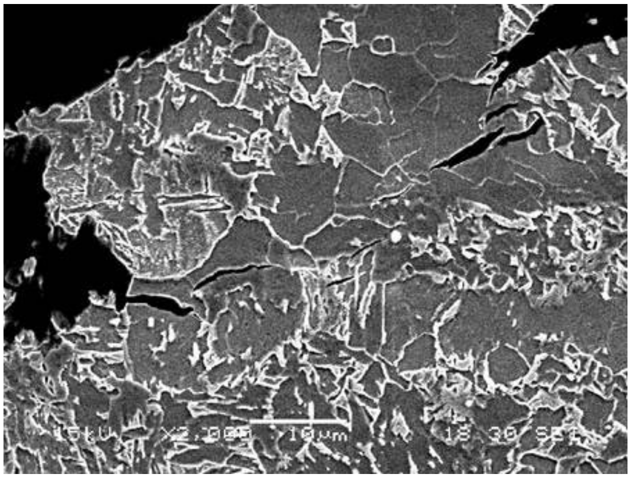

FIGURE 2. Fracture Profile from Sustained-Load Cracking Specimen of X100 Steel Tested in 100 MPa Hydrogen Gas

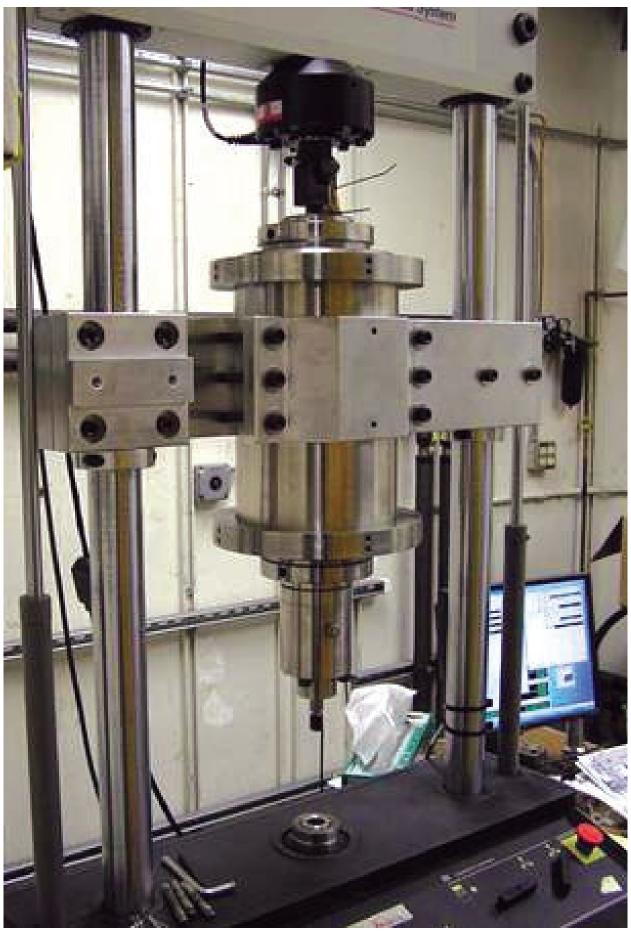

FIGURE 3. Pressure Vessel and Mechanical Test Frame in System for Conducting Fatigue Crack Growth Tests in High-Pressure Hydrogen Gas

at pressures up to 138 MPa. The leak rates past the sliding seals have exceeded expectations, leading to an unacceptable pressure decrease in the pressure vessel. Two solutions are being pursued to ensure the system can function as designed: working with vendors to redesign the sliding seals and effectively increasing the volume of the pressure vessel by adding a gas accumulator to the system.

Conclusions and Future Directions

- Sustained-load cracking thresholds were measured for X100 steel in hydrogen gas over a range of pressures. These data coupled with structural integrity modeling demonstrate that steel pipelines fabricated from X100 have favorable defect tolerance in hydrogen gas.
- Microscopy results provided the first insights into the hydrogen-assisted fracture mode for X100 steel. These results represent the first step in creating a physical model of hydrogen-assisted fracture for X100 steel.
- Measure the fatigue crack growth rates of technologically important pipeline steels such as X42 and X52 in high-pressure hydrogen gas. These measurements must be conducted on the base metal as well as welds (future).

FY 2008 Publications/Presentations

1. (invited) "Structural-Materials Considerations for Hydrogen Gas Containment", C. San Marchi, B. Somerday, K. Nibur, M. Yip, International Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA, Nov. 2007.

2. "Hydrogen-Assisted Fracture in Steels for Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, Feb. 2008.

3. "Effects of Hydrogen Gas on Steel Vessels and Pipelines", B. Somerday and C. San Marchi, in *Materials for the Hydrogen Economy*, R.H. Jones and G.J. Thomas, Eds., CRC Press, Boca Raton, FL, 2008, pp. 157-179.

4. "Measurement of Sustained-Load Cracking Thresholds for Steels in Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, submitted to *2008 Proceedings of the ASME PVP Conference*, 2008.

5. "Structural-Metals Considerations for the Containment of High-Pressure Hydrogen Gas", C. San Marchi, B. Somerday, K. Nibur M. Yip, submitted to *Proceedings of International Symposium on Materials Issues in a Hydrogen Economy*, 2008.