Thermal Barrier Coatings for Gas Turbines

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Output Power Depends on Rotor Inlet (T4) Temperature
Current T4 temperature exceeds melting temperature of the superalloys!
Superalloy Turbine Airfoils

Equiaxed (EQ)  Dir. Sol. (DS)  Single Xtal (SX)
Combination of advances in cooling and materials have enabled increases in turbine temperatures and energy efficiencies.
Coatings provide thermal barrier to prevent superalloy blades and vanes melting.
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
The Thermal Barrier Coating System

- Low thermal conductivity
- High strain compliance
- Extreme temperature gradient (~1°C/µm)

0.1–3 mm
- Oxidation product. Large growth strain
- Al reservoir for forming protective Al₂O₃

0.1–10 µm
- Interdiffusion with superalloy
- Capable of creep and plastic deformation

30–100 µm
- Ni-based superalloy structural component
- Susceptible to creep and cyclic fatigue

1–4 mm
- Internal surfaces of superalloy blade or vane cooled with air from engine

Engine Cooling Air
Rationale for Using Thermal Barrier Coatings for Turbine Components

• Original motivation was to extend the life of existing aero-turbine engines
• Additional benefits:
  • operate at higher gas temperature than melting point of superalloy
  • Minimize distortions due to transients

Rationale for Using Zirconia for Thermal Barrier Coatings

• Stabilized zirconia had the lowest thermal conductivities of any oxide @ 1985
• Demonstrated technology for refractory coatings – plasma-spraying – already existed
• Later experiments at NASA demonstrated that 7YSZ exhibited longest thermal cycle life
Some Requirements for a TBC

- Stable in air at temperatures in excess of 1400°C for long times
- Low thermal conductivity at high temperatures
  - Current 7YSZ coatings have conductivities < 1.5 W/mK
  - Need even lower thermal conductivity
- Negligible optical absorption
  - To avoid radiative heating by absorption from hot gases and surrounding parts
- Short optical scattering lengths
  - To minimize direct radiative heating
- Coating must stay on!
- High fracture toughness at all temperatures and resistant to thermal shock
  - Fracture toughness equal or greater than 7YSZ
- Chemical stability with alumina (Al2O3), the preferred oxide formed on alloy oxidation
- Coatings must be compliant, conformal and deposited on curved surfaces
- High-rate deposition of 150-250 micron thickness coatings needed
At high temperatures, conductivity always asymptotes to minimum value, $K_{\text{min}}$.

NB. Some oxides have a temperature independent conductivity above room temperature.

NB. Data shown from fully dense materials so no porosity contribution.
High-Temperature Thermal Conductivity Scaling

\[ \kappa_{\text{min}} = k_B \nu_m \Lambda_{\text{min}} \rightarrow 0.87 k_B \overline{\Omega}_{a}^{-2/3} \left( \frac{E}{\rho} \right)^{1/2} \quad \overline{\Omega}_{a} = \left[ M / \left( m \rho N_A \right) \right] \]
Minimization of Thermal Expansion Mismatch Stresses

To remain intact on the blade, the coating must withstand the stresses created by the thermal expansion mismatch strains.

Elastic strain energy in coating: 
\[ U_{\text{elastic}} = \frac{\sigma^2 h}{2E_{\text{coat}}} = \frac{E^2_{\text{coat}} \varepsilon^2_{\Delta T} h}{2} = \frac{h (\Delta \alpha \Delta T)^2 E^2_{\text{coat}}}{2} \]

Mismatch strain in coating: 
\[ \varepsilon_{\Delta T} = \Delta \alpha \Delta T \]

Condition for failure: strain energy release rate, \( G > \) fracture toughness of interface, \( \Gamma \)

The only way to reduce elastic strain energy is to lower the elastic modulus of the coating.

How?

