Multiscale Modeling of Grain Boundary Segregation and Embrittlement in Tungsten for Mechanistic Design of Alloys for Coal Fired Plants

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This UCR Project

GB = Grain Boundary

Using tungsten (W) based binary & ternary alloys as model systems...

Develop thermodynamic theories and models to predict a “new” type of high-T (premelting-like) GB segregation

Luo et al. at Clemson/UCSD

Develop multiscale modeling strategies to link GB segregation with GB embrittlement

Tomar et al. at Purdue

Experimental validation

Atomistic & quantum modeling of stress-strain

Continuum fracture modeling

Selected Results from Our Year-3 Efforts
Background: Grain Boundary (GB) Segregation

The Classical Models vs. New Perspectives

McLean-Langmuir:

\[ \frac{\Gamma}{\Gamma_0 - \Gamma} = \frac{X_C}{1 - X_C} \cdot e^{\frac{-\Delta g_{ads}}{kT}} \]

\[ \Delta g_{ads} = g_{GB} - g_C \]

Fowler-Guggenheim:

\[ \Delta g_{ads} = \Delta g_{ads}^{(0)} + z_1 \alpha_{Fowler} \frac{\Gamma}{\Gamma_0} \]

Monolayer? In reality, not necessarily

Background: Grain Boundary (GB) Embrittlement
The Classical Models vs. New Perspectives

Classical GB Embrittlement Models – Built on Langmuir-McLean Adsorption

Reduction of cohesion due to:
- Electronic effect (weakening the bonds);
- Atomic size (strain) effect; or
- Changing relative γ’s (the Rice-Wang Model)

New Perspective:
Segregation → GB Transition → Drastic Change in Properties

At High Temperatures & Alloying/Impurity Levels...
Segregation → GB “Melting” (Interfacial Disordering) → Embrittlement

S segregation → GB “melting” if $C_{S}^{GB} > 15\%$
→ GB Embrittlement

Atomistic Simulation: Chen et al., PRL 2010
Auger: Heuer et al., J. Nuclear Mater. 2002

Beyond “Monolayer”?

“Complexion” Transition (Bilayer)
Luo, Cheng, Asl, Kiely & Harmer
Science 333:1730 (2011)

Interfacial Disordering
(Liquid-Like GB “Complexion”)
**The Phenomenon**

**Unary Systems:**
- Surface Premelting ✓
- GB Premelting ???

Late 1980’s: Balluffi’s group suggested no GB premelting up to 0.999$T_{mel}$ in Al!

**Thermodynamically stable at** $T < T_{melting}$

**Multicomponent?**
- Enhanced by segregation
  - Sintering ✓ (Prior work)
  - Embrittlement ✓ (This study)
  - Coble creep? (Next UCR project)

**Can be stabilized at** $T < T_{solidus}$

**Ceramic Systems (Well Known)**

- **Vapor**
  - $\Delta T \equiv T_{eutectic} - T = 140^\circ C$
  - $\Delta T = 40^\circ C$

- **ZnO**
  - $\Delta T = 95^\circ C$

- **Ni-doped W**
  - $\Delta T = 95^\circ C$

- **Bi$_2$O$_3$-enriched film**
  - $\Delta T = 95^\circ C$

- **Ni-enriched film**
  - $\Delta T = 95^\circ C$

Luo et al., *Langmuir* 2005
Wang & Chiang, *JAmCerS* 1998

Luo et al., *APL* 2005

**ZnO Vapor**


Alsayed et al, *Science* 2005

**GB premelting in a colloidal crystal**

**Ice Surface (MD simulation)**

1 nm 1 nm 1 nm

**Ice Surface**

**Luo**
A subsolidus quasi-liquid film is thermodynamically stable if:

\[ \Delta G_{\text{amorph}} \cdot h < -\Delta \gamma \equiv \gamma_{gb}^{(0)} - 2\gamma_{cl} \]

Define & quantify:

\[ \lambda \equiv \frac{-\Delta \gamma}{\Delta G_{\text{amorph}}} \]

