VIII.4 R&D for Safety, Codes and Standards: Materials and Components Compatibility

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Project Start Date: October 1, 2003
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Optimize the reliability and efficiency of test methods for structural materials and components in hydrogen gas
- Generate critical hydrogen compatibility data for structural materials to enable technology deployment
- Create and maintain information resources such as the "Technical Reference for Hydrogen Compatibility of Materials"
- Demonstrate leadership in the international harmonization of standards for qualifying materials and components for high-pressure hydrogen service

Fiscal Year (FY) 2014 Objectives

- Demonstrate fatigue life measurements in gaseous hydrogen
- Determine boundary conditions for hosting "open-source" database of materials and materials properties in gaseous hydrogen
- Complete integration of automated gas-distribution manifold; establish cost estimates for variable-temperature testing hardware
- Foster growth of international collaboration and leadership on materials science of hydrogen embrittlement, in particular within the International Institute for Carbon-Neutral Energy Research (I2CNER)
- Leverage the partnership with the Japanese National Institute of Advanced Industrial Science and Technology (AIST) to supplement fracture testing database to influence materials testing standards; establish a roadmap for next phase collaboration with AIST (2015-2018)

Technical Barriers

This project addresses the following technical barriers from the Safety, Codes and Standards section (3.8) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Safety Data and Information: Limited Access and Availability

(F) Enabling national and international markets requires consistent RCS (regulations, codes and standards)

(G) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Safety, Codes and Standards Milestones

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

- Milestone 2.9: Publish technical basis for optimized design methodologies of hydrogen containment vessels to account appropriately for hydrogen attack. (4Q, 2013)
- Milestone 2.16: Demonstrate the use of new high-performance materials for hydrogen applications that are cost-competitive with aluminum alloys. (4Q, 2017)
- Milestone 2.3: Implement validated mechanism-based models for hydrogen attack in materials. (4Q 2016)
- Milestone 3.3: Reduce the time required to qualify materials, components, and systems by 50% relative to 2011 with optimized test method development. (1Q 2017)
- Milestone 3.4: Develop hydrogen material qualification guidelines including composite materials. (Q4, 2017)
- Milestone 4.8: Completion of the GTR Phase 2. (1Q, 2017)
- Milestone 5.2: Update materials compatibility technical reference. (4Q, 2011-2020)
- Milestone 5.4 Develop and publish database for properties of structural materials in hydrogen gas. (2Q, 2013)

FY 2014 Accomplishments

- Completed the initial test matrix to measure fatigue life of the stainless steel 21Cr-6Ni-9Mn in 103 MPa hydrogen gas. This testing satisfies the need to quantitatively evaluate methods recently published in the the Compressed Hydrogen Material Compatibility standard (CHMC1) from the CSA Group and to generate qualification data for lower-cost stainless steels.
- Completed review and gap analysis of "Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems" (report no. SAND2013-8904) in collaboration with the Hydrogen Delivery program element.
- Finalized design requirements and the procurement process for the variable-temperature testing in a hydrogen gas system.
- Devised a plan with international partner AIST to propose test methods to ASTM International for performing rising-displacement fracture threshold testing of structural metals in hydrogen gas.

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INTRODUCTION

A principal challenge to the widespread adoption of hydrogen infrastructure is the lack of quantifiable data on its safety envelope and concerns about additional risk from hydrogen. To convince regulatory officials, local fire marshals, fuel suppliers, and the public at large that hydrogen refueling is safe for consumer use, the risk to personnel and bystanders must be quantified and minimized to an acceptable level. Such a task requires strong confidence in the safety performance of high-pressure hydrogen systems. Developing meaningful materials characterization and qualification methodologies in addition to enhancing understanding of performance of materials is critical to eliminating barriers to the development of safe, low-cost, high-performance high-pressure hydrogen systems for the consumer environment.

APPROACH

The Materials and Components Compatibility project leverages decades of experience in high-pressure hydrogen systems, well-developed industry partnerships, and a core capability in hydrogen-materials interactions anchored by the Hydrogen Effects on Materials Laboratory to focus on three critical activities: (1) optimize materials characterization methodologies, (2) generate critical hydrogen compatibility data for materials to enable technology deployment, and (3) provide international leadership by assembling and maintaining a technical reference that is populated with vetted data and includes a technical assessment of the data and its application.

