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

- 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, ONEA etc on Volcanic Ash Composition selections

ARFL PTI 11717A 02 used at NASA for CMAS studies
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

Coating surface

Cross-section

EBC and degradations

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/SiO\textsubscript{2} 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

**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

![Diagram of EBC Systems](image.png)

- Advanced 2700°F bond coat systems
- RE-Si based Systems: grain boundary engineering designs and/or composite systems
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

Strength test data compared:

- 646-Specially alloy toughened t' like HfO$_2$
- 648-EBC Bond Coat Constituent
- 658-EBC HfO$_2$-Rare Earth-Alumino Silicate
- 660-Y$_2$Si$_2$O$_7$
- 657-Zr-RE silicate
- 669-Yb$_2$Si$_2$O$_7$
- 696-EBC Bond Coat Constituent
- 659-AE9762
- 681-HfO$_2$-Si
- 669-9762 with CMAS 1350C 50hr reacted
- 693-HfO$_2$-Si with CMAS 1350C 50hr reacted

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

![](image1.png)

HfO$_2$-Si illustrating notch distortion due to CMAS exposure at 1350°C for 50 hrs

![](image2.png)

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

![Fracture toughness vs Temperature graph](image3.png)

"Apparent Toughness Drop" due to strength decrease

- As processed HfO2-Si
- 1300C 20hr annealed HfO2-Si
- CMAS 1350C 50hr Reacted HfO2-Si
- As processed Yb2Si2O7
- CMAS 1350C 50hr Reacted Yb2Si2O7
- Si
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 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


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 point
  - Loss of $\text{SiO}_2$ due to volatility

![Diagram showing CMAS reaction and grain boundary phase composition](image)
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.

- CMAS concentrated region, SiO₂ content 20-30 mol% (SiO₂ 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

Oxidation kinetics vs Si content
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 O$_2$ 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

<table>
<thead>
<tr>
<th>Silicon content, at%</th>
<th>Bond coat systems</th>
<th>Cyclic life, hr</th>
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<tr>
<td>79</td>
<td>YbSi</td>
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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

CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr
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 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