Development and Property Evaluation of Selected HfO$_2$-Silicon and Rare Earth-Silicon Based Bond Coats and 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
  - 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
Outline

• **Environmental barrier coating (EBC) system development: needs and challenges**

• **Advanced bond coat development approaches, NASA HfO$_2$-Si bond coat systems**
  – Focused on oxidation resistance, high temperature strength, toughness and creep properties

• **Advanced Rare Earth – Silicon based 2700°F+ capable bond coat developments**
  – Development approaches
  – Oxidation resistance
  – Furnace and thermomechanical durability

• **Summary**
NASA EBC and CMC System Development

— 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 high strength and toughness
  • Resistance to heat-flux, high pressure combustion environment, creep-fatigue loading interactions
  • Bond coat cyclic oxidation resistance

— EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
  • Critical to reduce the EBC system Si/SiO$_2$ reactivity and their concentration tolerance

— EBC-CMC systems need advanced and affordable processing
  • Using existing infrastructure and alternative coating production processing systems, including Plasma Spray, EB-PVD and Directed Vapor EB-PVD, and/or emerging Plasma Spray - Physical Vapor Deposition
  • Affordable and safe, suitable for various engine components
Degradation Mechanisms for Si Bond Coat

- Silicon bond coat melts at 1410°C (melting point)
- Fast oxidation rates (forming SiO₂) and high volatility at high temperature
- Low toughness at room temperature (0.8-0.9 MPa m¹/²; Brittle to Ductile Transition Temperature about 750°C)
- Low strength and high creep rates at high temperatures, leading to coating delamination
- Interface reactions leading to low melting phases
  - A more significant issue when sand deposit Calcium- Magnesium –Alumino-Siliacte (CMAS) is present
- Si and SiO₂ volatility at high temperature (with and without moisture)
Design Requirements for 2700°F Bond Coat Systems

— High melting point and thermal stability
— Develop slow growing, adherent protective scales
  • High strength and low thermal expansion coefficient scales, and minimum element depletion in the bond coat due to the scale formation essential
— Provide oxidation and environment protection for SiC/SiC CMC substrate
  • Oxidation resistance in all operating temperature range, up to 1600°C, no pesting
— High creep strength and excellent fatigue resistance
  • High resistance to impact, erosion, and CMAS, and environment induced degradations
— Excellent bond strengths (important to provide strong bond for the EBC to the substrate!)
— Thermal expansion coefficient matching to the CMC substrate
— Thermal chemical and thermal mechanical compatibility with EBC and CMC
— Improved bond coat – CMC interface architecture and integration
— Ensure low oxygen activity at the bond coat – CMC interfaces
  • Preferably kinetics controlled and dynamic bond coat systems for durability
Advanced High Temperature and 2700°F+ Bond Coat Development

- Development approach:
  - Advanced compositions ensuring high strength, high stability, high toughness
  - Bond coat systems for prime reliant EBCs; capable of self-healing

- Other systems

- HfO$_2$-Si systems
  - High strength, high stability reinforced composites: HfO$_2$-Si and a series of Oxide-Si systems
  - HfO$_2$-Si based and minor alloyed systems for improved strength and stability

- Advanced 2700°F bond coat systems:
  - RE-Si based systems
  - Advanced 2700°F+ Bond Coat systems
  - Advanced 2700°F bond coat systems: RE-Si based Systems, grain boundary engineering designs and/or composite systems -
HfO$_2$-Si Bond Coats for Improved Temperature Capability, and High Temperature Strength

- A relatively low cost bond coat system, APS and EB-PVD processing capable
- Excellent oxidation resistance, also ensuring low oxygen activities at the EBC-CMC interface
- Upper use temperature 1400°C and can be up to 1482°C
- SiO$_2$-HfSiO$_4$-HfO$_2$ phase system at very high temperature
- Thermal expansion coefficient $\sim 5.5 \times 10^{-6}$/K
- Rare earth metal or other dopants added for improved stability
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HfO$_2$-Si and alloyed EBC bond coats using EB-PVD processing: achieving higher temperature capability

Plasma sprayed HfO$_2$-Si EBC bond coat
Experimental: Mechanical Specimen Configurations

