DEVELOPMENT OF ADVANCED ENVIRONMENTAL BARRIER COATINGS FOR SIC/SIC COMPOSITES AT NASA GRC: PRIME-RELIANT DESIGN AND DURABILITY PERSPECTIVES

Dongming Zhu

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

The work was supported by NASA Fundamental Aeronautics Program (FAP) Transformational Tools and Technologies (TTT) Project

Advanced Ceramic Matrix Composites: Science and Technology of Materials, Design, Applications, Performance and Integration
An ECI Conference, Santa Fe, NM
November 5-9, 2017
NASA’s Advanced Environmental Barrier Coating Systems for Ceramic Matrix Composites (CMCs):

— NASA Environmental Barrier Coatings (EBCs) development objectives

- Help achieve future engine temperature and performance goals
- Ensure system durability – towards prime reliant coatings and material systems
- Establish database, design tools and coating lifting methodologies
- Improve technology readiness

Fixed Wing Subsonic and Supersonics Aircraft

Hybrid Electric Propulsion Aircraft

Entry, Descending and Landing: Ultra High Ceramics and Coatings (UHTCC)
NASA Environmental Barrier Coating Development Goals

- Emphasize temperature capability, performance and durability
- Develop 2700°F environmental barrier coating technologies
  - For 2400°F (1316°C) and 2700°F (1482°C) Ceramic Matrix Composites (CMCs) in support of next generation turbine engines
  - Focus on advanced CMC combustors and highly loaded turbine airfoils
  - Particularly also emphasize highly loaded turbine blades

Temperature Capability

- 2800°F combustor TBC
- 2500°F Turbine TBC

Increase in $\Delta T$ across T/EBC

Step increase in the material’s temperature capability

- 3000°F SiC/SiC CMC airfoil and combustor technologies
- 2700°F SiC/SiC thin turbine EBC systems for CMC airfoils

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)

* Recession: <5 mg/cm² per 1000 hr (40-50 atm., Mach 1~2)
** Component strength and toughness requirements
Outline

- Environmental barrier coating systems: towards Prime-Reliant systems
  - Thermomechanical, environment and thermochemical stability of EBCs
  - Prime-reliant EBCs, initial design approach and requirements

- Advanced environmental barrier coating systems (EBCs) for CMC airfoils and combustors
  - NASA advanced turbine EBC coating system status
  - Development and testing, durability perspectives

- Design tool and life prediction perspectives of coated CMC components
  - Advanced Testing
  - Emphasizing thermomechanical, environment and thermochemical interactions

- Summary and future directions
Prime-Relaiant EBC Systems for Si-Based Ceramic Matrix Composites

- NASA’s advanced environmental barrier and bond coat development: Prime-reliant designs
  - High toughness and low conductivity EBC top coat
  - Alternating Composition Layered Coatings (ACLCs) and composite coatings, including improving impact resistance
  - Advanced doped multicomponent EBCs
  - Prime-reliant designed bond coats
  - Ultimately environmental resistant CMCs with high thermal conductivities

E.g.,

- Low expansion alloyed-HfO₂, and HfO₂ aluminates
- RE doped Hf, Hf RE silicate and/or multi-rare earth silicate EBCs
- 2700°F bond coats

**SiC/SiC CMC**
Fundamental Recession Issues of CMCs and EBCs

- Recession of Si-based Ceramics
  (a) Convective; (b) Convective with film-cooling
  - Low SiO₂ activity EBC systems
- Advanced rig testing and modeling
  Complex recession behavior of CMC and EBCs studied in NASA High Pressure Burner Rig, included film-cooled recession

Recession rate = const. \( V^{1/2} \frac{P_{(H₂O)}^2}{(P_{total})^{1/2}} \)

\[
\text{SiO}_₂ + 2\text{H}_₂\text{O}(g) = \text{Si(OH)}₄(g)
\]

(a) Convective; (b) Convective with film-cooling
**Fundamental Recession Issues of CMCs and EBCs - Continued**

— EBC stability evaluated on SiC/SiC CMCs in high velocity, high pressure burner rig environment

- Early generations of environmental barrier coatings - EBC systems, improved stability in turbine environments

![Graph showing weight loss of SiC over exposure time at different temperatures](image)

- Robinson and Smialek, J. Am. Ceram Soc. 1999

![Images of coatings](images)
Fundamental Recession Issues of CMCs and EBCs - Continued

EBC stability evaluated on SiC/SiC CMCs in high velocity, high pressure burner rig environment

- Early generations of environmental barrier coatings - EBC systems

![Graph showing specific weight change versus temperature and inverse temperature for different materials under high velocity burner rig conditions.](image)

