

## III.5 Hydrogen Embrittlement of Structural Steels

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### Overall Objectives

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

### Fiscal Year (FY) 2014 Objectives

- Complete triplicate measurements to establish reliable fatigue crack growth relationships for X65 girth weld fusion zone in 3,000 psi (21 MPa) hydrogen gas
- Complete duplicate measurements of fatigue crack growth relationships in hydrogen gas for model iron-carbon alloys with two different grain sizes in collaboration with the International Institute for Carbon-Neutral Energy Research

### 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 target addressed by this project is Pipeline Reliability/Integrity (Table 3.2.4).

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 2014 Accomplishments

- Reproducible fatigue crack growth rate ( $da/dN$ ) vs. stress-intensity factor range ( $\Delta K$ ) relationships were measured for X65 weld fusion zones in 3,000 psi (21 MPa) hydrogen gas. Comparing with results from FY 2013 suggests that the weld fusion zone and heat-affected zone are no more susceptible to hydrogen-accelerated fatigue crack growth compared to the base metal.
- Modified specimen geometry ESE(T) (eccentrically loaded, single edge tension) used in this study expands fatigue crack growth testing capabilities by allowing thinner walled pipes to be examined as well as different orientations of materials that would otherwise be precluded by employing the conventional C(T) (compact tension) specimen.



## 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 predictive models, which provide important insights such as the effects of microstructure on hydrogen-assisted fatigue crack growth. Successful implementation of these structural integrity and physics-based 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 the core capability in materials characterization at Sandia 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 as well as the welds, which are likely to be most vulnerable to hydrogen embrittlement. Such measurements are necessary to enable 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.

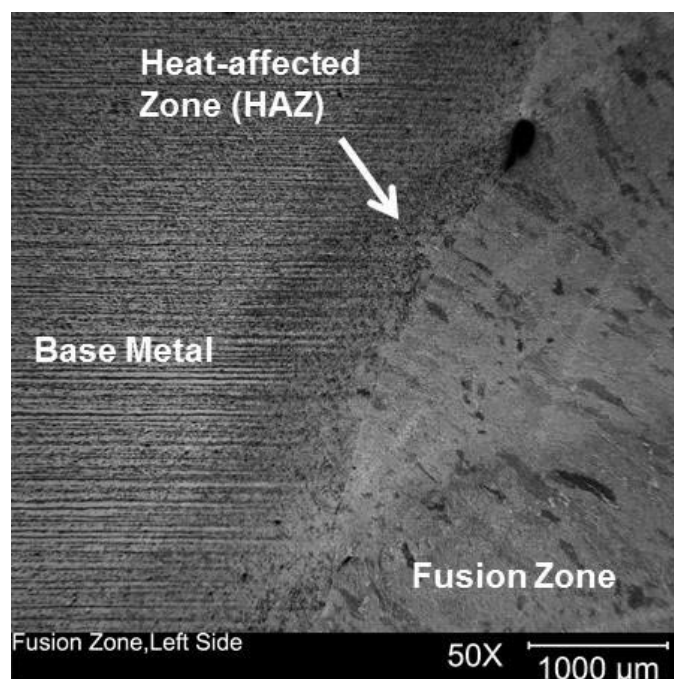
Following the establishment of reliable fatigue crack growth relationships for pipeline steel base metal, weld heat-affected zone, and weld fusion zone in hydrogen gas, a secondary approach of this project is to apply analytical techniques such as electron microscopy to define the mechanisms of hydrogen embrittlement for the purpose of developing physics-based predictive models. Such predictive models can provide quantitative insight into the effects of environmental, material, and mechanical variables on hydrogen embrittlement. For example, quantifying the effect of microstructure on hydrogen-accelerated fatigue crack growth can aid in the qualification of line pipe steels and their welds for hydrogen service.

## RESULTS

The  $da/dN$  vs.  $\Delta K$  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 measurement of fatigue crack growth relationships in this task supports the objective of establishing the reliability/integrity of steel hydrogen pipelines by enabling application of the ASME B31.12 code.

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-oriented gas metal arc weld was provided by an industry partner. An optical-microscope image revealing the base metal (BM), weld fusion zone (FZ), and weld heat-affected zone (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. In FY 2013, the  $da/dN$  vs.  $\Delta K$  relationships for the HAZ in 3,000 psi (21 MPa) hydrogen gas were measured and compared to the base metal. The emphasis for FY 2014 was measurement of the weld fusion zone (FZ) in 3,000 psi (21 MPa) hydrogen gas. As specified in ASME B31.12, the  $da/dN$  vs.  $\Delta K$  relationship was measured following ASTM Standard E647. 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. 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.

