Accelerating High Temperature Operation Development of High Entropy Alloys via High Performance Computation

Kenneth D Smith, Ryan Deacon, Soumalya Sarkar, John Sharon

E Hartford, CT

Michael Gao, Zongrui Pei, De Nyago Tafen

Albany, OR

Crosscutting Review
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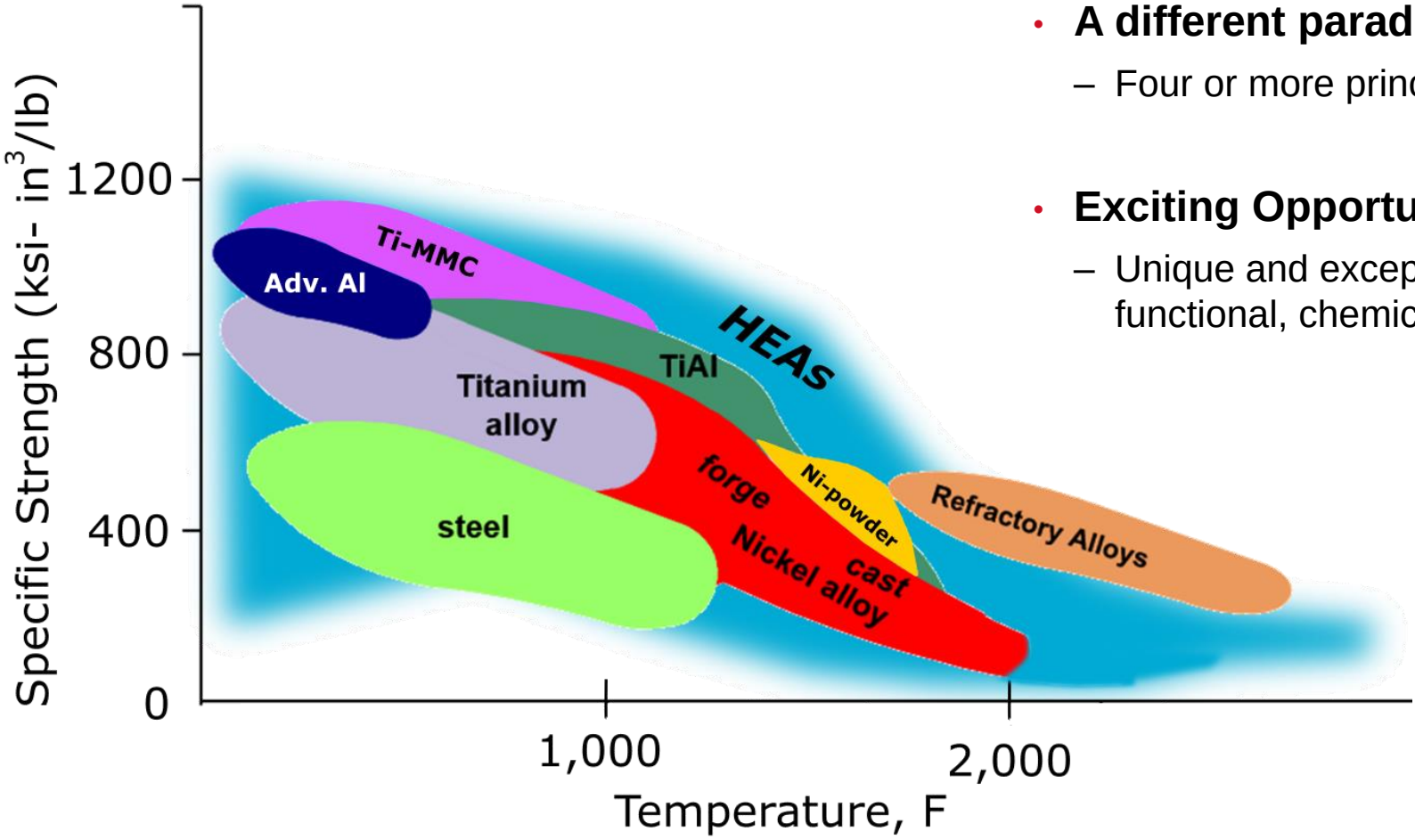
“New” Alloy Design – High Entropy



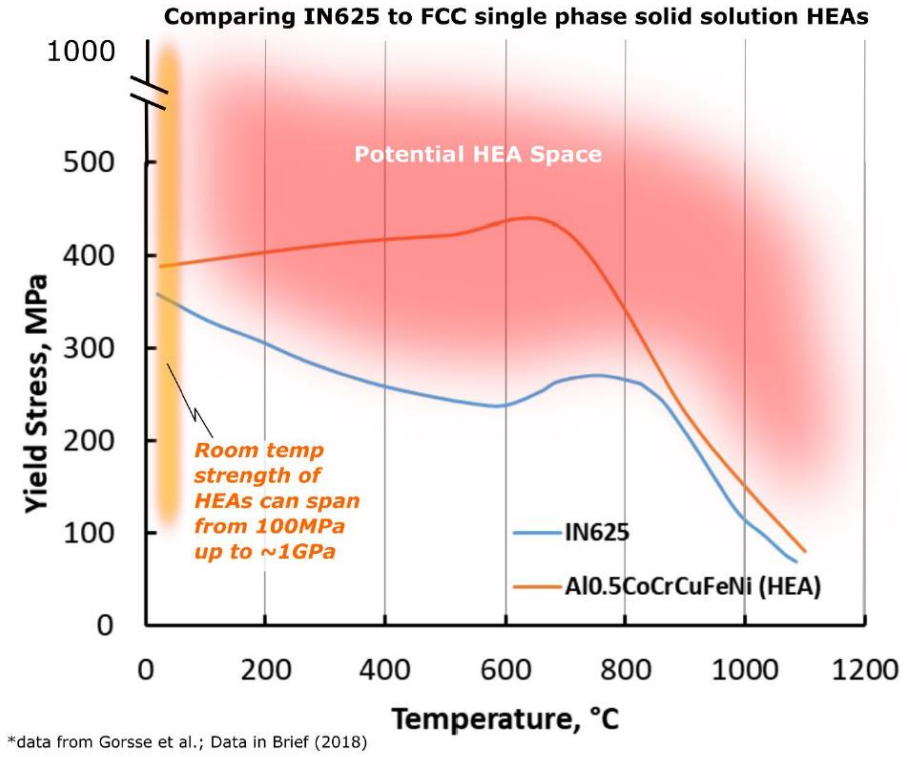
- **A different paradigm**
  - Four or more principal elements at ~ 5-35 at.%
- **Exciting Opportunities**
  - Unique and exceptional properties: mechanical, functional, chemical, etc.
- **Challenges**
  - Over 592 billion compositions for 3-6 principal elements from 72 metals.

How to approach the vast composition space & identify high performance alloys?

