The Development of HfO$_2$-Rare Earth Based Oxide Materials and Barrier Coatings for Thermal Protection Systems

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**Motivation**

- Thermal and environmental barrier coating (TBC) system development goals
  - High Temperature capability and high heat-flux cyclic durability
  - Excellent resistance to oxidation and combustion environment attacks
  - High toughness: resistance to impact and erosion being emphasized

### Temperature Capability

- **2500°F Turbine TBCs**
- **2850°F Combustor TBCs**

#### Step increase in temperature capability

- 2400°F (1316°C)
- 2700°F (1482°C)
- 3000°F+ (1650°C+)

#### Increase in ΔT across T/EBC

- **Single Crystal Superalloy**
- **Ceramic Matrix Composite**

- **Gen I**
- **Gen II – Current commercial**
- **Gen III**
- **Gen. IV**

#### Materials

- **SiC/SiC Turbine CMC coatings**
- **SiC/SiC CMC C/SiC and Si₃N₄ coatings**

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NASA Environmental Barrier Coating System Development – For Turbine Engines

- Emphasize temperature capability, performance and durability for next generation vehicle airframe or engine systems
- Increase Technology Readiness Levels for component system demonstrations

<table>
<thead>
<tr>
<th>Gas</th>
<th>TBC Bond coat</th>
<th>Metal blade</th>
<th>Gas</th>
<th>TBC Bond coat</th>
<th>Metal blade</th>
<th>Gas</th>
<th>EBC Bond coat</th>
<th>CMC airfoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>2900°F (T41)</td>
<td>2500°F TBCs</td>
<td>Tsurface 300°F increase</td>
<td>3200°F (T41)</td>
<td>2700-3000°F EBCs</td>
<td>Tsurface 200-500°F increase</td>
<td>3200°F (T41)</td>
<td>2700°F CMCs</td>
<td></td>
</tr>
<tr>
<td>2200°F TBCs</td>
<td>Tsurface</td>
<td>Baseline metal temperature</td>
<td></td>
<td></td>
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<td>2400°F CMCs</td>
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Current metal turbine airfoil system | State of the art metal turbine airfoil system 2500°F TBCs | 2700-3000°F CMC turbine airfoil systems
Challenges

– Current TEBCs limited in their temperature capability
  • >3000°F

– Preferably Oxide and Silicate Top Coat for oxidation and environment resistance
  • Stability (sintering resistance) and thermal expansion match with substrates

– Advanced TEBCs also required higher strength and toughness
  • In particular, resistance to combined higher heat flux, mechanical loading, harsh environment and the complex interactions

– TEBCs need to eb designed with high toughness, with improved impact and erosion resistance

– EBC systems processing Issues
Outline

— Advanced approaches for next generation environmental barrier and thermal protection system development

— Processing techniques for advanced EBCs
  • Air plasma spray
  • Plasma Spray – Physical Vapor Deposition (PS-PVD) and Plasma Spray – Physical Vapor Deposition processing
  • Electron Beam – Directed Vapor Deposition (EB-DVD) and/or Electron Beam - Physical Vapor Deposition (EB-PVD)

— Advanced thermal and environmental barrier coating systems
  • NASA EBC systems
  • Example systems for potential thermal protection system applications

— Summary and future directions
Advanced Environmental Barrier Coating Systems for Si-Based Ceramic Matrix Composites

- Focus on high stability HfO$_2$ layer with graded interlayer, environmental barrier and advanced bond coat developments
  - Alternating Composition Layered Coatings (ACLCs) and composite coatings
  - HfO$_2$-Aluminate and rare earth (RE) silicate EBCs
  - Processing approaches being developed for vapor deposition, plasma spray addressing high stability nano-composite systems

![Diagram of SiC/SiC CMC with interlayer composition](image)

- Low expansion alloyed-HfO$_2$, and HfO$_2$ aluminosilicate
- Interlayer: compositional layer graded system
- RE doped mullite-HfO$_2$, and/or rare earth silicate EBCs
- Ceramic composite bond coats

- Increased Si/SiO$_2$ activity
- Doped mullite with ACLC (Hf rich bands)
- Increased dopant RE/Transition metal concentrations & increased Al/Si ratio
- Doped mullite, HfO$_2$/Si (SiC/Si$_3$N$_4$) composite bond coat (High temperature capable with self-healing)

Examples:
- HfO$_2$-Y$_2$O$_3$-Yb$_2$O$_3$-Gd$_2$O$_3$-(SiO$_2$)
- HfO$_2$-Y$_2$O$_3$-Yb$_2$O$_3$-Gd$_2$O$_3$-Ta$_2$O$_5$-TiO$_2$-(SiO$_2$)
## Advanced Candidate Coating Material Systems

