Producing Zirconium Diboride Components with Complex, Near-Net Shape Geometries by Aqueous Room-Temperature Injection Molding

Valerie Wiesner
Profs. Jeffrey Youngblood and Rodney Trice

Purdue University
School of Materials Engineering

NSF Materials and Surface Engineering Grant CMMI-0726304
NASA Pathways Program, NASA Glenn Research Center
U.S. Dept. of Education GAANN Grant P200A10036
Advancing Ceramic Processing for Hypersonics

• Need for manufacturing complex-shaped ceramic components in aerospace
• Hypersonic flight speeds > Mach 5
  – Temperatures > 1900°C (3500°F)

Image from www.nasa.gov/missions/research/x43
Advancing Ceramic Processing for Hypersonics

- Need for manufacturing complex-shaped ceramic components in aerospace
- Hypersonic flight speeds > Mach 5
  - Temperatures > 1900°C (3500°F)

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB₂</td>
<td>3245</td>
<td>6.08</td>
<td>275-490</td>
<td>489-493</td>
</tr>
<tr>
<td>SiC</td>
<td>Dissociates 2245</td>
<td>3.21</td>
<td>480-580</td>
<td>410-444</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2072</td>
<td>3.9</td>
<td>200-700</td>
<td>393</td>
</tr>
<tr>
<td>Stainless Steel AISI316L</td>
<td>1400</td>
<td>8</td>
<td>515-620</td>
<td>193</td>
</tr>
<tr>
<td>Aluminum 7075</td>
<td>900</td>
<td>2.8</td>
<td>228-572</td>
<td>71</td>
</tr>
</tbody>
</table>

Advancing Ceramic Processing

• Ceramic injection molding
  – Net-shape production of parts possible
  – High-volume production
  – Pressureless sintering

Parts fabricated by injection molding powders.
Previous Work on Ceramic Injection Molding

• Ceramic injection molding
  – Net-shape production of parts possible
  – High-volume production
  – Pressureless sintering

• Polymer-based binder system in feedstock
  – Thermoplastic polymer
  – Wax (carnauba, paraffin)
  – Plasticizer or dispersant

Previous Work on Ceramic Injection Molding

• Ceramic injection molding
  – Net-shape production of parts possible
  – High-volume production
  – Pressureless sintering

• Polymer-based binder system in feedstock
  – Thermoplastic polymer
  – Wax (carnauba, paraffin)
  – Stearic acid

→ Energy-intensive heating and cooling of feedstock
→ Non-aqueous, multi-component binders

Ceramic Suspension Gel (CeraSGel)

- Suspension of ceramic powders in polymer gel
  - High ceramic content (~50 vol.%)
  - Minimal addition of water-soluble polymer (<5 vol.%)

Advantages
- Flowable at room temperature
- Yield-pseudoplastic
  - High yield point
  - Shear thinning

Sintered ZrB$_2$ specimen (right) formed by casting CeraSGels.
Injection Mold Design and Setup

- Force at constant rate exerted onto plunger to force CeraSGel out of chamber into mold
  - MTS setup

- Mold design
  - Mechanical characterization using ASTM C1323-10
  - Machine C-shape from ring

Mix powder + H₂O + dispersant and ball mill
Mix water + PVP by magnetic stirring
Add water-PVP mixture to ceramic slurry, ball mill
Load CeraSGel into mold chamber using syringe
Place mold between MTS platens, apply force at constant rate
Remove sample from mold, air dry
Burnout binder and pressureless sinter part to obtain a part near full density

**ZrB₂ CeraSGel Material Selection**

- **Pressureless sintering of ZrB₂ typically >2000°C**
  - ZrB₂ sensitive to oxygen impurities
  - B₄C sintering aid
  - Attrition mill using WC media
- Dispersant to maximize ZrB₂ powder loading
- PVP as binder to tailor flow properties

SEM images of a) as-received ZrB₂ powders (H.C. Starck Grade B); b) ZrB₂+B₄C powders after attrition milling with WC media resulting in d₅₀~0.5 μm.

Evaluate effect of PVP content in CeraSGels containing 48.6 vol.% ZrB$_2$+B$_4$C+WC
- 1 vol.% PVP
- 2 vol.% PVP
- 3 vol.% PVP

- Rheological behavior of CeraSGels
- Machinability in green state
- Density and composition after binder removal and pressureless sintering
- Mechanical strength of sintered samples
Vary PVP amount in CeraSGel

- 1 vol.% PVP
- 2 vol.% PVP
- 3 vol.% PVP

- pH of suspensions constant for PVP contents
  → PVP content does not alter pH
- Time-dependent response
- Use creep test approach to approximate yield shear stress for ZrB₂+B₄C+WC suspensions
  → Yield stress decreases with increasing polymer content

<table>
<thead>
<tr>
<th>Polymer Content</th>
<th>pH</th>
<th>Estimated Yield Stress [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol.%</td>
<td>8.85 ± 0.1</td>
<td>567</td>
</tr>
<tr>
<td>2 vol.%</td>
<td>8.91 ± 0.1</td>
<td>405</td>
</tr>
<tr>
<td>3 vol.%</td>
<td>8.89 ± 0.1</td>
<td>235</td>
</tr>
</tbody>
</table>
Machinable in Green State

- Prepare sample in green state
  - Even out surfaces by polishing
  - Chamfer edges

- Binder burnout and pressureless sintering
  - Ramp to 600°C (4°C/min), 1h hold (vacuum)
  - 1650°C (10°C/min), 1h hold, begin argon backfill
  - 1850°C (10°C/min), 1.5h hold in argon

Preparing green body for mechanical testing.

a) ZrB₂ sample in green state and b) after binder burnout and sintering.

