H-Mat Overview: Metals

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Overall Objectives

- Improve mechanistic understanding of hydrogen-assisted fracture with the goal of identifying high-strength steels (tensile strength >950 MPa) for high-pressure gaseous hydrogen service.
- Clarify the thermodynamic and kinetic role of water vapor on the hydrogen surface interactions with aluminum alloys to define engineering bounds (e.g., gas purity) for the potential use of high-strength aluminum in high-pressure gaseous hydrogen service.
- Develop a mechanistic understanding of hydrogen-induced crack nucleation in metals and a mechanics framework to establish similitude between laboratory testing and infrastructure deployment.
- Identify physical processes of hydrogen embrittlement in austenitic stainless steels to inform manufacturing processes that mitigate the adverse effects of high-pressure gaseous hydrogen environments.

Fiscal Year (FY) 2019 Objectives

- Develop interatomic potential for the Fe-C-H system to enable foundational study of hydrogen interactions in steel.
- Establish experimental and/or theoretical evidence that water vapor contributes to hydrogen-assisted fracture in hydrogen environments.
- Evaluate similitude of crack nucleation for different materials and different laboratory test geometries.
- Establish workflow for integration of experimental and computational study of austenitic stainless steels with sensitivity to the discrete grain structure and strain distribution on the grain scale.

Technical Barriers

The Hydrogen Materials Compatibility Consortium (H-Mat) addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Reliability and Costs of Gaseous Hydrogen Compression
- Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
- Other Fueling Site/Terminal Operation.

Technical Targets

H-Mat is conducting foundational studies of hydrogen-metals interactions and interpreting results in the context of strategies to mitigate (or moderate) hydrogen-assisted fatigue and fracture in engineering systems. While there are no specific DOE structural materials targets, these tasks are structured to provide the technical basis for materials selection that would reduce materials costs and enhance structural reliability of components for high-pressure hydrogen service. H-Mat is cross cutting and has implication across the infrastructure technology space.

FY 2019 Accomplishments

- Developed interatomic potentials for Fe-C-H system and included in Sandia's open-source molecule dynamics software LAMMPS,

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

providing a platform for study of fundamental hydrogen-steel interactions at the atomic scale.

- Completed density functional theory calculations that suggest that hydrogen is more strongly bound to water on aluminum surfaces than to aluminum in the absence of water, suggesting the importance of moisture in hydrogen-assisted fracture.
- Completed strain-based fatigue testing (in collaboration with University of California, Davis) that shows substantial effect of hydrogen on fatigue life, and crack growth that does not correlate with the material's grain structure.
- Developed an experimental and computational workflow to characterize oligocrystal test specimens and generate a digital representation of the test specimens toward the aim of illuminating grain-scale phenomena.

INTRODUCTION

The Hydrogen Materials Compatibility Consortium (H-Mat) addresses the challenges of hydrogen degradation by elucidating the mechanisms of hydrogen-materials interactions with the goal of providing science-based strategies that enable the microstructural design of metallic materials for enhanced resistance to hydrogen-assisted fatigue and fracture. The activities leverage the advanced computational capabilities, unique experimental facilities, and scientific expertise at the national laboratories to establish scientific frameworks to improve materials reliability in hydrogen infrastructure. In particular, computational materials science is exploited to improve materials design of metals and to provide the scientific basis for predictive materials performance tools. These activities are distinguished from previous studies by the innovative approaches to integrate state-of-the-art characterization techniques with computational studies that bridge length scales from the quantum to the continuum. This project addresses foundational scientific questions about materials-hydrogen interactions and applies this information to impact engineering outcomes. The activities include four principal topics:

1. High-strength ferritic steels—improve mechanistic understanding of hydrogen-assisted fracture with the goal of identifying high-strength steels (tensile strength >950 MPa) for high-pressure gaseous hydrogen service

2. High-strength aluminum alloys—clarify the thermodynamic and kinetic role of water vapor on the hydrogen surface interactions with aluminum alloys to define engineering bounds (e.g., gas purity) for the potential use of high-strength aluminum in high-pressure gaseous hydrogen service

3. Crack nucleation—develop a mechanistic understanding of hydrogen-induced crack nucleation in metals and a mechanics framework to establish similitude between laboratory testing and infrastructure deployment

4. Microstructural design of austenitic stainless steels—identify physical processes of hydrogen embrittlement in austenitic stainless steels to inform manufacturing processes that mitigate the adverse effects of high-pressure gaseous hydrogen environments.

