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

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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: $1M

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

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

Integration: Fabricate new alloy combinations (computational discovery) and measure fatigue performance (experimental)

Project Approach

Analysis suggests significant cost and weight reductions can be realized

- Relative component cost is estimated from the relative weight of material and material cost
  - Relative weight is determined from required thickness of material
  - Relative material cost is conservatively informed from price of bar material

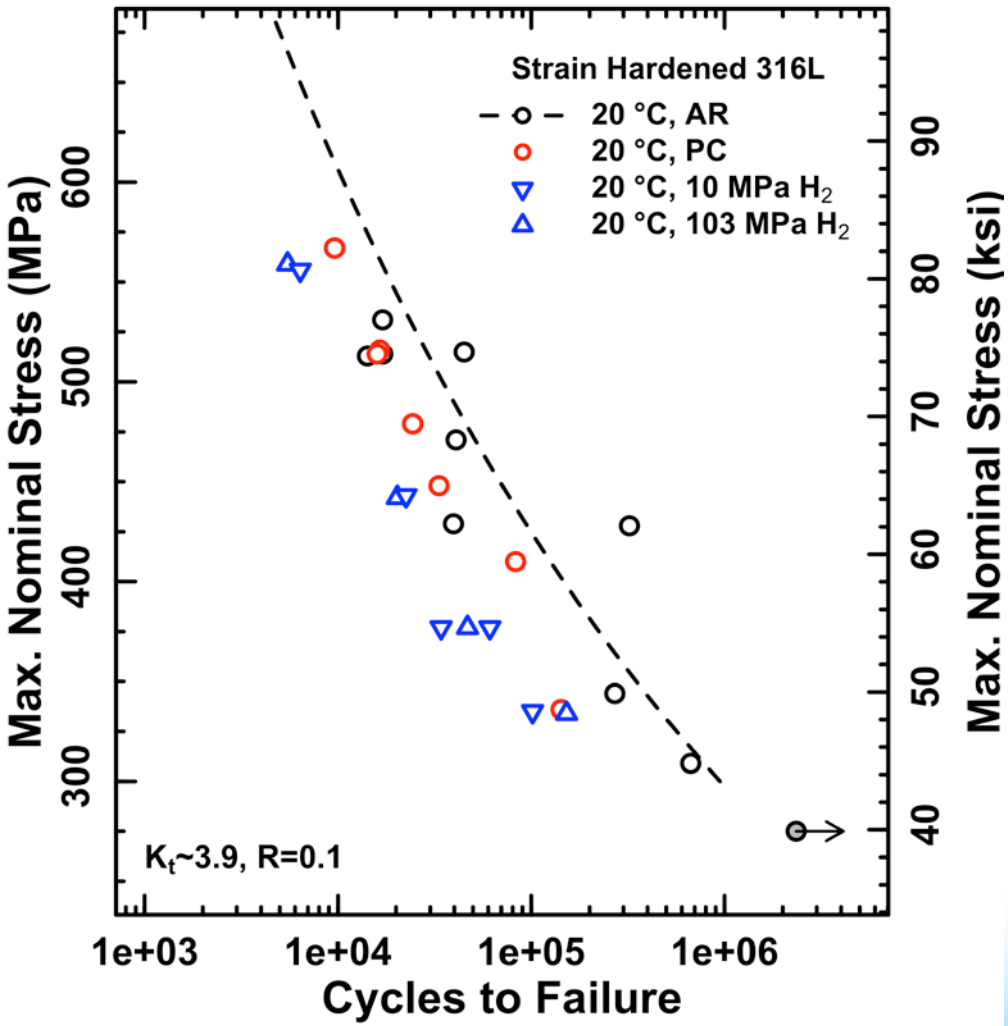
material	Relative material cost	Yield strength (MPa)	Relative weight	Relative material cost for component
316L (~12 wt% Ni)	1.0	140	1.0	1.0
XM-11 (~6 wt% Ni)	0.79	345	0.46	0.36
CW XM-11	1.6	620	0.17	0.27

- Stress-based fatigue life is used to design pressure systems
  - Fatigue experiments to compare performance for different commercial alloys
  - Testing standard already exists within the public domain (CSA CHMC1)
- Density functional theory (DFT) enables prediction of fundamental properties that correlate with behavior in hydrogen
  - Develop approach to calculate SFE and create database
  - Combine calculations with algorithms to guide composition selection

Project Objectives and Milestones

Objective/Milestone	Target date	Status / Impact
Review of literature to quantify correlations between measured hydrogen-affected mechanical properties and SFE	FY15Q1	Completed: *SFE captures relative trends within specific compositional ranges*
Fatigue life of 316L with hydrogen at low temperature	FY15Q2	Completed: *unique data establishing baseline and demonstrating the methodology*
VASP calculations for Ni and for Fe-Cr-Ni	FY15Q2	Ni calculations successful, Fe-Cr-Ni calculations are being refined (80% complete)
Computational and experimental measurements of SFE for alloys of interest	FY15Q3	Initial measurements of SFE for 316L completed, measurements for lower SFE 304L in progress (50% complete)
Hydrogen-assisted fatigue life of low-cost alloy to evaluate lower-cost test method and compare to baseline	FY16Q3	Demonstrated lower cost test method, which captures performance in gaseous hydrogen at room temp. (80% complete)
Go/No Go: Demonstrate potential to meet project targets through alloy selection or computational alloy design	FY16	XM-11 displays similar/better performance than type 316L at lower cost and lower weight

Fatigue performance quantified for high-strength (strain-hardened) type 316L at room temperature



