Multiscale Modeling of UHTC: Thermal Conductivity

John W. Lawson
NASA Ames Research Center

Murray S. Daw
Clemson University

Thomas H. Squire
NASA Ames Research Center

Charles W. Bauschlicher
NASA Ames Research Center

NASA Fundamental Aeronautics Program (FAP)
NASA Innovative Partners Program (IPP)
New materials modeling: interdisciplinary
- Computational chemistry
- Computational physics
- Computational engineering

Ablative composites
- Application: atmospheric re-entries
- Materials: PICA, Avcoat,…

Ultra high temperature ceramics (UHTC)
- Applications: leading edges
- Materials: ZrB$_2$ and HfB$_2$

UHTC modeling illustrate our approach

<table>
<thead>
<tr>
<th>Image</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="In-situ TEM image of UHTC" /></td>
<td>PICA: fibers w/ phenolic</td>
</tr>
<tr>
<td><img src="image2.png" alt="In-situ TEM image of UHTC" /></td>
<td>UHTC: HfB$_2$ w/ 20% SiC</td>
</tr>
</tbody>
</table>
UHTC for Sharp Leading Edges

*Sharp leading edge for hypersonic aircraft*
- Enhances vehicle performance
- Improves safety

*Higher temperature requirements*
- Shuttle RCC leading edge: T\~1650°C
- Sharp leading edged vehicles: T>2000°C

*UHTC advantages for sharp leading edges*
- Reasonable mechanical properties
- Oxidation resistance
- *High thermal conductivity*
  - Effective thermal radiation
  - Thermal shock resistance

Multiscale Modeling of UHTC

- **Materials modeling will:**
  - Discover fundamental mechanisms
  - Structure-property relationships
  - Design new materials
  - Accelerate material development

- **Framework integrates three methods:**
  - *Ab initio* – fundamental chemistry
  - *Atomistic* – thermal/mechanical
  - *Continuum* – macro properties

- **This talk focuses on thermal conductivity**
  - Atomic structure and bonding
  - Interatomic potential development
  - Lattice thermal conductivity simulations
  - Grain boundary thermal resistance
  - Imaged based FEM of GB networks

JL, Daw, Squire and Bauschlicher, (2012), submitted
UHTC: ZrB$_2$ and HfB$_2$

Alternating layers of Zr/Hf (red) and Boron (gray)

Graphitic Boron layers with Zr/Hf over each ring
Electron Localization Function (ELF)

Covalent bonding in Boron plane

Metallic bonding in Zr planes

Ionic bonding between Interlayers

Blue = High
Red = Low

Fundamental Properties: ZrB$_2$ & HfB$_2$

**Electronic Spectra**

- Total
- Zr d
- B p
- B s

**Zr d**

**B p**

**B s**

E-Ef (eV)

**Vibrational Spectra**

- ZrB$_2$
- HfB$_2$

**Zr/Hf modes**

**B modes**

Frequency (cm$^{-1}$)

Electronic properties essentially identical

Vibrational differences due to Zr/Hf mass difference
Tersoff Bond Order Potential

• **Two body terms** \((A, \lambda, B, \mu)\) energy

\[
E = \sum_{i \neq j} \left[ f_R^{[ij]}(d_{ij}) + b_{ij} f_A^{[ij]}(d_{ij}) \right]
\]

\[
f_R^{[ij]}(d) = A_{ij} \exp(-\lambda_{ij}d)
\]

\[
f_A^{[ij]}(d) = -B_{ij} \exp(-\mu_{ij}d)
\]

• **Bond order** \((\beta, \lambda_3, n, m)\)

\[
b_{ij} = (1 + \beta_i^n \zeta_{ij}^{n_i})^{-\frac{1}{2n_i}}
\]

\[
\zeta_{ij} = \sum_{k \neq i, j} f_C^{[ij]}(r_{ik}) \gamma_{ijk} g_i(\theta_{ijk}) \exp[\lambda_{3i}(d_{ij} - d_{ik})^{m_i}]
\]

• **Angular function** \((c, d, h)\)

\[
g_i(\theta) = 1 + c_i^2 / d_i^2 - c_i^2 / [d_i^2 + (h_i - \cos \theta)^2]
\]

