NASA/TM—2005-213857

Low Conductivity Thermal Barrier Coatings

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

September 2005

The NASA STI Program Office . . . in Profile

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:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***
- 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

NASA/TM—2005-213857

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

National Aeronautics and
Space Administration

Glenn Research Center

September 2005

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov

Low Conductivity Thermal Barrier Coatings

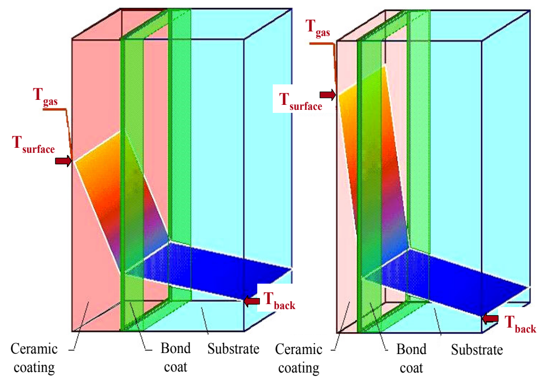
Dongming Zhu
U.S. Army Research Laboratory
Glenn Research Center
Cleveland, Ohio 44135

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

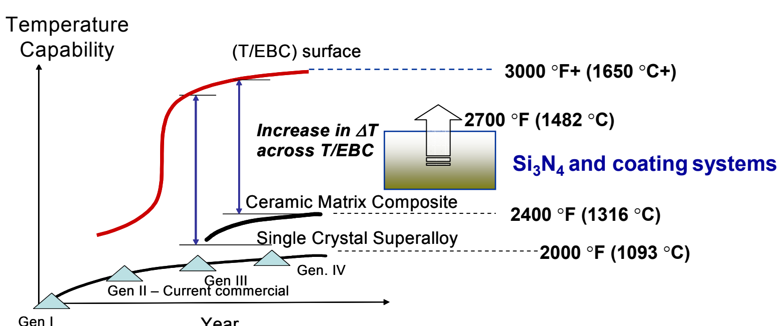
— Thermal and environmental barrier coatings (T/EBCs) can significantly increase gas temperatures, reduce cooling requirements, and improve engine fuel efficiency and reliability



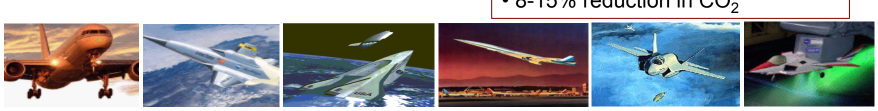
(a) Current TBCs (b) Advanced TBCs

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% NO_x reduction
- 8-15% increase in efficiency
- 8-15% reduction in CO_2



OBJECTIVES

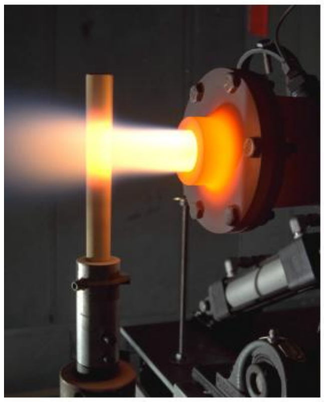
- Thermal barrier coating high-heat-flux testing
  - Conductivity measurements and coating degradation evaluation
  - Sintering and failure mechanisms
- Low conductivity thermal barrier coating development
  - Requirements and design considerations
  - Advanced oxide defect cluster coatings
- The 3000 °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**

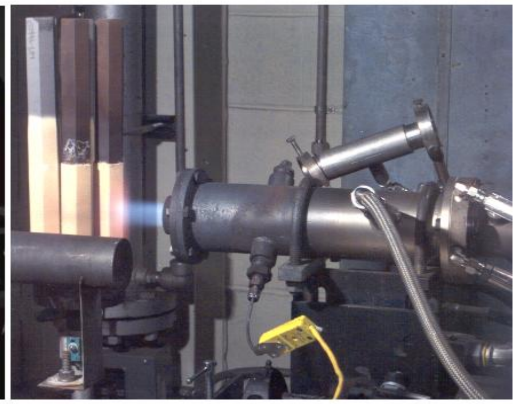
- Low conductivity thermal barrier coating development
- The 3000 °F (1650 °C) thermal and environmental barrier coatings for SiC/SiC ceramic matrix composites

Conventional 0.3 Mach Burner Rig

– Thermal barrier coating burner testing: relatively low heat flux ~20 W/cm^2



Burner rig bar specimen testing

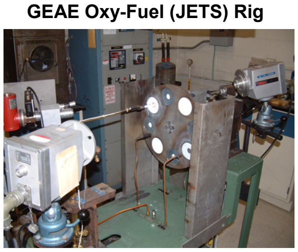


Hex bar specimen testing

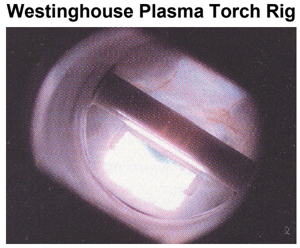
High Heat-Flux Test Approaches

– Oxy-fuel torch (GEAE), plasma torch (Westinghouse) and CO_2 laser (NASA, Purdue) high heat flux rigs are being used to assess coating failure mechanisms and durability

