

III.1 Hydrogen Embrittlement of Structural Steels

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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 2012 Accomplishments

A physics-based model for accelerated fatigue crack growth of steels in hydrogen gas with oxygen impurities was developed that enables the extrapolation of data over a range of hydrogen pressure, oxygen concentration, load-cycle frequency, and load ratio (R_K). This model demonstrates that the threshold level of oxygen required for mitigating accelerated fatigue crack growth of X52 steel in 21 MPa hydrogen gas is a function of load-cycle frequency and R_K .



Fiscal Year (FY) 2012 Objectives

- 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 3,000 psi (21 MPa)
- Measure the fatigue crack growth (da/dN vs. ΔK) relationship at constant H_2 gas pressure in X65 pipeline 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 Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines (Section 3.2.4)
- (K) Safety, Codes and Standards, Permitting (Section 3.2.4)

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

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 physics-based models, which provide important insights such as the effects of gas impurities (e.g., oxygen) and 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 code for hydrogen pipelines includes a fracture mechanics-based integrity management 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 physics-based models of hydrogen embrittlement in pipeline steels. The focus of this effort is to establish phenomenological models of hydrogen embrittlement in line-pipe steels using evidence from analytical techniques such as electron microscopy. These phenomenological models then serve as the framework for developing sophisticated finite-element models, which can provide quantitative insight into the effects of environmental, material, and mechanical variables. 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 damage-tolerant integrity management models applied to steel hydrogen pipelines. One such integrity management 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.

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 electric resistance seam weld.

The hydrogen-affected fatigue crack growth relationship (da/dN vs. ΔK) for the structural steel is the basic element in pipeline integrity management models. The ASME B31.12

code requires measurement of the fatigue crack growth relationship for pipeline steels at the hydrogen gas operating pressure. Previous results for pipeline and pressure vessel steels have demonstrated that gas species such as oxygen can favorably affect the fatigue crack growth relationship in hydrogen gas [1]. However, these studies have not systematically examined important variables such as the impurity partial pressure, hydrogen partial pressure, ΔK level, R ratio (K_{\min}/K_{\max}), and load-cycle frequency. Since the retarding effect of oxygen and other gas impurities on hydrogen-assisted fatigue crack growth may have technological benefits, the windows of variables that promote this positive effect need to be defined more quantitatively.

In the fourth quarter of FY 2011 and the first quarter of FY 2012, the effects of oxygen on the fatigue crack growth relationship for X52 base metal in hydrogen gas were measured for three hydrogen/oxygen gas mixtures: $H_2/10$ vppm O_2 , $H_2/100$ vppm O_2 , and $H_2/1,000$ vppm O_2 , in which the hydrogen gas partial pressure was approximately constant at 21 MPa. The da/dN vs ΔK relationships were measured at an R_K ratio (K_{\min}/K_{\max}) of 0.1 in all environments and at an additional R ratio of 0.5 in the $H_2/1,000$ vppm O_2 environment (Figure 1). Based on these trends, a model concept was conceived and developed in the second quarter of FY 2012, in which the onset of hydrogen-accelerated fatigue crack growth in the different hydrogen environments could be predicted.

The model was developed based on the following assumptions: 1) the onset of hydrogen-accelerated fatigue crack growth is activated by hydrogen uptake at the crack tip, which is impeded by oxygen adsorption on the crack-tip surface, 2) the rate of oxygen adsorption on the crack tip surface is governed by oxygen diffusion in the hydrogen

