Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

Innovative Development, Selection and Testing to Reduce Cost and Weight of Materials for BOP Components

PI: Christopher San Marchi, Co-PI: Jonathan Zimmerman

Team:

Michael Foster, Paul Gibbs, Aaron Gibson, Patricia Hough, Doug Medlin, Catalin Spataru (*Sandia National Laboratories, Livermore, CA*)

Kevin Nibur (*Hy-Performance Materials Testing*)

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Overview

Timeline

- Project start date: July 2014
- Project end date: Sept 2017

Technical Barriers

A. System Weight and Volume

B. System Cost

H. Balance-of-Plant (BOP) Components

Budget

- Total Project Budget: $2.475M (3yr)
  - Total Federal Share: $2.4M
  - Total Partner Share: $75K
  - Total DOE Funds Spent*: $1.775M

*As of 3/31/17

Partners

- *Hy-Performance Materials Testing*
  - Subcontractor: fatigue evaluation in hydrogen
- *Swagelok Company*
  - In-kind: materials, test specimens, design perspective
- *Carpenter Technology*
  - In-kind: materials manufacturing expertise

Relevance and Objectives

Problem: At low volumes, BOP components onboard light-duty vehicles collectively dominate cost of the hydrogen storage system

Objective: Identify alternatives to high-cost metals (annealed 316/316L stainless steel) for high-pressure BOP components

Barrier from 2012 Storage MYRDD	Project Goal
A. System Weight and Volume	Reduce BOP material weight by 50% Weight can be reduced by optimization of structural stresses
B. System Cost	Reduce BOP material cost by 35% Cost can be reduced by selecting lower cost materials and using less material
H. Balance-of-Plant (BOP) Components	Expand the scope of materials of construction for BOP Appropriate materials should be determined by relevant performance metrics such as fatigue properties

This objective is addressed from two perspectives: (1) engineering evaluation of commercial alloys; and (2) alloy discovery using first-principles computational tools.

Project Approach

Objective: Identify low-cost, light-weight alternatives to annealed type 316L austenitic stainless steels

- *Reduced nickel* content is prime candidate for *cost reduction*
- *High-strength* is prime candidate for *weight reduction*

Two parallel paths:

1. *Experimentally* evaluate fatigue properties of commercial austenitic stainless steels in hydrogen environments
   - Benchmark existing "standard": annealed type 316L
   - Evaluate alloys with lower-nickel content or high-strength condition
2. *Computational* materials discovery
   - Correlate stacking fault energy (SFE) with hydrogen effects
   - Develop high-throughput computational strategy to determine SFE
   - Use computational strategy to explore alloy additions to increase SFE

Project Approach

Analysis suggests significant cost and weight reductions can be realized

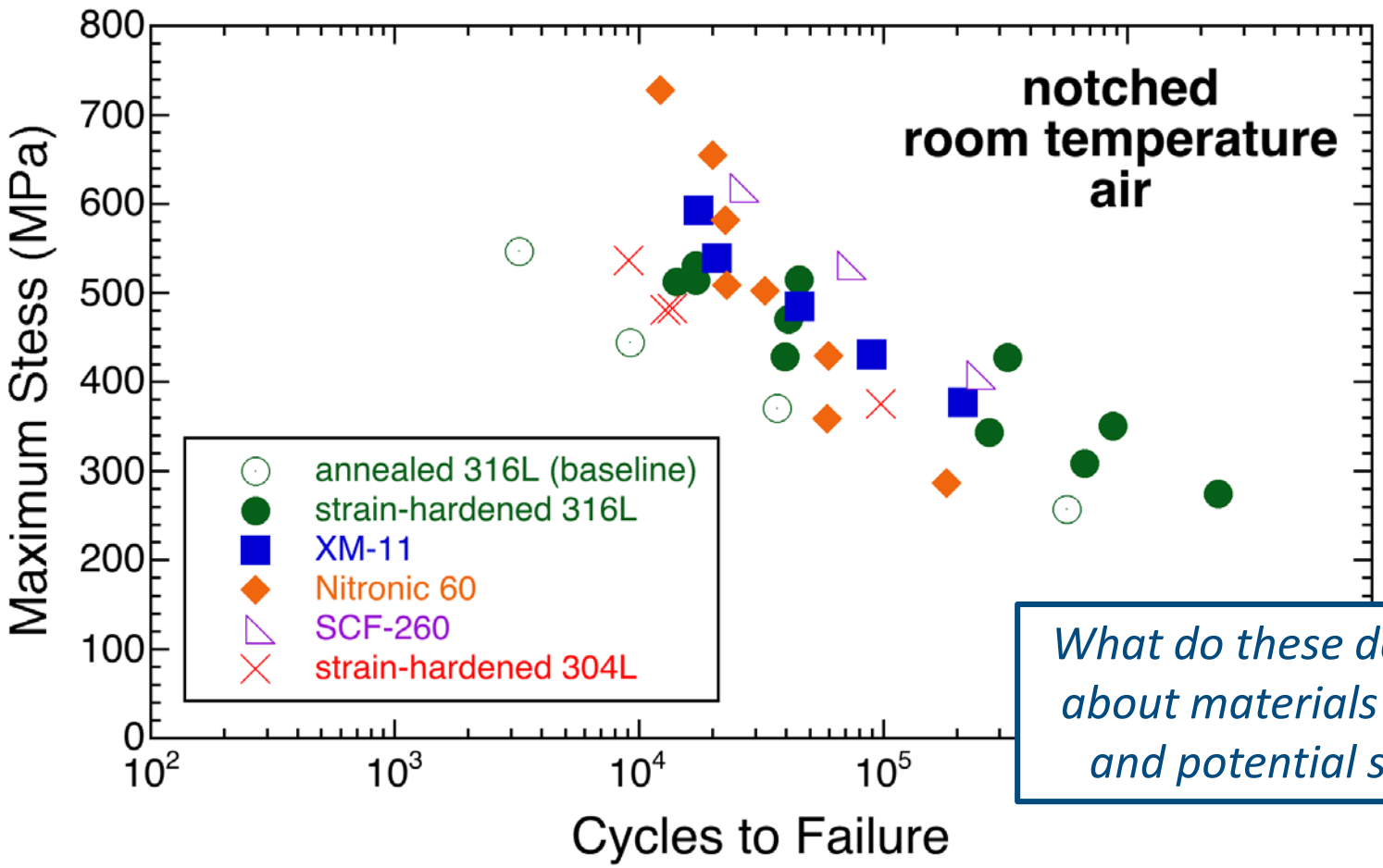
material	Sy (MPa)	UTS (MPa)	Cr	Ni	Mn	N	Typical allowable stress (MPa)
316L	280	562	17.5	12	1.2	0.04	115
CW 316L	573	731	17.5	12	1.2	0.04	218
304L	497	721	18.3	8.2	1.8	0.56	195
XM-11	539	881	20.4	6.2	9.6	0.26	207
Nitronic 60	880	1018	16.6	8.3	8.0	0.16	218
SCF-260	1083	1175	19.1	3.3	17.4	0.64	333

Wide range of strength (i.e., weight)

Wide range of Ni/Mn content (i.e., cost)

Project Approach

Fatigue measurements in hydrogen provide relevant performance metrics for assessing cost/weight reduction



What do these data tell us about materials selection and potential savings?

