



HARVARD

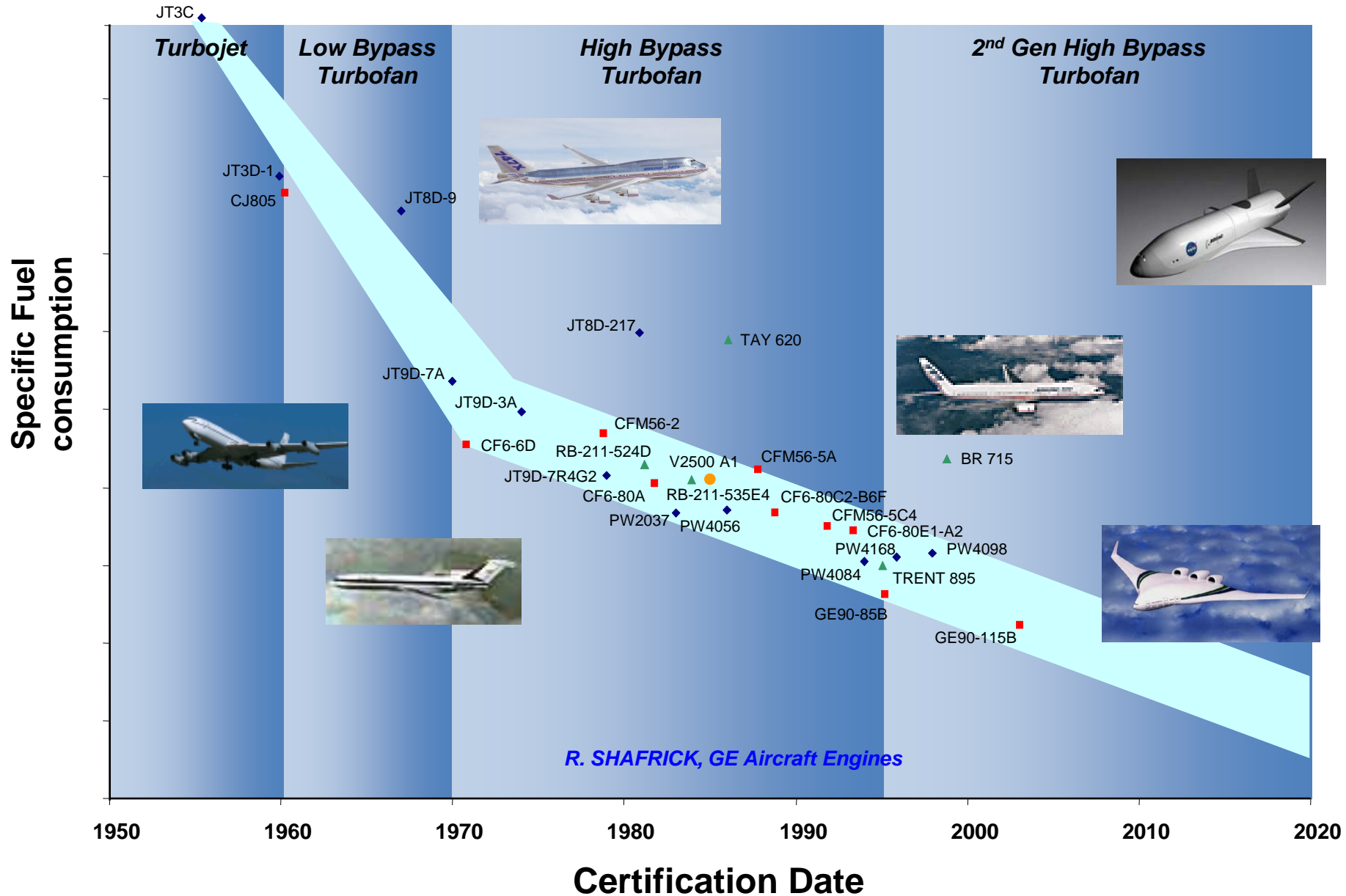
School of Engineering
and Applied Sciences