Program Objective

Demonstrate HPC models for temperature-dependent yield strength and oxidation models to guide new HEA identification and evaluation with performance similar to or better than Inconel 625 for deployment into AUSC power generation

- Advanced Ultra Supercritical (AUSC) operation needs higher temperature capable materials
- Nickel alloys present an economic challenge to AUSC adoption
  - Estimated to be 10 times the cost of ferritic steels[1]
- High Entropy Alloys (HEA) present an opportunity to use the vast compositional space to identify new candidate materials
- New computational methods needed to guide alloy selection



*data from Gorsse et al.; Data in Brief (2018)

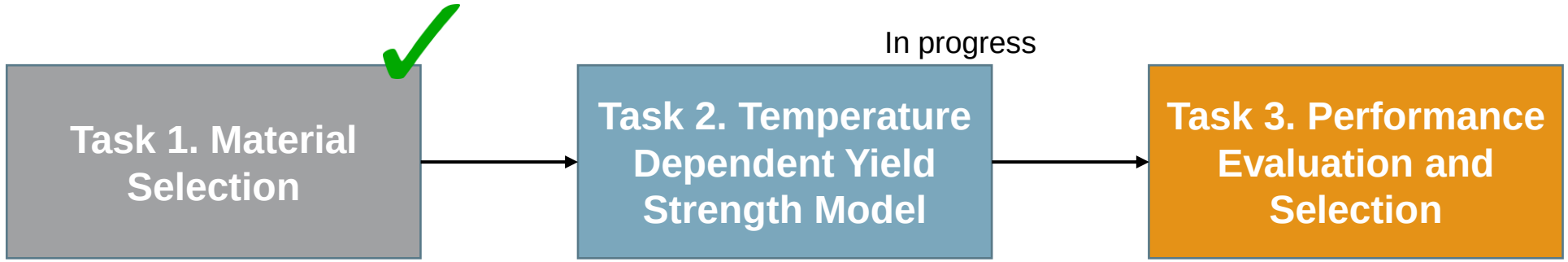
[1] G. Booras, J. Powers, C. Riley, H. Hendrix, "Engineering and Economic Analysis of an Advanced Ultra-Supercritical Pulverized Coal Power Plant with and without Post-Combustion Carbon Capture Task 7. Design and Economic Studies", DOE Contract DE-FE0000234 Final Report, 2015.

Advanced computational approaches to identify new HEAs

Selection Basis for Single Phase FCC Materials

Considerations	Advantages	Disadvantages
FCC Materials	- Ductility - Oxide formation - Lower cost materials match operating temperature ranges	- Limits on operating temperature
Precipitate Formation	- Computationally feasible with DFT and ML-searching algorithm - No complex computation/experiments to determine precipitation kinetics - Potential lower limit for strength	- Potentially limit maximum strength possible
Evolution in service	- No coarsening or strengthening phase depletion over time	- Doesn't limit all evolution - Limited long-time HEA testing completed to date
Economic	- Remove lengthy precipitation cycles from sluggish kinetics - Baseline for revised techno-economic analysis	- Materials development costs

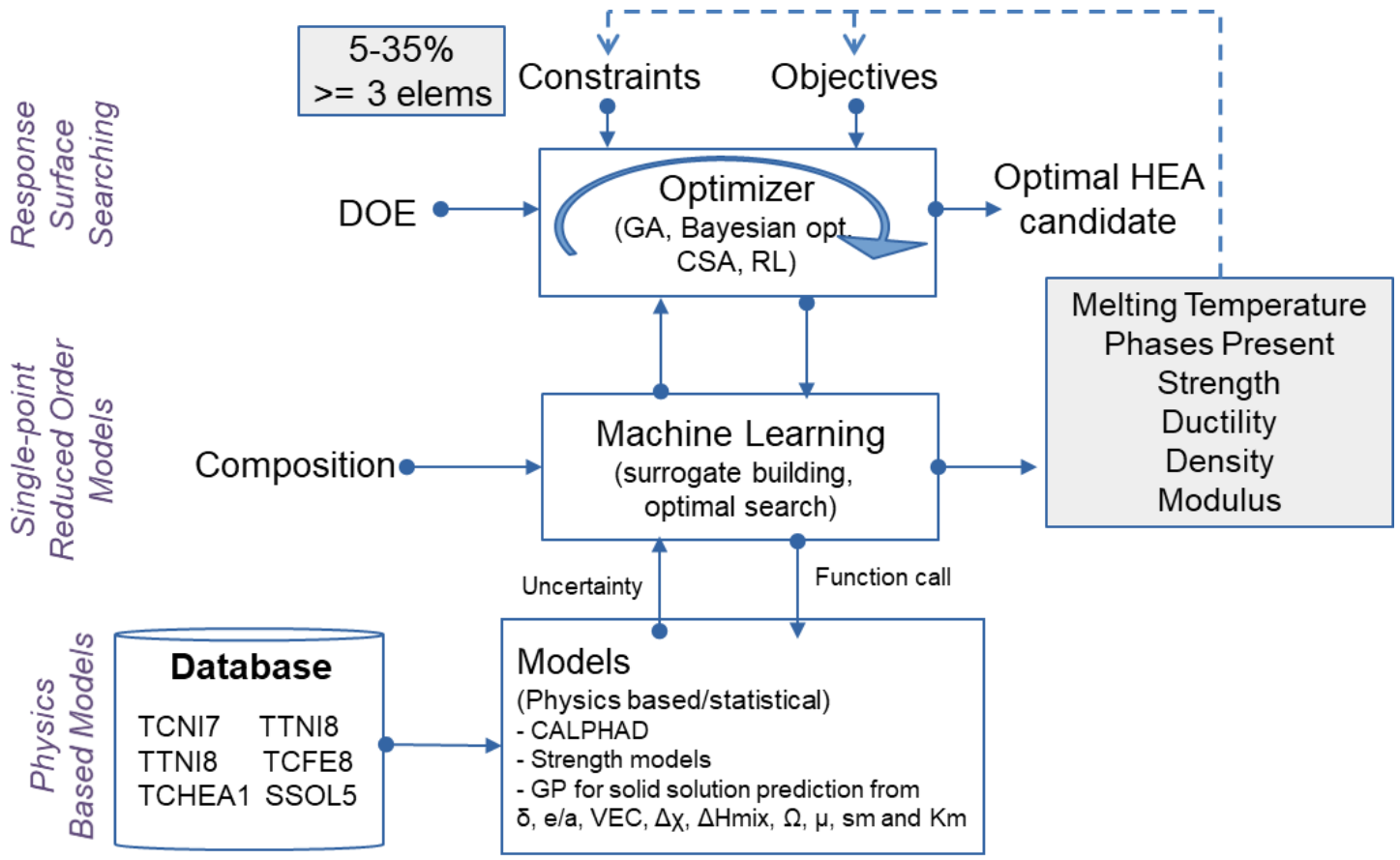
Overall Program Tasks



	Task 1. Material Selection	Task 2. Temperature Dependent Yield Strength Model	Task 3. Performance Evaluation and Selection
Activities	- Evaluate model approach to guide material selection for strength and oxidation - Change in HEA selection from new models	- Computational model for HEA yield stress of different HEAs at different temperatures - Reduced order model potential - Experimental validation data	- Evaluate model approach to guide material selection for strength and oxidation - Change in HEA selection from new models/criteria
Information Flow	- NETL: optimization criteria - RTRC: compositions	- NETL predictions - RTRC experimental results	- NETL revised strength/oxidation criteria - RTRC experimental results
Deliverables	1. NETL: Identify optimization criteria 2. RTRC: Identify candidate HEA	1. NETL: temperature dependent yield strength and potential for reduced order model 2. RTRC to measure yield strength and characterize oxides	1. NETL: Model refinements 2. NETL: Estimate oxide scale formation 3. RTRC: HEA changes based on any criteria revisions