Project Approach

Thermodynamics and density functional theory (DFT) enable prediction of fundamental properties

Two approaches for high-throughput calculation of SFE:

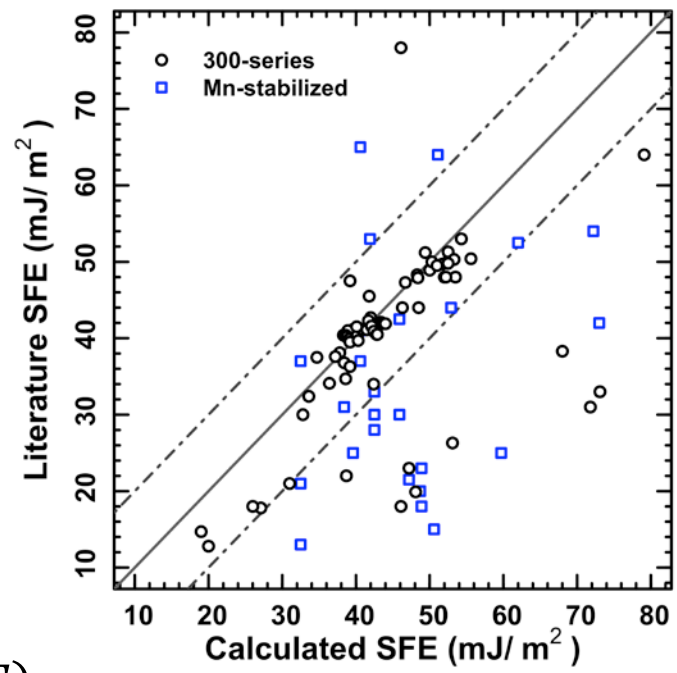
(1) analytic thermodynamic model that includes considerations of segregation, interfacial energy and magnetic entropy

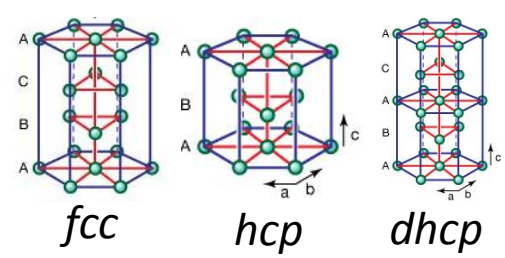
$$SFE(T) \approx 2\rho\Delta G^{\gamma\rightarrow\varepsilon}(T) + 2\sigma$$

Based on: Dumay, et al., Mater. Sci. A, 2008; Saeed-Akbari, et al., Met. Trans. A, 2010; Curtze, et al. Acta Mater. 2011

(2) coherent potential approximation (CPA) to DFT that includes considerations of thermal expansion and magnetic entropy

$$SFE(T) \approx \frac{F^{hcp}(T) + 2F^{dhcp}(T) - 3F^{fcc}(T)}{A}$$





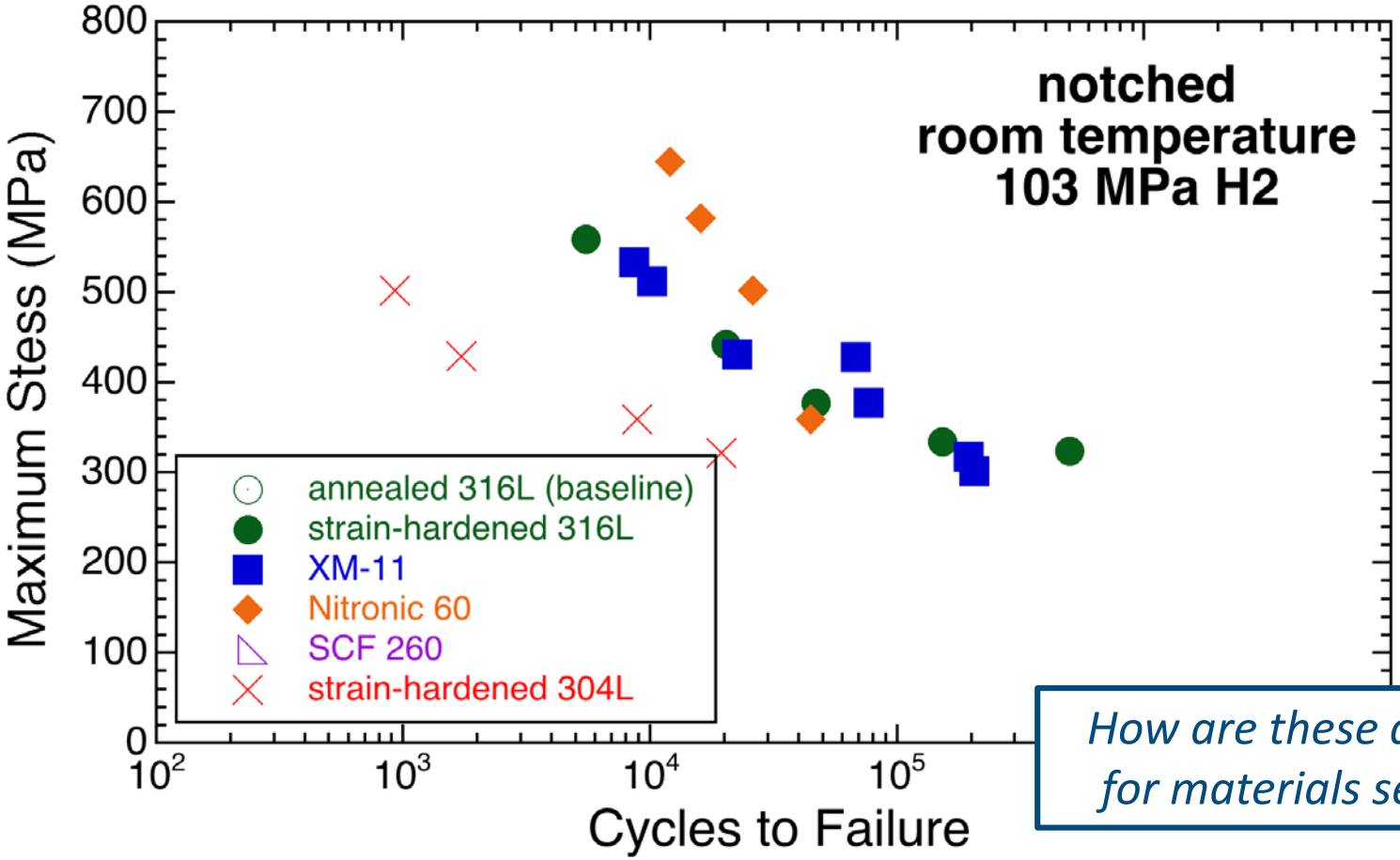
Original strategy of performing exact DFT calculations was found to be computationally intensive and not suitable for high-throughput screening