Daw, JL and Bauschlicher, Comp. Mat. Sci., (2011)
Lattice Thermal Conductivity

• Green-Kubo thermal conductivity tensor

\[ \kappa_{\mu\nu} = \frac{1}{Vk_B\tau^2} \int_0^\infty \langle J_{\mu}(\tau) J_{\nu}(0) \rangle d\tau \]

• Heat current \( J(x_i, v_i) \), energy \( e_i \), stress-tensor \( S_i \)

\[ J = \frac{1}{V} \left[ \sum_i e_i v_i - \sum_i S_i v_i \right] \]

\[ J = \frac{1}{V} \left[ \sum_i e_i v_i + \frac{1}{2} \sum_{i<j} (f_{ij} \cdot (v_i + v_j)) \cdot x_{ij} \right] \]

Heat Current Correlation Function

- Monoatomic systems (e.g. Si) have monoatomic decay
- $\text{ZrB}_2$ has longer period than $\text{HfB}_2$ at $T=300K$
- $\text{ZrB}_2$ at $T=1000K$ has longer period than $T=300K$

Correlation Function Power Spectra

- Correlations oscillates with metal-B optical modes
- $C_{xx}$ and $C_{yy}$ oscillate with in-plane mode frequency
- $C_{zz}$ oscillates with out-of-plane mode frequency
Lattice Thermal Conductivity: ZrB$_2$

- 8 independent, 10 ns simulations, $T=300K$
- 8x8x16 unit cell, 12,255 atoms
- $\kappa_{xx} = 60 \text{ W/(m.K)}$, $\kappa_{zz} = 40 \text{ W/(m.K)}$
Lattice Thermal Conductivity: HfB$_2$

- 8 independent, 10 ns simulations
- 8x8x16 unit cell (12 atoms) = 12,255 atoms
- $\kappa_{xx} = 76 \text{ W/(m.K)}$, $\kappa_{zz} = 65 \text{ W/(m.K)}$
Thermal Conductivity vs Temperature

- 8 independent, 10 ns simulations for each point
- Data fit to 1/T curves
Single Crystal ZrB$_2$ Data

- Electron & lattice thermal conductivity

\[ K = K_e + K_{lat} \]

- \( K_{lat} \) is 0.3\( \kappa \) from polycrystalline data
- Single crystal data
  - \( \kappa_{xx} = 140 \text{ W/mK}, \kappa_{zz} = 100 \text{ W/mK} \)
  - 1 sample, 1 measurement
  - Defects uncharacterized
  - \( \kappa_{xx} = 45 \text{ W/mK}, \kappa_{zz} = 30 \text{ W/mK} \) (lattice)
- More data needed for ZrB$_2$ and HfB$_2$

\( \Sigma 7 \) symmetric \textit{tilt} \\
(graphene GB structure)

\( \Sigma 7 \) symmetric \textit{twist}

Full \textit{ab initio}/MD analysis of two \textit{tilt} and two \textit{twist} boundaries

Swap atoms to create heat source/sink

\[ Q = \sigma_K \Delta T \]

\( \sigma_K \) is the Kapitza conductance
Simulation Results

Interface Conductance

<table>
<thead>
<tr>
<th></th>
<th>Ab Initio</th>
<th></th>
<th>DLB/Pot 1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$ (meV/Å²)</td>
<td>$\Delta_z$ (Å)</td>
<td>$\gamma$ (meV/Å²)</td>
<td>$\Delta_z$ (Å)</td>
</tr>
<tr>
<td>c-tilt</td>
<td>153(369)</td>
<td>-</td>
<td>112(238)</td>
<td>-</td>
</tr>
<tr>
<td>c-twist</td>
<td>157(375)</td>
<td>0.29</td>
<td>111(258)</td>
<td>0.29</td>
</tr>
<tr>
<td>a-tilt</td>
<td>227(1040)</td>
<td>-</td>
<td>107(1380)</td>
<td>-</td>
</tr>
<tr>
<td>a-twist</td>
<td>212(1230)</td>
<td>-</td>
<td>118(1430)</td>
<td>-</td>
</tr>
</tbody>
</table>

TABLE I: Energetics and thermal conductance for ZrB₂ grain boundary structures from empirical potentials (DLB/Pot 1) and ab initio/DFT. Units for $\gamma$ are meV/Å², $\Delta_z$ are Å and $\sigma_K$ are GW/(m²·K).