- HfO₂ based low k - APS
- HfO₂ based low k - EB-PVD
- Combustor coating
- Turbine coating

High pressure burner rig, 16 atm, 31 hr
Environmental Barrier Coating in Simulated Load-Fatigue Testing Environments (Laser High Heat Flux Rig)

- EBC $\text{Yb}_2\text{SiO}_5/\text{Yb}_2\text{Si}_2\text{O}_7/\text{Si}$ on Melt Infiltrated (MI) Prepreg SiC/SiC CMC substrates
- Tested in air, furnace isothermal at 1316°C; and in heat flux steam, at $T_{\text{EBC}}$ 1316°C, $T_{\text{CMC}}$ at ~1200°C
- Lower CMC failure strain observed in the steam-heat flux test environment
- Ytterbium mono-silicate recession observed in the test
- Thermal conductivity for monitoring coating delamination

Fatigue strains (amplitudes) – Time Plot
Thermal conductivity – Time Plot
Environmental Barrier Coating in Simulated Load-Fatigue Testing Environments (Laser High Heat Flux Rig) - Continued

- Crack and recession failure in air and steam tests

In Air; EBC cracking

In steam; EBC cracking and volatility

<table>
<thead>
<tr>
<th>Component</th>
<th>Type</th>
<th>Conc., At%</th>
<th>Conc., Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Calc</td>
<td>49.07</td>
<td>9.59</td>
</tr>
<tr>
<td>Si</td>
<td>Calc</td>
<td>9.79</td>
<td>3.36</td>
</tr>
<tr>
<td>Yb</td>
<td>Calc</td>
<td>41.14</td>
<td>87.04</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Advanced NASA EBC Developments

NASA advanced EBC systems emphasizing high stability HfO$_2$- and ZrO$_2$-RE$_2$O$_3$-SiO$_2$ EBC systems and HfO$_2$-Si and Rare Earth – Silicon bond coat systems
- NASA multicomponent Rare Earth RE$_2$Si$_{2-x}$O$_{7-2x}$, such as (Yb,Gd,Y)$_2$Si$_{2-x}$O$_{7-2x}$ environmental barrier systems
- Rare earth-doped HfO$_2$-ZrO$_2$, and HfO$_2$-doped Rare Earth (RE) silicates are among the advanced EBC systems
  - Improved high temperature stability and creep strength;
  - Facilitating nano-cluster formation with high concentration rare earth compound phases;
  - Improving CMAS resistance

TEM-EELS
Composition map
NASA EBC Bond Coat Systems

NASA EBC Systems

- HfO₂ - RE₂O₃-SiO₂/RE₂Si₂₋ₓO₇₋₂ₓ environmental barrier systems
  - Controlled silica content and rare earth dopants to improve EBC stability, toughness, erosion and CMAS resistance
  - HfO₂-Si based bond coat, controlled oxygen partial pressure
  - Advanced rare earth-Si composition systems for 2700°F+ long-term applications
- Early RE₂O₃-SiO₂-Al₂O₃ or YAG Systems
- Develop prime-reliant composite EBC-CMCs, HfSiRE(CN) systems

Bond coat systems for prime reliant EBCs; capable of self-healing
Development of Advanced HfO$_2$-Si Bond Coats

- Coating architecture and HfO$_2$ contents can be effectively controlled and optimized
- Si:Hf atomic ratio preferably 2:1 – 1:1
- Reported Spinodal decomposition of hafnium-silicate systems
Microstructures of Furnace Cyclic Tested GdYbSi(O) EBC Systems

- Cyclic tested cross-sections of PVD processed YbGdSi(O) bond coat
- Self-grown rare earth silicate EBCs and with some RE-containing SiO$_2$ rich phase separations
- Relatively good coating adhesion and cyclic durability

1500°C, in air, 500, 1 h cycles

- Complex coating architectures after the testing
- Designed with EBC like compositions – Self-grown EBCs

Composition (mol%) spectrum Area #1
SiO$_2$ 67.98
Gd$_2$O$_3$ 11.95
Yb$_2$O$_3$ 20.07

Composition (mol%) spectrum Area #2
SiO$_2$ 66.03
Gd$_2$O$_3$ 10.07
Yb$_2$O$_3$ 23.9
Microstructures of Cyclic Tested GdYbSi(O) EBC Systems - Continued

- Cyclic tested cross-sections of PVD processed YbGdSi(O) bond coat
- Self-grown rare earth silicate EBCs and with some RE-containing SiO₂ rich phase separations
- Interface growth instability

