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

Chris San Marchi (Primary Contact),
Brian Somerday
Sandia National Laboratories
7011 East Ave.
Livermore, CA 94550
Phone: (925) 294-4880
Email: cwsanma@sandia.gov

DOE Manager: Will James
Phone: (202) 287-6223
Email: Charles.James@ee.doe.gov

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) 2016 Objectives

- Evaluate relevant high hardenability (Ni–Cr–Mo) steels for advanced high-pressure storage.
- Develop material property database for hydrogen effects on materials.
- Establish coordinated fatigue life testing activities and data sharing with international stakeholders.
- Demonstrate low-temperature fatigue life method for austenitic stainless steels.

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 2016 Accomplishments

- Completed fatigue initiation testing of Cr–Mo steel specimens provided by the MATHRYCE project at two hydrogen gas pressures (30 and 100 MPa). Results show that the number of cycles for crack initiation decreases as hydrogen pressure increases from 30 to 100 MPa, confirming that fatigue testing at 30 MPa is nonconservative relative to the service pressure of 100 MPa.

- Initiated testing campaign on high hardenability (Ni–Cr–Mo) pressure vessels steels. This activity includes partnership with pressure vessel manufacturers from the United States, Europe, and Asia. Preliminary results show consistency with Cr–Mo pressure vessels steels, suggesting that Ni–Cr–Mo can be used for thicker wall hydrogen pressure vessels.
- Demonstrated public trial of Uniform Resource Locator-based GRANTA MI™ database of materials properties in hydrogen environments.

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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

Crack Initiation of Cr–Mo Steels

Sandia collaborated with the European Union-supported MATHRYCE project (www.mathryce.eu) to perform fatigue testing on notched specimens in high-pressure hydrogen gas. The tested materials were Cr–Mo steel, representative of pressure boundary materials in stationary hydrogen pressure vessels. The MATHRYCE project performed fatigue crack initiation and growth testing on these steels in lower-pressure hydrogen gas (less than 30 MPa) for the purpose of evaluating methods to inform fatigue life assessments of stationary pressure vessels. Since the testing systems operated by the MATHRYCE partners are limited to the lower pressure range, Sandia performed analogous fatigue testing on the Cr–Mo steel specimens at 100 MPa pressure in the Hydrogen Effects on Materials Laboratory. Sandia completed testing on the four instrumented specimens provided by the MATHRYCE project. Three of the specimens were tested in 100 MPa hydrogen gas (the upper limit expected for pressure vessels at refueling stations) with two different mechanical loading waveforms, i.e. sinusoidal and triangular. The fourth specimen was tested at 30 MPa to confirm the measurement by MATHRYCE. The results are summarized in Table 1.

TABLE 1. Summary of fatigue testing on notched Cr–Mo steel specimens

H_2 Pressure (MPa)	Waveform	Cycles for Crack Initiation
100	sinusoidal	763
100	sinusoidal	860
100	triangular	1017
30	triangular	2589
30	triangular	2764†
10	triangular	7136†
2	triangular	18292†

†measurements made by MATHRYCE program

The results in Table 1 demonstrate that increasing hydrogen pressure from 30 MPa to 100 MPa reduces the number of load cycles to initiate cracking at the notch, confirming that testing at 30 MPa cannot represent the service condition at 100 MPa. In addition, the number of cycles for crack initiation at 30 MPa as measured at Sandia is consistent with the result measured by MATHRYCE, validating the consistency of testing in the two laboratories (Sandia and MATHRYCE). These results represent the first attempt at quantification of crack initiation in gaseous hydrogen at high pressure (>70 MPa). These results suggest that the number of cycles to initiate a crack can be relatively low. A robust methodology for extrapolating crack initiation studies to design has not yet been achieved.

