Creating Materials and Energy Solutions

Science of Multicomponent Alloys – a Roadmap for Theoretical and Experimental Research

Matthew Kramer, Duane Johnson, Prashant Singh, Linlin Wang and Pratik Ray

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Alloy Design for Extreme Environments

Higher temperature → Higher energy efficiency

Challenges –
• High T oxidation
• Moisture
• Creep and high T deformation
• Toughness & manufacturability

Steels  Ni- superalloys  RM-silicides

Bond-coat

Creating Materials and Energy Solutions
Exploratory Development of Multi-Principal Element Alloys (MPEA)

- **Need:** Alloys that raise high-T strength limit above Ni-base alloys & provide oxidation and corrosion resistance.
- **Design:** MPEAs have more space to tune properties.
- **Musts:** include all relevant mechanisms (not just chemical)
- **Predict:** Need Global and Local Stability, and their origins
Semi-empirical approaches to MPEA design

\[ \Omega = \frac{T_M \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|} > 1.1 \]

Entropy (disordered phases) dominates enthalpy (ordered phases)

\[ T_M = \sum_{i=1}^{n} c_i (T_M)_i \]

\[ \delta = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i / \bar{r})^2} < 6.6\% \]

Similar to Hume-Rothery rule, i.e. minimize size differences in order to form the solid solutions

Y. Zhang, X. Yang and P.K. Liaw, JOM 64 (2012) 830

\[ \text{VEC} = \sum_{i=1}^{n} c_i (\text{VEC})_i \]

VEC < 6.87 bcc phases; VEC ≥ 8 fcc phases


Multiple stability criterion – potential for \textit{in-situ} functionalization?
Tuneable effects in MPEAs

Synthesis and Processing
- Easily trapped in metastable energy basins due to sluggish kinetics
- Single-phase vs multi-phase MPEAs – are there potential benefits of operating at the edge of stability, by tuning phase selection?

Key control parameters for processing
- Competing effects on heat treatment – overcomes activation barrier, reaches equilibrium

Schematic TTT diagram for a hypothetical alloy
Challenges in Disordered Systems

- **Experimental Measurement**: quenched or annealed samples.
- **Band calculations**: not always related to experimentally assessed (thermal and off-stoichiometric effects).

**Real World Processing**

- **Solid solution**
  - Liquid
  - Disorder
  - At. %
  - Infinitesimal amplitude (unstable) fluctuations
  - Finite amplitude (stable) partial order
  - Finite amplitude (stable) full order

- **ASRO**: Thermal and off-stoichiometric effects.
Modeling Disordered Solids: Thermodynamics

Direct calculation of energetics for Disordered/Partially-Ordered/Ordered States
- DFT-based multi-sublattice KKR-CPA (configurational averaging)

Thermodynamic Linear-Response calculations
- KKR-CPA based chemical or magnetic susceptibilities
- Directly calculate the energy associated with ASRO

Idea of CPA (Coherent Potential Approximation)

Velicky et. al., Phys Rev 165 (1968) 747
Problem Definition and Approach

**Grand Challenge:** to accelerate the discovery and optimization of these chemically complex alloys and leverage our theoretical and experimental capabilities for assessing their long-term stability.

- **Theoretical tools (KKR-CPA)**
- **Structural studies**
- **Stability in harsh environments**

Theory will inform experiments on new chemistries while experiments will be used to validate models and access kinetics.
Objectives

- Validation of the KKR-CPA code for MPEAs
- Modeling and experimental assessments of MPEAs with KKR-CPA and *in-situ* experiments for understanding the role of SRO, defects, vec and size effects
- Assessment of oxidation behavior of a model Al + Cr MPEA

Choice of alloy systems and techniques driven by these objectives
**Alloy Systems and Significance**

**ZrHfNb**
Model equiatomic alloy – Does Nb additions result in ordering? Does it transform hcp → bcc?

**TiZrHfAl**
Electron counting suggests possibility of brass-like structures

**AlCuNiTiZr**
Resolvable in to two quarternaries – AlCuNi(Ti,Zr) and Al(Cu,Ni)TiZr

**AlFeCoCrNi**
Likely to have high oxidation resistance, due to presence of Al and Cr. What is the effect of Al:Cr ratio? How do we control the microstructure of the alloy?

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**Objective 1:**
Model validation

**Objective 2:**
Exploring effects of SRO, vec and size mismatch through theory and experiments

**Objective 3:**
Assessment of High Temperature Oxidation resistance
Objective 1: Model validation – ZrHfNb alloys

ZrHfNb

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
</tr>
<tr>
<td>La-Lu</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
</tr>
</tbody>
</table>

2.06Å (hcp) 1.98Å (bcc)

Theoretical prediction: Nb additions promote B2 ordering, resulting in a hcp → bcc transition with increasing Nb content.
Objective 1: Model predictions

Key Issues – validate CPA code with predictions of the T dependent stability
Objective 1: Experimental conditions

\[(\text{Zr,Hr})_{1-x}\text{Nb}_x \text{ for } x = 0, 10, 20, 33 \text{ and } 40\]

High energy XRD at 11-ID-B at Advanced Photon Source, ANL
(PDF and Rietveld analysis)
heating and cooling rates
\(\sim 50^\circ\text{C/min}, \text{ hold 2 min every } 50^\circ\text{C}\)
exposure time = 0.25 s in flowing Ar
Objective 1: Experimental Assessments