As demonstrated in FY 2013, non-uniform crack fronts were observed in HAZ and FZ C(T) specimens. To mitigate deviation of the crack fronts during testing, C(T) specimens were thinned from their original 0.5 in (13 mm) to 0.25 in (6 mm) for the HAZ and FZ specimens. While this specimen

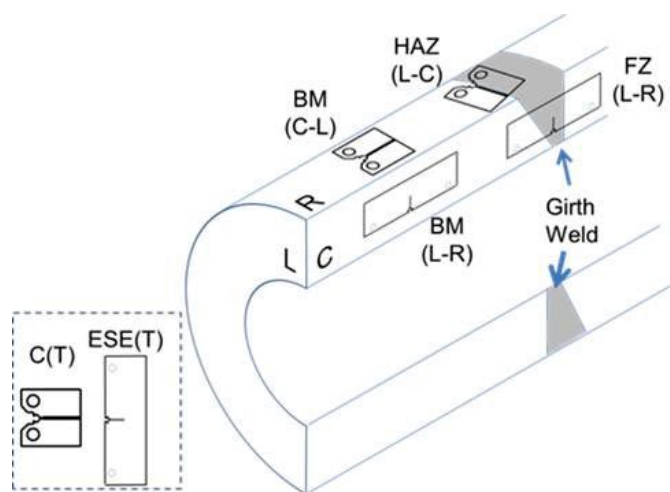


**FIGURE 1.** Optical-microscope image showing base metal, fusion zone, and HAZ of X65 weld.

modification improved results for the HAZ C(T) specimens, this thinning did not rectify non-uniform crack advance in the FZ C(T) specimens; therefore, both an alternate specimen geometry, i.e., the ESE(T), and crack propagation direction were adopted for the weld FZ, which improved crack front uniformity. Non-uniform crack fronts in the FZ were attributed to residual stress gradients [1] across the crack front. Figure 2 shows a schematic of the orientations and specimen geometries tested in this study with respect to the welded pipe. The first letter in parenthesis refers to the direction of applied load and the second letter refers to the crack propagation direction. Because of the residual stress gradient, the preferred orientation for the FZ specimens was longitudinal-radial (L-R). The ESE(T) specimens were extracted not only from the FZ but also from the BM (L-R and longitudinal-circumferential [L-C] orientations) for comparison. Uniform crack fronts were observed in all ESE(T) specimens.

The results from testing the X65 BM, HAZ, and FZ in 3,000 psi (21 MPa) hydrogen gas are shown in Figure 3. Tests performed in air at 10 Hz are also shown for comparison. The specimen orientation relative to the pipe is identified in parenthesis for each specimen tested and can be referenced in Figure 2, and tests performed in triplicate are identified by (x3). The FZ and BM circumferential-longitudinal (C-L) exhibited similar fatigue crack growth rates (FCGR) in hydrogen gas over the entire  $\Delta K$  range. The HAZ exhibited slightly lower crack growth rates in hydrogen gas for the lower  $\Delta K$  range but shows similar trends to the BM (C-L) and FZ in the higher range of  $\Delta K$ . These results indicate that the weld FZ and HAZ are no more susceptible to hydrogen-accelerated fatigue crack growth than the base metal.

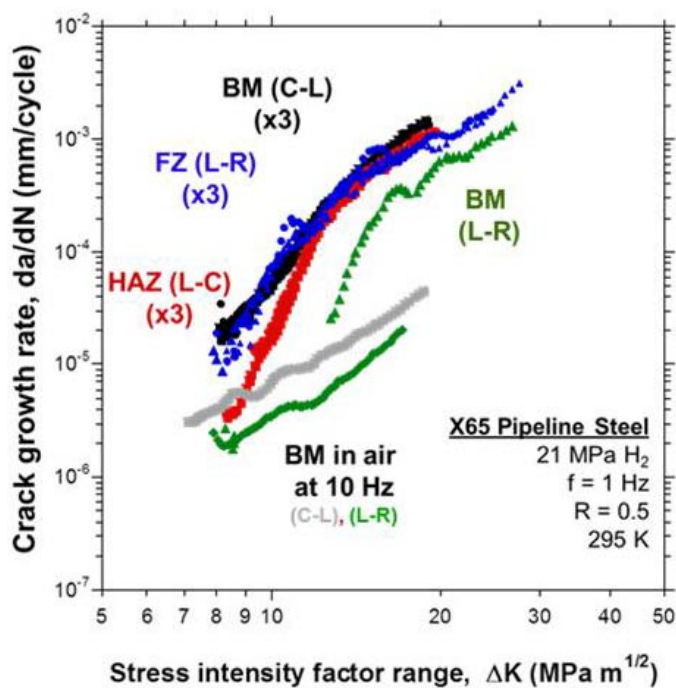
The effect of orientation on hydrogen-assisted FCGR is not well documented for line pipe steels, mainly



