Environmental Stability and Oxidation Behavior of HfO$_2$-Si and YbGd(O) Based Environmental Barrier Coating Systems for SiC/SiC Ceramic Matrix Composites

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NASA EBC and CMC System Development

- Emphasize temperature capability, performance and *long-term* durability
  - Highly loaded EBC-CMCs - Prime-reliant coatings
  - 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), impact and erosion

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**Temperature Capability**

<table>
<thead>
<tr>
<th>Year</th>
<th>Gen I</th>
<th>Gen II – Current commercial</th>
<th>Gen III</th>
<th>Gen. IV</th>
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<tbody>
<tr>
<td>Year</td>
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**Step increase in the material's temperature capability**

- 2800°F combustor TBC
- 2500°F Turbine TBC
- 2700°F (1482°C) SiC/SiC CMC 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), PtAl and NiAl bond coats

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**Increase in ΔT across T/EBC**

- 3000°F+ (1650°C+)
- 2700°F (1482°C)

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

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**Ceramic Matrix Composite**

**Single Crystal Superalloy**

**(T/EBC) surface**
Outline

• Advanced 2700°F capable EBC and bond coat developments
  - Rare Earth – Silicon, i.e., YbGd-Si (O) and YbGd-Lu-Si (O) and Hafnia-Si (HfO$_2$-Si) systems
  - Early systems cyclic oxidation results and Si composition optimizations
  - Focus on oxidation kinetics studies of selected EB-PVD coatings using TGA
  - Oxidation mechanisms and degradation mechanisms

• EBC - CMC system thermomechanical - environment testing, particularly using laser rigs
  - A Key step and capability for developments, and help composition optimization and

• Summary
NASA Advanced 2700°F Silicide Based Bond Coats – and EBC Systems Processing for Various Component Applications

- Advanced coating systems developed for various processing to improve Technology Readiness Levels (TRL)
- Composition ranges studied mostly from 50 – 80 atomic% silicon
  - PVD-CVD processing, for composition downselects - also helping potentially develop a low cost CVD or laser CVD approach
  - Compositions initially downselected for selected EB-PVD and APS coating composition processing

### PVD-CVD

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<th>GdYSi</th>
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<td>GdYSi</td>
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<tr>
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<tr>
<td>ZrSi+Ta</td>
<td>YbGdSi</td>
<td>GdYSi-X</td>
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<tr>
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<tr>
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<tr>
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<td>YbGdSi</td>
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### EB-PVD

- HfO2-Si 1;
  - REHfSi
  - GdYSi
  - GdYbSi 2
  - GdYb-LuSi
  - NdYSi

### APS*

- HfO2-Si
- YSi+RESilicate
- YSi+Hf-RESilicate

### FurnaceLaser/CVD/PVD

- REHfSi
- Hf-RESilicate
  - Used in ERA components as part of bond coat system
- Hf-RE-Al-Silicate
  - Used in ERA components as part of bond coat system
- APS*: or plasma spray related processing methods

**Process and composition transitions**

Oxidation Kinetics and Furnace Cyclic Behavior of RESi EBC Bond Coats -

- Some early multi-component PVD processed systems showed excellent oxidation resistance and furnace cyclic test (FCT) durability at 1500°C
- FCT and steam tests also performed for more advanced RESiO-Hf systems

![Graph showing specific weight gain vs. time for YGdSi bond coat on SiC/SiC, 1500°C](image)

Oxidation kinetics

An example of cross-sectional TGA tested specimen -
Oxidation Kinetics and Furnace Cyclic Behavior of RESi EBC Bond Coats - Continued

- Some early multi-component PVD processed systems showed excellent oxidation resistance and furnace cyclic test (FCT) durability at 1500°C
- FCT and steam tests also performed for more advanced RESiO-Hf systems
- FCT durability found to be closely related to temperature capability and oxidation resistance of the coating systems

An example of cross-section TGA tested specimen

FCT life, Testing in Air at 1500°C, 1 hr cycles
Oxidation Resistance of Plasma sprayed Based HfO$_2$-Si

- TGA weight change measurements in flowing O$_2$
- Parabolic oxidation kinetics generally observed
- Solid-state reaction is also involved with the systems, and more complex behavior at 1400 and 1500°C
- Improved oxidation resistance through APS plasma spray powder processing optimization (AE10219 II; Sulzer/Oerlikon Metco)

![Plasma spray processed microstructure](image)

- AE 10219: first Generation HfO$_2$-30wt%Si composite APS powders
- AE 10218 is HfO$_2$-30wt%Si composite APS powders used in NASA ERA liner component demonstrations
- AE 10219 Clad II is second Generation HfO$_2$-30wt%Si composite APS powders
Microstructures of Furnace Cyclic Tested GdYbSi(O) EBC Systems

- Cyclic tested cross-sections of early PVD processed YbGdSi(O) bond coat
- Self-grown rare earth silicate EBCs and with some RE-containing SiO\textsubscript{2} rich phase separations
- Relatively good coating adhesion and cyclic durability

1500°C, in air, 500, 1 hr cycles

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

Composition (mol\%) spectrum Area #1
- SiO\textsubscript{2} 67.98
- Gd2O\textsubscript{3} 11.95
- Yb2O\textsubscript{3} 20.07

Composition (mol\%) spectrum Area #2
- SiO\textsubscript{2} 66.03
- Gd2O\textsubscript{3} 10.07
- Yb2O\textsubscript{3} 23.9
Microstructures of Cyclic Tested GdYbSi(O) EBC Systems-
Continued

- Cyclic tested cross-sections of early 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 hr cycles

Outlined area

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<th>Composition (mol%)</th>
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<tbody>
<tr>
<td>SiO₂</td>
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<tr>
<td>Gd₂O₃</td>
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<tr>
<td>Yb₂O₃</td>
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Spot

<table>
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<tr>
<th>Composition (mol%)</th>
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<tbody>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Gd₂O₃</td>
</tr>
<tr>
<td>Yb₂O₃</td>
</tr>
</tbody>
</table>
Experimental: NASA Yb,Gd,Y Rare Earth Silicate EBCs

- Yb,Gd(Nd),Y (or RE-Silicate) Multi-Component Rare Earth Silicate EBCs
- Sometime using fine alternating HfO$_2$ and the silicates for top coats
- EB-PVD bond coat systems mostly focused on YbGdSi, YbGd-LuSi, and YbNdSi, and HfO$_2$-Si
- Initial compositions optimized for the EBC bond coats: RE:Si 1:2; and Hf:Si 1:2 – 1:1
- Coating processed on SiC/SiC ceramic matrix composites for studies
- Processed using Directed Vapor EB-PVD at Directed Vapor Technologies
Experimental: Oxidation and Durability Tests

— Test specimens with dimensions 25 mm diameter disc specimens for oxidation, laser heat flux and furnace cyclic test (FCT) – briefly reviewed
— Thermogravimetric analysis (TGA), using 0.5”x1” CVI SiC/SiC specimens
— Laser long-term thermomechanical fatigue + steam/CMAS water vapor cyclic test using 0.5”x6” dogbone specimens
Oxidation Kinetics of EB-PVD Processed YbGdSi(O) Based Coating

- Oxidation kinetics obtained at various temperatures in flowing O$_2$ for YbGdSi(O) (not necessarily processing optimized)
- Parabolic oxidation kinetics generally observed after initial transient stages
- Activation energy determined 110 kJ/mol
Oxidation Kinetics Comparisons of Several Advanced EB-PVD Processed EBC Systems Compared

- The EB-PVD Systems showed comparable oxidation rates and good oxidation resistance, tested up to 500 h
- Kinetics compared with LuGdSi (O) and HfO$_2$-Si (O) systems
- Further process improvements help improved oxidation resistance and durability

