IV.D.8 Innovative Development, Selection and Testing to Reduce Cost and Weight of Materials for BOP Components

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Subcontractor:
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Project Start Date: July 15, 2014
Project End Date: September 30, 2017

Overall Objectives

- Reduce weight of structural materials for balance of plant (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) 2016 Objectives

- Quantify fatigue life of commercially available low-nickel alloy with/without internal hydrogen at near-room and sub-ambient temperatures.
- Establish correlations of stacking fault energy (SFE) with performance metrics (e.g., tensile strength, ductility) known from project experiments and literature.
- Estimate SFEs for Fe-Cr-Ni-based and stainless steel alloys of interest and validate estimates against experimental measurements and literature values.
- Quantify cost and weight savings based on maximum allowable stress in the presence of hydrogen.

Technical Barriers

This project addresses the following technical barriers from Hydrogen Storage section of the Fuel Cell Technologies Office 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 2016 Accomplishments

- Notched stresslife fatigue data have been collected for XM-11 (21Cr6Ni9Mn) austenitic stainless steel at room and low (50°C) temperature with and without internal hydrogen.
- Normalization of the maximum cyclic stresses by the yield strength collapses hydrogen-assisted fatigue life data to a master curve, enabling extrapolation of the effects of both precharging and temperature on intrinsic fatigue performance in high-pressure hydrogen.
- Analysis of the available scientific literature reveals a general trend between stacking fault energy and reduction of area (i.e., tensile ductility) for service in hydrogen. Data also shows that this correlation persists with Mn-stabilized steels.
- Developed an atomic-level approach to calculate SFE including contributions due to magnetic entropy, which are significant for Fe-Cr-Ni alloys. This approach predicts a value of 35.4 mJ/m^2 for an alloy of approximate composition $Fe_{66}Cr_{14}Ni_{20}$, in close agreement to available literature.
- Quantified SFE for 316L stainless steel to be ~60–100 mJ/m^2 (a range consistent with the scientific literature) using transmission electron microscopy. Predicted a lower limit of 63 mJ/m^2 for the SFE of a low-Ni, high-Mn stainless steel alloy.

- Developed computational approach for alloy exploration based on optimizing SFE.

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INTRODUCTION

The primary objective of this effort is to identify alloys to replace Type 316/316L in hydrogen service for balance of plant (BOP) applications onboard fuel cell electric vehicles. 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 and (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 test program seeks appropriate trade-offs between materials cost and performance, such that hydrogen embrittlement can be effectively managed in design. This performance includes low temperature performance associated with refueling protocols at -40°C; the effect of hydrogen on fatigue as a function of temperature has not been previously reported. 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 framework is being developed that combines sophisticated optimization and uncertainty quantification with ab initio calculations. Our objective is to use this framework 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 DOE Fuel Cell Technologies Office 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 U.S. industry with 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

Using the method established during the first year of the project, fatigue life measurements were made for a low-Ni stainless steel alloy, XM-11 (21Cr6Ni9Mn). Overall, the observed life at a given stress level was observed to be the same or slightly better than annealed (the baseline material for this study) or strainhardened 316L. When tested at 20°C, this material demonstrates similar stress-life characteristics for both its as-received (AR) condition and H-precharged condition (PC). In contrast, the fatigue life when tested in 103 MPa external gaseous hydrogen was found to be noticeably less than the AR condition. Differences between the PC and external hydrogen testing could be attributed to the increase in yield strength observed to occur from the H-precharging process. Accounting for this increase aligns the results from PC specimens with those from testing in external hydrogen, with both data sets with hydrogen clearly occupying a single band below the average life of the AR condition, as shown in Figure 1. This suggests that H-precharging provides a method to efficiently probe the H-assisted fatigue performance of austenitic stainless steels.

Testing of XM-11 was also performed at a temperature of -50°C. Test results show a longer fatigue life at low temperature compared to room temperature for equivalent test conditions. As with the effect of H-precharging on fatigue at room temperature, normalization of the fatigue stress with yield strength collapses the fatigue life curves to a master curve for both temperatures with and without internal hydrogen, also shown in Figure 1.

