Thermal barrier coatings will be more aggressively designed to protect gas turbine engine hot-section components in order to meet future engine higher fuel efficiency and lower emission goals. In this presentation, thermal barrier coating development considerations and performance will be emphasized. Advanced thermal barrier coatings have been developed using a multi-component defect clustering approach, and shown to have improved thermal stability and lower conductivity. The coating systems have been demonstrated for high temperature combustor applications. For thermal barrier coatings designed for turbine airfoil applications, further improved erosion and impact resistance are crucial for engine performance and durability. Erosion resistant thermal barrier coatings are being developed, with a current emphasis on the toughness improvements using a combined rare earth- and transition metal-oxide doping approach. The performance of the toughened thermal barrier coatings has been evaluated in burner rig and laser heat-flux rig simulated engine erosion and thermal gradient environments. The results have shown that the coating composition optimizations can effectively improve the erosion and impact resistance of the coating systems, while maintaining low thermal conductivity and cyclic durability. The erosion, impact and high heat-flux damage mechanisms of the thermal barrier coatings will also be described.
Advanced Low Conductivity Thermal Barrier Coatings: Performance and Future Directions

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Collaborators

<table>
<thead>
<tr>
<th>GE Aviation</th>
<th>Howmet Coatings</th>
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<tbody>
<tr>
<td>Pratt and Whitney</td>
<td>Honeywell Engines</td>
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<tr>
<td>Rolls Royce-Liberty Works</td>
<td>UCSB</td>
</tr>
<tr>
<td>SUNY/Mesoscibe Tech.</td>
<td>Direct Vapor Technol.</td>
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Motivation

— Thermal barrier coatings (TBCs) can significantly increase gas temperatures, reduce cooling requirements, and improve engine fuel efficiency and reliability.
NASA Ceramic Coating Development Goals

— Meet engine temperature and performance requirements
  - improved engine efficiency
  - reduced emission
  - increase long-term durability
— Improve technology readiness
— The programs require a step-increase in coating capability
— Reliability critical

Step increase in temperature capability

<table>
<thead>
<tr>
<th>Temperature Capability</th>
<th>Year</th>
<th>Increase in $\Delta T$ across T/EBC</th>
</tr>
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<tbody>
<tr>
<td>2500°F Turbine TBCs</td>
<td>Gen I</td>
<td></td>
</tr>
<tr>
<td>2800°F Combustor TBCs</td>
<td>Gen II</td>
<td></td>
</tr>
<tr>
<td>3000°F+ (1650°C+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2700°F (1482°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400°F (1316°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000°F (1093°C)</td>
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</table>

3000°F SiC/SiC CMC coatings
2700°F SiC/SiC CMC and Si₃N₄ coatings
Outline

— Simulated high-heat-flux testing approaches
  • Laser high heat flux
  • Burner and laser high temperature erosion
  • High pressure burner and high heat-flux capability

— Low conductivity thermal barrier coating developments
  • Low conductivity TBC design requirements
  • Performance of low k four-component TBC systems
    Conductivity, and cyclic durability
  • High toughness Low k four- and six-component turbine airfoil
    TBC development – erosion resistance
  • CMAS interaction testing

— Future directions

— Summary
High Heat-Flux Test Approaches

- High-heat-flux tests crucial for turbine TBC developments
  - CO$_2$ laser simulated turbine engine high-heat-flux rig
  - Atmospheric burner rig simulated heat flux testing
  - High pressure burner rig simulated engine heat flux and pressure environments

Turbine blade TBC testing requirements
- $\Delta T \sim 450^\circ$F ($250^\circ$C) across 5mil coating
- Heat flux up to 400 W/cm$^2$

$T_{\text{surface}}$ 2400-2500°F (1316-1371°C)
$T_{\text{interface}}$ 1950°F (1066°C)

Distance from surface

$h_c=0.4 \text{ W/cm}^2\text{-K max}$
High Velocity Burner Erosion Rig and Laser high Heat Flux Erosion Test Rig for Turbine TBC Testing

- High precision particle feeder system
- Specimens under testing
- Mach 0.3-1.0 burner erosion rig
- Laser heat flux erosion rig
ZrO$_2$-(7-8) wt%Y$_2$O$_3$
Thermal Barrier Coating Systems

- Relatively low intrinsic thermal conductivity ~2.5 W/m-K
- High thermal expansion to better match superalloy substrates
- Good high temperature stability and mechanical properties
- Additional conductivity reduction by micro-porosity

