III.5 Hydrogen Embrittlement of Structural Steels

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

Overall Objectives

- Demonstrate the reliability/integrity of steel hydrogen pipelines subjected to cyclic pressure operating conditions
- Identify pathways for reducing the cost of steel hydrogen pipelines without compromising reliability/integrity

Fiscal Year (FY) 2013 Objectives

Establish reliable fatigue crack growth (da/dN vs ΔK) relationships for the fusion zone and heat-affected zone in X65 girth weld supplied by industry partner

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (Section 3.2.5):

(B) Reliability and Costs of Gaseous Hydrogen Compression

(D) High As-Installed Cost of Pipelines

(K) Safety, Codes and Standards, Permitting

Technical Targets

The principal targets addressed by this project are the following (Table 3.2.4 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan):

- Pipeline Reliability/Integrity

One salient reliability/integrity issue for steel hydrogen pipelines is hydrogen embrittlement. For steel pipelines, the central unresolved issue is the pipeline performance under 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 in design codes, e.g., American Society of Mechanical Engineers (ASME) B31.12. 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 2013 Accomplishments

Reliable fatigue crack growth (da/dN vs ΔK) relationships were measured for the X65 weld heat-affected zone (HAZ) in 3,000 psi (21 MPa) hydrogen gas. These results show that the weld HAZ is not more susceptible to hydrogen-accelerated fatigue crack growth compared to the base metal.

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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 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 structural integrity models in design codes 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 physics-based material models, which provide important insights such as the effects of gas impurities (e.g., oxygen) on hydrogen-affected fracture properties. Successful implementation of these structural integrity and material models enhances confidence in the design codes and enables decisions about materials selection and operating conditions for reliable and efficient steel hydrogen pipelines.

APPROACH

The approach of this project is to apply specialized materials testing capabilities to measure the fatigue crack growth rates of technologically relevant pipeline 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. Such measurements are necessary for enabling the application of structural integrity models in design codes. For example, the new ASME B31.12 code for hydrogen pipelines includes a fracture mechanics-based integrity management option, which requires material property inputs such as the fatigue crack growth relationship in hydrogen gas.

Following the establishment of reliable fatigue crack growth relationships for pipeline steel base metal, weld heat-affected zone, and weld fusion zone in hydrogen gas, a secondary approach of this project is to apply analytical techniques such as electron microscopy to define the mechanisms of hydrogen embrittlement for the purpose of proposing phenomenological models. These phenomenological models then serve as the foundation for developing analytical or numerical predictive models, which can provide quantitative insight into the effects of environmental, material, and mechanical variables on hydrogen embrittlement. Such predictive materials science models can enable the extrapolation of material data inputs required for structural integrity models.

RESULTS

The fatigue crack growth rate (da/dN) vs stress-intensity factor range (ΔK) relationship is a necessary material-property input into structural integrity models applied to steel hydrogen pipelines. One such integrity assessment methodology for steel hydrogen pipelines was recently published in the ASME B31.12 code. The measurements of crack propagation thresholds and fatigue crack growth relationships in this task support the objective of establishing the reliability/integrity of steel hydrogen pipelines.

Low-strength line pipe steels such as X52, X60, and X65 were selected for this task because of their stakeholder-recognized technological relevance for hydrogen pipelines. Generally, lower-strength steels are selected for hydrogen pipelines since these steels are less susceptible to hydrogen embrittlement. A section of X65 steel pipe containing a girth weld was provided by an industry partner. The emphasis in FY 2013 was to complete multiple measurements of the da/dN vs ΔK relationship for the weld fusion zone and heat-affected zone in 3,000 psi (21 MPa) hydrogen gas. An optical-microscope image revealing the base metal, weld fusion zone, and the HAZ is shown in Figure 1. This image demonstrates that the material regions have distinctly different metallurgical structures, particularly the base metal and fusion zone.

The hydrogen-affected fatigue crack growth relationship (da/dN vs ΔK) for the structural steel is the basic element in pipeline structural integrity models. The ASME B31.12 code requires measurement of the fatigue crack growth relationship for pipeline steels at the hydrogen gas operating pressure. Since the maximum pressure specified for hydrogen gas pipelines in the ASME B31.12 code is 3,000 psi (21 MPa), this upper-bound pressure was selected for the testing. As specified in ASME B31.12, the da/dN vs ΔK relationship was measured following ASTM Standard E647. Compact-tension crack-growth specimens were extracted from both the fusion zone and the HAZ such that the loading and crack propagation directions were in the longitudinal and circumferential orientations, respectively, relative to the pipe. In this way, the crack plane was fully contained in either the fusion zone or HAZ for the entire range of crack growth during the tests. Samples were extracted from the base metal for comparison. The load-cycle frequency selected for the testing was 1 Hz, consistent with previous testing on X52 line pipe steel in high-pressure hydrogen gas.

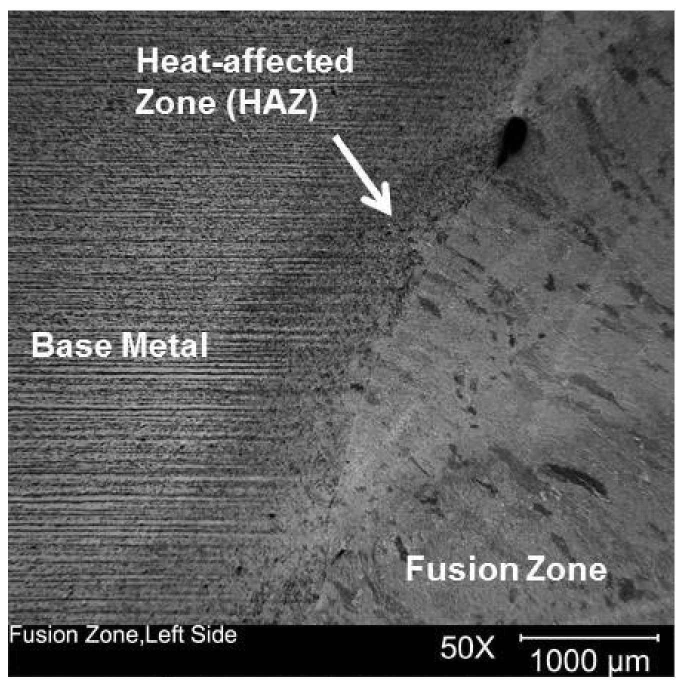

FIGURE 1. Optical-microscope image showing base metal, fusion zone, and HAZ of X65 weld.

Preliminary da/dN vs ΔK data for the X65 fusion zone and the HAZ revealed unexpectedly lower crack growth rates compared to X52 base metal in hydrogen gas at low ΔK values. Welds are expected to be more sensitive to hydrogen-assisted crack growth. Further analysis of the X65 weld fusion zone and the HAZ samples revealed that the pre-cracks deviated from their anticipated path, as shown for the fusion zone sample in Figure 2. The crack did not span the entire thickness of the specimen, instead exhibiting a non-uniform crack front, thus rendering the measured data unreliable. To mitigate the deviation of the crack front during pre-cracking, X65 fusion zone and HAZ compact tension samples were thinned from their original 13 mm (0.5 in) to 6 mm (0.25 in). Previous work has shown that thinner samples consistently exhibit more uniform crack fronts during pre-cracking while the change in sample geometry still conforms to ASTM E647 standard. In order to improve confidence in attaining a uniform crack front, side grooves were not machined and the specimen sides were polished to allow for observation of pre-cracks before initiating fatigue crack growth testing in hydrogen gas. The X65 HAZ specimen was observed to have uniform pre-crack fronts whereas the X65 fusion zone had non-uniform pre-crack fronts, e.g. significant crack growth on one side and negligible on the other.

The results from the X65 HAZ thinned specimen are shown in Figure 3 in comparison with X52 and X65 base metals. The data for the thinned specimen essentially overlay the original X65 HAZ data, both in 21 MPa H_2 gas. Both sets of data exhibit slightly lower crack growth rates at low ΔK values compared to the base metals, but all materials show similar trends at high ΔK values. The specimens were fractured after test completion and a side-by-side comparison of the two X65 HAZ specimens is shown in Figure 4. The optical images show that the thinned specimen exhibited a more uniform crack front during the pre-crack stage;

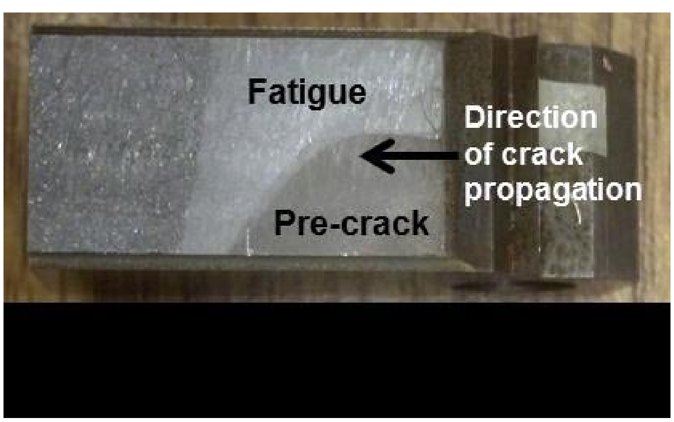

FIGURE 2. Optical-microscope image of fracture surface from compact tension specimen of X65 fusion zone showing a non-uniform pre-crack front (darker region, bottom right).

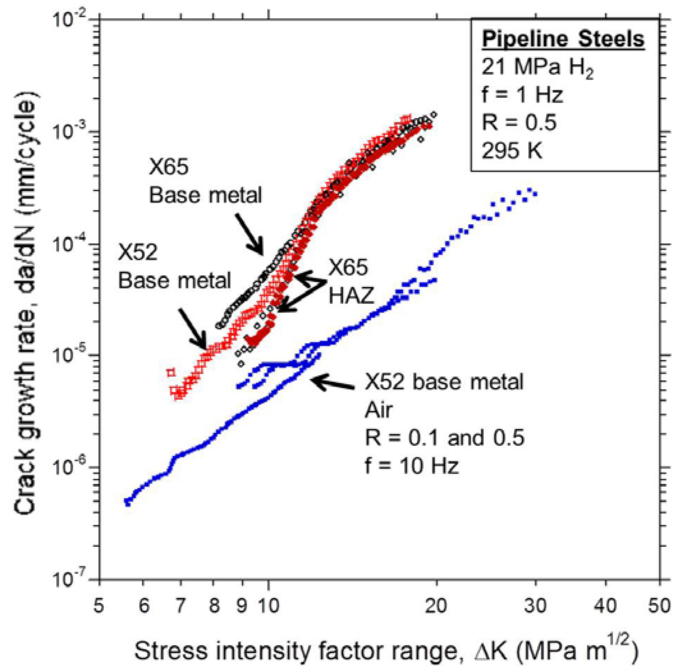

FIGURE 3. Fatigue crack growth relationships (da/dN vs ΔK) for X65 base metal and HAZ in 3,000 psi (21 MPa) hydrogen gas. The results are compared to measurements for X52 base metal in hydrogen gas and X52 base metal in air.

FIGURE 4. Optical-microscope images of fracture surfaces from compact tension of X65 HAZ specimens comparing pre-crack fronts. The top specimen was the original geometry and the bottom was thinned to 6 mm (0.25 in).

however, both exhibited similar uniformity during fatigue crack growth in hydrogen.

Since the thinned X65 fusion zone specimen was observed to have a non-uniform pre-crack, this fatigue crack growth test has not been performed in hydrogen. Further testing on the X65 fusion zone will be conducted in the fourth quarter of FY 2013 on a modified specimen geometry and orientation. These specimen modifications are required to attain the goal of establishing reliable measurements of the da/dN vs ΔK relationships for the weld-fusion zone.

CONCLUSIONS AND FUTURE DIRECTIONS

- Reliable da/dN vs ΔK relationships were measured for the X65 weld HAZ in 3,000 psi (21 MPa) hydrogen gas. These results show that the weld HAZ is not more susceptible to hydrogen-accelerated fatigue crack growth compared to the base metal.
- (future) Develop an alternate specimen geometry and orientation for reliable measurements of the X65 weld fusion zone. Complete triplicate measurements of the da/dN vs ΔK relationships for the weld fusion zone and HAZ to establish reliable material-property inputs for structural integrity models.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. "Elucidating the Variables Affecting Accelerated Fatigue Crack Growth of Steels in Hydrogen Gas with Low Oxygen Concentrations", B.P. Somerday, P. Sofronis, K.A. Nibur, C. San Marchi, and R. Kirchheim, *Acta Materialia*, 2013, doi: 10.1016/j.actamat.2013.07.001.

2. "Structural Materials Compatibility with Hydrogen", B.P. Somerday, I2CNER Annual Symposium, Kyushu University, Fukuoka, Japan, Jan. 2013.