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

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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: $1482^\circ$C

Molten CMAS Damage to Protective Coatings

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

- Need EBC materials resistant to CMAS glass attack above >1200°C

Eyjafjallajökull volcano eruption in Iceland (2010)

Dust storm in Phoenix, Arizona (2014)

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 $Y_2Si_2O_7$ material

- **CMAS glass on hot-pressed $Y_2Si_2O_7$ substrate**
  - Load substrate with CMAS glass ~35 mg/cm²
  - 20h heat treatments at 1200°C, 1300°C, 1400°C and 1500°C in air
  - Evaluate microstructure and composition of $Y_2Si_2O_7$/CMAS glass interface with SEM/EDS and EPMA

- **Cold-pressed pellet of $Y_2Si_2O_7$ and CMAS glass**
  - 80 wt.% $Y_2Si_2O_7$, 20 wt.% CMAS glass
  - 20h heat treatments at 1200°C, 1300°C, 1400°C and 1500°C in air
  - Analyze resulting phases using XRD
CMAS Glass on $Y_2Si_2O_7$ Substrate

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

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

![SEM image of CMAS/Y$_2$Si$_2$O$_7$ substrate cross-section](image)

- CMAS glass on surface
- Y$_2$Si$_2$O$_7$ substrate

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

- 1200°C
- 1500°C
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>1200°C for 20h</td>
<td>12.7 ± 2.5 µm</td>
</tr>
<tr>
<td>1300°C for 20h</td>
<td>80.9 ± 14.2 µm</td>
</tr>
<tr>
<td>1400°C for 20h</td>
<td>215.8 ± 17.6 µm</td>
</tr>
<tr>
<td>1500°C for 20h</td>
<td>217.6 ± 19.6 µm</td>
</tr>
</tbody>
</table>

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

1500°C
- CMAS glass on surface
- Y$_2$Si$_2$O$_7$ substrate
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

Alternate phase

Y$_2$Si$_2$O$_7$ substrate

1200ºC

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

CMAS glass on surface

Alternate phase

Y$_2$Si$_2$O$_7$ substrate

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 1500ºC
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 1500ºC
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

![Graph showing concentration vs. distance](image)
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