Calcium-Magnesium Aluminosilicate (CMAS) Interactions with Advanced Environmental Barrier Coating Material

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11th International Conference on Ceramic Materials and Components for Energy and Environmental Applications
Vancouver, B.C., Canada
June 18, 2015
Environmental Barrier Coatings for Ceramic Matrix Composites

- Improve air-breathing turbine efficiency by replacing metal-based components with ceramic matrix composites (CMCs)
- Environmental barrier coatings (EBCs) protect CMC components from oxidation and corrosion in hot section of gas turbine engines
  - Rare-earth silicates

Target: 1482°C

Molten CMAS Damage to Protective Coatings

- Particulates (i.e. sand, volcanic ash) ingested by engine melt into Calcium-Magnesium-AluminoSilicate (CMAS) glass above 1200ºC
- Molten CMAS degrade EBCs

Need EBC materials resistant to CMAS glass attack above >1200ºC

USA Today, “Massive dust storm sweeps through Phoenix” (2014)
High-Temperature Interactions between EBC Material and CMAS Glass

Objective:

• Evaluate thermo-chemical interactions between yttrium disilicate ($Y_2Si_2O_7$) EBC material and a desert sand glass at temperatures 1200ºC-1500ºC

• **Yttrium Disilicate ($Y_2Si_2O_7$)**
  – Comparable coefficient of thermal expansion to silicon-based CMCs
  – Water vapor resistance

• **Desert Sand (CMAS) Glass**
  – Actual sand sample
  – Relevant CMAS composition to aviation

Preparation of Desert Sand Glass

• As-received desert sand melted into glass
  – Heated at 10°C/min to 1550°C (1h)
  – Quenched melt in water
  – Grind glass frit in planetary mill
    zirconia milling media
  – Pass through sieve (<297 µm)

• Chemical analysis of glass by inductively coupled plasma atomic emission spectrometry (ICP-AES)

<table>
<thead>
<tr>
<th>Composition (mol.%)</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desert sand glass</td>
<td>27.8</td>
<td>4</td>
<td>5</td>
<td>61.6</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>Common CMAS glass¹,²</td>
<td>33</td>
<td>9</td>
<td>13</td>
<td>45</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Desert sand glass comprised of CMAS and trace oxides

Evaluate sand (CMAS) glass interactions with $\text{Y}_2\text{Si}_2\text{O}_7$ material

• **CMAS glass on hot-pressed $\text{Y}_2\text{Si}_2\text{O}_7$ substrate**
  - Load substrate with CMAS glass $\sim 35 \text{ mg/cm}^2$
  - 20h heat treatments at $1200^\circ\text{C}$, $1300^\circ\text{C}$, $1400^\circ\text{C}$ and $1500^\circ\text{C}$ in air
  - Evaluate microstructure and composition of $\text{Y}_2\text{Si}_2\text{O}_7$/CMAS glass interface with SEM/EDS and EPMA

• **Cold-pressed pellet of $\text{Y}_2\text{Si}_2\text{O}_7$ and CMAS glass**
  - 80 wt.% $\text{Y}_2\text{Si}_2\text{O}_7$, 20 wt.% CMAS glass
  - 20h heat treatments at $1200^\circ\text{C}$, $1300^\circ\text{C}$, $1400^\circ\text{C}$ and $1500^\circ\text{C}$ in air
  - Analyze resulting phases using XRD
CMAS Glass on $Y_2Si_2O_7$ Substrate

1. CMAS glass infiltration into $Y_2Si_2O_7$ substrate
2. Thermo-chemical interactions of $Y_2Si_2O_7$/CMAS glass

Heat $>1200^\circ$C, CMAS glass melts and penetrates/reacts with $Y_2Si_2O_7$ substrate

Region of interest after heat treatment
SEM Cross-Section of CMAS/Y$_2$Si$_2$O$_7$ substrate

- Scanning electron microscopy (SEM) to evaluate cross-sections of heat treated CMAS glass/Y$_2$Si$_2$O$_7$ substrates