(a) Plasma-sprayed coating

(b) EB-PVD coating
Sintering and Conductivity Increase of ZrO$_2$-(7-8) wt%Y$_2$O$_3$

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Significant conductivity increase at high temperature due to sintering

Accelerated failure due to phase stability and reduced strain tolerance

---

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Conductivity reduction by microcracks and microporosity</th>
<th>Intrinsic ZrO$_2$-Y$_2$O$_3$ conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma-sprayed TBC</td>
<td>20-hr rise at 1361°C</td>
<td>As received conductivity (Plasma Coating)</td>
</tr>
<tr>
<td>EB-PVD TBC</td>
<td>20-hr rise at 1316°C</td>
<td>As received conductivity (EB-PVD)</td>
</tr>
</tbody>
</table>
Sintering Kinetics of Plasma-Sprayed ZrO$_2$-8wt%Y$_2$O$_3$ Coatings

\[
\frac{k_c - k_c^0}{k_c^{\text{inf}} - k_c^0} = 102.2 \cdot \exp\left(-\frac{68228}{RT}\right) \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)
\]

\[
\tau = 572.5 \cdot \exp\left(\frac{41710}{RT}\right)
\]

Sintering Cracks and Delaminations

High heat flux surface sintering cracking and resulting coating delaminations

Ts\text{urface}=1280^\circ C
T_{\text{interface}}=1095^\circ C
\text{Thickness}=130 \, \mu m

Sintering Cracks and Delaminations - continued

Sintering strain corresponding to the thermal gradient across the coating ($T_{\text{surface}} = 1280^\circ\text{C}$, $T_{\text{interface}} = 1095^\circ\text{F}$)

\[
\text{strain (in\%) = } 0.40757 + 0.41 \cdot t \text{ (in hr)}^{0.2}
\]

Surface opening strain, %

Time, hours

100 µm
Low Conductivity and Sintering Resistant Thermal Barrier Coating Design Requirements

— Low conductivity ("1/2" of the baseline) retained at 2400°F
— Improved sintering resistance and phase stability (up to 3000°F)
— Excellent durability and mechanical properties
  • Cyclic life
  • Toughness
  • Erosion/impact resistance
  • CMAS and corrosion resistance
  • Compatibility with the substrate/TGO
— Processing capability using existing infrastructure and alternative coating systems
— Other design considerations
  • Favorable optical properties
  • Potentially suitable for various metal and ceramic components
  • Affordable and safe
Low Conductivity Thermal Barrier Coating Design Approaches

- Efforts on modifying coating microstructures and porosity, composite TBCs, or alternative oxide compounds

- Emphasize ZrO$_2$- or HfO$_2$-based alloy systems – defect cluster approach for toughness consideration

- Advantages of defect cluster approach
  
  • **Advanced design approach:** design of the clustering
  
  • **Better thermal stability:** point defects are thermodynamically stable
  
  • **Improved sintering resistance:** effective defect concentration reduced and activation energies increased by clustering
  
  • **Easy to fabricate:** plasma-sprayed or EB-PVD processes
Development of Advanced Defect Cluster Low Conductivity Thermal Barrier Coatings

— Multi-component oxide defect clustering approach (Zhu and Miller, US Patents No. 6,812,176, No.7,001,859, and No. 7,186,466)
  e.g.: $\text{ZrO}_2-\text{Y}_2\text{O}_3-\text{Nd}_2\text{O}_3(\text{Gd}_2\text{O}_3,\text{Sm}_2\text{O}_3)-\text{Yb}_2\text{O}_3(\text{Sc}_2\text{O}_3)$ systems

— Defect clusters associated with dopant segregation
— The nanometer sized clusters for reduced thermal conductivity, improved stability, and mechanical properties


Plasma-sprayed $\text{ZrO}_2-(\text{Y, Nd,Yb})_2\text{O}_3$
EB-PVD $\text{ZrO}_2-(\text{Y, Nd,Yb})_2\text{O}_3$
EELS elemental maps of EB-PVD $\text{ZrO}_2-(\text{Y, Gd,Yb})_2\text{O}_3$
Defect Clusters in a Plasma-Sprayed Y₂O₃, Nd₂O₃ and Yb₂O₃ Co-Doped ZrO₂-Thermal Barrier Coating