\( \lambda \) represents the thermodynamic tendency to stabilize a quasi-liquid film

Continuum approx. for metals:

\[ h_{EQ} \approx \xi \cdot \ln(\lambda / \xi) \]

\( \lambda \) scales the film thickness
A Prior Successful Example of Predictive Modeling: Extending Bulk CalPhaD Methods to GBs

Computed Lines of Constant $\lambda$: GB $\lambda$-Diagrams

**Experimental Validation:**
- HRTEM
- Auger
- Onset $T_{\text{sinter}}$ for W-X
- $D_{\text{GB}}(T, X)$

**Computed GB $\lambda$-diagram**

**Example of Predictability:** A counterintuitive prediction of $D_{\text{GB}} \downarrow$ as $T \uparrow$ was verified!

Shi & Luo
PRL 2010
One Major 3rd-Year Task of This UCR Project (as proposed)

Computing Ternary GB $\lambda$-Diagrams for W-Ni-X ($X = Zr, Co, Cr, Fe, Nb, Ti$)

\[ \lambda \equiv \text{Max} \left\{ \frac{\gamma_{GB} - 2\gamma_{cl}}{\Delta G_{amorph}} \right\} \]

**Ternary CalPhaD**

\[ \Delta G_{amorph}(X^{film}) = G_{liquid}(X^{film}) - \sum_i \mu_i^{solid} X_i^{film} \]

\[ G^f (T, X_A, X_B) = X_A G_A^0 + X_B G_B^0 + X_C G_C^0 + RT \left( X_A \ln X_A + X_B \ln X_B + X_C \ln X_C \right) + X_A X_B \sum_{j=0}^{n_{AB}} \Omega_{j}^{AB} (X_A - X_B)^j \]

**Redlich-Kister Expansion**

\[ + X_B X_C \sum_{j=0}^{n_{BC}} \Omega_{j}^{BC} (X_B - X_C)^j + X_C X_A \sum_{j=0}^{n_{CA}} \Omega_{j}^{CA} (X_C - X_A)^j + X_A X_B X_C G^{ABC} \]

**Statistical Thermodynamic Model (using CalPhaD data)**

\[ \gamma_{GB} = \frac{H_A^{vapor}}{3C_0V_A^{2/3}} \]

\[ \gamma_{cl}(X^{film}) = \frac{H_A^{fuse}}{C_0V_A^{3/2}} + \sum_{i \notin A} X_i^{film} \omega_{i-j}^{liquid} \left( \frac{2}{C_0V_A^{3/2}} + \frac{1.9RT}{C_0V_{Average}^{3/2}} \right) - \sum_{j \neq i} \sum_{i \notin A} \frac{X_i^{film} X_j^{film} \omega_{i-j}^{liquid}}{2C_0V_A^{2/3}} \]

**Practical Importance:**

- Engineering alloys often have many components or impurities
- Co-alloying to control GB behaviors?
Construct A Ternary GB $\lambda$-Diagram
(An Example: W-Ni-Fe, 1300 °C)

Considering ONLY the W-based BCC phase (& liquid phase)

Considering All Phases @ Bulk Equilibria
Computed $W$-Ni-$X$ ($X = \text{Cr, Zr, Co, Fe, Nb, Ti}$) Ternary GB $\lambda$-Diagram
(Considering Only BCC and Liquid Phases)

$T = 1300 \degree$
Computed $\textbf{W-Ni-X (X = Cr, Zr, Co, Fe, Nb, Ti)}$

Ternary GB $\lambda$-Diagram

(Considering All Stable Bulk Phases) $T = 1300 \, ^\circ\text{C}$

One Prediction: The co-alloying effect on promoting GB disordering of W-Ni-X (represented by the increase in $\lambda$) roughly follows the order: $\text{Cr} < \text{Zr} < \text{Co} < \text{Fe} < \text{Nb} < \text{Ti}$
Experimental Model Validation: Co-doping Effects in Ternary Alloys

For W-Ni-X (X = Zr, Co, Cr, Fe, Nb, Ti)

A custom-made furnace
- To remove ramping effects

Our Approach:
Density rate → The effect of co-alloying on promoting GB disordering (represented by the increase in computed $\lambda$)

Limitation: Chemical effect on GB diffusion not represented

The only exception in rankings

Ternary W-0.5Ni-0.5X (at. %)
Estimate Interfacial Width ($h_{EQ}$) from the Computed $\lambda$-Diagram?

