Advancing Development of Environmental Barrier Coatings Resistant to Attack by Molten Calcium-Magnesium-Aluminosilicate (CMAS)

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ICACC 2020
Daytona Beach, Florida
Replace current metal-based components with ceramic matrix composites (CMCs) to increase turbine engine efficiency
- Higher operating temperatures (>1200ºC)
- Lower (1/3) density than conventional metal-based components

6% increase in fuel efficiency → savings of ~$400,000/plane/year

CMC Degradation in Turbine Engine Environment

- Silicon carbide (SiC) CMCs susceptible to environmental attack at temperatures >800°C in oxygen and water vapor
  - Silica (SiO₂) scale formation that volatilizes in H₂O environment
  - Surface recession
- Require **environmental barrier coatings (EBCs)** to protect CMC component from harsh environment

Target: 1482°C
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**Intrinsic Material Selection Criteria**

- Coefficient of thermal expansion (CTE)
- Sintering resistance
- Low H₂O and O₂ diffusivity/solubility
- Phase Stability
- Low Modulus
- Limited coating interaction
Environmental Barrier Coating Failure Modes

EBC lifetime and design requirements determined by combination of extrinsic failure modes

Steam Oxidation

Hydroxide Formation/Recession

Erosion and FOD

CMAS Attack & Infiltration

Thermomechanical Durability
Molten CMAS Damage to Protective Coatings

- Particulates (i.e. sand, volcanic ash) ingested by engine melt into Calcium-Magnesium-Alumino-Silicate (CMAS) deposits above 1200ºC
- Molten CMAS degrades EBCs (chemical + mechanical)
  - CMAS infiltration of EBC due to lowered CMAS viscosity at elevated temperatures → CTE mismatch
  - Thermochemical interactions of CMAS with EBC → spallation

➢ Need EBC materials resistant to molten CMAS attack above >1200ºC

CMAS Mitigation Strategies for EBCs

- *Minimize* reactivity of coating material with CMAS deposits
  - Thermodynamic stability over reaction products

- *Maximize* reactivity of coating material with CMAS deposits to induce crystallization
  - Crystallized reaction product barrier
CMAS Mitigation Strategies for EBCs

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- Multi-layered T/EBC architecture
  - Sacrificial topcoat
  - Larger thermal gradient

Inform evaluation and selection of candidate EBC materials and coatings
Critical Questions

- How do the properties of CMAS change with composition?
- Can we quantify CMAS/EBC reactions?
- What materials are stable with CMAS?
- Can we design CMAS resistant EBCs?
- Can we develop accurate tests for CMAS?
**Critical Questions**

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**Experimental Measurements**
- Expose CMAS to various EBC materials
- Single-point analysis

**Experimental Thermodynamics**
- Determination of quantities with experimentation
- Single-point measurement for periodic trend modeling
- Calorimetry, mass spectrometry

**Computational Thermodynamics**
- First principles approach
- Periodic trends
- VASP, Thermo-Calc, FactSage
What Are the Various Types and Properties of CMAS?

<table>
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<tr>
<th></th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>AlO$_{1.5}$</th>
<th>FeO</th>
<th>CaO/SiO$_2$</th>
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<td>6</td>
<td>6</td>
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<tr>
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<td>2</td>
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<tr>
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<td>4</td>
<td>18</td>
<td>5</td>
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<td>5</td>
<td>20</td>
<td>5-20</td>
<td>0.125-0.5</td>
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<tr>
<td><strong>Engine Deposits</strong></td>
<td><strong>25-40</strong></td>
<td><strong>20-35</strong></td>
<td><strong>7-15</strong></td>
<td><strong>10-15</strong></td>
<td><strong>7-15</strong></td>
<td><strong>0.5-1.43</strong></td>
</tr>
</tbody>
</table>

“Minority” minerals such as NaO K$_2$O, etc may provide complexity

CaO/SiO$_2$ ratio is a critical factor in determining how CMAS will affect coatings
- Viscosity of melt
- Precipitation of apatite (Ca$_2$RE$_8$(SiO$_4$)$_6$O$_2$)
Sand Composition Viscosity

- Viscosity of glass related to how fast/far the glass will infiltrate
- Low CaO/SiO₂ CMAS ratios have higher viscosity
  - Engine deposits can vary in viscosity by 3 orders of magnitude
- Viscosity of synthetic sand (CMAS) glass measured using high-temperature viscometer with platinum spindle
- Estimate infiltration time needed to penetrate 200 μm TBC
  - 4.3 minutes at 1200°C
  - 11 seconds at 1500°C

How Do Different CMAS Compositions React with EBCs?

Decrementing Ca/Si Ratio

Yb$_2$Si$_2$O$_7$:CMAS

Apatite formation

RE$_2$Si$_2$O$_7$(xl) + 0.5CaO(CMAS) = 0.5CaRE$_4$Si$_3$O$_{13}$(xl) + 0.5SiO$_2$(CMAS)

No Apatite formation

RE$_2$Si$_2$O$_7$(xl) + 0.5CaO(CMAS) = RE$_2$Si$_2$O$_7$(xl) + 0.5CaO(CMAS)

POC: Jamesa Stokes

How Do Different CMAS Compositions React with EBCs?

1400° C/1hr
50:50 mol% ratio

POC: Jamesa Stokes

Decreasing Ca/Si Ratio

Increasing Cation (RE) Size

Yb$_2$Si$_2$O$_7$:CMAS

0.635

0.451

0.092

Er$_2$Si$_2$O$_7$:CMAS

Apatite formation

No Apatite formation

How Do Different CMAS Compositions React with EBCs?