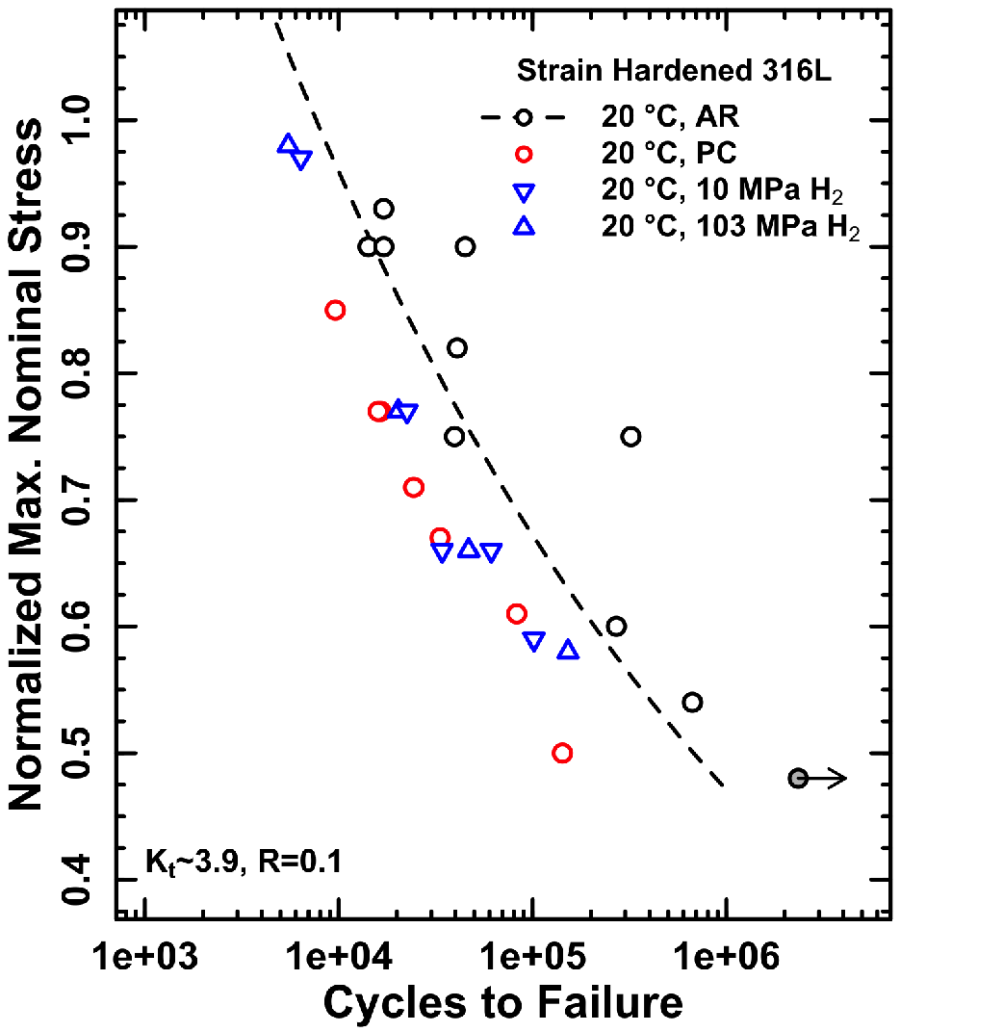
Notched tension-tension fatigue
AR = As Received
PC = Pre-Charged with Hydrogen

Ni = 12.04 wt%
S_y = 589 MPa

- Gaseous (external) hydrogen
  - **Measurable reduction of fatigue performance**
- H-pre-charged (internal)
  - **No reduction of fatigue performance**

Internal H results should be corrected for effects of pre-charging on flow stress

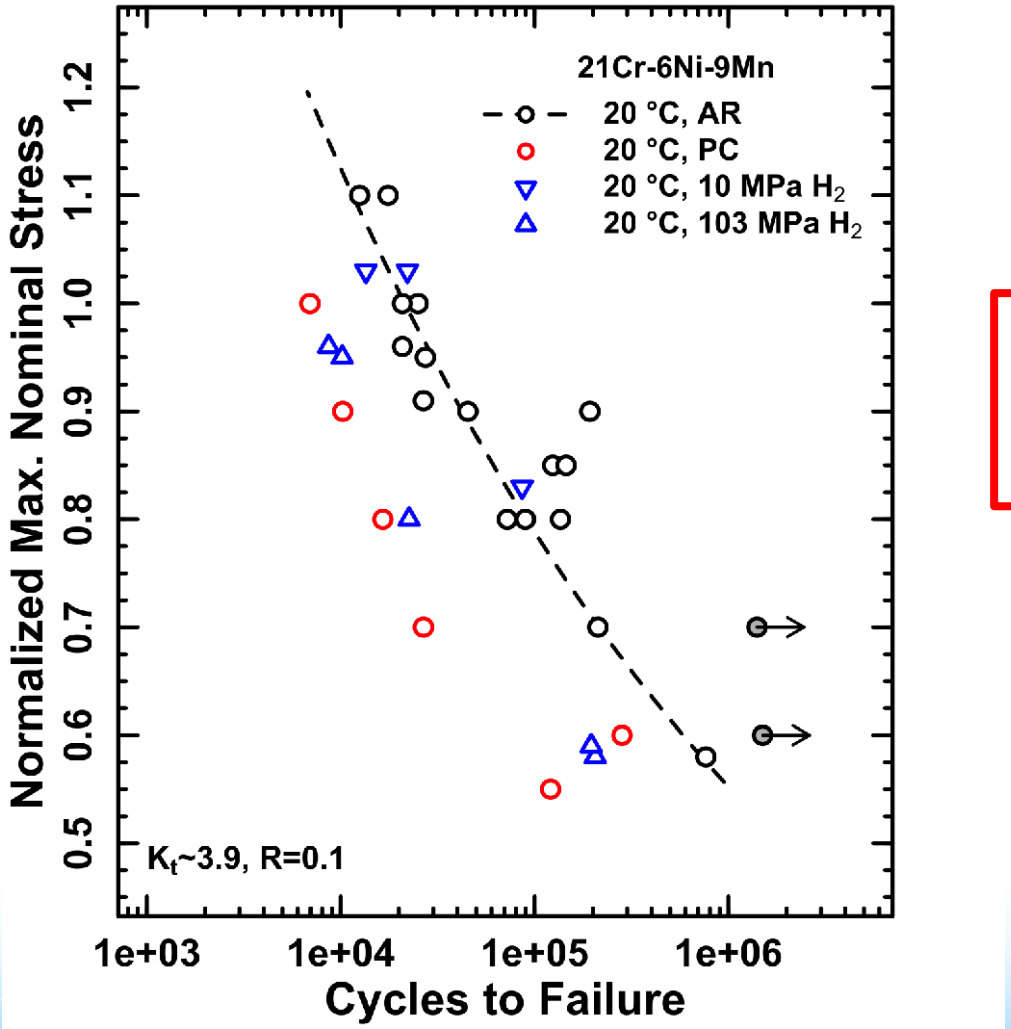
Normalization of fatigue performance shows that pre-charging and in-gas testing produces comparable results



- Internal H increases the flow stress (i.e. yield strength) compared to external H_2
- Apply normalization of the maximum fatigue stress by the yield strength: S_{max}/S_y
- Presentation in terms of normalized fatigue stress shows consistency between internal H and external H_2

Testing with internal H captures fatigue performance of 316L at room temperature

Fatigue performance quantified for low-Ni austenitic stainless steel: 21Cr-6Ni-9Mn (XM-11)



