SAND2017-7142PE

Computational Materials Discovery to Reduce Cost and Weight of Balance of Plant (BOP) Components in Hydrogen Storage Systems for Fuel Cell Vehicles

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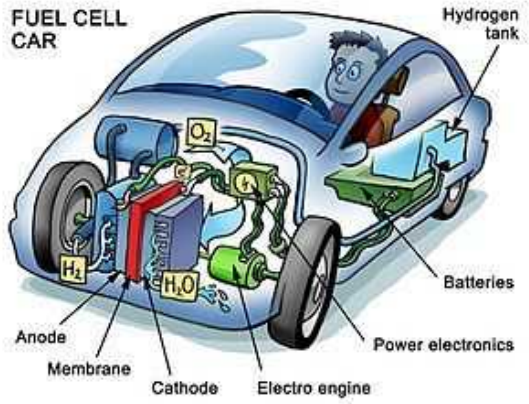
Advanced Computing Technology Team Meeting
July 12, 2017

Motivation: Lowering costs for hydrogen-fuel cell vehicles

- Hydrogen storage systems require a number of ancillary components to the primary storage vessel: tubing, valves, pressure regulators, pressure relief devices, pressure transducers.

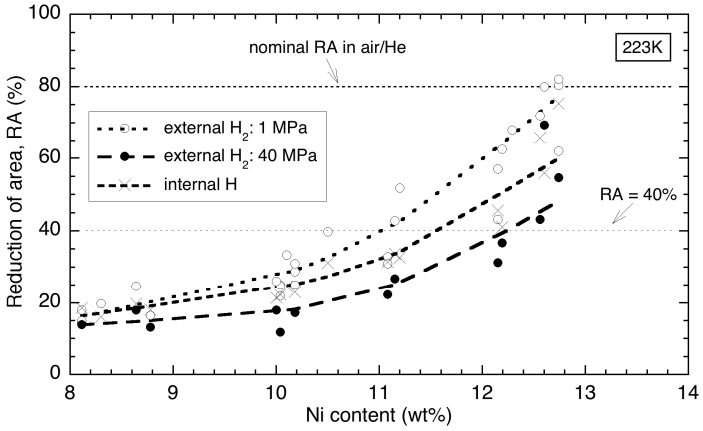


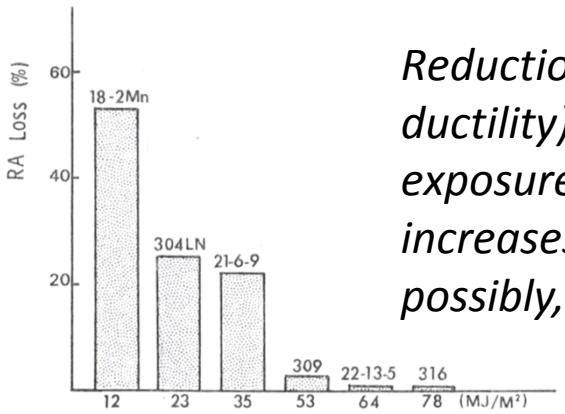
- Structural materials for these balance of plant (BOP) components typically include…
  - Annealed type 316L austenitic stainless steel (Ni content >12 wt%)
  - A286 precipitation-strengthened austenitic stainless steel (Ni ~30 wt%)
- BOP onboard vehicles accounts for:
  - 30-57% of total system cost
  - 15-20% of total system mass

Computation may offer a solution!

- ***Identify alternatives to high-cost metals for high-pressure BOP components***
  - Reduce cost by 35%
  - Reduce weight by 50%

Experimental observation: Hydrogen embrittlement is more severe for lower-Ni content stainless steels than for high-Ni content ones…





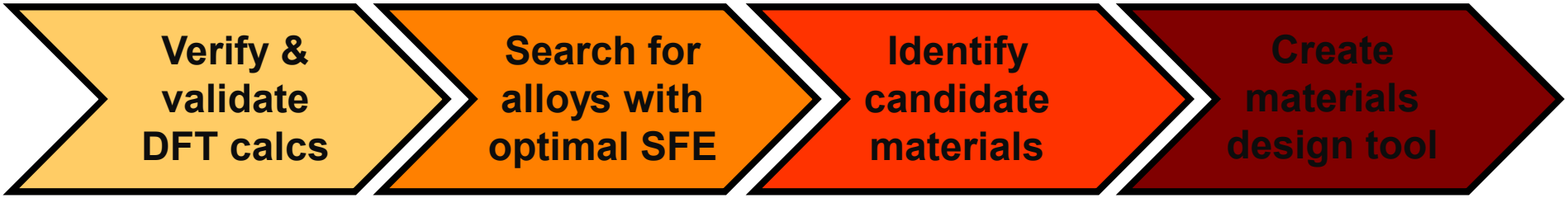
Reduction of area (tensile ductility) decreases with exposure to hydrogen, but increases with Ni content and, possibly, stacking fault energy.

Hypothesis: This effect could be due to the higher stacking fault energy (SFE) of steels with high-Ni content, i.e. higher SFE → increased dislocation mobility → more ductility.

- **Goal**: Use quantum-based computational approaches to discover alloy compositions that possess favorable material properties that correlate with mechanical performance in hydrogen environments (i.e. SFE).

Approach: Verify assumption; Use high-throughput computation to formulate "better" materials

- Survey existing literature to assess SFE relations to hydrogen effects on mechanical properties.
- Develop and implement density functional theory (DFT) based approaches for calculating SFE.
- Calculate SFE for known commercial (316L, 21-6-9) and research (10-8-2.5) alloys, and validate against literature values and experimental measurements.
- Develop algorithms to perform high-throughput, guided searches of Fe-Cr-Ni-Mn-Al composition 'space' to find alloys with optimal values of SFE.
- Work with industry partner (Carpenter Technology Corporation) to determine the feasibility and evaluate the economic benefit of synthesizing optimal alloys.
- Use DFT results to create a materials design tool useful to industry and scientific community.

