Computational Design and Experimental Verification of Refractory Metal-Based Alloys

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New Energy Conversion Technologies and High-Temperature Structural Materials

Turbine blade substrate metal temperature (°C) and temperature capability of structural materials
Project Goals

To demonstrate that computational methods and experimental techniques together can be appropriately used to develop novel materials.

To improve room temperature ductility of Cr-based alloys, the primary barrier for chromium to be considered as a viable high temperature material for fossil energy applications.

Accelerated development and commercialization of novel materials to enable advanced fossil energy systems.
Alignment with FE AR-Materials Program
Why Chromium?

**Advantages**

- High melting point (1873°C)
- Good strength up to 1300-1400°C
- Low density (7.1 g/cm³)
- Low CTE (4x10⁻⁶ /°C)
- High thermal conductivity
- Most abundant refractory element

**Challenges**

- Room temperature ductility and fracture toughness
- Oxidation resistance above 1000°C
- Creep strength
How do we use computational methods to develop new materials?

- Ductility
- Grain boundary segregation
- Creep strength
IMPROVING DUCTILITY OF CHROMIUM
Modifying Poisson’s ratio of Cr by alloying

First-Principles DFT Computations

- VASP package
- Projector augmented-wave pseudopotentials
- Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional
- Energy cutoff = 500 eV
- Convergence w.r.t. K-points: 1 meV
- Precision “high”
- semi-core 3p, 4p and 5p electrons treated as valence
- Spin polarization considered (antiferromagnetism)
- 2x2x2 supercell bcc lattice
- Binary: composition of Cr$_{15}$X$_{1}$ (X=6.25at%) in bcc structure
Modifying Poisson’s ratio of Cr by alloying
Modification of elastic properties of Cr via alloying with V

RUS measurements were made at LANL (Y. Suzuki, J. Betts)
Single crystals were grown at Ames Lab (T. Lograsso, D. Schlagel)

\[ \sigma_{P-N} = \frac{G}{1 - \nu} e^{-\frac{2\pi a}{b(1-\nu)}} \]

\[ b = \frac{1}{2}[111] \]
Cr-V Alloys
Fabrication and Testing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr</th>
<th>V</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>R7</td>
<td>99.96%</td>
<td>.04%</td>
<td></td>
</tr>
<tr>
<td>R8</td>
<td>74.29%</td>
<td>25.40%</td>
<td>.31%</td>
</tr>
<tr>
<td>R9</td>
<td>48.92%</td>
<td>50.50%</td>
<td>.58%</td>
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<tr>
<td>R10</td>
<td>23.75%</td>
<td>75.40%</td>
<td>.85%</td>
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</tbody>
</table>

**Blending of powders**

**HIP (1250 C – 103 MPa)**

**Heat Treatment 1300 C, 120 h**

**Extrusion 1200 C, 6:1 ratio**

**Diffusion Study**

**BDTT Determination**

- 3-Point Bend Tests (-40 C – 400 C)
- Tensile Tests (-40 C – 400 C)

Hailey Murdock
Jay Kruzic

**Mechanical testing**

Oregon State University
College of Engineering
Precipitates at GB

X. Song, West Virginia Univ.
J. Sears, NETL

Precipitates inside Grains

Cr-25V

Cr-50V

0.5 µm

500 nm

10 nm

$[010] C_{20}Cr_{25}V_{55}$
We are developing capability of modeling microstructures using Phase Field Method. Creep mechanisms, Oxidation scale growth, TBC/Bond Coat/Substrate degradation.
Program

Thermo Database

PanEngine

Phase Field

Kinetic Database
Interstitial Segregation

\[ F = \int_V \left\{ \frac{G_m(X_C, T)}{V_M} + f(X_C, \phi_1, \phi_2, T) + \frac{\epsilon^2}{2} \left[ \phi_1(\nabla \phi_2)^2 + \phi_2(\nabla \phi_1)^2 \right] \right\} dV \]

Sublattice Model

\[ e.g. \quad \text{Fe}(C, Va)_3 \quad \text{for BCC} (\alpha-\text{Fe}) \]
Segregation Energy

**GB Barrier & Segregation Energy**

\[ f(X_C, \phi_1, \phi_2, T) = \frac{W_c(T)y_c + W_v(T)y_{va}}{2} \phi_1^2 \phi_2^2 \]

**Segregation Parameters**

\[ \frac{W_c(T)y_c + W_v(T)y_{va}}{2} \phi_1^2 \phi_2^2 \]

**Chemical Potential of Interstitial**

\[ \mu_C = \mu_C^h + [W_c(T) - W_v(T)] \phi_1^2 \phi_2^2 \]