Alloy Selection

Machine Learning Framework for Alloy Discovery



User defines

- Up to 3 objectives
- Up to 3 constraints
- Elemental palette for consideration

Risks & mitigation

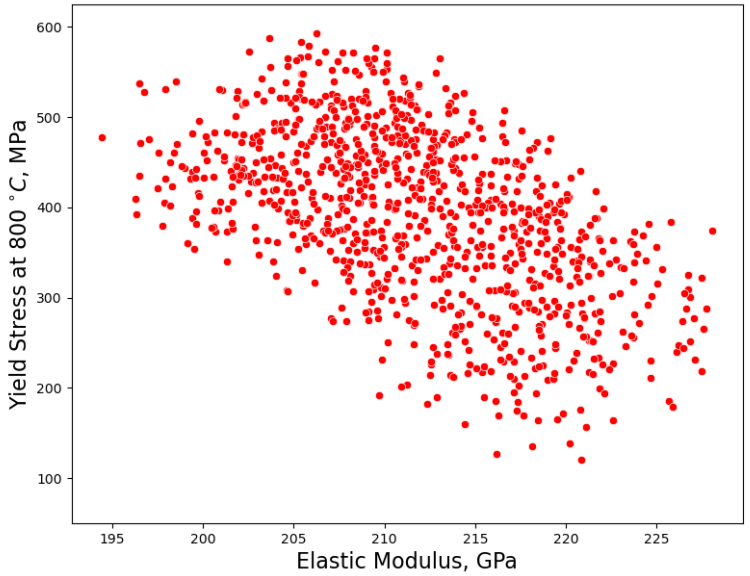
- Large search space with long computational time (e.g. CALPHAD prediction of T_{melt})
  - *Surrogate models*
- Limited data
  - *Multi-source models*
  - *Targeted experiments*

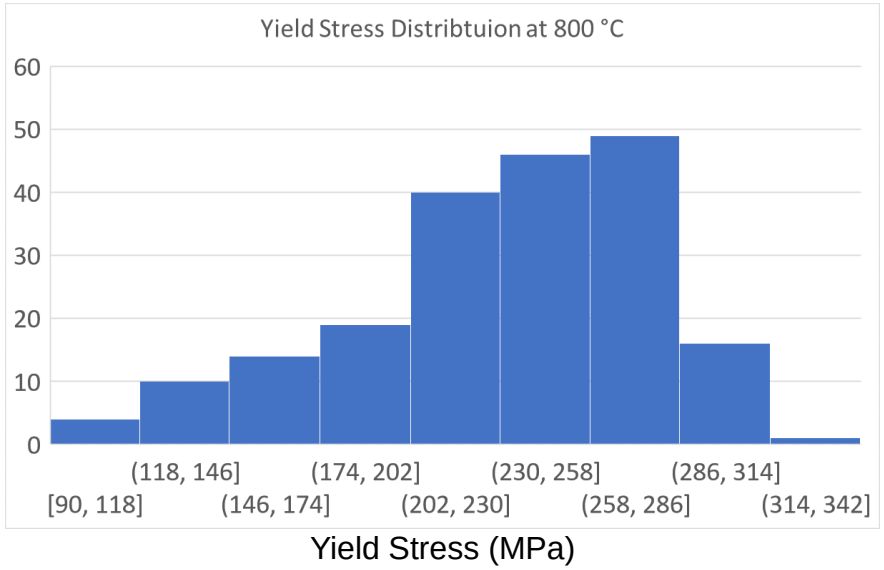
S. Sarkar, K. Smith, J. Sharon, R. Deacon, and G. V. Srinivasan, "Machine Learning-aided Accelerated Discovery of HEA for Turbomachinery Applications," (Oral) In 1st World Congress on High Entropy Alloys (HEA 2019), Seattle, WA.

Systematic approach to optimize performance within composition space

Compositional Searching

- Used machine-learning framework previously developed at RTRC to identify candidate HEA
  - 12 element palette to identify 2000 compositions during each run
  - Common Objectives: Maximize melt point; Maximize yield point at RT or 800 °C; Either: minimize density, minimize cost, or maximize modulus
  - Constraint: VEC greater than 6.8
- Next step is to filter the results to determine the actual space available





Set of conditions that allowed for complete run

HEA Selection

- List of candidates was narrowed down to 33 potential candidates
  - First required single FCC phase at end of Scheil solidification simulation
    - Most likely to be single phase or lower concentration of multiple phases
  - Reviewed calculated phase diagrams and yield strength
    - Identify HEAs with higher fraction of FCC phase present at 750 °C
    - Selected for a range of strength to validate strength predictions

- Set of 4 candidate HEA compositions identified
  - Alloys have been fabricated to produce small bars

HPC Tasks at NETL

- **NETL team**
  - Dr. Michael Gao
  - Dr. Zongrui Pei
  - Dr. De Nyago Tafen
- **Predict temperature-dependent yield stress**
  - Improve Curtin's model with DFT input on atomic volume, stacking faults energy, short-range order
  - Validate and refine the model
- **Predict atomic structure evolution (e.g., short-range order) as a function of temperature**
  - Ab initio molecular dynamics (AIMD) simulation
- **Predict oxidation resistance at key temperatures**
  - Oxygen diffusivity and transition metal diffusivities using AIMD
  - Correlate diffusivities with oxidation resistance
  - Validate and refine the model

Yield Strength Modeling

Predict Yield Strength

- **Keep the major elements (9 elements);**
- **Other elements may be considered for a finer searching;**
- **Varvenne-Curtin model;**
- **Volume is taken as the weighted Voronoi and elemental volumes;**
  - Voronoi volume in alloys considers interaction, but local, weakens the difference;
  - Elemental volume represents the upper boundary of volume;
  - $V = \theta V_{elem} + (1-\theta)V_{voro}, \theta = 0.5$ for this study; V_{elem}-DFT; V_{voro}-DFT.
- **Need to sample the concentration space (here by a step of 0.2);**
- **Both yield stresses at 0 K and 800 K are calculated.**