GEAE Oxy-Fuel (JETS) Rig



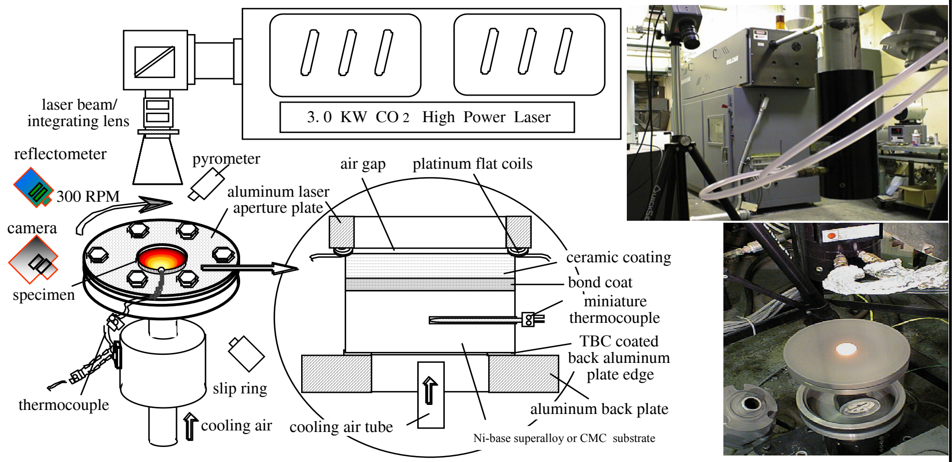
Westinghouse Plasma Torch Rig



NASA-GRC CO_2 Laser Rig

NASA CO_2 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

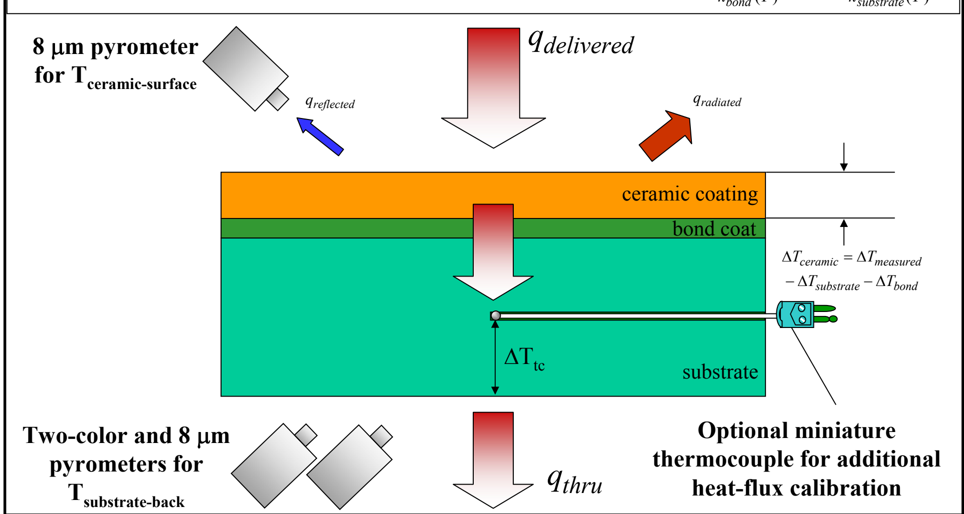


Thermal Conductivity Measurement by a Laser High-Heat-Flux Approach

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

Where

$$q_{thru} = q_{delivered} - q_{reflected} - q_{radiated} \quad \text{and} \quad \Delta T_{ceramic}(t) = T_{ceramic-surafce} - T_{metal-back} - \int_0^{l_{bond}} \frac{q_{thru}\cdot dl}{k_{bond}(T)} - \int_0^{l_{substrate}} \frac{q_{thru}\cdot dl}{k_{substrate}(T)}$$



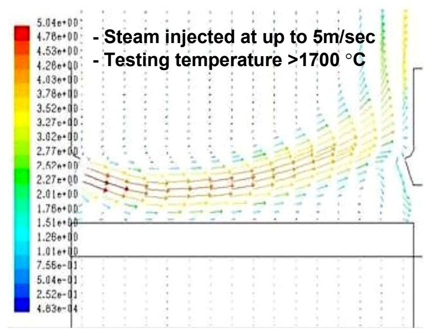
Laser Heat Flux Testing in Water Vapor Environments for Si-Based Ceramics/Coatings

- **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

Laser heat flux water vapor test rig

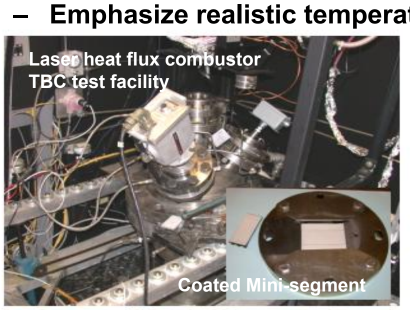
Specimen holder and water vapor jets

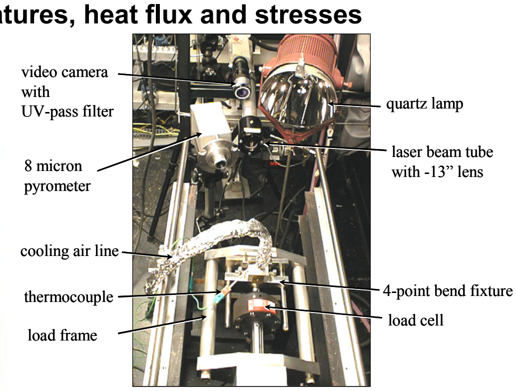

Specimen under testing

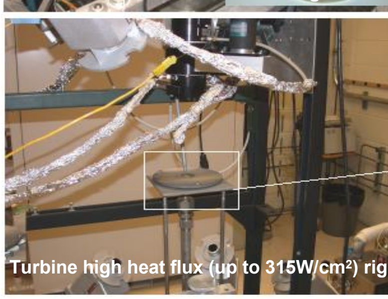


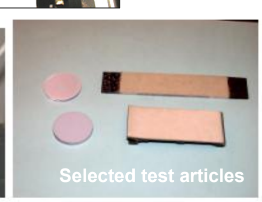
Laser High Heat Flux Combustor and Turbine Airfoil Rigs

