Low Conductivity Thermal Barrier Coatings

Dongming Zhu
U.S. Army Research Laboratory, Glenn Research Center, Cleveland, Ohio

September 2005
Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301–621–0134
- Telephone the NASA Access Help Desk at 301–621–0390
- Write to: NASA Access Help Desk NASA Center for AeroSpace Information 7121 Standard Drive Hanover, MD 21076
Low Conductivity Thermal Barrier Coatings

Dongming Zhu
U.S. Army Research Laboratory, Glenn Research Center, Cleveland, Ohio

Prepared for the
School of Materials Engineering Seminar
sponsored by Purdue University
West Lafayette, Indiana, February 28, 2005
Low Conductivity Thermal Barrier Coatings

Dongming Zhu
U.S. Army Research Laboratory
Glenn Research Center
Cleveland, Ohio 44135

Abstract

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. A fundamental understanding of sintering and thermal cycling degradation of thermal barrier coating systems under engine high-heat-flux conditions will provide insights into how to further maximize the coating capabilities. In this presentation, thermal barrier coating development considerations and requirements will be discussed. An experimental approach is established to monitor in real time the thermal conductivity of the coating systems subjected to high-heat-flux, steady-state and cyclic temperature gradients. It is demonstrated that the increasing and decreasing trends in thermal conductivity can be closely related to the coating sintering and subsequent delaminations. Advanced low conductivity thermal barrier coatings have also been developed using a multi-component defect clustering approach, and shown to have significantly improved thermal stability due to nano-sized and low mobility defect clusters associated with the paired rare earth dopant additions. The durability and erosion resistance of low conductivity thermal barrier coatings have been improved utilizing advanced coating architecture design, composition optimization, in conjunction with more sophisticated modeling and design tools.
**Motivation**

- Thermal and environmental barrier coatings (T/EBCs) can significantly increase gas temperatures, reduce cooling requirements, and improve engine fuel efficiency and reliability.

(a) Current TBCs  (b) Advanced TBCs

**Revolutionary Ceramic Coatings Greatly Impact Gas Turbine Engine Technology**

- Ceramic coatings are critical to future engine efficiency, power density, and compactness goals.

NASA UEET Goals
- 70% NOx reduction
- 8-15% increase in efficiency
- 8-15% reduction in CO2
OBJECTIVES

- Thermal barrier coating high-heat-flux testing
  - Conductivity measurements and coating degradation evaluation
  - Sintering and failure mechanisms

- Low conductivity thermal barrier coating development
  - Requirements and design considerations
  - Advanced oxide defect cluster coatings

- The 3000 °F (1650 °C) thermal and environmental barrier coatings for SiC/SiC ceramic matrix composites
  - Coating concept
  - Radiation conductivity evaluation
  - Advanced 3000 °F (1650 °C) coating durability evaluation

- Thermal barrier coating high-heat-flux testing

- Low conductivity thermal barrier coating development

- The 3000 °F (1650 °C) thermal and environmental barrier coatings for SiC/SiC ceramic matrix composites
Conventional 0.3 Mach Burner Rig

- Thermal barrier coating burner testing: relatively low heat flux ~20 W/cm²

Burner rig bar specimen testing  Hex bar specimen testing

High Heat-Flux Test Approaches

- Oxy-fuel torch (GEAE), plasma torch (Westinghouse) and CO₂ laser (NASA, Purdue) high heat flux rigs are being used to assess coating failure mechanisms and durability
NASA CO₂ Laser High-Heat-Flux Test Approach

- A uniform laser (wavelength 10.6 μm) power distribution achieved using an integrating lens
- Real time conductivity measurements by monitoring the ceramic surface and substrate temperatures at given heat flux

**Thermal Conductivity Measurement by a Laser High-Heat-Flux Approach**

\[ k_{\text{ceramic}}(t) = \frac{q_{\text{thru}}}{\Delta T_{\text{ceramic}}(t)} \]

Where

\[ q_{\text{thru}} = q_{\text{delivered}} - q_{\text{reflected}} - q_{\text{radiated}} \]

\[ \Delta T_{\text{ceramic}}(t) = T_{\text{ceramic}} - T_{\text{substrate-back}} \]

\[ q_{\text{delivered}} = \int_{t_0}^{t_f} \frac{dT_{\text{ceramic}}}{k_{\text{substrate}}(T)} \]

Two-color and 8 μm pyrometers for \( T_{\text{substrate-back}} \)

Optional miniature thermocouple for additional heat-flux calibration
Laser Heat Flux Testing in Water Vapor Environments for Si-Based Ceramics/Coatings

- Laser heat flux “steam” rig
  - Precise control of heat fluxes and temperatures
  - High temperature and high heat flux testing capabilities
  - Innovative “micro-steam environment” concept
  - Real-time specimen health monitoring capability

- Steam injected at up to 5m/sec
- Testing temperature >1700 °C

Laser High Heat Flux Combustor and Turbine Airfoil Rigs

- Emphasize realistic temperatures, heat flux and stresses

- Selected test articles

NASA/TM—2005-213857
Baseline 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

Thermal Conductivity Increase Kinetics of Plasma-Sprayed ZrO$_2$-8wt\%Y$_2$O$_3$ Coatings

- The conductivity reduction by microcracks and micro-porosity can not persist under high temperatures due to coating sintering
- The coating durability can be affected by sintering
Elastic Modulus of Free-Standing Plasma-Sprayed ZrO₂-8wt%Y₂O₃

- The coating “elastic modulus” also increases significantly with annealing and sintering.

