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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>2800°F combuster TBC</td>
<td>Gen II – Current commercial</td>
</tr>
<tr>
<td>2500°F Turbine TBC</td>
<td>Gen II</td>
</tr>
<tr>
<td>3000°F+ (1650°C+)</td>
<td>Gen III SiC/SiC CMC airfoils</td>
</tr>
<tr>
<td>2700°F (1482°C)</td>
<td>2700°F SiC/SiC thin turbine EBC systems for CMC airfoils</td>
</tr>
<tr>
<td>2400°F (1316°C) Gen I and Gen II SiC/SiC CMCs</td>
<td></td>
</tr>
<tr>
<td>2000°F (1093°C), PtAl and NiAl bond coats</td>
<td></td>
</tr>
</tbody>
</table>
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

ARFL PTI CMAS 02

NASA modified version

Wellman

Aygun

Rai

GE/Borom

Kramer

Smialek

Braue

Fully reacted

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

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

![Graph 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

Such as yttrium silicate

EBC and degradations
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

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

**Materials:**
- EB-PVD ZrO₂
- HfO₂-Yb₂O₃-
- Aluminosilicate
- Yb₂Si₂O₇
- Si
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
- HfO\textsubscript{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

![Graph showing strength test data compared for different EBCs and their reaction with CMAS.](image)

- Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} CMAS reacted tensile surface
- Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} 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 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)
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/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 ~ 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 $D(\text{REEs})$ 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 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

Grain boundary final phase – low SiO$_2$ and high Alumina
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
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 $O_2$ 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

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

- 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

![Diagram showing surface vertical cracks and delamination cracks.]

![Graph showing temperature and interface temperature with various points representing different compositions and conditions.]

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

- 7YSZ
- 7YSZ Laser heat flux
- 7YSZ burner heat flux rig

- In (Oxidation cycle time to failure), hours
- Erosion resistance, grams erodent required per 25 micrometer coating erosion

- Mach 0.3
- Oxidation-erosion

- Surface heat flux cyclic
- Furnace cyclic
- CMAS
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