- Very high thermal conductance (very low resistance)
- Experimental data indicate much lower values
- Not surprising given pristine grain boundaries
- Need: improved processing for improved GB properties
- Need: modeling more complex boundaries
Experimental Results: Polycrystalline ZrB$_2$

At 300K, $\kappa_{\text{tot}} = 55$ W/mK, $\kappa_e = 33$ W/mK, $\kappa_{\text{lat}} = 22$ W/mK

Microstructural Model: ZrB$_2$

What is effect of grain boundary network on thermal conductivity?

Estimate with Brick Layer Model

\[ \frac{1}{\kappa_{\text{eff}}} = \frac{1}{\kappa_0} + \frac{R_K}{d} \]

- $\kappa_{\text{eff}} = 48$ W/mK
- $\kappa_0 = 50$ W/mK
- $R_K = 1$ m$^2$K/GW
- $d = 6\mu$m

Very small reduction using MD resistances and BLM!

Imaged based FEM

- Larger reduction with realistic structures and parameters?
- Realistic microstructure
- Finite element mesh from OOF2
- MD thermal conductivity for grains
- Experimental interface resistance

Development of Steady State

Uniform thermal gradient (UTG) applied vertically across structure
Effective Thermal Conductivity

- Boundary conditions
  - Uniform temperature gradient (UGT)
  - Uniform heat flux (UHF)
- Transport direction
  - Vertical
  - Horizontal
- Evaluate effective properties

\[ \langle q \rangle = -k_{\text{eff}} \cdot \langle \nabla T \rangle \]

- Is microstructure “representative”???

\[ K_{\text{UHF}} \leq K \leq K_{\text{UTG}} \]
Effective Thermal Conductivity

<table>
<thead>
<tr>
<th>BC Type</th>
<th>Parameter</th>
<th>Vertical</th>
<th>Horizontal</th>
</tr>
</thead>
<tbody>
<tr>
<td>UGT</td>
<td>&lt;q&gt;</td>
<td>-27.32</td>
<td>19.05</td>
</tr>
<tr>
<td></td>
<td>&lt;dT/ds&gt;</td>
<td>1.56</td>
<td>-1.17</td>
</tr>
<tr>
<td></td>
<td>( \kappa_{\text{eff}} )</td>
<td>17.48</td>
<td>16.24</td>
</tr>
<tr>
<td>UHF</td>
<td>&lt;q&gt;</td>
<td>-28.13</td>
<td>28.05</td>
</tr>
<tr>
<td></td>
<td>&lt;dT/ds&gt;</td>
<td>1.68</td>
<td>-1.76</td>
</tr>
<tr>
<td></td>
<td>( \kappa_{\text{eff}} )</td>
<td>16.72</td>
<td>15.93</td>
</tr>
</tbody>
</table>

Comparison of results:
- BLM \( \kappa_{\text{eff}} = 15.4 \) (series model)
- Rule of mixtures \( \kappa_{\text{eff}} = 44.14 \) (parallel model)
- FEM has series and parallel contributions
- BLM has very good agreement with FEM
Conclusions

• NASA ARC computational materials modeling:
  • Ablative composites
  • Ultra high temperature ceramics
• Multiscale framework for UHTC:
  • \textit{Ab Initio} – bonding, electronic & vibrational spectra
  • Atomistic simulation – bulk and interfacial thermal conductivity
  • Continuum – microstructural modeling and effective properties
  • Iteration with experiment needed to “close” loop
• Modeling unanswered questions:
  • Interatomic potential fidelity
  • Complex grain boundary structural models and properties
• Experimental unanswered questions:
  • Single crystal thermal conductivity
  • Electronic vs lattice carrier breakdown
  • Grain boundary atomic structures and properties
  • Improved grain boundaries from improved processing