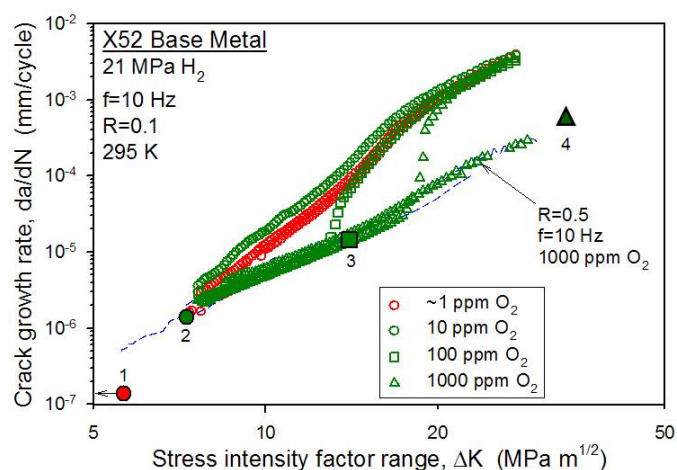


FIGURE 1. Fatigue crack growth rate (da/dN) vs stress-intensity factor range (ΔK) data for X52 steel in H_2/O_2 gas mixtures, high-purity hydrogen, and air. The symbols labeled 1, 2, 3, and 4 represent model predictions for the mechanical da/dN level required for $\theta_0 < 1$.

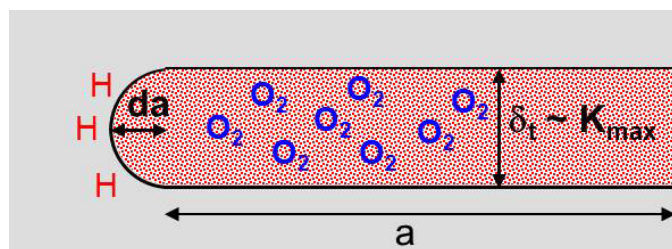


FIGURE 2. Schematic depicting the interactions between a mixed hydrogen/oxygen gas and a crack tip in steel opened at maximum load

gas, and 3) the extent of oxygen adsorption on the crack-tip surface depends on the area of new crack-tip surface created during each load cycle. These model elements are depicted in the schematic displayed in Figure 2. Prior to hydrogen-accelerated crack growth, the crack propagates in a manner dictated solely by mechanical driving forces. This “mechanical” crack growth rate, da/dN , is represented by the crack growth rates measured in an inert environment, i.e., air (blue dashed line in Figure 1). During this mechanical crack growth, the crack advances incrementally each load cycle, and the crack growth increment is equal to the measured da/dN . At the maximum load, the assumed relationship between the crack growth increment (da) and crack tip profile is shown in Figure 1. The new crack tip surface created during the load cycle is assumed to have a semicircular profile. The amount of oxygen adsorbed on this new crack tip surface is given by a simple mass balance: the adsorbed oxygen is equal to the flux of oxygen to the crack tip. The flux of oxygen in the crack channel is calculated using basic diffusion equations as well as the assumptions of steady state and a pressure equal to zero at the crack tip. The height of the crack channel is calculated from a fracture mechanics relationship between K_{max} and the crack opening. Based on these assumptions and relationships, an analytical expression was determined that relates the mechanical crack growth rate, da/dN , to the oxygen surface coverage, θ_o :

$$\frac{da}{dN} = \frac{Dp_o}{\theta_o \pi \nu RT} 0.6(1 - \nu_p^2) \frac{1}{E\sigma_0} \left(\frac{\Delta K}{\sqrt{a}(1 - R_K)} \right)^2$$

In this expression, D is the diffusivity of O_2 in the H_2 “matrix”, p_o is the partial pressure of oxygen in the bulk gas, ν is the load-cycle frequency, R is the gas constant, T is temperature, E is elastic modulus, σ_0 is yield strength, and a is the crack length. Although the original relationship was expressed in terms of K_{max} , this variable was replaced by the equivalent quantity $\Delta K/(1 - R_K)$ in order to include the R_K ratio.

Assuming that hydrogen uptake into the steel proceeds when oxygen delivered to the crack tip cannot cover the entire surface, i.e., $\theta_o < 1$, the model can predict the mechanical da/dN at the onset of accelerated crack growth.

