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) 2018 Objectives

- Provide the American Society of Mechanical Engineers (ASME) technical community with the technical basis for generalized assessment of fatigue crack growth of pressure vessel steels for high-pressure hydrogen service.
- Demonstrate fatigue life measurements at low temperature in high-pressure hydrogen with international partners to corroborate results from various testing institutions.
- Establish the technical basis for simplified fatigue life test methods to enable materials selection for hydrogen service in low-cycle applications (such as vehicle fuel systems).
- Obtain international consensus on materials testing methods and metrics for the SAE J2579 standard and for inclusion in the United Nations (UN) Global Technical Regulation (GTR no. 13 Phase II).

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[1]:

(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 Hydrogen Safety, Codes and Standards Milestones

This project will contribute to the 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)

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- 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 2018 Accomplishments

- Developed design curves for ASME pressure vessel steels (applicable to both Cr-Mo and Ni-Cr-Mo steels).
- Proposed design curves to ASME Pressure Vessel Committee as the basis for a code case that will allow pressure vessel design for high-pressure hydrogen without additional testing burden.
- Established the methods and the technical basis for materials acceptance criteria in the context of fuel systems for fuel cell electric vehicles with international experts.
- Performed round-robin testing with international partners to show consistency in fatigue life measurements in high-pressure gaseous hydrogen at low temperature (in context of materials requirements for SAE J2579 standard).
- Proposed materials testing methodology for hydrogen compatibility to UN GTR no. 13 Phase II Informal Working Group.
- Negotiated general consensus for the UN GTR with materials experts from the United States, Japan, Germany, European Union, Korea and China (a few details are still actively being negotiated, but general concepts have been accepted).

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 element of the Safety, Codes and Standards subprogram 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. In this laboratory, we focus on three critical activities:

1. Optimizing materials characterization methodologies
2. Generating critical hydrogen compatibility data for materials to enable technology deployment
3. Providing 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 temperatures. 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

Design Curves for Pressure Vessels

Nearly all of the fatigue data used to design high-pressure vessels for stationary hydrogen storage according to the ASME Boiler and Pressure Vessel Code was developed as part of this program in previous years. In general, stationary storage vessels for hydrogen are manufactured from SA-372 Grade J steel because, until recently, comprehensive data did not exist for any other steel. Recent work [1] contributed fatigue data for several high-hardenability steels (such as SA-723 Ni-Cr-Mo steels), which enables thicker vessel walls and larger sizes of storage vessels. Additionally, these recent data expanded the data range that can be used in design, essentially eliminating the overly conservative extrapolation of data to small defect sizes. A re-assessment of the older data sets for the Grade J steel and the newer data for Ni-Cr-Mo steels revealed consistency of the fatigue crack growth data for all of these steels, greatly expanding the parameter space for which fatigue crack growth data is available.

The new data were used to develop simplified design curves that bound the fatigue crack growth data for all the tested pressure vessel steels. The new design curves combine both the driving force (ΔK) and the load ratio (R) in a simple engineering relationship that appears to be relevant for a range of ASME pressure vessel steels. Formulation of these design curves was reported to the relevant ASME code committee and the concept was quickly embraced as a useful tool to advance pressure vessel design and eliminate, in some cases, the need and cost for additional testing. While a few fine points are still being discussed within the committee, a code case has been drafted that will significantly enable the design of high-pressure vessels for storage at hydrogen fueling stations.

The master design curves can be split into a family of design curves as shown in Figure 1. While previously only the upper envelope of data was available (i.e., $\Delta K > 10$ MPa $m^{1/2}$), the new design curves capture the behavior at lower ΔK and the transition between the two generalized regimes. By employing the design curves at lower ΔK, a significantly longer design life is allowed by design calculations (which are known to be conservative) because the crack growth rates have been shown to be lower than extrapolated from the upper curve alone. Additionally, the new data demonstrates limitations on the performance of high-strength steels and the need to advance our understanding of hydrogen effects on these steels to enable their use in hydrogen, for example through microstructural design.