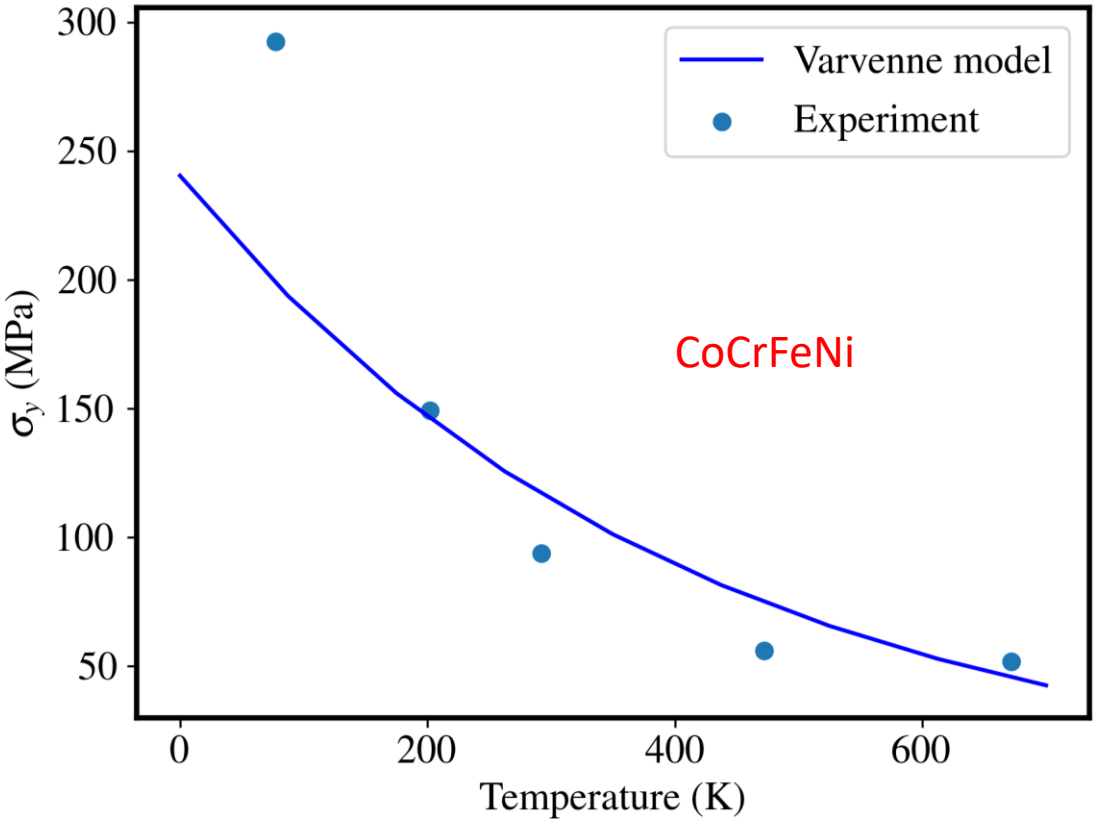
$$\Delta E_b = 0.274\alpha^{\frac{1}{3}} K_{\Delta E} f_{\Delta E} \left[\sum_n c_n \Delta V_n^2\right]^{\frac{1}{3}}$$

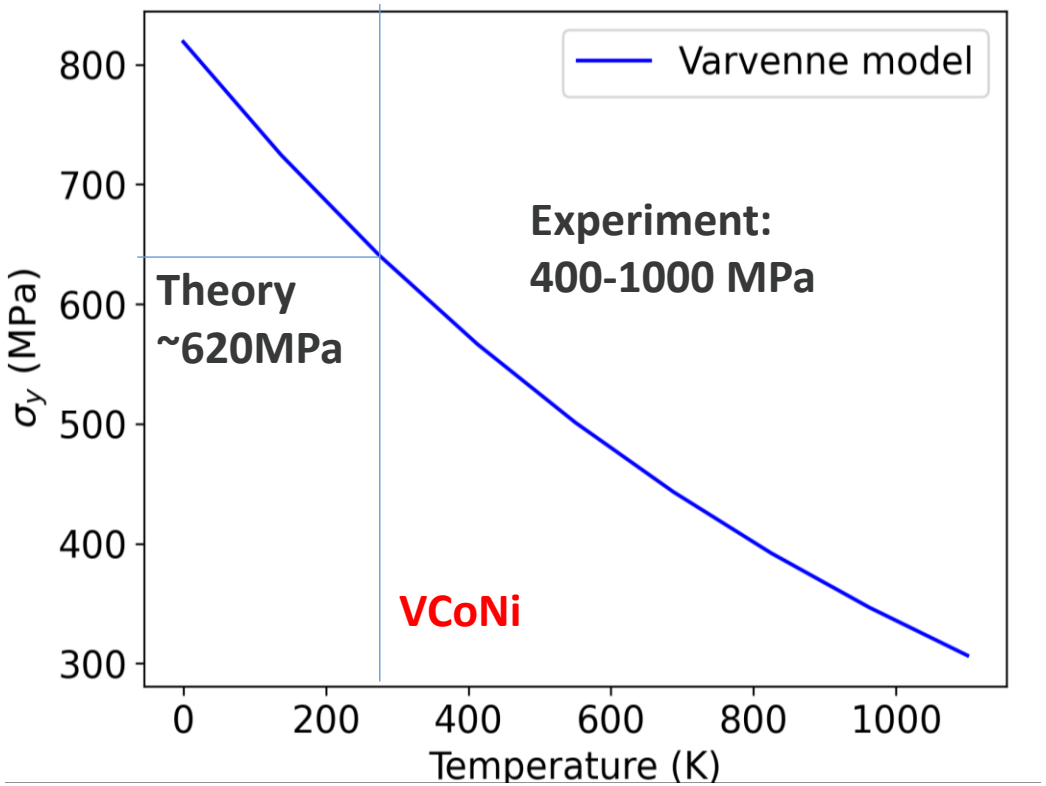
$$\tau_{ssi}(T, \dot{\epsilon}) = \tau_{0,ssi}\left[1 - \left(\frac{k_B T}{\Delta E_b} \ln \frac{\dot{\epsilon}_0}{\dot{\epsilon}}\right)^{\frac{2}{3}}\right]$$

C. Varvenne, A. Luque, W.A. Curtin, Theory of strengthening in fcc high entropy alloys, Acta Materialia 118 (2016) 164-176.

