IV.D.1 Innovative Development, Selection, and Testing to Reduce Cost and Weight of Materials for BOP Components

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Subcontractor

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Overall Objectives

- Reduce weight of structural materials for balance of plants (BOP) components by 50%
- Reduce cost of structural materials for BOP components by 35%
- Expand the scope of materials of construction for BOP components
- Identify simplified testing procedures to enable materials qualification

Fiscal Year (FY) 2015 Objectives

- Quantify fatigue life of baseline Type 316L austenitic stainless steel with internal hydrogen
- Develop framework to assess the stacking fault energy (SFE) of austenitic stainless steels with compositions that are consistent with technologically relevant alloys (e.g., Fe-(15-25Cr)-(2-20)Ni-(2-20)Mn)
- Establish a robust computational method for compositional and configurational variations in multi-component alloys (i.e., quantify the effects of randomly distributed elements on results of simulation with a relatively small number of atoms)
- Compare the fatigue response of baseline stainless steel in different environments (internal and external hydrogen) to establish the dependence on environment, including pressure

Technical Barriers

This project addresses the following technical barriers from Hydrogen Storage section of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(H) Balance of Plant (BOP) Components

Technical Targets

No specific technical targets have been set. This project is a basic study of materials of construction for BOP with the goals of identifying lower cost alternatives to the baseline of annealed Type 316L that can be implemented in lighter weight designs (i.e., high strength materials). The project targets are:

- Reduce weight of structural materials for BOP components by 50%
- Reduce cost of structural materials for BOP components by 35%

FY 2015 Accomplishments

- Fatigue life data for strain-hardened Type 316L stainless steel have been compared in gaseous (external) hydrogen at moderate-pressure (10 MPa), high-pressure (103 MPa) and with internal hydrogen
- For baseline material, the less expensive testing with internal hydrogen represents fatigue performance measured in moderate-pressure and high-pressure external hydrogen
- Simulation framework for predicting stacking fault energy has been demonstrated for pure nickel

INTRODUCTION

The primary objective of this effort is to identify alloys to replace Type 316/316L in hydrogen service for BOP applications onboard fuel cell electric vehicles (FCEVs).

Type 316/316L austenitic stainless steels are used extensively in hydrogen systems for their resistance to hydrogen embrittlement, which is attributed to the relatively high nickel content of Type 316/316L alloys. Nickel content, however, drives the cost of austenitic stainless steels, thus Type 316/316L alloys impose a cost premium compared to similar alloys with lower nickel content. Since the cost of BOP components is a large fraction of the cost of hydrogen fuel systems (even dominating the cost at low production volumes [1]), alternative materials are desired. In addition, Type 316/316L alloys are relatively low strength, thus high-pressure components tend to be heavy to accommodate the stresses associated with the pressure loads. Higher strength materials will reduce weight of the components (an added benefit for onboard components) and contribute to lower cost since less material is needed. However, engineering data to justify selection of lower cost and higher strength alloys for high-pressure hydrogen service are currently unavailable. Moreover, alloy design could enable low cost solutions to the specific needs of onboard hydrogen storage.

APPROACH

The objective of this project is addressed from two perspectives: (1) experimental evaluation of commercial alloys, (2) computational materials discovery of new alloys. In the first case, fatigue properties in hydrogen environments will be evaluated for low cost, high strength alloys and compared to the benchmark of annealed Type 316/316L. The use of fatigue stress as a performance based metric will be used for comparison with the goal of achieving 35% reduction of cost and 50% reduction of weight. The experimental activity does not seek to identify materials that are immune to hydrogen embrittlement. Rather, a comprehensive test program seeks appropriate trade-offs between materials cost and performance, such that hydrogen embrittlement can be effectively managed in design. In order to provide performance data, testing must be conducted at temperature consistent the temperature of maximum embrittlement for these alloys, which is reported to be in the range of 200–220 K from tensile testing; the effect of hydrogen on fatigue as a function of temperature has not been reported. The tasks in this project are organized to provide a methodical approach to effectively reach the proposed targets. An additional goal of the experimental activity is to demonstrate a straightforward, simplified methodology by which materials may be qualified for safe hydrogen service, including the use of internal hydrogen (saturation of the material with hydrogen by thermal precharging) as a robust substitute for testing in gaseous hydrogen.

The goal of the computational discovery activity, like the experimental activity, is to identify low-Ni content (and thus lower cost) stainless steel alloys to be used in BOP components that are compatible for hydrogen service. To achieve this goal from a computational perspective, a quantum based materials exploration and design (QMED) framework is being developed—one that combines sophisticated optimization and uncertainty quantification with ab initio calculations. This framework will be used to create a comprehensive database and materials design relations that identify stainless steel alloys that optimize stacking fault energy (indicative of hydrogen embrittlement resistance) with reduced Ni content. This effort represents a new initiative in the FCTO research portfolio to use computational materials science coupled with high performance computing to identify and evaluate low cost stainless steels that are tailored for hydrogen embrittlement resistance. This innovative approach will provide the DOE and United States industry a framework and computational tools to efficiently and effectively explore the design space for next generation materials used in fuel cell technologies.

