Ultra-High Temperature Thermal and Mechanical Properties of ZrB2-Based Ceramics

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Ultra-High Temperature Thermal and Mechanical Properties of ZrB$_2$-Based Ceramics

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Goals and Outline

• Goals
  – Understand the role of impurities (i.e., C), additives (i.e., SiC), isotopes ($^{10}\text{B}$ or $^{11}\text{B}$ in $\text{ZrB}_2$) on the thermal and mechanical properties of $\text{ZrB}_2$ based ceramics

• Outline
  – Thermal Conductivity of $\text{ZrB}_2$-based Ceramics
    • Historical studies vs. modern research studies
    • Missouri S&T studies – Thermal conductivity to 2000ºC+
  – Flexure Strength of $\text{ZrB}_2$-based Ceramics
    • Historical studies vs. modern research studies
    • Missouri S&T studies – Annealing; Flexure strength to 2300ºC+
  – Conclusions
Thermal Conductivity of ZrB$_2$-Based UHTCs
<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Relative Density (%)</th>
<th>Test Temperatures (°C)</th>
<th>Special Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tye and Clougherty</td>
<td>1970</td>
<td>100</td>
<td>100-1000</td>
<td>-</td>
</tr>
<tr>
<td>Tye and Clougherty</td>
<td>1970</td>
<td>90</td>
<td>100-1000</td>
<td>&quot;fluid energy milled&quot;</td>
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<tr>
<td>Branscomb and Hunter</td>
<td>1971</td>
<td>97.4</td>
<td>200-1300</td>
<td>0.92% impurity content</td>
</tr>
<tr>
<td>Fridlender et al.</td>
<td>1980</td>
<td>92</td>
<td>1000-2200</td>
<td>vibrogrinding (60hrs)</td>
</tr>
<tr>
<td>Andrievskii et al.</td>
<td>1980</td>
<td>95</td>
<td>100-900</td>
<td>-</td>
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<tr>
<td>Zimmermann et al.</td>
<td>2008</td>
<td>100</td>
<td>25-1327</td>
<td>attrition milled w/WC</td>
</tr>
<tr>
<td>Zhang et al.</td>
<td>2011</td>
<td>92.5</td>
<td>25-427</td>
<td>reaction processed (Zr+B)</td>
</tr>
<tr>
<td>Thompson et al.</td>
<td>2012</td>
<td>100</td>
<td>400-2000</td>
<td>attrition milled w/WC</td>
</tr>
</tbody>
</table>

1Tye and Clougherty, *Proceeding of the Fifth Symposium of Thermophysical Properties*, 396-401, 1970
3Fridlender, Neshpor, Ordan’yan, and Unrod, *Teplofizika Vysokikh Temperatur*, 17, 1210-1215, 1980
5Zimmermann, Hilmas, Fahrenholtz, Dinwiddie, Porter, and Wang, *J. of the American Ceramic Society*, 91, 1405-1411, 2008
7Thompson, Fahrenholtz, and Hilmas, *Journal of the American Ceramic Society*, 95, 1077-1085, 2012
• Broad range of reported conductivity values
• Slope of conductivity vs. temperature varies between positive and negative
  – Highest conductivities have negative slopes
  – Materials with positive slopes tend to have been milled (WC contamination)
• Large variation in 20 vol% conductivity values
  – 35 W/m•K difference @ 200°C
  – Multiple factors influencing overall conductivity

• Increasing SiC additions decrease thermal conductivity

• Decrease in conductivity w/temperature shows similar slope between different literature sources
 Missouri S&T – \( \lambda \) Thermal Conductivity

- **Total thermal conductivity,** \( \lambda_{\text{total}} = D \cdot C_p \cdot \rho \)
  - Laserflash thermal analysis, 25 - 2000° C in Ar
    - Diffusivity \( D \) – evaluated using Clark and Taylor method
    - Heat capacity \( C_p \) – comparison method and/or NIST JANAF
    - Density \( \rho \) obtained using Archimedes’ method + expansion w/ temp.