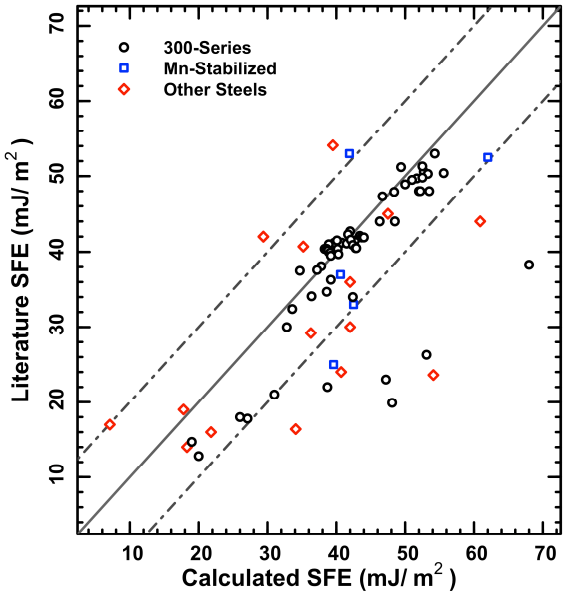


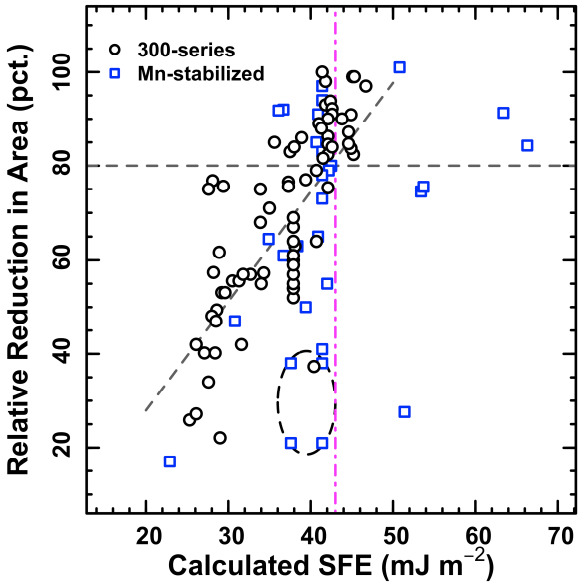
How does SFE trend with material sensitivity to H_2?

- Limited measurements of SFE are available, and investigations of hydrogen degradation generally do not report SFE.
- To enlarge data set, we used an analytic thermodynamic model that includes considerations of segregation, interfacial energy and magnetic entropy.

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

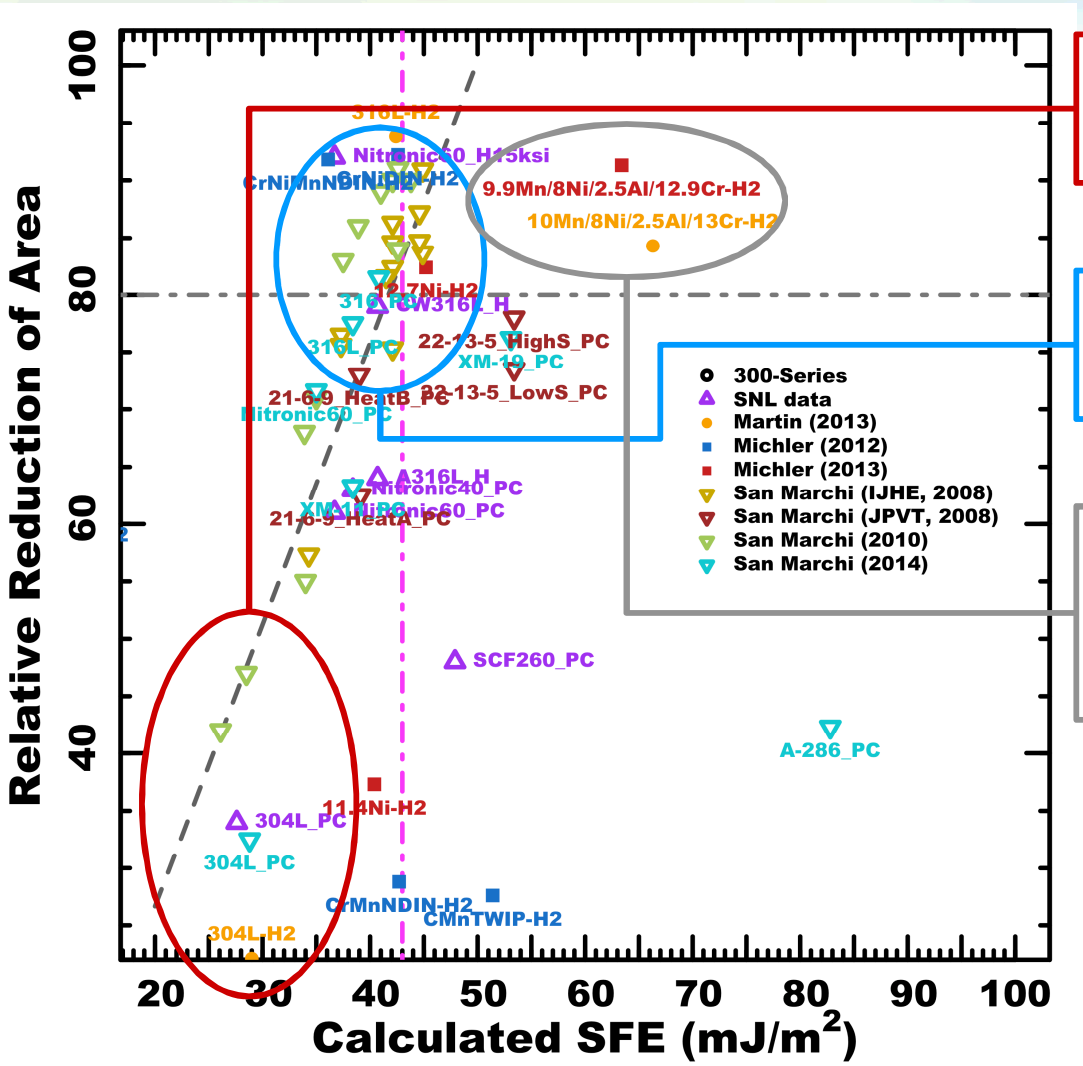
Based on: Dumay, et al., Mater. Sci. A, 2008; Saeed-Akbari, et al., Met. Trans. A, 2010; Curtze, et al. Acta Mater. 2011