High-Hardenability Pressure Vessel Steels

The partnership for testing high-hardenability (Ni–Cr–Mo) pressure vessel steels includes Fiba Technologies (United States), Tenaris-Dalmine (Europe/Italy), and Japan Steel Works (Asia/Japan). All of the partners are provided steel panels for extracting specimens or actual specimens. Testing has begun with steel panels (SA-372 Grade L) provided as part of previous work with the American Society of Mechanical Engineers (ASME) Project Team on Hydrogen Tanks. Sandia has two panels, one that satisfies the SA-372 Grade L strength specification (very high yield strength for hydrogen service, >1,000 MPa) and the other with an experimental heat treatment to achieve lower strength consistent with Grade J (yield strength of ~750 MPa). The fatigue crack growth rates for the low strength Ni–Cr–Mo pressure vessel steel is compared in Figure 1 with fatigue crack growth rates for several varieties of Cr–Mo pressure vessels steels. The Cr–Mo steels were tested in gaseous hydrogen at pressure of 45 MPa, while the Ni–Cr–Mo steel was tested at pressure of 106 MPa. The test frequency was either 1 Hz (4130X, Grade L) or 10 Hz (Grade J, 34CrMo4), while an R ratio of 0.1 was used for all tests. The different test configurations likely account for the modest differences in the observed fatigue crack growth rates, but in general, for high ΔK (>12 MPa $m^{1/2}$) the fatigue crack rates are consistent for these materials and test conditions. The steels from the partners will be consistent with SA-723, an ASME standard for Ni–Cr–Mo pressure vessel steels that includes yield strength criteria of around 700 MPa (Class 1). This relatively low strength is consistent with the Grade J steels from SA-372 and appropriate for hydrogen pressure vessels. The higher classes represent higher yield strength criteria (>825 MPa) and are unlikely to show sufficient fracture resistance in hydrogen environments to meet design requirements, such as those in ASME Boiler and Pressure Vessel Code VIII.3 [1]. Steels from the partners are expected in August 2016.

Information Resources

Granta agreed to a public trial of the Technical Database for Hydrogen Compatibility of Materials (https://granta-mi.sandia.gov). The initial effort to expand the content of the database includes the data from the technical reference, with the restriction of only including results measured in gaseous hydrogen environments. Recent publications on pipeline steels and pressure vessels steels will also be included in the database. This focus, we believe, serves the interests in a materials database of hydrogen effects previously expressed by ASME committee members (Project Team on Hydrogen Tanks and representatives from the ASME Pressure Piping Code [2]). The database will enable comparison of data from different sources, verification of materials and testing pedigrees, as well as potentially development of design data.

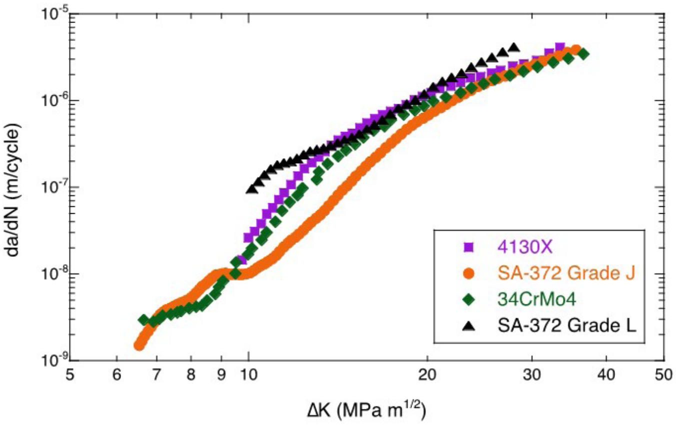

FIGURE 1. Fatigue crack growth rates comparing Ni–Cr–Mo pressure vessel steel (SA-372 Grade L) to Cr–Mo pressure vessel steels (4130X, SA-372 Grade J and 34CrMo4). The test pressure was 45 MPa, with the exception of the Grade L, where the test pressure was 106 MPa. Testing of the Grade L and 4130X was conducted at frequency of 1 Hz, while the other tests were conducted at frequency of 10 Hz. All tests were conducted with an R ratio of 0.1.

