High Temperature Degradation of Advanced Thermal and Environmental Barrier Coatings (TEBCs) by CaO-MgO-Al2O3-SiO2 (CMAS)

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12th Pacific Rim Conference on Ceramic and Glass Technology
(PACRIM 12)
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 ZrO$_2$-(7-8)wt%Y$_2$O$_3$ and Rare Earth Doped-Low Conductivity Thermal Barrier Coating Systems - Continued

Baseline 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.: 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- 30Y₂O₃</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
- SiO₂ – 3.5 ± 0.1
- Ca₂Mg₀.₄₆Al₀.₉₉Si₁.₅₂O₇ – 23.5 ± 0.7
- CaSiO₃ – 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

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.

Input oxide amounts

<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>FeO₃</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>

Output:
T = 1316.85 °C

2.3 mol% Y₂O₃ Baseline TBC

8 mol% Y₂O₃

Ionic_liq#2

Component   Mol
CaO         2.8e-1
MgO         9.3e-2
SiO₂        3.8e-1
FeO₁.₅      9.3-1
NiO         2.2e-2
ZrO₂        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: **12 YSZ 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**

**Grain Composition - mole (%):**

<table>
<thead>
<tr>
<th>Spots 1-3</th>
<th>(\text{ZrO}_2)</th>
<th>(\text{Y}_2\text{O}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nominal mole (%)</strong></td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td><strong>EDS mole (%)</strong></td>
<td>81 (1)</td>
<td>11.9(2)</td>
</tr>
</tbody>
</table>

**EDS mole (%)**

**Grain Boundary Composition - mole (%):**

<table>
<thead>
<tr>
<th>(\text{Zr})</th>
<th>(\text{Y})</th>
<th>(\text{Ca})</th>
<th>(\text{Mg})</th>
<th>(\text{Al})</th>
<th>(\text{Fe})</th>
<th>(\text{Ni})</th>
<th>(\text{Si})</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5%</td>
<td>72.2%</td>
<td>2.2%</td>
<td>0.6%</td>
<td>0.8%</td>
<td>1.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Spot 4.**

Elemental content from EDS.
Results: 30YSZ lower section of the hollow tube reacted with CMAS.

SEM image at high magnification.

Grain 1

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

Grain Boundary Composition - mole (%)

Elemental content from EDS.

cubic, YSZ + apatite phases
Results: 7DySH lower section of the hollow tube reacted with CMAS.

SEM image at high magnification.

Monoclinic and cubic, DySH

XRD pattern of the ground hollow tube.

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>

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

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

ZrO$_2$-30Y$_2$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.

\[ \text{ZrO}_2 \cdot 3.0\text{Y}_2\text{O}_3 \cdot 1.5\text{Nd}_2\text{O}_3 \cdot 1.5\text{Yb}_2\text{O}_3 \cdot 0.3\text{Sc}_2\text{O}_3 \]

Ionic potential trend of RE

ZrO\text{2-REO}_{1.5} \cdot  \Delta Hf more endothermic

Radius size trend of RE

ZrO\text{2-9.6Y}_2\text{O}_3 \cdot 2.2\text{Gd}_2\text{O}_3 \cdot 2.1\text{Yb}_2\text{O}_3

ZrO\text{2-3.0Y}_2\text{O}_3 \cdot 1.5\text{Sm}_2\text{O}_3 \cdot 1.5\text{Yb}_2\text{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.
• 7DySH, ZrO$_2$-9.5Y$_2$O$_3$-2.2Gd$_2$O$_3$-2.1Yb$_2$O$_3$ and 30YSZ samples had lower reactivity or more resistance to CMAS than the other coating compositions investigated in this study.

Acknowledgements

This work was supported by NASA Transformational Tools and Technologies Project, and also partially supported by the NASA-Army Research Laboratory Collaborative High Temperature Functionally Graded Sandphobic Coating and Surface Modification Research Project under NASA-Army Space Act Agreement SAA3-1460-1.