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

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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

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<th>GE Aviation</th>
<th>Howmet Coatings</th>
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<td>Pratt and Whitney</td>
<td>Honeywell Engines</td>
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<td>Rolls Royce-Liberty Works</td>
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<td>SUNY/Mesoscribe 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

Temperature Capability

2800°F (1532°C) combuster TBCs
2500°F (1371°C) Turbine TBCs

Increase in ∆T across T/EBC

Ceramic Matrix Composite
Single Crystal Superalloy

3000°F (1650°C) SiC/SiC CMC coatings
2700°F (1482°C) SiC/SiC CMC and Si₃N₄ coatings
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
- ΔT ~450°F (250°C) across 5mil coating
- Heat flux up to 400 W/cm²

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

Distance from surface

Heat flux

h_c=0.4 W/cm²-K max
High Velocity Burner Erosion Rig and Laser high Heat Flux Erosion Test Rig for Turbine TBC 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 conductivity and thermal properties of different coating types.]

- Conductivity reduction by microcracks and microporosity
- Intrinsic ZrO$_2$-Y$_2$O$_3$ conductivity
- As received conductivity (EB-PVD)
- As received conductivity (Plasma Coating)
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

Sintering Cracks and Delaminations - continued

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

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

![Graph showing sintering strain over time](image)

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

Yb, Nd rich region clusters

Yb rich region EDS

Overall EDS

Energy (keV)

Counts

~40Å

~11.4Å

9.07Å

(111)

5 nm

Overall EDS

Yb rich region 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

($k_0$, $k_5$ 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

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

Furnace Cyclic Behavior of ZrO$_2$-(Y,Gd,Yb)$_2$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)
Advanced Low Conductivity TBC Showed Excellent Cyclic Durability

Coating validated for down-selected low conductivity coating systems

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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 ZrO$_2$ low k coatings showed promise in improving erosion and impact resistance

Erosion and impact resistance, measured as the erodent Al$_2$O$_3$ weight required to penetrate unit thickness coating

Zhu & Miller, NASA R&T, 2004
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$\{TiO_2+Ta_2O_5\}$ systems

Primary stabilizer — Toughening dopants

Oxide cluster dopants with distinctive ionic sizes
Furnace Cyclic Test Lifetime and Thermal Conductivity of TiO\textsubscript{2} Doped Thermal Barrier Coatings

EB-PVD

YSZ-Nd-Yb
YSZ-Gd-Yb
YSZ-Sm-Yb
YSZ

Cycles to failure

Total dopant concentration, mol\%

FCT cycles to failure, hr

Thermal conductivity, W/m-K

Cubic low k 433 FCT life
Cubic 433+10TiO\textsubscript{2} low k FCT life
Cubic low k 433 low k thermal conductivity
Cubic 433+10TiO\textsubscript{2} low k thermal conductivity

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

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

Temperature, °C

Thermal conductivity, W/m-K

1/T·10^4, K^-1

Advanced Low k TBCs

ZrO_2-8wt%Y_2O_3 k20
ZrO_2-8wt%Y_2O_3 anti-sintering k20
PVD-ZrO_2-7wt%Y_2O_3 k20
PVD t' low k k20
PVD cubic low k k20

Plasma-sprayed and EB-PVD coatings
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.](image-url)
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 TiO$_2$ and Ta$_2$O$_5$. 

- 2175°F
- 50 µm Al$_2$O$_3$

![Graph showing erosion resistance comparison between advanced coatings and baseline coatings.](image)

100% increase

- ZrYGdYb Cubic+TT
- ZrYGdYb Cubic
- ZrYGdYb+TT
- ZYGNb+T
- ZrO$_2$-4Y (baseline)
Tetragonality of Multi-Component ZrO_2 being Evaluated and Correlated to Coating Performance

- Multi-component TiO_2/Ta_2O_5 and rare earth dopants increase the tetragonality (c/a ratio)
- Current efforts in optimizing the dopant composition ranges

![Graph showing tetragonality (c/a ratio) vs. RE dopant concentration with data points for 7YSZ, ZrO_2-MultiRE doped, and ZrO_2-RETiTa doped.]

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

17F1A5 powder - Instrument Comparison
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 $h_c 0.32$ W/cm$^2$·K
- Accelerated failure observed with CMAS interactions
- Advanced multi-component coatings completed 50 hr testing

Specimen under the rig test

(a) Upon initial heating

(b) After testing

Combustor TBC

Baseline coating

Advanced coatings 50 hrs

Turbine TBCs
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
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