Low-Temperature Testing Apparatus

Low-temperature evaluation of materials is critical to expansion of the alloys that can be used in vehicle applications (due, in part, to precooling requirements during refueling). This is the motivation for construction of a high-pressure testing system with the capability of controlling temperature as low approximately 200 K. Delivery of the low-temperature testing apparatus has been delayed several times by the vendor. The current estimate for receiving the autoclave for low-temperature testing is end of summer 2016. Other major hardware components have been purchased and integrated (to the extent possible). The initial focus of testing is anticipated to be austenitic stainless steels in coordination with international partners at MPA Stuttgart and Kyushu University. Preliminary data from other projects suggest that fatigue performance may not be limited by low temperature, but this hypothesis needs verification.

CONCLUSIONS AND FUTURE DIRECTIONS

- The qualification of high-hardenability steels (Ni–Cr–Mo) will be an important advance for storage as pressure vessels with thicker walls are needed to support high-pressure hydrogen storage for refueling. Evaluation of Ni–Cr–Mo steels in comparison to qualified Cr–Mo steels will be the focus of high-pressure fatigue and fracture testing the coming months.
- The Technical Database for Hydrogen Compatibility of Materials will show significant expansion before the end of FY 2016. The public trial will end and a longer-term solution must be negotiated with Granta. At the very least, the database will be distributed for free and GRANTA MI users will have access to the data.
- Completion of the system for low-temperature testing is critical to validation of low-temperature performance. Austenitic stainless steels will be the focus of international coordination of testing at low temperature once the low-temperature testing system is operational near the end of FY 2016.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. 2015 ASME PVP Heki Shibata Outstanding International Technical Session (awarded at the PVP 2016 conference): "Effects of Gaseous Hydrogen on Pressure Vessel Steels."

FY 2016 PUBLICATIONS/PRESENTATIONS

1. T. Michler, C. San Marchi, K. Berreth, J. Naumann, R.K. Misha, R.C. Kubic: "Microstructure, deformation mechanisms and influence of hydrogen on tensile properties of the Co based super alloy DIN 2.4711/UNS N30003." Mater Sci Eng A662 (2016) 36–45.

2. C. San Marchi, E.S. Hecht, I.W. Ekoto, K.M. Groth, C. LaFleur, B.P. Somerday, R. Mukundan, T. Rockward: "Overview of the DOE Hydrogen Safety, Codes and Standards Program, Part 3: Advances in research and development to enhance the scientific basis for hydrogen regulations, codes and standards." Intern J Hydrogen Energy (accepted; DOI: 10.1016/j.ijhydene.2016.07.014).

3. L. Zhang, B. An, T. Iijima, C. San Marchi: "Effect of gaseous hydrogen charging on nanohardness of austenitic stainless steels" (PVP2016-63390). Proceedings of the 2016 ASME Pressure Vessels & Piping Conference, 17–21 July 2016, Vancouver, BC, Canada.

4. 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." 6th International Conference on Hydrogen Safety (ICHS), 19–21 October 2015, Yokohama, Japan.

5. C. San Marchi, E.S. Hecht, I.W. Ekoto, K.M. Groth, C. LaFleur, B.P. Somerday, R. Mukundan, T. Rockward: "Advances in research and development to enhance the scientific basis for hydrogen regulations, codes and standards." 6th International Conference on Hydrogen Safety (ICHS), 19–21 October 2015, Yokohama, Japan.

6. C. San Marchi: "Fatigue testing methodologies in gaseous hydrogen." International Workshop on Hydrogen Embrittlement in Metal, at the Korean Society of Mechanical Engineers Annual Fall Conference, 13 November 2015, Jeju, Korea.

7. C. San Marchi: "Pressure cycling of all steel pressure vessels with gaseous hydrogen." Joint HYDROGENIUS and I2CNER International Workshop on Hydrogen-Materials Interactions 2016, 4 February 2016, Kyushu, Japan.

REFERENCES

1. American Society of Mechanical Engineers (ASME), Boiler and Pressure Vessel Code (BPVC), Section VIII, Division 3, Article KD-10.

2. American Society of Mechanical Engineers (ASME), Hydrogen Piping and Pipelines, B31.12, ASME Code for Pressure Piping.