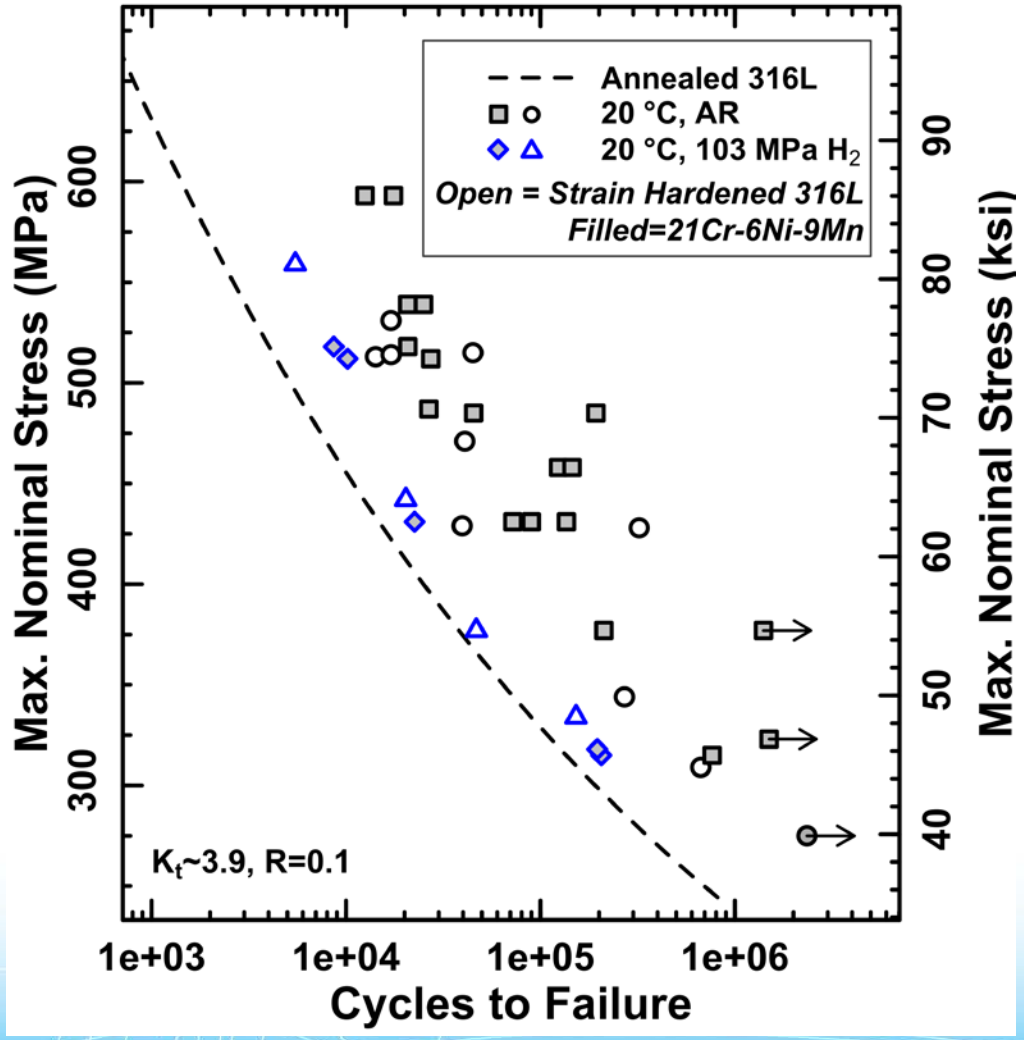
Annealed XM-11
Nominally 21Cr-6Ni-9Mn
S_y = 539 Mpa
Ni = 6 wt%

Nominally the same fatigue performance as the tested strain-hardened 316L

- Although data is sparse, there appears to be a measurable dependence on hydrogen pressure
- More testing is warranted

Accomplishment

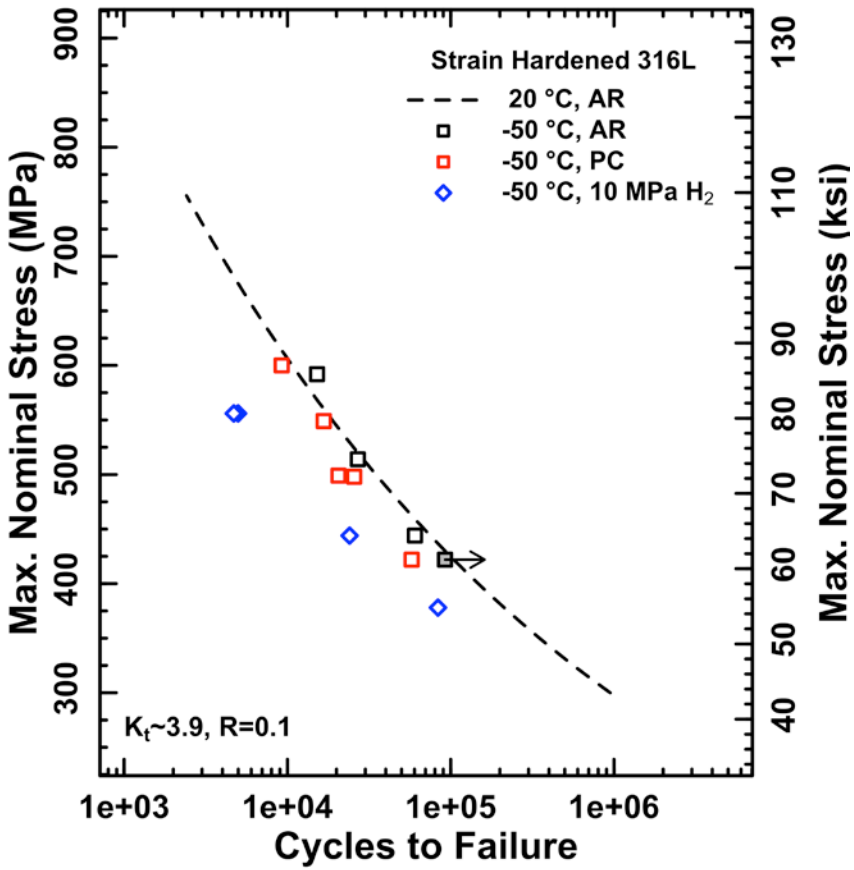
Direct comparison between fatigue performance of high-strength/low-Ni alloys & annealed 316L