Model Validation

Two systems: CoCrFeNi and VCoNi

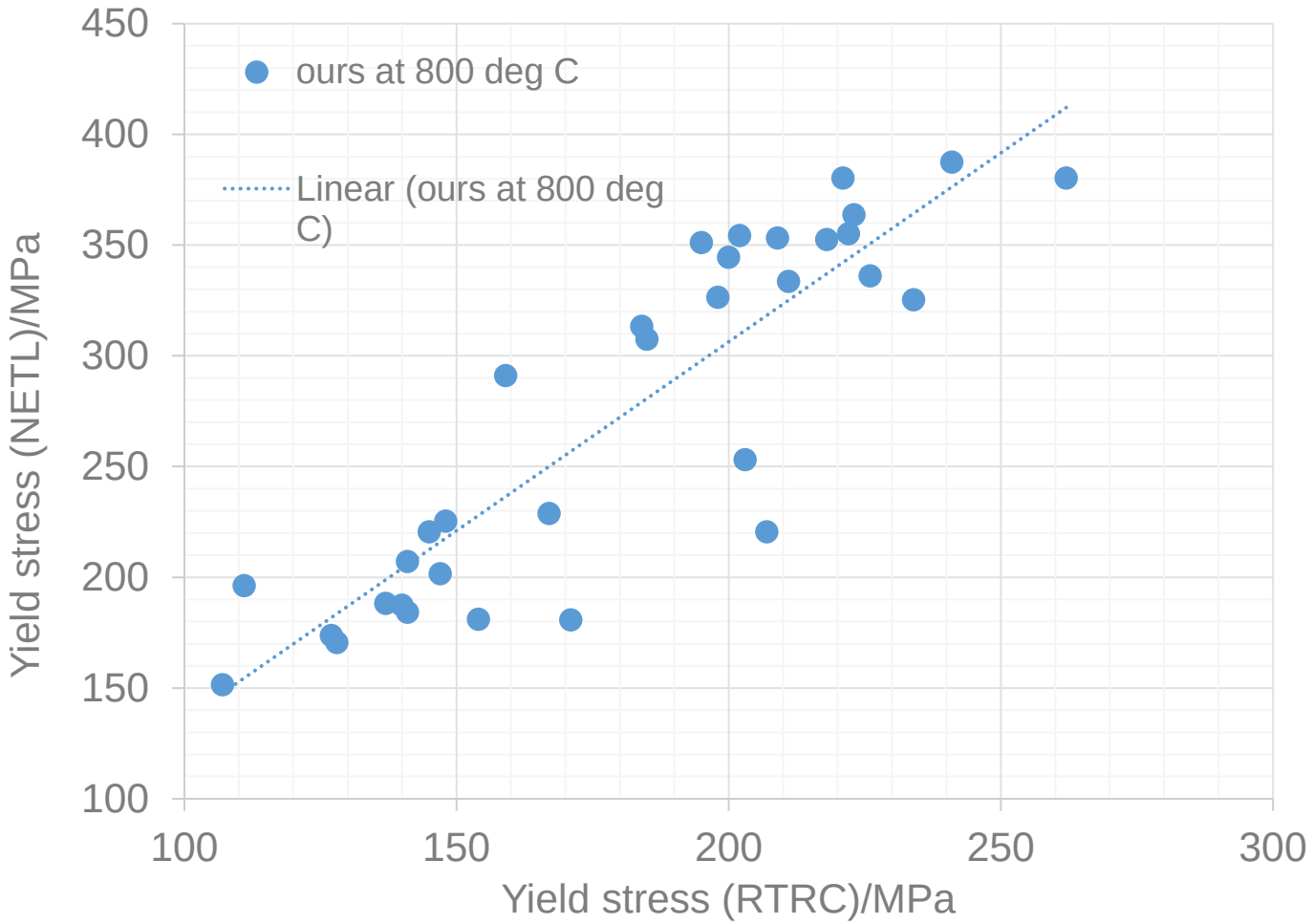




S.S. Sohn, A.K. da Silva, Y. Ikeda, F. Kormann, W.J. Lu, W.S. Choi, B. Gault, D. Ponge, J. Neugebauer, D. Raabe, Ultrastrong Medium-Entropy Single-Phase Alloys Designed via Severe Lattice Distortion, Advanced Materials 31(8) (2019).

Model Prediction for New Alloys

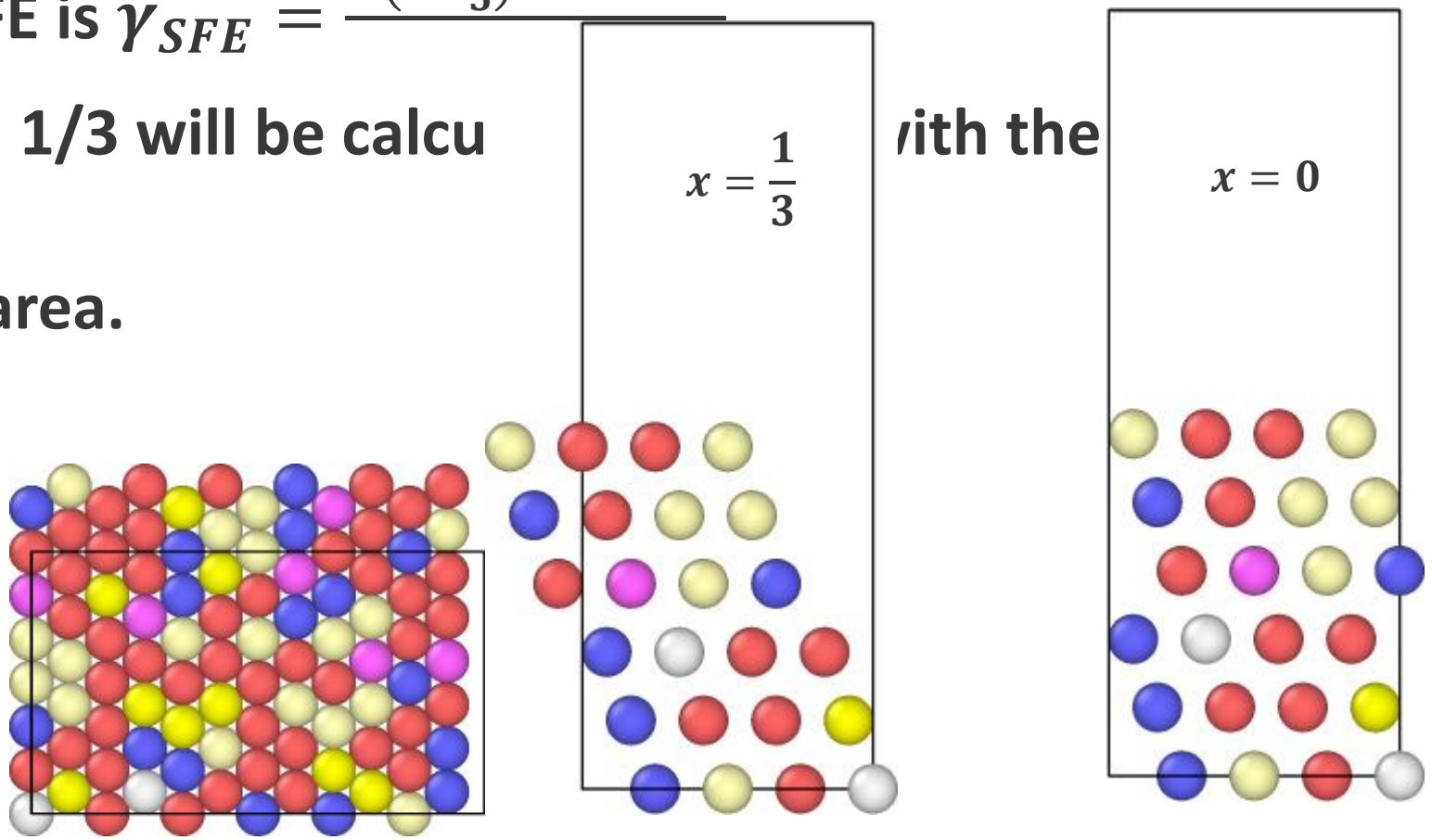
Comparison between NETL and RTRC results



Stacking Fault Energy (SFE) Calculations

DFT calculations at zero temperature; VASP package

- The formula to calculate SFE is $\gamma_{SFE} = \frac{E\left(x=\frac{1}{3}\right) - E(x=0)}{A}$
- The total energies *E* at x=0, 1/3 will be calcu ith the optimized parameters;
- The parameter A is the SF area.