Relative reduction of area (RRA) was found to track with SFE below a threshold value. Near and above this value, high SFE commonly corresponds with high RRA.

Thermodynamic model provides insights on hydrogen sensitivity and effects of composition variability



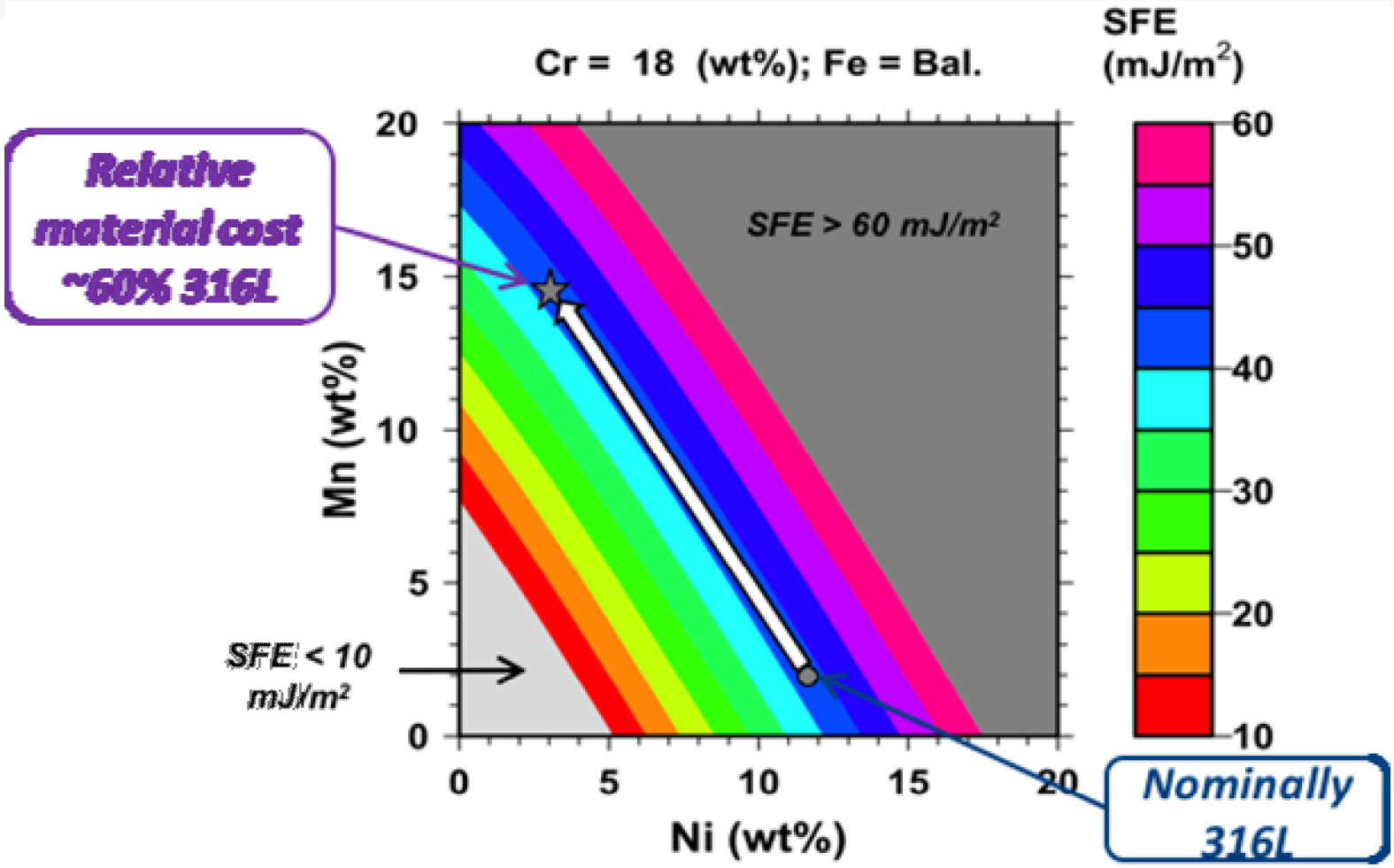
low SFE values indicate sensitivity to hydrogen degradation