- **Emphasize realistic temperatures, heat flux and stresses**



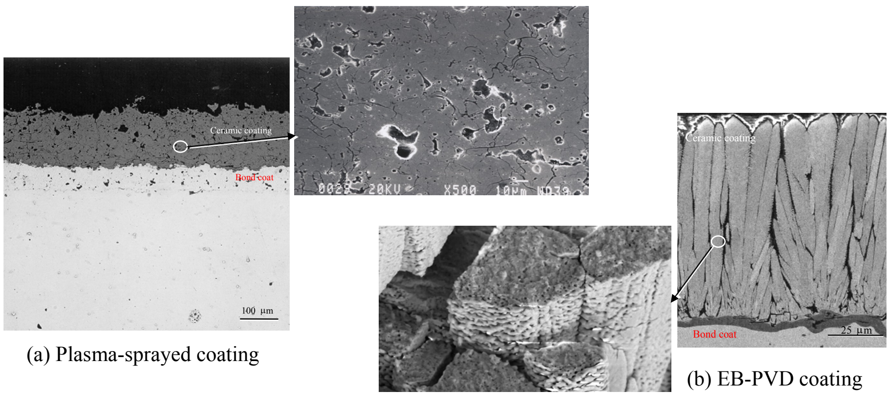






Baseline ZrO_2-(7-8) wt% Y_2O_3 Thermal Barrier Coating Systems

- 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

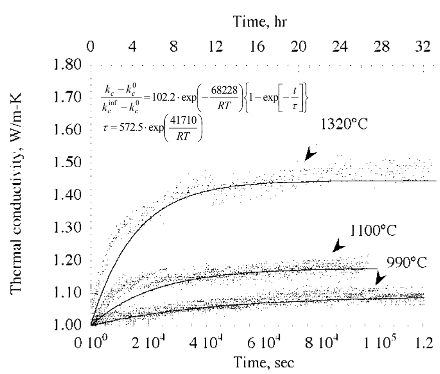


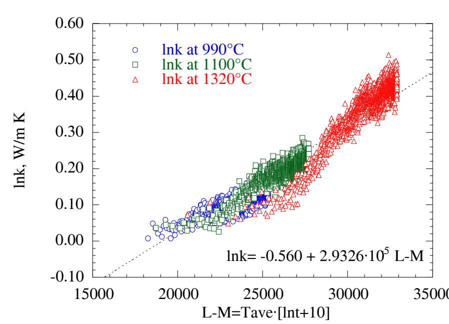
(a) Plasma-sprayed coating

(b) EB-PVD coating

Thermal Conductivity Increase Kinetics of Plasma-Sprayed ZrO_2-8wt% Y_2O_3 Coatings

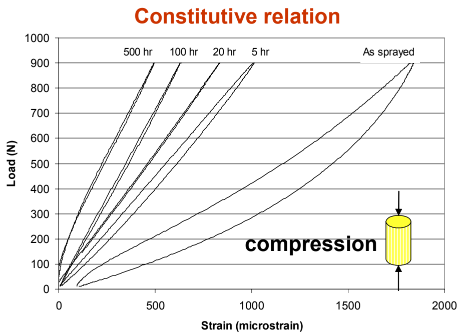
- The conductivity reduction by microcracks and micro-porosity can not persist under high temperatures due to coating sintering
- The coating durability can be affected by sintering

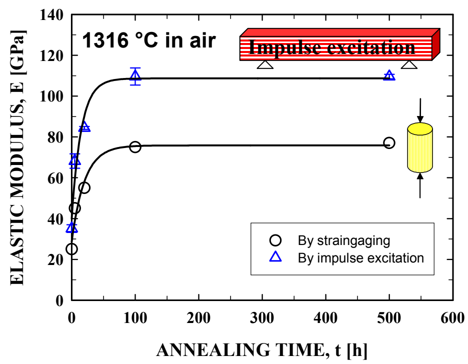




Elastic Modulus of Free-Standing Plasma-Sprayed ZrO_2-8wt%Y_2O_3

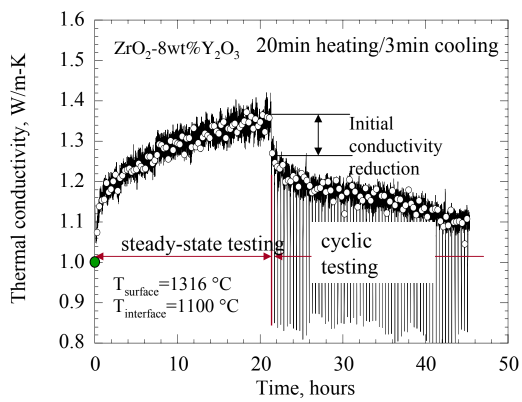
— The coating "elastic modulus" also increases significantly with annealing and sintering





