VIII.4 Hydrogen Materials and Components Compatibility

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End Date: Project continuation and direction determined annually by DOE

FY 2011 Objectives

(1) Populate Technical Reference on Hydrogen Compatibility of Materials
   - Summarize data from published technical documents in a Web-based resource.
   - Update published Technical Reference chapters to reflect new data from Sandia materials testing activities.

(2) Develop and Validate Materials and Components Test Methods
   - Enable technology deployment by generating critical material-property data for structural materials in hydrogen gas, emphasizing commercial materials tested in high-pressure hydrogen.
   - Optimize efficiency and reliability of standardized test procedures for generating design data for structural materials in high-pressure hydrogen gas.

(4) Provide Science-Basis for Codes and Standards Development
   - Perform testing and analysis to provide the technical basis for codes and standards.
   - Provide leadership in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses technical barriers from the Hydrogen Codes and Standards section of the Fuel Cell Technologies 2007 Multi-Year Research Plan:

(F) Limited DOE Role in the Development of International Standards
(I) Conflicts between Domestic and International Standards
(N) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Codes and Standards Milestones

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

- **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.
- **Milestone 25:** Draft regulation for comprehensive hydrogen fuel cell vehicle requirements as a GTR approved (UN Global Technical Regulation). (4Q, 2010)

FY 2011 Accomplishments

- Organized and convened Hydrogen Compatible Materials Workshop in November, 2010.
- Exercised leadership roles in developing standards (Society of Automotive Engineers [SAE] J2579 and Canadian Standards Association [CSA] Compressed Hydrogen Materials Compatibility [CHMC]1) for qualifying hydrogen compatibility of materials and components.
- Conducted materials testing designed to improve fatigue life methods in SAE J2579 and CSA CHMC1 standards.

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Introduction

A major barrier to 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 optimized materials qualification methodologies and assembling 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 assembled through the process of vetting, consolidating, and documenting materials data from journal articles and institutional reports. Gaps in the database content uncovered during the process of composing the Technical Reference are addressed through a materials testing activity. Results from this materials testing illuminate the pathways to optimize materials qualification methods, enabling efficient, high quality testing to support rapid technology deployment.

Approach

The focus of the Hydrogen Materials and Components Compatibility project is to optimize materials characterization methodologies, generate critical hydrogen compatibility data for materials to enable technology deployment, and compose the Technical Reference on Hydrogen Compatibility of Materials. Two activities proceed in parallel: generating new data and understanding through materials testing, and identifying and summarizing existing data from technical documents. 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), fatigue crack initiation and propagation test methods, and technology-critical material fabrication (e.g. welds) and service variables (e.g., temperature). The data from materials testing are rigorously reviewed to identify pathways to improve the test methods and to ensure the data are suitable for implementation in structural design.

As part of codes and standards advocacy, Sandia personnel provide leadership in the codes and standards development process through direct participation in organizations such as the American Society of Mechanical Engineers, CSA, and SAE. This participation ensures that the standards development organizations have the most current technical information on structural materials compatibility. Sandia personnel provide leadership in the development of both component design standards as well as materials testing standards.

Results

Sandia led a Hydrogen Compatible Materials Workshop on November 3, 2010. The goal of the workshop was to coordinate and plan international research and development (R&D) to harmonize characterization and design methodologies for hydrogen-compatible materials and components. The output from the workshop was a summary document that would guide international R&D and code development road mapping. The workshop format consisted of several overview presentations followed by a working meeting involving 35 leading experts from research labs, government, industry, and standards development organizations. The presentations were designed to provide the context for identifying gaps in technology research and development as well as standards development for structural materials in hydrogen containment.

In the documented results of the workshop, several high-priority gaps were identified in the areas of technology development, code development, and research. For example:

- High-strength, low-cost materials for long-life hydrogen service.
- Measurements of mechanical properties of structural metals in high-pressure hydrogen gas, in particular fatigue properties.
- Influence of welds on hydrogen compatibility of structures.
- Publicly available database for properties of structural materials in hydrogen gas.

The Sandia team has leadership roles in developing sections of the SAE J2579 (“Technical Information Report for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles”) and the CSA CHMC1 standards that are pertinent to qualifying structural metals for hydrogen containment. Currently, the potential for hydrogen effects on fatigue cracking of structural metals is not adequately addressed in the SAE J2579. The containment vessel is qualified for severe pressure-cycle service using hydraulic testing only. Sandia has provided the technical basis for the following safety qualification philosophy applied to the containment vessel:

- Certain structural metals exhibit minimal effects of hydrogen on fracture properties. For these structural metals, hydraulic testing is sufficient for qualifying the containment vessel for severe pressure cycling. Currently, two structural metals are in this category: 6061 aluminum and 316 stainless steel with greater than 12% nickel. Other structural metals can be included in this category provided the materials are subjected to four tests and meet the specified acceptance criterion for each test. The four tests (described in a new Appendix C.15) are the slow strain rate tensile test, two fatigue life tests, and the fatigue crack growth test, in which each test is conducted in hydrogen gas.
- Structural metals that do not meet the materials testing acceptance criteria in Appendix C.15 can still be selected for containment vessel components. In this case, the containment vessel must be subjected to both the hydraulic pressure cycling test and an additional severe pressure cycling test using hydrogen gas. The protocol for conducting this durability performance test using hydrogen gas has been included in the new Appendix C.14.

The SAE J2579 effort has involved coordination with international experts from the U.S., Japanese, and European automakers. The sections on qualifying structural metals for hydrogen containment are expected to also form the foundation for addressing hydrogen compatibility of metal components in the Global Technical Regulation (GTR).

The Sandia team has a leadership role in the new CSA Technical Advisory Group (TAG) for the CHMC1 standard. The content of this standard focuses on reliable test methods for structural materials in hydrogen gas. This standard was motivated by the lack of specific methods for qualifying structural metals for hydrogen service in component standards, such as the CSA standards for fuel cell vehicle components. Component standards that do not contain specific guidance for qualifying structural metals in hydrogen service can reference the CHMC1 standard. The CHMC1 document is scheduled for review by CSA in August 2011.

The fatigue life materials test is considered to be particularly relevant for many hydrogen containment components on fuel cell vehicles. For example, this test has been included in both the CSA CHMC1 and SAE J2579 standards. Fatigue life tests that employ smooth or notched specimens are intended to evaluate the effect of hydrogen on fatigue crack initiation. The output from fatigue life testing is an "S-N curve" for the material, which is a locus of points representing the number of cycles to failure (N) for a constant stress amplitude (S) applied to the test specimen. One of the principal objectives of the fatigue life testing in this Materials Compatibility task is to evaluate whether fatigue crack initiation dominates the number of cycles to failure. For this objective, it must be recognized that the number of cycles to failure (N) consists of the number of cycles for crack initiation (N_i) plus the number of cycles for crack propagation (N_p). Since tests on smooth or notched specimens are intended to evaluate the effect of hydrogen on crack initiation, the ratio of N_i/N should be nearly equal to 1. The first series of tests in this task were intended to establish the N_i/N ratio for a notched specimen geometry that is proposed for the CSA CHMC1 and SAE J2579 standards.

The S-N curve was measured for cylindrical, circumferentially notched specimens fabricated from the austenitic stainless steel 21Cr-6Ni-9Mn (21-6-9). Specimens from hydrogen-charged (200 wppm H) and non-charged 21-6-9 were tested at constant stress amplitudes, and the number of cycles to failure, N, were recorded for each test. The tests were conducted at a load ratio, R (ratio of minimum stress to maximum stress), equal to 0.1 and a load-cycle frequency of 1 Hz. In addition, each specimen was instrumented with an extensometer and the direct-current potential difference system to detect crack initiation. Results showing the number of cycles for crack initiation, N_i, and the number of cycles to failure, N, for both hydrogen-charged and non-charged specimens are summarized in Figure 1.

Two results are notable in Figure 1. First, hydrogen does not have a significant effect on the fatigue life of the 21-6-9 stainless steel. Second, the number of cycles for crack initiation, N_i, is approximately 50% of the total number of cycles to failure. The second observation indicates that the number of cycles to failure measured from the circumferentially notched specimen does not adequately approximate the number of cycles for crack initiation. This insight may influence the specimen geometry that is specified in the CSA CHMC1 and SAE J2579 standards.

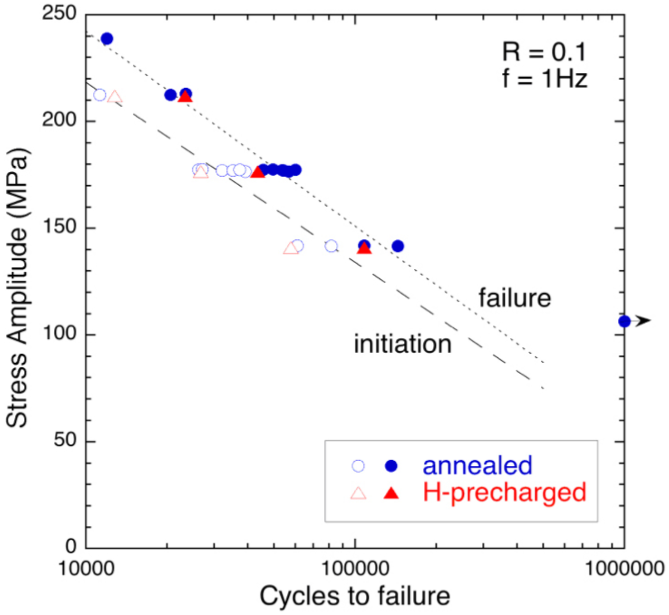

FIGURE 1. Stress amplitude (S) vs. number of cycles for crack initiation (N_i) and total number of cycles to failure (N) for hydrogen-charged and non-charged 21-6-9 stainless steel.

