III.21 Hydrogen Embrittlement of Structural Steels

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Objectives

1. Enable application of structural integrity models to steel hydrogen pipelines:
   - Measure fatigue crack growth rates and rapid-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

- Measured tensile properties of X52 and X100 pipeline steels in hydrogen gas as part of the DOE Pipeline Working Group materials-testing round robin.
- Demonstrated ability to measure fatigue crack growth rates of pipeline steels in high-pressure hydrogen gas using new laboratory capability.

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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 embrittlement 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 includes a fracture mechanicsbased design option, which requires material property inputs such as the threshold for rapid cracking and fatigue crack growth rate under cyclic loading. Thus, one focus of this project is to measure the rapid-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

A materials-testing round robin was coordinated by the DOE Pipeline Working Group with the objective of demonstrating that three participants (Sandia National Laboratories/California, Oak Ridge National Laboratory, and the National Institute of Standards and Technology) can provide reliable data on the mechanical properties of ferritic steels measured in high-pressure hydrogen gas. The emphasis for this round robin was measurement of tensile properties for two line pipe steels.

The tensile test matrix consisted of two steels (X52 and X100) and three environmental conditions (hydrogen gas, helium gas, and air). The steel products and tensile specimens were procured by Concurrent Technologies Corporation (a participant in the Pipeline Working Group) and supplied to the three laboratories. The intent of the test matrix was to produce triplicate results for each combination of steel and test environment. Sandia modified the test matrix to produce an initial set of duplicate results for each combination of steel and test environment. The reason for the modification was due to sub-optimal performance of the load cell located internal to the pressure vessel. It was decided to execute only part of the test matrix with this load cell, and the balance of the test matrix would be completed once the load cell performance was improved.

The modified test matrix was executed following procedures developed by participants in the round robin. Test procedures that were defined included the hydrogen and helium gas test pressures (14 MPa), the tensile strain rate (10^{-4}), and the test temperature (room temperature). Sandia successfully conducted the testing following the specified procedures, although two aberrations were noted. First, the gas pressure during testing in hydrogen and helium was not constant, but varied over about 1 MPa from the nominal pressure of 14 MPa. This pressure variation was due to gas leaks at the sliding seals in the pressure vessel. The second issue was apparent inaccurate labeling of some tensile test specimens. Specifically, two specimens labeled as X52 were evidently the other steel, X100. These aberrations did not affect the quality or reliability of the results.

Four properties were measured from the tensile tests, as summarized in Table 1: yield strength (S_y), ultimate tensile strength (S_u), elongation to fracture (El), and reduction of area at fracture (RA). These tensile properties were defined and measured following procedures outlined in ASTM International standards. The elongation to fracture was based on measurements of the original and final overall lengths of the tensile specimens. The gauge length for these measurements was approximately the gauge section of the tensile specimen (19 mm).

TABLE 1. Tensile properties of X52 and X100 line pipe steels measured in air, helium, and hydrogen.

Steel	Environment	S_y (MPa)	S_u (MPa)	El (%)	RA (%)
X52	air	429	481	31	79
X52	air	431	488	29	80
X52	helium	417	486	31	75
X52	helium	423	481	30	76
X52	hydrogen	430	495	24	49
X52	hydrogen	423	486	24	60
X100	air	769	919	20	74
X100	air	725	856	21	78
X100	helium	719	878	20	79
X100	helium	787	882	21	77
X100	hydrogen	755	914	13	38
X100	hydrogen	791	897	13	38

The data in Table 1 demonstrate some expected trends. The yield and tensile strengths of the X100 steel are significantly greater than strengths for the X52 steel. In addition, hydrogen degrades the ductility (elongation or RA) of both steels. The effect of hydrogen on ductility is more pronounced for the high-strength X100 steel. Other notable trends are that data for tests conducted in air and helium are similar and data are consistent within each set of duplicate tests.

The laboratory capability for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas was completed and initial testing was successfully demonstrated. The initial fatigue crack growth testing focused on the X100 steel from the round robin. A compact tension specimen fabricated from X100 was tested in 21 MPa hydrogen gas at a load cycle frequency of 1 Hz and a load ratio (R = minimum load/maximum load) equal to 0.5. The test was executed by imposing a sinusoidal loading wave form on the test specimen at fixed values of maximum load and minimum load, which resulted in an increasing stress-intensity factor range (ΔK) as the crack extended. The crack growth rate per load cycle (da/dN) measured as a function of applied ΔK is plotted in Figure 1. In this figure, the data measured in hydrogen gas are compared to another set of data measured in air. The data clearly demonstrate the effect of hydrogen on accelerating fatigue crack growth rates of steels. Although hydrogen has such a pronounced effect on fatigue crack growth rates, measurements such as those in Figure 1 enable the implementation of structural integrity models (e.g., Option B in ASME B31.12) that accommodate manifestations of hydrogen embrittlement.

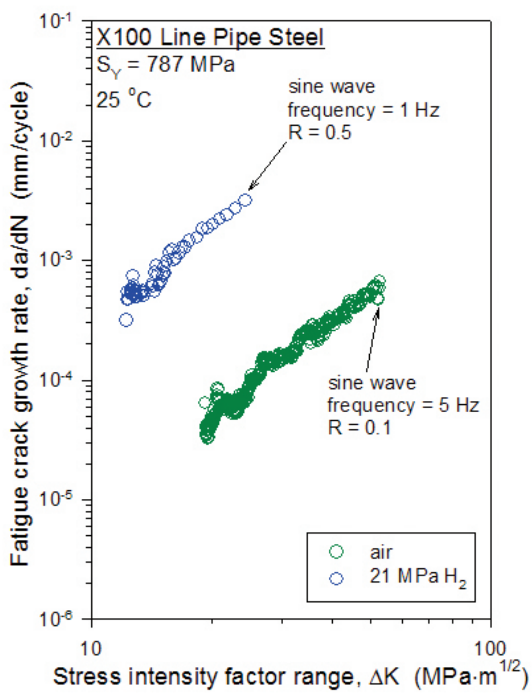

FIGURE 1. Fatigue crack growth rate per load cycle (da/dN) vs stress-intensity factor range (ΔK) data for X100 steel in hydrogen gas and air.

Conclusions and Future Directions

- Measurements of tensile properties for the materials-testing round robin and fatigue crack growth rates represent progress toward assuring reliability/integrity of steel pipelines for hydrogen gas service.
- (future) 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.

FY 2009 Publications/Presentations

1. (invited presentation) "Fracture Control of Hydrogen Containment Components", B. Somerday, *International Hydrogen Energy Development Forum 2009*, Fukuoka, Japan, Feb. 2009.

2. "On the Small Scale Character of the Stress and Hydrogen Concentration Fields at the Tip of an Axial Crack in Steel Pipeline: Effect of Hydrogen-Induced Softening on Void Growth", M. Dadfarnia, P. Sofronis, B. Somerday, I. Robertson, *International Journal of Materials Research*, vol. 99, 2008, pp. 557-570.

3. *Effects of Hydrogen on Materials: Proceedings of 2008 International Hydrogen Conference*, B. Somerday and P. Sofronis, eds., ASM International, Materials Park, OH, 2009, in press.

4. "Sustained Load Cracking of Steels for Hydrogen Storage and Delivery", K. Nibur, B. Somerday, D. Balch, and C. San Marchi, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.