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

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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 Gorée et al., Data in Brief (2018)*
# Selection Basis for Single Phase FCC Materials

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

<table>
<thead>
<tr>
<th>Activities</th>
<th>Information Flow</th>
<th>Deliverables</th>
</tr>
</thead>
</table>
| Evaluate model approach to guide material selection for strength and oxidation  
- Change in HEA selection from new models | - NETL: optimization criteria  
- RTRC: compositions  
- NETL predictions  
- RTRC experimental results | 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 revised strength/oxidation criteria  
- RTRC experimental results | 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 $T_{\text{melt}}$)
  - Surrogate models
- Limited data
  - Multi-source models
  - Targeted experiments

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
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.

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

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

Two systems: CoCrFeNi and VCoNi

Model Prediction for New Alloys

Comparison between NETL and RTRC results
The formula to calculate SFE is \[ \gamma_{SFE} = \frac{E(x=\frac{1}{3}) - E(x=0)}{A} \]

- The total energies \( E \) at \( x=0, 1/3 \) will be calculated by DFT with 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.
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 x 3 → 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

<table>
<thead>
<tr>
<th>D₀ (m²/sec)</th>
<th>Q (eV)</th>
<th>T (K)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.8×10⁻⁷</td>
<td>1.64</td>
<td>700 – 1700</td>
<td>DFT-Debye</td>
<td>Fang et al.</td>
</tr>
<tr>
<td>3.9×10⁻⁴</td>
<td>1.82</td>
<td>1000-1700</td>
<td>kMC</td>
<td>Fang et al.</td>
</tr>
<tr>
<td>2.8×10⁻⁴</td>
<td>1.95</td>
<td>1200-1700</td>
<td>MD-MEAM</td>
<td>Fang et al.</td>
</tr>
<tr>
<td>9.5×10⁻³</td>
<td>2.25</td>
<td>1000-1400</td>
<td>ReaxFF</td>
<td>Fang et al.</td>
</tr>
<tr>
<td>4.9×10⁻⁴</td>
<td>1.70</td>
<td>1123 – 1673</td>
<td>Potentiometric</td>
<td>Park, 1987</td>
</tr>
<tr>
<td>7.9</td>
<td>3.20</td>
<td>1073 – 1473</td>
<td>Internal oxidation</td>
<td>Barlow, 1969</td>
</tr>
<tr>
<td>1.82</td>
<td>3.12</td>
<td>1173 – 1573</td>
<td>Internal oxidation</td>
<td>Goto, 1967</td>
</tr>
<tr>
<td>26.8</td>
<td>3.08</td>
<td>1273 – 1623</td>
<td>Internal oxidation</td>
<td>Lloyd, 1972</td>
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<tr>
<td>8.93×10³</td>
<td>4.28</td>
<td>1323 – 1473</td>
<td>Gravimetric</td>
<td>Alock, 1969</td>
</tr>
<tr>
<td>1.21×10⁻³</td>
<td>2.49</td>
<td>623 – 1273</td>
<td>Desorption</td>
<td>Zhlobov, 1971</td>
</tr>
<tr>
<td>2.06×10⁻⁴</td>
<td>1.89</td>
<td>1273 – 1573</td>
<td>Electrochemistry</td>
<td>Kerr, 1972</td>
</tr>
</tbody>
</table>
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, \( P = 0 \) \( \Rightarrow \) \( V_0 \)

\[ a = 10.842 \text{ Å} \]
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.

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.
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
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