Constitutive relation

ANNEALING TIME, t [h]  
0 100 200 300 400 500 600

ELASTIC MODULUS, E [GPa]  
0 20 40 60 80 100 120 140

By straingaging  
By impulse excitation

Thermal Conductivity Response of Plasma-Sprayed ZrO₂-8wt%Y₂O₃ Coatings under Thermal Gradients

- Sintered coating delamination under thermal cycling.
ZrO$_2$-8wt%Y$_2$O$_3$/Mullite+BSAS/Si System under Steady-State Heat-Flux Testing

- Plasma-sprayed ZrO$_2$-8wt%Y$_2$O$_3$/mullite+BSAS TEBC system on SiC/SiC tested at 1482 °C (2700 °F)
- Coating delaminates at temperature due to sintering/creep

![Conductivity reduction due to sintering cracking induced delamination cracking](image1)

**Measured thermal conductivity**

**Predicted thermal conductivity**

---

Sintering Cracks and Delaminations

- High heat flux surface sintering cracking and resulting coating delaminations
  

![Surface vertical cracks and Delamination cracks](image2)

Increased Surface Sintering under Pulsed Heat Flux

— More severe surface sintering expected under pulsed heat flux

Surface Sintering Cracks and Delamination Under Pulsed Heat Flux Conditions

— Surface sintering, cracking and delaminations under pulsed heat flux
- Thermal barrier coating high-heat-flux testing

- **Low conductivity thermal barrier coating development**

- The 3000 °F (1650 °C) thermal and environmental barrier coatings for SiC/SiC ceramic matrix composites

<table>
<thead>
<tr>
<th><strong>Low Conductivity Thermal Barrier Coating Design Requirements</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>— Low conductivity (&quot;1/2&quot; of the baseline) retained under thermal gradient</td>
</tr>
<tr>
<td>— Improved sintering resistance and phase stability</td>
</tr>
<tr>
<td>— Better durability and mechanical properties</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>— Preferably use existing infrastructure and easy processing systems</td>
</tr>
<tr>
<td>— Other design considerations</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Low Conductivity Thermal Barrier Coating Design Approaches

- Many efforts on modifying coating microstructures and porosity, composite TBCs, or alternative oxide compounds
- Emphasize ZrO₂ or HfO₂-based alloy systems – defect cluster approach
- Advantages of defect cluster approach
  
  • **Advanced design approach**: design of the defect clustering at the molecular level
  
  • **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

Toughness Consideration

- The alloy based systems have higher fracture toughness than oxide compounds such as perovskite and pyrochlore oxides

![Normalized Toughness Graph](image)

Development of Advanced Defect Cluster Low Conductivity Thermal Barrier Coatings

- Multi-component oxide defect clustering approach (Zhu and Miller, US Patent No. 6,812,176)
  
  e.g.: \( \text{ZrO}_2\cdot\text{Y}_2\text{O}_3\cdot\text{Nd}_2\text{O}_3\cdot\text{Gd}_2\text{O}_3\cdot\text{Sm}_2\text{O}_3\cdot\text{Yb}_2\text{O}_3\cdot\text{Sc}_2\text{O}_3 \) systems

- Defect clusters associated with dopant segregation
- The 5 to 100 nm size defect clusters for significantly reduced thermal conductivity and improved stability

---

Defect Clusters in a Plasma-Sprayed \( Y_2\text{O}_3, \text{Nd}_2\text{O}_3 \) and \( \text{Yb}_2\text{O}_3 \) Co-Doped \( \text{ZrO}_2 \)-Thermal Barrier Coating

- \( \text{Yb}, \text{Nd} \) rich regions consisting of small clusters with size of 5 to 20 nm

---

NASA/TM—2005-213857
Low Conductivity Defect Cluster Coatings
Demonstrated Improved Thermal Stability

- Thermal conductivity significantly reduced at high temperatures for the low conductivity thermal barrier coatings
- Phase stability also improved

Thermal Conductivity of Dense Monolithic Specimens

- Lower conductivity observed for the N1 composition that has only slightly higher Gd, Yb concentrations
Advantages of Four-Component Defect Cluster Low Conductivity Coating Approach Demonstrated

- The coatings showed significantly lower thermal conductivity compared to two- or three-component systems under higher temperatures

![Graph showing thermal conductivity comparison between 2 or 3 component and 4 component coatings.](image)

Thermal Conductivity of Oxide Defect Cluster Coatings Tested at Higher Temperatures

- Cubic and $t'$ phase coatings showed lower thermal conductivity than baseline $\text{ZrO}_2-8\text{wt}\%\text{Y}_2\text{O}_3$
- Both composition regions are important for various applications

![Graph showing thermal conductivity comparison between different compositions.](image)
Furnace Cyclic Behavior of ZrO$_2$-(Y,Gd,Yb)$_2$O$_3$ Thermal Barrier Coatings

The cubic-phase ZrO$_2$-based low conductivity TBC durability can be further improved by an 8YSZ or low k t'-phase interlayer.

