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

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Project End Date: September 30, 2022

Overall Objectives

- Develop test methods and the technical basis for acceptance of welded austenitic stainless steel construction for hydrogen infrastructure and fuel systems (performance of welds).
- Provide technical basis to justify the long-term integrity of materials in the presence of kinetic barriers and mitigation strategies (kinetic barriers).
- Develop new test methods and provide critical assessment of methods to clarify and enable robust design strategies for hydrogen service (advanced test methods).
- Provide community with accessible resources to assess hydrogen embrittlement in engineering alloys and clear documentation of the technical basis for standardized test methods (informational resources).

Fiscal Year (FY) 2019 Objectives

- Evaluate fatigue life hole-drilled tubular specimen as a complement to the notched tension-tension fatigue life specimen.
- Assess fracture resistance test methodology for evaluation of humid gas (hydrogen) on aluminum.
- Evaluate fatigue crack growth on steels near threshold regime in gaseous hydrogen environment (i.e., crack propagation rates of 10^{-10} m/cycle).
- Provide literature-based assessment of key considerations for hydrogen-natural gas blends in transmission pipelines.

Technical Barriers

This project addresses the following technical barriers from the Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Safety Data and Information: Limited Access and Availability (A)
- Enabling National and International Markets Requires Consistent RCS (F)
- Insufficient Technical Data to Revise Standards (G).

Contribution to Achievement of DOE 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, 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)

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

- Milestone 3.4: Develop hydrogen material qualification guidelines including composite materials. (Q4, 2017)
- Milestone 4.9: Completion of the Global Technical Regulation (GTR) #13 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 2019 Accomplishments

- The American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel, Section VIII committee accepted Code Case 2938 that formalizes design curves for seamless Cr-Mo and Ni-Cr-Mo pressure vessel steels (SA-372 and SA-723) in gaseous hydrogen, which improves the design basis for high-pressure vessels.
- Technical Basis for Code Case 2938 was published in proceedings of the ASME Pressure Vessels and Piping Division Annual Conference.
- Fatigue crack growth results near threshold were demonstrated in gaseous hydrogen for the first time, suggesting a pathway to quantify fatigue threshold in high-pressure gaseous hydrogen.
- The SAE International (SAE) Fuel Cell Standards Committee approved standard SAE J2579 with a performance method for materials evaluation; international consensus on the method was led by this project and methods are being contributed to GTR #13 Phase 2.
- Testing results of the hole-drilled tubular tension specimen show fatigue life that is consistent with the test results utilizing the circumferentially notched tension specimen in SAE J2579, potentially providing an improved basis for evaluating welds.
- International collaboration on test methods for aluminum in high-pressure gaseous hydrogen suggest that the humid gas test (HPIS E103:2018) may be appropriate for humid air environments but may not be transferrable to "wet" hydrogen environments.

INTRODUCTION

A principal challenge to the widespread adoption of hydrogen infrastructure is insufficient technical data to define adequate safety margins without exposing 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, which includes materials performance in hydrogen service environments. Developing meaningful materials characterization and qualification methodologies (in addition to understanding 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.

The hydrogen compatible materials and components task has several broad goals:

1. Optimize the reliability and efficiency of test methods for structural materials and components in hydrogen gas.
2. Generate critical hydrogen compatibility data for structural materials to enable technology deployment.
3. Create and maintain information resources such as the "Technical Reference for Hydrogen Compatibility of Materials" and the Hydrogen Effects Database that enable efficient and appropriate system design
4. Demonstrate leadership in the international harmonization of standards for qualifying materials and components for service with high-pressure gaseous hydrogen.

Each of these objectives supports the development, optimization, implementation, and harmonization of hydrogen containment codes and standards, such as ASME Article KD-10 for stationary and transport vessels, ASME B31.12 for piping and pipelines, CSA HPIT1 for industrial truck fuel systems, SAE J2579 for compressed hydrogen storage systems on vehicles, United Nations GTR #13 Phase 2, and CSA CHMC1 for hydrogen containment material qualification.