RESULTS

Fatigue Life Measurements in Gaseous Hydrogen

Fatigue life assessment is a common design methodology that has only recently received attention in the context of qualifying materials for hydrogen service. In particular, the revised CHMC1 standard from CSA Group describes a materials qualification pathway that uses notched fatigue tests to qualify materials for hydrogen service.

Notched fatigue tests in high-pressure gaseous hydrogen were demonstrated at SNL for an austenitic stainless steel, 21Cr-6Ni-9Mn. Testing results (Figure 1) show a significant effect of high-pressure gaseous hydrogen (103 MPa) on the fatigue cycles to failure for nominally the same applied stress cycle. The results are also compared to previous testing in air with a more acute notch showing that the fatigue life in hydrogen is greater than for tests in air with a more acute notch. The significance of these results is not yet clear, as more data is necessary to clarify the trends. In general, the testing has shown that the testing configuration in gaseous hydrogen is feasible and provides basic trends that are

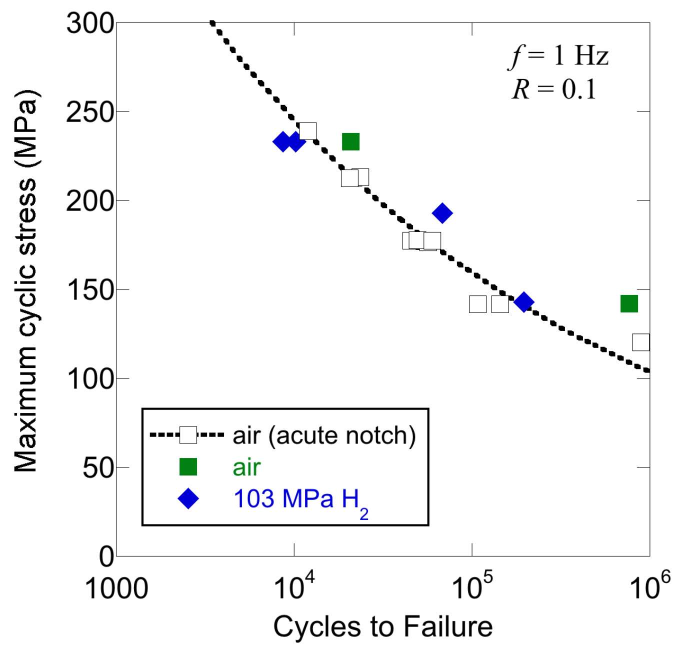

FIGURE 1. Stress amplitude cycles to failure plot for notched cylindrical fatigue tests, comparing tests in gaseous hydrogen with tests in air; open symbols represent tests in air with an acute notch, while closed symbols represent specimens with a notch as called out in CSA CHMC1.

consistent with expectations (e.g., power-law-like relationship between stress and cycles to failure).

Fatigue life assessment (e.g., using notched tensile fatigue tests) is anticipated to aid the qualification of lower cost materials for generic high-pressure hydrogen service; however, more work is necessary to demonstrate reproducibility and evaluate the effects of notch acuity in these tests. The effect of frequency must also be considered for fatigue testing, but has not been explored in this testing configuration.

"Open-Source" Database of Material Properties in Gaseous Hydrogen

Access to reliable and searchable materials properties measured in gaseous hydrogen is a significant limitation to selection of materials for hydrogen service. As part of the continued effort to provide access to materials selection information, Sandia teamed with Pacific Northwest National Laboratory to review the state of the art of polymeric materials in hydrogen systems, an effort jointly funded by the Hydrogen Delivery and the Safety, Codes and Standards programs. The resulting report included an extensive review of data and test methods for evaluating polymers in gaseous hydrogen and high pressure as well as an analysis of major gaps in knowledge and data related to selection of polymers for hydrogen service. Additionally, SNL is exploring methods to augment the Technical Reference for Hydrogen Compatibility of Materials (http://www.sandia.gov/matlsTechRef/) with a database of materials properties for both metals and polymers. As part of the Material Data Management Consortium (MDMC), an industry consortium organized by Granta Design, Sandia has engaged support for building the schema for incorporation of environmental variables in the Granta MI database structure with the aim of a comprehensive hydrogen effects in materials database. Discussions with Granta and individuals from MDMC suggest a precedent for data exchange using Web-based interface built on Granta database tools, such as Granta MI. Granta is the leader in materials information/database management solutions. Additional discussion is required to quantify the cost of maintaining an open platform for dissemination of materials properties measured in gaseous hydrogen.