Introduce a “shape factor” into the performance index, ie porosity/gaps.
Deposition of Thermal Barrier Coatings

- Deposition methods for introducing porosity for strain compliance
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**APS**
(Atmospheric Plasma Sprayed)

**EB-PVD**
(Electron Beam - Physical Vapor Deposited)
Deposition Effects on Microstructure

C. Levi, UCSB
Coating life usually limited by various fracture processes
Both low temperature and high temperature failures can occur
Need high fracture toughness at both low and high temperatures
Underlying mechanism of coating delamination are poorly understood
Thermal cycling lives are usually much shorter than constant temperature lives
Effect of Thermal Cycling on Coating Life

Failure typically by TBC buckling/spallation

“understood”

“not yet understood”

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

Balint-Hutchinson Code

TGO
BC
Substrate

Roughness Parameter $R_c$ (um)

- grit blasted
- polished

Temperature $T$, °C

Lower Cycle Temperature (°C)

Rumple Amplitude after 100 cycles (microns)

- Tolpygo-Clarke data
- GE simulation based on Balint-Hutchinson Model

100 regular 1-h cycles
isothermal 100h
Impact Resistance Requires High Fracture Toughness

Impact Damage

TBC spallation

1820 engine cycles
Luminescence Based Temperature and Damage Sensor

Non-contact method

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

- Luminescence lifetime is known to be temperature sensitive

  - Because of 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

*Luminescence decay times can be used measure temperature*
Example: Eu Doped TBC Sensor Layer

Superimposition of white light and UV luminescence images
Temperature Sensing Using Luminescence Lifetimes

10 micron sensor layer on EB-PVD coating

Calibration of luminescence lifetime provides basis for temperature measurements on engine components
Major Luminescence Transitions in Eu$^{3+}$ doped YSZ

![Diagram showing energy levels and transitions in Eu$^{3+}$ doped YSZ]
Luminescence Decay Measurement System

- **Pulsed Laser**: 248 nm, 355 nm, 532 nm
- **Electrical Trigger**
- **Furnace**
- **Coating**
- **Beam**
- **Sapphire Fiber**
- **Laser Filter**
- **PMT**
- **Oscilloscope**
TBC Interface Temperature in a Thermal Gradient

Diagram showing experimental setup for measuring temperature with various devices and components such as pyrometers, lasers, and light pipes. The diagram includes labels for a Superalloy, YSZ layer, Eu sensor layer, and high pressure cooling air.
TBC Interface Temperature in a Thermal Gradient

TBC thickness: 146 µm

Temperature (°C)
Top surface pyrometer

Temperature (°C)
Metal backsurface pyrometer

Metal temperature

Temperature (°C) measured by Luminescence
The Next Materials Frontier: Ceramic Matrix Composites

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

- Corrosion of GT components from pollution in the atmosphere, eg SO₂
  - Many of the metallic alloys in the engine were not designed to resist SO₂ corrosion
The chemical reactions that lead to thermal NOx formation are:

\[ \text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N} \]
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In the first reaction di-nitrogen is attacked by O to form NO and a nitrogen radical.

The nitrogen radical then attacks O\(_2\) to form another NO and regenerates the oxygen radical.

The overall reaction is given by:

\[ \text{N}_2 + \text{O}_2 \leftrightarrow 2(\text{NO}) \]

Highly endothermic: \(\Delta H_F = +90.4 \text{ kJ/mol}\)

NB. The formation rate of NOx is primarily a function of temperature and the residence time of nitrogen at that temperature.

**Combustion Reaction**

\[ \text{CH}_4 + 2\text{O}_2 + \text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2 + \text{CO} + \text{NO}_x + \text{heat} \]

**Zeldovich Mechanism for NOx Formation**

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**Combustion Creates NOx Pollution**
On land-based turbines, $NO_x$ can be reduced by steam injection into combustor.

*Aerospace turbines might need their own high-temperature catalytic converter.*
SO2 Corrosion Resistance

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.

Summary and Future Directions

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.
Turbine Aerodynamics, Heat Transfer, Materials, and Mechanics

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