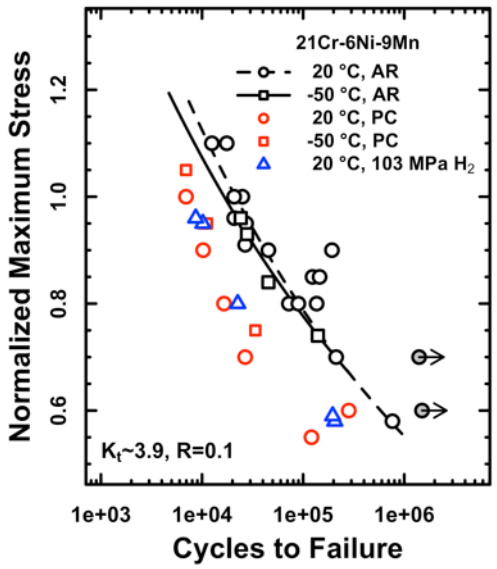
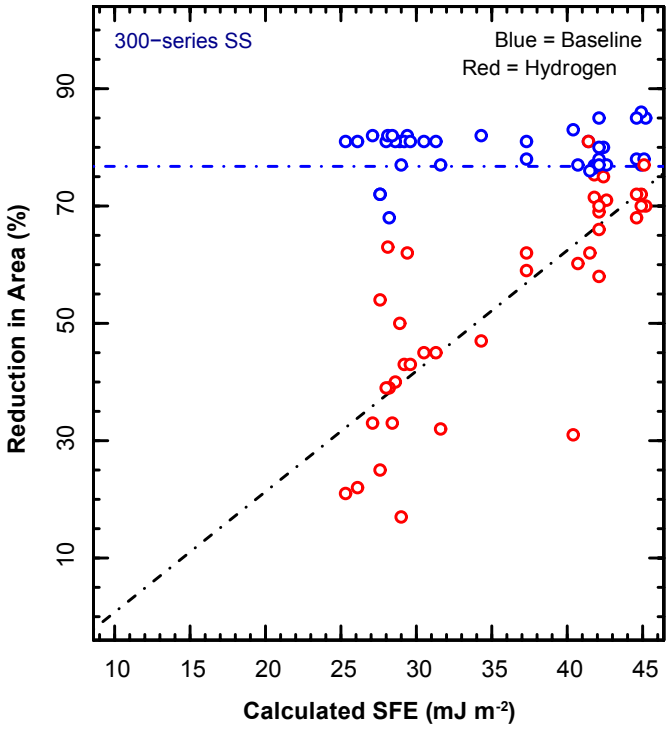


FIGURE 1. Tensiontension stresslife fatigue curves for notched specimens plotted as a function of the maximum imposed stress normalized by the yield strength for 21Cr6Ni9Mn austenitic stainless steel for the tested conditions. The lines on the plots represent fits to the AR data at room temperature (dashed) and at temperature of -50°C (solid). Shaded symbols with arrows represent test conditions that did not result in failure.



SS – Stainless steel

FIGURE 2. Reduction of area for various 300-series stainless steels from literature plotted as a function of calculated stacking fault energy for the alloy

Correlating Stacking Fault Energy to Hydrogen Degradation

To quantify the correspondence between stacking fault energy (SFE) and resistance to hydrogen degradation, we performed a systematic evaluation of the existing literature. Use of a thermodynamic model by Curtze et al. [2] that estimates SFE based on composition enabled consideration of a larger set of literature results than just those in which SFE was measured. Considering only 300-series stainless steels, several mechanical properties, including yield strength, were observed to have no correlation with SFE. However, the reduction of area in the presence of hydrogen shows a general decreasing trend with decreasing SFE value, as shown in Figure 2. The substantial decrease in reduction of area in hydrogen at low SFE with no corresponding variation in yield strength-based metrics suggests that hydrogen degradation in austenitic stainless steels is dependent on plastic strain generated during tensile testing. A similar trend has been established for Mnstabilized austenitic stainless steels, suggesting that Mn may be an effective replacement for Ni when considering alloys for hydrogen service.