APPROACH

There is no universal mechanism of hydrogen degradation in materials as hydrogen-materials interactions depend on the class of alloys. Moreover, hydrogen degradation can be a competition of distinct mechanisms that depend sensitively on details of the microstructure of metals, as well as the environment. The extreme mobility of hydrogen in metals as well as its transparency to most imaging techniques are the primary reasons for this lack of understanding. Consequently, the isolation, observation, and study of the mechanisms of hydrogen-materials interactions is very difficult, and a comprehensive understanding of hydrogen effects on materials has remained elusive. These challenges associated with study of hydrogen degradation cannot be overemphasized as state-of-the-art characterization techniques in high-pressure environments are antithetical to conventional scientific instrumentation (which are often ultra-high vacuum systems) and a significant

challenge for the materials science community. Additionally, the complex nature of engineering materials confounds efforts to develop rigorous understanding of the mechanisms of hydrogen-induced degradation processes. To address these challenges, this program exploits: (1) experimental study of model materials systems to aid interpretation of the measured materials response in hydrogen environments, (2) microstructurally informed modeling of the hydrogen-materials interactions in these model systems, (3) integration of the experimental and computational studies to evolve the sophistication of our understanding of hydrogen interactions with the microstructure and structure/morphology of engineering materials, and (4) development of predictive tools to aid materials design strategies.

There are few obvious solutions for significant advancement in the specification of materials that improve hydrogen resistance within established materials processing technologies. Microstructural design, however, has shown promise for improving performance of metals in hydrogen environments (e.g., grain boundary engineering in metals), but requires improved understanding of the mechanisms of hydrogen-induced degradation. This program, therefore, exploits model materials systems to elucidate degradation mechanisms. These studies will provide a scientific basis for microstructural design of metals, thus enabling materials design strategies that improve materials performance in hydrogen environments. In particular, these materials challenges will be addressed by combined experimental and computational approaches to understand discrete hydrogen-materials interactions and upscale to collective behavior at engineering length scales, thus providing predictive materials performance tools.