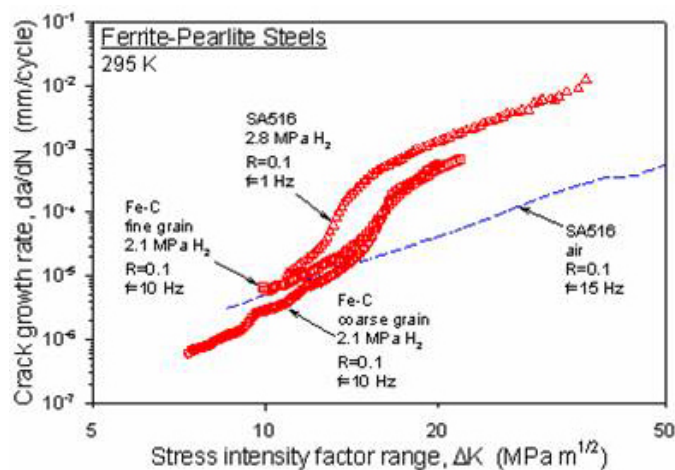
**FIGURE 2.** Schematic of gas metal arc welded pipeline with ESE(T) and C(T) specimens superimposed to show orientation tested for BM, HAZ, and FZ.

because geometrical constraints preclude testing in all orientations; however, the ESE(T) specimen geometry allows for BM samples to be extracted in the L-R orientation (see Figure 2). Additional tests were performed on BM ESE(T) specimens for the L-R orientation in both air and hydrogen gas as shown in Figure 3. The FCGR of BM (L-R) was 2 to 4 times lower in air and nearly an order of magnitude lower in hydrogen throughout the  $\Delta K$  range as compared to BM (C-L) tests in the respective environments. Microstructural banding is prevalent in pipeline steels with features elongated in the longitudinal and circumferential directions. Cracks propagating perpendicular to the banding (i.e., in L-R orientation) will encounter sequential planes of ferrite and pearlite which may affect FCGR. Previous work [2] showed lower hydrogen-assisted FCGR in fully pearlitic microstructures as compared to pure iron. This microstructural banding appears to play an important role in hydrogen-assisted FCGR for the X65 base metal when crack growth is perpendicular to the banded direction as demonstrated by the significantly lower FCGR in the BM (L-R) orientation.

In collaboration with the International Institute for Carbon-Neutral Energy Research, custom heats of two high-purity Fe-C materials were procured and delivered to Kyushu University (Fukuoka, Japan), a fine grain size (15  $\mu\text{m}$ ) heat and a coarse grain size (70  $\mu\text{m}$ ) heat. The goal was to assess whether the grain size in these model ferrite-pearlite steels



**FIGURE 3.** Fatigue crack growth rate relationships for X65 BM, HAZ, and FZ in 3,000 psi (21 MPa) hydrogen gas. The results are compared to measurements for X65 BM in air.



**FIGURE 4.** Fatigue crack growth rate relationships for fine and coarse grained model ferrite-pearlite steels. Data for a commercial ferrite-pearlite steel (SA516) is shown for comparison in air and hydrogen gas.

affects the onset of hydrogen-accelerated cracking. Tests on the model steels were performed at 10 Hz and  $R=0.1$  in 2.1 MPa hydrogen gas. Figure 4 shows the FCGR curves for the fine and coarse grain size steels along with data for a commercial ferrite-pearlite steel (SA516) in both air (15 Hz) and hydrogen gas (1 Hz) for comparison. Both model ferrite-pearlite steels exhibited the onset of hydrogen-accelerated fatigue crack growth at similar  $\Delta K$  ranges, suggesting that grain size does not have a pronounced effect. However, further testing (e.g., at higher load ratio,  $R$ ) is required to conclusively demonstrate such insensitivity of hydrogen-assisted FCGR to grain size.

