VII.3 Hydrogen Safety, Codes and Standards R&D: Materials Compatibility

Jay Keller (Primary Contact), Chris Moen, Brian Somerday and Chris San Marchi
Sandia National Laboratories
P.O. Box 969
Livermore, CA 94550
Phone: (925) 294-3316; Fax: (925) 294-2276
E-mail: jokelle@sandia.gov

DOE Technology Development Manager:
Antonio Ruiz
Phone: (202) 586-0729; Fax: (202) 586-9811
E-mail: Antonio.Ruiz@ee.doe.gov

Project Start Date: FY 2003
Project End Date: Project continuation and direction determined annually by DOE

Objectives

1. Technical Reference on Hydrogen Compatibility of Materials
   - Identify and document existing data from technical journals and institutional technical reports in an internet-based resource.
2. Materials Testing
   - Generate new data on compatibility of structural materials in hydrogen gas, emphasizing commercial materials tested in high-pressure gas. Establish procedures for generating reliable 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 Multi-year Research Development and Demonstration Plan:

(F) Control and Safety (Section 3.1.4.2)
(K) Durability (Section 3.1.4.2)
(D) High Capital Cost and Hydrogen Embrittlement of Pipelines (Section 3.2.4.2)
(B) Hydrogen Storage (Section 3.5.4.2
(E) Codes and Standards (Section 3.5.4.2)
(N) Insufficient Technical Data to Revise Standards (Section 3.6.4.2)

Contribution to Achievement of DOE Codes and Standards Milestones

This project will contribute to achievement of the following DOE Codes and Standards milestones from the Hydrogen 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 creating and maintaining the Technical Reference for Hydrogen Compatibility of Materials.
- **Milestone 21: Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012).** This project will enable the development and implementation of codes and standards by providing expertise and data on hydrogen compatibility of structural materials.

Accomplishments

- Completed version 1 of the Technical Reference for Hydrogen Compatibility of Materials. This internet-based resource consists of 14 material-specific chapters that provide guidance on selection of structural materials for applications such as pressure vessels, pipelines, and gas manifold components.
- Measured hydrogen-assisted cracking thresholds for industry-supplied pressure vessel steels in 100 MPa hydrogen gas, providing data that can be employed in new American Society of Mechanical Engineers (ASME) design codes for hydrogen pressure vessels. Threshold values for SA 372 Gr. J steel (90 $\text{MPa}\cdot\text{m}^{1/2}$) are approximately three-fold higher than values measured in previous studies.
- Measured tensile fracture resistance of hydrogen-exposed 316 stainless steels as a function of alloy composition, strain hardening, temperature, and stress concentration. Hydrogen-assisted fracture becomes more severe at nickel concentrations less than 12% and under an imposed stress concentration.
- Initiated collaborations with the Hydrogen Industrial Use and Storage (HYDROGENIUS) project at Kyushu University in Japan.

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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 tested 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 for the Hydrogen Compatibility of Materials. This effort is driven by the need for a materials guide, as identified in the draft Multi-Year Research, Development and Demonstration Plan (Table 3.6.5) issued in June 2003. 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 will be addressed through a materials testing activity.

Approach

Efforts during this year were directed toward the following project components: (1) Hydrogen-Compatible Materials and (2) Codes and Standards Advocacy. The purpose of the Hydrogen-Compatible Materials component is to enable the development of codes and standards by compiling existing data and generating new data on the mechanical properties of structural materials exposed to hydrogen gas. The focal point of the effort is composing The Technical Reference for Hydrogen Compatibility of Materials, which emphasizes data on the structural materials and service conditions of interest to stakeholders. Activities involve two parallel paths: identifying and documenting existing data from journals and reports, and generating new data through a materials testing program. The high-priority structural materials are carbon and low-alloy steels, stainless steels, and aluminum alloys. The data reflect salient service conditions, such as hydrogen gas pressure, temperature, and mechanical loading state.

As part of Codes and Standards Advocacy, Sandia is an active participant in the codes and standards development process through groups such as ASME and the Canadian Standards Association (CSA). This participation ensures that the standards and codes development organizations have the most current technical information on structural material compatibility and that the correct scientific knowledge base is developed in the most expedient way possible.