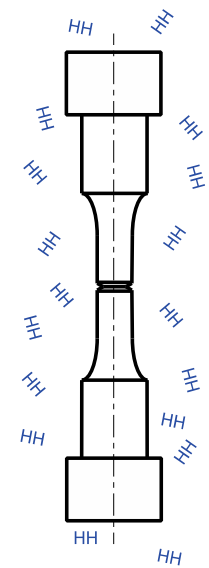
Project Objectives and Milestones

Objective/Milestone	Target date	Status / Impact
Go/No Go: Demonstrate potential to meet project targets through alloy selection or computational alloy design	FY16	High strength XM-11 results in weight reduction of almost 70% and cost reduction of 50% through the use of less material.
Assess fatigue strength, material weight and cost of two engineering alloys: (1) gall resistant alloy Nitronic 60, and (2) low-Ni, high-strength alloy XM-11	FY17Q1	Completed: *Both alloys perform at least as well as 316L on a per strength basis*
Evaluate compatibility of first-principles calculations with reduced-order models. Identify best-fit approach to use for construction of reduced-order models	FY17Q2	In progress. Database of ~650 alloys generated using first-principles approach.
Establish approvals for data sharing, including licensing and copyright assertion (if necessary) as well as documentation for computational tools	FY17Q3	Web interface allows flexible tool for exploring compositional dependence of SFE and potentially cost
Complete final program report, including recommendations for alloys to replace 316L	FY17Q4	*A diverse set of alloys meet minimum performance metrics and cost/weight targets*

Accomplishment

Fatigue life measured in gaseous hydrogen reveals several alloy options comparable to baseline material

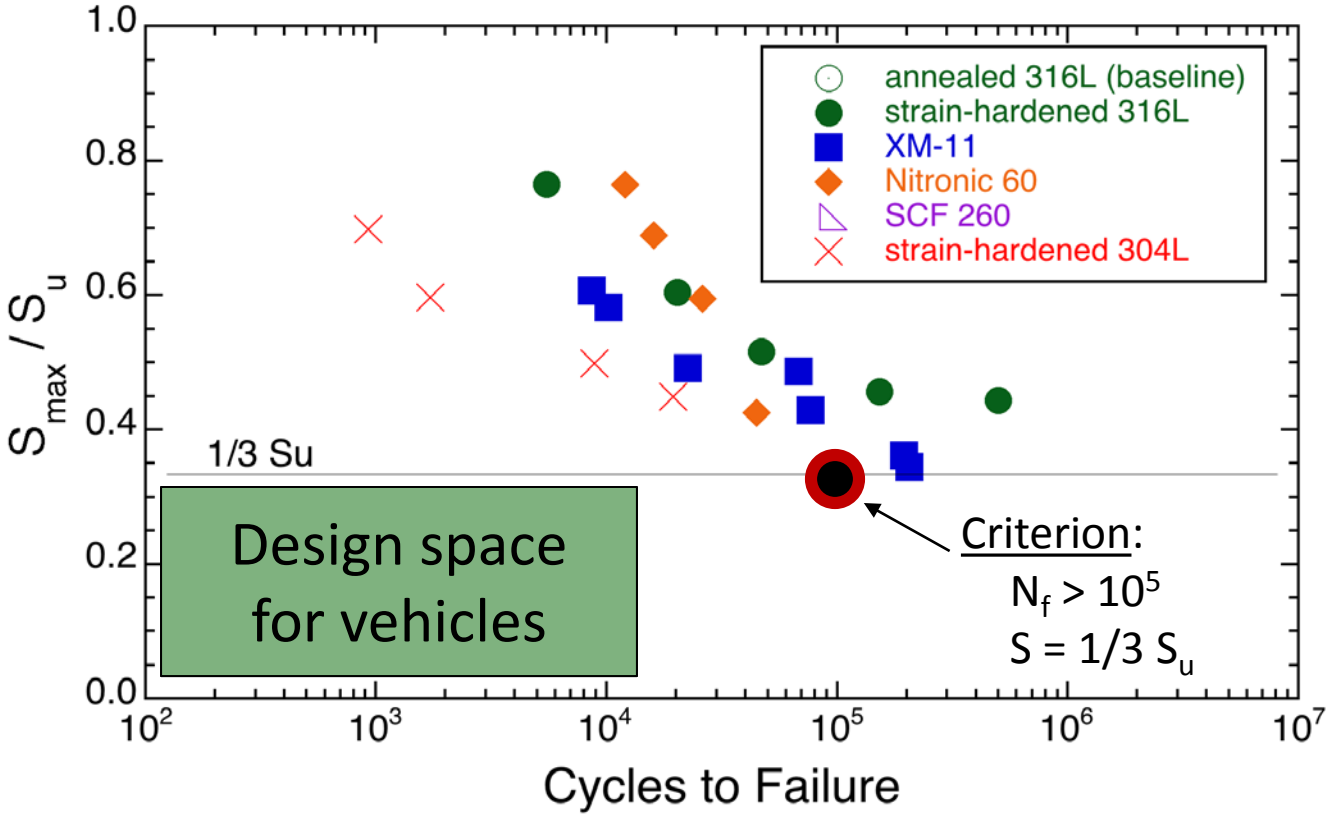




How are these data used for materials selection?