- Flexural specimens with dimensions 4x5x50 mm, machined from hot-pressed air plasma spray (APS) HfO$_2$-Si powders (billets size 75mmx50mmx10mm); test spans 20 and 40 mm
  - Using ASTM standards 1161 and 1211
  - Si concentration range from 25 to 70wt% in the HfO$_2$-Si systems
- The non-notched bar specimens used for strength, and creep testing
- Single edge V-notched beam (SEVNB) specimens used for toughness tests
- Test temperature range room temperature, 1200 up to 1500°C

![Specimen Diagram]

Specimen width = 4 mm

20 mm

50 mm

40 mm
Experimental: Oxidation and Durability Tests

— Test specimens with dimensions 25 mm diameter disc specimens for oxidation, laser heat flux and furnace cyclic test (FCT)
— Test specimens with dimensions 152x12.7 mm dog-bone, and 76x12.7 mm for tensile creep rupture and fatigue tests

• Tests were also conducted including
  o Thermogravimetric analysis (TGA)
  o FCT test
  o Laser + steam/CMAS water vapor cyclic test
  o Thermomechanical creep and fatigue
Oxidation Resistance of 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
- Excellent oxidation resistance and improved oxidation resistance through APS plasma spray powder processing optimization

- TGA weight change measurements at various temperatures
- AE 10219 is first Generation HfO$_2$-30wt%Si composite APS powders used in NASA ERA liner component demonstrations
- 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

Polished specimen microstructure after 1400°C test
High Strength EBC and Bond Coat Composition Development

- Bond coats and bond coat constituents designed with high strength to achieve the ultimate coating durability, compared with EBCs’ strengths.
- HfO$_2$-Si based systems showed high strength and high toughness.
- HfO$_2$-Si Bond coats showed high toughness
  - Toughness $>4-5$ MPa m$^{1/2}$ achieved
  - Emphasis on improving the lower temperature toughness
  - Annealing effects on improved lower temperature toughness being studied

![Fracture toughness vs. Temperature graph](image)

- May expect further increase from annealing
- Strength drop due to creep strength decrease

- Plot markers:
  - ○ As processed
  - △ 1300°C 20hr annealed
  - □ Si
The composites coatings have improved creep strength, and creep resistance at high temperatures. 

*Increased HfO$_2$-HfSiO$_4$ contents improve high temperature strength and creep resistance*
HfO$_2$-Si/Ytterbium Silicate EBC System Furnace Cyclic Durability Test at 1500°C

- Coating processed using Triplex Pro plasma spray processing, not necessarily fully optimized
- Long-term furnace cyclic durability tested 1500°C for 500 hr in air
- EBC with HfO$_2$-Si bond coat adherent (no any spallation) after testing
- Excellent oxidation resistance in protecting SiC/SiC
- SiO$_2$ loss in ytterbium silicate EBC (some area became ytterbia), and in the HfO$_2$-Si bond coat
- Some HfO$_2$ containing scales may be stable
Advanced 2700°F+ Bond Coats (Beyond HfO$_2$-Si)

**Development approach:**
- Advanced compositions ensuring high strength, high stability, high toughness
- Bond coat systems for prime reliant EBCs; capable of self-healing

High strength, high stability reinforced composites: HfO$_2$-Si and a series of Oxide-Si systems

HfO$_2$-Si based and minor alloyed systems

Advanced 2700°F bond coat systems: RE-Si based systems

Multicomponent RESi systems

Studied Zr, Hf, Ta, N, Al Dopants

RESi systems

HfO$_2$-RE-Si systems

HfO$_2$-RE-Al-Si systems

Advanced 2700°F+ Bond Coat systems
2700°F+ Advanced EBC Bond Coat Developments: Rare Earth Silicon Systems and Effect of Dopants

- Ytterbium, Yttrium and Gadolinium – Silicon or Silicide systems

- **Controlled silicon compositions and oxygen activities** to achieve good thermal expansion match with SiC/SiC CMCs and EBCs, and high melting points and stability

- **Focusing on multicomponent high temperature based systems** to ensure high temperature capability, oxidation resistance and durability

- **Emphasizing chemically and mechanically compatibility** with SiC/SiC CMCs and various environmental barrier coatings, *no free-standing silicon phases in composition designs*