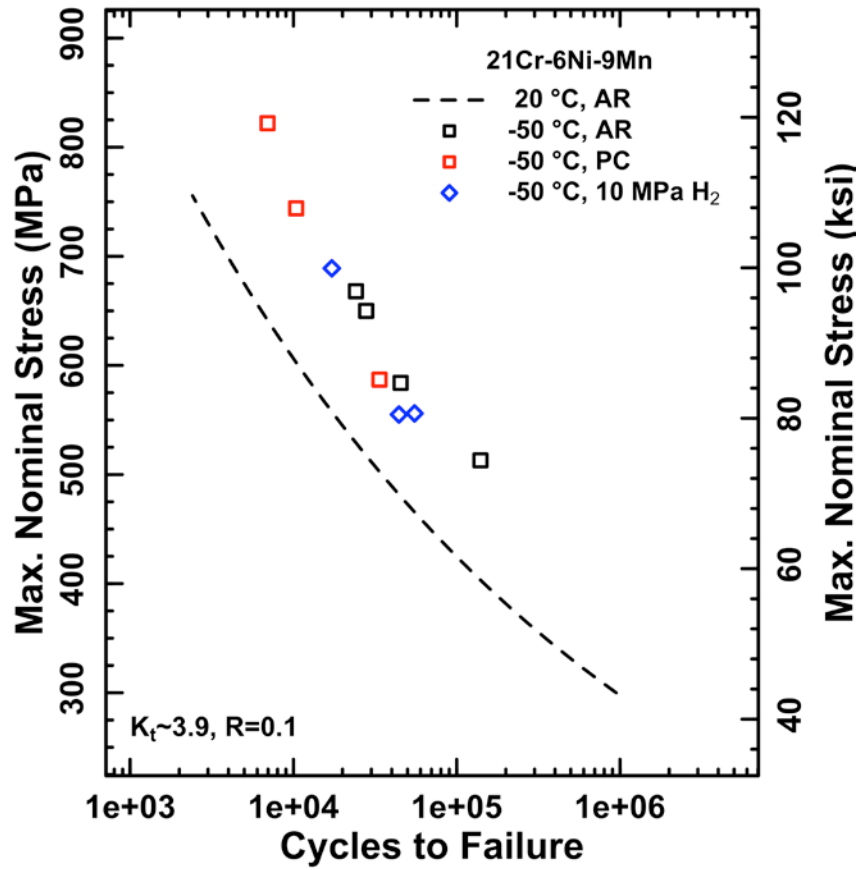


Fatigue life is longer for both the strain hardened 316L and XM-11 compared to the annealed 316L steel

- Applied fatigue stresses are greater than the yield strength for annealed 316L
- Environmental trends are the same for all materials

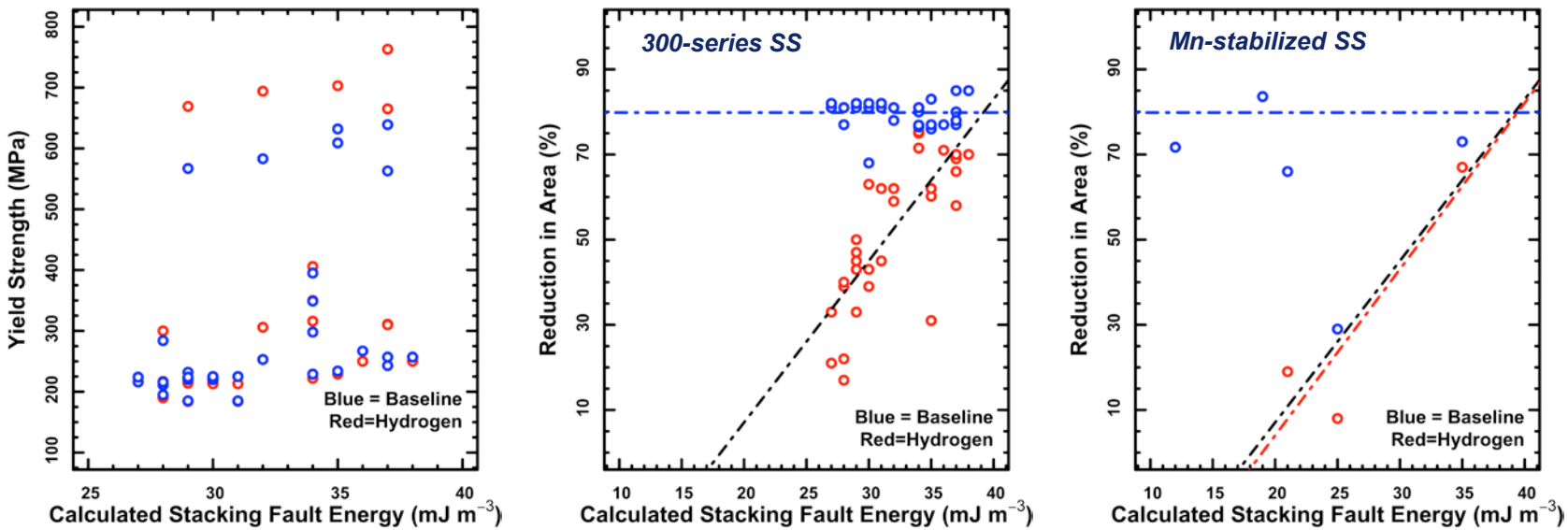
Fatigue performance quantified for low temperature





- **Fatigue life at -50°C is longer than at 20°C for low-Ni alloy**
  - Trend associated with greater flow stress at low temperature
  - Extensive testing at low temperature may **not** be necessary to sufficiently characterize fatigue performance

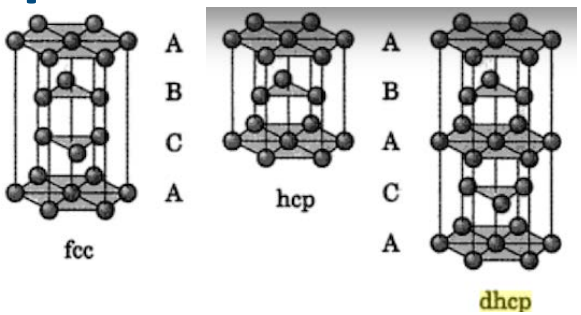
Literature data shows a correlation between stacking fault energy (SFE) and reduction of area in hydrogen



- Calculated estimates of SFE (using method by Curtze *et al.*) leverage experimental data.
- No definitive correspondence between yield strength (and other mechanical properties) and either the presence of hydrogen or SFE.
- Hydrogen pre-charged (PC) condition corresponds to an increase in the yield strength, while some data for external hydrogen shows a slight decrease.
- **Reduction of area in the presence of hydrogen proportional to SFE.** Variation of data suggests that other effects may also be present.
- **Trend found for 300-series and suggested for Mn-stabilized austenitic stainless steels.**

Estimation of SFE using quantum calculations

$$SFE = \frac{E^{hcp} + 2 * E^{dhcp} - 3 * E^{fcc}}{A}$$



- We use an indirect method of estimating SFE using free energies of various bulk crystal structures.

- Compared different density functionals; A few predict reasonable values of SFE, but most of the predict a negative SFE at zero temperature.

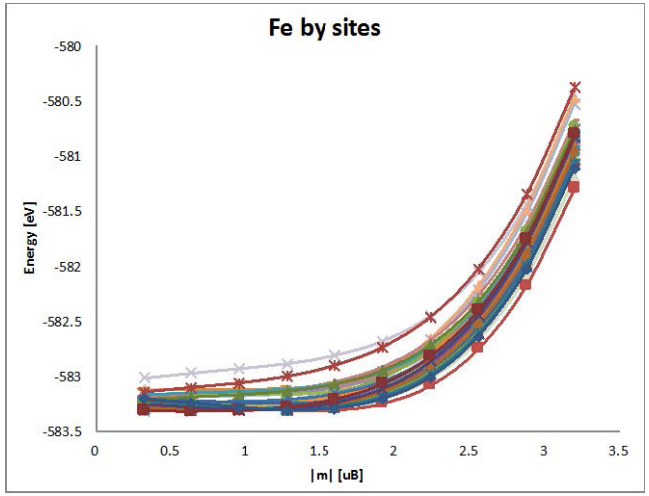
	FCC		HCP		dHCP		
	E/atom	V/atom	E/atom	V/atom	E/atom	V/atom	SFE (mJ/m^2)
PBE	-9.11	10.80	-9.12	10.63	-9.10	10.68	-21
PBEsol	-9.84	10.08	-9.86	10.07	-9.85	10.12	-152
PBE+U	-5.54	14.00	-5.55	13.82	-5.50	13.66	167
PW91	-7.72	10.81	-7.74	10.67	-7.73	10.73	-131
LDA	-10.25	9.78	-10.25	9.76	-10.24	9.78	36
AM05	-9.54	10.09	-9.59	10.00	-9.58	10.04	-388

