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

Dongming Zhu

Materials and Structures Division
NASA John H. Glenn Research Center
Cleveland, Ohio 44135

Thermal Barrier Coating IV Conference, Irsee, Germany
June 26, 2014
Acknowledgements

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
- **Fundamental NASA in-house CMAS properties** - Narottam Bansal and Valerie Weiner

The work was supported by NASA Fundamental Aeronautics Programs, and Aeronautical Sciences Project.

The work was also partially supported by Air Force Venture Program.

The author is grateful to

- Lynne M. Pfledderer and Oliver T. Easterday of the Air Force Research Laboratory, Managers of the Air Force Venture Program.
- Ralph Pawlik and Ron Phillips for their assistance in mechanical testing of EBC-CMC systems
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**

- **Increase in ΔT across T/EBC**
  - 2800°F combustor TBC
  - 2500°F Turbine TBC
  - 2700°F (1482°C) Single Crystal Superalloy
  - Ceramics Matrix Composite
  - 2700°F (1482°C) Gen III SiC/SiC CMCs
  - 3000°F SiC/SiC CMC airfoil and combustor technologies
  - 3000°F SiC/SiC thin turbine EBC systems for CMC airfoils

- **2000°F (1093°C), PtAl and NiAl bond coats**
- **2400°F (1316°C) Gen I and Gen II SiC/SiC CMCs**
- Gen I – Current commercial
- Gen II – Current commercial
- Gen III
- Gen. IV

www.nasa.gov
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 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

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 p402-408
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 $T_{\text{surface}}=1316^\circ F$, $T_{\text{interface}}=950^\circ F$
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

![CMAS and EBC interactions diagram]
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

EB-PVD ZrO₂
HfO₂-Yb₂O₃⁻
Aluminosilicate
Yb₂Si₂O₇
Si

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

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

- HfO$_2$-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
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 versus temperature](image)
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
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/RE₂O₃ ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE₂O₃ 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 ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE$_2$O$_3$ ratio ~ 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 $\sim1200^\circ\text{C}$ melting
  - Loss of $\text{SiO}_2$ due to volatility

![Diagram showing the effect of CMAS reactions on grain boundary phases.](image-url)
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 \( \text{Yb}_2\text{Si}_2\text{O}_7/\text{Si} \) 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

Specimen after testing
- Silica loss observed in the concentrated CMAS reacted regions

**HfO\textsubscript{2}-Rare Earth Silicate Composite EBC Systems - Continued**

Coating surface

**HfO\textsubscript{2} rich phase region**

**Rare earth silicate - apatite phase rich phase region**

CMAS concentrated region, SiO\textsubscript{2} content 20-30 mol% (SiO\textsubscript{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 $O_2$ 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 $1500^\circ C$
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
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