The Excess Free Energy:

$$G^x - \gamma_{gb}^{(0)} = \Delta G_{amorph} \cdot h + \Delta \gamma + \sigma_{interfacial} (h) = \Delta G_{amorph} \cdot h + \Delta \gamma \cdot f(h)$$

Interfacial (disjoining) Potential

$$\begin{cases} f(0) \equiv 0 \\ f(\infty) \equiv 1 \end{cases}$$

Continuum approx. for metals:

$$f(h) \approx 1 - e^{-h/\xi}$$

Coherent length

$$h_{EQ} \approx \xi \cdot \ln(\lambda / \xi)$$

GB $\lambda$-Diagram

Estimating $h_{EQ}$ & $\gamma_{gb}$

The Excess Free Energy: Interfacial (disjoining) Potential

$$\begin{cases} f(0) \equiv 0 \\ f(\infty) \equiv 1 \end{cases}$$

Continuum approx. for metals:

$$f(h) \approx 1 - e^{-h/\xi}$$

Coherent length

$$h_{EQ} \approx \xi \cdot \ln(\lambda / \xi)$$
High-T (Liquid-Like) vs. Classic (Solid-Like) GB Segregation
(To Establish a Unified Thermodynamic Framework?)

Premelting-Like Segregation
Interfacial Disordering

Multilayer Segregation on the Lattice
Wynblatt-Chatain [JMS 2005; 2006, MMA 2006]

Generally, more reduction in the GB energies ($\gamma_{GB}$'s) for forming liquid-like complexions in W-Ni and most other W-based alloys (due to the high $\gamma_{GB}^0$ of W)
A Useful Component for the “Materials Genome” Project?

Construct “Grain Boundary (GB) Diagrams”

Useful Materials Science Tool for Designing:
- Fabrication protocols utilizing appropriate GB structures to achieve optimal microstructures
- Co-doping strategies and/or heat treatment recipes to tune the GB structures for desired performance

Applications: To predict useful trends in:
- GB embrittlement
- Sintering
- Grain growth & microstructural involution
- Coble creep
- GB controlled corrosion & oxidation
- ...

Following the late Dr. R. M. Cannon’s transformative concept

Summary – Thermodynamics Thrust

We have …

• (Years 1 & 2) Derived the basic equations;
• (Years 1 & 2) Developed and tested the algorithms and MATLAB codes;
• (Years 2) Completed numerical experiments;
• (Year 3) Computed “GB $\lambda$-diagrams” for W-Ni-X ($X =$ Cr, Zr, Co, Fe, Nb & Ti) systems;
• (Year 3) Conducted experimental validation for ternary W alloys;
• (Year 3) Compared with classical segregation model in an effort to establish a unified framework; and
• Worked closely with the Purdue team to use our thermodynamic models and experimental results to support their multiscale modeling efforts to link GB segregation to mechanical properties.
PROBLEM DESCRIPTION

- The primary site of embrittlement of Nickel (Ni) – doped Tungsten (W) is at the grain boundary (GB).

- GB is interfacial region between two differently oriented W grains.

- Most of the Ni impurities concentrate at the GB region.

