Durability and CMAS Resistance of Advanced Environmental Barrier Coatings Systems for SiC/SiC Ceramic Matrix Composites

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Environmental Barrier Coating - CMAS Interaction Research Efforts

- Advanced EBC development – composition design and developments for improved CMAS resistance; thermomechanical-CMAS Interactions and durability – Zhu et al
- NASA-Air Force Venture and Viper Turbine Coating-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
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
- 2700°F (1482°C) SiC/SiC CMCs
- 3000°F SiC/SiC CMC airfoil and combustor technologies

Increase in $\Delta T$ across T/EBC

- 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 compositions, in particular, NASA modified version (NASA CMAS), and the Air Force Powder Technology Incorporated PTI 02 CMAS currently being used
- Saudi Sands used for past turbine coating studies
- CMAS SiO₂ content typically ranging from 43-49 mole%; such as NASA’s CMAS (with NiO and FeO)
- Collaborations on-going with the Air Force; also planned DLR, ONERA etc on Volcanic Ash Composition selections

ARFL PTI 11717A 02 used at NASA for CMAS studies

![CMAS EDS spectrum](image1.png)

**AFRL02 particle size distribution**
(34% Quartz, 30% Gypsum, 17% Aplite, 14% Dolomite, 5% Salt)

**Percentile Size (μm)**
- 10: 2.5 +/- 1.0
- 50: 8.5 +/- 2.0
- 90: 40.5 +/- 3.0

![CMAS image](image2.png)

**Fully reacted CMAS**

**As received**

**Fully reacted**
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 induced melting and failure
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$_3$
CMAS Related Degradations in EBCs

- Fatigue – environmental interaction is of great concern

A 20 micrometer thick EBC bond coated Prepreg SiC/SiC CMC after 40 hr, 20 Ksi, stress ratio R=0.05 fatigue testing in air
Current EBCs limited in their temperature capability, water vapor stability and long-term durability, especially for advanced high pressure, high bypass turbine engines

Advanced EBCs also require higher strength and toughness
- In particular, resistance to combined high-heat-flux, engine high pressure, combustion environment, creep-fatigue, loading interactions

EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
- Critical to reduce the EBC Si/SiO₂ reactivity and their concentration tolerance

EBC-CMC systems need advanced processing for realizing complex coating compositions, architectures and thin turbine configurations for next generation high performance engines
- Advanced high temperature processing of high stability cluster and nano-composites
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$_2$-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 EBCs and specific compounds.](image)

**Yb$_2$Si$_2$O$_7$ CMAS reacted tensile surface**

**Yb$_2$Si$_2$O$_7$ 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
EBC CMAS Surface Reactions

- Ytterbium- and yttrium-disilicate silicates 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 $\text{AEO/RE}_2\text{O}_3$ 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

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/RE₂O₃ ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE₂O₃ ratio ~ 0.22 for yttrium silicate – CMAS system

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 point
  - Loss of SiO$_2$ due to volatility

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

NASA modified CMAS

200 hr, 1500°C
Rare Earth Apatite Grain Growth

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

Ytterbium silicate system

Yttrium silicate system
Silica loss observed in the concentrated CMAS reacted regions

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

- 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: Designed with Improved Temperature capability and CMAS Resistance

- 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 also evaluated at 1500°C
High Stability Rare Earth Silicon Bond Coat with High Melting Point Coating Compositions: Designed with Improved Temperature capability and CMAS Resistance - Continued

- 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 or high heat flux test life evaluated at 1500°C up to 1000 hours with or without CMAS

An Yb-Gd2700°F EBC bond coat showed 500hr cyclic durability

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

- SiO$_2$ rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C
- More advanced compositions are being implemented for improved thermomechanical – CMAS resistance
Advanced EBC Compositions Improve the Resistance to CMAS

- Controlling CMAS wetting, viscosity, stability and melting points
- Providing better EBC protections for CMCs in CMAS environments
- EBC durability being validated under CMAS-mechanical loading

400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure
Advanced EBC Compositions Improve the Resistance to CMAS - Continued

- Controlling CMAS wetting, viscosity, stability and melting points
- Providing better EBC protections for CMCs in CMAS environments
- EBC durability initially validated under long-term CMAS-mechanical loading

400 hr, 69 Mpa creep rupture at EBC surface temperature 1400°C

202 hr, 69 MPa creep rupture at EBC surface temperature 1540°C; CMC failure
Creep-Fatigue of EBCs-CMCs in Complex Heat Flux and Simulated Engine Environments

- Long-term creep and fatigue used to validate EBCs at various loading levels
- Demonstrated 2700°F EBC and bond coat capability in complex environments

Fracture surface; 200+ hr at 2700°F+ creep rupture testing with CMAS; Advanced EBC protected CMCs

Advanced Bond Coat on CMC – intact after fatigue test with 15 ksi load and 2600-2700°F surface temperature for 460 hot hours

Stress-oxidation and stress-CMAS environmental testing
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 EBC compositions showed promise for CMAS resistance at temperatures up to 1500°C+, and in combined with mechanical loading
• We have better understanding of CMAS interaction 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
**EBC-CMAS Degradation under Thermal Gradients**

- **Effect of CMAS concentration on EBC-CMC system cyclic durability**
  - CMAS reacts with high SiO$_2$ activity layer and reducing melting point
  - Low tough reaction layers such as apatite phases
  - Interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue

![Thermal conductivity graphs](image)

- **EB-PVD ZrO$_2$**
- **HfO$_2$-Yb$_2$O$_3$-Aluminosilicate**
- **Yb$_2$Si$_2$O$_7$**
- **Si**

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