Thermochemistry of CaO-MgO-Al_{2}O_{3}-SiO_{2} (CMAS) and Advanced Thermal and Environmental Barrier Coating Systems

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Outline of Presentation

• Thermal and Environmental Barrier Coating Systems

• Experimental
  - Sample preparation and reaction with CMAS

• Results
  - Thermodynamic modeling of YSZ-CMAS system
  - Characterization:
    1 - Pristine NASA composition CMAS by XRD, ICP-OAS and DSC
    2 - CMAS reacted with the hollow tube coating specimens by SEM-EDS and XRD

• Summary
Baseline $\text{ZrO}_2$-(7-8)wt$\%$Y$_2$O$_3$ and Rare Earth Doped-Low Conductivity Thermal Barrier Coating Systems - Continued

Baseline $\text{ZrO}_2$-(7-8) wt$\%$Y$_2$O$_3$:
- Relatively low intrinsic thermal conductivity ~2.5 W/m-K
- High thermal expansion to better match superalloy substrates
- Good high temperature stability and mechanical properties
- Additional conductivity reduction by micro-porosity

Low Conductivity Defect Cluster Thermal Barrier Coatings

— Multi-component oxide defect clustering approach

e.g.: $\text{ZrO}_2$/HfO$_2$-Y$_2$O$_3$-Nd$_2$O$_3$(Gd$_2$O$_3$,Sm$_2$O$_3$)-Yb$_2$O$_3$(Sc$_2$O$_3$) systems

Primary stabilizer

Oxide cluster dopants with distinctive ionic sizes

— Defect clusters associated with dopant segregation
— The 5 to 100 nm size defect clusters for significantly reduced thermal conductivity (0.5-1.2 W/m-K) and improved stability
— Advanced TEBC systems for Ceramic Matrix Composites use the low k based compositions

TEBCs-CMAS Degradation is of Concern with Increasing Operating Temperatures
Experimental: sample preparation and heat treatment

- Air plasma sprayed coating (0.030” thickness) specimens on to 1/8” diameter graphite bar substrates then 1500 °C, 5 h sintering, resulting hollow tubes.
- NASA composition CMAS used for reaction at 1300 °C for 5h.

<table>
<thead>
<tr>
<th>Hollow Tube composition mole (%)</th>
<th>ρ (%) *</th>
<th>Average pore vol. (mm³) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂-12Y₂O₃</td>
<td>90(3)</td>
<td>35(2)</td>
</tr>
<tr>
<td>ZrO₂-18Y₂O₃</td>
<td>81(3)</td>
<td>-</td>
</tr>
<tr>
<td>HfO₂-7Dy₂O₃</td>
<td>89(3)</td>
<td>21(3)</td>
</tr>
<tr>
<td>ZrO₂-9Y₂O₃-4.5Gd₂O₃-4.5Yb₂O₃</td>
<td>100(3)</td>
<td>3(7)</td>
</tr>
<tr>
<td>ZrO₂-9.6Y₂O₃-2.2Gd₂O₃-2.1Yb₂O₃</td>
<td>90(3)</td>
<td>23(4)</td>
</tr>
<tr>
<td>ZrO₂-3Y₂O₃-1.5Nd₂O₃-1.5Yb₂O₃-0.3Sc₂O₃</td>
<td>90(3)</td>
<td>20(3)</td>
</tr>
<tr>
<td>ZrO₂-3Y₂O₃-1.5Sm₂O₃-1.5Yb₂O₃</td>
<td>98(3)</td>
<td>4(3)</td>
</tr>
</tbody>
</table>

*(ρgeometric*100/ρHe). **ρgeometric-ρHe.

(1:10 CMAS to sample mass ratio, concentration of 70-150 mg/cm²)

Hollow 12YSZ tube samples: (A) pristine; (B) before heat treatment in which it was half filled with CMAS powder, wrapped and sealed with Pt foil; (C) after heat treatment at 1310 °C for 30 min and unwrapped.
Results: characterization of NASA composition CMAS (as processed) before reaction

**Phase content (Wt. %)**
- Amorphous – 66.4 ± 0.9
- SiO$_2$ – 3.5 ± 0.1
- Ca$_2$Mg$_{0.46}$Al$_{0.99}$Si$_{1.52}$O$_7$ – 23.5 ± 0.7
- CaSiO$_3$ – 6.6 ± 0.4

Chemical analysis of the as-received NASA CMAS by ICP-OAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (wt. %)</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>Mg</td>
<td>3.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Al</td>
<td>6.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Si</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>5.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>1.10</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Trace elements found but not quantified are Ba, Cr, Cu, K, Mn, Na, Sr, Ti, Zr

X-ray diffraction patterns of the as-received CMAS sample.

DSC traces of CMAS during **heating** and cooling up to 1500 °C at 5 °C/min.

