High Temperature Multilayer Environmental Barrier Coatings Deposited Via Plasma Spray–Physical Vapor Deposition

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Work was supported by the NASA Fundamental Aeronautics Program under the Aeronautical Sciences Project

Pittsburgh, PA, October 12-16, 2014
Motivation

- Turbine engine materials require long lifetimes at elevated temperatures
- Ceramic matrix composites (CMCs) offer substantial benefits
  - Limited by water vapor attack
- Environmental barrier coatings (EBCs) are necessary to protect the underlying ceramic
- Candidate materials are limited
  - Need to be thin, stable and durable
- Traditional processing methods may not be able to meet the requirements
  - Plasma Spray-Physical Vapor Deposition (PS-PVD)
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- Bridges the gap between plasma spray and vapor phase methods
  - Variable microstructure
  - Multilayer coatings with a single deposition

- Low pressure (70-1400 Pa)
  High power (>100 kW)
  - Temperatures 6,000-10,000K

- High throughput\(^1\)
  - 0.5 m\(^2\) area, 10 μm layer in < 60s

- Material incorporated into gas stream
  - Non line-of-sight deposition

- Attractive for a range of applications
  - Solid oxide fuel cells, gas sensors, etc.

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PS-PVD Diagnostics

Optical Spectrometer

• Data collected *in-situ*
• Emission lines measured and tracked
  – Plasma gases and feedstock
• Conditions can be optimized for maximum vaporization
PS-PVD Diagnostics

Ar/He Plasma with Oxide

He I

Oxide

Ar I

Oxide

Ar/He Plasma

Intensity

Wavelength (nm)

600 620 640 660 680 700 720
PS-PVD Diagnostics

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Plasma temperature measurement

• Boltzmann distribution
• Assumes local thermal equilibrium
• Intensities of Ar I lines were used
  – 40 lines measured
  – 516 - 968 nm range

\[
T = (-m k_b)^{-1}
\]

![Graph showing plasma temperature measurement](image)

1:2 Ar:He
85-95 kW
**Yb$_2$Si$_2$O$_7$: As-Deposited**

- Yb$_2$Si$_2$O$_7$ (Yb-disilicate) has been considered as a potential next-generation EBC

- Deposited using PS-PVD processing (~115 μm)
  - Air plasma sprayed silicon bond coat (~75 μm)
  - SiC/SiC substrate

- Splat-like deposition with large porosity distribution

- Backscatter shows some localized variation in Si content
  - Bright regions are Si-deficient
  - Dark regions are Si-rich

- XRD shows coatings are fully disilicate after heat treating
  - Isothermal exposure to water vapor at 1316C for 500 hours shows little crystallographic change
Single Layer Yb-disilicate EBCs

- High heat flux testing showed increased degradation of Yb-silicate coatings

- Coatings tested in air and in a steam environment from 1400-1500C
  - Yb-disilicate was stable in air with some sintering and delamination at the bond coat
  - Steam environment testing resulted in significant porosity at the surface due to the formation of Si-hydroxide

- Although Yb-disilicate has some desirable properties as an EBC, its silica activity may still be too high for temperatures required for advanced engine components.
Qualitative Ranking of Candidate EBC Materials

| Oxide Composition | EBC Material
|-------------------|----------------|
| HfO<sub>2</sub> | yttrium-aluminum-garnet
| ZrO<sub>2</sub> [YSZ] | Lu<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>
| 2(Lu<sub>2</sub>O<sub>3</sub>) · 3(ZrO<sub>2</sub>) | Yb<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>
| 2(Y<sub>2</sub>O<sub>3</sub>) · 3(ZrO<sub>2</sub>) | Y<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>
| 3(Yb<sub>2</sub>O<sub>3</sub>) · 5(Al<sub>2</sub>O<sub>3</sub>) | Al<sub>2</sub>O<sub>3</sub> · TiO<sub>2</sub>
| 3(Y<sub>2</sub>O<sub>3</sub>) · 5(Al<sub>2</sub>O<sub>3</sub>) (yttrium-aluminum-garnet) | 2(Lu<sub>2</sub>O<sub>3</sub>) · 3(HfO<sub>2</sub>)
| Lu<sub>2</sub>O<sub>3</sub> · 2(SiO<sub>2</sub>) | Y<sub>2</sub>O<sub>3</sub> · 2(SiO<sub>2</sub>)
| Yb<sub>2</sub>O<sub>3</sub> · 2(SiO<sub>2</sub>) | Ba(Sr)O · Al<sub>2</sub>O<sub>3</sub> · 2(SiO<sub>2</sub>)
| (barium-strontium-aluminosilicate) | (strontium-aluminosilicate)
| SrO · Al<sub>2</sub>O<sub>3</sub> · 2(SiO<sub>2</sub>) | Al<sub>2</sub>O<sub>3</sub>
| 3(Al<sub>2</sub>O<sub>3</sub>) · 2(SiO<sub>2</sub>) (mullite) | TiO<sub>2</sub>
| CaO · 2(Yb<sub>2</sub>O<sub>3</sub>) · 3(SiO<sub>2</sub>) | CaO · 2(Yb<sub>2</sub>O<sub>3</sub>) · 3(SiO<sub>2</sub>)
| x(CeO<sub>2</sub>) · (ZrO<sub>2</sub>) | SiO<sub>2</sub>
| SiO<sub>2</sub> | Cr<sub>2</sub>O<sub>3</sub>