- GB thickness varies upon the level of saturation. (unsaturated:0.3nm, saturated:0.6nm)

- While the mechanical properties (yield stress, ultimate tensile strength, etc) of Ni-doped W varies by the change of Ni amount and the level of saturation, the quantitative relation to predict those mechanical properties are needed.
PROBLEM DESCRIPTION

Fully saturated tungsten
→ GB thickness = 0.6 nm

Consist of (100) and (210) orientation of atom array
Setup

Pure W

(100) (210)

(a)

Unsaturated W

~0.3 nm

(100) W+NI (210)

(b)

Saturated W

~0.6 nm

(100) W+NI (210)

(c)
RESULT – (1) PURE W

Typical tungsten properties:
Tensile strength : 1.5 ~ 4.2 GPa
Young’s modulus : 360 ~ 420 GPa

Q. Wei and et al, 2006, Acta Materialia

4.0 Gpa : Ultimate Tensile Strength
Yield strength : 1.5 GPa at 0.04 strain (approximated by 0.2% offset)
RESULT – (2) UNSATURATED (GB thickness = 0.3 nm)

Yield strength: at strain 0.04
The yield strength has dependent on the Ni volume fraction.

First peak: at strain 0.12
The first peak’s values has dependent on the Ni volume fraction.

Second peak: at strain 0.18
The second peak’s values are not depend on the Ni volume fraction.

Ultimate tensile strength: strain of 0.12~0.18
The maximum tensile strength are not depend on the Ni volume fraction for the unsaturated Ni-doped W.
RESULT – (3) SATURATED (GB thickness = 0.6 nm)

Yield strength: at strain 0.04
The yield strength has dependent on the Ni volume fraction.

First peak: at strain 0.16
The first peak’s values has dependent on the Ni volume fraction.

Second peak: at strain 0.24
The second peak’s values have the largest dependence on the Ni volume fraction.

Ultimate tensile strength: strain of 0.16~0.24
The maximum tensile strength are depend on the Ni volume fraction for the saturated Ni-doped W.
Comparison of the maximum tensile stress with the density of states (sum in the range of -1.3 ~ -1.0 eV) for f-orbital of unsaturated case saturated case
PHONON DISPERSION
PHONON DISPERSION

1st transverse curve for the direction of $[\xi 00]$, and $[\xi \xi 0]$.

Note that the pure W is idealistic atomic structure based on no GB assumption.

With existing of GB thickness larger than 0, more saturated form gives higher frequency which is related to the higher bond strength along the horizontal direction.

Although the atomic structure of pure W provides higher phonon frequency in overall, the stress-strain curve tells us that the substitution of Ni atoms with W plays a role of compensating the low frequency of phonon dispersion curve.
Cubic polynomial regressions for (a) total values of E-DOS (electron density of states) of unsaturated and saturated Ni-added W GB, (b) total values of phonon dispersion in direction of ($\xi00$) and ($\xi\xi0$)

\[
\frac{T_{\text{max}}}{T_{\text{ideal}}} = \frac{CE}{CD} \Phi f(t,n)g(w)
\]
A comparison of the GB strength as a function of Ni atomic fraction using the derived analytical expression and the CPMD results in the case of 0.3 nm thickness GB, and 0.6 nm thickness GB.
OBTAINING MICROSTRUCTURES


-From the tungsten microstructure morphology in the above paper, digitalization process has been gone through to extract grain boundary shape.

-With the assumption that grains are consist of 3 different orientation and GB to form a microstructure, grain types are assigned to grain region.
DETERMINISTIC FINITE ELEMENT EQUATIONS

- LaGrangian Kinetics Description

\[ \int_V s : \delta F dV - \int_{S_{int}} T \cdot \delta A dS - \int_{S_{ext}} T \cdot \delta u dS - \int_V \rho \frac{\partial^2 \mathbf{u}}{\partial t^2} \cdot \delta \mathbf{u} dV, \]

- Finite Element Descretization

\[ \mathbf{M} \ddot{\mathbf{u}} = -\mathbf{R} \]

- Solution of Equations (Newmark $\beta$ -Method)

\[
\begin{align*}
\ddot{\mathbf{u}}^{n+1} &= -\mathbf{M}^{-1}\mathbf{R}^n \\
\dot{\mathbf{u}}^{n+1} &= \dot{\mathbf{u}}^n + \frac{1}{2} \Delta t_n \left( \ddot{\mathbf{u}}^{n+1} + \ddot{\mathbf{u}}^n \right) \\
\mathbf{u}^{n+1} &= \mathbf{u}^n + \Delta t_n \dot{\mathbf{u}}^n + \frac{1}{2} \left( \Delta t_n \right)^2 \ddot{\mathbf{u}}^n 
\end{align*}
\]
PERCENTAGE OF EACH PHASES