System for Variable-Temperature Testing in Hydrogen Gas

Materials qualification for hydrogen fueling applications requires the measurement of materials properties, especially fatigue properties, in high-pressure gaseous hydrogen and low temperature. It is well known, for example, that certain materials such as austenitic stainless steels are most susceptible to hydrogen embrittlement at temperatures near 233 K (-50°C). Facilities for testing materials under the combined influence of variable temperature and high pressure do not exist nationally. Sandia maintains a core capability in hydrogen embrittlement of structural materials, in which the Hydrogen Effects on Materials Laboratory is the central asset. This laboratory features several specialized systems for measuring the mechanical properties of materials in high-pressure gaseous hydrogen; however, fatigue evaluation of materials is limited to testing at room temperature. Work is underway to add variable temperature testing to the fatigue testing capabilities in the Hydrogen Effects on Materials Laboratory.

The major components of the apparatus for variable-temperature testing in hydrogen has have been acquired. The final procurements are being made with investment from both Fuel Cell Technologies Office and the National Nuclear Security Administration. The Advancing Materials Testing in Hydrogen Gas workshop hosted by Sandia in March 2013 was instrumental in focusing attention on an internal cooling mechanism for the pressure vessel. A prototype cooling mechanism was designed and tested under ambient conditions. This mechanism is relatively simple in concept, consisting primarily of a copper-cooling block in contact with a stainless steel tube carrying cryogenic fluid (Figure 2a). This prototyping activity demonstrated that the target temperature of 223 K (-50°C) could be attained at a cylindrical stainless steel test specimen surrounded by the copper-cooling block. In parallel with this successful prototyping, a student intern at Boise State simulated the temperature distribution in the concept pressure vessel with internal cooling mechanism. Example results from these SolidWorks simulations are displayed in Figure 2b.

Once operational, this system will provide system designers with data necessary to develop robust, cost-effective low-temperature hydrogen systems for storage and dispensing applications.

International Collaboration with I2CNER

Significant resources are being invested around the world in hydrogen material research. I2CNER is one of the premier organizations dedicated to the advancement of hydrogen materials science. Through coordination of hydrogen materials science research in the U.S. and Japan, hydrogen technology can be accelerated. Dr. Brian Somerday leads the Hydrogen Materials Compatibility division of I2CNER, providing a direct link between hydrogen embrittlement studies across the Pacific. Dr. Somerday co-organized several high-profile events for I2CNER in FY 2014:

- Coordination meeting for the Hydrogen Materials Compatibility division at Yufuin, Japan, to promote interaction within the division and refine the research roadmap of the division (December 2013)
- The Joint HYDROGENIUS and I2CNER International Workshop on Hydrogen-Materials Interactions at the International Hydrogen Energy Development Forum in Fukuoka, Japan (January 31, 2014)

