Ceramic Materials for Extreme Environments

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Ultra-High Temperature Ceramics

**Aim:**
Design materials for extreme environments → UHTCs with increased strength, toughness, oxidation resistance

**Approaches:**
- Addition of refractory secondary phases: TM alloying
- Thermal treatment to trigger toughening mechanisms (pull-out, crack deflection)
- Combination of phases able to provide oxidation protection over a wide T range

**In this talk:**
A. Flexural strength up to UHT
B. Fracture toughness
C. Oxidation behavior

ZrB₂ + SiC + WC
A. Flexural strength

- C/ZrC results in clean ZrB$_2$ boundaries allowing for stable HT strength at ~350 MPa
- TM additives maintain and even increase the HT strength
- Exceptional HT strength for composites containing no or low SiC amount
- **WC: strength > 1 GPa** at 1800°C, fully retained at 2100°C
The baseline: ZrB₂ + 15 vol% SiC + WC

- SiC particles form an interconnected network.
- Above 1500°C SiO₂ forms → grain boundary sliding, strength decay
The good one: ZrB$_2$ + 0/5 vol% SiC + WC

- Isolated SiC particles
- Strength not hampered by SiO$_2$ glass at the grain boundaries, no grain boundary sliding
As sintered microstructure

- Fully dense
- Core-shell matrix grain: (Zr,W)B\textsubscript{2} on ZrB\textsubscript{2} core: shell=70:30 vol\%
- New mixed phases: WB, Zr-W-C
- Clean grain boundaries
Fractography after $\sigma_{1500}$, air

- ~62 $\mu$m modified thickness $\rightarrow$ 11 vol% modified material
- Outermost SiO$_2$ glass $\rightarrow$ flaws healer
- W droplets encased in ZrO$_2$ $\rightarrow$ intrinsic ZrO$_2$ toughening by metallic nanoparticles
TEM analysis after σ1500, air

- Increased dislocations activity in boride grains
- Grains refinement by formation of PDW at and across the core/shell boundary (2 μm → 50 nm)
TEM analysis after σ1500, air

- Phases with stacking faults: SiC, WB → pull-out, crack deflection
- GB: all clean, BUT SiC/SiC → softening
Modified scale & bulk

Fractography after σUHT, Ar

- No SiO₂ healing layer
- ~ 4 μm modified thickness (1500-2100°C) → 2 vol% modified material

- Plastic deformation in the boride at 2100°C
B. Fracture toughness

Introduction of secondary phases:

- Whiskers, nanotubes, graphene → critical handling, do not survive the sintering T
- Short/long fiber → $K_{lc}$ up to 7 MPa·m$^{1/2}$, BUT $\sigma_{RT-1500}$: 300-120 MPa, oxidation, costs
- SiC platelets → $K_{lc}$ up to 5 MPa·m$^{1/2}$, BUT control of the grain boundaries
C. Oxidation behavior

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Oxidation Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>ZrO₂ + glassy B₂O₃(l/g)</td>
</tr>
<tr>
<td>1100</td>
<td>naked ZrO₂</td>
</tr>
<tr>
<td>1500</td>
<td>columnar ZrO₂</td>
</tr>
<tr>
<td>1700</td>
<td></td>
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<tr>
<td>2200</td>
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</tbody>
</table>

**ZrB₂**

- 800°C: ZrO₂ + glassy B₂O₃(l/g)
- 1100°C: naked ZrO₂
- 1500°C: columnar ZrO₂
- 2200°C: glassy SiO₂-B₂O₃

**ZrB₂ + SiC**

- 800°C: active SiC oxidation
- 1100°C: glassy SiO₂-B₂O₃
- 1500°C: active SiC oxidation
- 1700°C: stable X-modified ZrO₂ compact scale
- 2200°C: dense ZrO₂

**ZrB₂ + SiC + X**

- 800°C: ZrO₂ + glassy X-modified SiO₂-B₂O₃
- 1100°C: stable X-modified ZrO₂ compact scale
- 1500°C: stable X-modified ZrO₂ compact scale
- 2200°C: dense ZrO₂
TM effect on the oxidation

1500°C

ZrB₂ + Zr W Ta Mo

110 µm 135 µm 35 µm 25 µm
30 µm 30 µm 20 µm 20 µm

It is fundamental to be aware of the oxidation behavior of g.b. phases

1650°C

240 µm 210 µm 510 µm 66 µm
50 µm 50 µm 100 µm 30 µm

ZrO₂ Ta₂O₅
TM effect on the oxidation

$\text{ZrB}_2 + \text{TM} \rightarrow (\text{Zr,TM})\text{B}_2$

$(\text{Zr,TM})\text{B}_2 + \text{O}_2 \rightarrow \text{ZrO}_2 + \text{TM}$

*depending on $\text{P}_\text{O}_2$ vs $\text{P}_{\text{B}_2\text{O}_3}$

<table>
<thead>
<tr>
<th>TM</th>
<th>inclusion</th>
<th>oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>MoB</td>
<td>MoO$_3$</td>
</tr>
<tr>
<td>Ta</td>
<td>TaB$_2$</td>
<td>Ta$_2$O$_5$ (+$\Delta$vol)</td>
</tr>
<tr>
<td>W</td>
<td>W</td>
<td>WO$_3$</td>
</tr>
</tbody>
</table>

$\text{ZrO}_2$ + nanoinclusions

$\text{ZrO}_2 + \Delta \text{vol}$

$\Delta \text{vol}$

$\text{WO}_3$
Concluding remarks

- **UHT zone** still rather unexplored
- **Super strong borides** with strength peaks of 1 GPa @ 1800°C and above 600 MPa @ 2100°C
- **Strength at UHT** increases by grain refinement upon dislocation intersection, plastic deformation and by ductile-phase toughening by W nanoparticles expelled by the solid solution
- **SiC** amount has to be carefully controlled: too much leads to creep, too little does not offer protection to oxidation.
- **Solid solutions** are beneficial as they provide a diffused source of guest cation → benefits on HT strength, toughness and oxidation.
- **Oxidation** behavior at UHT can be improved by functionalization of the oxide scale.
- **W** is a kind of magic!!! Benefits on HT properties and easy to track by imaging.
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Thank you for your attention!