Accomplishment

Engineering normalization of hydrogen-assisted fatigue data allows comparison of design performance



Common design criterion:

$S \leq 1/3\ S_u$

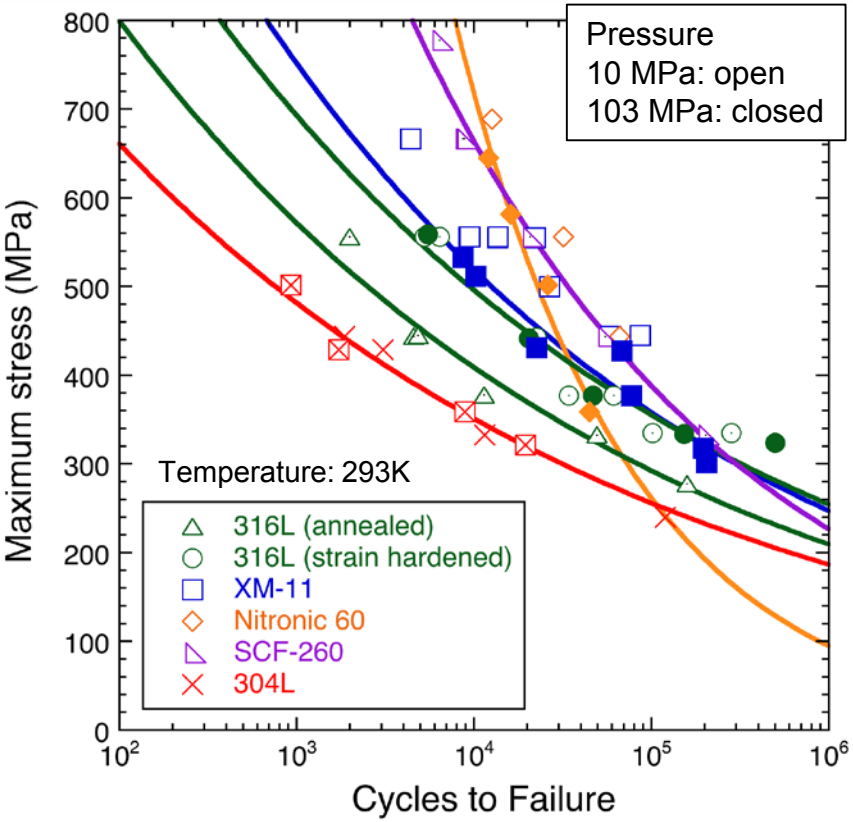
S_u = ultimate tensile strength

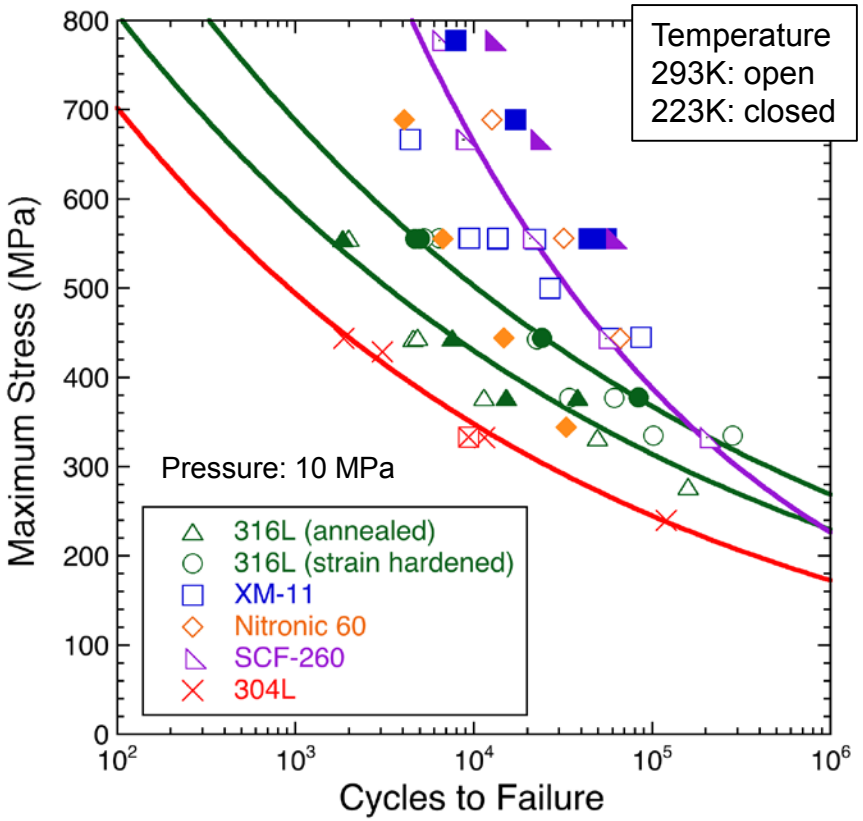
S = allowable stress (or design stress)

Conservative materials qualification metric for materials in the vehicle application has been proposed (collaboration with SCS program)

Accomplishment

Fatigue life testing at low temperature leads to similar conclusions about performance as at room temperature





- Pressure has modest effect, if any, on fatigue life
- Temperature has either no effect or increases fatigue life
- Nitronic 60 is an exception for both pressure and temperature

Accomplishment

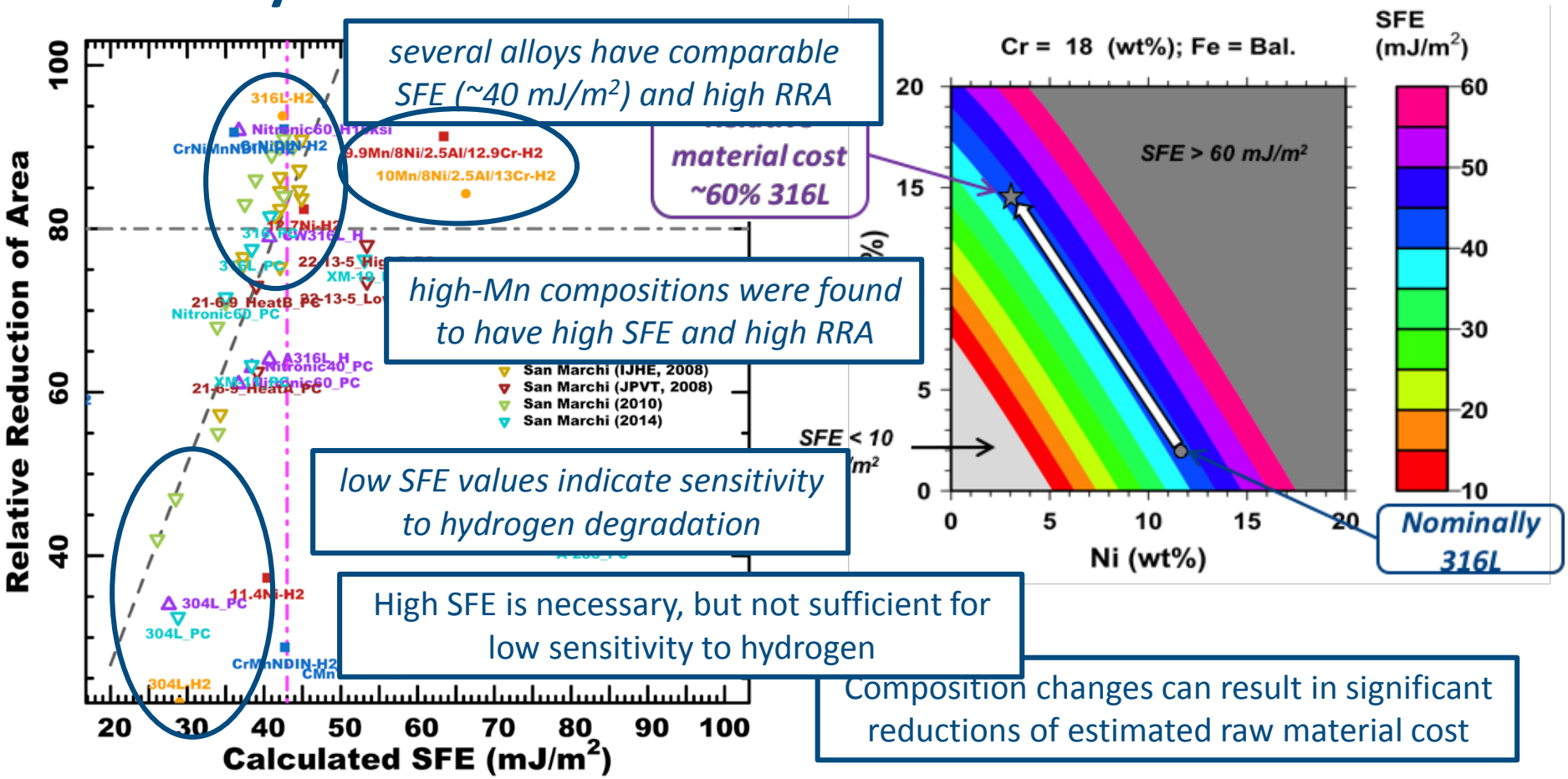
Assessment of fatigue performance demonstrates that cost and weight reduction targets can be achieved