RESULTS

Experimental Evaluation of Commercial Alloys

Fatigue life measurements of strain hardened Type 316L have been performed in gaseous hydrogen at moderate pressure of 10 MPa (1.5 ksi) by Hy-Performance Materials Testing and at high pressure of 103 MPa (15 ksi) by Sandia National Laboratories. The fatigue-life data for these two conditions are shown in Figure 1 along with data for the as-received (AR) material in air (AR, reference condition) and material with internal hydrogen (hydrogen precharged [PC]). Also shown in Figure 1 is a power-law fit to the data measured on the AR material (dashed black line). The relative variability in the data is represented by 95% confidence limits on the fit, shown by the red dashed lines in this figure.

The presence of external hydrogen reduces the fatigue life of strain-hardened Type 316L. The measured fatigue life in external hydrogen at pressure of 10 MPa and 103 MPa appear to overlay (Figure 1). This observation suggests that tests may not need to be performed at high pressure. While testing in external hydrogen indicated a clear decrease in performance for the strain-hardened Type 316L, testing the steel with internal hydrogen (PC) had no measurable effect on the fatigue life (Figure 1); since the stress-life data of the hydrogen-precharged Type 316L are within the confidence limits of the fit to the AR data. However, it is important to consider the 10–15% increase in yield strength typically observed in stainless steels with internal hydrogen. Figure 2 shows the same data with the fatigue stress amplitude normalized by the yield strength. When normalized, the fatigue-life data for internal hydrogen (PC) converge with the data for external hydrogen (both pressures). This is an important finding since it suggests that internal hydrogen can be a substitute for testing in high-pressure external hydrogen. More data is needed to determine if these observations can be extended to low temperature and with other materials (such as XM-11). Preliminary data (not shown here) suggest that

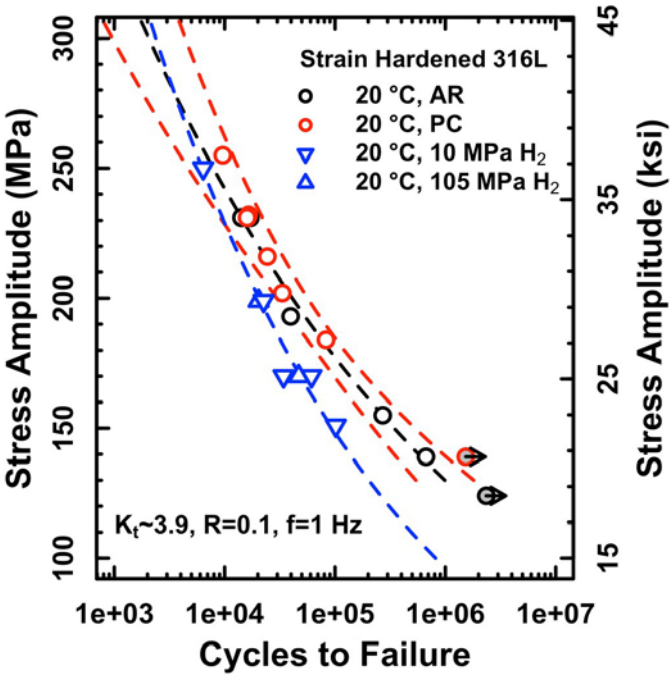

FIGURE 1. Stress-life fatigue curves of high-strength Type 316L austenitic stainless steel at 20°C (293 K), notched specimens ($K_t \approx 3.9$), loaded in tension-tension (R = 0.1): AR material, hydrogen-precharged condition, as well as in external gaseous hydrogen at pressure of 10 MPa and 103 MPa. The lines on the plots represent power-law fit to the data for the AR condition (black) and tests in external hydrogen (blue). The red curves represent 95% confidence limits for the AR data. Shaded symbol with arrows represent samples that did not fail.

