VIII.2 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" and the "Database 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) 2017 Objectives

- Perform fatigue and fracture tests on high-hardenability pressure vessel steels in high-pressure gaseous hydrogen, evaluating multiple alloys representing a range of strength.
- Demonstrate fatigue and fracture testing in high-pressure hydrogen at low temperature in the context of vehicle applications.
- Develop performance-based materials qualification metric for vehicle applications, emphasizing austenitic stainless steels.
- Major revision of Database on Hydrogen Compatibility of Materials to include recent fatigue and fracture data from the literature.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section 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

(G) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen 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, 2014)
- Milestone 2.16: Demonstrate the use of new high-performance materials for hydrogen applications that are cost-competitive with aluminum alloys. (4Q, 2017)
- Milestone 2.18: Implement validated mechanism-based models for hydrogen attack in materials. (4Q, 2018)
- 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 4.9: 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 2017 Accomplishments

- Documented fracture and fatigue performance of high hardenability pressure vessel steels in high-pressure hydrogen, showing that these alloys perform similarly to the pressure vessel steels currently used for stationary storage.

- Proposed a performance-based fatigue metric for qualifying materials for high-pressure service to the SAE Fuel Cell Safety Task Force, which significantly reduces the testing burden for materials qualification.
- Provided leadership to international partnership to develop low-temperature hydrogen testing capabilities in the United States, Europe, and Asia and to harmonize materials qualification methods for proposal to Global Technical Regulation (GTR) No. 13 Phase 2; draft proposal has general consensus.
- Developed schema for public access of hydrogen compatibility of materials database and greatly expanded available data records; database has substantial global visibility with hundreds of visitors, and nearly 8,000 page views, significantly extending the dissemination of data on hydrogen compatibility of materials.

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INTRODUCTION

A principal challenge to the widespread adoption of hydrogen infrastructure is the lack of quantifiable data to define safety margins and to mitigate potential hazards. 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 the 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. This activity develops scientifically defensible, accelerated testing strategies and critically evaluates test methodologies for quantifying hydrogen effects on materials. Additionally, the program engages the international scientific community to harmonize test methods, provide guidance on materials selection for hydrogen service and disseminate the latest scientific knowledge on the hydrogen compatibility of materials and suitability of components.

APPROACH

The Materials and Components Compatibility program element 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 and database that compile technical data relevant to understanding the effects of hydrogen on materials. To achieve these goals, the Hydrogen Effects on Materials Laboratory develops and maintains unique hardware and test methods for measuring fracture and fatigue behavior of materials in high-pressure gaseous hydrogen environments over a range of temperature. This program element also leverages state-of-the-art materials science characterization tools to advance the understanding of hydrogen–materials interactions in both structural and functional materials.

RESULTS

High-Hardenability Pressure Vessel Steels

Manufacturers of stationary hydrogen storage solutions have demonstrated interest in high hardenability pressure vessel steels, which enables larger storage systems to serve larger refueling stations. A memorandum of understanding with several pressure vessel manufacturers documents the common interest in high-hardenability (Ni-Cr-Mo) pressure vessel steels and includes Fiba Technologies (North America/United States), Tenaris-Dalmine (Europe/Italy), and Japan Steel Works (Asia/Japan). Three heats of Ni-Cr-Mo steels have been tested, including one of these steels in both a low-strength and high-strength condition (four steels with tensile strength in the range from 860 MPa to 1,150 MPa). Fracture results (Figure 1) demonstrate the basic trend of significantly lower fracture resistance for steels with tensile strength greater than 950 MPa [1]. While the fracture resistance is sensitive to the strength of the steel, fatigue results are decidedly different.

Fatigue crack growth rates for the tested steels are insensitive to composition and strength at low stress intensity factor range (ΔK). Testing was conducted primarily at 1 Hz with load ratio in the range of 0.1 to 0.7 in gaseous hydrogen at pressure of 106 MPa. An example of the measured fatigue crack growth rates (load ratio = 0.5) is shown in Figure 2, representing data for four Ni-Cr-Mo steels as well as two heats of Cr-Mo pressure vessel steel. These results are consistent for all steels, suggesting that a simple fatigue crack growth relationship can represent the performance of all Cr-Mo and Ni-Cr-Mo steels within this strength range; moreover, Ni-Cr-Mo steels perform similarly to the Cr-Mo steels, which are commonly employed in existing infrastructure. The high-strength steels transition to higher crack growth rates than the basic trend at higher ΔK as the maximum stress intensity factor approaches the fracture resistance – this is referred to as Stage III fatigue crack growth. This trend emphasizes the challenge of designing hydrogen pressure vessels with high strength steels.