Materials Discovery and Applications Group
Professor David R. Clarke
clarke@seas.harvard.edu

Thermal Barrier Coatings for Gas Turbines

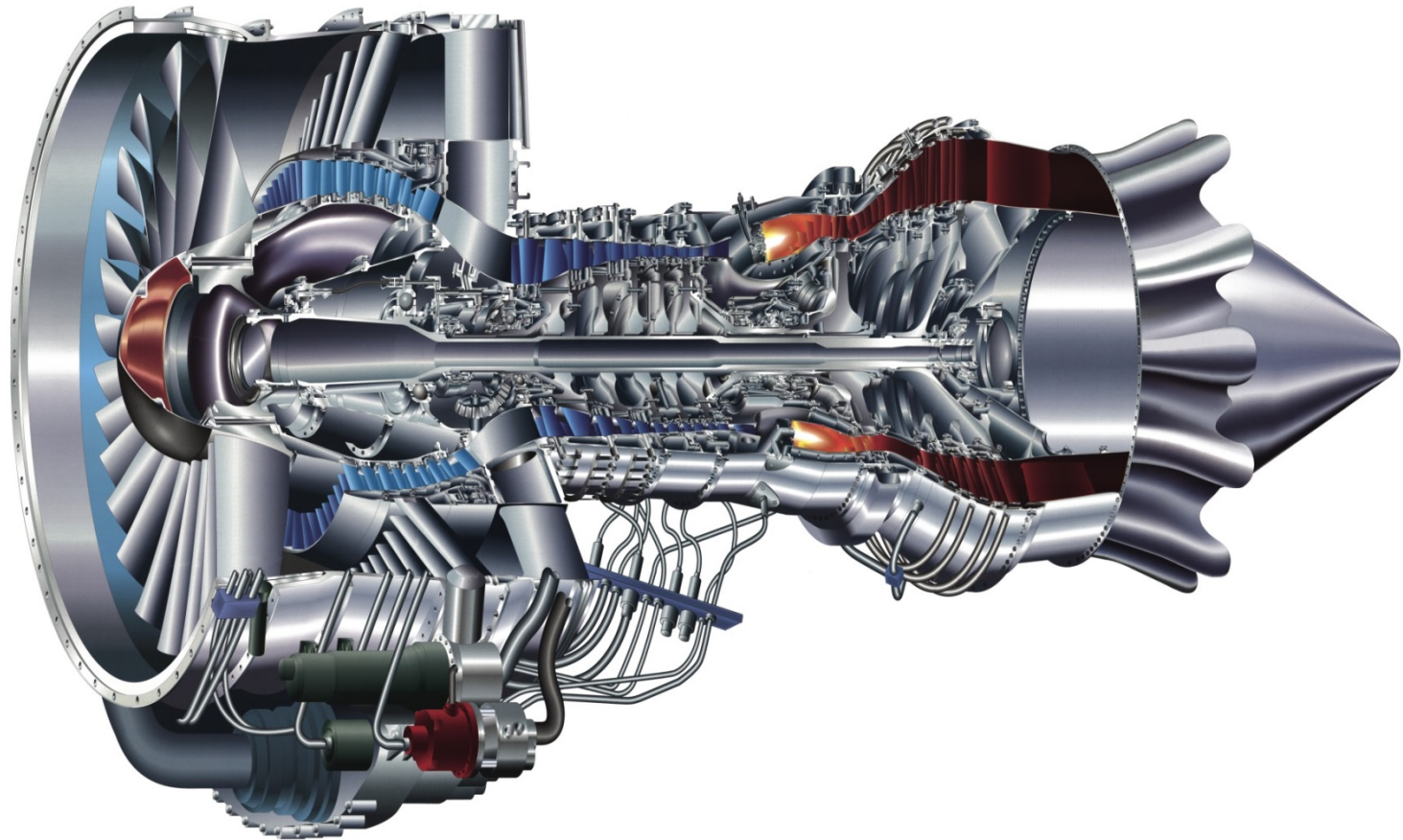
Institute of Advanced Studies,
Hong Kong University of Science and Technology