— Yb, Nd rich regions consisting of small clusters with size of 5 to 20 nm

Yb, Nd rich region clusters

Yb rich region EDS

Overall EDS
Low Conductivity Defect Cluster Coatings
Demonstrated Improved Thermal Stability

— Thermal conductivity significantly reduced at high temperatures for the low conductivity TBCs

(a) Plasma-sprayed coatings
(b) EB-PVD coatings
Thermal Conductivity of Defect Cluster Thermal Barrier Coatings

EB-PVD coatings (k₀, k₅ and k₂₀ are the initial thermal conductivity, and the conductivity at 5 and 20 hours, respectively)
Thermal Conductivity of Defect Cluster Thermal Barrier Coatings

— Thermal conductivity benefit of oxide defect cluster thermal barrier coatings demonstrated

(k₀, and k₂₀ are the initial thermal conductivity, and the conductivity at 5 and 20 hours, respectively)
Furnace Cyclic Behavior of $\text{ZrO}_2-(\text{Y, Gd, Yb})_2\text{O}_3$
Thermal Barrier Coatings

- $t'$ low $k$ TBCs had good cyclic durability
- The cubic-phase low conductivity TBC durability needed improvements

Furnace Cyclic Behavior of $\text{ZrO}_2-(\text{Y,Gd,Yb})_2\text{O}_3$
Thermal Barrier Coatings - Continued

- $t'$ low $k$ TBCs had good cyclic durability
- The cubic-phase low conductivity TBC durability initially improved by an 7YSZ or low $k$ $t'$-phase interlayer

![Graph showing cycles to failure vs. total dopant concentration](image-url)
**Advanced Low Conductivity TBC Showed Excellent Cyclic Durability**

Coating validated for down-selected low conductivity coating systems

- **Low conductivity EB-PVD turbine airfoil coating**
  - Tsurface=2480°F (1360°C)
  - Tinterface=2020°F(1104°C)
  - 6 min heating, 2 min cooling cycles

- **Low conductivity plasma-sprayed combustor coating**
  - Tsurface=3000°F(1650°C)
  - Tinterface=1670°F(910°C)
  - 3030, 3min heating & 1.5min cooling cycles completed

**Laser heat flux tests**

**Burner rig tests**
Advanced Low Conductivity Combustor Thermal Barrier Coating Developments

— Low k TBC coated components demonstrated in simulated engine environments
— Low k TBC being incorporated in advanced engine development programs

Low conductivity TBC flame tube and combustor deflector demos in Advanced Subsonic Combustion Rig (ASCR)

Low conductivity TBC combustor liner demonstration in Combustor rig
Low conductivity TBC: combustor liner demonstration
Low conductivity TBC Propulsion 21 flame tube and deflector demonstrations
Erosion and Impact Resistant Turbine TBC Development

— Multi-component ZrO₂ low k coatings showed promise in improving erosion and impact resistance

Erosion and impact resistance, measured as the erodent Al₂O₃ weight required to penetrate unit thickness coating

Zhu & Miller, NASA R&T, 2004

2200°F burner rig erosion
Advanced Multi-Component Erosion Resistant Turbine Blade Thermal Barrier Coating Development

- Rare earth (RE) and transition metal oxide defect clustering approach (US Patents No. 6,812,176, No.7,001,859, and 7,186,466; US patent application 11/510,574) specifically by additions of RE$_2$O$_3$, TiO$_2$ and Ta$_2$O$_5$
- Significantly improved toughness, cyclic durability and erosion resistance while maintaining low thermal conductivity
- Improved thermal stability due to reduced diffusion at high temperature

ZrO$_2$-Y$_2$O$_3$- RE$_1$ {e.g.,Gd$_2$O$_3$,Sm$_2$O$_3$}-RE$_2$ {e.g.,Yb$_2$O$_3$,Sc$_2$O$_3$} – TT{TiO$_2$+Ta$_2$O$_5$} systems

Primary stabilizer  Toughening dopants
Oxide cluster dopants with distinctive ionic sizes
Furnace Cyclic Test Lifetime and Thermal Conductivity of TiO₂ Doped Thermal Barrier Coatings

Unpublished work 2003
Furnace Cyclic Lifetime of Advanced Turbine Thermal Barrier Coatings

- Furnace cyclic life can be optimized with RE$_2$O$_3$ and TT additions
- Stability and volatility with too high TT concentrations