DSC traces of CMAS mixed with 18YSZ (1:2 mass ratio) during **heating** up to 1500 °C at 5 °C/min.
**Results:** Thermochemical modeling of YSZ – CMAS system using Thermocalc and TCOX6 database

**Calculated phase diagram of CMS-YSZ system.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>35</td>
</tr>
<tr>
<td>MgO</td>
<td>8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>45</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3</td>
</tr>
<tr>
<td>NiO</td>
<td>1</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>82</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>18</td>
</tr>
</tbody>
</table>

**Input oxide amounts**

**Fluoride**

- **Component:** CaO, MgO, SiO₂, ZrO₂, Y₂O₃
- **Mole:** 2.3 mol% Y₂O₃

**Baseline TBC T - 1316.85 °C**

- **Component:** CaO, MgO, FeO₁.₅, AlO₁.₅, NiO, SiO₂, ZrO₂, Y₂O₃
- **Mole:** 8.1e-3, 5.1e-5, 8.6e-8, 3.8e-3, 9.7e-1, 1.8e-2

**ZrO₂-tetragonal**

- **Component:** CaO, MgO, FeO₁.₅, AlO₁.₅, NiO, SiO₂, ZrO₂, Y₂O₃
- **Mole:** 8.1e-3, 5.1e-5, 8.6e-8, 3.8e-3, 9.7e-1, 1.8e-2

**Apatite**

- **Component:** CaO, MgO, FeO₁.₅, AlO₁.₅, NiO, SiO₂, ZrO₂, Y₂O₃
- **Mole:** 1.1e-1, 5.1e-5, 8.6e-8, 3.8e-3, 9.7e-1, 1.8e-2

**Ionic_liq#2**

- **Component:** CaO, MgO, FeO₁.₅, AlO₁.₅, NiO, SiO₂, ZrO₂
- **Mole:** 2.8e-1, 9.3e-2, 3.8e-1, 9.3-1, 2.2e-2, 2.7e-2
Results: SEM cross-section images at low magnification (lower cut section)

SEM cross – sectional electron images of the lower section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h.
Results: **12YSZ lower section of the hollow tube reacted with CMAS.**

SEM image of (reacted region) at high magnification.

XRD pattern of the ground hollow tube.

cubic, YSZ

Grains 1-3

<table>
<thead>
<tr>
<th></th>
<th>ZrO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal mole (%)</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>EDS mole (%)</td>
<td>81 (1)</td>
<td>11.9(2)</td>
</tr>
</tbody>
</table>

Spots 1-3.

Elemental content from EDS.

Spot 4.

Grain Boundary Composition - mole (%)

<table>
<thead>
<tr>
<th></th>
<th>Zr</th>
<th>Y</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20%</td>
<td>35.2%</td>
<td>6.6%</td>
<td>5.7%</td>
<td>2.4%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
</tbody>
</table>

Nominal mole (%) 88 12
EDS mole (%) 81 (1) 11.9(2)

Spots 1-3.
Results: 18YSZ lower section of the hollow tube reacted with CMAS.

SEM image at high magnification.

X-ray diffraction of the ground hollow tube.

Grain 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Nominal mole (%)</th>
<th>EDS mole (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>81</td>
<td>75(2)</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>18</td>
<td>19(1)</td>
</tr>
</tbody>
</table>

Elemental content from EDS.

cubic, YSZ + apatite phases

Grain Boundary Composition - mole (%)

Spot 1.

Spot 2.

Spot 3.
Results: 7DySH lower section of the hollow tube reacted with CMAS.

SEM image at high magnification.

Grain Composition - mole (%)

<table>
<thead>
<tr>
<th>Grain 2</th>
<th>HfO₂</th>
<th>Dy₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal mole (%)</td>
<td>93</td>
<td>7</td>
</tr>
<tr>
<td>EDS mole (%)</td>
<td>85(5)</td>
<td>7(1)</td>
</tr>
</tbody>
</table>

Monoclinic and cubic, DySH

XRD pattern of the ground hollow tube.

Elemental content from EDS.
Results Rare Earth Content versus apatite phase formation.

ZrO$_2$-18RE$_2$O$_3$ (RE = Y, Gd and Yb)

ZrO$_2$-18Y$_2$O$_3$

ZrO$_2$-13.9RE$_2$O$_3$ (RE = Y, Gd and Yb)

ZrO$_2$-12Y$_2$O$_3$

HfO$_2$-6.3Dy$_2$O$_3$

ZrO$_2$-6.3RE$_2$O$_3$ (RE = Y, Nd, Yb and Sc)

ZrO$_2$-6.0RE$_2$O$_3$ (RE = Y, Sm and Yb)

XRD patterns of the ground hollow tubes reacted with CMAS at 1310 °C for 5 h (lower cut section).
Results: content of the Rare-earth in the glass/silicate phase.

Depedence of the Rare-earth content in the glass/silicate phase versus Rare-earth content in the coating.
Results: content of the Rare-earth in the glass/silicate phase.

ZrO$_2$-3.0Y$_2$O$_3$-1.5Nd$_2$O$_3$-1.5Yb$_2$O$_3$-0.3Sc$_2$O$_3$

Ionic potential trend of RE

ZrO$_2$-REO$_{1.5}$ - $\Delta$Hf more endothermic

Radius size trend of RE

ZrO$_2$-3.0Y$_2$O$_3$-1.5Sm$_2$O$_3$-1.5Yb$_2$O$_3$

ZrO$_2$-9.6Y$_2$O$_3$-2.2Gd$_2$O$_3$-2.1Yb$_2$O$_3$
Summary

• Thermochemical reactions between CMAS and EBC and TBC materials were studied at 1310 °C for 5h.
• CMAS penetrated the samples at the grain boundaries and dissolved the EBC/TBC material to form silicate glassy and orthosilicate crystalline phases containing the rare-earth elements.
• Apatite crystalline phase was formed in the samples with rare-earth content higher than 12 mole (%) total of Rare-earths in the reaction zone.
• 18YSZ, 7DySH and ZrO_2-9.5Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3 samples have lower reactivity or more resistance to CMAS than the other coating compositions of this work.

Acknowledgements

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