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

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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)
  - Increase in temperature across T/EBC

Step increase in the material’s temperature capability

- **2700°F (1482°C) Gen I** and Gen II SiC/SiC CMCs
- **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**

Temperature Capability

- 2800°F combustor TBC
- 2500°F Turbine TBC
- 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
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 \( T_{\text{surface}} = 1316^\circ F \), \( T_{\text{interface}} = 950^\circ F \)

![Graph showing thermal conductivity and temperature over time]

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

Examples of CMAS degradation mechanisms include:

- **Eutectic**
- **SiO**
- **Recessed cavity**
- **Flow debond**
- **Si crack**
- **CMAS induced melting and failure**

And materials such as yttrium silicate and SiC/SiC CMC.
CMAS Related Degradations in EBCs - Continued

- CMAS effects on EBC temperature capability
  - Silicate reactions with NaO$_2$ and Al$_2$O$_3$ silicate

Phase diagrams showing yttrium di-silicate reactions with SiO$_2$, NaO and Al$_2$O$_3$
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

![Graphs showing thermal conductivity over time](image1)

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

- HfO$_2$ - RE$_2$O$_3$ - SiO$_2$/RE$_2$Si$_{2-x}$O$_{7-2x}$ environmental barrier systems
  - Controlled silica content and transition element and rare earth dopants to improve EBC stability and toughness
  - Develop HfO$_2$-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
- RE$_2$O$_3$ - SiO$_2$ - Al$_2$O$_3$ Systems
- Develop advanced NASA high toughness alternating layered systems
- Advanced 1500°C bond coats
Strength Results of Selected EBC and EBC Bond Coats
- CMAS Reaction resulted in Strength Reduction in Silicates

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

Strength test data compared

- **HfO₂-Si (Si-rich)**
- **Yb₂Si₂O₇**
- **Yb₂Si₂O₇ CMAS reacted tensile surface**
- **Yb₂Si₂O₇ CMAS reacted specimen fracture surface**

<table>
<thead>
<tr>
<th>EBCs</th>
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<tr>
<td>646-Specially alloy toughened t’ like HfO₂</td>
<td>648-EBC Bond Coat Constituent</td>
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<tr>
<td>648-EBC Bond Coat Constituent</td>
<td>658-EBC HfO₂-Rare Earth-Alumino Silicate</td>
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<tr>
<td>660-Y₂Si₂O₇</td>
<td>657-Zr-RE silicate</td>
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<tr>
<td>669-Yb₂Si₂O₇</td>
<td>669-9762 with CMAS 1350C 50hr reacted</td>
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<tr>
<td>696-EBC Bond Coat Constituent</td>
<td>659-AE9762</td>
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<tr>
<td>681-HfO₂-Si</td>
<td>681-HfO₂-Si</td>
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<td>669-9762 with CMAS 1350C 50hr reacted</td>
<td>693-HfO₂-Si with CMAS 1350C 50hr reacted</td>
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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

![HfO$_2$-Si illustrating notch distortion due to CMAS exposure at 1350°C for 50 hrs](image)

![Yb$_2$Si$_2$O$_7$ notch after CMAS exposure at 1350°C for 50 hrs](image)

![Graph showing fracture toughness vs. temperature](image)
EBC CMAS Surface Reactions

- Ytterbium and yttrium silicate reactions and dissolutions in CAMS

  **Ytterbium silicate surface CMAS melts:**
  - 50 hr at 1300°C
  - 5 hr at 1500°C

  **Yttrium silicate surface CMAS melts:**
  - 50 hr at 1300°C
  - 5 hr at 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
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 $\text{AEO/RE}_2\text{O}_3$ ratio $\sim 0.68$ for ytterbium silicate – CMAS system
  - Average $\text{AEO/RE}_2\text{O}_3$ ratio $\sim 0.22$ for yttrium silicate – CMAS system
Partitioning of Rare Earths in Apatite in Geo Systems: Medium Ionic Rare Earths 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 $D(\text{REEs})$ as a function of atomic number for series AP50 experiments. Note that AP50-2 and AP50-3 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

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

50 hr 150 hr 200 hr
Effect of CMAS Reaction on EBC Cyclic Durability in Thermal Gradient Laser Steam Rig

- Ytterbium silicate EBC $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Si}$ 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
- 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)
High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions

- Thermogravimetric analysis (TGA) in dry $O_2$ at $1500^\circ$C, tested up to 500 hr
- “Protective” scale of rare earth di-silicate forms in oxidizing environments
- Furnace cyclic test life evaluated at $1500^\circ$C

![TGA results vs. Si content](image)

**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

- SiO$_2$ 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
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