Future Work on Yield Strength Prediction

- **1. More calculations to test and understanding the misfit volumes;**
  - ➢The misfit volumes are calculated based on binary solute solution systems;
  - ➢However, for some binaries they form intermetallics rather than solid solutions;
  - ➢We may ignore them in calculating the average misfit volume;
  - ➢We will check this approximations when compared with experiments.
- **2. Calculations of stacking fault energies for the 4 selected HEAs;**
  - ➢Now optimizing the basic parameters, such as lattice parameters;
  - ➢Next adjusting the geometry of the stacking fault models;
- **3. Compare and improve the yield stress prediction when experimental results are available.**
  - ➢Refine the model as needed: considering stacking faults energy, short range order, etc.

E. Antillon, C. Woodward, S.I. Rao, B. Akdim, T.A. Parthasarathy, Chemical short range order strengthening in a model FCC high entropy alloy, Acta Materialia 190 (2020) 29-42.

Oxidation Prediction

Predict Oxidation Resistance

Modeling procedures

- **AIMD Code: VASP**
- **Canonical ensemble (NVT), temperature controlled by a Nose thermostat**
- **Cubic supercells between 100 and 256 atoms depending on compositions**
- **Simulation time ~ 30 to 100 ps depending on system size with time step of 1.0 fs**
- **Benchmark Calculations will be performed on pure Ni, binary alloys (Ni-Al and Ni-Cr) and ternary alloys Ni-Al-Cr.**

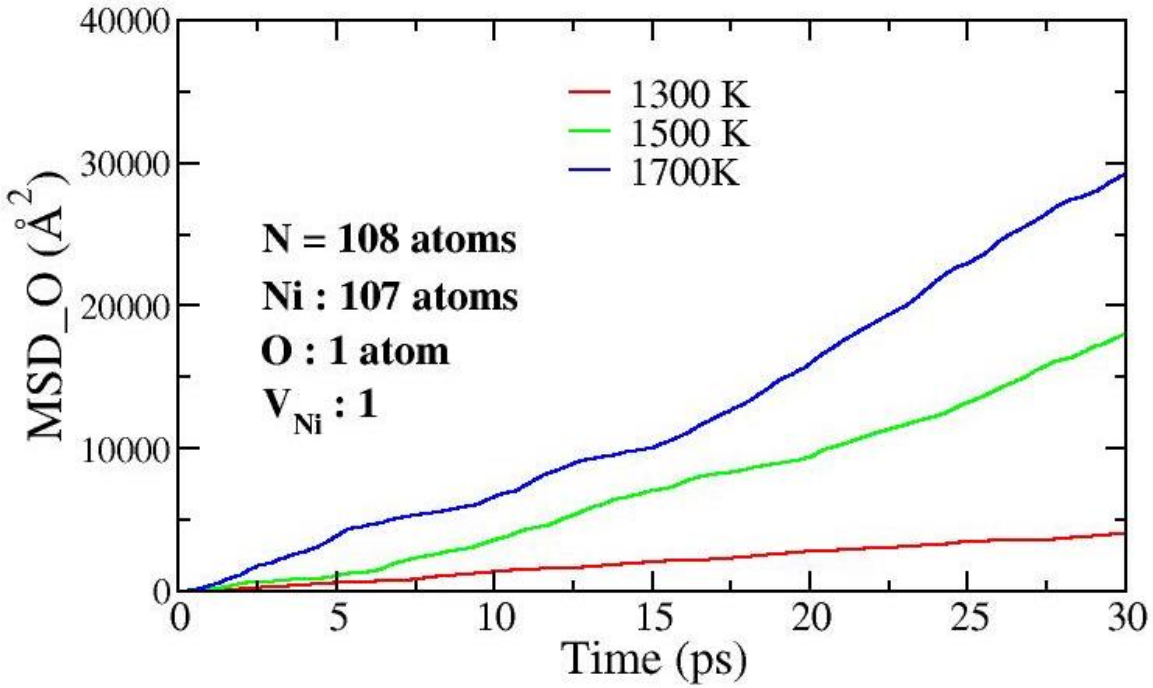
AIMD Benchmark Calculations

Oxygen diffusion in pure Ni

- **Supercell 3 x 3 x3 → 108 atoms**
- **O location: prefers octahedral position**
- **O prefers to be near Ni vacancy (Three locations were examined)**
- **Four temperatures were chosen: 1100 K, 1300 K, 1500 K, 1700 K**
- **Diffusion coefficients are calculated as follows:**

$$D_i = \lim_{t\to\infty} \frac{\langle |R_i(t) - R_i(0)|^2 \rangle}{6t}$$

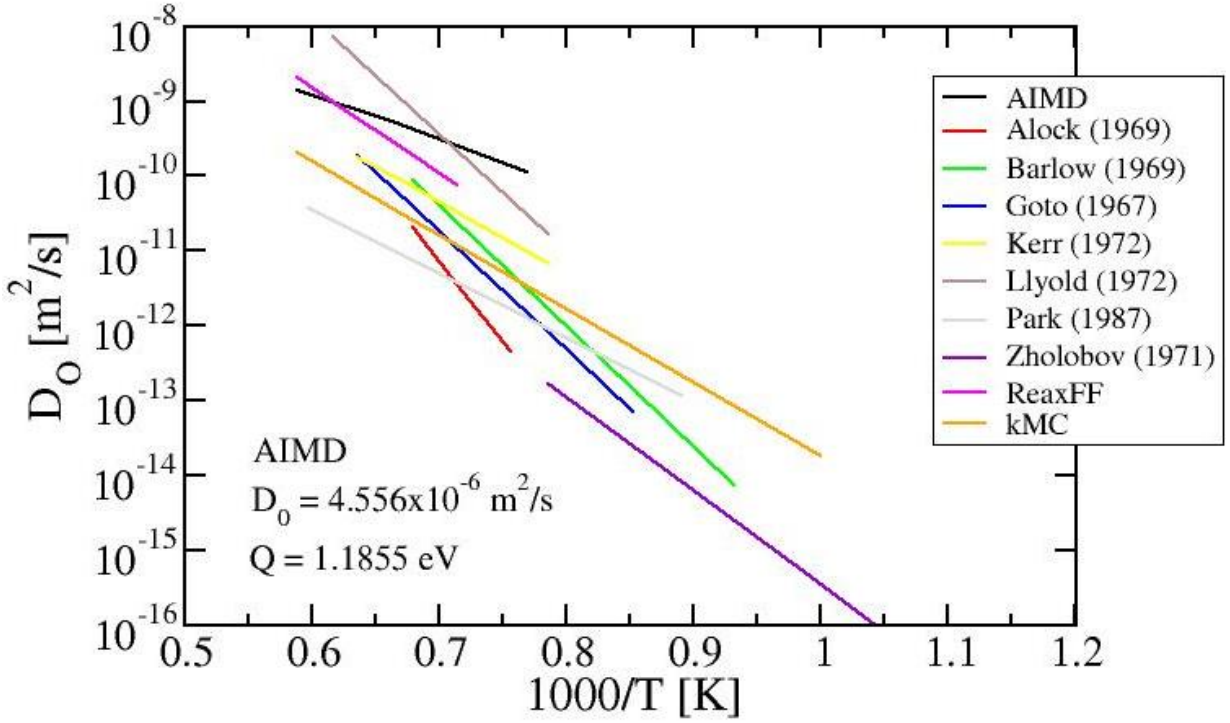
- $|R_i(t) - R_i(0)|^2$ **is the mean-squared displacement of atom i**