## CONCLUSIONS AND FUTURE DIRECTIONS

- Reliable  $da/dN$  vs.  $\Delta K$  relationships were measured for the X65 weld FZ in 3,000 psi (21 MPa) hydrogen gas. Comparison of results shows that weld FZ and HAZ are no more susceptible to hydrogen-accelerated fatigue crack growth compared to the base metal.
- (future) Orientation was shown to have a pronounced effect on crack growth rate, therefore, in order to compare the BM and HAZ results directly similar orientations should be tested. Tests on C(T) specimens from the BM in L-C orientation will provide a more direct comparison to results from completed tests on C(T) specimens in the HAZ.
- (future) ESE(T) specimens will be extracted from a friction stir welded X52 pipe provided by Oak Ridge National Laboratory for triplicate testing in 3,000 psi (21 MPa) hydrogen gas.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

- Best Poster Award: “Assessing Hydrogen Pipeline Reliability: Quantifying Susceptibility of Pipeline Steels to Hydrogen Gas-Accelerated Fatigue Crack Growth,” Brian Somerdar and Joe Ronevich, ASME 12<sup>th</sup> Fuel Cell Science, Engineering and Technology Conference Boston, MA, June 30 - July 2, 2014.
- Brian Somerdar and Chris San Marchi, DOE Hydrogen and Fuel Cells Program Awards, Hydrogen Delivery and Safety, Codes and Standards, 2014.

## FY 2014 PUBLICATIONS/PRESENTATIONS

- “Effect of Hydrogen Gas Impurities on the Hydrogen Dissociation on Iron Surface”, A. Staykov, J. Yamabe, and B.P. Somerdar, *International Journal of Quantum Chemistry*, vol. 114, 2014, pp. 626-635.
- “Measurement of Fatigue Crack Growth Relationships for Steel Pipeline Welds in High-Pressure Hydrogen Gas”, J.A. Ronevich and B.P. Somerdar, submitted to Second International Conference on Metals & Hydrogen, 2014.
- “Measurements of  $H_2$ -Assisted Crack Growth in Pipeline Steels at SNL”, J. Ronevich, B. Somerdar, C. San Marchi, and K. Nibur, Joint DOC/DOE/DOT Meeting on Hydrogen Fuel Research, NIST, Boulder, CO, Dec. 2013.
- (invited) “Modeling of Gaseous Impurity Inhibition of Hydrogen Environment Embrittlement”, B. Somerdar, A. Staykov, P. Sofronis, and R. Kirchheim, TMS 2014 Annual Meeting & Exhibition, San Diego, CA, Feb. 2014.
- “Structural Materials Challenges in the Deployment of Hydrogen Pipelines”, B. Somerdar, Hydrogen Transmission and Distribution Workshop, National Renewable Energy Laboratory, Golden, CO, Feb. 2014.
- (invited) “Addressing Critical Issues for Hydrogen Gas-Accelerated Fatigue Crack Growth in Pipeline Steels: Effects of Welds and Oxygen Gas Impurities”, B. Somerdar, University of Virginia, Charlottesville, VA, March 2014.
- “Assessing Hydrogen Pipeline Reliability: Quantifying Susceptibility of Pipeline Steels to Hydrogen Gas-Accelerated Fatigue Crack Growth”, B.P. Somerdar and J.A. Ronevich, ASME 12<sup>th</sup> Fuel Cell Science, Engineering and Technology Conference Boston, MA, June 30 – July 2, 2014.

## REFERENCES

- Neeraj, T., Gnaupel-Herold, T., Prask, H.J., Ayer, R., “Residual stresses in girth welds of carbon steel pipes: neutron diffraction analysis,” *Science and Technology of Welding and Joining*. Vol. 16, No.3, pp. 249-253, 2011.
- Cialone, H.J. and Holbrook, J.H. “Microstructure and fractographic features of hydrogen-accelerated fatigue crack growth in steels” in *Microstructural Science* Vol. 14, Eds. M.R. Louthan, I. LeMay, and G.F. Vander Voort, ASM, Metals Park, OH, (1987) pp. 407-422.

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