material	Allowable stress (MPa)	Relative weight	Cr	Ni	Mn	N	Relative cost	
316L	115	1.00	17.5	12	1.2	0.04	1.00	
CW 316L	218	0.28	17.5	12	1.2	0.04	0.42	
304L	195	0.34	18.3	8.2	1.8	0.56	0.35	
XM-11	207	**0.31**	20.4	6.2	9.6	0.26	**0.41**	***Low-nickel***
Nitronic 60	218	**0.28**	16.6	8.3	8.0	0.16	**0.40**	***Gall tough***
SCF-260	333	0.15	19.1	3.3	17.4	0.64	0.23	

- Verification of fatigue performance in the combination of low-temperature and high-pressure is needed
  - Effects of pressure and H-precharging suggest low-temperature conditions will not be limiting

Accomplishment

Thermodynamic model predictions provide insights on hydrogen sensitivity and effects of composition variability



several alloys have comparable SFE (~40 mJ/m²) and high RRA

material cost ~60% 316L

high-Mn compositions were found to have high SFE and high RRA

low SFE values indicate sensitivity to hydrogen degradation

High SFE is necessary, but not sufficient for low sensitivity to hydrogen

Composition changes can result in significant reductions of estimated raw material cost

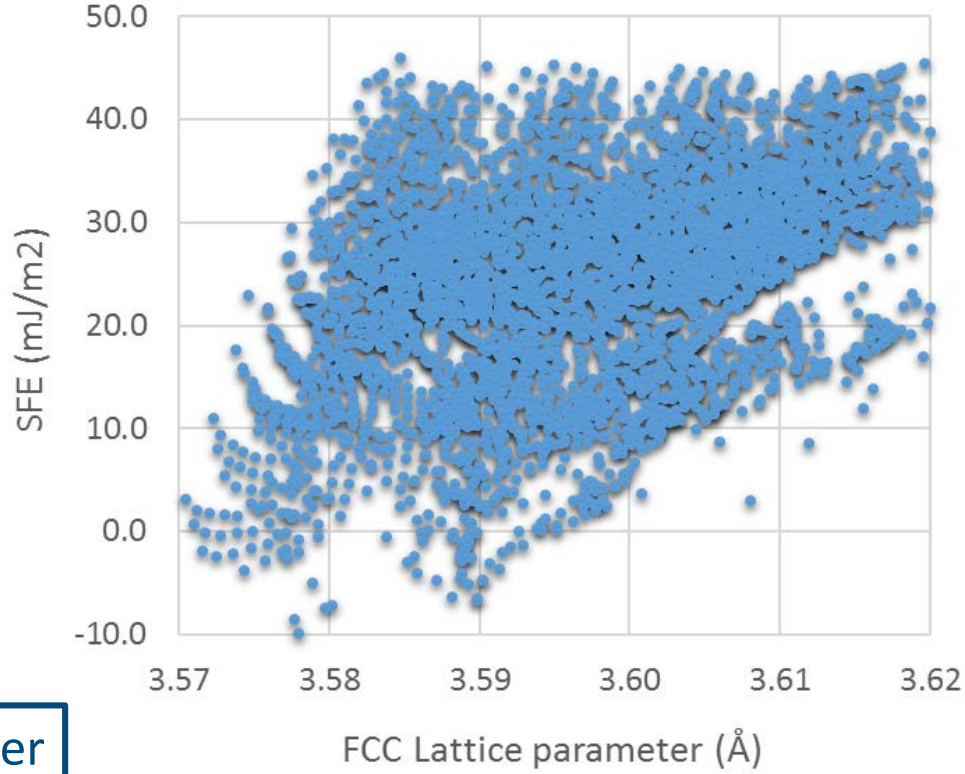
Accomplishment

DFT/CPA approach used to generate database of alloy compositions with fewer assumptions than TD model

We have predicted the SFE of ~4,000 stainless steel alloys

Current composition ranges:
Fe – 62 to 74 wt%, Ni – 0 to 20 wt%,
Cr – 16 to 24 wt%, Mn – 0 to 24 wt%,
Mo – 0 to 6 wt%, Si – 0 to 6 wt %

Alloys with larger lattice parameter for the austenitic (fcc) structure display a narrower range of variation centered around larger values of SFE.



