NASA’s Advanced Environmental Barrier Coatings Development for SiC/SiC Ceramic Matrix Composites: Understanding Calcium Magnesium Alumino-Silicate (CMAS) Degradations and Resistance

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Currently related NASA CMAS research activities:

- **Advanced EBC development** – composition design and developments for improved CMAS resistance
- **NASA-Air Force Venture and Viper CMAS Collaborative programs** - Zhu, James Smialek, Robert A. Miller, Bryan Harder
- **Formal NASA Intern Undergraduate Students** – Nadia Ahlborg and Dan Miladinovich
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Outline

- Environmental barrier coating (EBC) development: the CMAS relevance
- Some generalized CMAS related failures
- CMAS degradation of environmental barrier coating (EBC) systems: rare earth silicates
  - Ytterbium silicate and yttrium silicate EBCs
  - Some reactions, kinetics and mechanisms
- Advanced EBCs, HfO$_2$- and Rare Earth - Silicon based 2700°F+ capable bond coats
- Summary
NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

- **Emphasize material temperature capability, performance and long-term durability** - Highly loaded EBC-CMCs with temperature capability of 2700°F (1482°C)
  - 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
  - 2700°F (1482°C) EBC bond coat technology for supporting next generation
    - Recession: <5 mg/cm² per 1000 h
    - Coating and component strength requirements: 15-30 ksi, or 100-207 Mpa
    - Resistance to Calcium Magnesium Alumino-Silicate (CMAS)

Step increase in the material’s temperature capability

- **Temperature Capability**
  - 2800°F combustor TBC
  - 2500°F Turbine TBC
  - (T/EBC) surface

- **Increase in ΔT across T/EBC**

- **Ceramic Matrix Composite**
- **Single Crystal Superalloy**

- **3000°F+ (1650°C+)**
  - 3000°F SiC/SiC CMC airfoil and combustor technologies

- **2700°F (1482°C)**
  - 2700°F SiC/SiC thin turbine EBC systems for CMC airfoils

- **2700°F (1482°C) Gen III SiC/SiC CMCs**
  - 2400°F (1316°C) Gen I and Gen II SiC/SiC CMCs
  - 2000°F (1093°C), PtAl and NiAl bond coats
EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

- Emphasize improving temperature capability, performance and long-term durability of ceramic turbine airfoils

  • Increased gas inlet temperatures for net generation engines lead to significant CMAS-related coating durability issues – CMAS infiltration and reactions


Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests

- Synthetic CMAS, modified version (NASA), the Air Force PTI 02 CMAS currently being used
- Saudi Sands used for past turbine TBC studies
- CMAS SiO₂ content typically ranging from 43-49 mole%
- Collaborations on-going with the Air Force; also planned DLR, ONEA etc on Volcanic Ash Composition selections

ARFL PTI 02 is also used at NASA for CMAS studies

Fig. 4. The 10% MgO plane of the system CaO–MgO–Al₂O₃–SiO₂ showing the isotherms and fields of primary crystallization. A.T. Prince, J. Amer. Ceram. Soc., 37(9)1954 p402–408

Fully reacted
Thermal Gradient Tests - Thermal Barrier Coating Degradations

Coating cyclic failure with CMAS

7YSZ turbine EB-PVD laser rig cyclic tested, after 50 hr cyclic test at $T_{\text{surface}}$ 1230°C and $T_{\text{interface}}$ 1170°C
Thermal Gradient Tests of Infiltrated and Reacted Apatite Phase under Cyclic Testing – Thermal Barrier Coating Degradations

- Coating surface layer spallation in infiltrated or highly reacted apatite phase layer in high rare earth dopant TBC systems
- Thermal gradient cyclic testing at $T_{\text{surface}}=1316^\circ\text{F}$, $T_{\text{interface}}=950^\circ\text{F}$

![Diagram showing thermal conductivity and temperature over time](image)

After thermal gradient cyclic testing
CMAS Related Degradations in EBCs

- **CMAS effects**
  - Significantly reduce melting points of the EBCs and bond coats
  - Cause more severe degradations with thin airfoil EBCs
  - CMAS increase EBC diffusivities and permeability, thus less protective as an environmental barrier
  - Reduced mechanical properties: such as strength and toughness reductions
  - Leads to grain boundary attack thus disintegrate EBCs
  - CMAS interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue

![Diagram showing CMAS interactions and EBC degradations](image-url)
CMAS Related Degradations in EBCs - Continued

- **CMAS effects on EBC temperature capability**
  - Silicate reactions with NaO₂ and Al₂O₃ silicate

Phase diagrams showing yttrium di-silicate reactions with SiO₂, NaO and Al₂O₃
EBC-CMAS Degradation under Thermal Gradients

- **Effect of CMAS concentration on EBC-CMC system cyclic durability**
  - CMAS reacts with high SiO₂ activity layer and reducing melting point
  - Low tough reaction layers such as apatite phases
  - Interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td>Tsurface</td>
<td>1500</td>
</tr>
<tr>
<td>Tinterface</td>
<td>1316</td>
</tr>
</tbody>
</table>

**EB-PVD ZrO₂**

**HfO₂-Yb₂O₃⁻**

**Aluminosilicate**

**Yb₂Si₂O₇**

**Si**

More severe degradation and delamination:
- Tsurface: 1500°C
- Tinterface: 1316°C
NASA EBC Systems

- **HfO₂ -RE₂O₃-SiO₂/RE₂Si₂-xO₇-2x** environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Develop HfO₂-Si based + X (dopants) and more advanced rare earth composite compound composition systems for 2700°F+ long-term applications
  - Develop prime-reliant composite EBC-CMC interfaces for fully integrated EBC-bond coat systems

- **RE₂O₃-SiO₂-Al₂O₃ Systems**
- Develop advanced NASA high toughness alternating layered systems
- Advanced 1500°C bond coats
Selected EBC systems

- HfO₂-RE-Si, along with co-doped rare earth silicates and rare earth alumino-silicates, for optimized strength, stability and temperature capability
- CMAS infiltrations can reduce the strength

![Diagram of Strength Results of Selected EBC and EBC Bond Coats]

Strength test data compared:
- Yb₂Si₂O₇ CMAS reacted tensile surface
- Yb₂Si₂O₇ CMAS reacted specimen fracture surface
Effect of CMAS Reaction on Toughness of HfO$_2$-Si Bond Coat and Yb$_2$Si$_2$O$_7$ EBC

- HfO$_2$-Si bond coat and ytterbium di-silicate fracture toughness studied
  - HfO$_2$-Si toughness >4-5 MPa m$^{1/2}$ achieved at higher temperature
  - Annealing heat treatments at 1300°C improved lower temperature toughness
  - CMAS effect unclear due to the compounded effects of possible 1350°C CMAS reaction degradation and annealing
- Ytterbium silicate EBC toughness may also be reduced due to CMAS reactions
  - More measurements are needed
EBC CMAS Surface Reactions

- Ytterbium and yttrium silicate reactions and dissolutions in CAMS

Ytterbium silicate surface CMAS melts: 50 hr 1300°C

Ytterbium silicate surface CMAS melts: 5 hr 1500°C

Yttrium silicate surface CMAS melts: 50 hr 1300°C

Yttrium silicate surface CMAS melts: 5 hr 1500°C
EBC Reacted Apatite Phases under Long-Term Testing at 1500°C – Ytterbium silicate EBC

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases
- Difference in partitioning of ytterbium vs. yttrium in apatite

Composition in apatite (100 hr):
EBC Reacted Apatite Phases under Long-Term Testing at 1500°C: Yttrium Silicate EBC

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases
- Difference in partition of ytterbium vs. yttrium
  - Average AEO/RE$_2$O$_3$ ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE$_2$O$_3$ ratio ~ 0.22 for yttrium silicate – CMAS system

Composition in apatite (100 hr):
Stoichiometry of the Reacted Apatite Phases under Long-Term Testing at 1500°C

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 hr testing
- Difference in partitioning of ytterbium vs. yttrium in apatite
  - Average AEO/RE$_2$O$_3$ ratio $\sim$ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE$_2$O$_3$ ratio $\sim$ 0.22 for yttrium silicate – CMAS system

Partitioning of Rare Earths in Apatite in Geo Systems: Medium Ionic Rare Earth Reported higher Partitioning Coefficients

– Reported partition of Rare Earths in Apatite

Fig. 1. Comparison of $D_{\text{REE}}$ values calculated from SIMS analyses (open squares) and LA-ICPMS analyses.

