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 1482C (2700F)
  – Limited recession and good adhesion

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

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**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>
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<tbody>
<tr>
<td>mol%</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>
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</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
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  - 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)

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- Bond coat significantly densified and \( \text{HfO}_2 \) had more rounded microstructure
  - Little or no \( \text{Si}/\text{SiO}_2 \) 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
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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 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
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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 1500°C for 50h

• Evaluate reacted pellet using X-ray diffraction (XRD) to compare with observed coating results

![Comparison of samples before and after treatment](image-url)
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 ≥1300°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