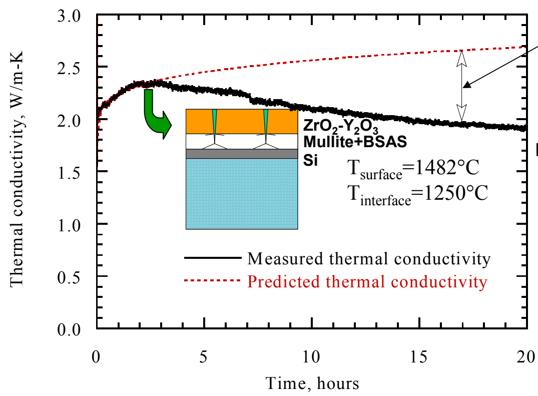
Thermal Conductivity Response of Plasma-Sprayed ZrO_2-8wt%Y_2O_3 Coatings under Thermal Gradients

— Sintered coating delamination under thermal cycling



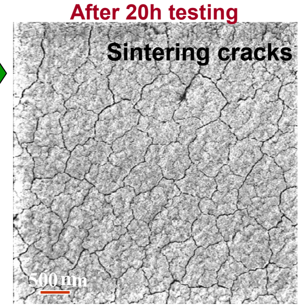
ZrO_2-8wt%Y_2O_3/Mullite+BSAS/Si System under Steady-State Heat-Flux Testing

- Plasma-sprayed ZrO_2-8wt%Y_2O_3/mullite+BSAS TEBC system on SiC/SiC tested at 1482 °C (2700 °F)
- Coating delaminates at temperature due to sintering/creep



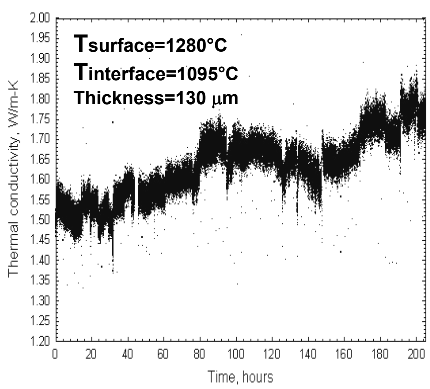
Conductivity reduction due to sintering cracking induced delamination cracking

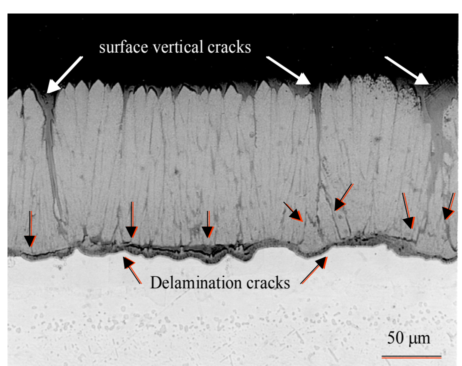
After 20h testing



Sintering Cracks and Delaminations

- High heat flux surface sintering cracking and resulting coating delaminations
  - Kokini and Takeuchi, Mat. Sci. and Eng., 189 (1994), pp. 301-309.
  - Zhu and Miller, J. Mater. Res. 14(1999). Mater. Sci. Eng. A245(1998), 212-223.

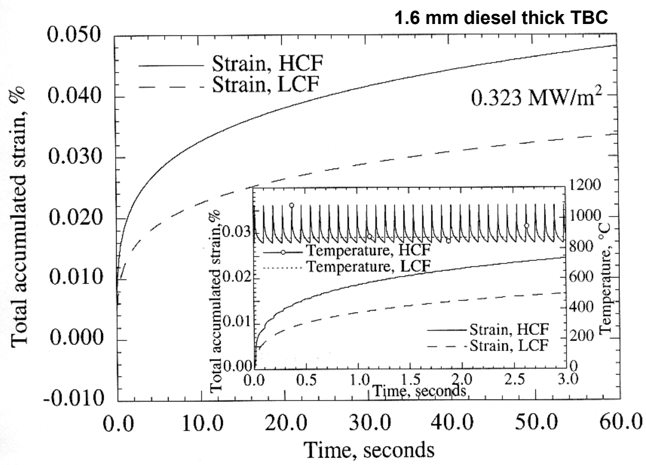




Zhu et al., Surf. Coat. Tech., 138 (2001), 1-8

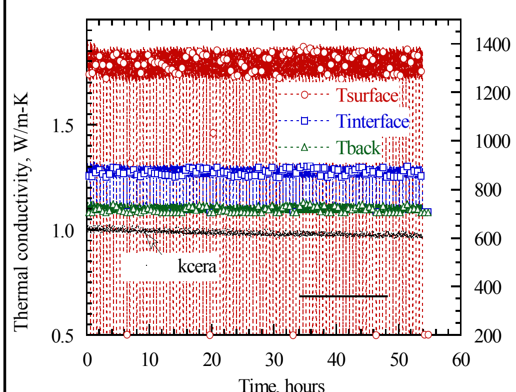
Increased Surface Sintering under Pulsed Heat Flux

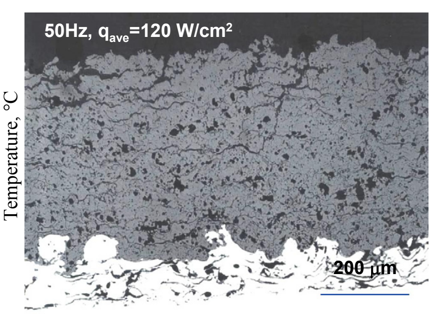
— **More severe surface sintering expected under pulsed heat flux**