<table>
<thead>
<tr>
<th>Type</th>
<th>Percentages by Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB</td>
<td>7.53 %</td>
</tr>
<tr>
<td>Phase1</td>
<td>17.41 %</td>
</tr>
<tr>
<td>Phase2</td>
<td>40.43 %</td>
</tr>
<tr>
<td>Phase3</td>
<td>34.63 %</td>
</tr>
</tbody>
</table>

For each cases, three different GB properties are applied.

→ Maximum Tensile strength that is

1. Larger than that of grains
2. Same as that of grains
3. Smaller than that of grains
FRAMEWORK

→ All cohesive surfaces serve as potential crack paths.
→ FE meshes are uniformly structured with “cross-triangle” elements to give maximum flexibility for resolving crack extensions and arbitrary fracture patterns.
→ Center-cracked tungsten specimens under tensile loading.
→ Initial crack : 20 µm
→ The boundary velocity $V$ (1m/s) is imposed with a linear ramp from zero to $V$ in the initial phase of loading.
→ The specimen is stress free and at rest initially.
COMPARISON FOR COHESIVE ENERGY DISSIPATION

When $T = 155$ nsec

High Strength GB

Medium Strength GB

Low Strength GB

Interfacial Multiphysics Lab (https://engineering.purdue.edu/~tomar)
COMPARISON FOR CRACK PROPAGATION DIRECTION

When $t = 155$ nsec

Low Strength GB

High Strength GB

Medium Strength GB

Low Strength GB
COMPARISON OF PRIMARY CRACK AND MICROCRACKS

High Strength GB

Medium Strength GB

Low Strength GB

Primary crack

Micro crack

Primary crack

Micro crack

Primary crack

Micro crack

TIME [ nsec ]

Percentage

TIME [ nsec ]

Percentage

TIME [ nsec ]

Percentage
THE RELATION BETWEEN ENERGY DISSIPATION VS CRACK DENSITY

Therefore, \( \Phi \cdot \Delta \cdot \left( \frac{a \times b}{h^2} \right) \cdot C \) can be explained as energy dissipation per unit crack length or crack density. C is a constant.

In our case of simulation, \( C = 12.5 \)

\[ CE = 12.5 \cdot \Phi \cdot \Delta \cdot \left( \frac{a \times b}{h^2} \right) \cdot CD \]

By substituting the equation \( \Delta = \frac{2 \cdot \Phi}{T_{\text{max}}} \) to the above equation,

we obtained a relation of \( CE = 25 \cdot \frac{\Phi^2 \cdot (a \times b)}{T_{\text{max}} \cdot h^2} \cdot CD \)
THE RELATION BETWEEN ENERGY DISSIPATION VS CRACK DENSITY

\[ CE = 25 \cdot \frac{\Phi^2 \cdot (a \times b)}{T_{\text{max}} \cdot h^2 \cdot CD} \]
CONCLUSIONS

- Analyses demonstrate that the failure of a tungsten involves inter-granular cracks, intra-granular cracks, and significant microcracking.

- By applying different properties of GBs, plots of cohesive energy dissipation display various patterns of energy release. Property of ductility and brittleness are known as temperature dependent, however, the findings in this study indicates that the tungsten microstructural failure can have both ductile and brittle pattern of failure decided also by property of GBs. (GBs have 7.53% by volume)

- The level of microcracking goes greater in the interfaces of grains as strength of GBs becomes lower.

- A significant microcracking occurs during failure. Surface energy study in this research indicates m value to be around 14 for such microstructure with no time dependent. This finding can contribute to predict the level of microcrack over primary crack at other time frames.

- In literature, continuum and analytical fracture mechanics work usually neglects contribution of GBs to overall microstructural fracture strength. The findings in this work indicate property of GB act major role in crack propagation pattern as well as crack initiation time.