RESULTS

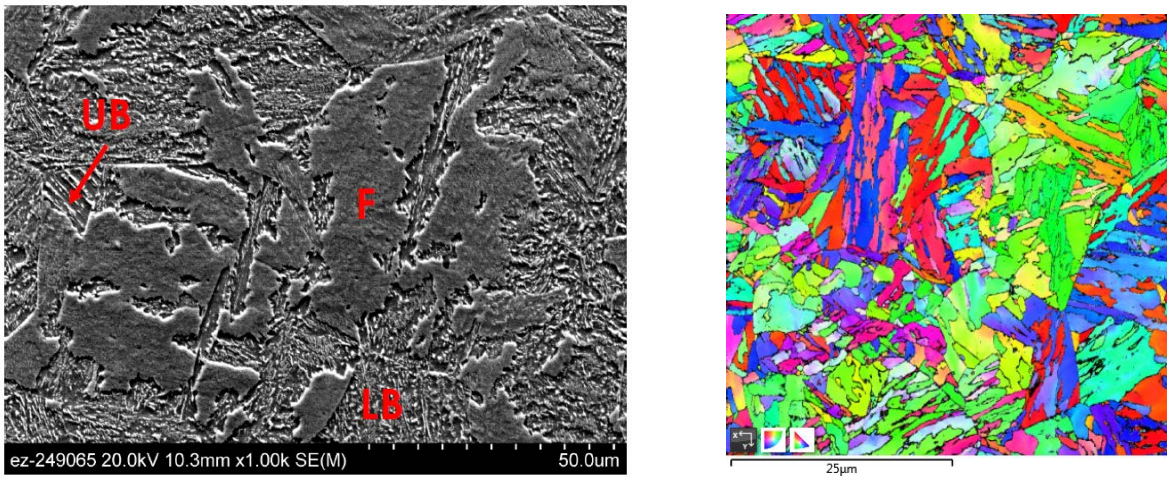
High-Strength Ferritic Steels

High-strength ferritic steels (as defined here by tensile strength >950 MPa) are typically not used in hydrogen service because the fracture resistance is significantly degraded by hydrogen. The Hydrogen Pipeline and Piping Code (ASME B31.12), for example, requires fracture resistance in hydrogen to be greater than 55 MPa $m^{1/2}$ for design basis of pipelines, while high-strength ferritic steels typically display fracture resistance near 20 MPa $m^{1/2}$ in gaseous hydrogen. In contrast, a wide variety of microstructurally distinct, low-strength steels perform similarly in hydrogen. To better understand these observations, we are combining both computational and experimental approaches to the study of high-strength ferritic steels.

To illuminate basic hydrogen-microstructure interactions, molecular dynamics simulations are being implemented. The first step was to develop a Fe-C-H interatomic potential that enables the study of hydrogen in fundamental microstructural units. Based on an extensive literature search, two versions of Fe-C-H ternary bond order potentials have been developed and incorporated in the open-source LAMMPS code for molecular dynamics simulations. Extensive testing of the interatomic potential shows both potentials are suitable for studying hydrogen effects in Fe-C steels because they agree with experimental or ab initio results on (a) cohesive energies, lattice constants, and elastic constants of different phases; (b) diffusion energy barriers, defect trapping energies, interstitial formation energies, and swelling volumes of carbon and hydrogen in face-centered cubic and body-centered iron; (c) the α-γ-δ Fe transition and the Bain path; and (d) the formation of the Fe_3C cementite precipitate. It is worth noting that simulations of the Fe_3C cementite phase are most challenging as potentials do not easily capture compound structures. This development enables the study of Fe-C microstructures involving the Fe_3C cementite precipitates as well as other phases.

In parallel to computational developments, Sandia National Laboratories, Oak Ridge National Laboratory, and Colorado School of Mines have been working collaboratively to develop a moderate-strength bainitic microstructure with a target tensile strength of 1,000 MPa. A higher strength bainitic microstructure (1,300 MPa) displayed fracture resistance in hydrogen comparable to conventional steels with strength of around 1,000 MPa, suggesting that the bainitic microstructure could show superior fracture resistance in hydrogen at lower strength (fracture resistance generally shows an inverse relationship with strength). Researchers at Oak Ridge have systematically studied heat treatments of this Ni-Cr-Mo steel and

established procedures to produce a bainitic microstructure with strength near the target. Colorado School of Mines has also modified the heat treatment of a material from a separate study to achieve the targeted strength with a bainitic microstructure as shown in Figure 1. This material will form the basis for study of hydrogen-assisted fracture at Sandia's Hydrogen Effects on Materials Laboratory and will be complemented by materials heat-treated by Oak Ridge National Laboratory.



(a) (b)

Figure 1. Secondary electron image from scanning electron microscope (a) showing phases in steel from Colorado School of Mines (UB = upper bainite, LB = lower bainite, F = ferrite). The lack of ferrite is evident in the electron backscattered diffraction image (b) of the same steel heat treated to higher strength (nominally 1,000 and 1,300 MPa respectively).

High-Strength Aluminum Alloys

Aluminum alloys are generally considered resistant to high-pressure gaseous hydrogen. High-strength aluminum alloys, however, are susceptible to stress corrosion cracking in humid environments. Consequently, moisture in hydrogen is a potential concern for this class of materials. There are several studies showing that a broad range of aluminum alloys are not degraded in high-pressure gaseous hydrogen. However, an active debate remains about the suitability of aluminum alloys for hydrogen service. One argument is that small concentrations of water (on the order of 5 ppm) in high-pressure hydrogen represent a sufficient partial pressure of water to induce stress corrosion cracking in susceptible alloys. Another hypothesis is that adsorbed water on aluminum surfaces (since they are hydrophilic) can catalyze the uptake of hydrogen into aluminum, essentially defeating the kinetic barrier to hydrogen ingress into aluminum and inducing hydrogen-assisted fracture. The goal of this activity is to provide a clear scientific description of the role of water-hydrogen-aluminum interactions and demonstrate the engineering implication of these interactions.