Results

Technical Reference

The first version of the Technical Reference for Hydrogen Compatibility of Materials was completed in May 2007. Version 1 of the Technical Reference consists of 14 material-specific chapters, each of which summarizes data culled from the peer-reviewed technical literature and institutional technical reports. Four of the total 14 chapters were completed since the last annual report: ferritic stainless steels, duplex stainless steels, non-heat treatable aluminum, and carbon steels. The chapter on carbon steels is particularly important, since carbon steels are the leading candidate structural materials for hydrogen gas pipelines.

Materials Testing

Construction of the glove box for preparing crack-growth specimens in a low-oxygen environment was completed. The function of the glove box is to limit the extent of oxide formation on the crack surface after loads are applied to the test specimens, enabling hydrogen uptake into the specimens during subsequent exposure to hydrogen gas. The glove box and associated argon gas purifier were successfully operated, and the target of 1 ppm oxygen in the glove box was achieved.

While the crack-growth specimens have not yet been analyzed for the DOT 3T and DOT 3AAX steels, final results have been determined for the SA 372 Grade J steel. The crack-growth thresholds for SA 372 Grade J are plotted in Figure 1 along with literature data for similar pressure vessel steels in high-pressure hydrogen gas. The thresholds for SA 372 Grade J are about 90 MPa·m$^{1/2}$, which are significantly greater than values for the 4145 and 4147 steels at 100 MPa hydrogen gas pressure. While the metallurgical origin of the

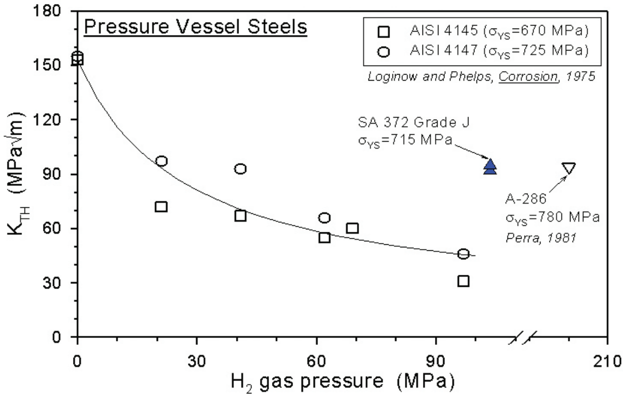

FIGURE 1. Crack-growth thresholds for SA 372 Grade J and two similar pressure vessel steels (4145 and 4147) in high-pressure hydrogen gas. Results are also shown for the stainless steel A-286.

dramatically higher crack-growth threshold for SA 372 Grade J has not been identified, the improved properties may reflect changes in steelmaking practices that have evolved over the last 30 years.

Testing of hydrogen-exposed 316 stainless steels has continued in collaboration with a piping and valve component manufacturer. This testing has been motivated not only by the needs of industrial stakeholders but also by ASME priorities. Testing of hydrogen-exposed 316 stainless steel has focused on the effects of alloy composition, strain-hardened microstructures, sub-ambient temperature, and stress concentration on tensile deformation and fracture. The results show that reducing nickel content lowers the reduction of area (RA), indicating greater susceptibility to hydrogen-assisted fracture. The effect of stress concentration was assessed by testing tensile specimens with circumferential notches. Measurements of the ratio of RA measured from hydrogen-exposed specimens to RA for non-exposed specimens (i.e., relative ductility) for both smooth and notched specimens as a function of temperature demonstrate that the RA ratios at 298, 258, and 223 K are similar in 316 stainless steels that have approximately 135 wppm dissolved hydrogen. However, the RA ratio is notably lower for the notched specimens compared to the smooth specimens, indicating that stress concentration significantly affects hydrogen-assisted fracture.

The effort to install a system for conducting materials testing under dynamic loading in high-pressure hydrogen gas has made significant progress. One of the primary components of the system, a mechanical test frame manufactured by MTS, was delivered in September 2006. Most of the lab infrastructure needed to support the testing system has been acquired and assembled, including a manifold designed and constructed by Sandia personnel that will deliver high-pressure hydrogen and helium gases to the testing system. Delivery of the pressure vessel to Sandia has been delayed by several months due to difficulties associated with two electrical feedthroughs supplied by subcontractors. The latest delivery date communicated by the vessel manufacturer, Autoclave Engineers, is June 30, 2007.

Technical Interactions

A relationship was established with the HYDROGENIUS project operating at Kyushu University in Japan. The HYDROGENIUS project is lead by Professor Yukitaka Murakami and is funded by the Ministry of Economy, Trade and Industry in Japan. The primary objective of the project is to study hydrogen embrittlement of structural materials in hydrogen energy infrastructure. The emphasis of much of the current materials testing in HYDROGENIUS is hydrogen-assisted fatigue crack propagation in 316 stainless steel. Interactions will continue with Professor Murakami and the HYDROGENIUS project to share information and work in areas of mutual interest.

Conclusions and Future Directions

- Data collected for version 1 of the Technical Reference for Hydrogen Compatibility of Materials will provide some guidance on the performance of carbon and low-alloy steels, stainless steels, and aluminum alloys in hydrogen gas environments. More data are needed to ensure the design methodologies in evolving codes and standards can be fully implemented.
- The hydrogen-assisted cracking thresholds measured for SA 372 Grade J steel in 100 MPa hydrogen gas (90 $\mathrm{MPa{\cdot}m^{1/2}}$) are unexpectedly high. This cracking threshold approaches the value for high-strength stainless steels, suggesting that conventional, low-cost steels may be attractive candidates for stationary hydrogen gas storage vessels.
- The hydrogen compatibility of 316 stainless steels is sensitive to alloy composition and stress concentration. The performance of 316 stainless steels in hydrogen gas may be optimized for nickel concentrations greater than 12%. Hydrogen-assisted fracture in 316 stainless steel components will be promoted near stress risers, e.g., at threads and fittings.
- Compose new chapters for version 2 of Technical Reference for Hydrogen Compatibility of Materials (e.g., 310, 321, and 17-4 PH stainless steels).
- Measure fatigue crack growth rates in the chromium-molybdenum steel SA 372 Grade J in high-pressure hydrogen gas.
- Measure cracking thresholds and fatigue crack growth rates in a nickel-chromimum-molybdenum pressure vessel steel (e.g., SA 372 Grade M) in high-pressure hydrogen gas.
- Continue testing of 316 stainless steels, emphasizing measurement of fatigue crack growth rates and performance of welds.

Special Recognitions & Awards/Patents Issued

1. R&D award from Hydrogen, Fuel Cells and Infrastructure Technologies Program Office for accomplishments in Hydrogen Safety, Codes and Standards.

FY 2007 Publications/Presentations

Presentations

1. (invited) B. Somerday and C. San Marchi, “Structural Materials Challenges in the Hydrogen Economy Infrastructure”, Hydrovision 2006, The Hydrogen Economy 2006 workshop, Portland, OR, August 2006.

2. C. San Marchi and B. Somerday, “The Effects of Gaseous Hydrogen on Structural Materials”, Codes and Standards Tech Team Meeting, Livermore, CA, January 2007.

3. (invited) B. Somerday, C. San Marchi, K. Nibur, and D. Balch, “Hydrogen-Assisted Fracture of Steels for High-Pressure Gas Containment”, International Hydrogen Energy Development Forum and Workshop, Fukuoka, Japan, February 2007.

4. B. Somerday, C. San Marchi, and K. Nibur, “Sandia Hydrogen Safety, Codes and Standards: Materials Compatibility”, Hydrogen Safety Panel Meeting, Livermore, CA, February 2007.

5. C. San Marchi and B. Somerday, “Effects of high-pressure gaseous hydrogen on structural metals”, SAE World Congress, Detroit, MI, April 2007.

Publications

1. C. San Marchi, B. Somerday, J. Zelinski, X. Tang, and G.Schiroky, “Mechanical Properties of Super Duplex Stainless Steel 2507 After Gas Phase Thermal Precharging with Hydrogen”, Metallurgical and Materials Transactions A, 2007, in press.

2. C. San Marchi and B. Somerday, “Effects of High-Pressure Gaseous Hydrogen on Structural Metals”, Document No. 2007-01-0433, SAE World Congress, 2007.

3. B. Somerday, K. Nibur, D. Balch, and C. San Marchi, “Hydrogen-Assisted Fracture of a Cr-Mo Steel for High-Pressure Gas Containment”, Proceedings of International Hydrogen Energy Development Forum & Workshop, Fukuoka, Japan, 2007.

4. C. San Marchi, D. Balch, K. Nibur, and B. Somerday, “Effect of High-Pressure Hydrogen Gas on Fracture of Austenitic Steels”, Journal of Pressure Vessel Technology, 2007, in press.

5. C. San Marchi, B. Somerday, X. Tang, and G. Schiroky, “Effects of Alloy Composition and Strain Hardening on Tensile Fracture of Hydrogen-Precharged Type 316 Stainless Steels”, International Journal of Hydrogen Energy, 2007, in review.