1500°C, in air, 500, 1 hr cycles

Outlined area Composition (mol%)
SiO₂ 66.72
Gd₂O₃ 8.62
Yb₂O₃ 24.66

Spot Composition (mol%)
SiO₂ 96.15
Gd₂O₃ 1.2
Yb₂O₃ 2.64
Advanced EBC developments – Some Hybrid Air-Plasma Spray/EB-PVD Turbine Combustor EBC Systems and Qualification Tests

- Achieved low thermal conductivity ranging from 1.0 - 1.7 W/m-K
- Demonstrated high pressure environmental stability at 2600-2650°F, 12-20 atm. in the high pressure burner rig
- Surface recession or micro-spallation for less tougher coating systems

2” diameter ND3 EBC/SiC/SiC specimen after testing in the high pressure burner rig At 2600°F+, 200 m/s
Erosion and Impact Aspects: Early Mach 0.3 Ballistic Impact Tests of HfO$_2$-Si Bond Coat EBC Systems

- Advanced high toughness EBCs tested with comparable performance of best TBCs
- More advanced EBC compositions currently also in developments

![Graph showing projectile velocity vs. spalled area and energy](image)

- 7YSZ and low k TBCs
- ZrRETT
- ATES series
- ND2
- ND3
- ND6
- ND7
- SUP-ERA7.4 EBC
- t'-ZrO2/NASA EBC
- Cubic low k ZrO2 k-NASA EBC

![Images of spalled samples](images)
Advanced EBC Coating Material Strength Evaluations

- High strength EBCs and bond coats are critical for prime-reliant designs
  - Multicomponent EBCs and first-generation HfO$_2$-Si bond coat achieved 150-200 MPa strength at high temperature (1400°C+)
  - Multicomponent silicates showed improved high temperature strengths compared to baseline yttrium and ytterbium silicates
  - High strength and high toughness are critical for erosion and fatigue cracking resistance
High Heat Flux and CMAS Resistance are Ensured by Advanced High Melting Point Coating, and Multi-Component Compositions

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 h 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

High Heat Flux and CMAS Resistance Tests of Advanced EBC Systems

- Multicomponent rare earth silicate EBC showed improved performance
- Silicate based coatings still sensitive to CMAS concentrations (estimated variation between average CMAS at 25 mg/cm² to more concentrated region CMAS at 75 mg/cm²)
- Some coating damage occurred for EBCs in JETS tests at higher CMAS loading regions

Laser rig test of advanced coating systems
Thermal Gradient Tensile Creep Rupture Testing of Advanced Turbine Environmental Barrier Coating SiC/SiC CMCs

- Advanced high stability multi-component hafnia-rare earth silicate based turbine environmental barrier coatings being successfully tested for 1000 hr creep rupture
- EBC-CMC creep, fatigue and environmental interaction is being emphasized
Advanced environmental barrier coatings – Prepreg CMC systems demonstrated long-term EBC-CMC system creep rupture capability at stress level up to 20 ksi at $T_{EBC}$ 2700°F, $T_{CMC}$ interface ~2500°F

- The HfO$_2$-Si based bond coat showed excellent durability in the long term creep tests

EBCs on Gen II CMC after 1000 h fatigue testing

Hybrid EBCs on Gen II CMC after 1000 h low cycle creep fatigue testing
High Heat Flux Thermomechanical fatigue Tests of Advanced NASA EBC-Bond Coats Systems on CMCs

- Laser High Heat Flux thermomechanical fatigue testing of a HfO$_2$-Si and NASA advanced EBC baseline with steam at 3 Hz, 2600-2700°F, and 69 MPa maximum stress with stress ratio 0.05, completed 500 h testing

- $T_{\text{surface}} = 1500-1600^\circ\text{C}$
- $T = 1320-1350^\circ\text{C}$
- Heat Flux = 170 W/cm$^2$
- Specimen had some degradations

3 hz fatigue testing at 10 ksi loading
Completed 500 hr testing

Testing proving vital failure mechanisms in a simulated test environments
EBC-CMC Thermal Gradient Creep Rupture and Delamination Modeling

- An equivalent stress model is established for EBC multicrack stress intensity modeling: emphasize creep, thermal gradient and stress rupture interactions
- Benchmark failure modes established in EBC systems, strong bond coat beneficial

EBC-CMC Thermal Gradient Creep Rupture and Delamination Modeling – Bond Coat Stiffness Effect

Advanced EBCs designed with higher strength and stiffness to improve creep, fatigue, and cyclic durability

Fatigue Tests of Advanced RESi Bond Coats and EBC Systems

- APS and PVD processed 2700°F bond coats on CMC: focus on fatigue testing at temperatures 2400-2700°F
- EBC bond coats critical to prime-reliant coating system designs