<table>
<thead>
<tr>
<th>Material Systems</th>
<th>Temperature capability</th>
<th>Thermal expansion</th>
<th>Resistance to oxidation and combustion environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfO$_2$-RE$_2$O$_3$</td>
<td>~3000°C</td>
<td>8-10x10$^{-6}$ m/m-K</td>
<td>Excellent</td>
</tr>
<tr>
<td>HfO$_2$-Rare earth silicates</td>
<td>~1900-2900°C</td>
<td>8-10x10$^{-6}$ m/m-K</td>
<td>Excellent</td>
</tr>
<tr>
<td>Rare earth silicate</td>
<td>~1800-1900°C</td>
<td>5-8.5x10$^{-6}$ m/m-K</td>
<td>Good</td>
</tr>
<tr>
<td>Rare earth – aluminates and Alumino silicate</td>
<td>~1600-1900°C</td>
<td>5-8.5x10$^{-6}$ m/m-K</td>
<td>Good</td>
</tr>
<tr>
<td>HfO2-Si and RE-Si bond coat</td>
<td>Up to 2100°C</td>
<td>5-7x10$^{-6}$ m/m-K</td>
<td>Good</td>
</tr>
</tbody>
</table>
Plasma Sprayed Processing of Environmental Barrier Coatings

- Focused on advanced composition and processing developments using and coupled with more state-of-the-art techniques
- Improved processing envelopes using high power and higher velocity, graded systems processing for advanced TEBCs and thermal protection systems
An advanced Electron Beam Vapor (EB-DVD) approach developed by Directed Vapor Technologies, Inc (DVTI)

Flexible in multi-component coating processing and composition controls

Progress made in advanced bond coat, EBC and some top coat developments of environmental barrier coating systems

Significant processing advancement in co-deposition and multi-component coating developments with current NASA EBC compositions for high Technology Readiness Levels (TRLs) EBC component processing

Collaborative work also in the EBC top coat development with Penn State University
Plasma Sprayed-Physical Vapor Deposition (PS-PVD) and Plasma Sprayed- Thin Film (PS-TF) Processing of Thermal and Environmental Barrier Coatings

- NASA PS-PVD and PS-TF coating processing using Sulzer technology
- EBC is being developed for next-generation SiC/SiC CMC turbine airfoil coating processing
  - High flexibility coating processing – PVD and/or splat coating processing at lower pressure (at ~1 torr)
  - High velocity vapor, near non line-of-sight coating processing for complex-shape components
Thermal Conductivity of Near Dense HfO₂-Y₂O₃

- Thermal conductivity decreases with increasing yttria dopant concentration
- Lighter weight can be achieved by increasing yttria content
- Some porosity in the hot-pressed specimens can affect the conductivity measurements
Thermal Conductivity of Near Dense HfO$_2$-Y$_2$O$_3$: Plus Rare Earths: Multicomponents

- Multi-component oxide defect clustering approach

HfO$_2$-Y$_2$O$_3$-Nd$_2$O$_3$(Gd$_2$O$_3$,Sm$_2$O$_3$)-Yb$_2$O$_3$(Sc$_2$O$_3$) – TT(TiO$_2$+Ta$_2$O$_5$) systems

- Primary stabilizer
- Oxide cluster dopants with distinctive ionic sizes
- Toughening dopants

- HfO$_2$ based multi-rare earth doped coatings showed low thermal conductivity and excellent high temperature stability
Radiative Diffusion Models Developed for Understanding the Coating Radiative Conductivity at High Temperature

- The diffusion conduction equations

\[
q_{total} = k_{cond} \frac{dT}{dx} + \frac{16\sigma \cdot n^2 \cdot T_{ave}^3}{3(a + \sigma_s)} \frac{dT}{dx} = \left( k_{cond} + \frac{16\sigma \cdot n^2 \cdot T_{ave}^3}{3(a + \sigma_s)} \right) \frac{dT}{dx}
\]

\[
k_{effective} = k_{cond} + \frac{16\sigma \cdot n^2 \cdot T_{ave}^3}{3(a + \sigma_s)} = k_{cond} + k_{rad}
\]

\(q_{total}\) = Total heat flux

\(k_{cond}\) = Intrinsic lattice conductive thermal conductivity

\(k_{rad}\) = radiation thermal conductivity

\(k_{effective}\) = effective thermal conductivity

\(\sigma\) = Stefan-Boltzman constant \(5.6704 \times 10^{-8}\) W/(m\(^2\)-K\(^4\))