![Graph showing the relationship between cycles to failure and total RE$_2$O$_3$ dopant concentration with TT concentration.](image-url)
Cyclic Life of Four-Component Thermal Barrier Coatings

— Furnace and high heat flux cyclic life being optimized for long-term durability

Temperature, K

ln (Cycle time to failure), hours

1/T, 1/K
Thermal Conductivity of Selected Low k Thermal Barrier Coatings

![Graph showing thermal conductivity of various materials as a function of temperature.](#)
Impact Resistance of Advanced Multi-component Low Conductivity Thermal Barrier Coatings

- Improved impact/erosion resistance observed for advanced low conductivity six-component coatings

![Graph showing erosion resistance comparison between advanced coatings and baseline.](chart.png)
Erosion Resistance of Advanced Multi-component Low Conductivity Thermal Barrier Coatings

- The original cubic low k coating showed significant increase in erosion resistance due to the incorporation of TiO₂ and Ta₂O₅
Tetragonality of Multi-Component ZrO₂ being Evaluated and Correlated to Coating Performance

- Multi-component TiO₂/Ta₂O₅ and rare earth dopants increase the tetragonality (c/a ratio)
- Current efforts in optimizing the dopant composition ranges

Area detector x-ray diffractometer used for EB-PVD coatings

<table>
<thead>
<tr>
<th>RE dopant concentration</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>1.010</td>
</tr>
<tr>
<td>6</td>
<td>1.020</td>
</tr>
<tr>
<td>8</td>
<td>1.030</td>
</tr>
<tr>
<td>10</td>
<td>1.040</td>
</tr>
<tr>
<td>12</td>
<td>1.050</td>
</tr>
</tbody>
</table>

Higher TT dopant conc.: 7YSZ, ZrO₂-MultiRE doped
Lower TT dopant conc.: ZrO₂-RETiTa doped
Impact Failure of Advanced Multi-Component Low Conductivity Thermal Barrier Coatings

- Surface sintering and impact densification zones observed, with subsequent spallation under the erodent further impacts
- Toughened structures observed

SEM micrographs of advanced thermal barrier coating after impact/erosion damage

Secondary electron image

Backscattered electron image
Impact Failure of Advanced Multi-Component Low Conductivity Thermal Barrier Coatings

Effect of erosion parameters will be modeled and validated
High Heat Flux Testing of Turbine EB-PVD Thermal Barrier Coatings to Study CMAS Effect

- Specimens typically tested at \( T_{\text{surface}} \sim 2400^\circ\text{F}, T_{\text{interface}} 2000^\circ\text{F} \)
- Heat flux up to 250-300 W/cm\(^2\), cooling heat transfer coefficient up to \( h_c 0.32 \text{ W/cm}^2\text{K} \)
- Accelerated failure observed with CMAS interactions
- Advanced multi-component coatings completed 50 hr testing
Future Directions for Low Conductivity TBC Development

— Emphasize high heat flux durability and erosion resistance

- Optimize high toughness erosion resistant turbine coatings
- Improve turbine airfoil TBCs with up to 3x erosion resistance
- Emphasize creep, fatigue, erosion, and CMAS interactions
- Develop multilayered damping and erosion coatings
- Develop turbine blade TBC life prediction model
Future Directions for Low Conductivity TBC Development

- Emphasize thin ceramic matrix composite turbine coating processing
  - Advanced processing for integrated TEBCs
  - Ceramic nanocomposite and nanotube-based TEBCs for improved durability and optical properties
  - Embedded sensors
  - Life prediction methodology and design tool development

**CMC Turbine Blade coatings**

- $T_{\text{surface}} > 1482^\circ\text{C} (2700^\circ\text{F})$
- $T_{\text{coating/CMC interface}} < 1316^\circ\text{C} (2400^\circ\text{F})$
- High temperature capability thermal and radiation barrier
- Energy dissipation and chemical barrier interlayer
- Environmental barrier
- Advanced bond coat
- Ceramic matrix composite (CMC)

CMC combustor liner and vane
Summary

- Four-component low k TBC systems developed for low k combustor applications

- Advanced turbine airfoil TBCs being developed with combined low conductivity and high toughness

- Improved erosion/impact resistance observed for the multi-component coating t’ and t’/cubic nano-composite systems

- Coatings being optimized for cyclic life, thermal conductivity and erosion/impact and CMAS resistance

- High heat flux durability, multifunctional coatings and lifing models being emphasized in the current research programs