Fuel Efficiency in the Aeroturbine Industry

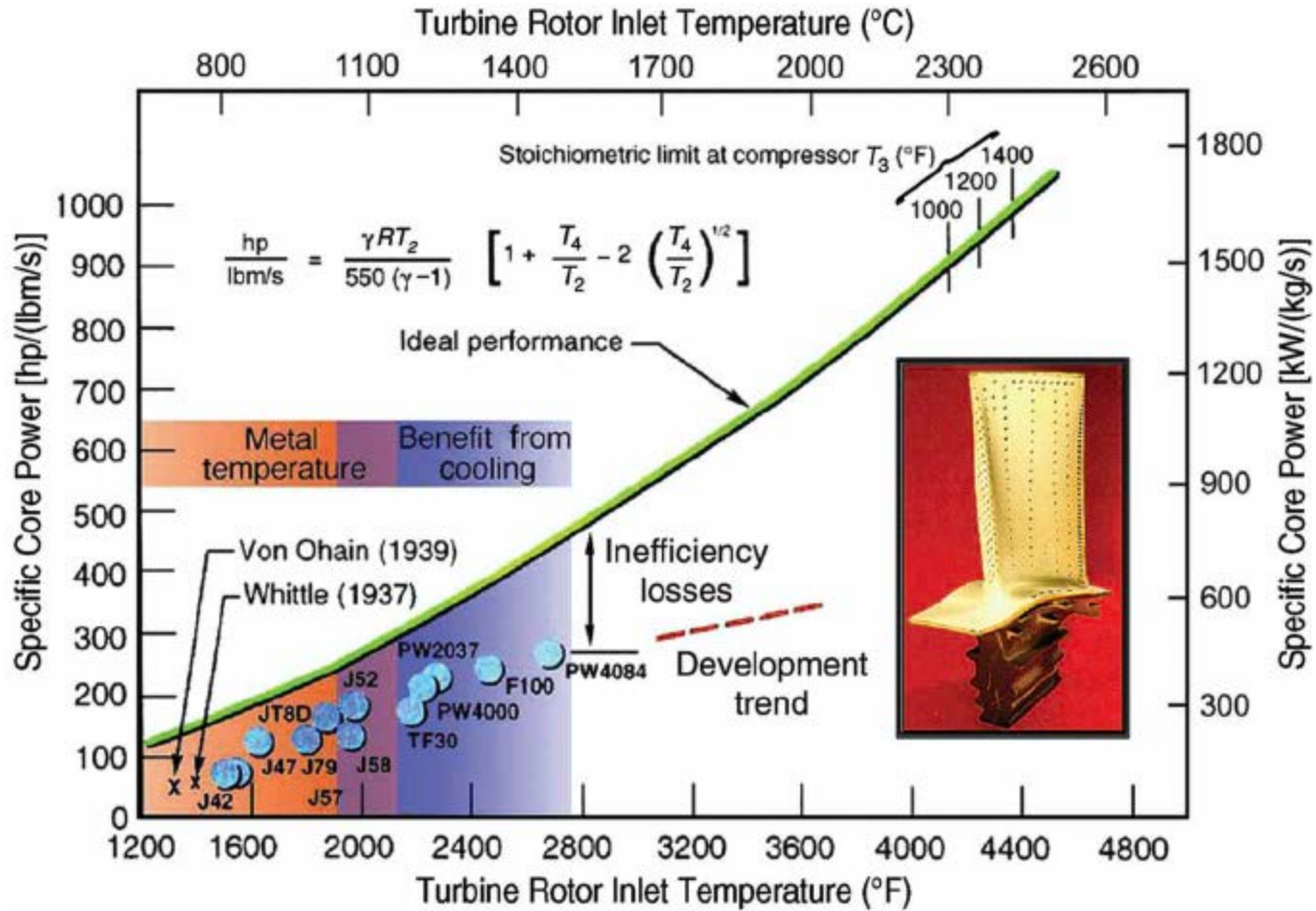




High By-pass Aeroturbine