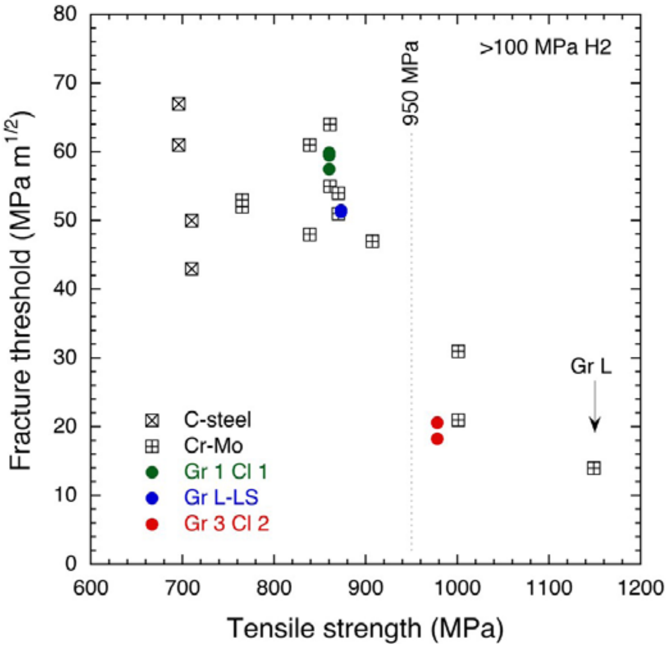

FIGURE 1. Fracture threshold determined from elastic–plastic fracture toughness measurements in gaseous hydrogen at pressure of 106 MPa. Carbon steel [2,3] and Cr-Mo steel [4,5] data from previous studies in hydrogen at pressure of 103 MPa and displacement rate of 1.5 and 3 mm/h, respectively. Each data point represents an individual test.

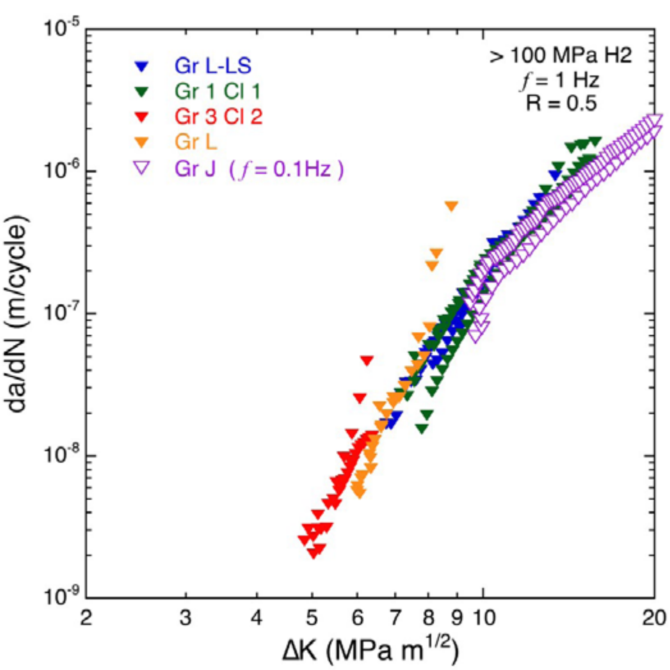

FIGURE 2. Comparison of fatigue crack growth rates for Ni-Cr-Mo pressure vessel steels and Ni-Cr pressure steels in high-pressure gaseous hydrogen at load ratio of 0.5. The Ni-Cr-Mo data (Gr L-LS, Gr 1 Cl 1, Gr 3 Cl 2, Gr L) was generated at a frequency of 1 Hz in hydrogen at pressure of 106 MPa [1], while the data for Cr-Mo steel (two heats of Gr J) was generated at a frequency of 0.1 Hz in hydrogen at pressure of 103 MPa from Refs. [6,7].

