Integrated Design and Rapid Development of Refractory Metal Based Alloys for Fossil Energy Applications

Ömer Doğan, Michael Gao, Paul King
New Energy Generating Technologies and High-Temperature Structural Materials

Refractory Metals and Ni

<table>
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<th>Melting T °C</th>
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Major issues with refractory metals

- Low ductility and fracture toughness at low temperatures
- Poor oxidation resistance at high temperatures
Integrated Design of Refractory Metal Based Alloys For Fossil Energy Applications

*The project goal is to develop refractory metal based alloys utilizing integrated design approach.*

Integrated design uses computational methods with experimental verification and available knowledge base to design alloys according to the requirements of processing, microstructure and properties.

- **Thermodynamics** (DFT, CALPHAD)
- **Kinetics** (DFT, CALPHAD)
- **Process Requirements**
  - Ductility (DFT, Dislocation Dynamics)
- **Microstructure Requirements**
  - Grain boundary segregation (MD)
  - Second phase particles (CALPHAD)
- **Performance Requirements**
  - Creep strength (DFT, CALPHAD)
  - Fracture toughness (DFT, DD)
  - Corrosion resistance (CALPHAD)

As a result of integrated design, the efficient development of materials requires much less experimental work, thus reducing the time and cost involved in alloy development.
Integrated Design of Refractory Metal Based Alloys for Fossil Energy Applications

• Improving ductility and fracture toughness through substitutional alloying
• Thermodynamic evaluation of promising systems
• Kinetic evaluation of relevant alloy systems
• Grain boundary segregation of C, N, O, and S in the refractory alloys
• Ductile – Brittle transition (DBT) in refractory alloys
• Improving creep strength
• Improving high temperature oxidation resistance
Improving ductility and fracture toughness through substitutional alloying

- First principles quantum mechanical calculations
- Experimental verification: tensile & fracture toughness
Thermodynamic evaluation of promising systems

- DFT calculations & CALPHAD modeling
- Experimental verification: Thermal analysis, XRD, TEM, SEM

Enthalpy convex hull plot of Al-Cr from first principles DFT calculations

An efficient and reliable way to study phase diagrams is to combine first principles DFT calculations, critical experiments and CALPHAD modeling.
Kinetic evaluation of relevant alloy systems

• **DFT calculations of diffusivities (CMU)**
  – Interstitial (O, N and C) diffusion in refractory metal based alloys will be studied using first-principles quantum-mechanical calculations

• **Experimental diffusivity measurements (CMU)**
  – Substitutional diffusion coefficients for promising systems will be measured and incorporated into the DICTRA kinetic database
Grain boundary segregation of C, N, O, and S in the refractory alloys

- Molecular dynamic simulations coupled with DFT calculations
- Experiments: HRTEM, Analytical TEM

Carbon concentration as a function of misorientation of adjacent grains

(a–d) Simulations of Al-Pb microstructures for 0–3 at.% Pb, respectively. (e–g) The Pb atom positions highlighted for frames (b–d), respectively.


Hofman: Surf interf Ana 19 (1992) 601
Ductile – Brittle Transition (DBT) in Refractory Metal Based Alloys

- Dislocation dynamics simulations to study interactions between the crack tip and dislocations

- Experimental study to understand the ductile-brittle transition

\[ \text{DBT} \]

Is it lack of dislocation nucleation? Is it lack of dislocation mobility?

Improving Creep Strength of Refractory Metal Based Alloys

- Explore strengthening second phase particles in terms of high temperature stability, lattice coherency, and coarsening behavior in candidate alloy systems
- Fabricate designated binary/ternary/higher degree alloys and characterize them using XRD, TEM, SEM, and optical microscopy


82Nb-8Al-10Ru

Ru₂NbAl
Improving High Temperature Oxidation Resistance of Refractory Metal Based Alloys

- Thermodynamic calculations to identify stable oxides at high temperatures, to determine solubility of alloying elements and elements entering from the environment both in the scale and in the bulk alloy.
- Kinetic computations will be performed to determine growth rates of the oxide scales.
- High temperature oxidation experiments (continuous and cyclic) will be performed and oxide scales will be characterized using XRD, ESCA, Auger spectroscopy, and SEM.

