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# SANDIA NATIONAL LABORATORIES
# HYDROGEN PRODUCTION AND DELIVERY PROGRAM

QUARTERLY PROGRESS REPORT FOR JANUARY 1–MARCH 31, 2012

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**RECIPIENT:** SANDIA NATIONAL LABORATORIES

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# TASK 2: ENABLING HYDROGEN EMBRITTLEMENT MODELING OF STRUCTURAL STEELS

**COVERING PERIOD:** JANUARY 1, 2012 THROUGH MARCH 31, 2012

**DATE OF REPORT:** APRIL 27, 2012

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## FY 2012 MILESTONES/DELIVERABLES

| Task | Planned | Status |
|---|---|---|
| **Task 2: Enabling Hydrogen Embrittlement Modeling of Structural Steels** | | |
| ***Subtask 2.1: Measurement of Fracture Properties of Structural Steels in High-Pressure $H_2$*** | | |
| 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 | 6/12 | In progress |
| ***Subtask 2.2: Effect of Gas Impurities on Fracture Properties in $H_2$*** | | |
| Quantify the relationship between $H_2$ pressure and the threshold level of oxygen impurity concentration required to mitigate hydrogen-accelerated fatigue crack growth of X52 steel. | 9/12 This milestone is deferred at the lower funding target. | |
| ***Subtask 2.3: 2012 International Hydrogen Conference*** | | |
| Organize and convene the 2012 International Hydrogen Conference at Jackson Lake Lodge, Grand Teton National Park, WY | 9/12 | In progress |

## OBJECTIVE

The principal objective of this project is to provide an experimental component to the development of prognosis models for steel hydrogen gas pipelines. These models include both mechanism-based simulations of hydrogen embrittlement as well as structural integrity analyses to predict safety margins for pipelines. The aim of the experimental effort is to establish physical models of hydrogen embrittlement in steels and to generate material properties that serve as model inputs. The focus of the latter is on fracture mechanics properties such as crack propagation thresholds and fatigue crack growth relationships.

## BACKGROUND

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. While hydrogen embrittlement compromises the structural integrity of steel components, decades of research and industrial experience have allowed many salient variables that affect hydrogen embrittlement of steels to be identified. As a result, established paths exist to manage hydrogen embrittlement in steels and to quantify safety margins for steel hydrogen containment structures. For example, fatigue crack growth aided by hydrogen embrittlement is a potential failure mode for steel hydrogen containment structures subjected to pressure cycling. Applying appropriate structural integrity models coupled with measuring relevant material properties in hydrogen gas allows quantification of safety margins against fatigue crack growth in hydrogen containment structures.

## STATUS

The fatigue crack growth rate (da/dN) vs stress-intensity factor range ($\Delta K$) relationship is a necessary material-property input into damage-tolerant life prediction models applied to steel hydrogen pipelines. One such life prediction 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 (FY08) 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 ERW seam weld.

The hydrogen-affected fatigue crack growth relationship (da/dN vs $\Delta K$) for the structural steel is the basic element in pipeline life-prediction 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 FY11Q4 and FY12Q1, 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 ppm $O_2$, $H_2$/100 ppm $O_2$, and $H_2$/1000 ppm $O_2$, in which the hydrogen gas partial pressure was approximately constant at 21 MPa. The da/dN vs ΔK relationships were measured at an R ratio ($K_{min}/K_{max}$) of 0.1 in all environments and at an additional R ratio of 0.5 in the $H_2$/1000 ppm $O_2$ environment (Figure 1). Based on these trends, a model concept was conceived and developed in FY12Q2, 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 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, $\theta_O$:

$$\frac{da}{dN}=\frac{Dp_O}{\theta_O \pi \nu RT}0.6(1-\nu_P{}^2)\frac{1}{E\sigma_0}\left(\frac{\Delta K}{\sqrt{a}(1-R)}\right)^2$$

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, $\sigma_0$ 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 $\Delta K/(1-R)$ in order to include the R ratio.

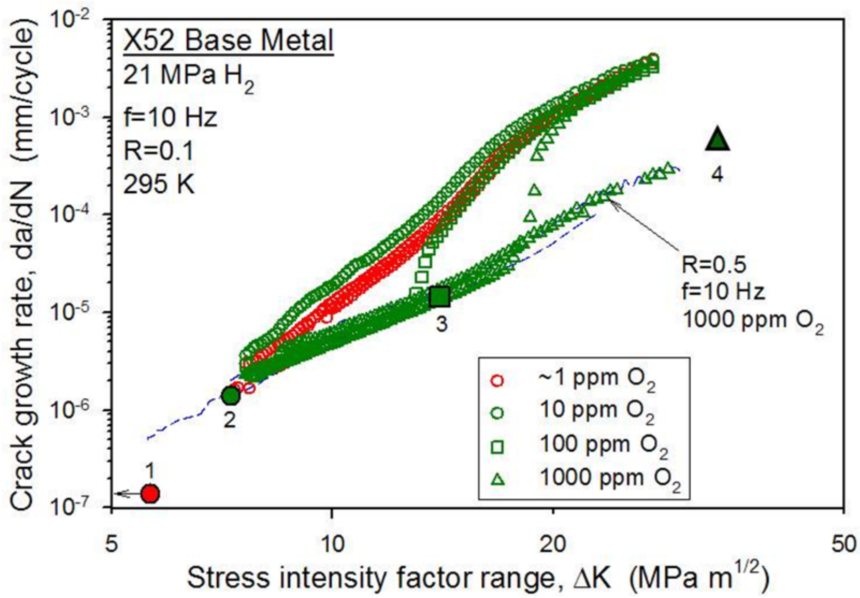


**Figure 1.** Fatigue crack growth rate (da/dN) vs stress-intensity factor range ($\Delta K$) data for X52 steel in hydrogen/oxygen gas mixtures, high-purity hydrogen, and air. The symbols labeled 1, 2, 3, and 4 represent model predictions for the mechanical da/dN level required for $\theta_O < 1$.

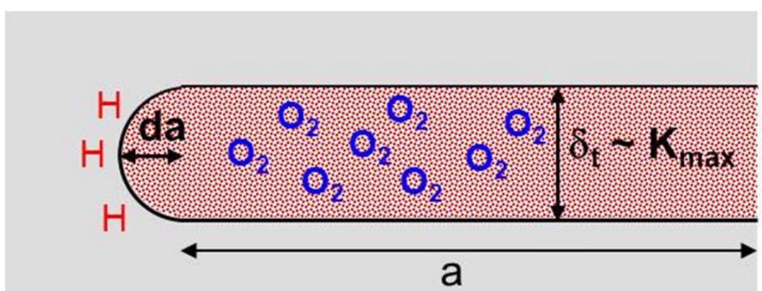


**Figure 2.** Schematic depicting the interactions between a mixed hydrogen/oxygen gas and a crack tip in steel opened at maximum load.

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 ppm and 100 ppm. 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 1000 ppm and the R 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 ppm 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 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).

#### REFERENCES

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

### PLANS FOR NEXT QUARTER AND KEY ISSUES

The primary objective for FY12 Q3 is to prepare fatigue crack growth test specimens from girth welds in pipeline steels. ExxonMobil has supplied a generous quantity of girth weld in an X65 steel pipe (Figure 3). Test specimens will be prepared from this X65 girth weld.


**Figure 3.** X65 steel girth weld supplied by ExxonMobil.

## PUBLICATIONS / PRESENTATIONS

- "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, R. Kirchheim, 2012 TMS Annual Meeting & Exhibition, Orlando FL, March 2012.