Additional testing may focus on developing a simplified testing strategy to verify consistency of other steel classes over an extended load ratio range using these results as a benchmark. With this benchmark data, the number of specimens and the time for testing other steels can, in principle, be substantially reduced while ensuring performance in hydrogen. It should also be noted that the fracture tests in gaseous hydrogen were performed at the conclusion of fatigue testing (rather than using separate specimens for evaluating fracture resistance), which also reduces the number of test specimens needed to characterize the steels.

Performance Methods for Materials Qualification

Establishing robust performance metrics for materials qualification is challenging because materials are often selected for multiple characteristics, which depend on the specifics of the design. However, when properties can be bounded by general performance requirements, criteria can often be established. The H2 Compatibility Expert Team from the SAE Fuel Cell Safety Task Force has been engaged in conversation to develop internationally harmonized materials performance metrics for several years. Previously, progress on this discussion had been inhibited by lack of relevant fatigue data; however, active research programs (such as funded by the hydrogen storage subprogram, but also internationally) have recently made data available for assessment and these data are actively being discussed to inform performance metrics for in the SAE Fuel Cell Safety Task Force. The Safety, Codes and Standards subprogram, which developed the tension-tension notched fatigue test method for hydrogen, has proposed a performance metric of $\geq 10^5$ cycles at a maximum fatigue stress of one-third of the tensile strength, as shown in Figure 3. This simple performance metric can be applied to fatigue testing in gaseous hydrogen for either the smooth fatigue specimen (load ratio of -1) or the notched fatigue specimen (load ratio of 0.1). In both test methods, the target is to verify that the maximum allowable stress in the material is less than the fatigue limit (implying infinite life design) using a relatively small number of tests and avoiding extensive fatigue life testing. While not yet formally adopted, the proposed criterion is the first step toward a performance-based materials qualification metric and has been discussed as a possible proposal for discussion at the GTR no. 13 Phase 2 negotiations.

The H2 Compatibility Expert Team at SAE has also been engaged in information sharing toward developing testing capability for fatigue testing in high pressure gaseous hydrogen at low temperature, in addition to developing the test methods for materials qualification. Three international institutes (namely Kyushu University, MPA Stuttgart and Sandia National Laboratories) are independently developing new capability for testing in the combination of high-pressure and low-temperature, and sharing their experience toward

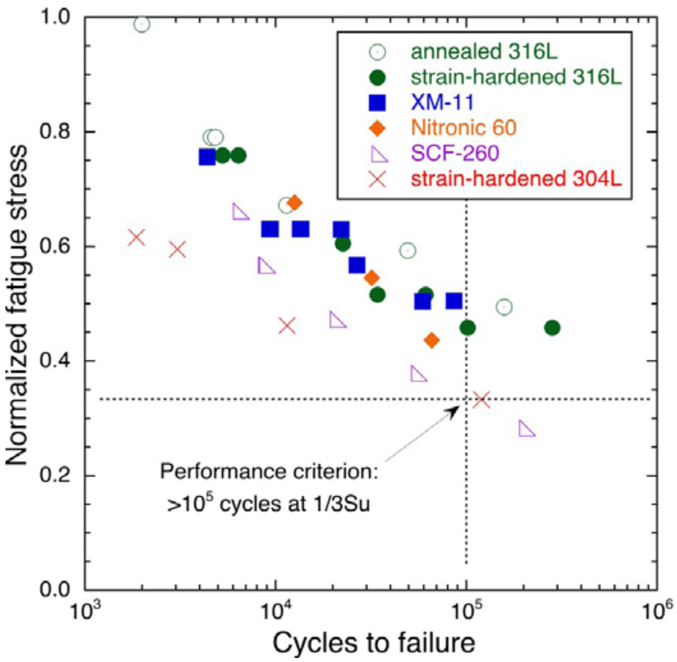

FIGURE 3. Fatigue life curves for several austenitic steels measured in gaseous hydrogen at pressure of 10 MPa (tension-tension notched fatigue: stress concentration factor of 3.9, frequency of 1 Hz, and load ratio of 0.1), plotted for maximum fatigue stress normalized by the tensile strength (Su). The proposed materials qualification metric is indicated on the plot: >10^5 cycles to failure at maximum fatigue stress representing one-third of the tensile strength of the material.

coordinated testing to verify test methods for qualification of materials for vehicle components. The H2 Compatibility Expert Team meets quarterly at the SAE Fuel Cell Safety Task Force meetings, but these meetings are supplemented by technical exchanges almost monthly via teleconference. The technical institutes seek to complete a testing campaign by the end of 2017 to compare equivalent tests from each institute. These results will aid test method development and will also help establish the limiting conditions for fatigue performance in gaseous hydrogen.

