IX.3 Materials Compatibility

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Project End Date: Project continuation and direction determined annually by DOE

Objectives

(1) Technical Reference on Hydrogen Compatibility of Materials
   - Compile historical data from published technical documents in an Internet-based resource.
   - Update published Technical Reference chapters to reflect new data from current applied research activities.

(2) Materials Testing
   - Fill gaps in database by generating benchmark data on compatibility of structural materials in hydrogen gas, emphasizing commercial materials tested in high-pressure gas.
   - Establish procedures for generating reliable, conservative design data for structural materials in high-pressure hydrogen gas.

(3) Codes and Standards Advocacy
   - Participate in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines (Section 3.2.4)
(G) Storage Tank Materials and Costs (Section 3.2.4)
(N) Insufficient Technical Data to Revise Standards (Section 3.7.4)

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 6**: Materials compatibility technical reference updated (2Q, 2009). This project directly addresses the milestone by continuing to augment the content of the Technical Reference on Hydrogen Compatibility of Materials, both through the evaluation of published data as well as the generation of new data.
- **Milestone 21**: Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012). This project enables the development and implementation of codes and standards by providing expertise and data on hydrogen compatibility of structural materials.

Accomplishments

- Completed new Technical Reference chapters on “stabilized” austenitic stainless steels (i.e., 321 and 347) as well as 2XXX and 7XXX aluminum, increasing the total number of chapters to 21. Updated chapter on duplex stainless steels with data from Sandia materials testing activity.
- Completed measurements of sustained-load cracking thresholds on Ni-Cr-Mo pressure vessel steel American Society of Mechanical Engineers (ASME) SA-372 Grade L in 100 MPa hydrogen gas. These measurements serve as benchmark data for implementing design standards such as ASME Article KD-10.
- Measured cracking thresholds of Cr-Mo pressure vessel steels in 100 MPa hydrogen gas using “crack initiation” test method. Comparison of these “crack initiation” thresholds to the sustained-load cracking thresholds (i.e., “crack arrest” thresholds) indicates that the sustained-load cracking thresholds may be non-conservative.
- Measured fatigue crack growth rates of the Cr-Mo pressure vessel steel ASME SA-372 Grade J in 100 MPa hydrogen gas. These tests represent the successful operation of the new Sandia laboratory capability for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas.

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Introduction

A major barrier to the development of a hydrogen economy and the deployment of hydrogen technologies is the lack of validated safety codes and standards. The purpose of this project is to provide the technical basis for assessing the safety of hydrogen-based systems with the accumulation of knowledge feeding into the development or modification of relevant codes and standards. The materials compatibility effort focuses on developing a resource entitled the Technical Reference on Hydrogen Compatibility of Materials. This effort is driven by the need for a materials guide, as identified in the Multi-Year Research, Development and Demonstration Plan (Table 3.7.5). The content of the Technical Reference is being developed by identifying and documenting materials data from journal articles and institutional reports. Voids in the database uncovered during the process of composing the Technical Reference are addressed through a materials testing activity.

Approach

The focal point of this Materials Compatibility project is composing the Technical Reference on Hydrogen Compatibility of Materials. To accomplish this objective, two activities are proceeding in parallel: identifying and compiling existing data from technical documents, and generating new data through a materials testing program. The high-priority structural materials featured in these activities are low-alloy and carbon steels, austenitic stainless steels, and aluminum alloys. The materials testing activity emphasizes high hydrogen gas pressures (>100 MPa), fracture mechanics methods, and material fabrication and service variables (e.g., welds, temperature). The data from materials testing are critically reviewed to ensure measurements reflect lower-bound fracture properties and enable structural design.

As part of codes and standards advocacy, Sandia personnel are actively engaged in the codes and standards development process through direct participation in standards development organizations such as ASME, Canadian Standards Association, and International Organization for Standardization. This participation ensures that the standards development organizations have the most current technical information on structural material compatibility. Sandia personnel provide guidance in the development of both component design standards as well as materials testing standards.

Results

Technical Reference

Three new chapters were completed for the electronic, Internet-based version of the Technical Reference, increasing the total number of chapters to 21. These new chapters cover the "stabilized" austenitic stainless steels (i.e., 321 and 347) as well as the 2XXX and 7XXX aluminum alloys. The chapter on 321 and 347 stainless steels was composed in response to needs expressed by stakeholders. The chapters on 2XXX and 7XXX aluminum are the first in the Technical Reference on high-strength aluminum alloys, a technologically important class of alloys that are being considered as lower-cost alternatives to stainless steels in components such as fittings.

Materials Testing

Sustained-load cracking measurements were completed on the Ni-Cr-Mo pressure vessel steel ASME SA-372 Grade L in 100 MPa hydrogen gas. The SA-372 Grade L could be desirable for fabrication of high-pressure hydrogen gas vessels, since the steels can be heat treated more effectively in thick sections. Panels of the SA-372 Grade L were obtained from an industrial partner, who removed the panels from a seamless pipe and heat treated the panels to two different strength levels. One strength level (1,050 MPa yield strength) met the standard specification for SA-372 Grade L steel, while the other strength level (760 MPa yield strength) was substantially reduced to enhance the hydrogen compatibility of the steel. Measurements of the sustained-load cracking thresholds (K_{TH}) are plotted in Figure 1, and the different thresholds for the two strength levels of steel are readily apparent. The lower-strength SA-372 Grade L steel has a K_{TH} value that is similar to the Cr-Mo steel SA-372 Grade J, which was tested previously (Figure 1). Since this Cr-Mo steel is currently used in hydrogen gas pressure vessels, the results suggest that heat treating SA-372 Grade L to a lower strength level could represent a technologically attractive condition for this steel in stationary hydrogen pressure vessels. Similar to previous measurements of K_{TH} for the Cr-Mo pressure vessels steels (Figure 1), measurements for the Ni-Cr-Mo steel SA-372 Grade L are motivated by the materials qualification specifications in ASME Article KD-10.

Fracture toughness tests (i.e., measurements of the threshold for crack propagation under rising displacement) were conducted on the three Cr-Mo pressure vessel steels previously tested under static displacement. The static-displacement procedure is used to measure K_{TH}, where the threshold is defined at crack arrest. In contrast, the fracture toughness tests under rising displacement yield the threshold at crack initiation

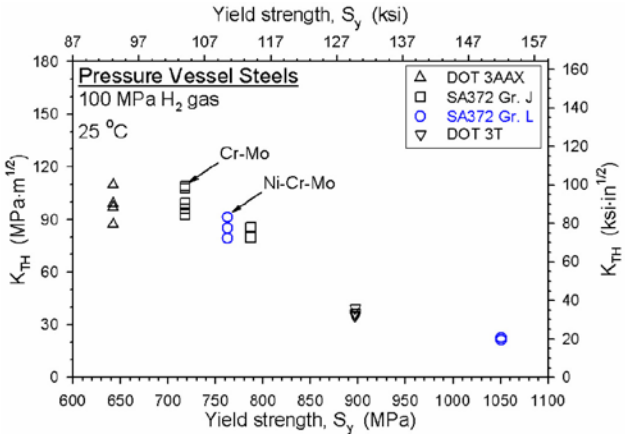

FIGURE 1. Benchmark values of K_{TH} measured in 100 MPa hydrogen gas for the Ni-Cr-Mo pressure vessel steel SA-372 Grade L. Included in the plot are previous data measured for Cr-Mo pressure vessel steels in 100 MPa hydrogen gas.

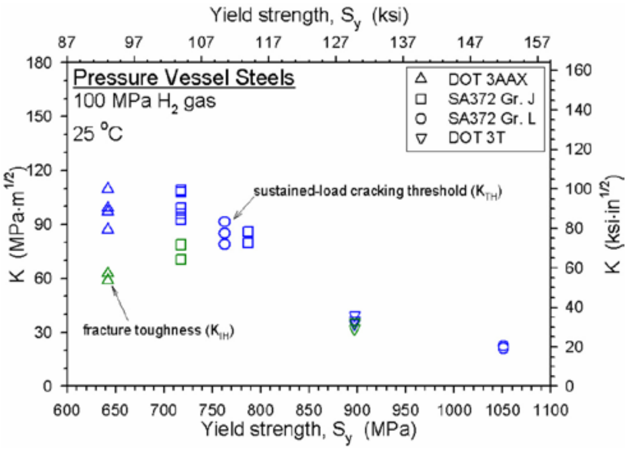

FIGURE 2. Comparison of fracture toughness values (i.e., "crack initiation" thresholds) to sustained-load cracking thresholds (i.e., "crack arrest" thresholds) for Cr-Mo pressure vessel steels in 100 MPa hydrogen gas.

(K_{IH}). The fracture toughness data in 100 MPa hydrogen gas are plotted in Figure 2 to compare these results to the sustained-load cracking thresholds. Figure 2 shows that the fracture toughness and sustained-load cracking measurements are comparable for the highest-strength steel (DOT 3T), but the fracture toughness is notably lower than the sustained-load cracking threshold for the DOT 3AAX and SA-372 Grade J steels. This latter comparison indicates that the "crack arrest" method for measuring the threshold is not the most conservative measurement of crack propagation resistance in hydrogen gas for the lower-strength steels. Since the ASME Article KD-10 currently only requires measurement of the threshold using "crack arrest" methods, these results could lead to consideration of including "crack initiation"(i.e., fracture toughness) measurements as well.

Fatigue crack growth tests in high-pressure hydrogen gas were conducted on three heats of the Cr-Mo pressure vessel steel SA-372 Grade J. The execution of these tests demonstrates the successful effort to develop a capability for conducting fatigue crack growth tests in hydrogen gas up to 100 MPa, and this capability is one of only four known to exist or be in development (the other three are in Japan and the United Kingdom). Fatigue crack growth testing is needed to support the development and implementation of hydrogen containment design codes such as ASME Article KD-10. This code specifies testing to measure fatigue crack growth rates in hydrogen gas to design against fatigue failure, which is promoted by pressure cycling in hydrogen containment components. The fatigue crack growth testing on SA-372 Grade J represents a collaborative effort with an industrial partner. This industrial partner supplied the materials and will use the data (Figure 3) to design a hydrogen gas pressure vessel following ASME Article KD-10.

