CMAS Interactions with Advanced Environmental Barrier Coatings Deposited via Plasma Spray-Physical Vapor Deposition

B. J. Harder, V. L. Wiesner, and D. Zhu

NASA Glenn Research Center, Cleveland OH 44135

N. S. Johnson

Colorado School of Mines, Golden CO 80401

Work supported by the Transformative Tools and Technologies (TTT) Project as part of the Transformative Aeronautics Concepts (TACP) Program
Motivation

• Incorporation of Si-based ceramics into turbine hot section has substantial benefits
  – Limited by water vapor attack

• Environmental barrier coatings (EBCs) are necessary to protect the underlying ceramic

• Current NASA goals require durable coating systems at 1482°C (2700°F)
  – Limited recession and good adhesion

• Traditional processing methods may not be able to meet the requirements
  – Plasma Spray-Physical Vapor Deposition (PS-PVD)
Plasma Spray-Physical Vapor Deposition (PS-PVD)

• Bridges the gap between plasma spray and vapor phase methods
  – Variable microstructure
  – Multilayer coatings with a single deposition

• Low pressure (70-1400 Pa)
  High power (>100 kW)
  – Temperatures 6,000-10,000K

• High throughput\(^1\)
  – 0.5 m\(^2\) area, 10 μm layer in < 60s

• Material incorporated into gas stream
  – Non line-of-sight deposition

• Attractive for a range of applications
  – Solid oxide fuel cells, gas sensors, etc.

**Yb$_2$Si$_2$O$_7$/Si-HfO$_2$ EBCs**

- Bulk SiC substrates 0.5” x 0.75”

- Bond coat was Si-HfO$_2$
  - “Bricks and Mortar” structure
  - Starting powder 30/70 mol% HfO$_2$/Si

- SiO$_2$-lean Yb-silicate
  - 35 mol% Yb$_2$O$_3$ bal SiO$_2$
  - Fully reacted 85/15 wt% Yb$_2$Si$_2$O$_7$/Yb$_2$SiO$_5$
  - After deposition coating contained some free SiO$_2$ (~10 wt%) 

- Heated in air to 1300°C for 20hr prior to CMAS exposure
CMAS Exposure

- CMAS composition was melted at 1500°C and quenched
- CMAS was milled and tape cast at a loading of ~29 mg/cm²
- Tape area for exposure ~ 2mm x 2mm
  - Total tape weight before burnout 1.50 - 2.0 mg
- Binder burnout at 500°C (6 hr)
- Ramp rate ~5°C/min to target temp
- Cross-section through center of reacted zone

### CMAS Composition (mol%)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>23.3</td>
<td>6.4</td>
<td>3.1</td>
<td>62.5</td>
<td>4.1</td>
<td>0.5</td>
<td>0.05</td>
</tr>
</tbody>
</table>
1200°C/10hr

• Tape became shiny and exhibited wetting on the surface of the coating

• Total 'affected zone' was ~5mm

• Macro image showed the glass did not go fully molten
1200°C/10hr

- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10μm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration
1200°C/10hr

- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10μm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration
1200°C/10hr

- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10µm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration
1300°C/10hr

- Tape completely wet surface and coating raised off surface by ~0.75mm
- Total ‘affected zone’ was ~7mm
- Macro image showed coating was thinned near the center of the tape
1300°C/10hr

- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb$_2$SiO$_5$
- Bond coat significantly densified and HfO$_2$ had more rounded microstructure
  - Little or no Si/SiO$_2$ present after reacting with CMAS
1300°C/10hr (Top Coat)

- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb$_2$SiO$_5$
- Bond coat significantly densified and HfO$_2$ had more rounded microstructure
  - Little or no Si/SiO$_2$ present after reacting with CMAS
1300°C/10hr (Top Coat)

- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of $\text{Yb}_2\text{SiO}_5$
- Bond coat significantly densified and $\text{HfO}_2$ had more rounded microstructure
  - Little or no Si/SiO$_2$ present after reacting with CMAS

Unreacted

With CMAS

$\text{Yb}_2\text{SiO}_5$

$\text{Yb}_2\text{Si}_2\text{O}_7$

SiO$_2$

10 μm

CMAS with trace Yb
1300°C/10hr (Bond Coat)

- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb$_2$SiO$_5$
- Bond coat significantly densified and HfO$_2$ had more rounded microstructure
  - Little or no Si/SiO$_2$ present after reacting with CMAS
1300°C/10hr (Bond Coat)

- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb$_2$SiO$_5$
- Bond coat significantly densified and HfO$_2$ had more rounded microstructure
  - Little or no Si/SiO$_2$ present after reacting with CMAS
1400°C/1hr

- Tape completely wet surface and roughened surface of the coating
- Total ‘affected zone’ was ~6.5mm
- Macro image shows significant porosity in the EBC top coat
Even after 1 hour at 1400°C, there was significant damage to the coating.