PVP Effect on Density and Internal Porosity

- **Archimedes density test**
  - True density (TD) = 6.17 g/cm³
  - Based on 86 wt.% ZrB₂, 4 wt.% B₄C and 10 wt.% WC

<table>
<thead>
<tr>
<th>PVP content</th>
<th>Relative density (TD%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol.%</td>
<td>99.4 ± 0.3</td>
</tr>
<tr>
<td>2 vol.%</td>
<td>100.5 ± 0.4</td>
</tr>
<tr>
<td>3 vol.%</td>
<td>98.2 ± 0.8</td>
</tr>
</tbody>
</table>

- Specimens prepared with 3 vol.% PVP had lowest density
- ~21% linear shrinkage
PVP Effect on Density and Internal Porosity

Scanning electron microscopy (SEM)

- Dense microstructure
- Grain size dependence

<table>
<thead>
<tr>
<th>PVP content</th>
<th>Relative density (TD%)</th>
<th>Average grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol.%</td>
<td>99.4 ± 0.3</td>
<td>9.8 ± 6.2</td>
</tr>
<tr>
<td>2 vol.%</td>
<td>100.5 ± 0.4</td>
<td>10.6 ± 5.3</td>
</tr>
<tr>
<td>3 vol.%</td>
<td>98.2 ± 0.8</td>
<td>7.7 ± 3.7</td>
</tr>
</tbody>
</table>

Unclear if polymer content affects grain size of sintered part
Energy dispersive spectroscopy (EDS)

- B$_4$C grains surrounded by ZrB$_2$ grains
- No presence of oxygen detected

Cross section of specimen prepared with 1 vol.% PVP CeraSGel.
Phase Analysis of Sintered Specimens

• Tungsten formed solid solution with ZrB$_2$
  $\rightarrow$ ZrB$_2$ peaks shifted to higher angles after sintering

• No oxide phases detected

✓ Binder content did not seem to affect sintered ceramic compositions

XRD spectra of sintered ZrB$_2$ specimens prepared with 1, 2 and 3 vol.% PVP CeraSGels and of attrition milled ZrB$_2$/B$_4$C/WC powders.
Mechanical Strength of Sintered Parts

ASTM C 1323-10\textsuperscript{1}

Ultimate strength at ambient temperatures

\textendash Requires compressive loading of C-ring specimens

\[ R = \frac{(r_o - r_i)}{\ln(r_o/r_i)} \]

\[ r_a = \frac{r_o + r_i}{2} \]

\[ \sigma_{\theta_{\text{max}}} = \frac{PR}{btr} \left| \frac{r_o - r_a}{r_a - R} \right| \]

Geometry of C-ring specimen for ASTM C 1323-10 (modified from standard\textsuperscript{1}).

Effect of PVP on Average C-ring Strength of ZrB$_2$ Samples

- C-ring strength values lower than anticipated
  - ASTM C 1323-10 not comparable to other flexure tests
- Grain sizes comparable to literature
- Defects introduced during forming

<table>
<thead>
<tr>
<th>PVP Content in vol.% (wt.%)</th>
<th>Relative density (TD%)</th>
<th>Average C-ring strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (0.3)</td>
<td>99.4 ± 0.3</td>
<td>31 ± 12</td>
</tr>
<tr>
<td>2 (0.7)</td>
<td>100.5 ± 0.4</td>
<td>73 ± 15</td>
</tr>
<tr>
<td>3 (1.0)</td>
<td>98.2 ± 0.8</td>
<td>75 ± 27</td>
</tr>
</tbody>
</table>

Evaluate ZrB$_2$-based CeraSGels with varying PVP contents and powder loadings
Conclusions and Future Work

- **Rheology of ZrB$_2$+B$_4$C+WC CeraSGels**
  - Flow properties suitable for room-temperature processing
  - Effective yield point decreased with increasing PVP content
- **Machinable in green state**
- **Dense (>98%TD) ZrB$_2$ samples produced by pressureless sintering**
  - 21% linear shrinkage
  - PVP did not affect final composition
- **Mechanical characterization using ASTM C 1323-10**
  - C-strength increased with increasing PVP content

Prepare and evaluate CeraSGels and resulting C-ring specimens containing >3 vol.% PVP with varying solids loading.