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

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

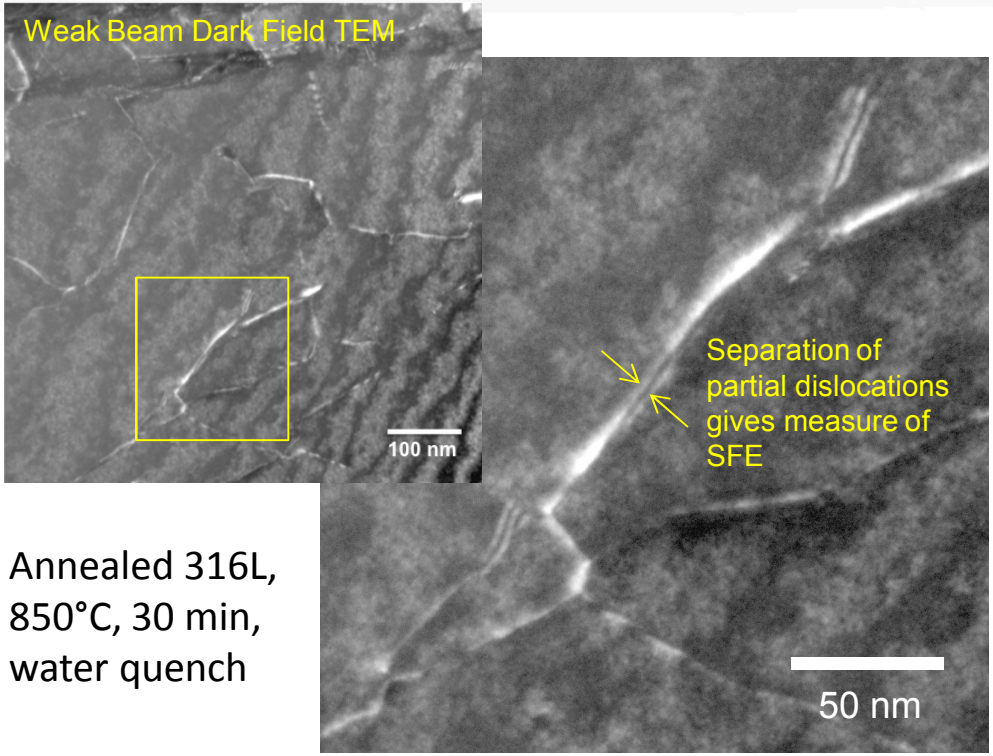
High SFE is necessary, but not sufficient for low sensitivity to hydrogen

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

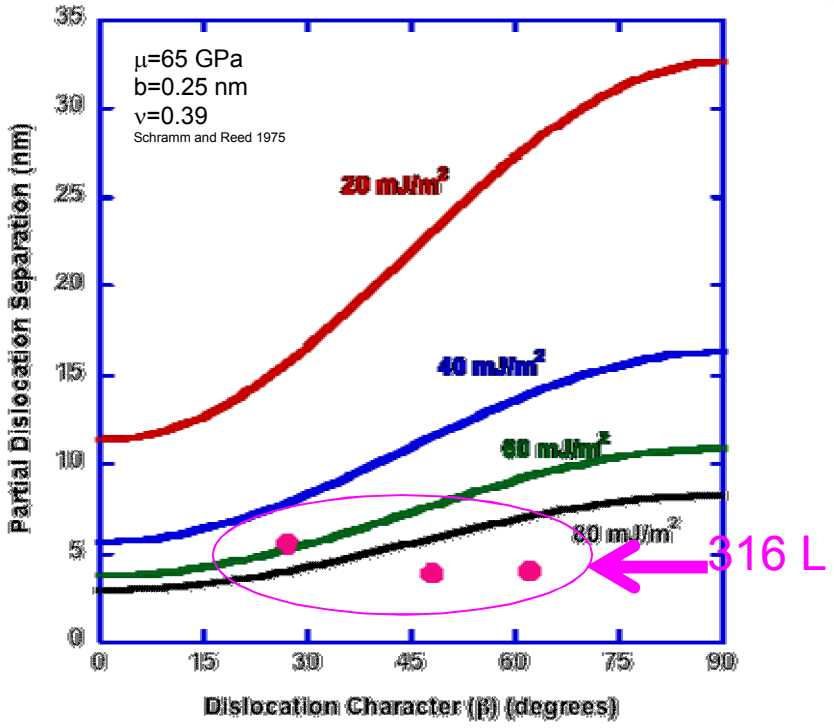


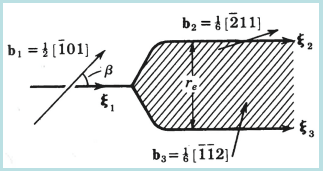
Microscopy measurements of stacking fault energy

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





ref. Hirth & Lothe, Theory of Dislocations 1992

Analytical expression for partial dislocation spacing as function of SFE:

Shear modulus, Burgers vector

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

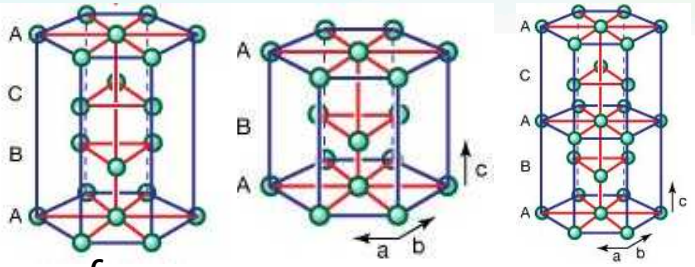
partial separation, SFE

- Measurements on 316L give **SFE ~60-100 mJ/m²** (c.f. XRD ~78 mJ/m² (Schram and Reed 1975))
- Measurements of high-Mn alloy tested by Michler *et al.* gives **SFE ≥ 63 mJ/m²**
- These high values are pushing this technique's limits of due to narrow separation of partial dislocations.