**Diffusion Flux of Interstitial**

\[ J_C = -\frac{C_c}{C_A} \left( c_c M_A + c_A y_{va} M_C \right) \nabla \mu_C \]
GB Segregation-3D

300 Grains, 200 Orientations
Segregation Kinetics

Fe-C BCC ($\alpha$-Fe)
Effect of Segregation Parameters

$$f(X_C, \phi_1, \phi_2, T) = \frac{W_C(T)y_c + W_v(T)y_{va}}{2} \phi_1^2 \phi_2^2$$
Summary on Phase Field Modeling

- **Completed**
  - Parallel code
  - Multi-component, Multi-orientation, Polycrystal
  - GB Segregation of Interstitial Solutes
  - Integration with CALPHAD Databases
  - Ready for Real Systems

- **In Progress**
  - Integration with FFT for Mechanical Property Evaluation
  - Integration with First-Principles DFT and KMC Calculations
CREEP STRENGTH IN CHROMIUM ALLOYS
SEARCHING FOR ORDERED PHASES

Something like these microstructures

For improved creep resistance
And ideally contribute to the oxidation resistance
Ordered phases:
(1) $\text{Cr}_2\text{Ti.cF24}$ (Laves), $T_{\text{crit}}=1370^\circ\text{C}$
(2) $\text{AlNi.cP2}$ (CsCl), $T_m=1638^\circ\text{C}$
(3) $\text{AlNi}_2\text{Ti.cF16}$, $T_m=1500^\circ\text{C}$
<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Parameters</th>
<th>Cr.cI2</th>
<th>AlNi$_2$Ti.cF16</th>
<th>AlNi.cP2</th>
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</thead>
<tbody>
<tr>
<td>$a$ [cal]</td>
<td>2.87</td>
<td>5.8898</td>
<td>2.8890</td>
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<tr>
<td>$a$ [exp]</td>
<td>2.91</td>
<td>5.87</td>
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<tr>
<td>$C_{11}$ [GPa]</td>
<td>426</td>
<td>218</td>
<td>214</td>
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<tr>
<td>$C_{12}$ [GPa]</td>
<td>56</td>
<td>145</td>
<td>138</td>
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<tr>
<td>$C_{44}$ [GPa]</td>
<td>95</td>
<td>94</td>
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<tr>
<td>$B$ [GPa]</td>
<td>179</td>
<td>169</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>$G$ [GPa]</td>
<td>124</td>
<td>65</td>
<td>75</td>
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<tr>
<td>$\nu$</td>
<td>0.219</td>
<td>0.330</td>
<td>0.300</td>
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misfit = 0.9%          misfit = 1.0%
Fig. 4  Al-Cr-Ni isothermal section at 1000 °C [2008Gru1]

Chen Metall Mater Tran. 40A (2009) 2980

Fig. 1  Al-Ni-Ti isothermal section at 1000 °C [2007Sch]

ASM Ternary Handbook

Fig. 1—Solid-state phase equilibria at 900 °C (≤75 at. pct Al) and 600 °C (>75 at. pct Al).
$\Delta H_f = -55.8 \pm 2.2$ [exp, Hu et al.]
-63.8 [Calphad]
-49.1 [DFT calculations]
Cr Solubility in AlNi$_2$Ti.cF16

DFT: 2x2x2 supercell (128 atoms); electronic spin polarization considered.
Experimental Work

- Process Cr-Ni-Al-Ti alloys
- Characterize microstructure
- Verification of AlNi$_2$Ti second phase
<table>
<thead>
<tr>
<th>Milestones</th>
<th>Milestone Date</th>
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<tr>
<td>Establish computational methods to study</td>
<td>12/31/2009</td>
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<tr>
<td>(i) effects of alloying elements on dislocation mobility</td>
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<td>(ii) segregation of impurities at grain boundaries,</td>
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<td>(iii) formation of ordered phases.</td>
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<td>Preliminary results of computational work on the three tasks above.</td>
<td>03/31/2010</td>
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<td>Experimental results on identification of ordered phases predicted by</td>
<td>06/30/2010</td>
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<td>computations</td>
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<td>Demonstrated improved ductility for Cr alloys</td>
<td>09/30/2010</td>
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Deliverables


• Thermodynamic Assessment of V-Rare Earth Systems, W. Chan, M. C. Gao, Ö. N. Doğan, P. King, submitted to *Journal of Phase Equilibria and Diffusion*.


Future Plans

Further improve computational methods to realistically simulate complex alloy systems and coatings.

Apply the computational methods that we have developed to other high temperature alloys.

Develop high temperature materials for FE applications to support AR goal of “Advanced Materials for Zero-Emission Power Plants”.