Computational and Experimental Development of Novel High Temperature Alloys


2015 Crosscutting Technology and Research Meeting
April 29, 2015

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The High Temperature challenge

Higher temperatures $\rightarrow$ Higher energy efficiencies

Challenges –
- High T oxidation
- Moisture
- Creep and high T deformation
- Toughness & manufacturability
- Highly variable coal combustion environments

The problem:
- Are there effective ways of tweaking existing systems?
- Can we develop a new alloy system?

Key metrics:
- High melting temperatures
- Microstructural stability
- Toughness $\geq 20$ MPa$\cdot$m$^{1/2}$
- Oxidative Stability

Ni based alloys approaching limits
Conceptual approach

Rapid screening of phase space: base alloy selection
(Deliverable: semi-empirical model for multicomponent systems)

Characterization & testing of the base alloy
(Deliverable: identify failure modes and alloy requirements)

Alloying additions guided by ab-initio studies
(Deliverable: Chemical modification for enhanced stability)

Microstructural modifications and gradients
(Deliverable: Processing methods for graded microstructures)

Toughness, deformation and high T strength
(Deliverable: Optimizing strength via processing techniques)

Oxidative damage: mechanisms and models
(Deliverable: Establish and improve oxidative limits)

Alloy development by multi-stage hierarchical screening

Ray et. al., JOM 62 (2010) 25


Ray et.al., App Surf Sci 301(2014) 107


Bell et. al., under preparation

Ray et. al., under preparation
# Enthalpies of multicomponent alloys

## Table: Combinations of Elements

<table>
<thead>
<tr>
<th># of elements</th>
<th>Combinations</th>
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<tbody>
<tr>
<td>3</td>
<td>3160</td>
</tr>
<tr>
<td>4</td>
<td>82160</td>
</tr>
<tr>
<td>5</td>
<td>$1.58 \times 10^6$</td>
</tr>
<tr>
<td>6</td>
<td>$2.40 \times 10^7$</td>
</tr>
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</table>

$$\Delta H = \phi_1 \Delta H_{AB}(\alpha) + \phi_2 \Delta H_{BC}(\beta) + \phi_3 \Delta H_{CA}(\gamma)$$

Individual binaries calculated using Miedema’s equation:

$$\Delta H = c_A c_B \left( f_A^A \Delta H^{i/c}_{AB} + f_B^B \Delta H^{i/c}_{BA} \right)$$

Mass balance constraints:

$$\sum_{i=1}^{3} \phi_i = 1$$

$$\phi_1 \alpha + \phi_3 (1 - \gamma) = x_A$$

$$\phi_2 \beta + \phi_1 (1 - \alpha) = x_B$$

$$\phi_3 \gamma + \phi_2 (1 - \beta) = x_C$$

Alloy selection: the NiAl-Mo system

<table>
<thead>
<tr>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
</tr>
<tr>
<td>1539</td>
<td>1670</td>
<td>1902</td>
<td>1857</td>
<td>1244</td>
<td>1540</td>
<td>1495</td>
<td>1453</td>
<td>1083</td>
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<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
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<tr>
<td>1526</td>
<td>1852</td>
<td>2467</td>
<td>2617</td>
<td>2200</td>
<td>2250</td>
<td>1963</td>
<td>1552</td>
<td>961</td>
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<tr>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>920</td>
<td>2227</td>
<td>3014</td>
<td>3407</td>
<td>3180</td>
<td>3027</td>
<td>2443</td>
<td>1772</td>
<td>1065</td>
</tr>
</tbody>
</table>

Requisites
- High temperature oxidation resistance
- High thermal stability

Bei & George, Acta Mater 53(2005) 69

Passivating elements
- Al
- Si
- Cr
- Ga
- Ge

High melting + poor oxidation
Low melting + good oxidation
Mix of oxidation and melting & possibly creep strength
Processing and microstructures

- Arc-melted
- Directionally solidified
- Liquid phase sintered
- Stable microstructures at 1500°C (12 hrs)
Fracture toughness of NiAl-Mo alloys

Mo forms the “backbone” for this alloy – creep and toughness

- Toughness of NiAl $\sim 5 \text{ MPa}\cdot\text{m}^{1/2}$
- Toughness of Mo-Si-B alloys $\sim 12 \text{ MPa}\cdot\text{m}^{1/2}$

Fracture toughness ascertained using four point bending method

![Four point bending method diagram]

Force applied perpendicular to the growth direction [ (0 0 1) direction]
Fracture toughness of NiAl-Mo alloys

- Fracture toughness of NiAl-15%Mo [drop-cast] ~ 10 MPa·m^{1/2} (J. Kruzic, OSU)
- Fracture toughness of NiAl-15%Mo [DS] ~ 20 MPa·m^{1/2}

Flexural Strength
- Drop-cast ~ 400 MPa
- DS alloys ~ 850 MPa

DS alloys shows a larger strain to failure
Fracture toughness of NiAl-Mo alloys

Presence of Mo dendrite pull-outs indicate a contribution towards toughening.