Use density functional theory (DFT) to provide high accuracy estimates of SFE

$$SFE(T) \approx \frac{F^{hcp}(T) + 2F^{dhcp}(T) - 3F^{fcc}(T)}{\sqrt{3}a_{fcc}^2/4}$$

$$F = E\big(V(T), m(T)\big) - T * S_{mag}(m(T))$$



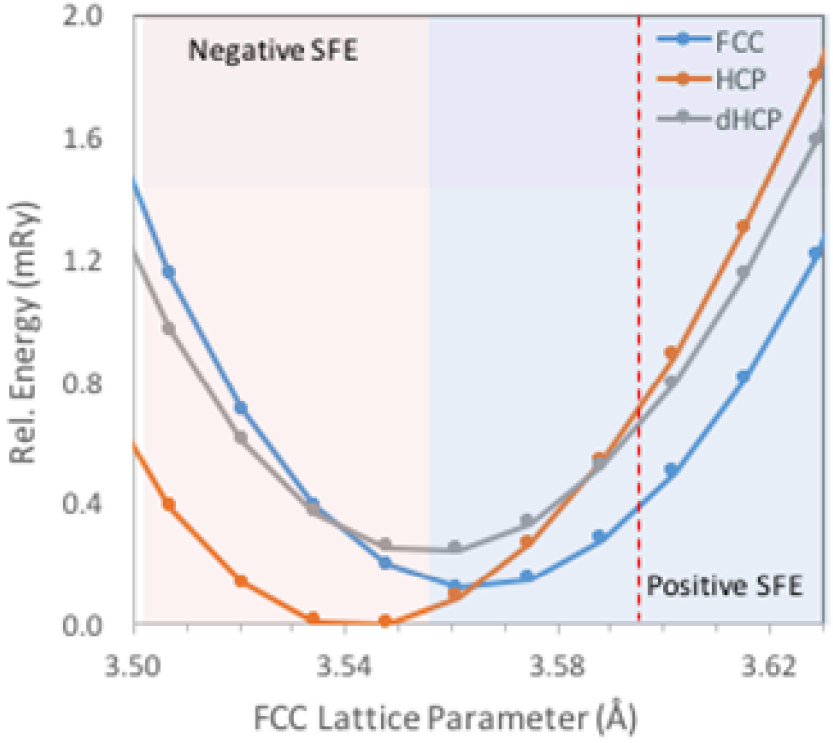
Two approaches for calculation of SFE:

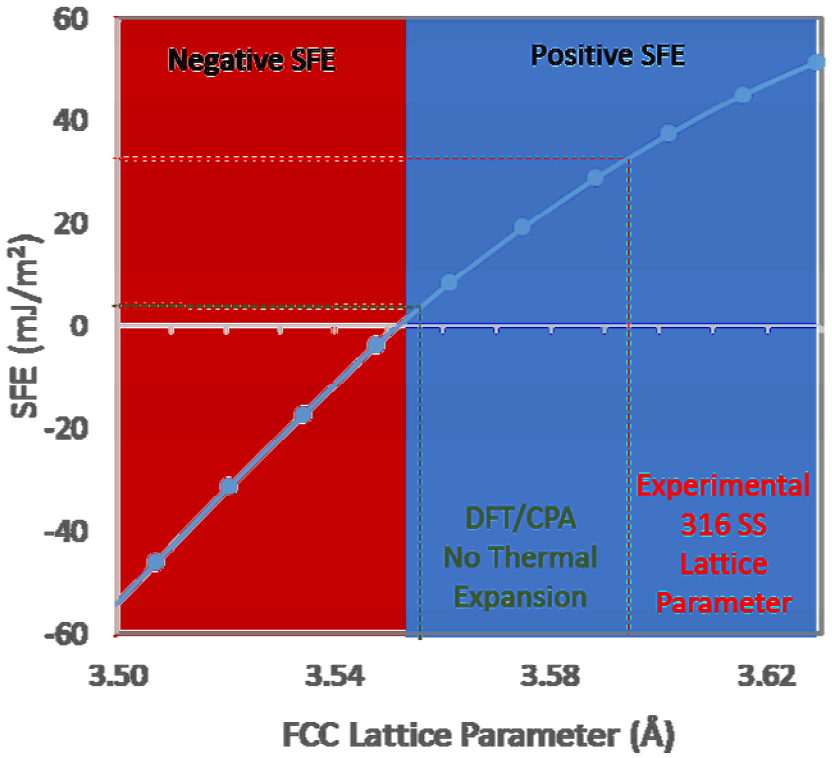
(1) Full *ab initio* calculation of SFE (explicit atoms of each species):

a. Generate a special quasi-random structure for a given composition to obtain a statistically random configuration.
b. Use DFT to perform a geometry optimization to determine the enthalpy and the magnetic/spin moment vectors.
c. Use longitudinal spin-fluctuation (LSF) Monte Carlo to determine the magnetic/spin entropy.
d. Repeat for three crystallographic phases

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

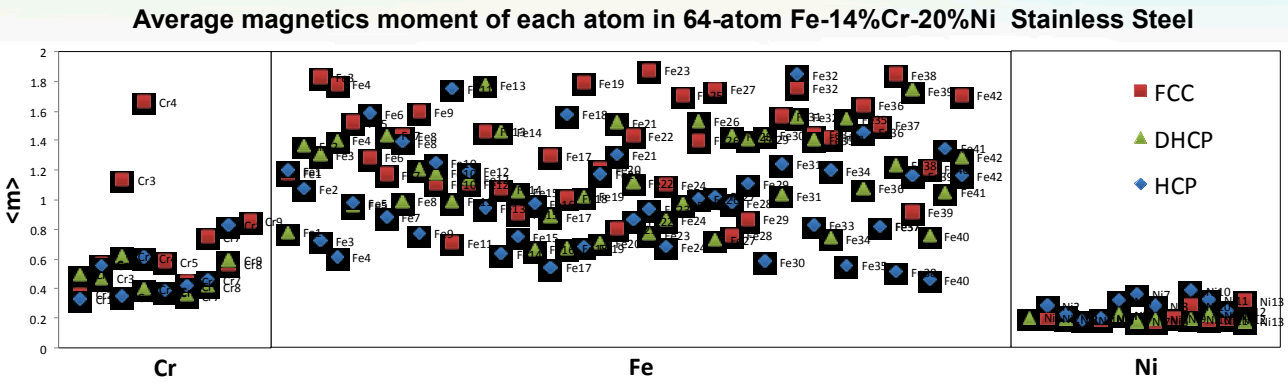
Thermal lattice expansion and magnetic entropy are critical to DFT prediction of SFE