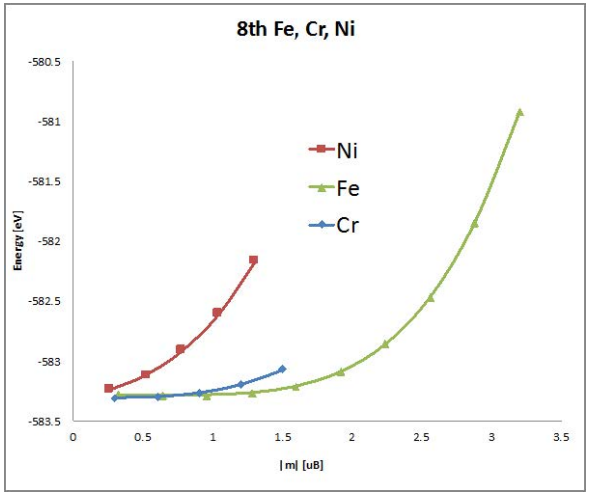
- May indicate instability of the different crystal phases (e.g. fcc) at low temperature, and the **necessity to include aspects relevant at higher temperatures**, such as thermal expansion of the lattice and inclusion of spin (magnetic) entropy.
- Previous studies by Reyes-Huamantinco *et al.* (2012) suggest that magnetic excitations are the main entropy contributor to the SFE in stainless steels.

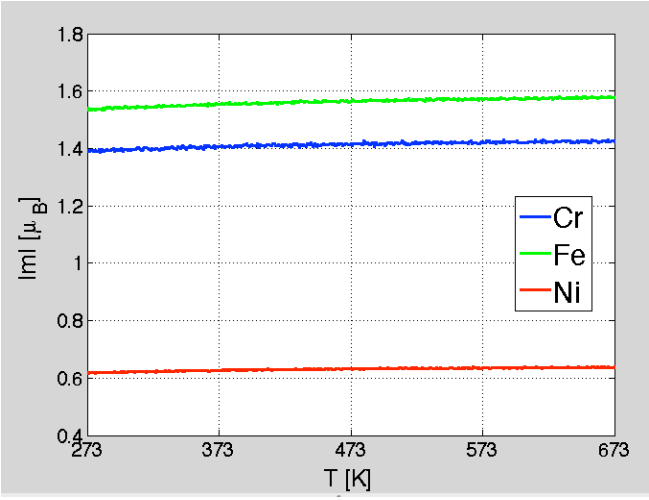
Impact of temperature and magnetism on SFE

- Calculate SFE from combining free energies (F) of different structures: $F = E(V,m) - T*S_{mag}(m)$
- Volume (V) and magnetic moments (m) depend on temperature (T).
- Assumption: Single-site magnetic fluctuations can be captured by a magnetic Hamiltonian describing local spin fluctuation (LSF) : $H_{mag} = \Sigma_i \, Energy(m_i)$
- Approach: use VASP to calculate LSF energies and a Monte-Carlo technique to obtain magnetic moments at finite temperatures that minimize H_{mag}:

14% Cr, 20% Ni, **fcc**





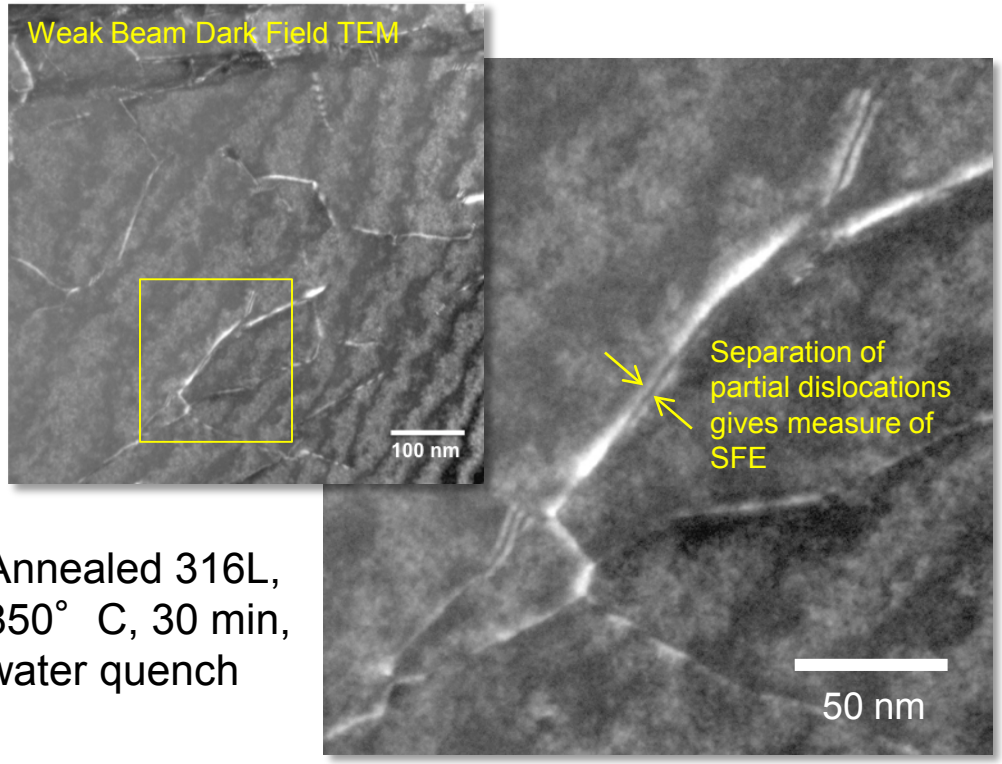


✓ Similar calculations will be performed for **hcp** and **dhcp** phases after which the **SFE** can be obtained.