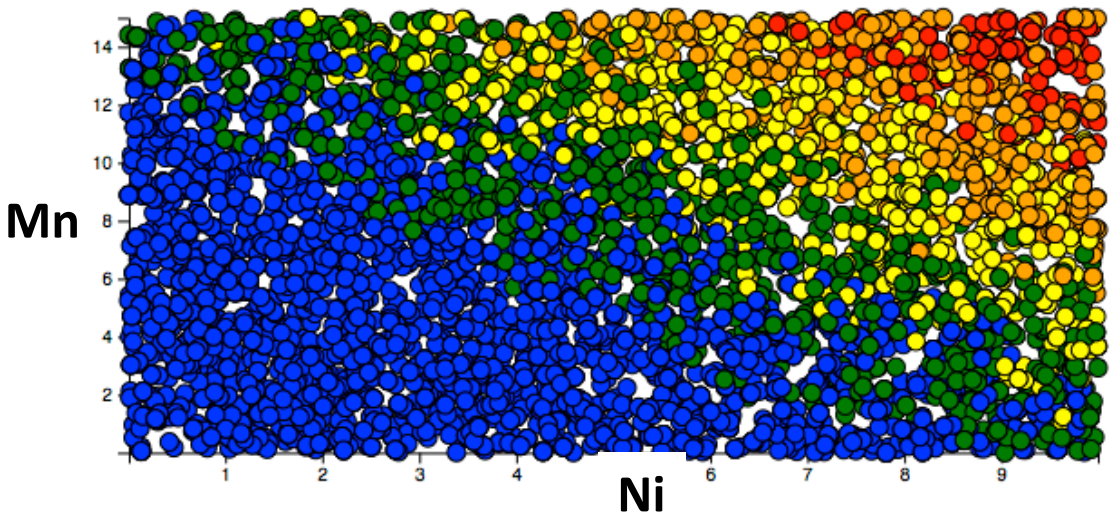
Calculations suggest lattice parameter (an easier quantity to measure) could serve as a proxy for SFE

Still to do: Comparison with thermodynamic model predictions

Accomplishment

Web-based "design" tool integrates the SFE models and cost metrics for rapid alloy screening

Simulation of SFE contours in Ni-Mn space



Cost Inputs

Iron	0.045
Chromium	0.94
Nickel	4.51
Manganese	0.88
Molybdenum	6.92
Silicon	0.91
Copper	2.59
Aluminum	0.87

Update costs

X-Axis: Ni Y-Axis: Mn

The fields below allow for configuring a filter on the points displayed. Leaving one of the fields below "blank" implies no bound.

Filter: Cr

The fields below allow for configuring the color of the data points based on configurable properties.