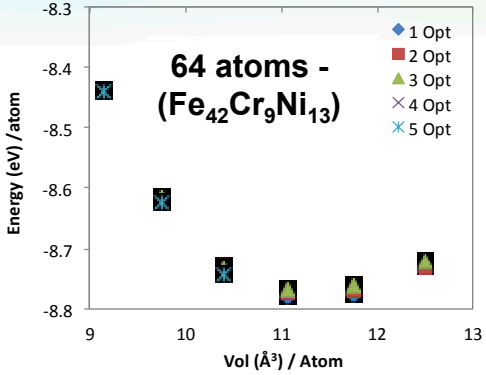


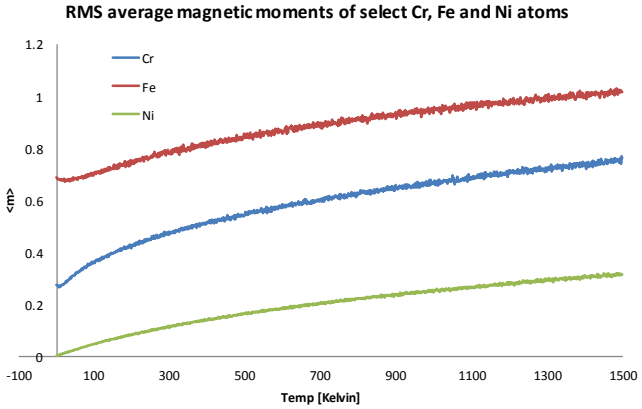


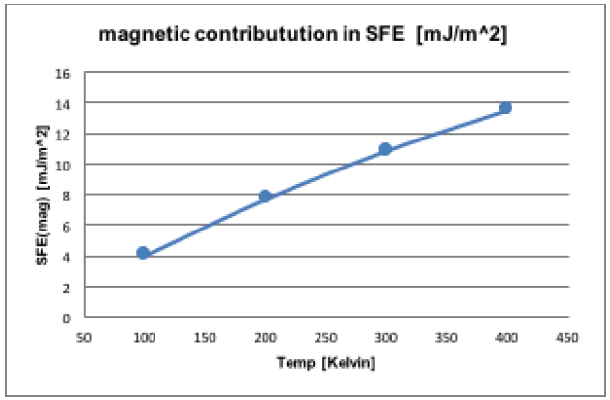
- SFE is estimated by a difference between energies of FCC, HCP and dHCP structures, which are very small, particularly at the room temperature lattice size.
- Thus, SFE prediction can be very sensitive to how well lattice size is predicted.
- These dependencies are what make accurate prediction of SFE using DFT-based methods a formidable challenge.

Full DFT computation of SFE requires a large computational effort









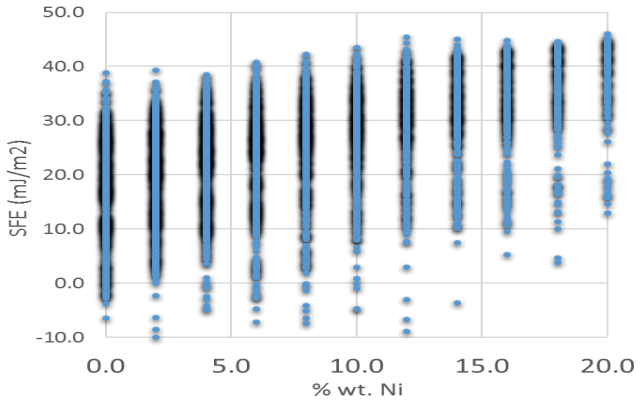
Strategy of performing exact DFT calculations is computationally intensive and not suitable for high-throughput screening

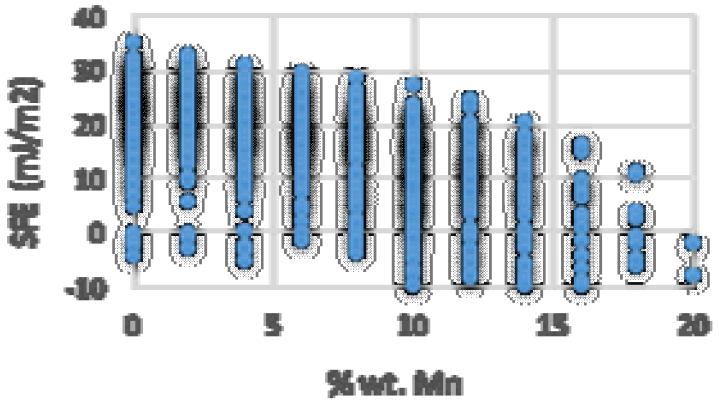
Geometry optimization of a given phase and composition:
384 processors x 48 hours runtime = ***18,432 cpu—hours***
Estimation of magnetic/spin entropy of a 64-atom system:
552 DFT calculations x 128 processors x 8 hours = ***565,248 cpu-hours***

Cohesive potential approximation (CPA) method introduces computational efficiencies to SFE estimation

- A small series (12) of DFT/CPA calculations is used to construct an energy-volume curve for the fcc phase and determine the theoretical lattice parameter.