- **Yb$_2$Si$_2$O$_7$:CMAS**
- **Er$_2$Si$_2$O$_7$:CMAS**
- **Y$_2$Si$_2$O$_7$:CMAS**

| Decreasing Ca/Si Ratio | 0.635 | 0.451 | 0.092 |

Increasing Cation (RE) Size

- Apatite formation
- No Apatite formation

**POC: Jamesa Stokes**


1400$^\circ$C/1hr
50:50 mol% ratio
How Do Different CMAS Compositions React with EBCs?

- Yb$_2$Si$_2$O$_7$:CMAS
- Er$_2$Si$_2$O$_7$:CMAS
- Y$_2$Si$_2$O$_7$:CMAS
- Gd$_2$Si$_2$O$_7$:CMAS

- 1400°C/1hr
- 50:50 mol% ratio

POC: Jamesa Stokes

Decreasing Ca/Si Ratio
- 0.635
- 0.451
- 0.092

Increasing Cation (RE) Size

Apatite formation

How Do Different CMAS Compositions React with EBCs?

- Amount of apatite phase changed as a function of glass composition and RE cation species
  - Smaller RE cannot stabilize with CaO-lean compositions
  - As RE size increases, stabilization is possible but preferential liquid formation may hinder apatite formation

- Not all RE-disilicate systems have ideal CTE matches for SiC/SiC systems (~4x10^-6 /°C)

- Mixing of these silicate systems may aid in promoting crystallization of molten deposits across a range of CaO:SiO₂ ratios

POC: Jamesa Stokes, Brian Good
Can We Design New EBC Compositions for CMAS Resistance?

- Density Functional Theory (DFT) can be used to predict disilicate crystal structures
- Yb-disilicate $\beta$-phase chosen as ideal phase
- When dopant atomic radii are significantly larger than the radius of Yb, the structure is more likely to be disrupted
- Results are supported by initial testing of doped Yb-silicate compositions
- CMAS resistance testing of doped coatings is ongoing

POC: Brian Good, Jamesa Stokes
Can we measure CMAS reactions or stability?

- Drop coating material in molten CMAS or lead borate
- Measured change in temperature is related to reactivity with solvent
- Determine enthalpy of solution ($\Delta H_s$), mixing ($\Delta H_{mix}$) and reaction ($\Delta H_{reaction}$)
- Compare the stability of both the coating material and reaction products
- Results incorporated into a thermodynamic database

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POC: Gustavo Costa

Can we calculate CMAS reactions or stability?

- First principles methods using density functional theory (DFT) can provide thermodynamic quantities

- Phonon calculations for RE-silicate materials can generate:
  - Heat capacity ($c_p$)
  - Entropy
  - Coefficient of Thermal Expansion (CTE)
  - Enthalpy of formation

- RE-silicates challenging due to complex electronic structure

- Initial results with heat capacity ($c_p$) and entropy are encouraging
How will CMAS React with Coatings?

- Yb-silicate does not react strongly with CMAS but affords no protection in the coating system.
- Tested with a CMAS loading of 35 mg/cm².
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms.

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- Tested with a CMAS loading of 35 mg/cm²
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms
- TEM results have indicated significant SiO₂ present between the grains of Yb₂Si₂O₇
  - Infiltration may occur quickly at very low concentrations

POC: Valerie Wiesner, Bryan Harder
How can we accurately test EBCs with CMAS?

- Duration of engine exposure vs. ash concentration (DEvAC)

How can we accurately test coatings with CMAS?

**Assumptions**
- 575 kg/s air intake during cruise
- 1 x 10^5 cm² engine surface area
- 1% CMAS ingested sticks
- 30,000 ft altitude

How can we accurately test coatings with CMAS?

- Majority of testing 10-100 mg/cm²
- Little known at lower concentrations
  - May affect long term operation
  - Unknown degradation modes
- Require continuous exposure for ‘realistic’ test

How can we accurately test EBCs with CMAS?

- CMAS deposition can be performed with modified Mach 0.3 – 1.0 burner test rig at NASA GRC
- Computational fluid dynamics (CFD) modeling predicts CMAS glass particles injected into the burner should be molten by the time they reach/impinge on the target
- ‘Low’ CMAS feeding rates can be achieved with consistency/repeatability
  - Continuous exposures at temperature/thermal cycling to better simulate cumulative engine exposure
Critical Questions

- How do the properties of CMAS change with composition?
  
  Ca/Si ratio and viscosity are critical properties, and trace oxides may affect reactivity.

- Can we quantify CMAS/EBC reactions?
  
  Calorimetry and experimentation can provide quantities for determining periodic trends.

- What materials are stable with CMAS?
  
  Calorimetry and computational methods are beginning to measure material stabilities.

- Can we design CMAS resistant EBCs?
  
  Computational methods are in the early stages, but are showing promise for materials design.

- Can we develop accurate tests for CMAS?
  
  More ‘realistic’ methods are being developed, but nothing will be perfect (besides an engine).
Summary

- Development of CMAS resistant architectures will require a combined approach of experiment and theory.

- While experimental measurements can provide valuable point information about reactions, thermodynamics should be used to generate a map for periodic trends.

- Computational methods will assist in the development of near-term trends, and will become more predictive/prescriptive in the future.

- Testing in ‘realistic’ environments is critical for model validation.
Acknowledgments

• Amjad Almansour
• Pete Bonacuse
• Joy Buehler
• Rick Rogers

Support from NASA’s Transformational Tools and Technologies (TTT) Project at NASA Glenn Research Center