APPROACH

The materials and components compatibility R&D effort seeks fundamental understanding of hydrogen effects on materials and applies that understanding to (1) assess design implications of hydrogen infrastructure, (2) develop and assess scientifically defensible, accelerated test methodologies for fracture and fatigue testing of materials in hydrogen environments (emphasizing high-pressure environments and temperatures over the full range relevant to hydrogen technologies), (3) develop selection criteria and requirements for codes and standards for fuel cell technology components in hydrogen service, and (4) extend the scientific literature on hydrogen effects on materials. The Hydrogen Effects on Materials Laboratory (HEML), which 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, is the cornerstone of this effort. The output of this effort includes (1) optimized test methodologies, (2) critical data that enable the rapid deployment of vehicle, infrastructure, and stationary components, and (3) open-source informational resources. This activity also leverages state-of-the-art materials science characterization tools at Sandia National Laboratories to advance the understanding of hydrogen-materials interactions in both structural and functional materials, resulting in publications and conference presentations that enhance our science-based understanding of hydrogen effects and apply scientific principles to engineering assessment of materials and components performance in hydrogen technologies. To achieve these goals, this activity engages internationally in safety, regulation, and codes and standards discussion and development, provides leadership in these activities, and participates in international conferences.

RESULTS

Performance of Welds

Hydrogen compatibility of welds has received limited attention in the literature, although many components and systems rely on the use of welds. Extracting test specimens from relevant welds is challenging due to the geometrical configuration of typical welds in relation to standardized test specimens. In some cases, surrogate welds can be generated exclusively for extraction of test specimens as reviewed in [1], but not all weld configurations are suitable for extraction of test specimens. Orbital tube welds, for example, are a standard method for assembling gas manifolds, but they cannot be easily tested in fatigue and fracture configurations. Using the circumferentially notched tension (CNT) specimen as an analog, the hole-drilled tubular tension (HDTT) specimen was developed for fatigue life testing of orbital tube welds. The concept is simple: produce a stress concentration in the welded tube that is analogous to the stress concentration in the CNT. While the geometry of the HDTT and CNT are substantially different, the stress concentration factor (Kt) is designed to be similar, meaning that the mechanics of the two specimens are similar in the elastic limit. Using the CNT as the baseline, the tension-tension fatigue life data of the two specimens were compared in the context of the performance-based metric developed for and documented in the SAE J2579 standard (appendix B). As shown in Figure 1, when the fatigue life data are presented with the stress normalized to account for differences of the strength of the material, the fatigue life curves for two different tube materials and orbital welded tube are consistent with the data determined from CNT specimens (annealed and strain-hardened materials respectively). These results suggest a new configuration for evaluating relevant component and welded-component configurations for hydrogen service (such as tubing). More work is necessary to measure and compare fatigue life data of the HDTT and welded-HDTT specimens in the presence of hydrogen, as well as to understand the mechanics of the tubular specimen. Additionally, the HDTT configuration provides a platform for investigation of crack nucleation and initiation of relevant components and welds.

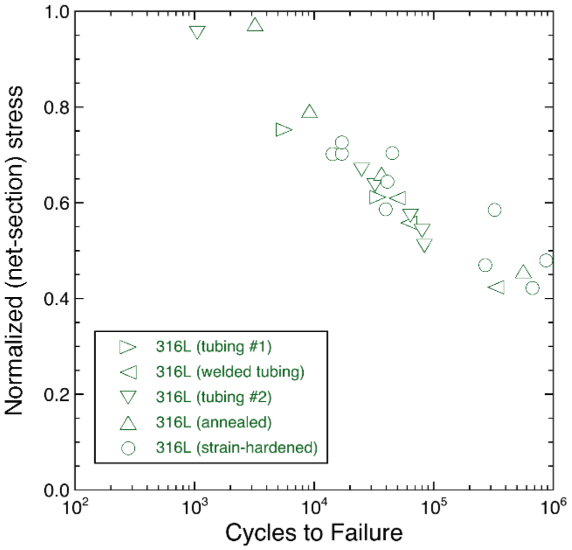

Figure 1. Fatigue life curves for HDTT (tubing) and CNT (annealed and strain-hardened) type 316L stainless steels, showing consist material response for the two configurations (load ratio: R = 0.1; frequency: *f* = 1 Hz; temperature: T = 293 K; as-fabricated condition).

Kinetic Barriers

The detailed physics of hydrogen-aluminum surface interactions have not been adequately described in the literature. It has been hypothesized that the native oxide on aluminum is a kinetic barrier to the uptake of gaseous hydrogen into the aluminum metal. Indeed, fracture and fatigue testing have shown that mechanical properties are not degraded in pure gaseous hydrogen [2]. Native aluminum surfaces, on the other hand, are hydrophilic, meaning moisture adheres to the aluminum surfaces. Water on aluminum surfaces has been shown (in the Hydrogen Materials Compatibility Consortium [H-Mat] program) to stabilize hydrogen on aluminum surfaces, creating a potential pathway to defeat the kinetic barrier to hydrogen uptake into the metal from aluminum surfaces. Furthermore, the fracture resistance of many aluminum alloys is degraded in humid air, and “wet” hydrogen has been shown to induce cracking in some high-strength aluminum alloys. Collectively, these observations raise questions about the structural integrity of aluminum alloys in gaseous hydrogen and the potential for water in the hydrogen stream to induce subcritical fracture.

