
Songge Yang\textsuperscript{1}, Mohammad Asadikiya\textsuperscript{1}, Vadym Drozd\textsuperscript{2}, \textit{Yu Zhong}\textsuperscript{1}

\textsuperscript{1}Worcester Polytechnic Institute
\textsuperscript{2}Florida International University
Content

1. Introduction
2. Alloy design Approaches
3. Computational Details
4. Result and discussion
Objective/Vision

Develop a novel *modeling* approach, which can quickly design new high performance structural alloys for the application of FE power plants.

The long-term goal is to use the developed efficient hybrid computational model to predict the composition range of the new alloys with different elemental systems based on the specific application requirement.

In addition, new high performance structural alloys are to be designed based on the predictions from the model.
Current Challenges for Ab Initio

The prediction reliability of DFT simulations at elevated temperatures is still not comparable to which at 0K. Supercell is needed DFT calculations for HEA. DFT is mainly limited to certain equimolar stoichiometries.

.......
High entropy alloys

- High hardness and superb specific strength
- Superior mechanical performance at elevated temperatures
- Exceptional ductility and fracture toughness at cryogenic temperatures
- High wear resistance
- Significant resistance to corrosion and oxidation

Ashby map showing fracture toughness vs. yield strength (Gludovatz et al. (2014))
Specific-yield strength vs. Young’s modulus: HEAs compared with other materials, particularly structural alloys. HEAs are among the materials with highest specific strength and with a wide range of Young’s modulus.
The frequency with which elements are used in the 408 multi-principal element alloys (MPEAs). Al, Co, Cr, Cu, Fe, Mn, Ni and Ti are by far the most commonly used elements [D.B. Miracle and O.N. Senkov (2017)].
Alloy Design Approaches

High-throughput calculations of phase diagrams (HT-CALPHAD)

High-throughput Density functional theory calculation (HT-DFT)

VEC-Composition generations

HT-CALPHAD

Compositions Screening

Generations of Special quasi-random structures (SQS)

Calculations of Enthalpy of formation

Calculations of elastic properties

Good compositions screened by HT-CALPHAD would be used to generate SQS structures
Alloy Design Approaches

✓ **HT-CALPHAD simulations**
  Predictions of phase stability in the Al-Cr-Co-Fe-Ni system with the HEA thermodynamic database, down-selecting more than 3000 compositions (based on VEC phase stability criteria)

✓ **Special quasi-random structure (SQS) generation:**
  Binary, ternary and quaternary SQS structures for the random FCC, BCC and HCP alloys in Fe-Ni-Co-Cr system were generated using the Alloy-Theoretic Automated Toolkit (ATAT)

✓ **DFT**
  - Vienna ab initio simulation package (VASP)
  - Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional
  - Cutoff energy 520 eV (700 eV for elastic properties calculations)
  - Monkhorst-Pack k-point meshes with density not less than 1000 pra (7000 pra for elastic properties calculations) (per-reciprocal-atom)
Phase formation rules in HEAs

**Hume-Rothery rules**

**Valence electron concentration (VEC)**

Formation of solid solution:

1. Atomic size difference ≤ 15%
2. Same crystal structure
3. Same valence
4. Similar electronegativity

Hume-Rothery electron concentration rule

Definite crystal structure will occur at a particular electron concentration.

Fe = 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^2\) 3d\(^6\)

### Valence electron concentration (VEC)

The valence electron concentration (VEC) is defined as:

$$ VEC_{(sys)} = \sum_{i=1}^{n} C_i (VEC)_i $$

- $C_i$ : atomic percentage

#### Al-Cr-Co-Fe-Ni system

- $(VEC)_{Al} = 3$
- $(VEC)_{Cr} = 6$
- $(VEC)_{Fe} = 8$
- $(VEC)_{Co} = 9$
- $(VEC)_{Ni} = 10$

#### Reference

Impact of phase formation parameters on phase stabilities in HEAs

**Main conclusions:**
- $\text{VEC} < 6.87$, BCC stable
- $6.87 \leq \text{VEC} < 8$, BCC+FCC stable
- $\text{VEC} \geq 8$, FCC stable

**Problems:**
- Very limited experimental compositions
- What is the role of temperature?
- How does it work in real case?
Very wide range of Al compositions to choose (20~53mol.%)-TCHEA3