- **Determine electronic** \( \lambda_{\text{electron}} \) & **phononic** \( \lambda_{\text{phonon}} \) contributions
  - \( \lambda_{\text{total}} = \lambda_{\text{electron}} + \lambda_{\text{phonon}} \) where \( \lambda_{\text{electron}} = 2.44 \times 10^{-8} \sigma T \) (Wiedemann-Franz)
  - Electrical conductivity \( \sigma \) measured at temp T by 4-point probe

- **Tailor \( \lambda \) for UHTC applications**
  - Maximize \( \lambda \)
    - Hypersonic vehicle leading edges
    - Studying “phase pure” ZrB\(_2\) (reactive processing and isotope affects)
  - Minimize \( \lambda \)
    - Hypersonic thermal protection systems and high temperature refractories
    - Researching solid solution and second phase additives
λ for As-Received ZrB$_2$

- Hot pressed as-received ZrB$_2$ (H.C. Starck, Grade B)
- Electron contribution dominates thermal conductivity in ZrB$_2$
- Phonon contribution decreases to nearly zero above 1200°C
λ of As-Received ZrB₂ vs. ZrB₂ with WC

- WC contamination typically obtained when attrition milling
  - $\lambda_{\text{total}}$ decreases for both 1 and 2 wt% WC additions
  - ~50 W/m-K decrease at 200°C
  - ~10 W/m-K decrease at 2000°C

- WC additions decrease both $\lambda_{\text{electron}}$ and $\lambda_{\text{phonon}}$ contributions to $\lambda_{\text{total}}$ below the Debye temperature
- Above Debye, electron contribution is decreased by WC

*W seems to affect the electron contribution (↓ carrier concentration?)

$\lambda_{\text{total}}$ as a Function (Zr,Ti)B$_2$ (SS)

- (Zr,Ti)B$_2$ solid solution with 0 to 50 vol% TiB$_2$ additions
- $\lambda_{\text{total}}$ decreases with increasing TiB$_2$ SS content
  - Largest effect seen below 1000$^\circ$C
  - Increase in $\lambda$ with increasing temperature for 25 and 50 vol% TiB$_2$
• Steady decrease in electronic portion of $\lambda_{\text{total}}$ with increasing TiB$_2$ SS

• Little change to phonon contribution up to 10 vol% TiB$_2$ addition but 50 vol% reduced phononic portion to nearly zero
WC and TiB$_2$ Addition Comparison

- Not all additions have the same affect
  - $\lambda$ decreased significantly with WC addition compared to TiB$_2$
  - 0.4 vol% WC provided similar $\lambda$ as 50 vol% TiB$_2$
λ vs. Temperature – ZrB₂+C

- As-received ZrB₂ hot pressed w/varrying carbon additions
  - Not milled in order to avoid contamination (i.e., WC)
  - 1 wt% ZrH₂ added to eliminate B₄C formation
- 0 through 0.375 wt% C
  - Carbon in SS
  - Decrease in λ with increasing C additions

- >0.375 wt% C produces material w/carbon as a stable second phase
  - Little change in λ with increasing carbon
- λ of 0 wt% C still higher than compositions with 0.5 to 1 wt% C additions
High Purity Reaction Hot Pressed ZrB\textsubscript{2}

\[ \text{ZrH}_2 + \text{B} \rightarrow \text{ZrB}_2 + \text{H}_2 \text{ (2100° C)} \]

- ZrB\textsubscript{2} reactively hot pressed from ZrH\textsubscript{2} and B powders to 98.8% density of theoretical
- High conductivity achieved because of the high density and low impurity content
Summary – Thermal Conductivity

• \( \lambda \) strongly affected by impurities and second phases
• \( \lambda \) dominated by the electron contribution

High \( \lambda \) material
  – Few ways to increase \( \lambda \)
    • Produce fully dense material
    • Decrease impurities (reaction process)
    • Increase grain size
  – Possibilities for the future
    • Improve phonon conduction
      – Study isotope affects
    • Increase electron conduction
      – Increase carrier concentration
      – Increase mean free path

Low \( \lambda \) material
  – Many ways to lower \( \lambda \)
    • SS additions (C, WC, TiB\(_2\))
    • Second phases (SiC)
    • Increasing porosity
  – Phonon modes are easiest to disrupt
    – Research required to understand role of electron conduction
Flexure Strength of ZrB$_2$-Based UHTCs
• Limited studies of ZrB$_2$ at elevated temperatures
  – Rhodes: various densities and grain sizes – 4 pt, Ar
  – Melendez-Martinez: 87% dense, GS ~20µm – 4 pt, air
  – Zhu: >97% dense, GS ~ 10µm – 4pt, air, TEOS coated

• Strength of ZrB$_2$ decreases for increasing grain size for all temperatures
ZrB$_2$-SiC Strength vs. Temperature