To probe the fundamental surface interactions, density functional theory is being employed to describe the energetics of surface structures at the atomistic scale. These studies have systematically explored the interaction of hydrogen on bare aluminum surfaces, the effect of adsorbed water on the energetics of hydrogen surface interactions, the role of an oxygen chemisorbed overlayer on hydrogen surface interactions, and the combined influence of the oxygen and water on the hydrogen surface interaction. Figure 2 shows the lack of hydrogen binding to bare aluminum and the stabilization of hydrogen on the aluminum surface through the formation of the hydronium ion. An oxygen overlayer enhances the binding of hydrogen to the surface, but the energy landscape remains insufficient to dissociate the diatomic hydrogen molecule.

In complementary work at the component scale, fracture specimens of aluminum are being exposed to high-pressure gaseous hydrogen doped with relatively high levels of moisture. The constant displacement fracture configuration is being used to explore potential synergy of moisture in gaseous hydrogen, which

is a common configuration for stress corrosion cracking. With this method, cracking is determined ex situ after some predetermined exposure time. These tests require several weeks of static exposure to ensure sufficient time is given to transition kinetic barriers. Tests are underway at the time of writing, but indications are that moisture has not initiated cracking in 100 MPa "wet" hydrogen. After 1,000 hours of exposure, the test samples (consisting of three high-strength aluminum alloys) will be removed and the specimens will be interrogated for environmental-assisted cracking.