Recognizing the importance of moisture to structural integrity of aluminum alloys, the High Pressure Institute (HPI) of Japan has developed a standard (HPIS E103:2018) to evaluate the effect of humidity on aluminum alloys for fuel cell vehicle applications. While this method is relevant for the external air environment, the method was developed to also be a surrogate for water impurity in fuel-cell-grade hydrogen at high pressure. However, testing has not been performed to evaluate the efficacy of testing in humid air as a surrogate for water impurity in high-pressure hydrogen (as proposed by HPI). The goal of this activity is to apply the fracture method proposed by HPI to evaluate high-strength aluminum alloys in “wet” high-pressure hydrogen and determine whether the method can effectively “screen” aluminum alloys for hydrogen embrittlement phenomena in relevant fuel-cell-grade hydrogen environments. At the time of writing, constant displacement fracture specimens of three aluminum alloys (2219-T851, 7050-T7451, 7475-T7351) have been exposed to gaseous hydrogen at a pressure of approximately 100 MPa with water impurity of nominally 100 ppm (by volume) for 1,000 hours in the high-pressure environment. Indications are that no cracking was observed in these displacement-controlled fracture test specimens, but this conclusion needs to be verified upon removal of the specimens from the pressurized environment. These preliminary results suggest that low concentrations of water in high-pressure hydrogen do not degrade the fracture resistance of these high-strength aluminum alloys in the T7 and T8 tempers.

It should be noted that this activity seeks to evaluate test methods for evaluating hydrogen-assisted fracture in aluminum alloys in the context of potential kinetic barriers that may bias results toward positive testing outcomes. While this activity is focused on engineering test method development and evaluation, it is complemented by fundamental studies on hydrogen-aluminum interactions in the H-Mat program, which provides theoretical context to understanding potential kinetic barriers. Additionally, this activity is complemented by international research activities at the Japanese Automotive Research Institute and the University of Stuttgart in Germany, which support the Fuel Cell Standards Committee (Safety Task Force) at SAE and, in particular, the development of the SAE J2579 standard for the fuel system on fuel cell vehicles. Test results from these international programs are leveraged in the context of SAE to develop science-based methods for materials evaluation for fuel cell vehicles.

Advanced Test Methods

The ASME committee from Section VIII of the Boiler and Pressure Vessel Code voted positively on design curves for pressure vessel steels for high-pressure stationary storage of gaseous hydrogen. The design curves are described in Code Case 2938, which supplements the design rules in Article KD-10 (BPVC VIII.3). The technical basis for the design curves was presented at the ASME Pressure Vessels and Piping (PVP) conference in July 2019 [3]. These design curves represent a significant technology advance as they provide a basis for design of high-pressure vessels without the need for extensive testing in gaseous hydrogen environments, which substantially reduces the cost of pressure vessel development. Moreover, the design curves demonstrate the fatigue response over a larger operating range (namely lower ΔK), which has eliminated some of the conservativism in designs and enabled greater design life.

Many questions remain about the applicability of the design curves. The Code Case limits the use of design curves to Cr-Mo and Ni-Cr-Mo pressure vessel steels with tensile strength less than 915 MPa. This limit is a conservative upper bound on strength and even increasing the limit modestly to 950 MPa would have substantial benefit to manufacturers. Additionally, fatigue crack growth rates at $\Delta K < 5$ MPa $m^{1/2}$ are very limited, although establishing reliable fatigue thresholds (i.e., ΔK below which $da/dN < 10^{-10}$ m/cycle) will affect design strategy as pressure vessels can potentially be designed for infinite life. However, generation of data at low fatigue crack growth rates ($<10^{-8}$ m/cycle) in high-pressure gaseous hydrogen is challenging for several reasons including the time required to complete tests at low crack growth rates (which can be weeks) and the special testing protocols required to access low crack growth rates. Nevertheless, this activity seeks to develop and optimize test protocols to access the fatigue crack growth threshold. Figure 2 shows preliminary testing results at the fatigue crack growth threshold for a pipeline steel. These test results are characterized by low pressure, which was used to facilitate control of the load cycle; consequently, initial testing also utilized pipeline steel to enable verification of the protocols by comparison with existing data at low pressure. The curves in this image also show the design (master) curves from Code Case 2938, which are extrapolated from high pressure and high crack growth rates. While more data and further refinement of the methods are needed, these results suggest that the power-law behavior of fatigue crack growth in stage II is maintained to low crack growth rates and, consequently, the design curves may approximate fatigue behavior to rates as low as the threshold. If these results can be generalized, the value of the design curves can be extended to lower crack growth rates and the pressure vessel community can improve confidence of their safety margins for high-pressure hydrogen vessels.