Information Resources

The Database for Hydrogen Compatibility of Materials uses the Granta database tool software. It is currently publicly accessible through a web-based interface at https://granta-mi.sandia.gov. Public access to this database is made available by special agreement with Granta and hosted by Sandia National Laboratories. The database has experienced over 20,000 hits, and nearly 8,000 page views by hundreds of unique visitors. The database is undergoing a major revision for release at the end of Summer 2017. Recently published data is being integrated into the database by soliciting authors to aid the incorporation of their data into this state-of-the-art tool. The database enables comparison of data from different sources, verification of materials and testing pedigrees, and may eventually be the basis for prescriptive design data. While the database enables quantitative access to materials properties measured in gaseous hydrogen by institutes throughout the world, the Technical Reference provides interpretation of the data and specific guidance on materials selection for hydrogen service for nonexperts. The updated database content will greatly facilitate the revision of the Technical Reference by providing the authors with advanced comparison tools and wider range of data from which to establish concrete recommendations and confirm broadly applicable trends where appropriate.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Testing of high-hardenability pressure vessels steels with a range of strength show that hydrogen-accelerated fatigue crack growth is similar to the pressure vessel steels currently in service, while fracture resistance of pressure vessels steels displays a steep reduction when tensile strength exceeds 950 MPa.
- A simple method for evaluating fatigue performance in hydrogen has been proposed. The method consists of tension-tension fatigue life testing of notched specimens and a conservative performance-based metric of >10^5 cycles to failure at maximum fatigue stress of one-third of the tensile strength.
- The Database on Hydrogen Compatibility of Materials is receiving a major upgrade, which will be transitioned to public access at the end of summer.
- Low-temperature testing in high-pressure gaseous hydrogen will be the focus of the next method development campaign, allowing for evaluation of the limiting conditions for fatigue behavior of austenitic stainless steels for vehicle and vehicle refueling applications. This testing represents a significant advancement of capabilities for hydrogen testing within the United States and is being coordinated with an international team of experts developing similar testing capability to support GTR no. 13 Phase 2 discussions.

FY 2017 PUBLICATIONS/PRESENTATIONS

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2. B.P. Somerday, J.A. Campbell, K.L. Lee, J.A. Ronevich, C. San Marchi: "Enhancing safety of hydrogen containment components through materials testing under in-service conditions." *Intern J Hydrogen Energy* 42 (2017) 7314–7321.

3. B. An, Z. Hua, T. Iijima, C. Gu, J. Zheng, C. San Marchi: "Scanning Kelvin probe force microscopy study of hydrogen distribution and evolution in duplex stainless steel" (PVP2017-66121), Proceedings of the 2017 ASME Pressure Vessels & Piping Conference, 16–20 July 2017, Waikoloa, HI.

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4. K.A. Nibur, B.P. Somerday, C. San Marchi, J.W. Foulk III, M. Dadfarnia, P. Sofronis, G.A. Hayden: "Measurement and interpretation of threshold stress intensity factors for steels in high-pressure hydrogen gas," SAND2010-4633, Sandia National Laboratories, Livermore, CA.

5. K.A. Nibur, B.P. Somerday, C. San Marchi, J.W. Foulk, M. Dadfarnia, P. Sofronis: "The relationship between crack-tip strain and subcritical cracking thresholds for steels in high-pressure hydrogen gas." *Metall Mater Trans* 44A (2013) 248–269.

6. B.P. Somerday, K.A. Nibur, and C. San Marchi: "Measurement of fatigue crack growth rates for steels in hydrogen containment components," 3rd International Conference on Hydrogen Safety (ICHS3), September 2009, San Sebastian, Spain.

7. B.P. Somerday, C. San Marchi, and K.A. Nibur: "Measurement of fatigue crack growth rates for SA-372 Gr. J steel in 100 MPa hydrogen gas following Article KD-10" (PVP2013-97455), ASME Pressure Vessels and Piping Division Conference, American Society of Mechanical Engineers, 14–18 July 2013, Paris, France.