  Note: Electronic and magnetic entropy effects, at 300K, are included self-consistently using the longitudinal spin fluctuation (LSF) method.
- Optimal cell volume is determined by spline interpolation and scaled to include thermal expansion (~0.5%). This results in a lattice parameter and SFE consistent with experimental results for 316 stainless steel, for example.
- Construct hcp and dhcp unit cells based on the above optimal cell volume.
- Calculate free energy for each phase (fcc, hcp, dhcp).
- Estimate SFE using the axial next-nearest-neighbor Ising (ANNNI) model.



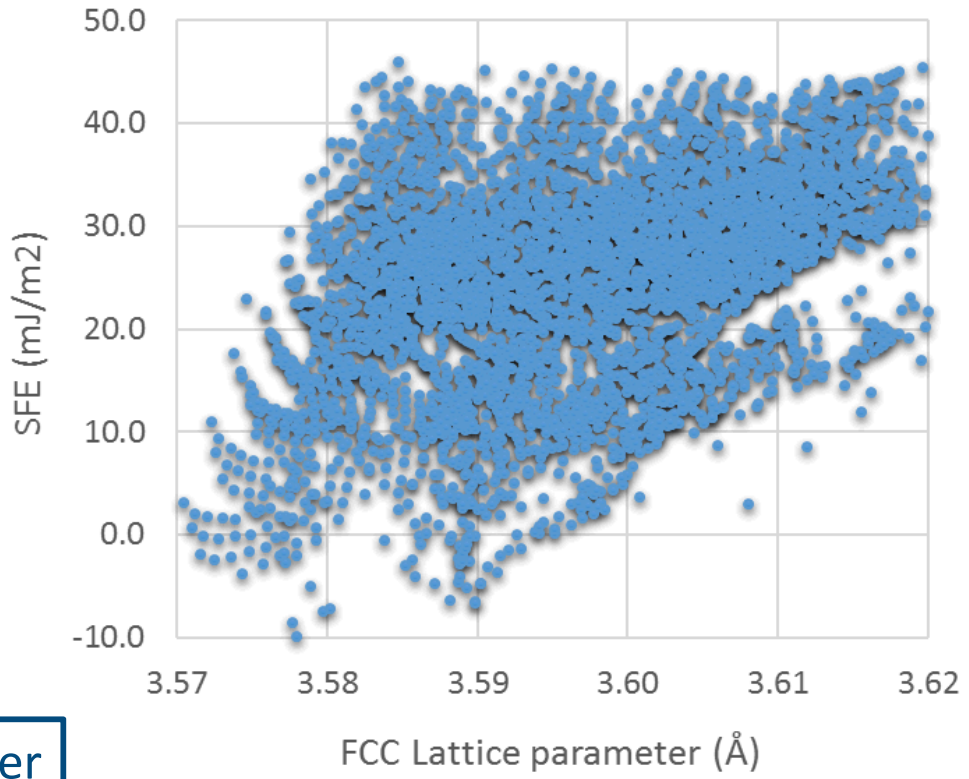


DFT/CPA approach used to generate database of alloy compositions with fewer assumptions than TD model

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.

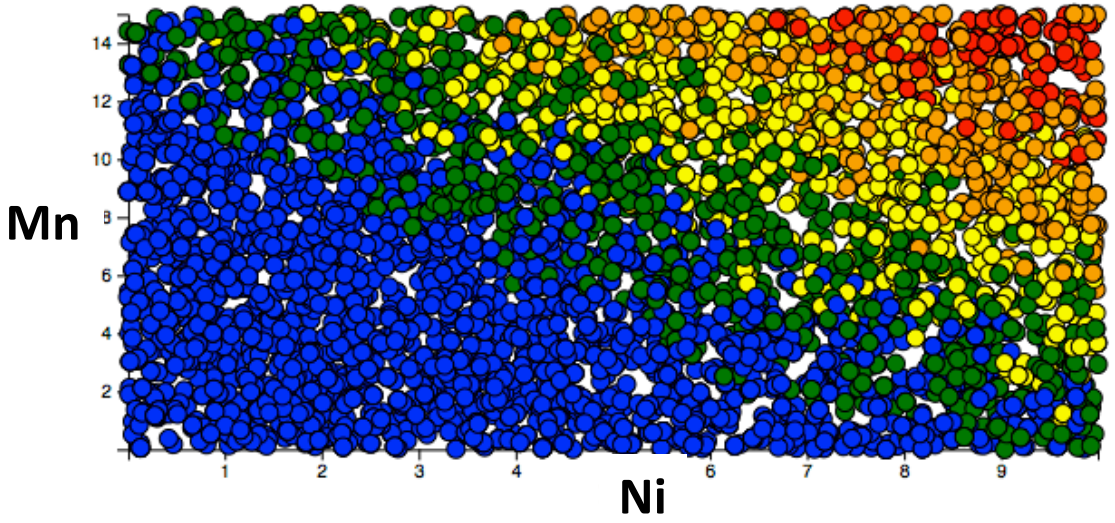


Calculations suggest lattice parameter (an easier quantity to measure) could serve as a proxy for SFE

In Progress: Comparison with thermodynamic model predictions

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.