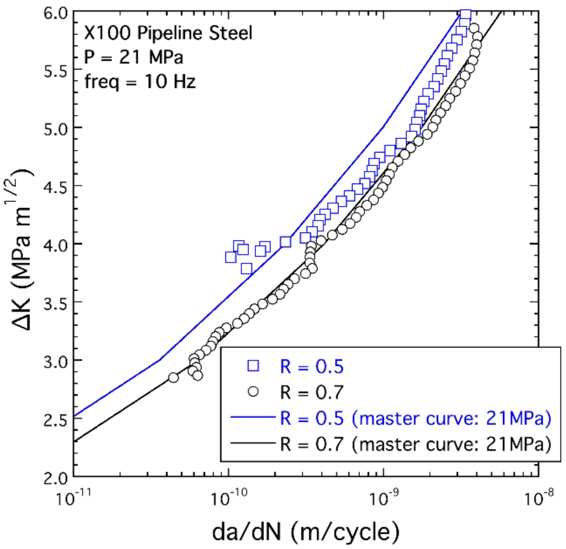

Figure 2. Fatigue crack growth rate of X100 pipeline steel in high-pressure gaseous hydrogen in the fatigue threshold regime

Informational Resources

Informational resources are designed to provide a distribution framework to communicate materials compatibility information to the hydrogen community. The Technical Reference (http://www.sandia.gov/matlsTechRef/) and Sandia Hydrogen Effects Database (https://granta-mi.sandia.gov) are examples of the sustained informational resources. The database in particular experienced nearly 70,000 page views in the last fiscal year from more than 3,700 unique IP addresses. A significant update to the Technical Reference is also planned to incorporate the advances in available fatigue and fracture data measured in high-pressure gaseous hydrogen, including data from the database. These updates will emphasize the ASME Code Case 2938 and its supporting data, the significant output from the Fuel Cell Technologies Office investment in evaluating structural integrity of pipeline steels for hydrogen service including welds, and the technical basis for the testing methodologies developed for SAE J2579 and the United Nations GTR.

In addition to the sustained informational resources, several presentations have been developed to communicate key concepts of and dispel misconceptions about the materials compatibility landscape [2, 4, 5]. Most notably, there has been an increase in activity around gas blending, namely injecting hydrogen into natural gas infrastructure. The implication of gas blending on the structural integrity of natural gas infrastructure is complicated and generally not well understood outside the materials community [6]. Small amounts of hydrogen (even less than an atmosphere) can have profound effects on fatigue crack growth and fracture resistance of typical ferritic steels [2, 4, 5]. Despite significantly enhanced fatigue crack growth and reduced fracture resistance, natural gas infrastructure with injected hydrogen can maintain its structural integrity if the systems are adequately managed; for example, by assessing defects in the system and controlling pressure fluctuations. Thousands of kilometers of hydrogen pipeline exist in the United States, although the rigor by which these systems are managed exceeds that of typical natural gas infrastructure. Additionally, impurities in natural gas (e.g., oxygen, carbon monoxide) will theoretically mitigate the effects of hydrogen-enhanced fatigue [2] under most circumstances (such as slow, modest pressure changes), provided the impurity content is sustained over the life of the system. While experimental study of the effects of gas blends on behavior of materials is beyond the scope of this program, dispelling misinformation and educating the community on the technical principles of materials compatibility (in pure hydrogen and gas blends) will continue to be an important contribution of this activity.

CONCLUSIONS AND UPCOMING ACTIVITIES

The materials and component compatibility R&D portfolio has contributed to several recent advances in codes and standards, including SAE J2579 Appendix B and ASME Code Case 2938. However, more work is necessary to improve the methods in these documents as well as disseminate results and lessons learned.

