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

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Advancing Ceramic Processing for Hypersonics

• Need for manufacturing complex-shaped ceramic components in aerospace
• Hypersonic flight speeds > Mach 5
  – Temperatures > 1900°C (3500°F)
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<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>
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<tr>
<td>Al₂O₃</td>
<td>2072</td>
<td>3.9</td>
<td>200-700</td>
<td>393</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>AISI316L</td>
<td>1400</td>
<td>8</td>
<td>515-620</td>
<td>193</td>
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<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.

Image from http://www.aremco.com/wp-content.jpg
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 ZrB₂ 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

CeraSGel Injection Molding Process

1. **Load CeraSGel into mold chamber using syringe**
2. **Burnout binder and pressureless sinter part to obtain a part near full density**
3. **Add water-PVP mixture to ceramic slurry, ball mill**
4. **Mix powder + H₂O + dispersant and ball mill**
5. **Mix water + PVP by magnetic stirring**
6. **Place mold between MTS platens, apply force at constant rate**
7. **Remove sample from mold, air dry**
8. **Mix powder + H₂O + dispersant and ball mill**
9. **Sample in green state**
10. **Sample after binder burnout and sintering**

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
Rheological Dependence on Polymer Content

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 ZrB$_2$+B$_4$C+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 (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>
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<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
Elemental Analysis of Sintered Specimens

Energy dispersive spectroscopy (EDS)

- $\text{B}_4\text{C}$ grains surrounded by $\text{ZrB}_2$ 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

- Requires compressive loading of C-ring specimens

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

\[ R = \frac{(r_o - r_i)}{\ln(r_o/r_i)} \quad r_a = \frac{r_o + r_i}{2} \]

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

Effect of PVP on Average C-ring Strength of ZrB₂ 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 ZrB₂-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