**1200ºC**
Interface between Y$_2$Si$_2$O$_7$ substrate/CMAS glass after heat treatment

**1500ºC**

Area of interest
SEM Cross-Section of CMAS/Y$_2$Si$_2$O$_7$ substrate

- CMAS glass penetration into Y$_2$Si$_2$O$_7$ substrates
  - Infiltration depth increases with temperature

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Depth of CMAS Infiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200ºC for 20h</td>
<td>12.7 ± 2.5 µm</td>
</tr>
<tr>
<td>1300ºC for 20h</td>
<td>80.9 ± 14.2 µm</td>
</tr>
<tr>
<td>1400ºC for 20h</td>
<td>215.8 ± 17.6 µm</td>
</tr>
<tr>
<td>1500ºC for 20h</td>
<td>217.6 ± 19.6 µm</td>
</tr>
</tbody>
</table>

Interface between Y$_2$Si$_2$O$_7$ substrate/CMAS glass after heat treatment
SEM Cross-Section of CMAS/Y$_2$Si$_2$O$_7$ substrate

- CMAS glass penetration into Y$_2$Si$_2$O$_7$ substrates
  - Infiltration depth increases with temperature

- Thermo-chemical interactions
  - Precipitation of alternate phase in CMAS glass and infiltrated region

![CMAS glass on surface](image1.png)
![CMAS glass on surface](image2.png)

1200ºC Interface between Y$_2$Si$_2$O$_7$ substrate/CMAS glass after heat treatment

1500ºC
EDS Mapping of Interaction Region

- Yttrium incorporated into CMAS glass
  - Yttrium signal detected above substrate surface in glass
  - $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ oxyapatite silicate phase expected

- Calcium infiltrated $\text{Y}_2\text{Si}_2\text{O}_7$ substrate
  - Depth of calcium infiltration corresponds to microstructural deformation in interaction region

Interface between $\text{Y}_2\text{Si}_2\text{O}_7$ substrate and CMAS glass after 20h heat treatment at 1500°C
Quantification of Composition by EPMA

• Electron probe micro-analysis (EPMA)
  – Evaluate composition along line normal to substrate surface

BSE image of $Y_2Si_2O_7$ substrate and CMAS glass after 20h heat treatment at 1500°C
Quantification of Composition by EPMA

- Electron probe micro-analysis (EPMA)
  - Evaluate composition along line normal to substrate surface
  - Quantify variation in elemental composition from CMAS glass through $Y_2Si_2O_7$ substrate after various heat treatments

- **Ca** detected throughout CMAS glass and interaction region
- No **Ca** in substrate
- Minimal **Al** or **Mg** in interaction region

- Compare Ca content in specimens heat treated at different temperatures
Average CaO Content by EPMA

- CaO content in glass decreases with temperature
- CaO content in interaction region constant
  - Depth of interaction region increases with temperature
- No CaO detected in substrate
Identifying Alternate Phase using XRD

- Heat treat powder pellets containing 80 wt.% EBC powder ($Y_2Si_2O_7$) and 20 wt.% CMAS glass
- Evaluate reacted pellet using X-ray diffraction (XRD)

**Alternate phase:** $Ca_2Y_8(SiO_4)_6O_2$ oxyapatite silicate phase
Conclusions and Current Efforts

- Desert sand (CMAS) glass reacted with $Y_2Si_2O_7$ yielding $Ca_2Y_8(SiO_4)_6O_2$ oxyapatite silicate phase
  - Formed by dissolution of $Y_2Si_2O_7$ in CMAS glass followed by precipitation during cooling
  - Similar reaction observed for $Y_2SiO_5$

- Depth of CMAS infiltration increased with increasing heat treatment temperature
  - More significant pore formation and microstructural deformation in interaction region compared with $Y_2SiO_5$

- Evaluate other advanced EBC materials’ high-temperature interaction with desert sand (CMAS) glass