Creep and Fatigue Test with CMAS

Air Plasma Sprayed APS YSi+Hf-RESilicate EBC Bond Coat series on Royce Royce HTC CVI-MI SiC/SiC (with CMAS) 1400°C, at 10 ksi, **400 h**

EB-PVD HfRE$_2$Si$_{2-x}$O$_{7-x}$ EBC/GdYbSi(O) bond coat on CVI-MI SiC/SiC (with CMAS) 1537°C, 10ksi, **300 h** fatigue (3 Hz, R=0.05)

Fatigue Tested

PVD GdYSi(O) coated on Hyper Them 12C-461-002 #17 1316°C, 10ksi, **1000 h** fatigue (3 Hz, R=0.05)

PVD GdYbSi(O) bond coat, 1316°C, 15ksi, **1169 h** fatigue (3 Hz, R=0.05) on GE Prepreg SiC/SiC

EB-PVD RE$_2$Si$_{2-x}$O$_{7-x}$ EBC/HfO$_2$-Si bond coat on 3D CVI+PIP SiC/SiC 1482°C, 10ksi, SPLCF fatigue at 3 Hz, R=0.5 (**300 h** furnace tested, **500 h** in laser thermal gradient)

Advanced EBC coated airfoil tests
EBC-CMC Turbine Element Fatigue Testing

- Testing approaches developed for EBC-CMC trailing edge thermomechanical testing
- High heat flux capability to simulate required high thermal gradients and more complex temperature distributions in a turbine engine
- Mechanical loading to simulate the high pressure turbine airfoil pressure (ballooning) effects
- EBC-CMC durability being evaluated, planned incorporation of stream jet environments

EBC coated Trailing Edge (TE) “wedge” testing in high heat flux and mechanical fatigue loading

Maximum Principal Strain vs. Airfoil Internal Pressure
The results showed complex coating cycling behavior, and out of phase strain cycles also on the EBC coated sides.

Possibly changed neutral axes of the deflections of the CMC thin and thick walls.

Challenges for modeling along with thermal in-phase and out-phase loading.
SiC/SiC Turbine Airfoil Trailing Edge Tests

- Subelement wedge testing and high temperature tests, aiming at understanding the CMC and EBC degradations

Summary

- **Prime-Reliant and durable EBCs are critical to emerging SiC/SiC CMC Hot-Section component technologies**
  - The EBC development built on a solid foundation from past experience, evolved with the current state of the art compositions with higher temperature capabilities and stabilities
    - Multicomponent EBC oxide-doped silicates showed promise with improved stabilities, strength and toughness, and durability in various tests
    - HfO$_2$-Si and RE-Si bond coats, along with RESiHfCN potentially for realizing prime-reliant EBC designs
    - Advanced testing help scale-up for components and EVC-CMC modeling

Current emphases and future paths:
- Better understanding of the coating failure mechanisms, and helping develop coating property databases and validate life models, aiming at more robust EBC-CMC designs
- Continue to focus on coating composition and processing improvements, simulated engine environment testing and performance modeling
- Design high strength, strain tolerant, CMAS resistant top coat; and dense, low diffusion and high toughness EBC and bond coats
- Self-repairing and/or self-growing of slow growth adherent EBC coatings, minimizing silica separation
Acknowledgements

• The work was supported by NASA Fundamental Aeronautics Program (FAP) and Transformational Tools and Technologies (TTT) Project – Janet Hurst and Dale Hopkins

In particular, the contributions from the following:

NASA EBC-CMC Team, In particular, Jim DiCarlo (retired), Jim Smialek, Dennis Fox, Bryan Harder, Robert A. Miller, Janet Hurst, Martha Jaskowiak, Ram Bhatt, Doug Kiser, Amjad S. Almansour, Mike Halbig, Valerie Wiesner, Nate Jacobson, Narottam Bansal, Francisco Sola-Lopez, and Serene Farmer, (NASA GRC)

Craig Robinson (Chief, Environmental Effects and Coatings Branch); Joe Grady (Chief, Ceramic and Polymer Composites)

Ron Phillips and Ralph Pawlik for assistance in mechanical testing
John Setlock, Don Humphrey, and Mike Cuy for their assistance in the TGA and furnace cyclic testing, respectively

Sue Puleo and Rick Rogers: X-ray Diffraction
Ram Bhatt in the collaborative work for EBC-CMC integrations
Bob Pastel, Test support
Louis Ghosn and Yoshida Yamada: FEM modeling

Collaborators include:

Sulzer Metco (US) - Mitch Dorfman; Chis Dambra
Directed Vapor Technologies, International – Derek Hass and Balvinder Gogia
Praxair Surface Technologies – John Anderson, Li Li, Michael Helminiak
Southwest Research Institute – Ronghua Wei (PVD coating processing)

in supporting the coating processing