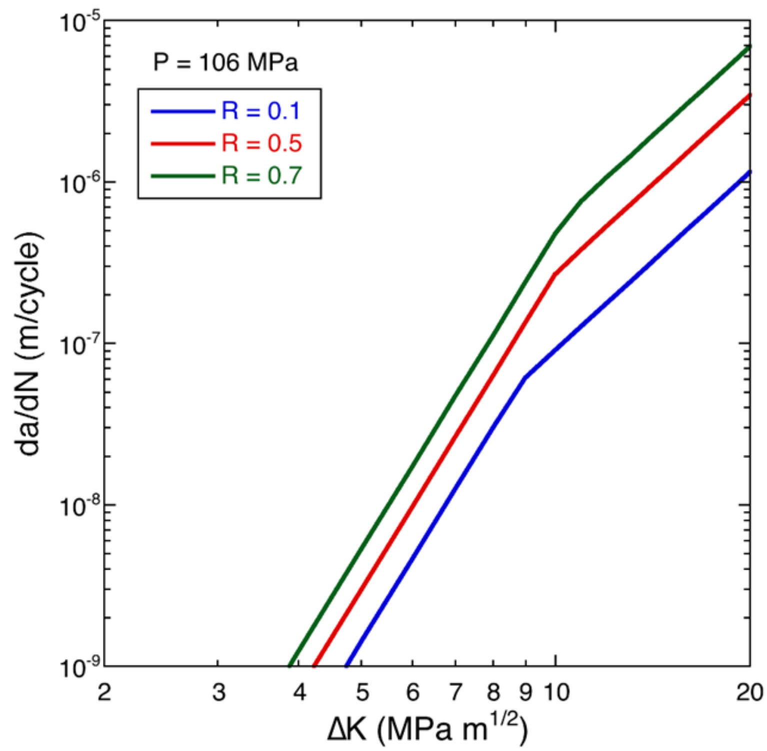

Figure 1. Master design curves for Cr-Mo and Ni-Cr-Mo pressure vessel steels at several load ratios (R)

Fatigue Life Methods

Fatigue life methods are an important and, in some cases, necessary alternative to fracture-mechanics-based design methods. Unlike the ASME codes, which specify design basis, many industries use performance-based requirements, which are design agnostic. Vehicle standards, for example, define performance requirements of components and systems rather than specifying design requirements. Performance-based standards allow for design innovation when components and systems can be tested, such as in vehicle crash tests. Performance-based standards, however, can be difficult to realize for structural materials because the transference of the performance of a structural material to the performance of a component is generally design specific. Nevertheless, with understanding of the application and the system performance requirements, it is possible to identify simple relevant performance metrics that materials must satisfy without specifying the design.

We have led an international team of materials experts for several years with the aim of developing performance-based materials testing requirements for hydrogen compatibility. While initial activities of the expert team on materials compatibility identified a long list of testing requirements that would have been overly burdensome to manufacturers, the team negotiated comparatively simple test metrics specific to the vehicle application. These metrics have been formalized in the SAE J2579 standard with technical justification and have been proposed to the GTR no.13 Phase II Informal Working Group. For the first time, this definition of test metrics enables relatively simple screening of materials for hydrogen compatibility, as discussed in a joint publication with materials experts from the United States, Japan, and Germany [2]. While the developed test metrics are specific to the vehicle application, the performance-based concept for hydrogen compatibility can be extended to other applications where the design is not defined by the standard or code.

As part of the international activity to develop a performance-based protocol for hydrogen compatibility of materials, a modest test program was developed such that the participating laboratories could compare results on identical specimens. This activity provided a common understanding of the testing requirements, challenges with execution of the tests, and consistency of test results from different laboratories. The results are summarized in Ref. [2], along with rationale for the methods. An important outcome of this testing activity was a consensus that the limiting temperature for fatigue performance for austenitic stainless steels is room temperature. Previously, it was assumed that hydrogen effects are greatest at low temperature (around 220 K), close to the lower end of the temperature range specified for the application space (usually considered to be 233 K). Through this testing activity (and subsequently corroborated by complementary testing activities [3]), it was realized collectively that fatigue life in this class of materials is similar or shorter at room temperature than at low temperature, both in air and in hydrogen (Figure 2). While this idea had been proposed previously, it was the collective testing activity that enabled consensus among the hydrogen compatibility experts. As a result, the testing protocols were simplified, requiring fatigue life testing at room temperature in hydrogen, which is already challenging enough, but less challenging than testing at low temperature in high-pressure hydrogen.

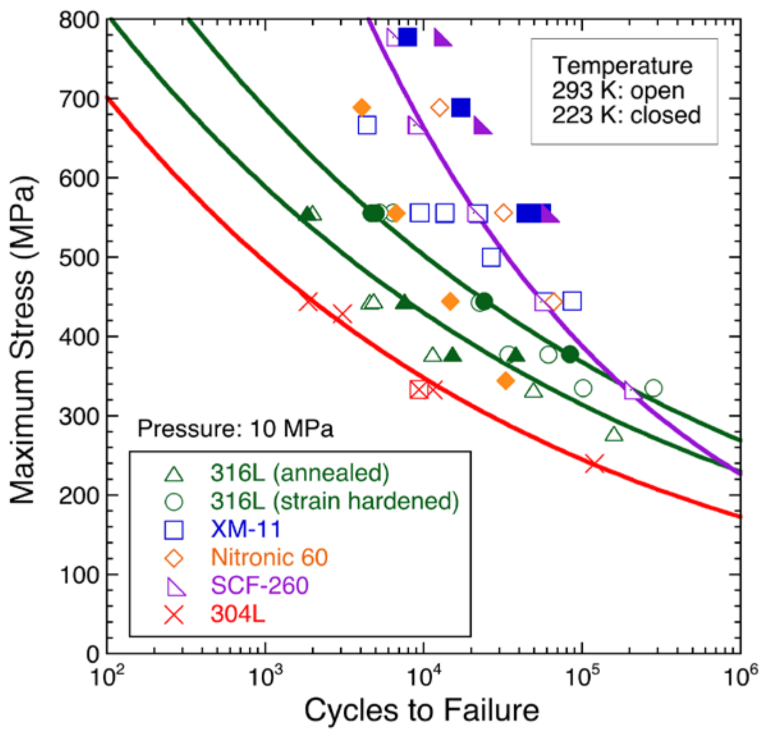

Figure 2. Fatigue life curves for several austenitic stainless steels, showing effect of temperature of fatigue in gaseous hydrogen at pressure of 10 MPa

In summary, working closely with international materials experts and SAE, consensus was reached for the first time on a simple performance-based protocol for screening materials for high-pressure hydrogen service. A collaborative testing activity across multiple test laboratories aided consensus building and further simplification of the testing protocols. The protocols have been proposed for inclusion in GTR no. 13 Phase II and there is general agreement among materials testing experts participating in the GTR discussions (including United States, Japan, European Union, Korea, and China). Acceptance of welded components remains an open question and should be a focus of continued work.

CONCLUSIONS AND UPCOMING ACTIVITIES

- A variety of common pressure vessel steels show similar fatigue behavior in high-pressure gaseous hydrogen, and this behavior can be captured with a relatively simple set of design curves that account for the load ratio.
- The fatigue design curves developed for pressure vessels are the basis for a code case being debated in the ASME committee on high-pressure vessels.
- Materials requirements for hydrogen compatibility in the fuel system of vehicles have been developed in collaboration with an international team of materials experts; the requirements have been incorporated into SAE J2579 and are being negotiated for inclusion in the UN GTR no. 13.
- A scientific paper on performance-based materials requirements for the high-pressure components on the vehicle was jointly authored with international experts from Japan and Germany.
- Hydrogen-assisted fatigue and fracture of welded austenitic stainless steels and aluminum alloys represent high-priority research topics based on discussion with standards organizations and industry participants; in particular, demonstration that welded stainless steel can meet similar requirements as base materials may enable the replacement of fittings with welded joints, while validation of testing protocols for the unique characteristic fracture behavior of aluminum alloys is still needed.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. J. Ronevich, C. San Marchi. "Effects of Gaseous Hydrogen on Austenitic Stainless Steel Welds." Presented at International Hydrogen Infrastructure Workshop Bilateral Safety Meeting, 13 September 2018, Boston, MA. SAND2018-10200PE.
2. C. San Marchi. "Master Curves for Fatigue Crack Growth of Ferritic Steels in Gaseous Hydrogen." Presented at meeting of Study Group on Materials Testing and Qualification for Hydrogen Service, 20 July 2018, Prague, Czech Republic. SAND2018-8867PE.
3. J. Ronevich, et al. "Effects of Gaseous Hydrogen on Austenitic Stainless Steel Welds." Presented at meeting of Study Group on Materials Testing and Qualification for Hydrogen Service, 20 July 2018, Prague, Czech Republic. SAND2018-8850PE.
4. C. San Marchi, J. Yamabe, M. Schwarz, H. Matsunaga, S. Zickler, S. Matsuoka, H. Kobayashi. "Global Harmonization of Fatigue Life Testing in Gaseous Hydrogen." *Proceedings of the 2018 ASME Pressure Vessels & Piping Conference*, 15–20 July 2018, Prague, Czech Republic. Paper PVP2018-84898.
5. C. San Marchi (in collaboration with SAE Fuel Cell Safety Task Force). "Proposed Test Method to Establish Hydrogen Compatibility of Materials for Fuel Cell Vehicles." Presented by Glenn Scheffler to GTR no. 13 Phase 2 informal working group, June 2018, Seoul, Korea. SAND2018-6478PE.
6. C. San Marchi. "R&D for Safety, Codes and Standards: Materials Compatibility." Presented at Joint Tech Team Meeting, Delivery, Storage and Safety, Codes and Standards, 28–29 March 2018, Troy, MI. SAND2018-3050C.
7. C. San Marchi (invited), J. Ronevich. "Dispelling Myths about Gaseous Hydrogen Environmental Fracture and Fatigue." Presented at TMS Annual Meeting, 11–15 March 2018, Phoenix, AZ. SAND2018-2718C.

8. C. San Marchi, J. Ronevich. "Basis of FCGR Laws for Fatigue Crack Growth of PV Steels in Gaseous Hydrogen." Presented at ASME Boiler and Pressure Vessel Committee Code Week, 2–9 February 2018, Las Vegas, NV. SAND2018-1098PE.
9. C. San Marchi (in collaboration with SAE Fuel Cell Safety Task Force). "Proposed Test Method to Establish Hydrogen Compatibility of Materials for Fuel Cell Vehicles." Presented to GTR no. 13 Phase 2 informal working group, 5–7 February 2018, Torrance, CA. SAND2018-0857PE.
10. C. San Marchi, P. Gibbs, J. Foulk, K. Nibur. "Fatigue Life of Austenitic Stainless Steels in Hydrogen Environments." Paper presented at 43rd MPA Seminar, 11–12 October 2017, Stuttgart, Germany (co-sponsored).

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1. C. San Marchi, P. Bortot, J. Felbaum, Y. Wada, J.A. Ronevich. "Fatigue and Fracture of High-Hardenability Steels for Thick-Walled Hydrogen Pressure Vessels." Presented at International Conference on Hydrogen Safety, Hamburg, Germany, 11–13 September 2017.
2. C. San Marchi, J. Yamabe, M. Schwarz, H. Matsunaga, S. Zickler, S. Matsuoka, H. Kobayashi. "Global Harmonization of Fatigue Life Testing in Gaseous Hydrogen." *Proceedings of the 2018 ASME Pressure Vessels & Piping Conference*, 15–20 July 2018, Prague, Czech Republic. Paper PVP2018-84898.
3. T. Iijima, H. Enoki, J. Yamabe, B. An. "Effect of High Pressure Gaseous Hydrogen on Fatigue Properties of SUS304 and SUS316 Austenitic Stainless Steel." *Proceedings of the 2018 ASME Pressure Vessels & Piping Conference*, 15–20 July 2018, Prague, Czech Republic. Paper PVP2018-84267.