Transition suppressed ~ 200°C Sluggish on cooling

Initial transition ~ 1000°C

In-situ experiments in line with CPA showing Nb promotes B2 formation

Transition to a cubic phase is observed

\[
\begin{align*}
\text{Pm3m} & \\
a &= 7.901 \text{Å} \\
\text{Pmmm} & \\
a &= 2.78 \text{ Å} \\
b &= 5.10 \text{ Å} \\
c &= 6.44 \text{ Å}
\end{align*}
\]
Objective 2a: Effect of SRO and Defects – TiZrHfAl

Phase selection sequence in ZrHfNb alloys (function of T and Nb):

\[ \text{hcp} \rightarrow \text{orthorhombic} \rightarrow \text{disordered cubic} \rightarrow \text{B2} \]

TiZrHf ternary alloys

- Low T P6\(_3\)/mmc phase (hcp)
- High T Im-3m phase (B2, predicted)

Structurally, TiZrHf is similar to low Nb content alloys in ZrHfNb system. By adding Al,

1. electron counting suggests existence of brass like structure (implying ordered vacancies)
2. In other cubic systems like AlFeCoCrNi, Al addition promotes B2 ordering and phase separation
 Objective 2a: Model predictions – thermodynamics

- Adding Aluminum **promotes** the A2 phase
- **A2 and A3 compete at low %Al, but A2 is lowest**  
  *(A1: fcc; A2: bcc; A3: hcp)*

Structural transition occurs as a function of composition
Objective 2a: Model predictions – effect of defects

Model hints a possible defect mediated phase selection mechanism

Discovery of a γ-brass like structure in MPEA

Structure solved by a combination of synchrotron and single-crystal diffraction
Objective 2b: Relative role of vec and size

AlCuNiTiZr 
Resolvable in to two quarternaries – 
AlCuNi(Ti,Zr) and Al(Cu,Ni)TiZr

Size effects 
vec effects

Work in progress:
• Model calculations (lots of competing structures)
• Will be followed by suitable experiments

Model predicts bcc motif, but with significant ordering

Experimental Assessments: 
AlCuNiTi_{1-x}Zr_x
X = 0, 0.25, 0.5, 0.75, 1.0
Objective 2b: Effect of size mismatch

- Cast samples found to have AlCu$_2$Ti ‘Heusler’ type structure.
  - Al(Cu, Ni)$_2$(Ti, Zr), Fm-3m.
  - Lattice parameter:
    - AlCuNiTi - 5.95 Å
    - AlCuNiTi$_{0.5}$Zr$_{0.5}$ - 6.06 Å
    - AlCuNiZr - 6.16 Å

Phase analysis of cast alloys

Are these structures thermodynamically stable?
Objective 2b: Effect of size mismatch

- Single-crystal diffraction indicated the formation of twinned structure
- Annealing results in clear peak splitting – does this result in a $\text{Ni}_2\text{MAI} + \text{Cu}_2\text{MAI}$ Heusler phases?

Is this transition driven by size or chemistry (electron effects!) Going forward, these are the critical questions to be answered
Objective 3: Assessment of Oxidation behavior

Rapid cooling traps single phase, annealing results in two-phase structure
Objective 3: Assessment of Oxidation behavior

Key questions –
- How does the microstructure change during oxidation – can we develop a “skin” in-situ
- Temperature limits imposed by oxidation on the current alloy.

XRD pattern from the oxide scale corresponds to single-phase $\alpha$-$\text{Al}_2\text{O}_3$. 
Objective 3: Assessment of Oxidation behavior

Oxide scale, after 100 hours of oxidation at 900°C shows the formation of exclusive Al₂O₃ layer.

Oxide scale after 5 hours of oxidation indicates the formation of both Al₂O₃ and Cr₂O₃, with the latter forming in the external region and the former forming in the internal oxide/alloy interface.
Objective 3: Effect of Al:Cr ratio

- Given the relatively low stability of chromia, increased Al content helps with oxidation.

- But the initial formation of \( \text{Cr}_2\text{O}_3 \) promotes the growth of \( \text{Al}_2\text{O}_3 \), hence extremely low Cr content may not be desirable either.
Milestone Report and Future Work

Milestone 1: Model validation – completed

Milestone 2a: Defect mediated phase selection – completed
Milestone 2b: Effect of varying Cu:Ni ratio in Al(CuNi)TiZr alloys, synchrotron studies on Al(TiZr)CuNi alloys for ascertaining definitively the role of size and vec on phase selection

Milestone 3: Assessment of Oxidation behavior and estimation of Al:Cr ratios – completed

Implications for Alloy Design:
• Designing strong and tough alloys through defect mediated mechanisms in conjunction with vec/size constraints and oxidation resistance
• **Significance of processing:** Accessing metastable structures with long residence times, kinetically – need for better understanding of solidification processing
Outcome – Novel Design concepts for MPEAs

Singh, et al., nature computational materials (In press)

Designing high strength refractory alloys through control on size and vec – Collaboration with Prof. Ganesh Balasubramanian, Lehigh University
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Milestone 1: Validation of the KKR-CPA approach for MPEAs

Milestone 2: Demonstrate possibilities of defect mediated phase selection and vacancy ordering

Milestone 3: Assessment of oxidation resistance, and determination of Al:Cr range for enhanced oxidation resistance

Upcoming Deliverable
Determine the relative role of size effects and vec on phase selection