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

Low Conductivity Thermal Barrier Coating Design Requirements

— **Low conductivity ("1/2" of the baseline) retained under thermal gradient**

— **Improved sintering resistance and phase stability**

— **Better durability and mechanical properties**
  - Cyclic life
  - Erosion/impact resistance

— **Preferably use existing infrastructure and easy processing systems**

— **Other design considerations**
  - Favorable optical properties
  - Suitable for various metal and ceramic components
  - Affordable and safe

Low Conductivity Thermal Barrier Coating Design Approaches

– Many 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

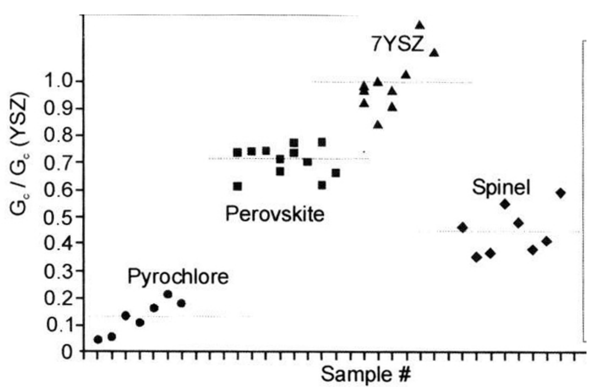
– Advantages of defect cluster approach

- **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



Bast and Schumann, Ceram. Eng. Sci. Proc. 23(2002), 525-532

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*)

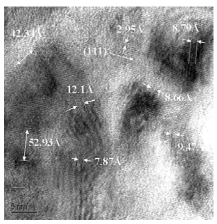
e.g.: ZrO_2-Y_2O_3-Nd_2O_3(Gd_2O_3,Sm_2O_3)-Yb_2O_3(Sc_2O_3) systems

Primary stabilizer

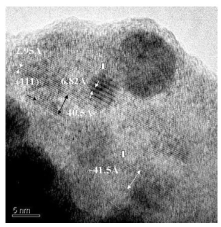
Oxide cluster dopants with distinctive ionic sizes

— **Defect clusters associated with dopant segregation**

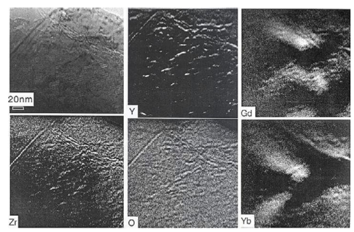
— **The 5 to 100 nm size defect clusters for significantly reduced thermal conductivity and improved stability**



Plasma-sprayed ZrO_2-13.5mol%(Y, Nd,Yb)$_2O_3$



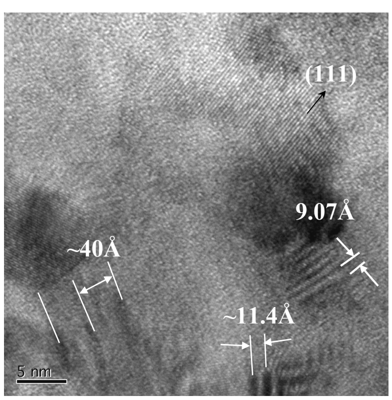
EB-PVD ZrO_2-12mol% (Y, Nd,Yb)$_2O_3$



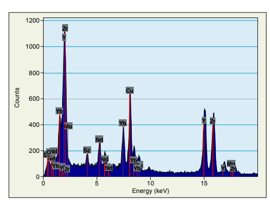
EELS elemental maps of EB-PVD ZrO_2-14mol%(Y, Gd,Yb)$_2O_3$

Defect Clusters in a Plasma-Sprayed Y_2O_3, Nd_2O_3 and Yb_2O_3 Co-Doped ZrO_2-Thermal Barrier Coating

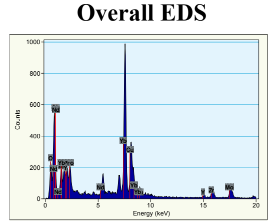
— **Yb, Nd rich regions consisting of small clusters with size of 5 to 20 nm**