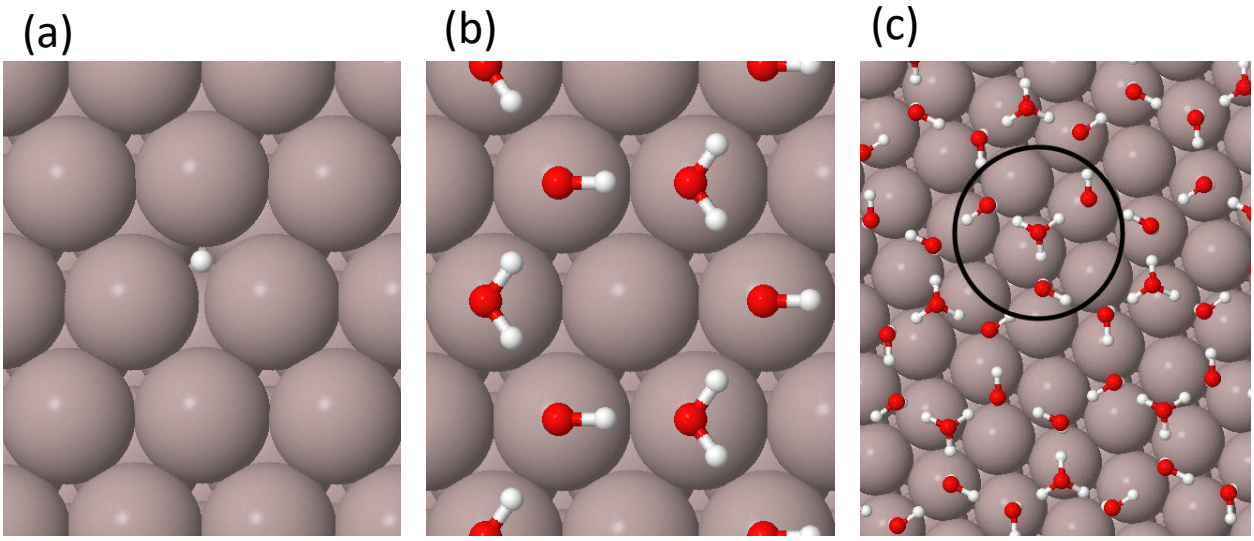


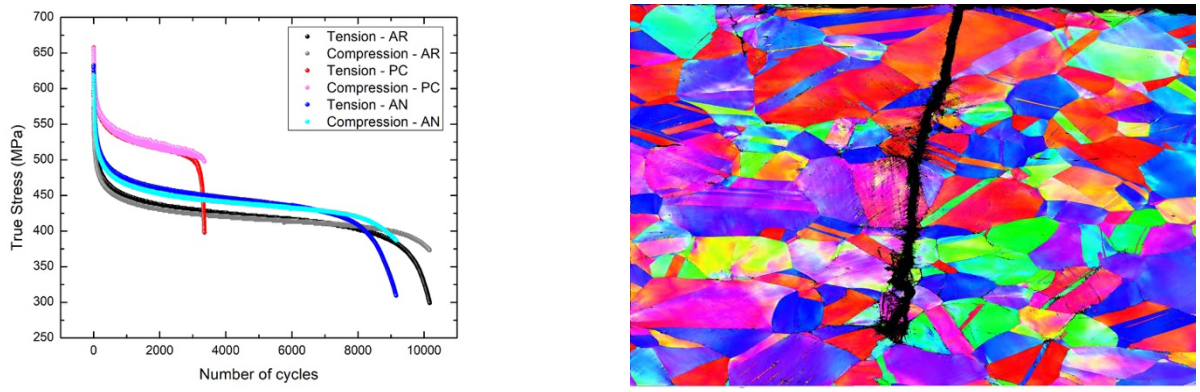
Figure 2. (a) A hydrogen adatom on Al(111). (b) Our hypothesized structure of a water monolayer. (c) The result of adding H atoms to this water monolayer. The circled structure is a hydronium ion.

Crack Nucleation

Crack nucleation is a difficult phenomenon to characterize and generalize. Previous work suggests that hydrogen effects on fatigue crack nucleation at stress concentrations in austenitic stainless steels are similar, at least in the high-cycle regime. Moreover, the notched test geometry was exploited to show that quantitative information on both crack nucleation and crack propagation could be extracted from the same test specimen. These observations suggest an opportunity to develop a framework to quantify crack nucleation and potentially take credit in engineering design for the time to nucleate a crack. The study of crack nucleation has two main thrusts: (1) characterization of the mechanics of engineering test specimens to develop generalized engineering parameters that characterize crack nucleation (such as relative stress), and (2) characterization of damage at microstructural length scales to inform the mechanisms of damage accumulation. The latter task is intended to aid the development of higher fidelity parameters to characterize crack nucleation and the transition to crack propagation, which could ultimately be used in design assessments.

Appropriate constitutive models that capture the cyclic plastic response of the material are a necessary element of the mechanics characterization. Through an informal collaboration with the University of California, Davis, the cyclic response in fully reversed, strain-controlled fatigue tests (of smooth round specimens) is demonstrating the character of plastic deformation in 316L austenitic stainless steel, providing inputs to the constitutive model, and elucidating features of crack initiation under fatigue loading. Strain-controlled tests in situ in gaseous hydrogen are not currently possible, thus thermal hydrogen precharging is used as a surrogate for tests in gaseous hydrogen. While the implications of this testing are still emerging, the fatigue tests show substantial effects of hydrogen on fatigue life, while postmortem analysis shows seemingly random crack paths (i.e., cracking is not biased to a particular microstructural feature) (Figure 3). To aid characterization of microstructural damage, techniques to instrument the middle-tension specimen for crack nucleation are being developed. This specimen has the

advantage that it is flat, which (if tests can be interrupted early in the crack nucleation process) enables detailed microstructural interrogation at the early stage of fatigue crack nucleation. Preliminary results are consistent with postmortem evaluation. While still in the early stages of study, collectively these observations suggest that fatigue damage is stochastic and not governed by microstructural details, which supports the hypothesis that a generalized framework for quantification of crack nucleation can be based on mechanics.



(a) (b)

Figure 3. Stress response curves (a) for 316L stainless steel (strain amplitude of 0.2%) showing uniformity of tension-compression cycles for the as-received material (AR) and material thermally treated in air (AN) compared to the substantially lower fatigue life of hydrogen-precharged material (PC). Electron backscattered diffraction inverse pole figure (b) showing transgranular fatigue crack propagation in relation to the microstructure.