Al-Cr-Co-Ni-Fe systems (transition from FCC to BCC)

1. HT-CALPHAD simulations

1.1 Preliminary results of Al-Cr-Co-Ni-Fe systems (2D screening)

- No multiphase region
- Melting point region of BCC phase
- FCC appears
- Single FCC phase appears

41 compositions are generated and calculated
1. HT-CALPHAD simulations

1.2 Preliminary results of Al-Cr-Co-Ni-Fe systems (3D screening)

Temperature range of BCC phase

Temperature range of FCC phase

3312 VEC-Compositions are calculated
1. HT-CALPHAD simulations

1.2 Preliminary results of Al-Cr-Co-Ni-Fe systems (3D screening)

Temperature-density-VEC diagram of BCC phase

Temperature-density-VEC diagram of FCC phase
1. **HT-CALPHAD simulations**

1.2 Preliminary results of Al-Cr-Co-Ni-Fe systems (3D screening)

\[ \Delta T \text{-density-VEC diagram of BCC phase} \]

\[ \Delta T \text{(C)-BCC} \]

\[ \Delta T \text{(C)-FCC} \]
Special Quasi-random Structure

What is Special Quasi-random Structure (SQS)?

small-unit-cell periodic structures in random substitutional alloys

Why do we introduce SQS concept?

SQS can be regarded as the best possible periodic unit cell representing a given random alloy.

Fig. The input unrelaxed atomic structures of 64-atom quaternary SQS
All of the pairs

All of the triplets

All of the quadruplets

Random structures have lower energy of configuration!

\[ E(\sigma_1, \sigma_2, \sigma_3 \ldots \sigma_n) = \sum_\alpha m_\alpha J_\alpha \Pi_\alpha(\delta) = \sum_{\{ij\}} m_{ij} J_{ij} \delta_i \delta_j + \sum_{\{ijk\}} m_{ijk} J_{ijk} \delta_i \delta_j \delta_k + \sum_{\{ijkl\}} m_{ijkl} J_{ijkl} \delta_i \delta_j \delta_k \delta_l + \ldots \]

\[
\bar{\Pi}_\alpha(\delta) = \frac{1}{N_\delta M_\alpha} \sum_\beta \equiv \alpha \Pi \delta_i
\]
SQS generation

2. Correlation function

Example: Fe3Ni (only consider pairs)

<table>
<thead>
<tr>
<th>Ideal mismatch</th>
<th>SQS1</th>
<th>SQS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,1 = 0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>2,2 = 0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>2,3 = 0.25</td>
<td>0.25</td>
<td>0.458</td>
</tr>
<tr>
<td>2,4 = 0.25</td>
<td>0.25</td>
<td>0.333</td>
</tr>
</tbody>
</table>

SQS1 is more random than SQS2

The more atoms match the correlation function, we could get more random SQS structures

Binary:
Substitutional model: \( A_{1-x}B_x \)
Ideal correlation mismatch = \( \langle \prod_{k,m} \rangle_R = (2x - 1)^k \)

A=0.5 B=0.5 ideal mismatch=0
A=0.75 B=0.25 ideal mismatch=0.25
A=0.66 B=0.33 ideal mismatch=0.1111

Number of points considered for cluster expansion
2. Generated SQS structures

SQS structures:

- 16 and 32 atoms per unit cell for binary systems
- 32 atoms per unit cell for ternary systems
- 32 and 64 atoms per unit cell for quaternary system
- 200 atoms per unit cell for quinary systems

Atomic arrangement tested:

- Face Center Cubic structures (FCC)
- Body Center Cubic structures (BCC)
### 3. Elasticity constant (DFT calculation)

**Fe$_{0.25}$Ni$_{0.25}$Co$_{0.25}$Cr$_{0.25}$ alloy**

<table>
<thead>
<tr>
<th>V, Å$^3$/atom</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.05</td>
<td>DFT</td>
<td>This work (64 atoms SQS)</td>
</tr>
<tr>
<td>11.09</td>
<td>DFT</td>
<td>This work (32 atoms SQS)</td>
</tr>
<tr>
<td>11.19</td>
<td>DFT</td>
<td>Gao et al. (2017)</td>
</tr>
<tr>
<td>11.27</td>
<td>EXP</td>
<td>Y.-F. Kao et al. (2009)</td>
</tr>
<tr>
<td>11.37</td>
<td>EXP</td>
<td>G. Laplanche et al. (2018)</td>
</tr>
<tr>
<td>11.57</td>
<td>EXP</td>
<td>B.Liu et al. (2016)</td>
</tr>
</tbody>
</table>