Integrated Design of Chromium Based Alloys for Fossil Energy Applications

- We selected Cr to demonstrate that integrated design methodology works well in developing new high temperature materials based on refractory metals.
- Cr based alloys show considerable promise due to:
  - relatively low cost
  - relatively low density
  - good high temperature strength

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Donachie – Superalloys, ASM International, 2002
1) Binary solubility in Cr
2) Liquidus temperature
Ductility and Toughness vs. Poisson ratio

Crystalline metals (purity ≥ 99.9%)

[1]. S.F. Pugh, Phil. Mag., 45 (1954) 823


Amorphous alloys
Amorphous + crystalline composite

Phil. Mag. Lett. 85 (2005) 77
What Is Poisson’s Ratio?

Poisson's ratio is the ratio of the relative contraction strain, or transverse strain (normal to the applied load), divided by the relative extension strain, or axial strain (in the direction of the applied load).

Uniaxial compression

\[ \nu = -\frac{\varepsilon_{\text{tran}}}{\varepsilon_{\text{axial}}} \]

- \( \nu \) is the resulting Poisson's ratio
- \( \varepsilon_{\text{tran}} \) is transverse strain
- \( \varepsilon_{\text{axial}} \) is axial strain.

General Hook’s law

\[ \varepsilon_x = \frac{1}{E} [\sigma_x - \nu (\sigma_y + \sigma_z)] \]
\[ \varepsilon_y = \frac{1}{E} [\sigma_y - \nu (\sigma_x + \sigma_z)] \]
\[ \varepsilon_z = \frac{1}{E} [\sigma_z - \nu (\sigma_x + \sigma_y)] \]

\[ \nu = \frac{3 - 2(G/B)}{6 + 2(G/B)} \]

G = polycrystalline shear modulus
B = bulk modulus

Poisson ratio is all about G/B ratio
Desirable: high B, low G
Intrinsic property; can be calculated without experimental information
Computational Details

• VASP package is used
• 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 compositions
• Ternary compositions in bcc structure
Bulk Modulus Calculations

\[ B = -\left( V \frac{\partial P}{\partial V} \right)_{E_{\text{min}}} = V \frac{\partial^2 E}{\partial V^2} \bigg|_{E_{\text{min}}} \]

Cubic polynomial fitting. There are other EOS (equation of state) such as Murnaghan equation, Birch-Murnaghan equation.

Antiferromagnetism of Cr must be included into calculations to validate the predicated physical properties.
Polycrystalline Shear Modulus


\[ G^3 + \frac{9B+4C'}{8} G^2 - \frac{3C_{44}(B+4C')}{8} G - \frac{3C_{44}C'B}{4} = 0 \]

\[ C' = \frac{1}{2}(C_{11} - C_{12}) \quad B = \frac{1}{3}(C_{11} + 2C_{12}) \]

G=shear; B=bulk modulus; C_{11}, C_{12} and C_{44} are elastic constants

Applying orthorhombic strain

Mehl et al, Phys Rev B 41 (1990) 10311

\[ \varepsilon_o = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2(1-\delta^2) \end{pmatrix} \]

\[ \Delta E(\delta) = E(0) - E(\delta) = (C_{11} - C_{12})V_0\delta^2 + O[\delta^4] \]

Applying monoclinic strain

\[ \varepsilon_m = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2(4-\delta^2) \end{pmatrix} \]

\[ \Delta E(\delta) = E(0) - E(\delta) = \frac{1}{2}C_{44}V_0\delta^2 + O[\delta^4] \]
Validation of Computation

**Bulk modulus**

- **Cal.** vs. **Exp.**
- Elements: Al, Zr, Hf, Nb, Cr, Ta, Mo, W
- **Y-axis:** Bulk Modulus (GPa)
- **X-axis:** Elements

**Elastic constants**

- **C11**, **C12**, **C44**
- **Cal.** vs. **Exp.**
- **Y-axis:** Elastic constants (GPa)
- **X-axis:** Elastic constants

**Poisson ratio**

- **Cal.** vs. **Exp.**
- Elements: V, Cr, Nb, Mo, Ta, W, Al
- **Y-axis:** Poisson's ratio
- **X-axis:** Elements

**References**

Current status

- We have done similar calculations on ternary systems based on the promising binaries
- Currently, we are working on establishing phase diagrams for the promising ternary systems
Future Work

• Continue thermodynamic investigation to identify a promising multi-component system
• Kinetic studies on the identified multi-component system
• Designing an alloy with sufficient creep strength within the multi-component system
• Further modifying the alloy composition for high-temperature oxidation resistance

Above tasks will be accomplished utilizing various computational tools and experimental work