Fig. 3. Plots of $D(\text{REE})$ as a function of atomic number for series AP50 experiments. Note that AP50-2 and AP30-3 with low total REE contents have more pronounced enrichments in middle REEs than AP50-1 and AP50-4.


Effect of CMAS Reactions on Grain Boundary Phases

- CMAS and grain boundary phase has higher Al$_2$O$_3$ content (17-22 mole%)
  - Eutectic region with high Al$_2$O$_3$ content ~1200°C melting
  - Loss of SiO$_2$ due to volatility

Fig. 4. The 10% MgO plane of the system CaO-MgO-Al$_2$O$_3$-SiO$_2$ showing the isotherms and fields of primary crystallization. A.T. Prince, J. Amer. Ceram. Soc., 37(9) 1954 p 402-408

200 hr, 1500°C
Rare Earth Apatite Grain Growth

- Grain growth of apatite phase at 1500°C at various times:
  - 50 hr
  - 150 hr
  - 200 hr
Effect of CMAS Reaction on EBC Cyclic Durability in Thermal Gradient Laser Steam Rig

- Ytterbium silicate EBC Yb$_2$Si$_2$O$_7$/Si on CMC
- CMAS fully infiltrated
- Failed after 40 cycles (1hr cycle) under combined laser thermal gradient CMAS+steam at 1400-1500°C
- Accelerated recession leading to cracking and porous coatings
HfO$_2$-Rare Earth Silicate Composite EBC with Yb-Si Bond Coat Systems

- Generally showed good resistance in CMAS and CMAS-steam tests
  - Composite system for achieving balanced CMAS resistance and water vapor stability at 1500°C
  - Compositions being further optimized

Specimen after testing

Coating surface

Back surface
HfO$_2$-Rare Earth Silicate Composite EBC Systems - Continued

- Silica loss observed in the concentrated CMAS reacted regions

Coating surface

HfO$_2$ rich phase region

Rare earth silicate - apatite phase rich phase region

CMAS concentrated region, SiO$_2$ content 20-30 mol% (SiO$_2$ loss in the steam water vapor tests)

Cross-section (surface region)
High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions

- Thermogravimetric analysis (TGA) in dry O₂ at 1500°C, tested up to 500 hr
- “Protective” scale of rare earth di-silicate forms in oxidizing environments
- Furnace cyclic test life evaluated at 1500°C

![Diagram showing TGA results vs. Si content and FCT life of RE-Si coatings]
High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

- Demonstrated CMAS resistance of NASA RESi System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9mol%)
CMAS Reaction Kinetics in Bond Coats

- SiO₂ rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C

CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr
Turbine TEBC Life Aspects due to CMAS Degradations and Other Mechanisms

- Reduced cyclic life due to the CMAS infiltration

![Graph showing temperature/Interface temperature vs. ln (Oxidation cycle time to failure), hours]

- Zr2.5Y0.75Gd0.75Yb
- Zr2.0Y1.5Gd1.5Yb
- Zr1.6Y1.2Gd1.2Yb
- Zr2.5Y0.75Gd0.75Yb
- Zr2.0Y1.5Gd1.5Yb
- Zr1.6Y1.2Gd1.2Yb
- Zr2.5Y0.75Gd0.75Yb
- Zr2.0Y1.5Gd1.5Yb

![Graph showing erosion resistance, grams erodent required per 25 micrometer coating erosion vs. 1/T, 1/K]

- Zr1.6Y1.2Gd1.2Yb
- 7YSZ
- 7YSZ
- 7YSZ Laser heat flux
- 7YSZ burner heat flux rig
Summary

• CMAS degradation remains a challenge for emerging turbine engine environmental barrier coating – SiC/SiC CMC component systems
• CMAS leads to lower melting point of EBC and EBC bond coat systems, and accelerated degradations
• NASA advanced HfO$_2$-Si and, in particular Rare Earth - Silicon based bond coat compositions showed promise for CMAS resistance at temperatures up to 1500°C
• We have better understanding of CMAS integration with rare earth silicates, and in controlling the compositions for CMAS resistance while maintaining high toughness
• We are developing better standardized CMAS testing, and working on CMAS induced life reductions, helping validate life modeling