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

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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 lifing methodologies
• Improve technology readiness

Guided Entry: Peak Heating

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<tr>
<th>Altitude</th>
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<tr>
<td></td>
<td>23 km</td>
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<table>
<thead>
<tr>
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<td>15247 kmph</td>
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Entry, Descending and Landing: Ultra High Ceramics and Coatings (UHTCC)

Fixed Wing Subsonic and Supersonics Aircraft

Hybrid Electric Propulsion Aircraft
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

![Diagram showing temperature capability and development goals for environmental barrier coatings.](image)

**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 environment resistant CMCs with high thermal conductivities

![Diagram of EBC System](image)

- **SiC/SiC CMC**
- **Low expansion alloyed-HfO₂ and HfO₂ aluminates**
- **RE doped Hf, Hf RE silicate and/or multi-rare earth silicate EBCs**
- **2700°F bond coats**
- **EBC Bond Coat**
- **SiC/SiC CMC**

Examples of RE-doped Hf silicates:
- HfO₂-Y₂O₃-Yb₂O₃-Gd₂O₃-(SiO₂)
- HfO₂-Y₂O₃-Yb₂O₃-Gd₂O₃-Ta₂O₅-TiO₂-(SiO₂)
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. \( V^{1/2} \frac{P_{\text{H₂O}}}{(P_{\text{total}})^{1/2}} \)

\[
\text{SiO}_2 + 2\text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)
\]
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 SiC weight loss with exposure time at different temperatures](image)

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

![SEM images of Combustor and Turbine 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

- HfO₂ based low k - APS

- SiC/SiC under high velocity

- Tyranohex SA (16 atm, 30m/s)

- Tyranohex SA (6 atm, 200m/s)

- BSAS Baseline

NASA EBC stability development goal: 5 mg/cm²-h

Specific weight change, mg/cm²-h vs. 1/T, K⁻¹

Temperature, °C

1600 1500 1400 1300 1200 1100 1000

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

- EBC Yb$_2$SiO$_5$/Yb$_2$Si$_2$O$_7$/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$_{EBC}$ 1316°C, T$_{CMC}$ 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

In steam-jet, EBC cracking and recession

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

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<th>Component</th>
<th>Type</th>
<th>Conc., At%</th>
<th>Conc., Wt%</th>
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<td><strong>Total</strong></td>
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EDS 25D
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
- HfO$_2$ -RE$_2$O$_3$-SiO$_2$/RE$_2$Si$_{2-x}$O$_{7.2x}$ environmental barrier systems
  - Controlled silica content and rare earth dopants to improve EBC stability, toughness, erosion and CMAS resistance
  - HfO$_2$-Si based bond coat, controlled oxygen partial pressure
  - Advanced rare earth-Si composition systems for 2700°F+ long-term applications
- Early RE$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ or YAG Systems
- Develop prime-reliant composite EBC-CMCs, HfSiRE(CN) systems
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 SiO₂ 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
SiO₂ 67.98
Gd₂O₃ 11.95
Yb₂O₃ 20.07

Composition (mol%) spectrum Area #2
SiO₂ 66.03
Gd₂O₃ 10.07
Yb₂O₃ 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%)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Gd₂O₃</th>
<th>Yb₂O₃</th>
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<tr>
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<td>66.72</td>
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Spot
Composition (mol%)

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<tr>
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<th>SiO₂</th>
<th>Gd₂O₃</th>
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<tr>
<td></td>
<td>96.15</td>
<td>1.2</td>
<td>2.64</td>
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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 tough coating systems

2” diameter ND3 EBC/SiC/SiC specimen after testing in the high pressure burner rig At 2600°F+, 200 m/s

High pressure burner rig tested new ND series Hybrid EBC systems coated on 2” diameter Gen II Prepreg SiC/SiC CMCs
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

![Spalled area vs. energy graph](image)

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

![Sample images](image)
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

![Graph showing flexure strengths of selected EBC materials](image)
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 $T_{\text{EBC}} 2700^\circ F$, $T_{\text{CMC}}$ interface $\sim 2500^\circ F$

- 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
- $T_{\text{surface}} = 1500$-$1600^\circ$C
- $T = 1320$-$1350^\circ$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 HfRE₂Si₂₋ₓO₋ₓ EBC/GdYbSi(O) bond coat on CVI-MI SiC/SiC (with CMAS)
1537°C, 10ksi, 300 h fatigue (3 Hz, R=0.05)

Advanced EBC coated airfoil tests

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 RE₂Si₂₋ₓO₋ₓ EBC/HfO₂-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)
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

Modeled testing
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

Strains Measurements for Coated Airfoil Trailing Edge Subelements at High Loads
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
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