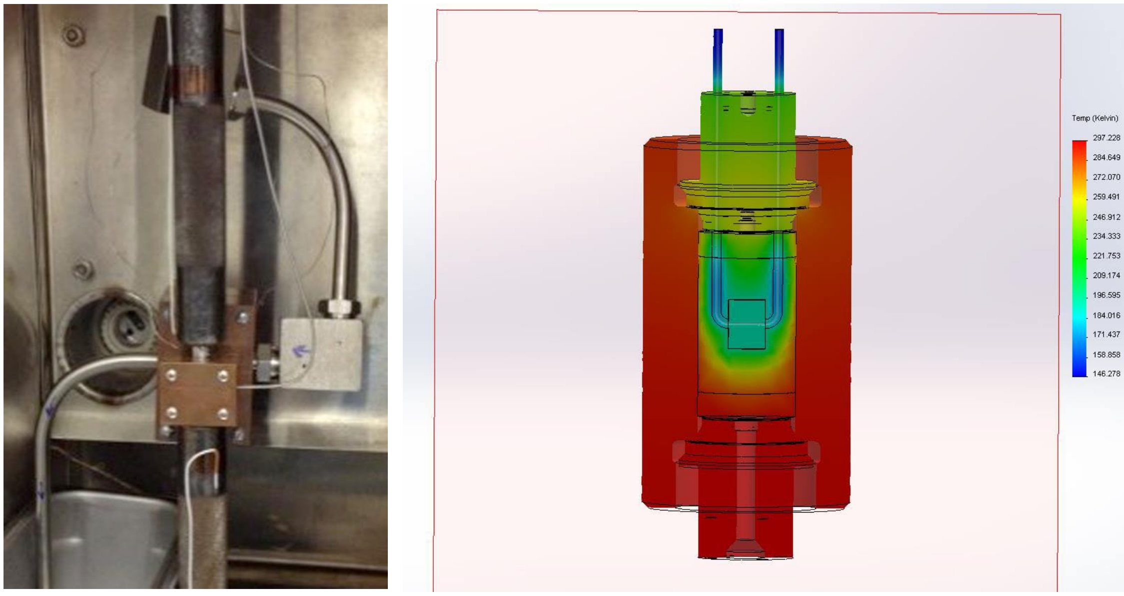

FIGURE 2. (a) Prototype cooling mechanism consisting of copper cooling block with stainless steel tubing carrying cryogenic fluid. (b) SolidWorks simulation of temperature distribution in pressure vessel with internal cooling mechanism.

Leveraging Partnership at AIST

International harmonization of methods for qualifying materials for hydrogen service is widely recognized as critical to the deployment of hydrogen technologies. Sandia interacts broadly with international partners to promote unified test methods, including research collaboration with staff from AIST (who visit Sandia regularly). The Sandia team hosted the SNL-AIST Workshop on High-Pressure Hydrogen Storage Systems in January 2014. The main outcomes of the workshop were (i) a plan for proposing revision of ASTM testing standards to include special requirements for testing gaseous hydrogen, (ii) identification of opportunities for risk analysis around materials and pressure vessels, and (iii) extension of materials testing activities in gaseous hydrogen. Future testing activities are contingent on budgets. Figure 3 shows the foundational data generated collectively by SNL and AIST; these data are anticipated to influence testing standards, such as those from ASTM International. Several papers were prepared jointly by SNL and AIST to be presented at the ASME 2014 Pressure Vessel and Piping Division Conference.

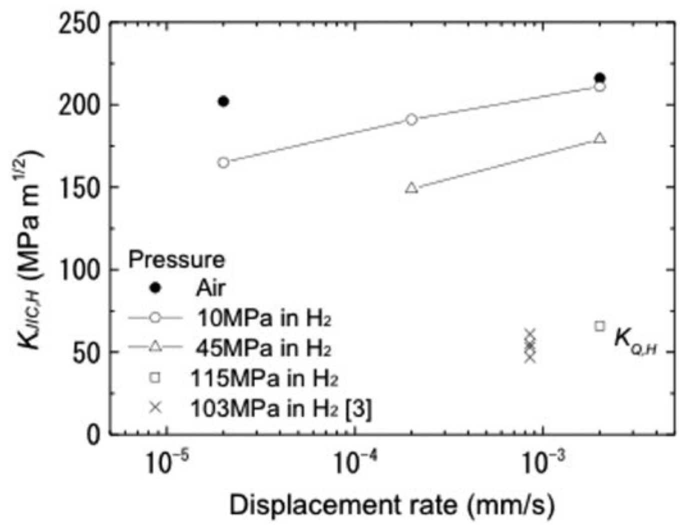

FIGURE 3. Rising-displacement fracture thresholds measured for SA372 Grade J pressure vessel steel in air and high-pressure hydrogen gas. Data points in plot represent measurements from both SNL (cross symbols) and AIST (other symbols).

CONCLUSIONS AND FUTURE DIRECTIONS

- Fatigue life testing on the stainless steel 21Cr-6Ni-9Mn in 103 MPa hydrogen gas has two potential impacts, quantitative evaluation of methods recently published in the CSA CHMC1 standard and qualification data for a lower-cost stainless steel.
- Progress in developing the variable-temperature testing system bolsters the core capability for materials characterization in high-pressure hydrogen and assures critical testing can be performed on technologically pivotal materials such as stainless steels.
- International partnerships with I2CNER and AIST provide access to basic science related to materials behavior in hydrogen and data that enable the development of international standards for materials testing and component qualification.