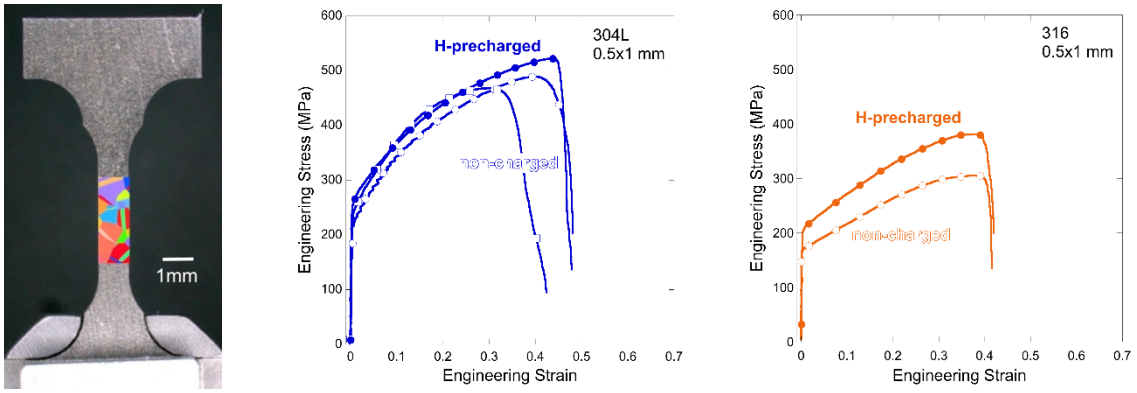
Microstructural Design of Austenitic Stainless Steels

To study the effects of boundaries on hydrogen-mediated plasticity and hydrogen-assisted fracture, a test method has been developed to produce specimens with a relatively small ensemble of grains (Figure 4). The small number of grains aids observation of behavior on length scales relevant to discrete grain behaviors, which are believed to be important in hydrogen-assisted fracture. Additionally, a computational framework for simulating deformation locally at the grain scale (generally called crystal plasticity) complements the experimental capability and provides a platform for parametric study. To adequately validate the model and verify trends, the experimental and computational activities are integrated through testing and simulating identical configurations of grains. Therefore, grain scale phenomena can be characterized experimentally as well as accessed digitally. To achieve complementary experimental and computational test specimens, techniques have been developed to produce and characterize the grain structure of individual experimental test specimens and reproduce the structures digitally.

In one method, the faces of the experimental specimen are mapped by electron backscattered diffraction, providing the crystallographic orientation of each pixel in a surface scan. Sandia's open-source SPPARKS software is used with surface boundary conditions to evolve physics-based synthetic grain morphology in the interior of the test piece from the surface boundary condition. Newly developed computational algorithms are necessary to translate the experimental diffraction output to computationally accessible input for the grain-architecture simulation (see SAND2019-11720C). While the specimen preparation techniques are continuously being improved, specimen-preparation techniques have evolved sufficiently that the crystallography (i.e., grain structure) of the surfaces of 304L and 316L austenitic stainless steel test specimens have been elucidated adequately for digital reconstruction and mechanical simulation.

The small size of the specimens (<1 mm x 1 mm cross section) preclude testing in high-pressure gaseous hydrogen. Therefore, thermal hydrogen precharging is used to produce a uniform high concentration of hydrogen prior to experimental testing. Preliminary results demonstrate the expected variability of the stress-strain response of these materials due to the highly anisotropic behavior of the austenitic stainless

steel lattice (crystallography) and the small number of grains in the test specimen (Figure 4). In other words, rather than producing a uniform and reproducible response as observed in polycrystalline specimens, in contrast, the stress-strain response of oligocrystals (specimens with just a "few" grains) is dominated by a small population of the grains in the specimen; therefore each specimen is unique. These initial tests will be used to tune the crystal plasticity model for exploration of the role of hydrogen in localizing deformation and evolving fracture in austenitic stainless steels. We hypothesize that certain microstructural configurations are more susceptible to hydrogen-assisted fracture and manufacturing techniques can be optimized to control these configurations.



(a) (b) (c)

Figure 4. Image of tensile specimen (a) with the grain structure map superimposed. Stress-strain response of 304L (b) and 316 (c) oligocrystal test specimens in the non-charged and hydrogen-precharged condition.