Some eutectic regions also showed the eutectic lamellae pull-outs.

Bell et al., article under preparation
Fracture toughness of NiAl-Mo alloys

Mo serves to deflect crack path thereby imparting toughening

Mo additions also appear to induce a small amount of plasticity
Effect of temperature on oxidation

Evolution of the oxide scale with temperature

As temperature increases, NiMoO$_4$ regions grow larger, but they start disappearing above 1100 °C. NiAl$_2$O$_4$ and NiO seem to predominate above 1125 °C.
Stability of NiMoO$_4$

Comparisons – spalled vs adherent scale

2 hrs @ 1100 °C

Major differences –

- The amount of NiMoO$_4$ and NiO is drastically reduced in the coupon surface.
- The $\alpha$-Al$_2$O$_3$ and MoO$_2$ are virtually absent in the spalled scale.
- NiAl$_2$O$_4$ shows up in both cases as a major phase.

A physical model for oxidation

Consider the oxidation of a Mo rich region of the surface.

Initial oxidation of Mo results in the formation of MoO₃ which later volatilizes.

$$\text{Mo} + \frac{3}{2} \text{O}_2 \rightarrow \text{MoO}_3$$

NiMoO₄ forms at the interface along with alumina

$$2\text{MoO}_3 + 2\text{NiAl} + \frac{3}{2}\text{O}_2 \rightarrow 2\text{NiMoO}_4 + \text{Al}_2\text{O}_3$$

NiMoO₄ dissociates progressively

$$\text{NiMoO}_4 \rightarrow \text{NiO} + \text{MoO}_3$$

The NiO reacts with the underlying Al₂O₃ to form the spinel interphase

$$\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$$

NiMoO₄ dissociates: poor oxidation;
NiMoO₄ doesn’t dissociate: $\beta \rightarrow \alpha$ transformation with 20% volume change

Ray et al., article under preparation
Coating methodologies

Coating process: Electrodeposition (Ni) and pack cementation (Al); anneal at 1350°C for 2 hours

Accurate statistical models of electroplating and pack cementation for controlling thickness
Oxidation of NiAl

Pure β-NiAl – Massive scale spallation during cyclic oxidation at 1250°C

Approaches –
- Enhanced melting temperature
- Microstructure

Ray et al., JOM 62 (2010) 65
Alloying additions: computational screening

\[ T_m = 0.032 \frac{E^c}{k_B} \]

Rose-Ferrante theory of Universal Binding Curve

\[ E^c = x_1 E_1^c + x_2 E_2^c + x_3 E_3^c - \Delta H_f \]


- Ab-initio calculations using VASP
- GGA potentials
- 54 atom unit cell (3 x 3 x 3)
**Ab-initio** studies on the role of PGM additions

\[
T_m = 0.032 \frac{E^c}{k_B}
\]

\[
E^c = x_1 E_{1}^c + x_2 E_{2}^c + x_3 E_{3}^c - \Delta H_f
\]

Formation enthalpies estimated using the VASP code with GGA potentials

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cohesive E (kJ/mol)</th>
<th>Metal</th>
<th>Cohesive E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>327</td>
<td>Ir</td>
<td>670</td>
</tr>
<tr>
<td>Ni</td>
<td>428</td>
<td>Pd</td>
<td>376</td>
</tr>
<tr>
<td>Rh</td>
<td>554</td>
<td></td>
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</tr>
</tbody>
</table>
Effect of PGM additions on oxidation

Pure β-NiAl – Massive scale spallation during cyclic oxidation at 1250°C

Addition of 6 atom% of PGM results in a significant increase in the oxidation resistance

Ray et al., JOM 62 (2010) 65
The role of grain size

β-NiAl

β-NiAl + 9% Ir

β-NiAl + 9% Ir + 0.05% Hf

Brammer et.al., article under preparation
Failure mechanisms for the coatings

- Pre-existing cracks provide oxidation pathways.
- Integrity is a function of NiMoO$_4$ formation vs Al$_2$O$_3$ coverage.
- T dependence is function of Al$_2$O$_3$ growth rate and MoO$_3$ vapor pressure
Oxidation behavior of coated alloys 1150°C

Optimal coating approach:

Double layered coatings

Pre-oxidized at 1100°C for 5 hours

Bell et al., article under preparation
Perspectives

• Semi-empirical techniques assisted in initial selection; further work resulted in an alloy with high melting temperature and adequate toughness, with oxidatively stable coatings.