Computational Materials Discovery

We calculate an alloy's SFE from a combination of cohesive energies for the face-centered cubic (fcc), hexagonal close-packed (hcp) and double hcp (dhcp) crystal structures. To include the effect of temperature, we assume the material to be in a paramagnetic state (i.e., net zero magnetic moment) and determine the average value of individual atomic magnetic moments based on statistical mechanics and the system's temperature. The computational expense associated with this approach is quite considerable as a total of 70,656 processors are used for approximately 8 hr to obtain the magnetic/spin contribution to the SFE. Figure 3 shows a distribution of average magnetic/spin moments determined for a $Fe_{66}Cr_{14}Ni_{20}$ alloy. Using this distribution, we estimate the magnetic/spin entropy to be 9.5 mJ/m^2 at 300 K, a value in close agreement with published results [3]. We combine this entropy contribution with the enthalpy corresponding to a configuration of very similar composition for a total SFE of 35.4 mJ/m^2. Unfortunately, upon examining other alloy compositions we determined that the initial electron spin configuration can significantly impact the enthalpy calculated for the system. It is unclear whether this issue can be addressed without drastically increasing the cost of these calculations.

We have developed a computational approach to enable automated exploration of the material composition space (1) to explore and understand tradeoffs with regard to composition effects on SFE and (2) to identify compositions that maximize SFE values. The software infrastructure consists of a combination of tools for model exploration, tools for data analysis and visualization, our own implementation

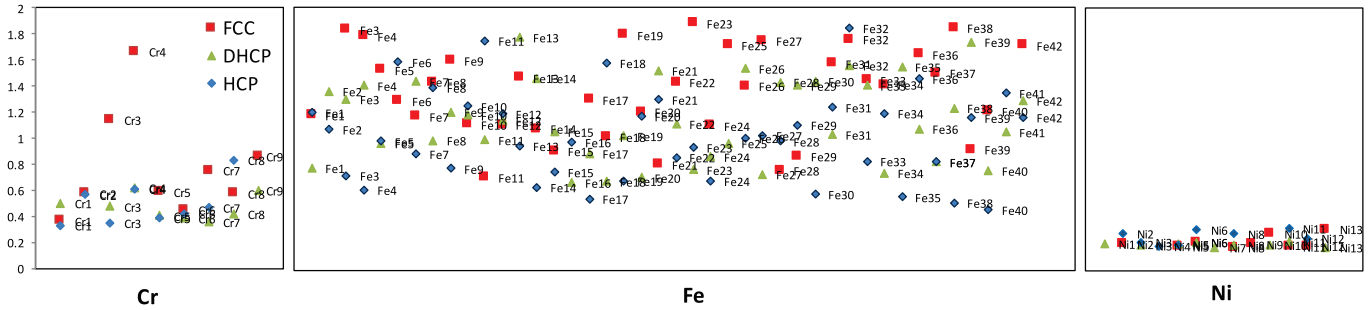


FIGURE 3. Comparison of average magnetic moments of all atoms within a 64-atom system between different structural phases, fcc, dhcp and hcp, at a temperature of 300 K

of the thermodynamic model, and code to enable interfacing between all of these pieces.

Transmission Electron Microscopy Measurements of Stacking Fault Energy

We have used transmission electron microscopy to investigate dislocation structures in stainless steel alloys, and to measure the SFE in order to validate the predictions of our modeling. By measuring the width associated with partial dislocation dissociation (shown in Figure 4), we determined that 316L has a SFE value in the range of 60–100 mJ/m^2, consistent with measurements of SFE = 78 mJ/m^2 reported in the literature [4]. We have also examined dislocations in a low-Ni, high-Mn stainless steel alloy and estimated a lower limit to the alloy's SFE of about 63 mJ/m^2.