Incorporation of volume and temperature effects should improve the accuracy of SFE estimates

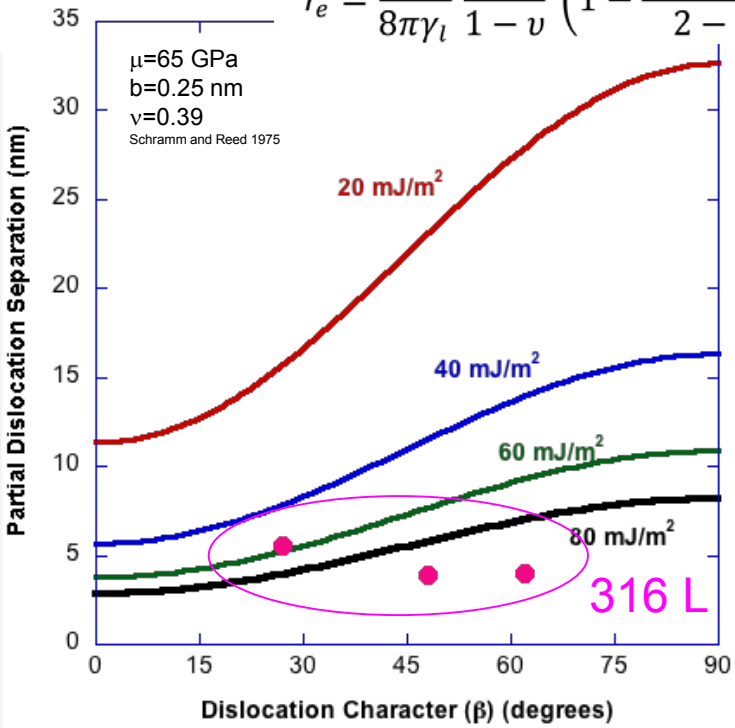
Microscopy measurements of SFE

Approach: Weak beam dark field TEM measurements to determine fault widths as function of dislocation character (angle of Burgers vector with respect to line direction)



Annealed 316L, 850° C, 30 min, water quench

$$r_e = \frac{\mu b^2}{8\pi\gamma_l}\frac{2-\nu}{1-\upsilon}\left(1-\frac{2\nu\cos 2\beta}{2-\upsilon}\right)$$



Initial measurements on 316L give **SFE ~60-100 mJ/m²** (c.f. XRD ~78 mJ/m² (Schram and Reed, 1975))

Next step: compare against lower SFE material (e.g.,304L ~18 mJ/m² from XRD)

Response to Previous Year Reviewers' Comments

- "The approach is generally good by including both experimental and computational effort. However, there is no clear indication how the experimental result will be used to validate the computational model."
- "Overall the effort's approach is well thought out. The integration of the experimental and computational paths could be better defined…"
- "It is not clear how the computational model will be validated."
  - Experimental effort now includes microscopy measurements of SFE to be used for validation.
  - Using literature survey findings to guide which low-Ni alloys should possess favorable mechanical performance, e.g. Mn-substituted steels, measuring fatigue life.
- "It's unclear if the SFE alone is a good descriptor for the performance of these alloys in this application. This is mentioned ..., and literature searching is proposed to address it."
  - Survey and analysis reveals that SFE does not correlate with some mechanical properties, e.g. yield strength, but **does** correlate with reduction of area in hydrogen. Potential correlation between SFE and fatigue performance is being evaluated by the experimental work.
- "…the project goals are to reduce system weight by 50% and system cost by 35%. It should be clarified … that the reductions are intended for BOP components only…"
  - Relevance and Objectives slide has been updated to clarify that weight and cost savings are with regard to BOP component materials.

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 implies significant changes in material strength due to hydrogen pre-charging and/or low temperature. An approach needs to be established on how to incorporate these changes into fatigue life predictions.
- **Resolution**: Smooth tensile samples are currently being made to measure the strength of the various conditions to account for these changes.

- **Challenge**: Currently examining extent to which temperature-related contributions to free energy affect SFE values. If influence is significant, high throughput nature of calculations may be compromised.
- **Resolution**: Use simple compositions to establish the magnitude of this effect, and its computational cost/speed relative to the overall calculations.

- **Challenge**: Is there a way for computational approach and knowledge of SFE have more immediate impact in the near-term?
- **Resolution**: Use thermodynamic method by Curtze *et al*. to provide an estimate of SFE for a given alloy composition, and couple with Dakota to rapidly survey composition 'space'.

Future Work

Remainder of FY16:

- Perform testing of smooth tensile bars to assess strength under various conditions, i.e. hydrogen pre-charged, low-temperature
- Quantitatively predict the SFE for 3 tertiary (Fe-Cr-Ni) compositions relevant to commercial austenitic stainless steels → include temperature effects
- Computationally quantify SFE for commercial alloys and Fe-Cr-Ni-Mn-Al alloys
- Create software infrastructure to optimize alloy composition
- ***Go/No Go***: Identify one or more candidate materials that potentially meet 35% reduction of cost and 50% reduction of weight using alternative commercial alloys

FY17:

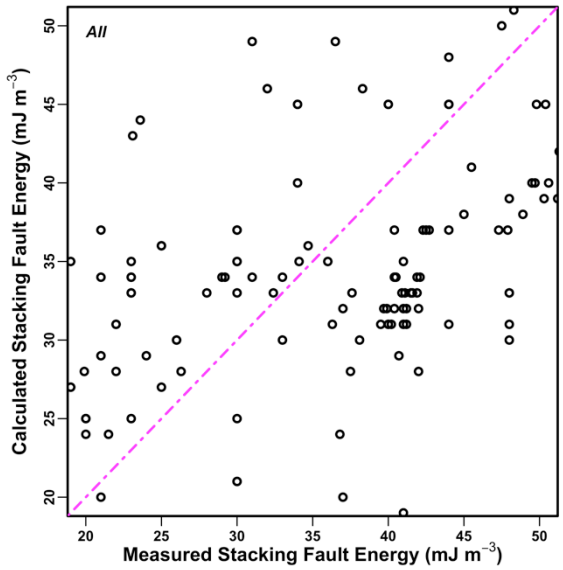
- Quantify fatigue behavior of high-strength alternatives to annealed type 316/316L, e.g. Mn-substituted alloys, N-strengthened alloys
- Combine software infrastructure with DFT calculations to optimize alloy composition and quantify trends in estimated SFE
- Identify one or more candidate materials that potentially meet reduction targets using alternative commercial alloys **or** computational alloy design