- SiC additions to ZrB$_2$ increase strength at all temperatures
  - Grain size and residual stress effect
- Currently no strength data for ZrB$_2$-SiC system above 2000ºC
- Effect of grain size on high temp strength has not been investigated
Other Additions to ZrB$_2$

- Silicide additions can offer improved strength over SiC additions
- Lower melting point than ZrB$_2$-SiC eutectic (2270°C)
  - MoSi$_2$ - 2030°C; TaSi$_2$ - ~2200°C
- Mechanical behavior of ZrB$_2$ with silicide additions above 1500°C is unknown
SiC Particle Size/Shape Controls Strength

- SiC particulate phase fit as an ellipse

$K_{IC} = 3.8 \text{ MPa} \cdot \text{m}^{1/2}$
$K_{IC} = 2.6 \text{ MPa} \cdot \text{m}^{1/2}$

ASTM C 1161-2b, 10 samples per data point

Residual Stresses in ZrB$_2$-SiC

- ZrB$_2$-30 vol% SiC(6H)
  - Advantageous properties (high RT $\sigma$)
  - $\sim 2$ ppm/$^\circ$C difference in CTE
    - Thermal residual stresses upon cooling after hot pressing or sintering
    - SiC in compression
    - ZrB$_2$ in tension

- Residual stresses
  - Neutron diffraction using Zr$^{11}$B$_2$-30%SiC
    - Milled with SiC milling media
  - ZrB$_2$ is in tension (455 MPa)
  - SiC in compression (-878 MPa)
  - Stresses accumulate below 1400$^\circ$C
  - Can the stresses be manipulated to improve thermomechanical properties?

10 $\mu$m

= compression
= tension
Neutron Diffraction – ZrB$_2$ Phase

Zr$^{11}$B$_2$ (110)

$\epsilon=1.01E-3$ (540 MPa)
Calculated Stresses

- Calculated stresses vs. crystallographic directions
  - Stiffness coefficients from Okamoto (ZrB$_2$) and Yao (α-SiC)
    Yao, *Journal of the American Ceramic Society*, 90 (10), 2007

<table>
<thead>
<tr>
<th>(h k l)</th>
<th>$E_{hkl}$ (GPa)</th>
<th>$\varepsilon$</th>
<th>Calculated $\sigma$ (MPa)</th>
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<td>498</td>
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<td>390</td>
<td>7.18E-04</td>
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<tr>
<td>1 1 1</td>
<td>557</td>
<td>9.61E-04</td>
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<td>1 1 2</td>
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<td>3 0 0</td>
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<td>1 0 4</td>
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<td>7.45E-04</td>
<td>313</td>
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**Average**: 455 Tensile

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<tr>
<th>(h k l)</th>
<th>$E_{hkl}$ (GPa)</th>
<th>$\varepsilon$</th>
<th>Calculated $\sigma$ (MPa)</th>
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<td>-1.94E-03</td>
<td>-937</td>
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<tr>
<td>1 0 1</td>
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<td>0 0 6</td>
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<td>-1.51E-03</td>
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<td>1 0 2</td>
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<td>1 0 8</td>
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<tr>
<td>1 1 6</td>
<td>426</td>
<td>-1.92E-03</td>
<td>-815</td>
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</tbody>
</table>

**Average**: -878 Compressive

# Annealing Study

**ZrB$_2$-30vol% SiC (milled using SiC media)**

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Annealing Temperature (ºC)</th>
<th>Time at Temperature (Hrs)</th>
<th>Cooling Rate (ºC/min)</th>
<th>Applied Pressure (MPa)</th>
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<tbody>
<tr>
<td>20-0</td>
<td>2000</td>
<td>0</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>19-2</td>
<td>1900</td>
<td>2</td>
<td>30</td>
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<tr>
<td>18-2</td>
<td>1800</td>
<td>2</td>
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</tr>
<tr>
<td>17-2</td>
<td>1700</td>
<td>2</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>16-2</td>
<td>1600</td>
<td>2</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>15-2</td>
<td>1500</td>
<td>2</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>14-2</td>
<td>1400</td>
<td>2</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>13-72</td>
<td>1300</td>
<td>72</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>12-72</td>
<td>1200</td>
<td>72</td>
<td>30</td>
<td>0</td>
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<tr>
<td>10-0-32</td>
<td>1000</td>
<td>0</td>
<td>2 (below 1500 ºC)</td>
<td>32</td>
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<tr>
<td>10-0-100</td>
<td>1000</td>
<td>0</td>
<td>2 (below 1500 ºC)</td>
<td>100</td>
</tr>
</tbody>
</table>
RT Flexure Strength after Annealing