Such predictions are indicated by the symbols labeled 1, 2, 3, and 4 in Figure 1. Considering points 2 and 3, these predictions represent the mechanical da/dN required for hydrogen uptake in the cases of bulk oxygen concentrations equaling 10 vppm and 100 vppm. As shown in Figure 1, the predicted mechanical da/dN levels are approximately equal to the levels at the onset of accelerated cracking for these two cases. Considering point 4, this is the predicted da/dN for hydrogen uptake when the bulk hydrogen concentration is 1,000 vppm and the R_K ratio is 0.5. The model accurately predicts that da/dN at the point of hydrogen uptake and accelerated crack growth is beyond the final point in the measured data set. The correlation between model predictions and experimental data is consistent with the notion that the onset of accelerated crack growth is controlled by the mechanical crack growth rate, which in turn governs the extent of oxygen adsorption on the freshly exposed crack tip. The prediction represented by point 1 is for the case of 1 vppm oxygen. In this case, the mechanical da/dN for hydrogen uptake is substantially lower than the da/dN at the onset of accelerated crack growth. The interpretation here is that thresholds for two mechanical variables must be exceeded for accelerated crack growth: a threshold level of da/dN for hydrogen uptake and a threshold level of K_{max} to activate the embrittlement. For the high-purity hydrogen case, oxygen does not hinder hydrogen uptake, but accelerated cracking is not activated until a critical K_{max} is reached.

The oxygen-diffusion model provides insights into the mechanical variables that dictate the onset of accelerated crack growth for steel in hydrogen/oxygen environments. This model can also be used to quantify the mechanical variables that affect the onset of accelerated cracking for components such as pipelines that contain hydrogen with small concentrations of oxygen. For example, the model demonstrates that higher R_K ratios lead to higher mechanical da/dN for hydrogen uptake and accelerated crack growth. This indicates that the onset of accelerated crack growth is displaced to higher mechanical da/dN when the components operate at higher pressure ratios (p_{min}/p_{max}). Thus, the reliability/integrity of a component containing hydrogen/oxygen is enhanced at higher pressure ratios.

The hydrogen diffusion model was developed in collaboration with Prof. Petros Sofronis (University of Illinois/International Institute for Carbon-Neutral Energy Research) and Prof. Reiner Kirchheim (University of Göttingen/International Institute for Carbon-Neutral Energy Research).

In the third quarter of FY 2012, fatigue crack growth specimens were prepared from the girth weld in a section of X65 steel pipe supplied by ExxonMobil (Figure 3). The fatigue crack growth rate, da/dN , vs. stress-intensity factor range, ΔK , relationship for the girth weld in hydrogen gas will be measured from these specimens.



FIGURE 3. X65 steel girth weld supplied by industry partner

Conclusions and Future Directions

- The development of a physics-based model for accelerated fatigue crack growth of steels in hydrogen gas with oxygen impurities enables the extrapolation of data over a range of hydrogen pressure, oxygen concentration, load-cycle frequency, and load ratio (R_K). This model demonstrates that the threshold level of oxygen required for mitigating accelerated fatigue crack growth of X52 steel in 21 MPa hydrogen gas is a function of load-cycle frequency and R_K .
- (future) Measure the fatigue crack growth (da/dN vs ΔK) relationship at constant H_2 gas pressure in X65 pipeline girth weld supplied by industry partner.

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FY 2012 Publications/Presentations

1. "The Effect of Trace Oxygen on Gaseous Hydrogen-Accelerated Fatigue Crack Growth in a Low-Strength Pipeline Steel", B. Somerday, C. San Marchi, K. Nibur, P. Sofronis, and R. Kirchheim, 2012 TMS Annual Meeting & Exhibition, Orlando FL, March 2012.
2. "Gaseous Hydrogen-Assisted Fatigue Crack Growth in X52 Linepipe Steel", B. Somerday, C. San Marchi, and K. Nibur, MS&T 2011, Columbus OH, October 2011.

References

1. C. San Marchi and B.P. Somerday, *Technical Reference on Hydrogen Compatibility of Materials*, SAND2008-1163, Sandia National Laboratories, Livermore, CA, 2008.