Yb rich region clusters



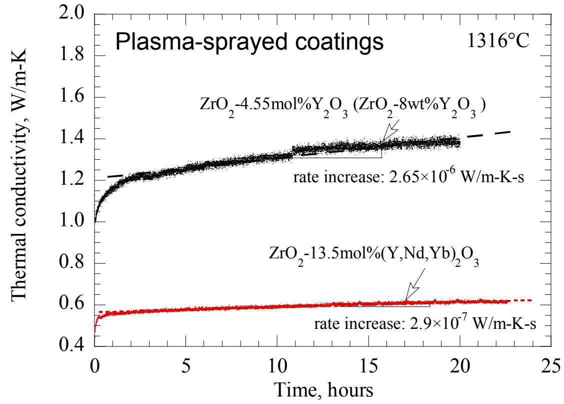
Overall EDS



Yb rich region EDS

Low Conductivity Defect Cluster Coatings Demonstrated Improved Thermal Stability

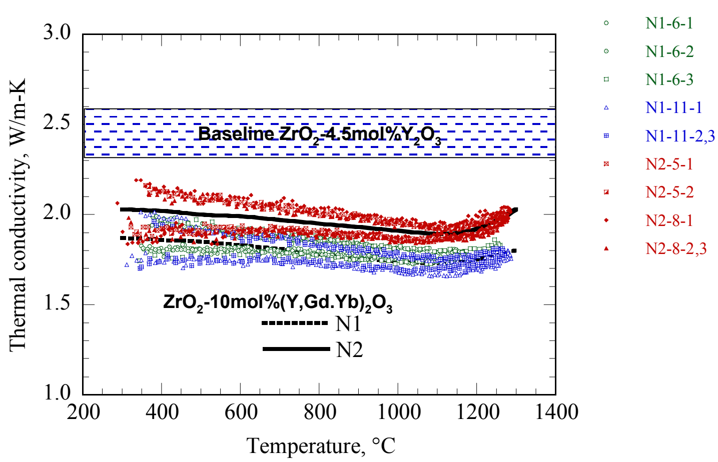
- Thermal conductivity significantly reduced at high temperatures for the low conductivity thermal barrier coatings
- Phase stability also improved



m1

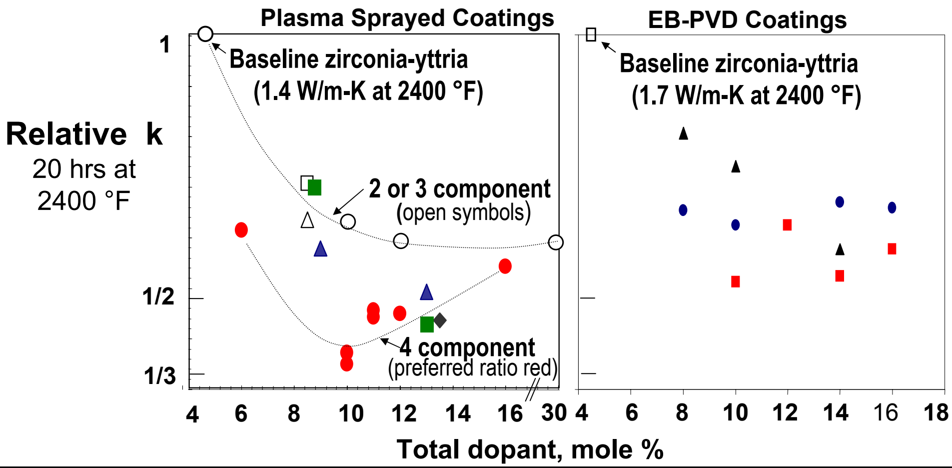
Thermal Conductivity of Dense Monolithic Specimens

- 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

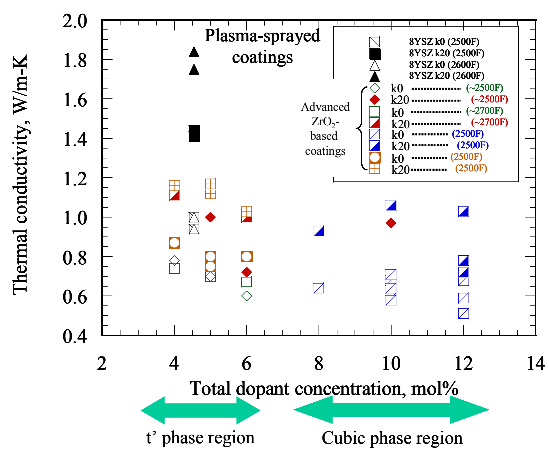
— The coatings showed significantly lower thermal conductivity compared to two- or three-component systems under higher temperatures



Thermal Conductivity of Oxide Defect Cluster Coatings Tested at Higher Temperatures

— Cubic and t' phase coatings showed lower thermal conductivity than baseline ZrO_2-8wt%Y_2O_3

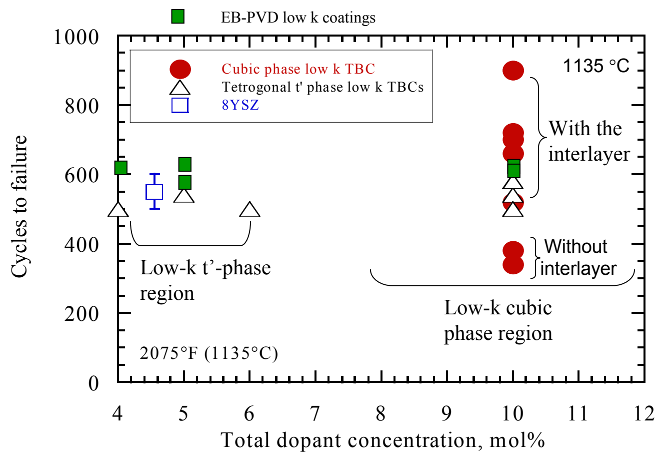
— Both composition regions are important for various applications



Furnace Cyclic Behavior of ZrO_2-$(Y,Gd,Yb)_2O_3$ Thermal Barrier Coatings

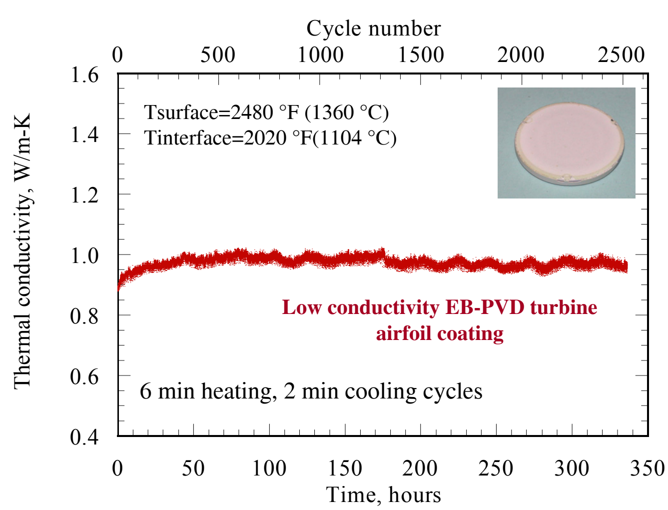
— The cubic-phase ZrO_2-based low conductivity TBC durability can be further improved by an 8YSZ or low k t'-phase interlayer