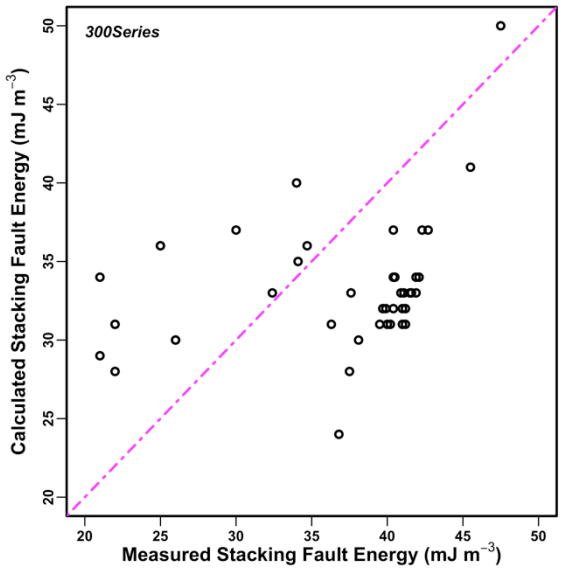
Summary

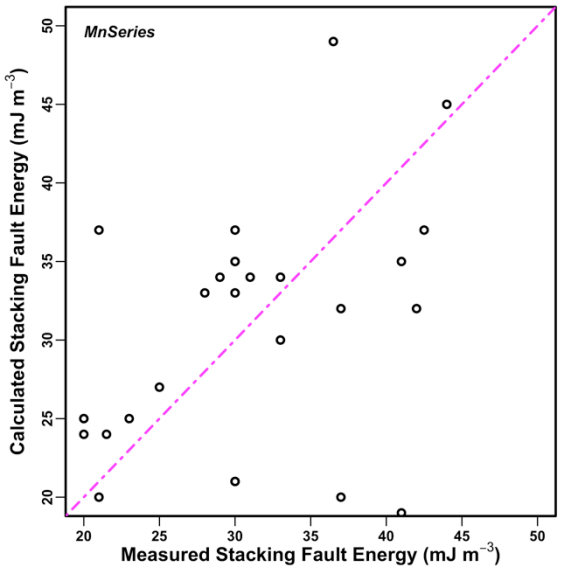
- Fatigue performance in external hydrogen can be captured by a simplified test method with internal (pre-charged) hydrogen.
  - Proper normalization of applied stress is crucial to interpreting results
- Strain hardening provides a route to increase fatigue life for 'baseline' annealed materials. **(reduced wall thickness = lower component weight)**
- Annealed XM-11 has the same fatigue performance as the tested strain-hardened 316L. **(lower cost material)**
- Testing at low temperature suggests that limiting behavior is determined by room temperature performance.
- Literature survey and analysis shows that SFE correlates with reduction of area in the presence of hydrogen for 300-series austenitic stainless steels.
- Use of DFT to estimate SFE indicates instability of the austenitic phase at low temperature; necessary to include thermal expansion and magnetic entropy
- TEM is providing data to validate calculations of SFE for alloys
- TEM and extended fatigue analysis (e.g. fractography) are being used to add value to understanding of behaviors and bridge observations at different length scales

Technical Back-Up Slides

Using limited literature data to correlate SFE with mechanical properties in hydrogen







'Everything':

- *0 < Total Alloy wt % <50*
- *0 < SFE < 60*

Restrict to 300-series SS

- *8 < Ni wt% < 13*
- *0 < Mn wt% < 2*
- *0 < C wt% < 0.1*

Restrict to C-Mn stabilized

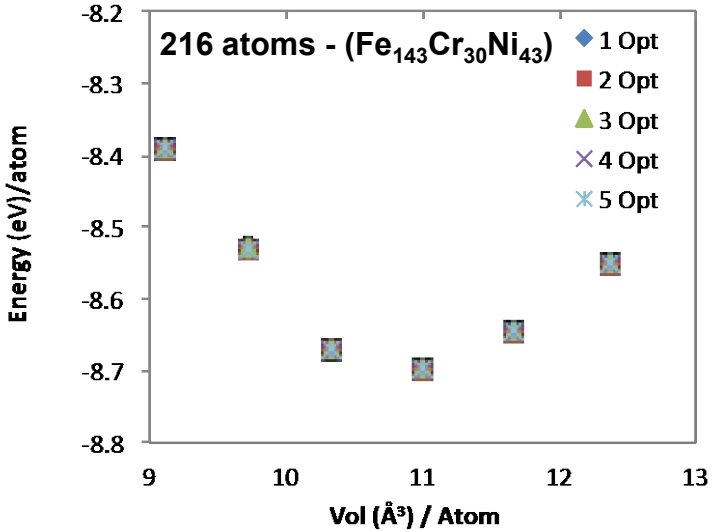
- *2 < Mn wt% < 30*

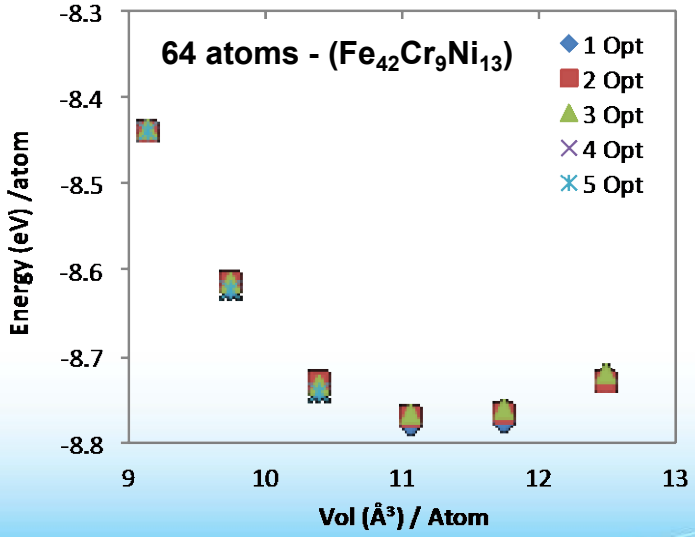
As SFE of steel is difficult to measure experimentally, and investigations of hydrogen degradation generally do not report the stacking fault energy, we use the thermodynamic model by Curtze et al.: $\gamma_{SFE} = 2\rho\Delta G^{\gamma\rightarrow\varepsilon} + 2\sigma$

Calculated values display some systematic error toward predicting low SFEs, but appear to represent an acceptable approximation to observed values, enabling calculation of stacking fault energy for alloys with reported hydrogen interactions.

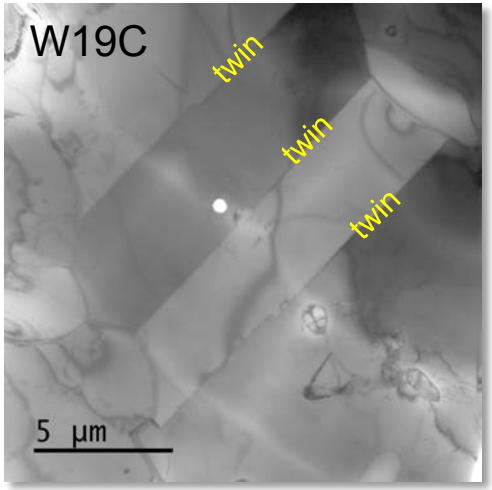
Calculation results: Effect of alloy concentration

- Goal – determine the effect of alloy configuration; what size unit cell is needed to limit energetic and structural variability?
- DFT/PBE was used to construct volume/atom vs. energy/atom curves for 5 randomly generated austenitic stainless steel alloys
  - Two different size unit cells were considered: 216 (top) and 64 (bottom) atoms
- Virtually no variability in energy/atom and volume/atom was observed for the two different unit cells
- Result – a 64 atom unit cell is sufficient for minimizing alloy configuration variability