Average properties (numbers in parentheses are for 32 atoms SQS structure)

<table>
<thead>
<tr>
<th>Averaging scheme</th>
<th>Bulk modulus, GPa</th>
<th>Young's modulus, GPa</th>
<th>Shear modulus, GPa</th>
<th>Poisson's ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voigt</td>
<td>$K_V = 167.0$ (157.4)</td>
<td>$E_V = 245.0$ (247.4)</td>
<td>$G_V = 97.6$ (99.9)</td>
<td>$\nu_V = 0.2554$ (0.2380)</td>
</tr>
<tr>
<td>Reuss</td>
<td>$K_R = 166.7$ (155.89)</td>
<td>$E_R = 201.1$ (205.1)</td>
<td>$G_R = 77.4$ (80.1)</td>
<td>$\nu_R = 0.2989$ (0.2807)</td>
</tr>
<tr>
<td>Hill</td>
<td>$K_H = 166.8$ (156.62)</td>
<td>$E_H = 223.4$ (226.6)</td>
<td>$G_H = 87.5$ (90.0)</td>
<td>$\nu_H = 0.2768$ (0.2589)</td>
</tr>
</tbody>
</table>

**64 atoms SQS cell**

**32 atoms SQS cell**
Calculated elastic property: Fe_{0.25}Ni_{0.25}Co_{0.25}Cr_{0.25} alloy
Main Conclusions

1. The high-throughput CALPHAD approach shows the capability of the simulation of phase stability on Al-Cr-Co-Ni-Fe systems.
   - BCC structures have higher solidus temperatures and single phase temperature ranges when VEC is between 5.5 to 6.5
   - FCC structures have higher solidus temperatures and single phase temperature ranges when VEC is larger than 8.0

2. The calculated elastic properties of generated SQS structures show good agreement with the experimental data for the Fe-Ni-Cr-Co quaternary system.
Acknowledgment

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- Help from the program manager: Maria Reidpath
  
- Collaborations on DFT: Dr. Michael Gao, Dr. Yi Wang
- Help from Computherm providing database
Thank you!
Fe-Ni system: 16 atoms vs. 32 atoms per unit cell (FCC)

\[ H = E(A_{1-x}B_x) - [(1-x)E(A) + xE(B)] \]

Enthalpy of Mixing  
Energy of SQS structures  
Energy of pure A  
Energy of pure B

Ref. state is FCC

16 atoms SQS
32 atoms SQS

Pandat FCC

Fe\textsubscript{0.875}Ni\textsubscript{0.125}  
Fe\textsubscript{0.75}Ni\textsubscript{0.25}  
Fe\textsubscript{0.625}Ni\textsubscript{0.375}  
Fe\textsubscript{0.5}Ni\textsubscript{0.5}  
Fe\textsubscript{0.375}Ni\textsubscript{0.625}  
Fe\textsubscript{0.25}Ni\textsubscript{0.75}  
Fe\textsubscript{0.125}Ni\textsubscript{0.875}
\[ \delta = E \varepsilon \]

Bulk modulus Voigt average\( (K_V) \)
\[ 9K_V = (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31}) \]

Bulk modulus Reuss average\( (K_R) \)
\[ \frac{1}{K_R} = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31}) \]

Bulk modulus Hill average\( (K_H) \)
\[ 2K_H = (K_R + K_V) \]

Young's modulus\( (E) \)
\[ E = 2G(1 + \mu) \]

Shear modulus Voigt average\( (G_V) \)
\[ 15G_V = (C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66}) \]

Bulk modulus Reuss average\( (G_R) \)
\[ \frac{15}{G_R} = 4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66}) \]

Bulk modulus Hill average\( (G_H) \)
\[ 2G_H = (G_R + G_V) \]

Poisson's modulus\( (\mu) \)
\[ \mu = (3K - 2G)/(6K + 2G) \]