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



Advanced Low Conductivity Coatings Showed Excellent High Temperature Cyclic Durability

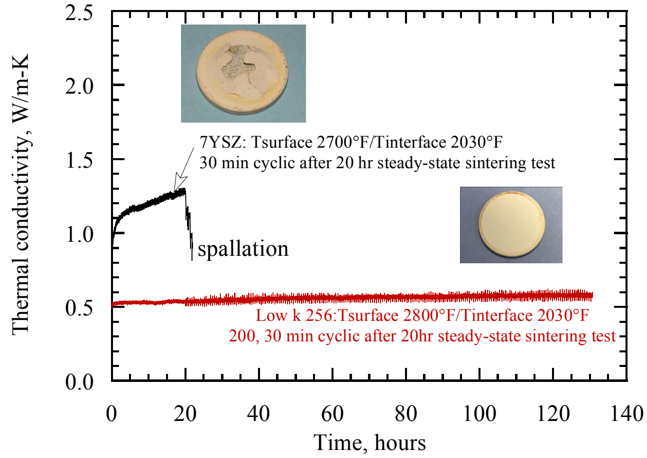
— The low conductivity turbine airfoil thermal barrier coatings successfully tested under simulated engine thermal gradient cyclic conditions



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

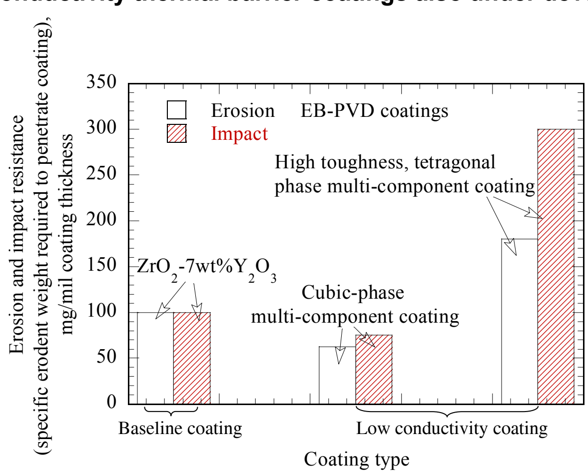
— The low conductivity combustor coatings showed better performance than baseline coating at the 2700 to 2800 °F

— The 3000 °F (1650 °C) capable ZrO_2 and HfO_2 based combustor thermal barrier coatings also successfully developed



Development of Advanced Erosion Resistant Turbine Blade Thermal Barrier Coatings

— High toughness, multi-component defect cluster erosion resistant low conductivity thermal barrier coatings also under development

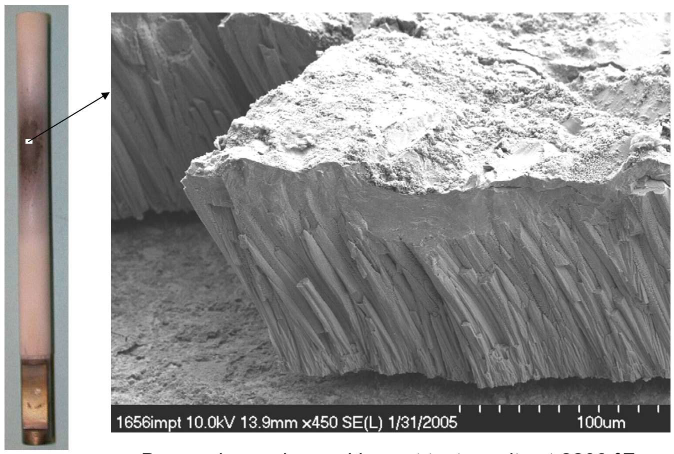


Burner rig erosion and impact test results at 2200 °F

Test specimen

Advanced Impact/Erosion Resistant Thermal Barrier Coatings

— **Improved toughness and strain tolerance**



Burner rig erosion and impact test results at 2200 °F

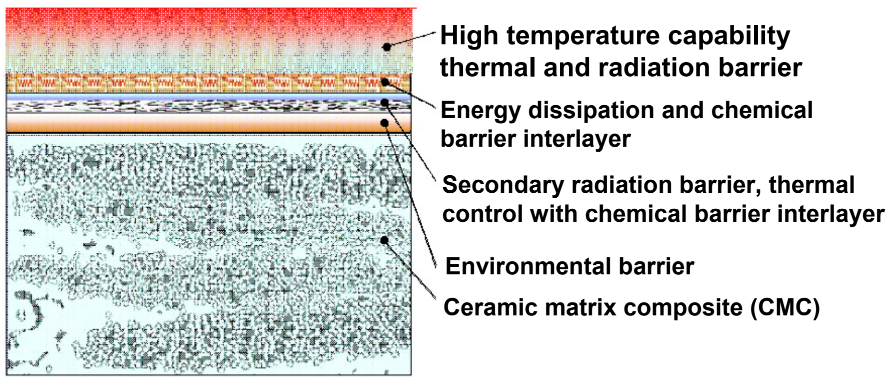
- Thermal barrier coating high-heat-flux testing