\(n\) = Refractive index, 2.2

\(a\) = Absorption coefficient, cm\(^{-1}\)

\(\sigma_s\) = Scattering coefficient, cm\(^{-1}\)

\(\overline{T}\) = Average temperature of the material, K

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<thead>
<tr>
<th>q(_{r1})</th>
<th>q(_{r2})</th>
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<tbody>
<tr>
<td>(T_{g1})</td>
<td>(T_{g2})</td>
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<td>(T_{s1})</td>
<td>(\text{D})</td>
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<tr>
<th>(\nu_{c1})</th>
<th>(\nu_{c2})</th>
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<tr>
<td>Regions of optical thickness</td>
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Evaluation of Radiation Flux Resistance of Oxide Coating Systems

HfO$_2$ based multi-rare earth doped coatings showed low thermal conductivity.
Advanced Multi-Component TEBC Developed For Integrated to SiC/SiC and C/SiC Systems

— The emphasis placed on graded systems and thermomechanical stability
— Strong interest in highly stable oxide-silicate and composites
— Aiming at better understanding the phase stability and solid-state reaction kinetics of multi-phase systems

Oxide-silicate nano-composites (bright areas are Hf- and/or RE-rich phases; dark areas are silica-rich phases)
Fundamental Understanding Needed in Stability of Multi-Component EBC Compositions

- Mechanical strength and toughness of multi-component EBCs may still need to be improved as compared to intrinsically tougher nano-structured turbine TBCs.

NASA early EBC top coat compositions (Hf-RE-silicate systems) after 1500°C 60 hr cyclic testing.

In comparison:

- NASA t' phase Zr-RE four- or six-component compositions.
Air Plasma Spray Processing Focused on Advanced Multi-Component EBC composition Optimization and Supporting Hybrid APS-PVD EBC Development

— Mechanical strength and toughness of multi-component EBCs may still need to be improved as compared to intrinsically tougher nano-structured turbine TBCs

NASA advanced APS EBC (Hf-RE-Alumino-Silicate system) Optimization and Controlled Grain boundary phases

NASA Hybrid APS and EB-DVD/PVD EBC Optimization
EBC Processing using Plasma Spray-Physical Vapor Deposition (PS-PVD)

- Demonstrated vapor-like coating deposition for thermal barrier and environmental barrier coating applications using Sulzer processed powders
  - Advanced powders developed/being developed under NASA programs using NASA specifications
- Initial properties being evaluated
  - Potentially high stability (thermodynamically) processing as EB-DVD/PVD
  - Potential issue with relatively less-stable systems such as silicates due to phase separations
Initial PS-PVD Processing of Advanced TEBCs

- The emphasis is placed on initial turbine environmental barrier coating compositions, processing feasibility in realizing advanced EBC design architectures
- Low conductivity micro-pore silicates obtained
Thermal Conductivity of Early PS-PVD Yb$_2$Si$_2$O$_7$ Coating

— Micro-Porous and composite PS-PVD ytterbium silicate systems showed low thermal conductivity
— Porosity estimated based on composite thermal conductivity modeling
Laser Rig Heat Flux Thermal Gradient Tests For Thermal Conductivity Measurements of PS-PVD Systems

- PS-PVD three-layer systems, with the low conductivity $\text{ZrO}_2/\text{ZrO}_2+\text{Ytterbium silicate composite/Ytterbium silicate TEBCs}$ processed on SiC/SiC, improving the temperature capability
- Laser rig tests also showed relatively low thermal conductivity
Laser Rig Heat Flux Thermal Gradient Tests Validating the Coating and Materials Systems up to Temperature

- Directed Vapor processed EBCs tested for 50, 1 hr cycles at the coating surface temperature of near 1700°C without failure
Summary and Future Directions

• Advanced high temperature thermal and environmental barrier coating systems being developed using advanced EBC compositions and processing, potentially good candidates for thermal protection system applications

• Demonstrated feasibility to process complex and advanced graded EBC systems using APS, EB-DVD and PS-PVD approaches

• Demonstrated uniqueness of each processing methods and processing scale-up capability

• Achieved higher temperature capability, lower thermal conductivity, better environmental stability and incorporating toughening phases of the multicomponent coating systems

• Develop robust processing for APS, EB-DVD, PS-PVD, and process scaleups

• Further develop advanced testing approaches to ensure prime-reliant EBC systems
Acknowledgements

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