Mean-squared displacement of O diffusion in Ni

AIMD Benchmark Calculations (Cont.)

Oxygen Diffusion in Ni



AIMD predicted O diffusion coefficients plotted against available literature data.

Available literature data of O diffusion coefficients

D_0 (m^2/sec)	Q (eV)	T (K)	Method	Ref.
8.8×10^{-7}	1.64	700 – 1700	DFT-Debye **	Fang et al.
3.9×10^{-4}	1.82	1000-1700	kMC **	Fang et al.
2.8×10^{-4}	1.95	1200-1700	MD-MEAM **	Fang et al.
9.5×10^{-3}	2.25	1000-1400	ReaxFF **	Fang et al.
4.9×10^{-6}	1.70	1123 – 1673	Potentiometric	Park, 1987
7.9	3.20	1073 – 1473	Internal oxidation	Barlow, 1969
1.82	3.12	1173 – 1573	Internal oxidation	Goto, 1967
26.8	3.08	1273 – 1623	Internal oxidation	Llyold, 1972
8.93×10^{3}	4.28	1323 – 1473	Gravimetric	Alock, 1969
1.21×10^{-3}	2.49	623 – 1273	Desorption	Zholobov, 1971
2.06×10^{-4}	1.89	1273 – 1573	Electrochemistry	Kerr, 1972

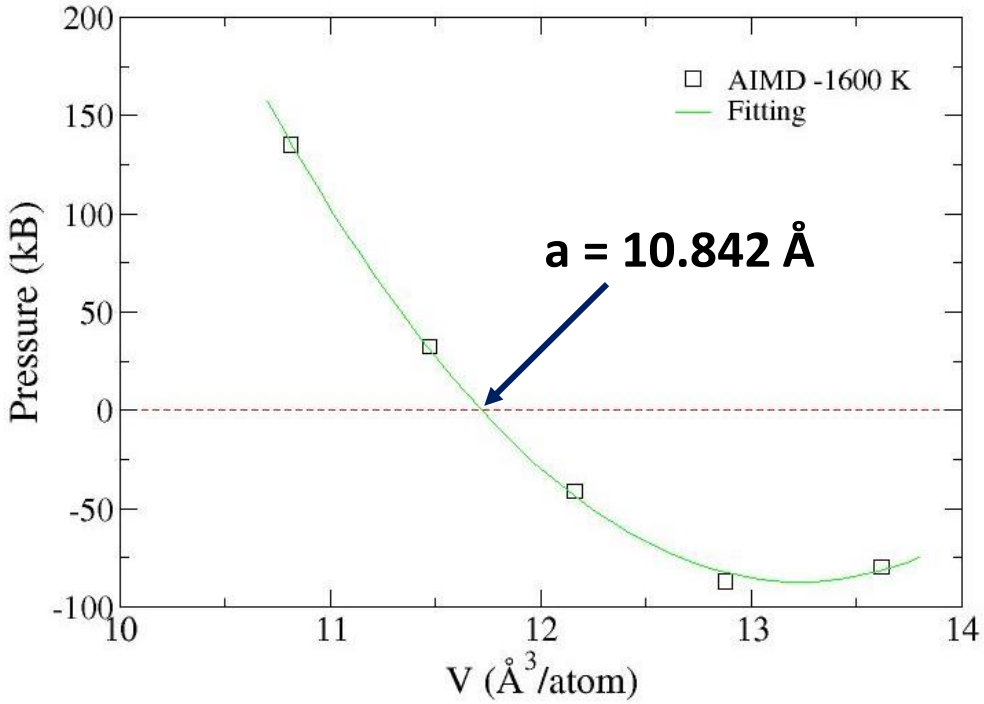
Calculating Lattice Constant at Finite T

Equation of State: P = F(V)

- NVT dynamics
- A series of simulation cell volumes is performed
- Time averaged Pressure is calculated as function of volume
- Equation of state:

$$P = aV^2 + bV + c$$

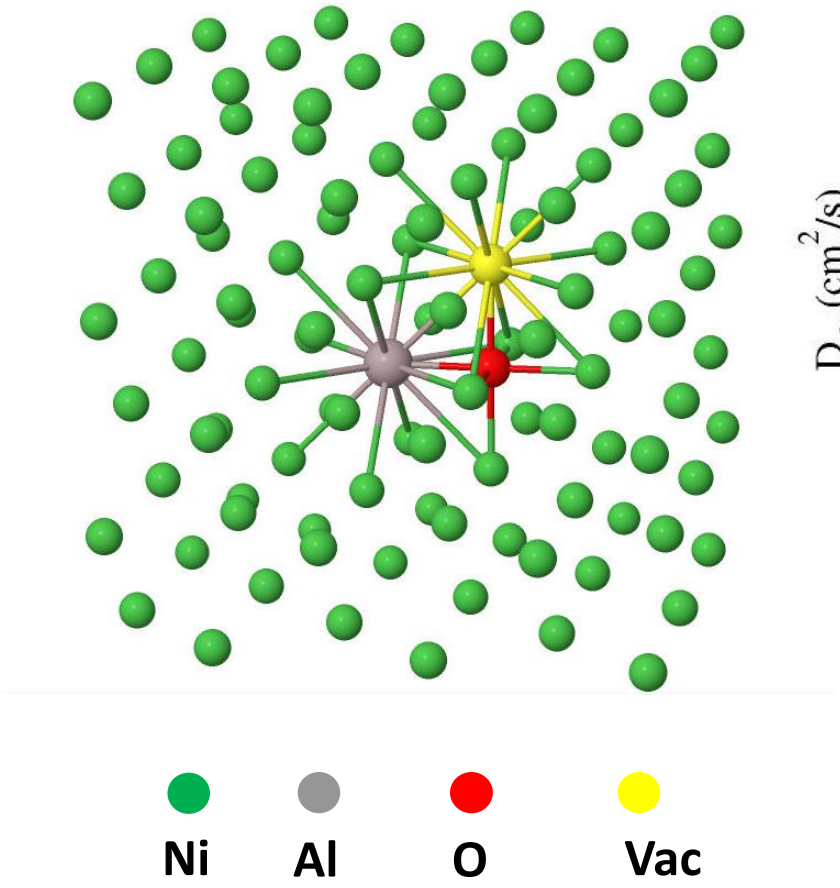
- At equilibrium, $P = 0 \implies V_0$

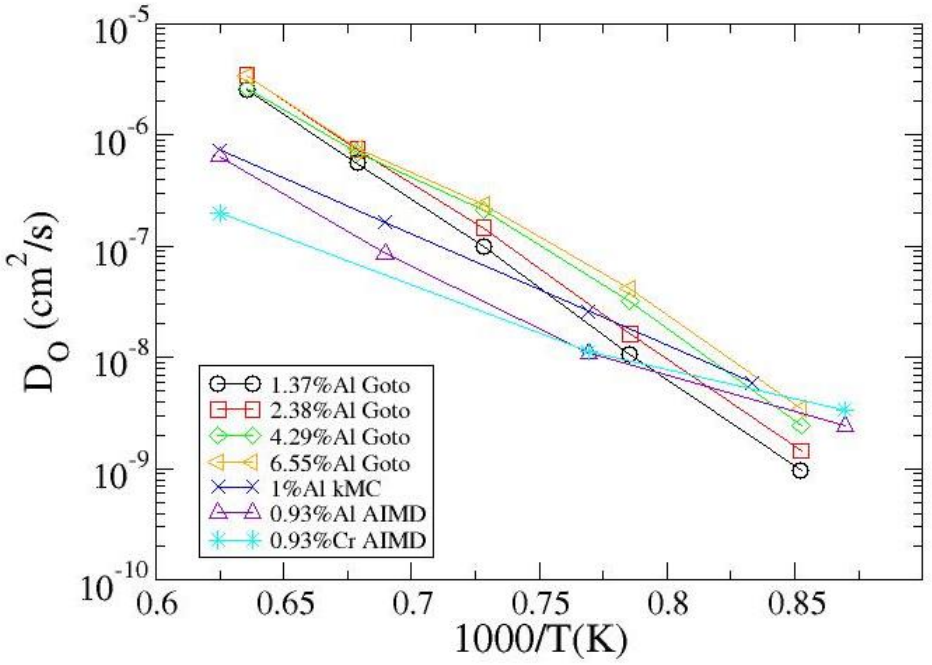


O Diffusion in Binary Ni-Al and Ni-Cr Alloys

Case of Ni-0.93%Al and Ni-0.93%Cr

- Dilute Al and Cr in Ni
- 3 x 3 x 3 Supercell: 106 Ni, 1 Al or Cr, 1 O and 1 Vac.
- O occupies an octahedral interstitial formed by Ni, Al/Cr and Vac.

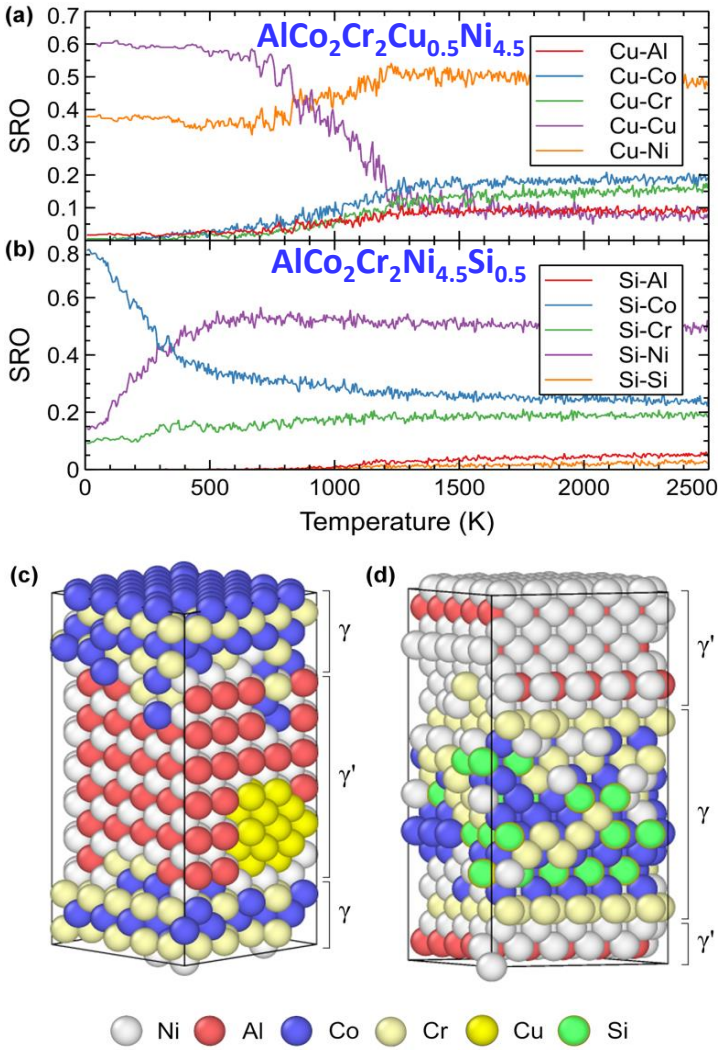




Expt: Goto et al. J. Japan Inst. Metals, 34, 319 (1970).
kMC: Alfonso & Tafen (2015)

Future Work on Predicting Oxidation Resistance

- Complete AIMD Simulations of Ni-Al and Ni-Cr binary alloys (for dilute and non-dilute concentrations) and predict O diffusivity as a function of temperature.
- Apply AIMD to predict O diffusivity in Ni-Al-Cr and other ternary alloys.
- Investigate the oxidation resistance of down-selected HEAs using AIMD: Predict the O diffusivity as a function of temperature
  - Validate and refine the model as necessary.
- Using AIMD investigate the effect of short-range order in HEAs by simulating the evolution of the atomic structures as a function of temperature.



M. Detrois, Z. Pei, K.A. Rozman, M.C. Gao, J.D. Poplawsky, P.D. Jablonski, J.A. Hawk, Partitioning of tramp elements Cu and Si in a Ni-based superalloy and their effect on creep properties, Materialia 13 (2020) 100843.

Conclusions and Future Work

Conclusions and Future Work

- Conclusions
  - Identified HEA candidates for computational evaluation
  - Determining major computational effects influence for strength and oxidation
  - Validating procedures versus literature materials

- Future Work
  - Experimental characterization: yield strength at temperature and oxidation
  - Compare yield strength model with experiments and identify model improvements
  - Evaluate oxygen diffusivity as a measure of oxidation kinetics from experiments

Acknowledgement and Disclaimer

- Acknowledgment: "This material is based upon work supported by the Department of Energy HPC4Materials Award under CRADA NETL-AGMT-1031."