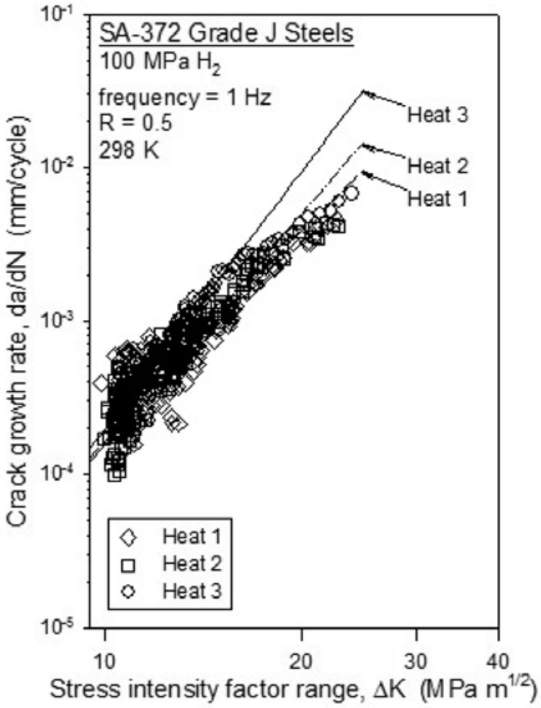

FIGURE 3. Fatigue crack growth rates measured for three heats of the Cr-Mo pressure vessel steel SA-372 Grade J in 100 MPa hydrogen gas.

Conclusions and Future Directions

- The Technical Reference on Hydrogen Compatibility of Materials continues to evolve as intended, where new chapters are created in response to stakeholder needs and existing chapters are updated to include data generated from the materials testing activity.
- Benchmark sustained-load cracking data that are required to qualify pressure vessel steels for high-

pressure hydrogen service according to ASME Article KD-10 have now been generated for the technologically relevant Ni-Cr-Mo steels as well as the Cr-Mo steels.

- Results showed that the sustained-load cracking threshold (i.e., "crack arrest" threshold) may be non-conservative relative to the fracture toughness (i.e., "crack initiation" threshold) measured in hydrogen gas, which could lead to changes in the test methods in ASME Article KD-10.
- Fatigue crack propagation rates measured for the Cr-Mo pressure vessel steel ASME SA-372 Grade J in hydrogen represent a rare data set at 100 MPa gas pressure and enable qualification of this steel for high-pressure hydrogen service according to ASME Article KD-10.
- (future) Create new Technical Reference chapter on nickel alloys and update chapters on ferritic steels with data from materials testing activity.
- (future) Evaluate the effects of load cycle frequency on fatigue crack growth rate of ferritic steels in hydrogen gas.
- (future) Compare fatigue crack growth data for stainless steels tested in hydrogen gas vs. hydrogen-precharged condition.
- (future) Develop reliable methods for measuring fracture response of aluminum alloys in hydrogen gas.
- (future) Engage domestic and international stakeholders to develop materials qualification standards for pressure manifold components (i.e., fittings, regulators, etc.).

FY 2009 Publications/Presentations

1. *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.

2. (invited presentation) "Hydrogen Effects in Materials", B. Somerday, *3rd European Summer School on Hydrogen Safety*, Belfast, UK, July 2008.

3. (invited presentation) "Hydrogen-Assisted Fracture of Austenitic Stainless Steels", C. San Marchi et al., *2008 International Hydrogen Conference*, Moran, WY, Sept. 2008.

4. (invited presentation) "Variables Affecting Measurement of Sustained Load Cracking Thresholds in Hydrogen Gas", K. Nibur and B. Somerday, *ISO/TC 58/WG 7 Workshop on H2 Test Methods,* Atlanta, GA, Sept. 2008.

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

6. "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.

7. "Hydrogen-Assisted Fracture of Welded AISI 316 Austenitic Stainless Steel", X. Tang, G. Schiroky, C. San Marchi, and B. Somerday, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH , 2009, in press.

8. "Characterization of Hydrogen-Assisted Fracture Mechanism by Fracture Surface Topography Analysis (FRASTA)", T. Kobayashi, B. Somerday, C. San Marchi, and K. Nibur, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.

9. "Effect of Internal Hydrogen on Fatigue Strength of Type 316 Stainless Steel", C. Skipper, G. Leisk, A. Saigal, D. Matson, and C. San Marchi, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH , 2009, in press.

10. "Measurement of Fatigue Crack Growth Rates for Steels in Hydrogen Containment Components", B. Somerday, K. Nibur, and C. San Marchi, submitted to *3rd International Conference on Hydrogen Safety.*