- Low conductivity thermal barrier coating development

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

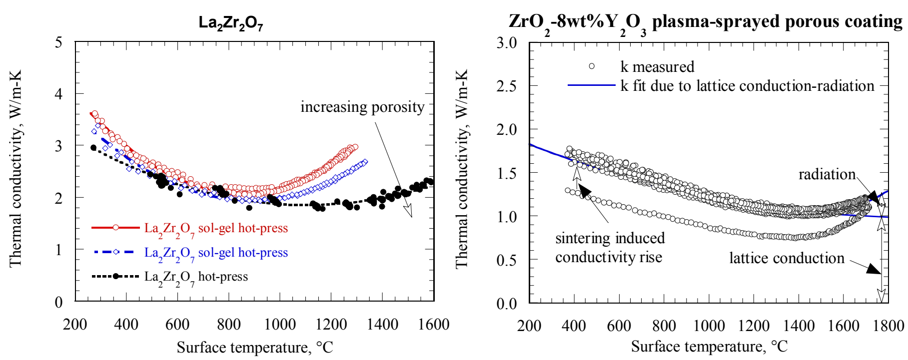
Advanced 3000 °F (1650 °C) Coatings For SiC/SiC CMCs

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



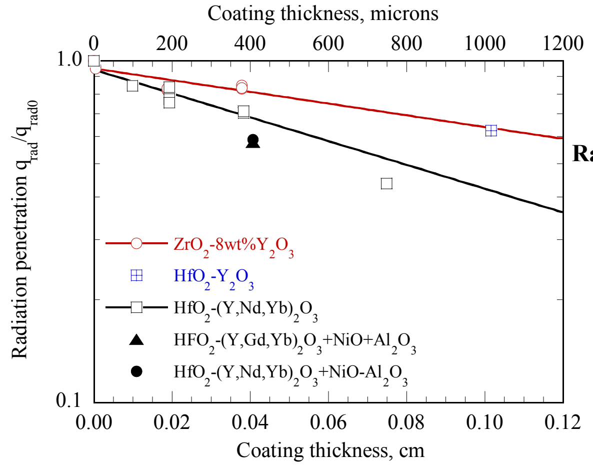
Coating Radiation Performance Evaluation and Radiation Barrier Coatings Development

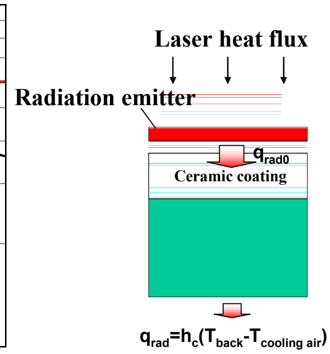
- — Radiation conductivity evaluated using the laser heat flux approach
- — Significant conductivity increase due to increased radiation at high temperatures especially under thermal gradients



Evaluation of Radiation Thermal Conductivity of T/EBC Systems at High Temperatures

— Advanced HfO_2 coatings demonstrated improved radiation resistance compared to the baseline ZrO_2-8wt%Y_2O_3 coating

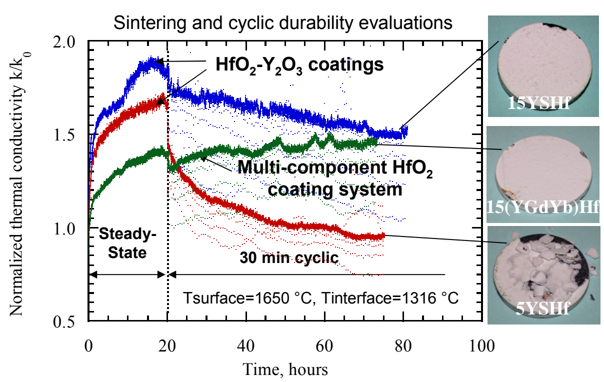


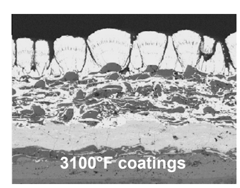


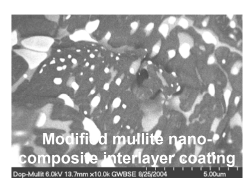
Advanced 3000 °F (1649 °C) Coatings Development for SiC/SiC Combustor Liner and Vane Applications

— 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







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**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
September 2005

3. REPORT TYPE AND DATES COVERED
Technical Memorandum

4. TITLE AND SUBTITLE
Low Conductivity Thermal Barrier Coatings

5. FUNDING NUMBERS
WBS–22–714–20–09

6. AUTHOR(S)
Dongming Zhu

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135 – 3191

8. PERFORMING ORGANIZATION REPORT NUMBER
E – 15227

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NASA TM—2005-213857

11. SUPPLEMENTARY NOTES
Viewgraphs prepared for the School of Materials Engineering Seminar sponsored by Purdue University, West Lafayette, Indiana, February 28, 2005. Responsible person Dongming Zhu, organization code RMD, 216–433–5422.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified - Unlimited
Subject Categories: 23, 24, and 27
Available electronically at http://gltrs.grc.nasa.gov
This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

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.

14. SUBJECT TERMS
Thermal barrier coatings; Environmental barrier coatings; Thermal conductivity; Erosion; Thermal radiation

15. NUMBER OF PAGES
27

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102