• Computational methods were not used for down-selecting materials on the basis of oxidation resistance, due to a relatively small playground once criteria for high melting temperature and tough “backbone” phase were fulfilled.
Expanding the toolbox

- Need for more accurate models for materials genomics, especially with multiple principal components which presents a greater complexity of challenges
- Standard DFT based approaches are more suited to ordered materials rather than disordered solid solutions like HEAs
- Looking ahead – use computational tools for oxidation resistance, while selecting alloy systems that retain structural stability with temperature (Entropically Stabilized Alloys – studied using KKR-CPA) when oxidized (system selection using new computational tools – GSSNEB)
Short Range Ordering in N-component Alloy

- Atomic SRO can be calculated using *all-electron, first-principles KKR-CPA-based linear-response code* addressing inhomogeneous chemical fluctuations.
- We can uniquely identify atomic SRO in alloy using *Concentration Wave analysis* using an analytic N-dimensional transform for Gibbs’ (chemical) space.
- Approach was tested and verified on
  - Ternary A2 (bcc) Nb$_{25}$Al$_{25}$Ti$_{50}$
  - Quinary A1 (fcc) Ni$_{20}$Cu$_{20}$Al$_{20}$Ti$_{20}$Zr$_{20}$
Ti$_{50}$Nb$_{25}$Al$_{25}$: SRO unstable eigenmodes

*SRO indicate the unstable chemical modes*
All mode determined simultaneously, just like for (second-order) phonon modes.

Lowers energy

Costs energy

-0.1
0
0.05
0.1

$S^{(2)}(k)$

Nb-Ti
Nb-Al
Al-Ti

-0.1
-0.05
0
0.05
0.1

Temperature Scale
Theory spinodal $T_{sp} = 1750$ K
Experimental B2 order: 1713 K

First unstable mode (H-point)
$k_0 \rightarrow <100> = <111>$

Strong partially-ordered B2 (H-pt) ordering

Alloy-specific partially-ordered B2 phase

B2
<111>
Nb/Al

SRO in Quinary NiTiZrAlCu

Direct Calculation KKR-CPA
Formation Energy = +16.4 mRyd
$T_c = 1610$ K

Experimental findings – HEA by MA, multiphase intermetallics by casting

SRO: $k_0 = [000]$ Clustering
SRO: Unstable Modes (Zr-Cu)
$S^{(2)}$: competing Zr-Al, Zr-Cu, Ti-Al
$T_{sp} = 1510$ K (estimated)

Real Space decomposition of $S^{(2)}$ upto 5-shells.

<table>
<thead>
<tr>
<th>Shell_{RS}/Modes</th>
<th>Zr-Al</th>
<th>Zr-Cu</th>
<th>Ti-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{0}^{(2)}$</td>
<td>+10.4</td>
<td>+9.39</td>
<td>+8.55</td>
</tr>
<tr>
<td>$S_{1}^{(2)}$</td>
<td>-0.07</td>
<td>+2.37</td>
<td>-0.55</td>
</tr>
<tr>
<td>$S_{2}^{(2)}$</td>
<td>-0.01</td>
<td>-1.92</td>
<td>-0.05</td>
</tr>
<tr>
<td>$S_{3}^{(2)}$</td>
<td>-0.10</td>
<td>-4.27</td>
<td>+0.12</td>
</tr>
<tr>
<td>$S_{4}^{(2)}$</td>
<td>-0.01</td>
<td>+0.50</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
Kinetic Barriers for MnBi: HTP to LTP

- In HTP, interstitial Mn couples anti-ferromagnetic and reduces magnetization.
- Interstitial-vacancy pair (Mn\textsubscript{i}-V\textsubscript{Mn}) only costs 0.3 eV when separated by 1 atom.
- Barrier in between is as high as 1.7-2 eV, which limits kinetic for HTP → LTP.
- Kinetically stable HEA desirable for mechanical properties.
Summary

Thermodynamic stability of competing phases

Synthesis: different degree of deviation from equilibrium

Thermal analysis and phase evolution, Tm (DTA, DSC)

Oxidation resistance (cyclic and isothermal kinetics)

Structural analysis – microstructures, ordering (SEM, TEM, PXRD, synchrotron)

Thermo-kinetic modeling and alloy optimization

“Explore the development of graded oxidation resistant microstructures with high-entropy precursors”

Theoretical models for guiding experimental design

Experimental: synthesis and characterization

Optimized high-entropy alloy