- The guidance on welds in SAE J2579 is rather generic, which motivates the development of the HDTT specimen and potentially a broader spectrum of fatigue life test geometries that utilize the concept of similitude with the CNT specimen. Testing of HDTT specimens with and without welds in the presence of hydrogen is underway to confirm the results in the absence of hydrogen that demonstrate the utility of the HDTT geometry. The learning will then be applied to other relevant weld configurations, as well as to the requirements in applications beyond SAE J2579.
- The ASME Code Case enables design of steel pressure vessels based on fracture mechanics, although some important gaps remain, including data and methods that access the fatigue crack growth threshold as well as resolution on fatigue crack growth of steels with tensile strength in the range of 915–950 MPa.
- Preliminary results on aluminum suggest that moisture (within the impurity range for fuel-cell-grade hydrogen) does not degrade aluminum relative to tests in air, suggesting that the proposed standard for humid gas testing is not relevant to high-pressure hydrogen environments. Additional evaluation may be needed to ensure these preliminary results are not sensitive to kinetic limitations.
- The Technical Reference and the Sandia Hydrogen Effects Database are referenced extensively in the codes and standards community. The Technical Reference in particular is due for significant updates. Additionally, enhancing communications through safety workshops and venues (such as the Hydrogen Safety Panel) are planned to disseminate science-based understanding to the broader energy sector and the expanding energy communities considering hydrogen technologies.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. C. San March, J.A. Ronevich, J. Sabisch, J.D. Sugar, D.L. Medlin, and B.P. Somerday, “Effect of Microstructural and Environmental Variables on Ductility of Austenitic Stainless Steels,” International Conference on Hydrogen Safety, Adelaide, Australia, September 24–26 2019.
2. C. San Marchi, et al, “Discussion Topics for Study Group Meeting,” Study Group on Materials Testing and Qualification for Hydrogen Service, San Antonio, TX, July 19, 2019, SAND2019-8905PE.
3. C. San Marchi, J. Ronevich, P. Bortot, Y. Wada, J. Felbaum, and M. Rana, “Technical Basis for Proposed Master Curve for Fatigue Crack Growth of Ferritic Steels in High-Pressure Gaseous Hydrogen in ASME Section VIII-3 Code,” (PVP2019-93907) Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, San Antonio, TX, July 14–19, 2019.
4. J. Ronevich, C. San Marchi, and D.K. Balch, “Evaluating the Resistance of Austenitic Stainless Steel Welds to Hydrogen Embrittlement,” (PVP2019-93823) Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, San Antonio, TX, July 14–19, 2019.
5. C. San Marchi, J.A. Ronevich, J. Campbell, and B. Davis, “R&D for Safety, Codes and Standards: Materials and Components Compatibility,” DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, April 2019, SAND2019-3280C.
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7. C. San Marchi and J.A. Ronevich, “Testing to Establish Suitability of Aluminum Alloys for Use in Fuel Cell-Grade Hydrogen,” SAE Fuel Cell Safety Task Force, Materials Expert Team, February 2019, SAND2019-1705PE.

8. C. San Marchi and J.A. Ronevich, “Federal Research on Emerging Fuels – The Integrity Impact of Transporting Hydrogen via Existing Pipeline Systems,” webinar for Pipeline Research Council International, December 2018, SAND2018-14013PE.
9. C. San Marchi and J.A. Ronevich, “Hydrogen Embrittlement Considerations for Distribution of Gaseous Hydrogen by Pipeline,” invited talk at Pipeline Research Council International quarterly meeting, October 2018, SAND2018-12184PE.
10. C. San Marchi, “Proposed Test Method to Establish Compatibility of Materials for Fuel Cell Vehicles,” Informal Working Group of Global Technical Regulation number 13, Phase 2, Brussels, Belgium, October 2018, SAND2018-11454PE.

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1. J. Ronevich, C. San Marchi, and D.K. Balch, “Evaluating the Resistance of Austenitic Stainless Steel Welds to Hydrogen Embrittlement,” (PVP2019-93823) Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, San Antonio, TX, July 14–19, 2019.
2. C. San Marchi and J. Ronevich, “Dispelling Myths about Gaseous Hydrogen Environmental Fracture and Fatigue,” TMS Annual Meeting, Phoenix, AZ, March 11–15, 2018, SAND2018-2718C.
3. C. San Marchi, J. Ronevich, P. Bortot, Y. Wada, J. Felbaum, and M. Rana, “Technical Basis for Proposed Master Curve for Fatigue Crack Growth of Ferritic Steels in High-Pressure Gaseous Hydrogen in ASME Section VIII-3 Code,” (PVP2019-93907) Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, San Antonio, TX, July 14–19, 2019.
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