SFE 40 50 60 70

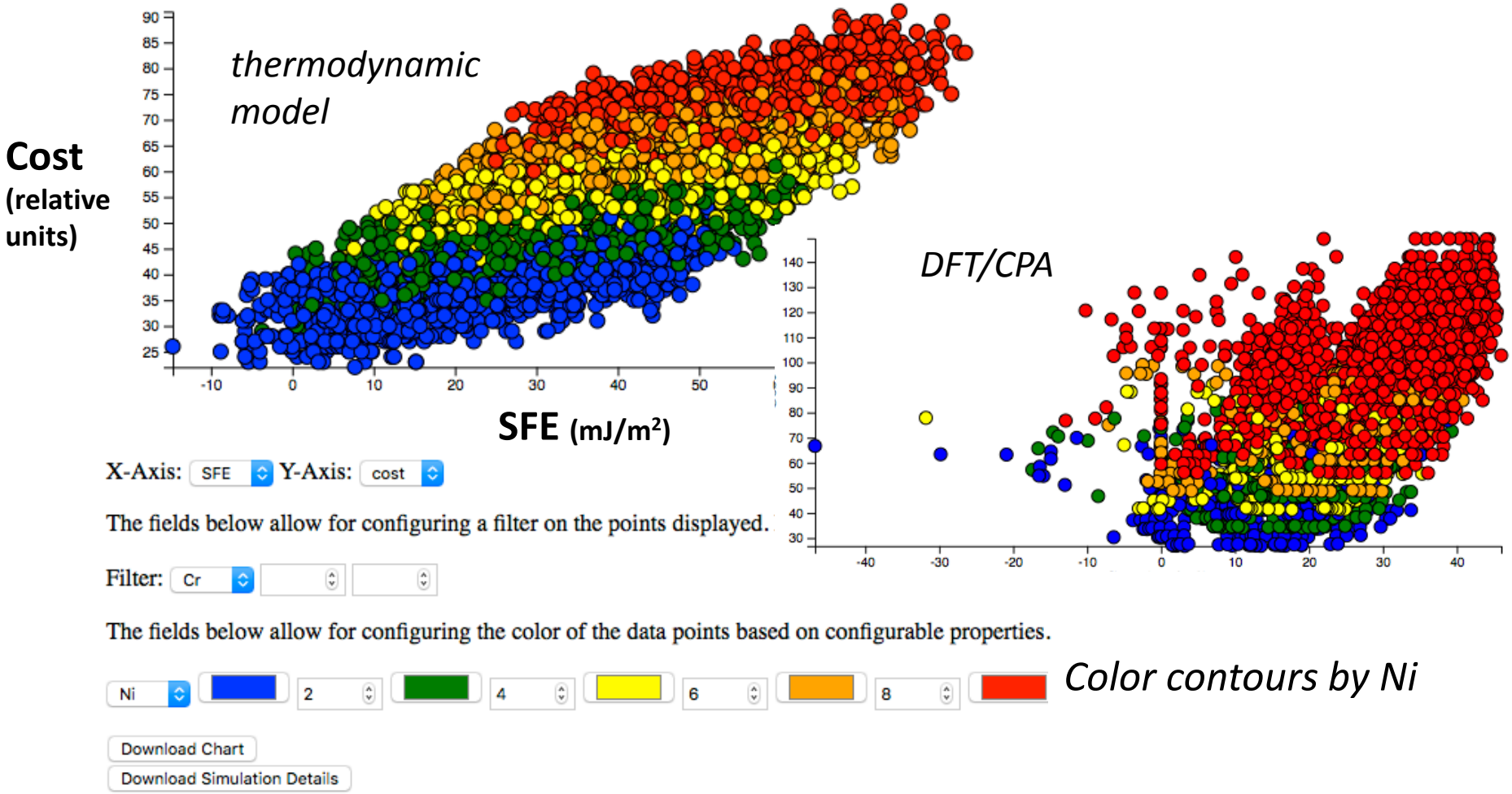
Color contours by SFE

Download Chart

Download Simulation Details

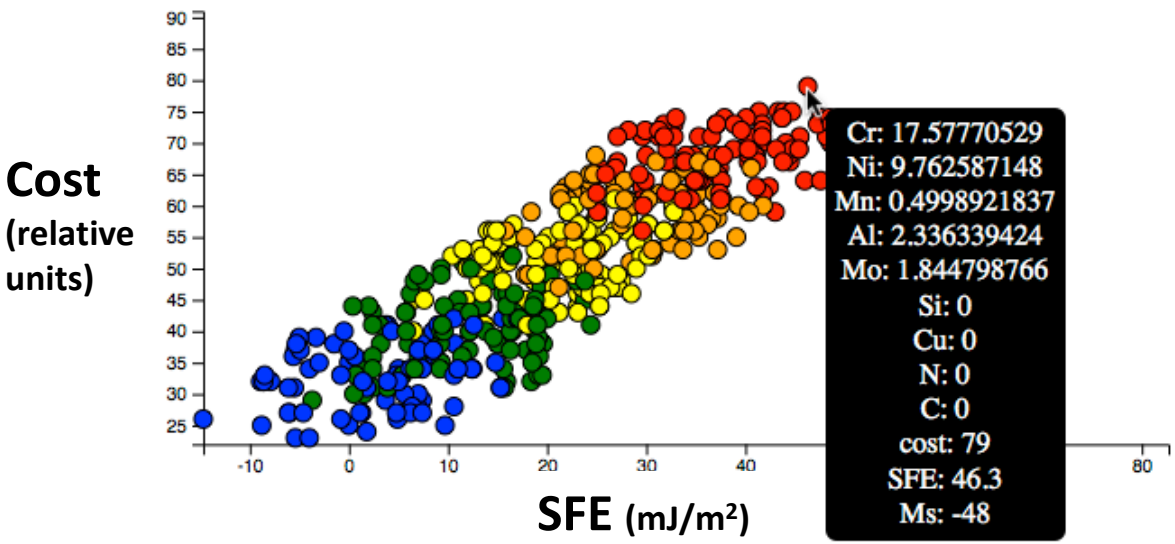
Accomplishment

Multi-dimensional simulation results can be used to assess the effects of composition on SFE and cost



Accomplishment

Filters in the web-tool allow narrowing ranges of any field and all characteristics are accessible at cursor tip



Simulation of Ni contours in cost-SFE space includes:

- Fe
- Cr
- Ni
- 0 < Mn < 1
- Mo
- Cu
- Si
- Al

X-Axis: SFE Y-Axis: cost

The fields below allow for configuring a filter on the points displayed. Leaving one of the fields below "blank" implies no bound.

Filter: Mn 0 1

The fields below allow for configuring the color of the data points based on configurable properties.

Ni 2 4 6 8

Color contours by Ni

Download Chart

Download Simulation Details

Response to Previous Year Reviewers' Comments

- "One concern is the feasibility of the DFT calculations, which have proven to be more complex than expected."
- "It is unclear whether the computational efforts with the SFE will provide a useful outcome in recommending other materials for hydrogen applications."
  - Development and use of thermodynamic model – a method amenable to high-throughput calculation – has identified a regime of SFE values where hydrogen sensitivity can be minimized.
  - CPA approach enables high-throughput calculations while including some of the fidelity characteristic of DFT, e.g. thermal expansion, magnetic entropy contribution to energy.
- "The project could have a reasonable impact…, but the reviewer is not totally convinced that the project will identify new materials.."
  - Fatigue analysis has enabled identification of commercial alloys (e.g. XM-11, Nitronic 60) that afford cost and/or weight savings over the baseline alloy while ensuring good performance within a designated design space.
- "The team should consider Cr as a variable, in addition to Ni."
  - The thermodynamic model and the CPA approach have been used to assess effect of Cr composition on SFE. Results show slight decrease in SFE with increasing content of Cr, which should have deleterious effect on hydrogen performance.

Collaborations and Partnerships

- Sandia National Laboratories
  - Core DOE capability for high-pressure hydrogen testing
  - Leverage between NNSA and EERE customers
  - Deep expertise in mechanical metallurgy of austenitic stainless steels
  - Advanced computing tools
- Hy-Performance Materials Testing (Kevin Nibur)
  - Commercial testing expertise in pressure environments
  - Unique commercial capabilities in the US
- Swagelok Company (Shelly Tang)
  - Component manufacturer
  - Materials selection and engineering analysis
  - Deep understanding of manufacturing with austenitic stainless steels
- Carpenter Technology (Sam Kernion)
  - Steel manufacturer
  - Metallurgical expertise and cost analysis

Remaining Challenges and Barriers

- **Challenge**: Fatigue data demonstrate performance of a range of compositions and strengths; however, international community questions the application of the notched geometry for materials qualification
- **Resolution**: The notched method enables quantification of crack initiation for deeper understanding of fatigue behavior. Also solid mechanics models are being used to assess the strains and stresses around the notch to better understand the applicability of the notched geometry

- **Challenge**: Tools for prediction of SFE must be made accessible
- **Resolution**: A platform for flexible assessment of SFE trends with compositional variables has been developed using a thermodynamic method. The platform will also allow sampling of large databases from DFT calculations

- **Challenge**: Can empirical and computational paths intersect each other?
- **Resolution**: Early investigation of SFE-RRA trend led to consideration of high-Mn commercial alloys. Regarding hydrogen effects on design, degradation of fatigue behavior was not observed to depend on SFE; consider alternative metrics.

Future Work

Remainder of FY17:

- Complete fatigue testing
  - high-pressure testing (SCF-260)
  - low temperature testing (H-precharged)
- Assess crack initiation behavior for different environmental conditions and conduct preliminary assessment of stress and strain fields in notch toward understanding short crack behavior
- Complete web-based tool for SFE estimations based on composition
  - Include larger database of CPA estimates and compare with thermodynamic model
  - Improve cost assessment methodology

Potential follow-on activities:

- Apply concepts to aluminum alloys
- Deeper exploration of testing parameters (specimen size, frequency, etc)
- Additional testing and solid mechanics modeling to develop framework for short crack behavior (toward design for higher stresses – finite life)
- Study of deformation and crack growth mechanisms in hydrogen-assisted fatigue
- Expansion of web-based tool for estimations of other intrinsic material properties that have relevance to performance characteristics

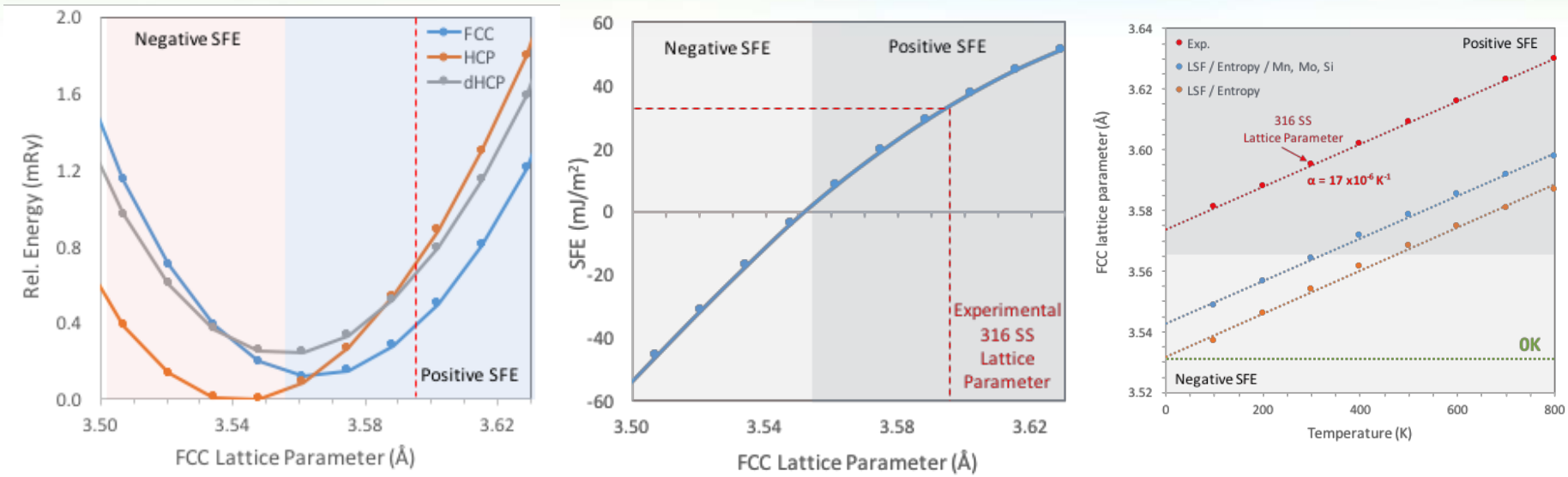
Any proposed future work is subject to change based on funding levels