Best Water Vapor Resistance

If silicon-free oxides can be adapted as EBCs, significantly higher stabilities are possible

\[
\text{Flux} = 0.664 \left( \frac{v_x \rho_x L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si(OH)}_4} \rho_x} \right)^{0.33} \frac{D_{\text{Si(OH)}_4}}{RTL} K a_{\text{SiO}_2} \left( P_{H_2O} \right)^2
\]

Under relevant turbine engine conditions:
Silicon Carbide: \( J = 0.48 \text{ mg/cm}^2\text{-hr} \)
\( Y_2SiO_5 + Y_2Si_2O_7: J = 0.12 \text{ mg/cm}^2\text{-hr} \)
\( Y_2Si_2O_5 + Y_2O_3 J = 2 \times 10^{-4} \text{ mg/cm}^2\text{-hr} \) (CTE issues)

Compiled by Jim Smialek in
Review: N. Jacobson et al.
T/EBC Multilayer Coatings

- Rare earth silicates have some desirable properties for EBCs, but SiO₂ activity may still be too high for temperatures required for advanced engine components.

- The addition of an oxide layer on the surface shows promise for reducing the temperature of the EBC and improving durability.

- Topcoat of rare earth doped t’ ZrO₂ provides erosion resistance equaling or surpassing other vapor processed coatings.

- Columnar microstructure in the topcoat reduces the in-plane modulus to a value of 25-30GPa.
Thermal Conductivity Testing

- In situ measurement
- 8 μm pyrometer on the surface and backside
- High power CO₂ laser high-heat-flux system
  - Capable up to 315 W/cm²
- Sample approximately 1” in diameter

$$k_{\text{ceramic}}(t) = \frac{q_{\text{thru}} \cdot l_{\text{ceramic}}}{\Delta T_{\text{ceramic}}(t)}$$

$$q_{\text{thru}} = q_{\text{delivered}} - q_{\text{reflected}} - q_{\text{radiated}}$$

$$\Delta T_{\text{ceramic}}(t) = T_{\text{ceramic-surface}} - T_{\text{metal-back}} - \int_{0}^{l_{\text{bond}}} \frac{q_{\text{thru}} \cdot dl}{k_{\text{bond}}(T)} - \int_{0}^{l_{\text{substrate}}} \frac{q_{\text{thru}} \cdot dl}{k_{\text{substrate}}(T)}$$

![Diagram of thermal conductivity testing setup](image)

Optional steam at 10-12 psi
3-Layer T/EBC

- Sample surface heated with high heat flux laser
  - Provides thermal gradient

- Tested for 10 heating cycles (1 hour each)
  - 1470°C surface temperature
  - 1350°C interface temperature
  - 1150°C backside temperature

- Microstructure showed some changes due to the gradient testing
  - Doped ZrO₂ topcoat sintered
  - Yb₂Si₂O₇ EBC layer did not change
  - Silicon bond coat showed signs of melting in various locations

- Sintering also observed in thermal conductivity measurement
  - k₀: 1.75 W/mK
  - k₁₀: 2.15 W/mK
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  - \( k_{10} \): 2.15 W/mK
Silicon Infiltration

- Microstructure indicated melting of Si bond coat
  - Silicon infiltration of Yb-silicate layer
  - Rapid sintering and delamination

- 1370°C maximum calculated interface temperature
  - Impurities would suppress the melting temperature from 1410°C

- Delamination isolates the top layer oxide and increases sintering
Conclusions and Future Work

• PS-PVD processing is a promising technique for depositing next-generation thermal and environmental barrier coatings on advanced engine components.

• The addition of a more thermally capable oxide topcoat on RE-silicate materials could improve performance as a T/EBC.

• The low melting silicon bond coat is the limiting factor for these coatings with surface temperatures approaching 1500°C.

• Future T/EBCs will use a more thermally capable bond coat, which should allow for thinner coatings and better performance, and will be tested under steam conditions and under mechanical loading with thermal gradient.