Baseline is ~700 MPa

All samples annealed below 1400ºC had a higher strength at room temperature

Baseline is ~700 MPa

ASTM C 1161-02b, 4-point bending, 10 samples per data point
Annealing Study – Different Composition

• **Sample preparation**
  - ZrB$_2$ (H.C. Starck, Grade B)
  - 30 vol% $\alpha$-SiC powder (H.C. Starck, UF-10)
  - 2 wt% B$_4$C (H.C. Starck, HD-20)
  - Milled using WC-6%Co milling media (0.24 wt% WC)
  - Hot pressed at 1950°C/32 MPa

• **Annealing**
  - Temperatures from 1300 to 1600°C
  - Times of 10 to 50 hours
  - Ar overpressure (1 atm)
Heat treatment increases flexure strengths by 12% at 1600°C – 10% reduction in room temperature strength.

Heat treatment increases elastic modulus by 34% at 1600°C.

Need additional heat treatments - higher pressure - Higher test temperatures.

Eric's strength box for graduation
Heat Treatment Microstructure

Microstructures

- ZrB$_2$
- SiC
- B$_4$C

Grain Size

- No additional phases identified by XRD
- EDS shows no additional discreet phases present
  - i.e. no W-rich phase typical of ZrB$_2$-SiC ceramics produced by milling with WC media
- No variation in grain size
  - $\sim$1.9±1.0 µm for ZrB$_2$
  - $\sim$1.2±0.5 µm for SiC
2500° C+ Environmental Chamber

- PID controlled induction heater
- 2-color optical pyrometer (1500-3000°C)
- Instron 4204 universal test frame
- Vacuum/gas flow control
- Fully articulated 4-pt fixture
- Capable of >2500°C
ZrB$_2$ Microstructure

ZrB$_2$ + 0.5 wt% C, hot pressed at 2150ºC/1 hour, 32 MPa, He

- **Density**
  - 6.04 g/cc, >99.2% RD

- **Grain Size**
  - 19.7 ± 13.0 µm (>2000 grains)

- **Strength in 4-point bending**
  - Room temp (ASTM C1161-02c)
  - Elevated temp (ASTM C1211-02c)
    - Air
      - TEOS sol coated, heat treated to 700ºC/1 hour in air, repeated 4x
    - Argon
      - 100ºC/min to 200ºC below temperature, then 50ºC/min to temperature, hold for 5 min
      - Variable crosshead speed

- Held for extended time at 2150ºC to grow grains and reduce tendency for creep at temperatures over 1800ºC (as observed by Rhodes *et al.*)
ZrB$_2$ Strength vs. Temperature

- **Strength in air:** ~380 MPa at RT, ~400 MPa at 1200$^\circ$C, ~110 MPa at 1600$^\circ$C
  - Oxidation affects strength above 1300$^\circ$C
- **Strength in Ar:** ~170 MPa at 1500$^\circ$C, ~300 MPa at 2200$^\circ$C, ~220 MPa at 2300$^\circ$C
- **Strength of material in present study** is greater than historical material, particularly above 2000$^\circ$C, with similar grain size and density
• 2400°C test resulted in a melted flexure bar
• ZrB₂ – C eutectic at 2390°C – Verified!
• The solution for higher temperature testing?:
  - Use ZrB₂-ZrC (2660°C eutectic) or ZrB₂-ZrC₀.88 (2830°C eutectic)
Summary – Mechanical Properties

- Strength of ZrB$_2$-30% SiC improved by annealing
  - Can be annealed to affect the stress state
    - Appropriate annealing temperature affected by impurities
  - Increased to >900 MPa from ~700 MPa after annealing at 1000°C under a 100 MPa applied load
    - Milled using SiC media
  - At a test temperature of 1600°C: ~375 MPa (as-processed) and ~440 MPa (annealed for 10 hours at 1500°C)
    - Milled using WC media
- Strength of ZrB$_2$ (~20 µm grain size)
  - ~380 MPa at RT
  - Strength decreased rapidly in air above 1200°C due to oxidation despite protective silica coating...need testing in Ar to verify behavior in this region (near stress relaxation temp.!) (~170 MPa at 1500°C & increased to ~300 MPa at 2200°C (Ar))
UHTC community needs to be testing properties to "ultra-high" temperatures.