Hydrogen containment component stakeholders have expressed interest in aluminum alloys due to their compatibility with hydrogen gas and low cost relative to stainless steels. Consequently, Sandia has included modern, high-performance aluminum alloys in its materials testing activity. Although aluminum alloys are generally considered to be resistant to hydrogen-assisted fracture in dry hydrogen gas, some questions remain about applying reliable test methods. Sandia has conducted some preliminary fatigue crack growth testing on 7475-T7351 aluminum in 103 MPa hydrogen gas. Testing duration was greater than 60 hours, and the cyclic plastic deformation associated with fatigue testing was intended to promote the exposure of "fresh" (non-oxidized) metal surface to hydrogen gas. However, even in this testing condition, the results in Figure 2 show essentially no difference between the test in hydrogen gas and a test performed in laboratory air. These initial results support the notion that aluminum alloys have superior hydrogen compatibility among common structural metals.

Conclusions and Future Directions

In FY 2011:

- Hydrogen Compatible Materials Workshop identified important technology gaps:

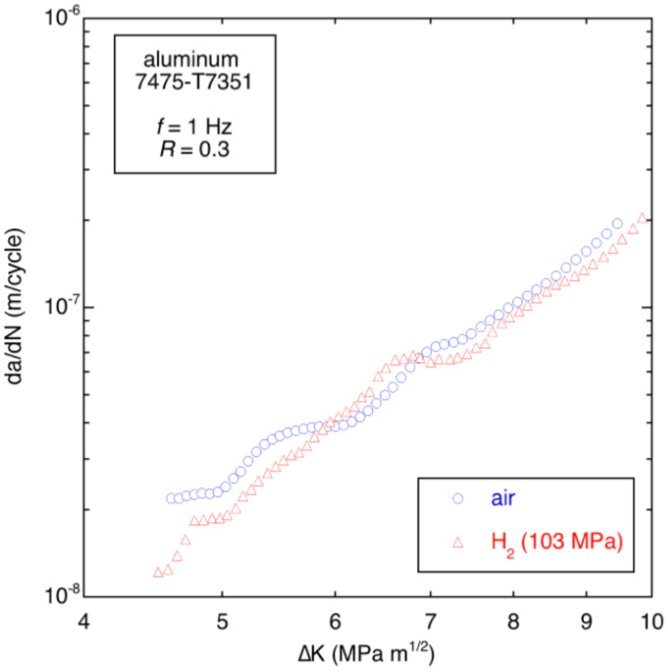

FIGURE 2. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) relationships for 7475-T7351 aluminum in 103 MPa hydrogen gas and air.

  - Workshop output guides R&D prioritization.
- Methods developed for qualifying hydrogen compatibility of materials and components in two standards: SAE J2579 and CSA CHMC1.
- Materials testing motivated by standards development:
  - Improving fatigue life testing methods impacts SAE J2579 and CSA CHMC1.

Future Work:

- Establish optimum methods for measuring fatigue properties of steels in high-pressure hydrogen for inclusion in standards.
- Measure hydrogen-affected properties of representative stainless steel welds in gas distribution manifolds.
- Complete first draft of CSA CHMC1 standard.
- Procure pressure vessel with variable-temperature feature for new fatigue testing capability.

FY 2011 Publications/Presentations

1. (invited) "Addressing Hydrogen Embrittlement in the Fuel Cell Vehicle Standard SAE J2579", B. Somerday, International Hydrogen Energy Development Forum 2011, Fukuoka, Japan, Feb. 2011.

2. (invited) "Improving the Fatigue Resistance of Ferritic Steels in Hydrogen Gas", B. Somerday, I^{2}CNER Kick-off Symposium, Fukuoka, Japan, Feb. 2011.

3. "Hydrogen Effects on Materials for CNG / H_2 Blends", B. Somerday, D. Farese, and J. Keller, International Hydrogen Fuel and Pressure Vessel Forum 2010, Beijing, China, Sept. 2010.

4. "Fracture and Fatigue Tolerant Steel Pressure Vessels for Gaseous Hydrogen", K. Nibur, C. San Marchi, and B. Somerday, Proceedings of the ASME 2010 Pressure Vessels & Piping Division / K-PVP Conference (PVP2010), July 18–22, 2010, Bellevue, Washington, USA.

5. "Austenitic Stainless Steels", C. San Marchi, in *Gaseous Hydrogen Embrittlement of Materials in Energy Technologies*, R. Gangloff and B. Somerday, Eds., Woodhead Publishing, Cambridge, UK, 2011, in press.

6. "Mechanical Test Methods for Gaseous Hydrogen Embrittlement ", K. Nibur and B. Somerday, in *Gaseous Hydrogen Embrittlement of Materials in Energy Technologies*, R. Gangloff and B. Somerday, Eds., Woodhead Publishing, Cambridge, UK, 2011, in press.

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