James Mueller Lecture:

“Thermal Barrier Coatings for Gas Turbines”

Materials Discovery and Applications Group

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Engineering Ceramics Division, American Ceramic Society, Daytona Beach, January 2015
Gas Turbines

Schematic

INTAKE  COMPRESSION  COMBUSTION  EXHAUST

Air Inlet  Combustion Chambers  Turbine

Cold Section  Hot Section

Siemens Power Generation 340 MWe

D. R. Clarke, Harvard University, Jan 2015
Fuel Efficiency in the Aeroturbine Industry

D. R. Clarke, Harvard University, Jan 2015
Replacing coal with natural gas turbines decreases CO2, Hg, radioactive and dust emissions, and is also more energy efficient.
What 1% Improvement in Gas Turbines Could Buy Us

2009 data

Ashby, Materials and the Environment, Elsevier

NB. 30% of natural gas is used to produce electricity. 1% improvement > all renewables

D. R. Clarke, Harvard University, Jan 2015
Output Power Depends on Turbine Inlet (T4) Temperature

Dimiduk and Perepezko, MRS Bull 639 2003

D. R. Clarke, Harvard University, Jan 2015
Thermal barrier coatings have enabled a jump in turbine temperatures and energy efficiencies.

Yttria-stabilized zirconia coatings
~ 150 – 500 micron thick

Thermal gradient
~ 150-200 K/mm

D. R. Clarke, Harvard University, Jan 2015
Thermal conductivity asymptotes to a minimum value at high temperatures.

Kingery et al, ca 1955

Zirconias -- Levi

D. R. Clarke, Harvard University, Jan 2015
The Minimum Thermal Conductivity

**Approach:**

Adopt Debye equation and express it's high-temperature limit in terms of measurable physical parameters.

\[ \kappa \rightarrow \kappa_{\text{min}} \quad ; \quad \kappa = C_V \frac{v_m \Lambda}{3} \rightarrow k_B v_m \Lambda_{\text{min}} \]

Dulong-Petit equation: \( C_V \rightarrow 3k_B \) as \( T > \Theta_D \)

Mean phonon velocity:

\[ v_m = \left( \frac{1}{v_p^3} + \frac{2}{v_S^3} \right)^{-1/3} \]

Over wide range of Poisson ratio:

\[ v_m = A \left( \frac{E}{\rho} \right)^{1/2} \]

Combining these approximations:

\[ \kappa_{\text{min}} \rightarrow 0.87k_B N_A^{2/3} \frac{m^{2/3} \rho^{1/6} E^{1/2}}{M^{2/3}} \]

\[ \Theta_D = 3.39 \frac{\hbar}{k_B} N_A^{1/3} \frac{m^{1/3} E^{1/2}}{M^{1/3} \rho^{1/6}} \]

In terms of atomic volume

\[ \kappa_{\text{min}} = k_B v_m \Lambda_{\text{min}} \rightarrow 0.87k_B \Omega_a^{-2/3} (E/\rho)^{1/2} \]

D. R. Clarke, Harvard University, Jan 2015
High-Temperature Thermal Conductivity Scaling

\[ \kappa_{\text{min}} = k_B \nu_m \Lambda_{\text{min}} \rightarrow 0.87 k_B \bar{\Omega}_a^{-2/3} (E/\rho)^{1/2} \]

\[ \bar{\Omega}_a = \left[ M / (m \rho N_A) \right] \]

D. R. Clarke, Harvard University, Jan 2015
Grain size effect on thermal conductivity can be significant at low temperatures but decreases with increasing temperatures until at highest temperatures there is little or no effect.

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Y-doped ZrO$_2$

Meta-stable tetragonal ($t'$) 7YSZ
- Low Y: $t'$ -> monoclinic
- High Y: $t'$ -> cubic

Lower thermal conductivity than 7YSZ, but no ferroelastic toughening at high temperature

Y$_2$O$_4$-doped ZrO$_2$

Transformable ($t$ -> $m$)

Non-transformable tetragonal
Fracture toughness increases with increasing Y$_2$O$_4$

ZrO$_2$ solid solution

High temperature M-T in YTaO$_4$

F = fluorite (cubic)
O = orthorhombic
$t$ = tetragonal

Phase diagram: Leckie et al. 2010

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Particular interest in compositions along ZrO$_2$-YTaO$_4$ Binary do not require structural vacancies to be stable. Consequently, no conductivity decrease by oxygen vacancies is possible.

$Y^{3+}_{1-x}Ta^{5+}_{1-x}Zr^{4+}_{2x}O^{2-}_{2}$ compositions do not require structural vacancies to be stable.

Consequently, no conductivity decrease by oxygen vacancies is possible.
Multi-phase Yttria-Tantala-Zirconia with Low Thermal Conductivity

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Variation of Thermal Conductivity with Composition

Obtained by interpolation from conductivity measured at different compositions


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• YTaO$_4$ undergoes *reversible* phase transformation, \( m \rightarrow t \), in which is, evidently, ferroelastic, involving atomic displacement and twinning, and maybe useful as a high temperature toughening mechanism.