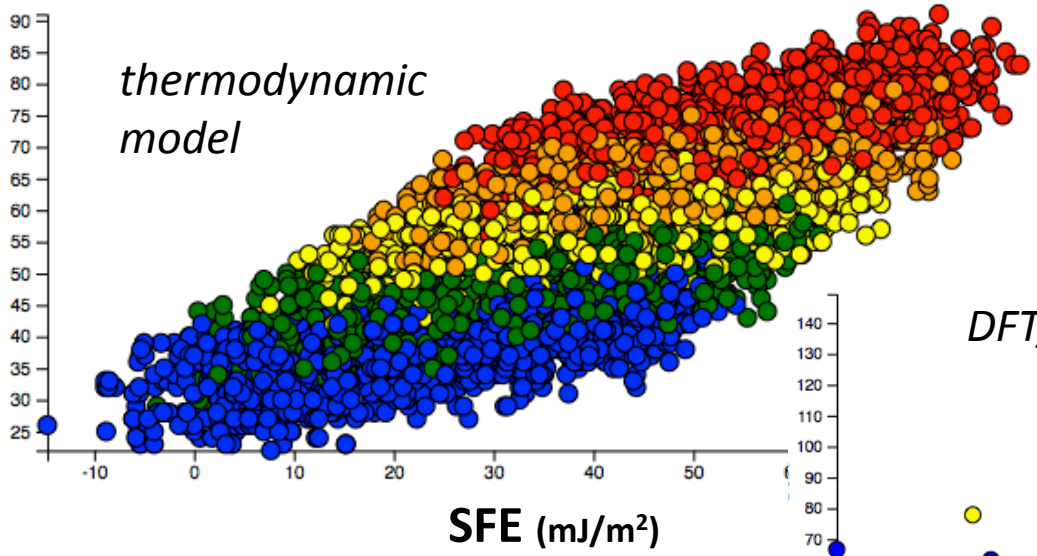
SFE 40 50 60 70

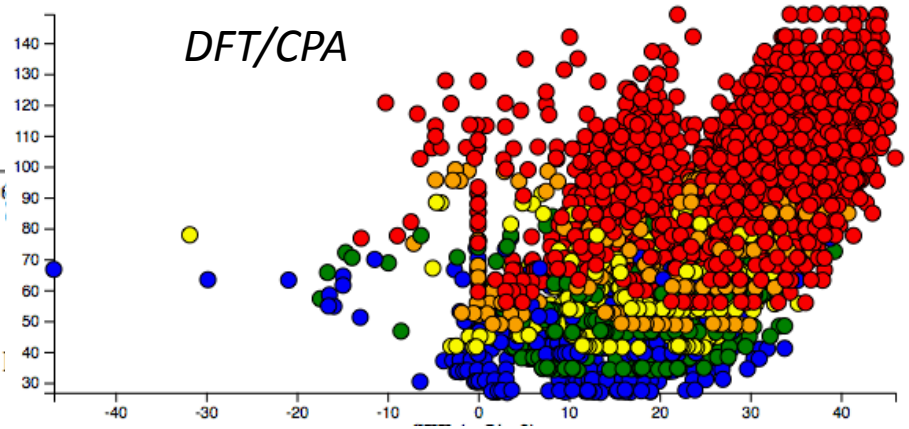
Color contours by SFE

Download Chart
Download Simulation Details

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

Cost (relative units)





X-Axis: SFE Y-Axis: cost

The fields below allow for configuring a filter on the points displayed.

Filter: Cr

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

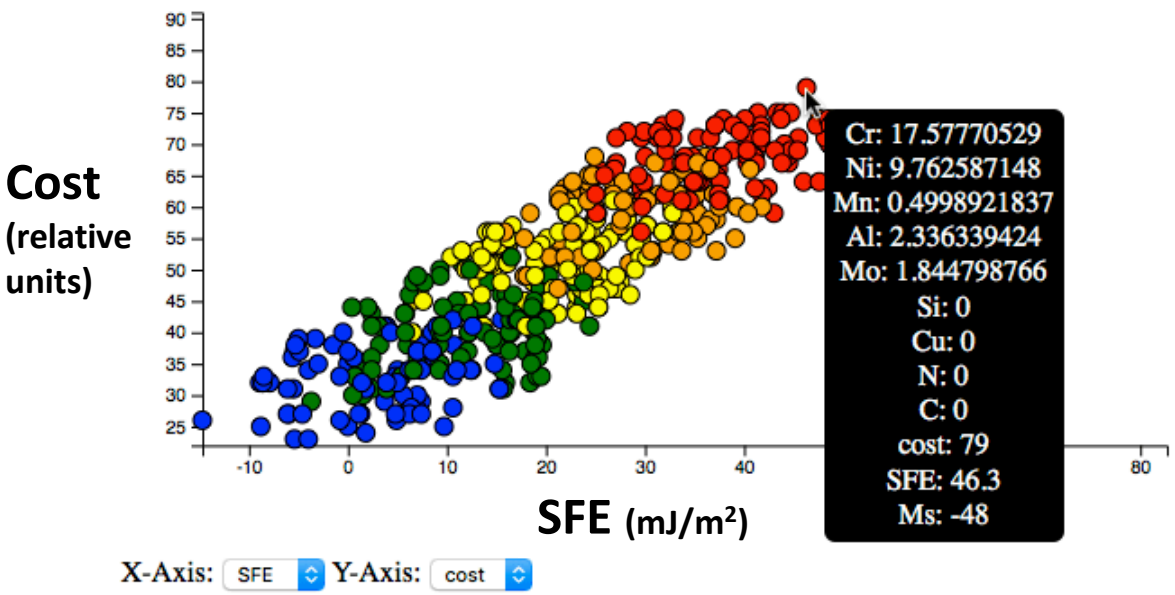
Ni 2 4 6 8

Color contours by Ni

Download Chart

Download Simulation Details

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

Color contours by Ni

Future Work

Remainder of FY17:

- 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:

- Study of deformation and crack growth mechanisms in hydrogen-assisted fatigue
- Apply concepts to aluminum alloys
- Expansion of web-based tool for estimations of other intrinsic material properties that have relevance to performance characteristics