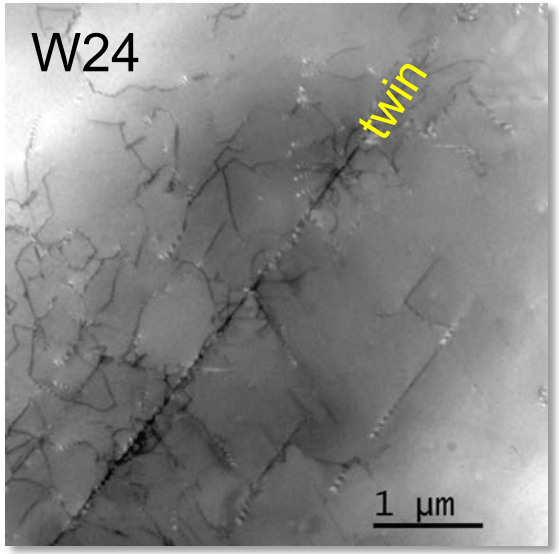




Applying TEM to investigate dislocation and stacking fault configurations in Al-containing austenitic SS alloys



Twin boundaries, defects closely related to stacking faults are observed in all the alloys



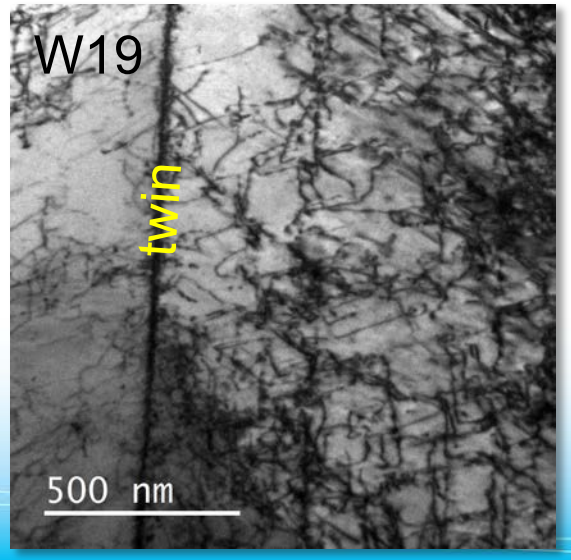
Strong crystallographic alignment of dislocation lines along {111} planes.

Collaboration with Thorsten Michler, Adam Opel AG (Germany)

T. Michler, Int. J. Hydrogen Energy 38 (2013)

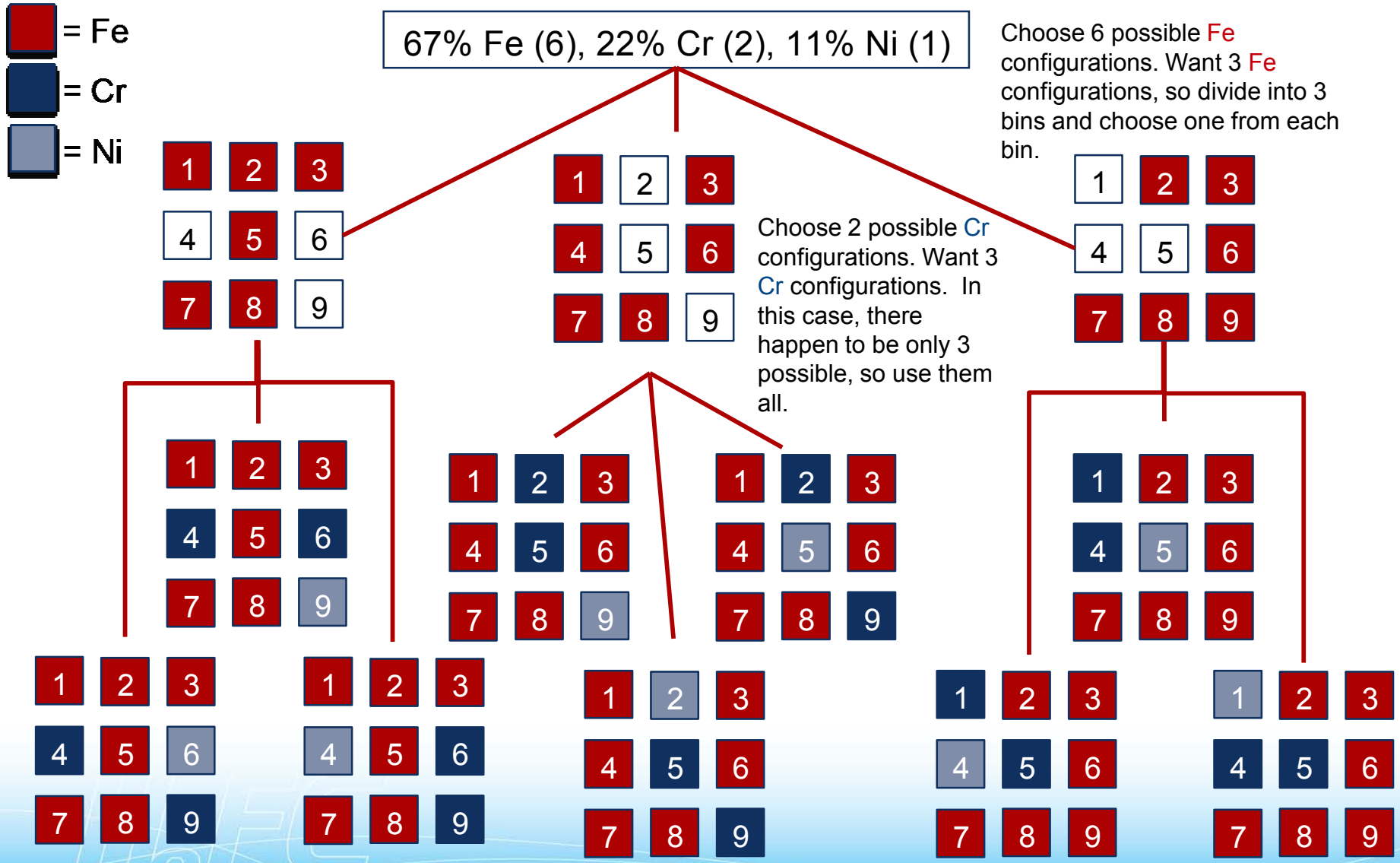
Alloy Compositions from Thorsten Michler

Alloy	C	Si	Mn	Cr	Ni	Cu	Al
W19	0,12	<0,2	10	13	8	-	2,5
W19C	0,12	<0,2	10	17	8	-	2,5
W24	0,05	0,2	12	18	8	3	0,1



Signature of low stacking fault energy?

Nested sampling/design of experiments preserves composition and separates effects

- Randomly sample composition space.
  - Simultaneously sample %Fe and %Cr over defined ranges. %Ni is defined in terms of the other two.
- Given a composition, design of experiments-based approach to choose Fe configuration.
  - Partition all possible Fe configurations into bins, with # bins = # Fe configurations desired.
  - Choose one configuration randomly from each bin.
- Given composition and Fe configurations, design of experiments-based approach to choose Cr configuration.
  - Partition all possible Cr configurations (where no Cr occupies same site as Fe) into bins, with # bins = # Cr configurations desired.
  - Choose one configuration randomly from each bin.
  - Ni configuration is now also fully defined, i.e., Ni occupies all sites not occupied by Fe or Cr.

Notional configuration generation for 9-atom system