- **Low temperature oxidation resistance and pesting issues** are also addressed in the developments
NASA Advanced 2700°F Silicide Based Bond Coats – System Processing for Various Component Applications

- Advanced systems developed and processed 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
  - Viable EB-PVD and APS systems downselected and tested; development new PVD-CVD approaches

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<th>PVD-CVD</th>
<th>EB-PVD</th>
<th>APS*</th>
<th>FurnaceLaser/CVD/PVD</th>
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<td>YbGdYSi</td>
<td>GdYSi</td>
<td>REHfSi</td>
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<td>YbGdYSi</td>
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<td>Process and composition transitions</td>
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APS*: or plasma spray related processing methods

Rare Earth Silicon Systems and Multi-Dopants for Stability

- Silicon-rich phase separations can limit high temperature stability
- Further thermal stability and mechanical strength can be improved by:
  - Composition controls (e.g. optimize silicon contents and addition of dopants)
  - Multi-dopant composition designs for reduced Si/SiO\(_2\) activity

Yb\(\text{Si}_x\) (no additional dopant)
Exposed to 1100°C for 20 h

Undoped material: shows separation of Si-rich/silica-rich phase

\((\text{Y},\text{Hf})\text{Si}_x\)
1100°C for 20 h

When dopant included: The Si-rich/silica-rich phases converted to more stable HfO\(_2\) - Hafnium silicate, and yttrium silicate containing phases
Advanced Bond Coats for Turbine EBCs – Oxidation Resistance

- 1500°C (2732°F) capable RESiO+X series EBC bond coat compositions and related composite coatings developed for combustor and turbine airfoil applications
- Oxidation kinetics studied using TGA in flowing O₂
- Parabolic or pseudo-parabolic oxidation behavior observed

Parabolic rate constant $K_p$ as a function of silicon content

Oxidation kinetics of a YbGdSi(O) bond coat

An oxidized bond coat after 1500°C 100 h creep testing
Furnace Cycle Test Results of Selected RESi and ZrSi + Dopant Bond Coats

- Testing in Air at 1500°C, 1 hr cycles

- Multi-component systems showed excellent furnace cyclic durability at 1500°C
High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

- Demonstrated CMAS resistance of RESi at 1500°C, 100 hr
Processing Advancements and Improvements for RE Si Bond Coats in EBC Systems

- Selected EBC system processed by EB-PVD and plasma Spray: Doped RE Si (+Hf) Bond Coat + advanced multi-component EBC Top Coat on woven SiC/SiC CVI-SMI CMC

- Creep testing conducted with 15 ksi load and laser thermal gradient

EBC System after 100 hr creep testing with 2700°F coating surface temperature and 2500°F CMC back temperature

- RE(Hf) silicate EBC Top Coat
- RESi Composite Bond Coat System: Striations indicate EB-PVD layers with compositional variations
- Excellent compatibility

Bond coat remains generally well-adhered to CMC substrate after the CMC failure, except some top bond coat composition segregation or processing defective regions
Fatigue Tests of Advanced Bond Coats and EBC Systems

- Strength and Fatigue cycles in laser heat flux rigs in tension, compression and bending
- Fatigue tests at 3 Hz, 2600-2700°F, stress ratio 0.05, surface tension-tension cycles
- Early fatigue-CMAS durability demonstrated

**Creep-fatigue durability test summary**

![Graph](image)

Tested, SA Tyrannohex with bond coat only

Tested, SA Tyrannohex with EBC system 188

Achieved long-term fatigue lives (near 500 hr) with EBC at 2700°F

Example of fatigue test EBC systems on Tyrannohex SiC composites
Summary

- Advanced HfO$_2$-Si and Rare Earth - Silicon based bond coat compositions developed
- The coatings showed excellent oxidation resistance and protection for CMCs
- HfO$_2$-Si showed excellent strength, fracture toughness, its upper use temperature may be limited to 1400°C due to higher silica activity, in particular in the CMAS environments
- The initial silicon content range of the Rare Earth-Silicon coatings was down-selected, multicomponent systems designed for further improved stability
- The rare earth – silicon based coatings showed 1500°C operating temperature viability and durability on SiC/SiC ceramic matrix composites
- The rare earth – silicon based coatings compositions will be down-selected; and further processing optimization planned
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