CONCLUSIONS AND UPCOMING ACTIVITIES

High-strength ferritic steels—Preliminary study supports the notion that bainitic microstructures have potential for greater fracture resistance in hydrogen than, for example, high-strength martensitic phases. Model microstructures have been developed with bainitic microstructure and relatively low strength (~1,000 MPa tensile strength). Test specimens have been prepared to evaluate the model microstructure, while a more systematic study of heat treatments to produce materials is being concluded. In parallel, an interatomic potential for the Fe-C-H system has been implemented in LAMMPS and is being exploited in fundamental studies of hydrogen-microstructure interactions aimed at providing direction for microstructural development.

High-strength aluminum alloys—To date, the scientific evidence suggests that moisture should not influence the response of aluminum alloys in hydrogen (although stress corrosion cracking may still be an issue from the external air environment). However, more work is necessary to confirm this evidence. For example, a non-cracking response is not a definitive conclusion for the experimental evaluation of hydrogen-assisted fracture in aluminum alloys in the presence of "wet" hydrogen, since the test method employs an air-passivated crack, which may act as a strong kinetic barrier to hydrogen uptake. In practice, a defect can evolve during service (e.g., fatigue crack), creating fresh metal surface that is not passivated by exposure to air and may, thus, be susceptible to hydrogen ingress. Two follow-on tests are being considered: (1) evaluate specimens in the same "wet" environment under dynamic loading (i.e., a fatigue test); and (2) identify materials and/or heat treatments that are known to be strongly susceptible to stress corrosion cracking. The next step in the computational studies is to evaluate the surface interactions of hydrogen and water on alumina, which is more representative of actual aluminum surfaces than the chemisorbed oxygen overlayers.

Crack nucleation—Observations from fatigue experiments and constitutive models suggest that crack nucleation can be captured by generic mechanics models. Modeling, in combination with testing, of multiple geometries (circumferentially notched, middle tension, hole-drilled tube) is being pursued in an effort to test the hypothesis that crack nucleation can be generalized. High-resolution interrogation of fatigue damage along with molecular dynamics simulation are intended to elucidate mechanisms of damage accumulation.

Microstructural design of austenitic stainless steels—A workflow has been developed to explore hydrogen effects on tensile behavior of oligocrystal specimens of austenitic stainless steels. In addition to exploiting crystal plasticity models for elucidating the process of hydrogen-assisted fracture in austenitic stainless steels, state-of-the-art characterization tools are being pursued to improve the fidelity of our digital representation of the test specimens. In particular, the crystallographic 3-D architecture of the test specimens is being mapped by X-ray computed tomography on Sandia state-of-the-art hardware. This is an emerging technology that can complement beamline experiments at synchrotron sources.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. C. San Marchi and K.L. Simmons, "H-Mat Overview: Metals, Science-Based Advancement of Materials for Hydrogen Technologies," presentation for Joint Hydrogen Delivery, Codes and Standards Storage Tech Team, March 12, 2019, SAND2019-2740C.
2. R. Sills, "Re-Examining HELP: Mechanism, Hypothesis, or None-of-the-Above?" (PVP2019-93614), ASME Pressure Vessel and Piping (PVP) Division Conference, San Antonio, TX, July 2019, SAND2019-8072C.
3. X.W. Zhou, M. Foster, J.A. Ronevich, and C. San Marchi, "Technology Maturity of Molecular Dynamics Studies of Hydrogen Embrittlement in Fe-C Based Steels," presentation at Materials Science and Technology (MS&T) 2019 Annual Meeting, September 2019, SAND2019-8194C.
4. T.R. Smith, C. Alleman, and C. San Marchi, "Investigating Hydrogen-Assisted Deformation of Oligocrystalline Austenitic Stainless Steel," presentation at Materials Science and Technology (MS&T) 2019 Annual Meeting, September 2019, SAND2019-11720C.
5. C. San Marchi, P.J. Gibbs, K.A. Nibur, G. Bergel, and J.W. Foulk III, "Assessing Hydrogen-Assisted Fatigue Crack Initiation and Propagation in Austenitic Stainless Steels," presentation at Materials Science and Technology (MS&T) 2019 Annual Meeting, September 2019, SAND2019-11725C.
6. D. Oliveira, J. Gibeling, and C. San Marchi, "Low-Cycle Fatigue Behavior of Strain-Hardened 316L Stainless Steel for Hydrogen Fuel Cell Vehicles," presentation at Materials Science and Technology (MS&T) 2019 Annual Meeting, September 2019.