The t'-phase low conductivity TBCs achieved at least baseline 8YSZ life.

Advanced Low Conductivity Coatings Showed Excellent High Temperature Cyclic Durability

The low conductivity turbine airfoil thermal barrier coatings successfully tested under simulated engine thermal gradient cyclic conditions.

---

NASA/TM—2005-213857
The low conductivity combustor coatings showed better performance than baseline coating at the 2700 to 2800 °F.

The 3000 °F (1650 °C) capable ZrO2 and HfO2 based combustor thermal barrier coatings also successfully developed.

Advanced 2800 to 3000 °F Low Conductivity Coatings
Developed for Metallic Combustor Applications

Development of Advanced Erosion Resistant Turbine Blade Thermal Barrier Coatings

High tougheness, multi-component defect cluster erosion resistant low conductivity thermal barrier coatings also under development.
Advanced Impact/Erosion Resistant Thermal Barrier Coatings

— Improved toughness and strain tolerance

Burner rig erosion and impact test results at 2200 °F

- Thermal barrier coating high-heat-flux testing

- Low conductivity thermal barrier coating development

☐ The 3000 °F (1650 °C) thermal and environmental barrier coatings for SiC/SiC ceramic matrix composites
Advanced 3000 °F (1650 °C) Coatings For
SiC/SiC CMCs

- Low thermal conductivity
- High temperature stability
- Excellent thermal stress resistance
- Enhanced radiative flux resistance and radiation cooling
- Improved environmental protection
- Designed functional capability

High temperature capability
thermal and radiation barrier
Energy dissipation and chemical barrier interlayer
Secondary radiation barrier, thermal control with chemical barrier interlayer
Environmental barrier
Ceramic matrix composite (CMC)

Coating Radiation Performance Evaluation and Radiation Barrier Coatings Development

- Radiation conductivity evaluated using the laser heat flux approach
- Significant conductivity increase due to increased radiation at high temperatures especially under thermal gradients

La₂Zr₂O₇ sol-gel hot-press
La₂Zr₂O₇ sol-gel hot-press
La₂Zr₂O₇ hot-press

ZrO₂-8wt%Y₂O₃ plasma-sprayed porous coating

La₂Zr₂O₇

increasing porosity

k measured
k fit due to lattice conduction-radiation
sintering induced conductivity rise
lattice conduction
Evaluation of Radiation Thermal Conductivity of T/EBC Systems at High Temperatures

- Advanced HfO₂ coatings demonstrated improved radiation resistance compared to the baseline ZrO₂-8wt%Y₂O₃ coating.

```
Coating thickness, microns

Radiation penetration q_rad/q_rad0

Laser heat flux

Radiation emitter

Ceramic coating

q_rad = h(T_back - T_cooling air)
```

Advanced 3000 °F (1649 °C) Coatings Development for SiC/SiC Combustor Liner and Vane Applications

- The hafnia (zirconia) top coating/modified mullite intermediate layer systems demonstrated excellent cyclic durability and radiation resistance at 1650 °C (3000 °F).
- Advanced high temperature ceramic bond coats also developed.

```
Sintering and cyclic durability evaluations

Normalized thermal conductivity k/k₀

Tsurface=1650 °C, Tinterface=1316 °C
```
### Summary and Conclusions

- High-heat-flux testing approaches established for low conductivity thermal barrier coating development
- Real-time monitoring of coating thermal conductivity demonstrated as an effective technique to assess coating performance
- The low conductivity thermal barrier coatings demonstrated improved thermal stability and cyclic durability
- High toughness, erosion resistant turbine airfoil thermal barrier coating development showed significant progress
- Advanced 1650 °C (3000 °F) thermal/environmental systems developed for Si-based ceramics
**Low Conductivity Thermal Barrier Coatings**

Dongming Zhu

**National Aeronautics and Space Administration**
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191


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 requirements will be discussed. An experimental approach is established to monitor in real time the thermal conductivity of the coating systems subjected to high-heat-flux, steady-state and cyclic temperature gradients. Advanced low conductivity thermal barrier coatings have also been developed using a multi-component defect clustering approach, and shown to have improved thermal stability. The durability and erosion resistance of low conductivity thermal barrier coatings have been improved utilizing advanced coating architecture design, composition optimization, in conjunction with more sophisticated modeling and design tools.

Thermal barrier coatings; Environmental barrier coatings; Thermal conductivity; Erosion; Thermal radiation