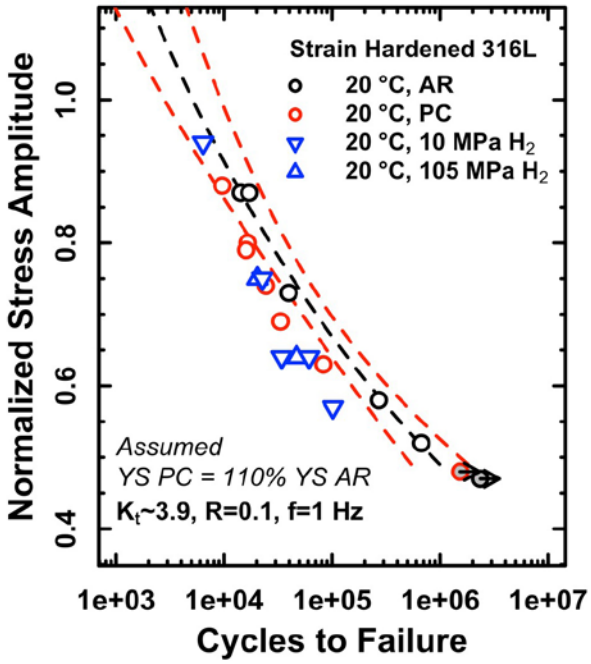

FIGURE 2. Stress-life curves normalized by yield strength (same data as Figure 1)

the same trends can be applied to strain-hardened Type 316L at low temperature and to Type XM-11 at room temperature. Testing is underway to substantiate these preliminary data and observations.

Computational Materials Discovery

The literature is unclear on the correlation between intrinsic properties such as SFE and the effects of hydrogen. As low SFE is known to correlate with propensity for both planar slip of dislocations (as opposed to cross-slip), as well as martensite formation, this suggests that hydrogen's effect on SFE might preferentially favor specific deformation mechanisms and mechanical behavior that imply resistance to the effects of hydrogen.

The SFE for ternary stainless steel alloys using large supercells (450 atoms) have been calculated from first principles (within density functional theory). We considered a perfect lattice and a lattice with three stacking faults. The initial composition considered was 66% Fe, 14% Cr, and 20% Ni. No temperature effects were included and the paramagnetic phase (that sets in experimentally above the transition temperature) was constrained by imposing zero total magnetic moment. The initial spin configuration was modeled by a random distribution of local magnetic moments on the Fe sublattice. Two different exchange-correlation functionals, GGA and GGA+U have been considered. In both cases the convergence of the total energy is very slow, taking thousands of iterations for each spin configuration and resulting in several days of computation time using several hundred processors. Furthermore, variations in initial spin configuration lead to different converged states. Within GGA+U, the SFE of the Fe-Cr-Ni alloy was found to range from 150 mJ/m^2 to 500 mJ/m^2 depending on the spin configuration. An alternative, indirect approach is also being pursued to calculate SFE using smaller supercells within the axial interaction model (used by Vitos, et al. [2,3]). Within this model, SFE can be estimated using calculated energies from hexagonal close-packing (hcp), double hcp and face-centered cubic lattice structures.

We have refined our sampling approach to assess the influence of atom configuration (for a given target composition) on SFE. We changed our approach from a space-filling approach based on a location-level view (i.e., determining the element that would populate each specific site) to one that employs perturbations that preserve sample properties and has a configuration-level view with respect to each element. For example, if the material composition is 66% Fe, 23% Cr, 11% Ni, we enumerate all of the possible Cr location combinations and all of the possible Ni location combinations. We then sample various Cr and Ni combinations and fill in the remaining locations with Fe. Testing is still underway, but preliminary results indicate that we can maintain space-filling properties, meet target

composition, and reduce the occurrence of duplicates to a manageable level.

To verify the predictive capability, SFE of commercial alloys and experimental alloys is being measured. SFE is very difficult to measure; high fidelity measurements require advanced high resolution imaging such as transmission electron microscopy (TEM). Specimens of annealed Type XM-11 austenitic stainless steels and experimental high manganese-aluminum austenitic stainless steels are being evaluated. Our TEM observations of the Mn-Al stainless alloy shows deformation structures characteristic of planar slip, although the alloy was designed to mitigate planar slip. Systemic diffraction contrast imaging and analyses are being used to glean information concerning the defect arrangements and their relationship with respect to other features in the microstructure. Our goal is to determine whether the planar slip in this material is due to low SFE, second phase particles, or other aspects of the microstructure. Diffraction contrast images of dislocations of Type XM-11 commercial alloy and the experimental Mn-Al stainless alloy are provided in Figure 3.

CONCLUSIONS AND FUTURE DIRECTIONS

- Testing of the baseline Type 316L shows that consistent fatigue results can be extracted from testing with internal and external hydrogen environments; additionally, for external hydrogen, fatigue life testing appears insensitive to pressure in the range of 10 MPa to 100 MPa
- Test methods must be verified at low temperature and for alloys that display greater effects of hydrogen
  - Preliminary results at low temperature are in qualitative agreement with tests at room temperature for Type 316L
  - Preliminary results from Type XM-11 suggest the test method can be applied to alloys that are more susceptible to hydrogen, but lower cost
- Two commercial, technologically relevant alloys have been selected for fatigue evaluation: Type XM-11 and Nitronic 60
- The computational framework for predicting SFE is being optimized to enhance the efficiency of evaluating commercial austenitic stainless steels and technologically relevant experimental alloys

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. C. San Marchi, Certificate of Recognition for Technical Committee Service, Materials and Fabrication, American Society of Mechanical Engineers, Pressure Vessels and Piping Division, 2015, presented at the ASME 2015 Pressure Vessels & Piping Division Conference, Boston, MA, 22 July 2015.