- Yb-silicate topcoat was aggressively attacked, resulting in large pores within a mixture of residual glass and Yb₂Si₂O₇.
- Bond coat porosity increased significantly although evidence of CMAS presence was limited:
  - Si/SiO₂ present and limited evidence of dissolution/reprecipitation.
Even after 1 hour at 1400°C, there was significant damage to the coating. Yb-silicate topcoat was aggressively attacked, resulting in large pores within a mixture of residual glass and Yb$_2$Si$_2$O$_7$. Bond coat porosity increased significantly although evidence of CMAS presence was limited. Si/SiO$_2$ was present and limited evidence of dissolution/reprecipitation.
• Even after 1 hour at 1400°C, there was significant damage to the coating
• Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and Yb$_2$Si$_2$O$_7$
• Bond coat porosity increased significantly although evidence of CMAS presence was limited
  – Si/SiO$_2$ present and limited evidence of dissolution/reprecipitation
1400°F/1hr (Bond Coat)

- Even after 1 hour at 1400°C, there was significant damage to the coating.
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within a mixture of residual glass and Yb$_2$Si$_2$O$_7$.
- Bond coat porosity increased significantly although evidence of CMAS presence was limited.
  - Si/SiO$_2$ present and limited evidence of dissolution/reprecipitation.
• Even after 1 hour at 1400°C, there was significant damage to the coating
• Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and Yb$_2$Si$_2$O$_7$
• Bond coat porosity increased significantly although evidence of CMAS presence was limited
  – Si/SiO$_2$ present and limited evidence of dissolution/reprecipitation
Identifying Phase Development using XRD

• Heat treated powder pellets in air
  – 75/25 wt.% EBC powder (\(\text{Yb}_2\text{Si}_2\text{O}_7\)) with CMAS glass
  – 75/25 wt.% “Bond Coat” material (\(\text{HfSiO}_4\)) with CMAS glass
  – Heated in air to 1200, 1300, 1400 and 1500ºC for 50h

• Evaluate reacted pellet using X-ray diffraction (XRD) to compare with observed coating results
Solid State Reaction of CMAS with Yb$_2$Si$_2$O$_7$

- Ca$_2$Yb$_8$(SiO$_4$)$_6$O$_2$ (silicate oxyapatite) not detected in reacted powder pellets by XRD
  - Only Yb$_2$Si$_2$O$_7$ phase detected

- Previous study$^1$ suggests some dissolution occurs, though not quantifiable by XRD
  - Crystalline Yb$_2$Si$_2$O$_7$ content decreased with no second phase developing

---

Solid State Reaction of CMAS to HfSiO$_4$

### Phases Detected in All Pellets
- Hafnium Silicate (HfSiO$_4$)
- Hafnium Oxide (HfO$_2$)
- Silicon Oxide (SiO$_2$)

SEM/EDS confirms CMAS composition suggesting CMAS is amorphous glass $\geq 1300^\circ$C
Conclusions

- A two-layer environmental barrier coating system of Si-HfO$_2$ and Yb$_2$Si$_2$O$_7$ was deposited via Plasma Spray-Physical Vapor Deposition (PS-PVD) and samples were exposed to CMAS isothermally in air at a loading of 29 mg/cm$^2$.

- At 1200°C the attack of the EBC topcoat was limited to less than 10 microns, but the reaction layer was not an oxyapatite phase.

- Above 1200°C the CMAS composition aggressively attacked the Yb-silicate resulting in dissolution of the topcoat but no additional phases were observed.

- The Si-HfO$_2$ layer was infiltrated with CMAS, which reached the substrate, but the bond coat remained intact (albeit with some glass present).

- Phase analysis of heat treated mixtures of CMAS with Yb$_2$Si$_2$O$_7$ and HfSiO$_4$ provided similar results of limited secondary phases forming from reaction.

- Overall, these two-layer systems do not provide adequate protection against CMAS either from penetration or melt stabilization.
Acknowledgements

• Kang Lee
• Ed Sechkar
• Scott Panko
• Nate Jacobson
• Terry McCue
• Rick Rogers
• Joy Buehler