• **Effect of ZrO$_2$ solid solution in YTaO$_4$**:
  – Stabilizes the tetragonal phases, decreasing the \( t-m \) transformation temperature and increasing the fraction of non-transformable tetragonal phases retained at room temperature
  – Solid solution creates mass disorder that decreases the phonon mean free path. Evident in:
    • the increase in Raman peaks width
    • the decrease in thermal conductivity
  – Suppresses grain growth
  – Lower thermal conductivity
Zr$^{4+}$ Stabilizes the high-temperature Tetragonal Phase

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The Thermal Management Challenge

D. R. Clarke, Harvard University, Jan 2015
Porosity Reduces Conductivity and Scatters Thermal Radiation

D. R. Clarke, Harvard University, Jan 2015
Temperature Distribution For Different Coating Designs

Liguo Chen, Phd Thesis

D. R. Clarke, Harvard University, Jan 2015
Temperature Distribution For Different Coating Designs

Liguo Chen, Phd Thesis

D. R. Clarke, Harvard University, Jan 2015
Basis of Optical Probing of a TBC

TBCs are optically turbid media – highly scattering but are translucent. Hence some light can penetrate through to the TGO underneath the TBC.

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Luminescent ions can be incorporated into the crystal structure of the coating material to act as sensors.

- Luminescence lifetime is known to be temperature sensitive.

- Because of the translucency of TBC materials, visible lasers and luminescence can be used to measure temperatures of sensors buried in a coating.

- Multiple sensor layers can be applied to measure the temperature at any depth.
Example: Eu Doped TBC Sensor Layer

Superimposition of white light and UV luminescence images

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Temperature Sensing Using Luminescence Lifetimes

10 micron Eu-doped sensor layer in a EB-PVD YSZ coating

Calibration of luminescence lifetime provides basis for temperature measurements on engine components

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TBC Interface Temperature in a Thermal Gradient

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TBC thickness: 146 µm

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Effect of Thermal Cycling on Coating Life

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Life of TBC is often limited by morphological instability (“rumpling”) of the metal bond coat on thermal cycling causing incompatibilities with TBC. More stable alloys needed.

Coating surface on thermal cycling.
0-300 cycles to 1150°C in air. ~ 400 micron field of view

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TBC Interface after 100 One-hour Cycles to 1150°C

Low magnification

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Evolution of Interface Separation Leading to Failure

D. R. Clarke, Harvard University, Jan 2015

Tolpygo, Murphy, Clarke
Key concepts:

- All alumina contains small (ppm) concentrations of Cr$^{3+}$ in solid solution
- Each Cr$^{3+}$ ion emits photons with an energy dependent on its own local strain environment
- Frequency shift proportional to mean stress in a polycrystalline alumina

\[ \Delta v_{R2} = 7.62 \sigma_m \]

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Optical properties of YSZ

TBCs are optically turbid media – highly scattering but translucent
Hence some light can penetrate through to the TGO underneath the TBC
Multi-spectral Luminescence Imaging to Reveal Stress Variations

- Illuminate coating with uniform laser beam, 514.3 nm
- Collect R-line luminescence on a CCD through a tunable Fabry-Perot filter
- Tune filter through the luminescence frequency band recording an image at each frequency step
- Invert spectral images to determine R1 shift and hence stress at each image pixel
- Map stress distribution over coating

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1.15 – 1.20 GPa

WA12

WA15

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1.10 – 1.15 GPa
1.05 – 1.10 GPa
1.00 – 1.05 GPa
0.95 – 1.00 GPa
0.90 – 0.95 GPa
0.85 – 0.90 GPa
0.80 – 0.85 GPa
$0.75 - 0.80 \text{ GPa}$
0.70 – 0.75 GPa
0.65 – 0.70 GPa
0.60 – 0.65 GPa

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0.55 – 0.60 GPa
0.50 – 0.55 GPa
Green areas correspond to areas where the mean stress below 0.7 GPa

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Defect Rearrangement Model (Wachman) predicts that damping peak occurs at:

\[ T_p = \frac{E_i}{k_B \ln \omega \tau} \]

Activation energy for hopping

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The Next Materials Frontier: Ceramic Matrix Composites

- Higher temperature capability
- High corrosion resistance
- Toughening mechanisms:
  - Microcracking
  - Fiber pull out
  - Crack bridging
- 90% cooling air reduction
- Reduced emissions

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Future Limits To Gas Turbines: Unresolved Challenges

- Atmospheric pollution from engine exhausts
  - Chemical reactions produce NOx -- will limit max combustion temperature

- Melting of ingested sand can erode TBC -- CMAS

- Corrosion of metallic components from pollution in the atmosphere, eg SO₂
  - Many of the metallic alloys in the engine were not designed to resist SO₂ corrosion

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On land-based turbines, NOx can be reduced by steam injection into combustor.

*Aerospace turbines might need their own high-temperature catalytic convertor*
Growing problem: rising SO2 levels in air in many cities around the world
Probably will require extensive modification of bond-coat alloys.
Growing problem: rising SO2 levels in air in many cities around the world. Current bond-coat alloys were designed for much lower SO2 levels. Solution: probably will require extensive modification of bond-coat alloys.
Identifying the next generation thermal barrier coatings remains a major challenge

- Low thermal conductivity at high temperatures is a necessary but not sufficient criterion.
- Thermal conductivity at low temperatures is relatively un-important and not a good guide to high-temperature conductivity
- High fracture toughness at high temperatures is also a necessary requirement.
- Thermal barrier coatings are part of a dynamically evolving and interacting system.
- Bond-coat and superalloy must also be morphologically stable, especially on thermal cycling

Future Directions

- Development of in-situ monitoring, particularly of coating temperatures and damage.
- Operation in air containing higher SO2 concentrations.
- Coatings for turbines using alternative fuels.
- Plenty of inter-disciplinary research and development opportunities
- Success will require a large scale, multidisciplinary approach and extensive collaborations
Office of Naval Research, Steve Fishman and Dave Shifler

Vladimir Tolpygo, Andi Limarga, Molly Gentleman, Sam Shian, Yang Shen,

Vanni Lughi, Liguo Chen, Matthew Chambers, John Nychka, Mary Gurak

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Bauke Heeg, Luminium

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