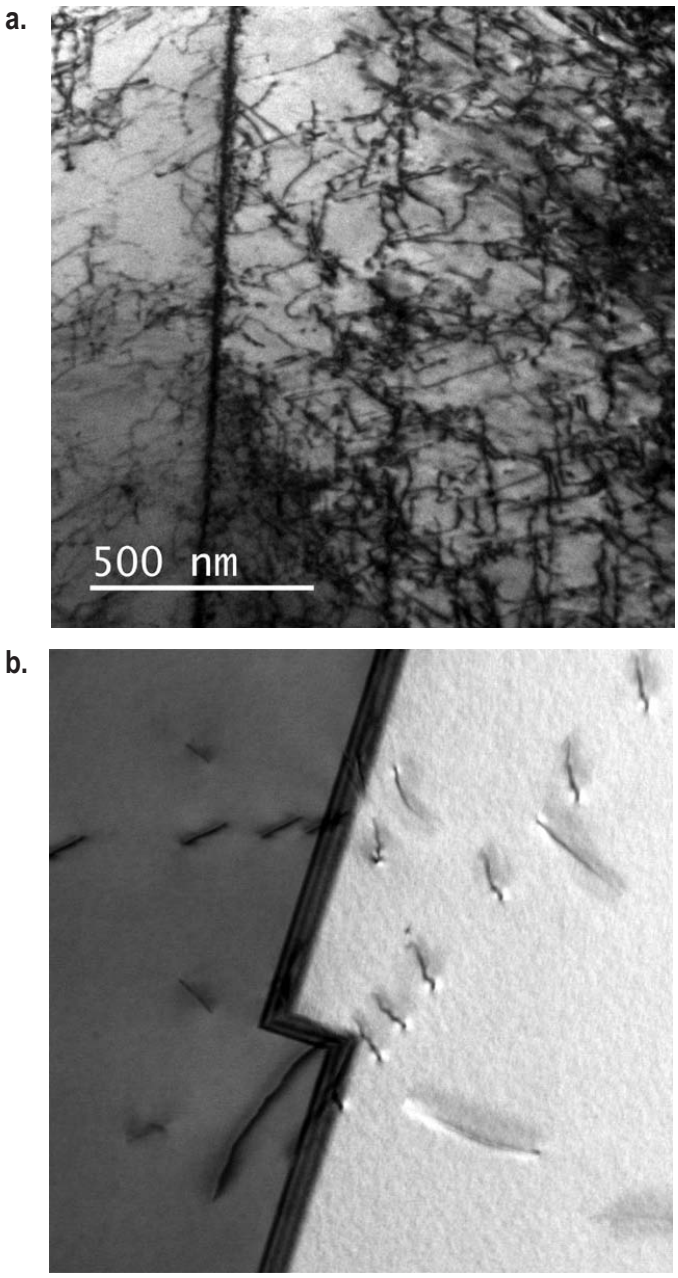

FIGURE 3. Diffraction contract images of dislocations in (a) experimental Mn-Al austenitic stainless steel, and (b) commercial Type XM-11 austenitic stainless steel

FY 2015 PUBLICATIONS/PRESENTATIONS

1. C. San Marchi, J.A. Zimmerman, K. Thuermer, X. Tang, S. Kernion, K.A. Nibur, "Stress-based fatigue performance of austenitic stainless steel in hydrogen environments," (PVP2015-45421), *Proceedings of the ASME 2015 Pressure Vessels & Piping Division Conference*, Boston MA, 19-23 July 2015.

2. C. San Marchi (presenter), "Hydrogen Energy Research at Sandia," (SAND2014-19188 PE), presented at SAE H_2 Compatibility Workshop, 9 March 2015.

3. C. San Marchi (presenter), "Innovative Development, Selection and Testing of Materials to Reduce Cost and Weight of BOP Components," (SAND2015-1912 O), in-person presentation at Swagelok Company, 11 March 2015.

REFERENCES

1. DOE Fuel Cell Technologies Office Record # 13010.

2. L. Vitos, J-O. Nilsson, B. Johansson. Acta Materialia 54 (2006) 3821–3826.

3. L. Vitos, P.A. Korzhavyi, B. Johansson. Phys Rev Lett 96 (2006) 117210.