Advanced Low Conductivity Thermal Barrier Coatings: Performance and Future Directions (Invited paper)

Dongming Zhu and Robert A. Miller
NASA Glenn Research Center
21000 Brookpark Road, Cleveland, Ohio 44135

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

Dongming Zhu and Robert A. Miller

Durability and Protective Coatings Branch, Structures and Materials Division
NASA John H. Glenn Research Center
Cleveland, Ohio 44135, USA

Contact: Dr. Dongming Zhu
(216) 433-5422
Dongming.Zhu@nasa.gov

35th International Conference On Metallurgical Coatings And Thin Films (ICMCTF 2008)
San Diego, California, April 27-May 2, 2008
Acknowledgments

This work was supported by NASA Fundamental Aeronautics (FA) Program Supersonics and Subsonic Rotary Wing Projects.

Collaborators

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

Thermal barrier coatings (TBCs) can significantly increase gas temperatures, reduce cooling requirements, and improve engine fuel efficiency and reliability.

(a) Current TBCs  (b) Advanced TBCs
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

Temperature Capability

- 2800°F combustor TBCs
- 2500°F Turbine TBCs

Step increase in temperature capability

(T/EBC) surface

Increase in $\Delta T$
across T/EBC

1. 2700ºF combustor TBCs
2. 2500ºF Turbine TBCs
3. 3000°F SiC/SiC CMC coatings
4. 2700°F SiC/SiC CMC and Si$_3$N$_4$ coatings

2800°F (1482°C)
2700°F (1482°C)
2400°F (1316°C)
2000°F (1093°C)
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
  - CO₂ 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

- \( \Delta T \sim 450°F (250°C) \) across 5mil coating
- Heat flux up to 400 W/cm²

\[ T_{\text{surface}} = 2400-2500°F \ (1316-1371°C) \]
\[ T_{\text{interface}} = 1950°F \ (1066°C) \]
\[ h_c = 0.4 \text{ W/cm}^2\cdot\text{K max} \]
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$_3$

— Significant conductivity increase at high temperature due to sintering
— Accelerated failure due to phase stability and reduced strain tolerance

![Graph showing the comparison of thermal conductivity for Plasma-sprayed TBC and EB-PVD TBC coatings. The graph includes arrows indicating conductivity reduction by microcracks and microporosity, as well as the intrinsic ZrO$_2$-Y$_2$O$_3$ conductivity after 20-hour rise at various temperatures.](image-url)
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

$T_{\text{surface}}=1280^\circ\text{C}$
$T_{\text{interface}}=1095^\circ\text{C}$
Thickness=$130 \mu\text{m}$

Sintering Cracks and Delaminations - continued

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

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

Surface opening strain, %

**Time, hours**

0 hr, 46 hr, 200 hr, mean strain

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.: ZrO$_2$-Y$_2$O$_3$-Nd$_2$O$_3$(Gd$_2$O$_3$,Sm$_2$O$_3$)-Yb$_2$O$_3$(Sc$_2$O$_3$) systems

— Defect clusters associated with dopant segregation

— The nanometer sized clusters for reduced thermal conductivity, improved stability, and mechanical properties

Defect Clusters in a Plasma-Sprayed Y$_2$O$_3$, Nd$_2$O$_3$ and Yb$_2$O$_3$ Co-Doped ZrO$_2$-Thermal Barrier Coating

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

![Image of TEM analysis showing Yb, Nd rich regions and EDS spectra.](image)

Yb, Nd rich region clusters

Yb rich region EDS

Overall EDS

Energy (keV)

Counts

20
15
10
5
0

1200
1000
800
600
400
200
0

Cu

Mo

Zr

Y

Yb

Nd

O

Overall EDS

Yb rich region EDS

Energy (keV)

Counts

20
15
10
5
0

1200
1000
800
600
400
200
0

Cu

Mo

Zr

Y

Yb

Nd

O
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

\(k_0\), \(k_5\) and \(k_{20}\) 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 ZrO$_2$-(Y,Gd,Yb)$_2$O$_3$
Thermal Barrier Coatings

- low k TBCs had good cyclic durability
- The cubic-phase low conductivity TBC durability needed improvements

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
Advanced Low Conductivity TBC Showed Excellent Cyclic Durability

— Coating validated for down-selected low conductivity coating systems

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
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 RE₂O₃, TiO₂ and Ta₂O₅
- Significantly improved toughness, cyclic durability and erosion resistance while maintaining low thermal conductivity
- Improved thermal stability due to reduced diffusion at high temperature

ZrO₂-Y₂O₃-RE₁ {e.g., Gd₂O₃,Sm₂O₃}-RE₂ {e.g., Yb₂O₃,Sc₂O₃} – TT{TiO₂+Ta₂O₅} systems

Primary stabilizer ──> Oxide cluster dopants with distinctive ionic sizes

Toughening dopants
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 cycles to failure vs. total RE$_2$O$_3$ dopant concentration.](image)
Cyclic Life of Four-Component Thermal Barrier Coatings

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

Temperature, K

In (Cycle time to failure), hours

1/T, 1/K

- Zr2.5Y0.75Gd0.75Yb (ln)
- Zr2.0Y1.5Gd1.5Yb (ln)
- Zr1.6Y1.2Gd1.2Yb (ln)
- Zr2.5Y0.75Gd0.75Yb (Ln)
- Zr2.0Y1.5Gd1.5Yb (Ln)
- Zr1.6Y1.2Gd1.2Yb (Ln)
- Zr2.5Y0.75Gd0.75Yb (2h) (Ln)
- Zr2.0Y1.5Gd1.5Yb (2h) (Ln)
- Zr1.6Y1.2Gd1.2Yb (2h) (Ln)
- 7YSZ (ln)
- 7YSZ (Ln)
- 7YSZ (2h) (Ln)
- 7YSZ
- 7YSZ Laser heat flux
- 7YSZ burner rig
Thermal Conductivity of Selected Low k Thermal Barrier Coatings

![Graph showing thermal conductivity vs temperature for different coatings](image)
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 and baseline coatings at 2200°F with 650 micron Al₂O₃]
The original cubic low k coating showed significant increase in erosion resistance due to the incorporation of TiO$_2$ and Ta$_2$O$_5$. 

![Graph showing erosion resistance comparison]

**Erosion Resistance of Advanced Multi-component Low Conductivity Thermal Barrier Coatings**

- **2175°F 50 µm Al$_2$O$_3$**: 100% increase

**Erosion resistance (Erodant amount required per mil coating removal, g/mil)**

- Advanced coatings
- Baseline
Tetragonality of Multi-Component ZrO$_2$ being Evaluated and Correlated to Coating Performance

- Multi-component TiO$_2$/Ta$_2$O$_5$ 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

![Chart showing tetragonality of multi-component ZrO$_2$](chart.png)
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 Tsurface ~2400°F, Tinterface 2000°F
- Heat flux up to 250-300 W/cm², cooling heat transfer coefficient up to $h_c \approx 0.32$ W/cm²·K
- Accelerated failure observed with CMAS interactions
- Advanced multi-component coatings completed 50 hr testing

Specimen under the rig test

Combustor TBC

Advanced coatings 50 hrs

Baseline coating

(a) Upon initial heating

(b) After 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
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