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:
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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:

- 2700°F (1482°C) Gen I and Gen II SiC/SiC CMCs
- 2700°F (1482°C) Gen III SiC/SiC CMCs
- 3000°F+ (1650°C+) 3000°F SiC/SiC CMC airfoil technologies
- 2500°F Turbine TBC 2700°F SiC/SiC thin turbine EBC systems for CMC airfoils
- 2800°F combustor TBC 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

![Diagram of TBC Surface Temperature vs Time](image1.png)


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 SiO$_2$ 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

Steady state laser thermal gradient test
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 $T_{\text{surface}}=1316^\circ\text{F}$, $T_{\text{interface}}=950^\circ\text{F}$

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

Such as yttrium silicate
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

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

**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**
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

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

![HfO$_2$-Si notch distortion](image1)

![Yb$_2$Si$_2$O$_7$ notch](image2)

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Yb$_2$Si$_2$O$_7$ notch after CMAS exposure at 1350°C for 50 hrs

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Fracture toughness, MPa m$^{1/2}$

"Apparent Toughness Drop" due to strength decrease
EBC CMAS Surface Reactions

- Ytterbium and yttrium silicate reactions and dissolutions in CAMS

Ytterbium silicate surface CMAS melts: 50 hr  
1300°C

Yttrium silicate surface CMAS melts: 50 hr  
1300°C

Ytterbium silicate surface CMAS melts: 5 hr  
1500°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 $\text{AEO}/\text{RE}_2\text{O}_3$ ratio $\sim 0.68$ for ytterbium silicate – CMAS system
  - Average $\text{AEO}/\text{RE}_2\text{O}_3$ ratio $\sim 0.22$ for yttrium silicate – CMAS system

Partitioning of Rare Earths in Apatite in Geo Systems: Medium Ionic Rare 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 $D$(REEs) 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 $\text{Al}_2\text{O}_3$ content (17-22 mole%)
  - Eutectic region with high $\text{Al}_2\text{O}_3$ content ~1200°C melting
  - Loss of $\text{SiO}_2$ due to volatility

Grain boundary final phase – low $\text{SiO}_2$ and high Alumina

200 hr, 1500°C

Fig. 4. The 10% $\text{MgO}$ plane of the system $\text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2$ showing the isotherms and fields of primary crystallization. A.T. Prince, J. Amer. Ceram. Soc., 37(9) 1954 p402-408
Rare Earth Apatite Grain Growth

- Grain growth of apatite phase at 1500°C at various times
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

![Graph showing temperature over time](image1.png)

Coating spalled after 40 hr test

Failed coating surface
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
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)
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 formed in oxidizing environments
- Furnace cyclic test life evaluated at 1500°C

FCT life of RE-Si coatings

TGA results vs. Si content
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
Turbine TEBC Life Aspects due to CMAS Degradations and Other Mechanisms

- Reduced cyclic life due to the CMAS infiltration

![Image](40x686 to 98x744)
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