- (future) Formalize schema for material property database in Granta MI.
- (future) Commission variable-temperature testing in hydrogen gas system to integrate subsystems and demonstrate functionality.
- (future) Continue critical evaluation of test methods in CSA CHMC1, including rate effects (AIST collaboration) and "safety factor method" option.
- (future) Develop R&D project with industry partner(s) to evaluate and improve resistance of high-strength structural metals to hydrogen-assisted fracture.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Brian Somerday and Chris San Marchi, DOE Hydrogen and Fuel Cells Program Awards, Hydrogen Delivery and Safety, Codes and Standards, 2014.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. C. San Marchi and B.P. Somerday, "Comparison of stainless steels for high-pressure hydrogen service" (PVP2014-2881), accepted for ASME 2014 Pressure Vessel and Piping Division Conference, Anaheim CA, 20–24 July 2014.

2. T. Iijima, B. An, C. San Marchi, B.P. Somerday, "Measurement of fracture properties for ferritic steel in high-pressure hydrogen gas" (PVP2014-28815), accepted for ASME 2014 Pressure Vessel and Piping Division Conference, Anaheim CA, 20–24 July 2014.

3. B. An, T. Iijima, C. San Marchi, B.P. Somerday, "Micromechanisms of hydrogen-assisted cracking in super duplex stainless steel investigated by scanning probe microscopy" (PVP2014-28181), accepted for ASME 2014 Pressure Vessel and Piping Division Conference, Anaheim CA, 20–24 July 2014.

4. (invited) J. Ronevich, B. Somerday, C. San Marchi, H. Jackson, and K. Nibur, "Fracture Resistance of Hydrogen Precharged Stainless Steel GTA Welds", SteelyHydrogen 2014: Second International Conference on Metals & Hydrogen, Ghent, Belgium, May 2014.

5. (invited) B. Somerday, "Technological and Industrial Progress in Hydrogen and Fuel Cells in the U.S.", International Hydrogen Energy Development Forum 2014, Fukuoka, Japan, Jan. 2014.

6. C. San Marchi and B.P. Somerday, "Design philosophies for high-pressure hydrogen storage systems". Presented at the AIST-SNL Workshop on High Pressure Hydrogen Storage Systems, Livermore CA, January 24, 2014 (SAND2014-0538P).

7. H.F. Jackson, C. San Marchi, D.K. Balch, B.P. Somerday, "Effect of low temperature on hydrogen-assisted crack propagation in 304L/308L austenitic stainless steel fusion welds". Corros Sci 77 (2013) 210-221.

8. C. San Marchi, B.P. Somerday, K.A. Nibur, "Development of methods for evaluating hydrogen compatibility and suitability", accepted to Intern J Hydrogen Energy.

9. L.A. Hughes, B.P. Somerday, D.K. Balch, C. San Marchi, "Hydrogen compatibility of austenitic stainless steel tubing and orbital tube welds", accepted to Intern J Hydrogen Energy.

10. R.R. Barth, K.L. Simmons, C. San Marchi, "Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems: Applications, Properties and Gap Analysis" SAND2013-8904 (October 2013).

11. C. San Marchi, B.P. Somerday, K.A. Nibur, "Measuring fracture properties in gaseous hydrogen", presented at International Workshop on Hydrogen Embrittlement in Natural Gas Pipelines, Seoul, Korea, November 27, 2013 (SAND2013-10058P).

12. C. San Marchi, "Hydrogen transport in metals", invited presentation at Korean Research Institute of Standards and Science, Daejeon, Korea, November 2013 (SAND2013-10059P).

13. C. San Marchi, K.A. Nibur, "Materials qualification for hydrogen service using CSA CHMC1", presented at to Japanese stakeholders during informational meeting at SNL/CA, November 8, 2013 (SAND2013-9607P).

14. M. Dadfarnia, B.P. Somerday, P.E. Schembri, P. Sofronis, J.W. Foulk, III, K.A. Nibur, and D.K. Balch, "On Modeling Hydrogen Induced Crack Propagation Under Sustained Load", *JOM*, 2014, in press.

15. B.P. Somerday and M. Barney, "Measurement of Fatigue Crack Growth Relationships in Hydrogen Gas for Pressure Swing Adsorber Vessel Steels", *Journal of Pressure Vessel Technology*, 2014, accepted for publication.

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