- We must report processing procedures, grain size(s), impurities, other microstructural effects.

UHT test capabilities at Missouri S&T:
- Thermal diffusivity to 2800°C

Conclusions:
- Thermal diffusivity to 2800°C, perhaps to 2500°C
- Electrical resistivity to 1200°C
- Concept for increasing capability to 2000°C
- Four-point bending to 2800°C, well, perhaps to 2600°C
- Testing in a simulated hypersonic environment to 2800°C, well, perhaps we don't have this capability…or do we?
Acknowledgements

• **Thermal property studies**
  – Dr. Matt Thompson, now at St. Gobain-Norpro
  – Greg Harrington, PhD candidate
  – Jason Lonergan, PhD student

• **Mechanical property studies**
  – Prof. Jeremy Watts, now a Research Professor at Missouri S&T
  – Eric Neuman, PhD candidate
Conclusions

• UHTC community needs to be testing properties to “ultra-high” temperatures
  – We must report processing procedures, grain size(s), impurities, other microstructural effects

• UHT test capabilities at Missouri S&T
  – Thermal diffusivity to 2800° C
    • well, perhaps to 2500° C
  – Electrical resistivity to 1200° C
    • Concept for increasing capability to 2000° C
  – Four-point bending to 2800° C
    • well, perhaps to 2600° C
  – Testing in a simulated hypersonic environment to 2800° C
    • well, perhaps we don’t have this capability…or do we?
Mechanical Properties

- Strength tested up to 1800°C
- Range of relative density values
- ZrB$_2$ and HfB$_2$
  - Nominally pure
  - SiC additions
  - Carbon additions
- Porosity reduces strength despite a decrease in grain size
- SiC reduces grain growth
- Carbon improves resistance to crack propagation and reduces elastic modulus

50 ksi $\approx$ 350 MPa

Density a large factor in thermal conductivity
- Has to be accounted for when researching affects of other variables
- Can be corrected using Maxwell-Eucken equation

Maximizing density is crucial for obtaining highest conductivity

Depending on mechanical requirements density can be used to lower conductivity for specific applications
Argon Stress-Strain Curves

- No visible oxidation scale
- Linear elastic failure
  - Test curves for samples tested in argon are not compliance corrected
Stress-Strain Curves

- Linear elastic failure for all temperatures
  - No bending observed in bars after testing
- Significant oxidation damage visible at 1400 and 1600°C
ZrB$_2$ + 0.5 wt% C Processing

- **Density**
  - Archimedes method (ASTM C373-88)
- **Grain Size**
  - Etched Na$_{0.5}$K$_{0.5}$OH, ~300° C, ~1s
  - Image analysis, >2000 grains
- **Flexural Strength**
  - Ambient (ASTM C1161-02c)
  - Elevated temperature (ASTM C1211-02c)
    - **Air**
      - TEOS sol coated, heat treated to 700° C/1 hour in air, repeated 4x
      - 10° C/min to temperature, hold for 10 min
    - **Argon**
      - 100° C/min to 200° C below temperature, then 50° C/min to temperature, hold for 5 min
      - ASTM B-bar configuration, 4-point bend, fully articulated fixture
      - Variable crosshead speed

---

**Ball mill**
- ZrB$_2$ (grade B)
- Hexanes, 48 hours

**Rotavap**
- Grind -50Mesh

**Ultrasonic dispersion**
- ZrB$_2$ and phenolic resin in acetone

**Load pressing die**
- BN coated graphite die
- 63.5 mm x 63.5 mm x 5 mm billets

**Hot pressing**
- Char at 800° C/1 hour, Ar/10H$_2$
- Vacuum isothermal reaction holds at 1250, 1450, 1600° C
- 20° C/min to 2150° C/1 hour, 32 MPa, He

**Diamond machining**
- Coarse grind – 120 grit
- Cut bar blanks – 120 grit
- Finish grind to ASTM B-bar – 600 grit
- Polish
  - 600 grit > 1200 grit > 6 μm > 3 μm > 1 μm
  - ~45° chamfer with 15 μm
Conclusions

• Thermal Properties
  – Thermal conductivity of “phase-pure”, dense ZrB$_2$ is:
    • 110 W/m•K at RT and 55 W/m•K at 2000° C
  – SiC additions decrease thermal conductivity ZrB$_2$ is:
    • 110 W/m•K at RT and 55 W/m•K at 2000° C

• Mechanical Properties
  – Flexure strength of ZrB2-30%SiC: