VIII.2 Hydrogen Safety, Codes and Standards R&D: Materials Compatibility

Chris Moen (Primary Contact), Jay Keller, Brian Somerday, Chris San Marchi
Sandia National Laboratories
P.O. Box 969
Livermore, CA 94550
Phone: (925) 294-3709; Fax: (925) 294-2606
E-mail: cmoen@sandia.gov

DOE Technology Development Manager: Antonio Ruiz
Phone: (202) 586-0729; Fax: (202) 586-2373
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
   - 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 data base 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

- In response to requests from stakeholders, created hardcopy version of the first 14 chapters of the Technical Reference on Hydrogen Compatibility of Materials (Sandia Report SAND2008-1163). Completed new Technical Reference chapters on martensitic stainless steels and polymers, increasing the total number of chapters to 18.
- Completed measurements of crack growth thresholds on Cr-Mo pressure vessel steels (DOT 3AAX, SA 372 Gr. J, DOT 3T) in hydrogen gas at pressures from 41 to 100 MPa. These measurements serve as benchmark data for implementing design standards such as American Society of Mechanical Engineers (ASME) Article KD-10.
- Measured tensile fracture resistance of hydrogen-exposed 316 stainless steels as a function of both alloy composition and temperature. These results demonstrate that low nickel content and low temperature represent a critical intersection of variables, where the tensile ductility of hydrogen-exposed 316 stainless steel is reduced by about 75%.
- Assembled system for conducting materials tests in hydrogen gas under dynamic loading.

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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 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 and Canadian Standards Association. 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

The first 14 chapters of the Technical Reference on Hydrogen Compatibility of Materials were prepared as an institutional technical report by Sandia National Laboratories (report number SAND2008-1163). This hardcopy version of the Technical Reference was requested by stakeholders in hydrogen energy infrastructure. The report was distributed to stakeholders in the industrial gas, automotive, and energy companies as well as standards development organizations. Beyond these first 14 chapters, four new chapters were prepared to bring the total number of chapters to 18 in the on-line version of the Technical Reference. These latter chapters are on martensitic stainless steels (e.g., 400-series, 17-4 PH), semi-austenitic stainless steels (e.g., 17-7 PH), and polymers. Although the martensitic stainless steels are attractive for certain components in hydrogen energy infrastructure due to their high strength, the mechanical property data demonstrate that these materials are not compatible with hydrogen gas.

Materials Testing

All of the planned testing for measuring benchmark sustained-load cracking thresholds of Cr-Mo pressure vessel steels was completed. Benchmark sustained-load cracking thresholds were measured for three steels: SA 372 Grade J, DOT 3T, and DOT 3AAX. Most of the testing was conducted in 100 MPa hydrogen gas, which is the upper pressure limit allowed in the ASME design code for hydrogen pressure vessels (Article KD-10). The DOT 3T steel was also tested in 41 MPa hydrogen gas to determine whether the relatively low sustained-load cracking thresholds in this steel would increase at lower gas pressure. The sustained-load cracking thresholds (K_{TH}) are summarized in Figure 1. The data in Figure 1 show that the susceptibility to hydrogen-assisted fracture increases (i.e., cracking thresholds decrease) as the material strength increases. This trend is quite general

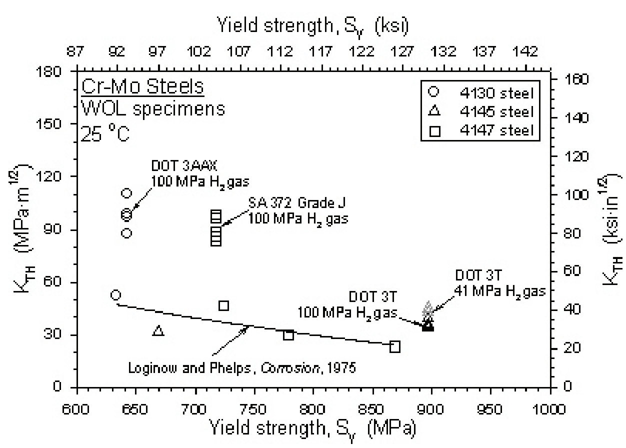

FIGURE 1. Benchmark values of the threshold for sustained-load cracking in hydrogen gas (K_{TH}) for three Cr-Mo pressure vessel steels. The cracking thresholds are plotted as a function of yield strength. Values for the DOT 3T steel are shown for two gas pressures.

for structural metals exposed to hydrogen gas and has important technological implications, since high-strength materials are attractive for components subjected to high pressures. Figure 1 also shows that the cracking threshold for DOT 3T steel increases only incrementally when the hydrogen gas pressure is lowered from 100 MPa to 41 MPa.

Testing of hydrogen-exposed 316 stainless steels continued in collaboration with a piping and valve component manufacturer. Previous results demonstrated that nickel content is an important variable governing susceptibility to hydrogen-assisted fracture, where lower nickel content exacerbates hydrogen-assisted fracture. In addition, literature results for stainless steels reveal that susceptibility to hydrogen-assisted fracture is sensitive to temperature. The intersection of these two variables had not been explored, so measurements were conducted on hydrogen-exposed tensile specimens of 316 stainless steel as a function of nickel content and temperature. Results from this testing are summarized in Figure 2. The effects of nickel content on hydrogen-assisted fracture are compounded at 223 K, leading to a reduction in ductility of about 75% in low-nickel alloys. This result has significant technological importance, since 316 stainless steel is considered one of the most hydrogen-compatible structural metals and is a favored material for small-volume components in hydrogen manifolds such as tubing, fittings, and valves.

All components for the system designed to conduct materials tests in hydrogen gas under dynamic loading were received and assembled. An image of the custom-designed pressure vessel coupled to the mechanical test frame is shown in Figure 3. Although the system has been assembled, there remains a significant challenge in achieving acceptable sealing around the pull rod that transmits force to the test specimen in the pressure vessel. While the pressure drop in the vessel associated

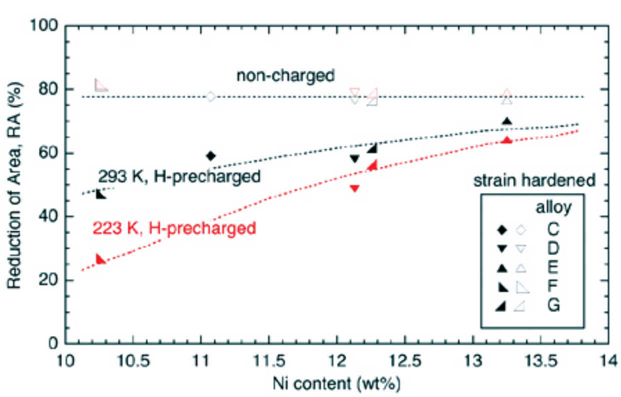

FIGURE 2. Reduction of area measured from strain-hardened 316 stainless steel alloys containing approximately 140 wppm hydrogen. The reduction of area is plotted as a function of nickel concentration for tests conducted at room temperature (293 K) and at low temperature (223 K).

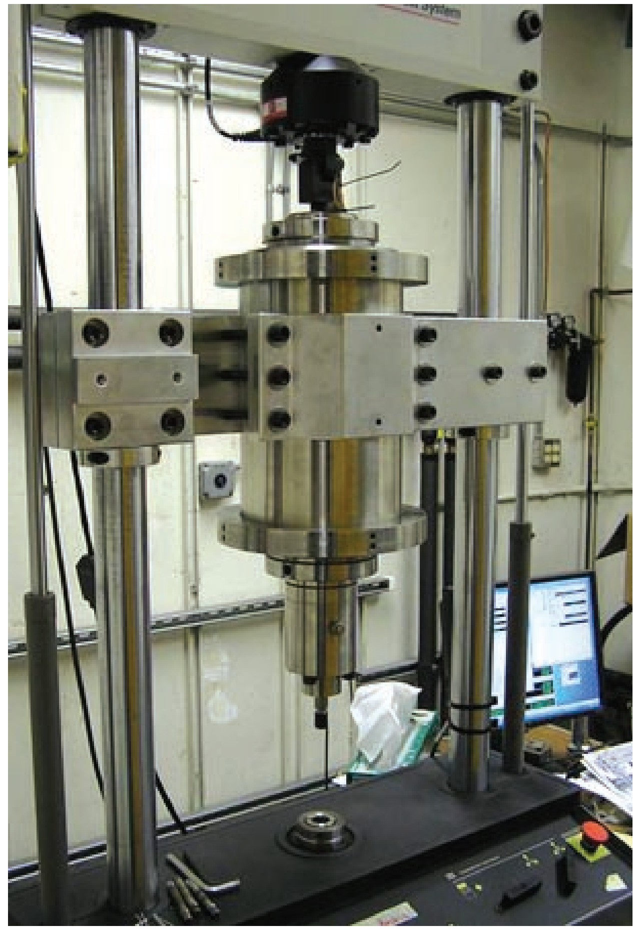

FIGURE 3. Pressure vessel and mechanical test frame in system for conducting materials tests under dynamic loading in high-pressure hydrogen gas.

with the gas leak rate past the sliding seals does not significantly compromise short-term tests, pressure cannot currently be maintained for the extended times (days to weeks) necessary for fatigue crack growth testing. Several solutions have been identified, including alternate seal designs as well as a gas replenishment system.

Conclusions

- The hardcopy version of the first 14 chapters of the Technical Reference on Hydrogen Compatibility of Materials allows this resource to be more easily referenced.
- The sustained-load cracking thresholds measured for SA 372 Gr. J, DOT 3T, and DOT 3AAX steels in high-pressure hydrogen gas serve as benchmark data for implementing design standards such as ASME Article KD-10.
- Although 316 stainless steel is considered compatible with hydrogen, materials testing results

reveal a vulnerability to hydrogen-assisted fracture at low nickel content and low temperature.

Future Directions

- Compose new chapters on 310 stainless steel, 321 stainless steel, precipitation-hardening aluminum, and nickel alloys for the Technical Reference.
- Measure sustained-load cracking thresholds of a Ni-Cr-Mo pressure vessel steel in 100 MPa hydrogen gas.
- Measure fatigue crack growth rates of 316 stainless steels containing thermally precharged hydrogen.
- Measure fatigue crack growth rates of Cr-Mo and Ni-Cr-Mo pressure vessel steels in 100 MPa hydrogen gas.
- Include aluminum alloys in materials testing.

FY 2008 Publications/Presentations

1. (invited) "Structural-Materials Considerations for Hydrogen Gas Containment", C. San Marchi, B. Somerday, K. Nibur, M. Yip, International Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA, Nov. 2007.

2. (invited) "Structural Design Methods and Materials Testing for Hydrogen Components", B. Somerday, International Hydrogen Energy Development Forum 2008, Fukuoka, Japan, Feb. 2008.

3. "Hydrogen-Assisted Fracture in Steels for Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, Feb. 2008.

4. "Hydrogen Containment Materials", B. Somerday and C. San Marchi, in *Solid-State Hydrogen Storage: Materials and Chemistry*, 2008, in press.

5. "Measurement of Sustained-Load Cracking Thresholds for Steels in Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, submitted to *2008 Proceedings of the ASME PVP Conference*, 2008.

6. "Hydrogen-Assisted Fracture of Type 316 Stainless Steel at Sub-ambient Temperature", X. Tang, G. Schiroky, C. San Marchi, B. Somerday, submitted to *2008 Proceedings of the ASME PVP Conference*, 2008.

7. "Structural-Metals Considerations for the Containment of High-Pressure Hydrogen Gas", C. San Marchi, B. Somerday, K. Nibur M. Yip, submitted to *Proceedings of International Symposium on Materials Issues in a Hydrogen Economy*, 2008.

8. "Thermodynamics of Gaseous Hydrogen and Hydrogen Transport in Metals", C. San Marchi and B. Somerday, submitted to *Proceedings of MRS 2008 Spring Meeting*, 2008.