![Graph showing oxidation kinetics comparison](image)

- Activation energy 110.6 kJ/mol
- Activation energy 136.5 kJ/mol
Microstructures of the Advanced EBCs after the Oxidation Tests

– RE-Si system: forming RE silicate “scales”, fully compatible with EBCs
– Reaction and oxidation mechanisms are being further studied, particularly RE containing SiO$_2$ phase stability
– Further process improvements can help improve the oxidation resistance and durability

Cross-section micrograph of YbGdSi(O) tested at 1500°C, 500hr
Microstructures of the Advanced EBCs after the 500 hr Oxidation Tests in O\textsubscript{2} - Continued

- HfO\textsubscript{2}-Si bond coat: forming HfSiO\textsubscript{x} based scales bond coat, compatible with EBCs
- Reaction and stability being studied
- Further process improvements can help improve the oxidation resistance and durability

Cross-section micrograph of HfO\textsubscript{2}-Si tested at 1500°C, 500hr
Microstructures of the Advanced EBCs after the Oxidation Tests - Continued

- Surface Morphologies of YbGdSi Bond Coat only on CMC after Oxidation at 1400°C, 300 hr

Area – all image region

Composition (mol%)
- GdO₃: 3.49
- Yb₂O₃: 13.84
- SiO₂: 82.67

Area A Composition

Composition (mol%)
- GdO₃: 7.73
- Yb₂O₃: 30.54
- SiO₂: 61.73
Microstructures of the Advanced EBCs after the Oxidation Tests - Continued

- Surface Morphologies of YbGdSi Bond Coat only on CMC after Oxidation at 1400°C, 300hr
- Observed SiO₂ rich phase separation with fine rare earth silicate phases
- Solubility of HfO₂ and rare earth oxides/silicates also being studied using TEM
CMAS Resistance for the Rare Earth-Silicon Coatings

- CMAS resistance of Yb-GdSi (O) at 1500°C, 100 hr
- Higher stability and CMAS resistance observed due to its High Melting Point Coating Compositions
- Observed the Apatite phase formation
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

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

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

Testing proving vital failure mechanisms in a simulated test environments
NdYb silicate EBC-RESi bond coat EBC coatings on 3D-architecture CVI-PIP SiC-SiC CMC (EB-PVD processing), tested in combined CMAS and steam thermomechanical fatigue, completed ~300 h testing.

Steam and CMAS attacked coating surface at 2700°F.
High Heat Flux Thermomechanical fatigue Tests of Advanced NASA EBC-Bond Coats Systems on CMCs - Continued

- NdYb silicate EBC-RESi bond coat EBC coatings on 3D architecture CVI-PIP SiC-SiC CMC (EB-PVD processing), tested in combined CMAS and steam thermomechanical fatigue, completed ~300 h testing

### Oxide Component Mole Conc.

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<th>Component</th>
<th>Mole Conc.</th>
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<tr>
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<tr>
<td>MgO</td>
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</table>
| SiO2 rich phases separation in CMAS Nd and Yb dissolutions

Steam and CMAS attacked coating surface at 2700°F
Summary

• RE - Silicon and HfO$_2$-Si bond coats with multicomponent rare earth silicate EBCs processed using EB-PVD, and the oxidation kinetics investigated

• The coatings generally showed very good oxidation and cyclic resistance for CMCs with targeted designed bond coat compositions, at 1500°C and up to 500 h tests

• The EBC bond coats grow rare earth silicates or HfSiO$_x$ “scales”, compatible with the EBC systems

• Stability of RE, Hf containing SiO$_2$ rich phases from the phase separation being further evaluated

• Long-term environment durability testing conducted to evaluate the coatings in more complex load, CMAS and/or steam environments, simulating turbine airfoil conditions

• The results helping further design and processing improved environmental barrier coating systems, for achieving more robust, prime-reliant EBC systems
Acknowledgements

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