CONCLUSIONS AND FUTURE DIRECTIONS

- Testing and analysis of strain-hardened 316L and XM-11 austenitic stainless steels reveals that normalization of stress values by yield strength collapses fatigue life data to a master curve, enabling extrapolation of the effects of hydrogen condition and temperature on performance.
- Analysis of literature shows that, for 300-series and Mn-stabilized stainless steels, stacking fault energy (SFE) appears to correlate with metrics for ductility for service in hydrogen.
- An atomic-level approach has been used to calculate SFE for Fe-Cr-Ni-based alloys, which produces predictions in close agreement with the available literature. A computational approach has been developed for alloy exploration based on optimizing SFE, and can be configured to use either thermodynamic models or ab initio calculations as an input/analysis tool.
- SFE has been measured for 316L stainless steel, and bounded for a low-Ni, high-Mn stainless steel alloy.
- In the final year of this project, commercial high-strength (i.e., strain-hardened) alloys will be evaluated to assess their potential for achieving the weight savings target. In addition, our computational framework will be more fully developed and used to explore a wide range of compositions within the Fe-Cr-Ni-Mn-Al system. Initial surveys will be performed using the available thermodynamic model, while avenues for improving the efficiency and consistency of ab initio calculations will be pursued.

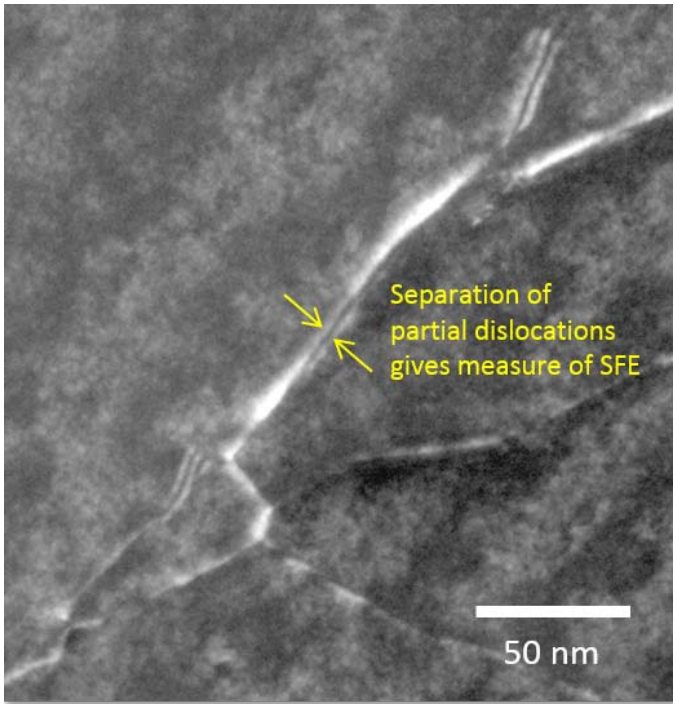


FIGURE 4. Transmission electron microscopy image of dislocation splitting in 316L stainless steel imaged using weak-beam dark-field. Measurement of the partial dislocation separation provides a measure of stacking fault energy.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. C. San Marchi (presenter), "Fatigue testing methodologies in gaseous hydrogen," (SAND2015-9931C), presented at the

International Workshop on Hydrogen Embrittlement in Metal, Jeju, Korea, 13 November 2015.

2. P.J. Gibbs (presenter), "Hydrogen Influences on Notched Fatigue Life of Stainless Steels," (SAND2016-1544C), presented at the 2016 TMS Annual Meeting and Exhibition, Nashville, TN, 17 February 2016.

3. P.J. Gibbs, K.A Nibur, X. Tang, C. San Marchi, "Comparison of Internal and External Hydrogen on FatigueLife of Austenitic Stainless Steel," (PVP2016-63563), *Proceedings of the ASME 2016 Pressure Vessels and Piping Conference*, Vancouver, Canada, 17–21 July 2016.

4. P.J. Gibbs, K.A. Nibur, C. San Marchi, "Fatigue behavior of austenitic steels with hydrogen," (SAND2016-1283A), *Abstract for the 2016 International Hydrogen Conference*, Moran, WY, 11–14 September 2016.

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1. DOE Fuel Cell Technologies Office Record # 13010.

2. S. Curtze et al., "Thermodynamic modeling of the stacking fault energy of austenitic steels," *Acta Materialia* 59 (2011): 1068–1076.

3. L. Vitos et al., "Stacking fault energy and magnetism in austenitic stainless steels," *Physica Scripta* 77 (2008): 065703.

4. R.E. Schramm and R.P. Reed, "Stacking fault energies of seven commercial austenitic stainless steels," Metallurgical Transactions A 6A (1975): 1345–1351.

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