Summary

- Assessment of fatigue performance of a diverse range of alloys demonstrates that material cost and weight reduction targets can be achieved
  - 35% reduction of cost
  - 50% reduction of weight
- Additional infrastructure is needed to verify performance under the combination of high pressure and low temperature
  - Although extrapolation of data suggests low temperature will not be limiting condition
- SFE can be a useful screening tool for assessing sensitivity to hydrogen
  - SFE alone is not a predictive metric of alloy performance in hydrogen
  - However, low SFE shows a tendency for greater sensitivity to hydrogen-induced cracking and degradation
  - Degradation of fatigue behavior was not observed to depend on SFE
- Web-based materials “design” tool provides insight to effects of composition on SFE and cost
  - Tool can easily be expanded to other materials and characteristics

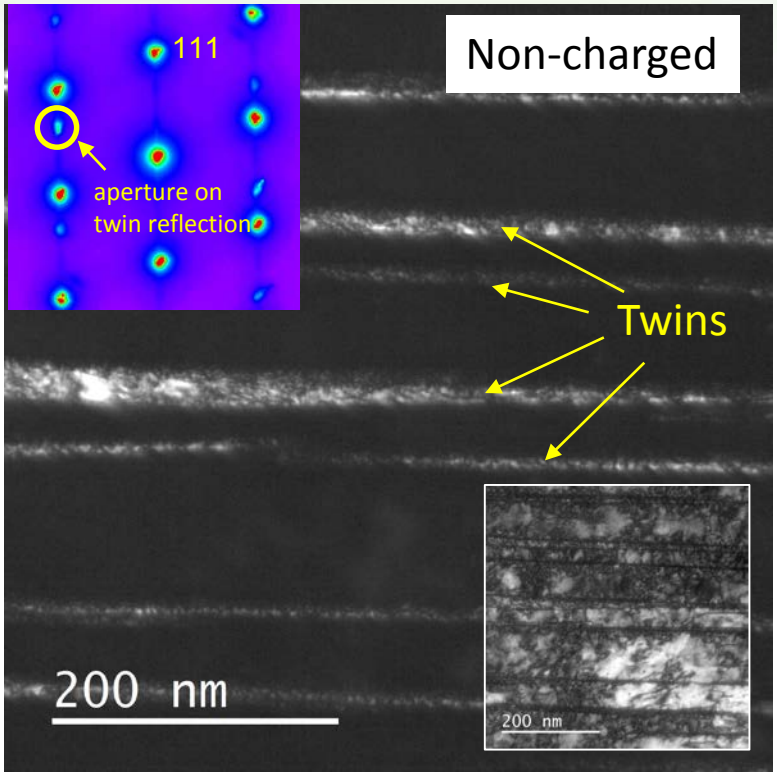
Technical Back-Up Slides

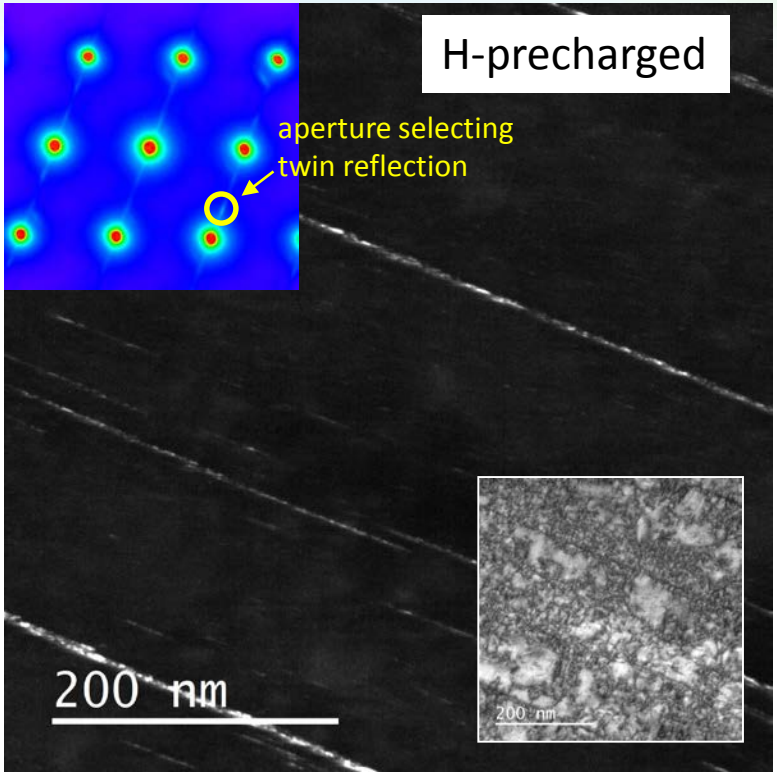
Thermal lattice expansion and magnetic entropy are critical to DFT prediction of Stacking Fault Energy



- SFE is estimated by a difference between energies of FCC, HCP and dHCP structures. These differences are very small, particularly at the room temperature lattice size.
- Thus, the predicted value of SFE can be very sensitive to how well lattice size is predicted. Even small differences in lattice size ($\lesssim$ 1%) due to consideration of magnetic entropy and the presence of low-concentration constituent elements (e.g. Mo, Si) can have a profound effect on SFE prediction.
- These dependencies are what make accurate prediction of SFE using DFT-based methods a formidable challenge.

High-resolution microstructural studies show differences in fatigue-induced deformation near the fracture surface





- Dark field imaging confirms presence of nanoscale twins in XM-11
- Nanoscale twins appear significantly thinner in the presence of hydrogen, which may affect fatigue crack initiation
- High resolution observations are needed to determine whether second-phases (e.g., epsilon martensite) are present.