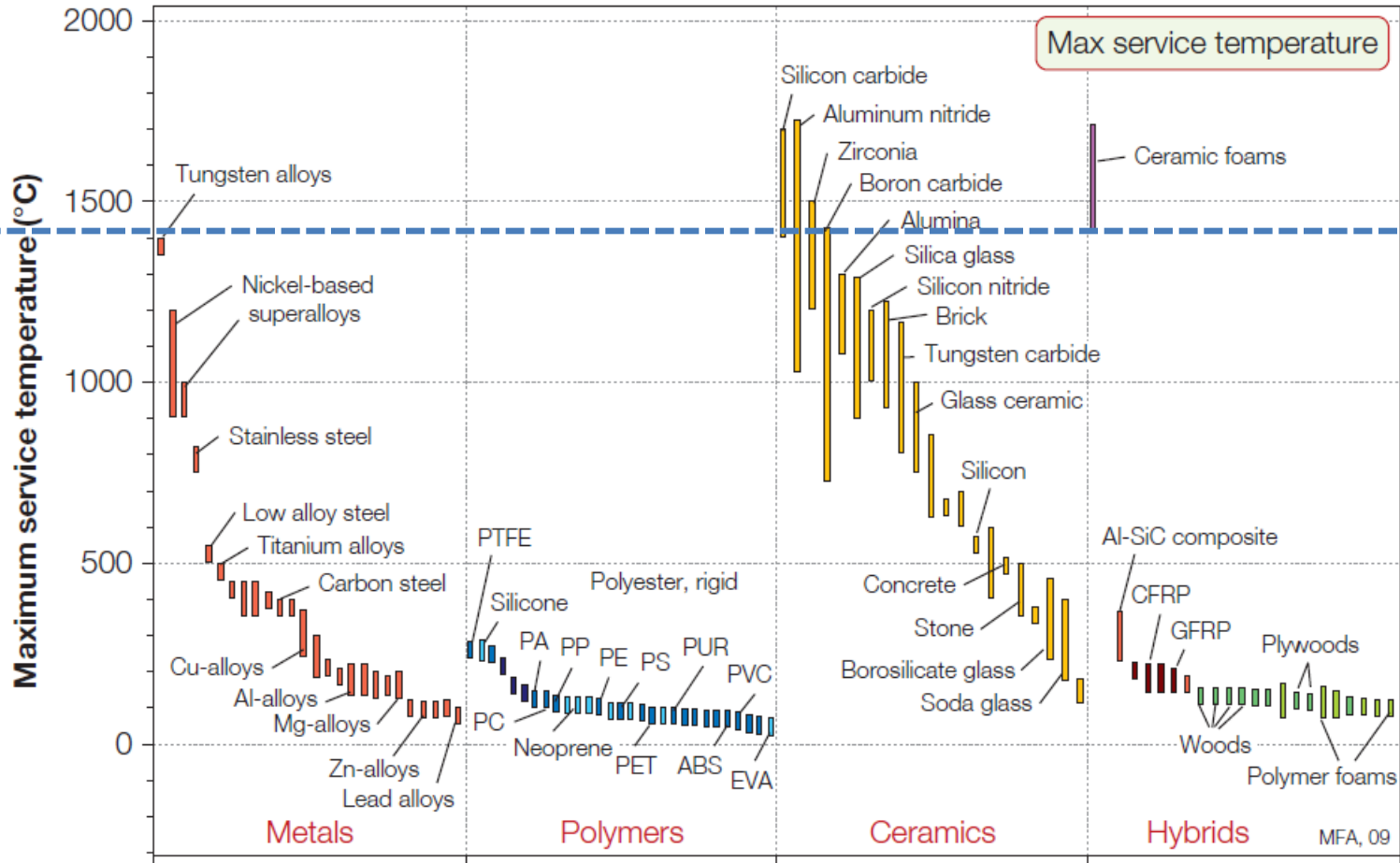


Output Power Depends on Rotor Inlet (T4) Temperature



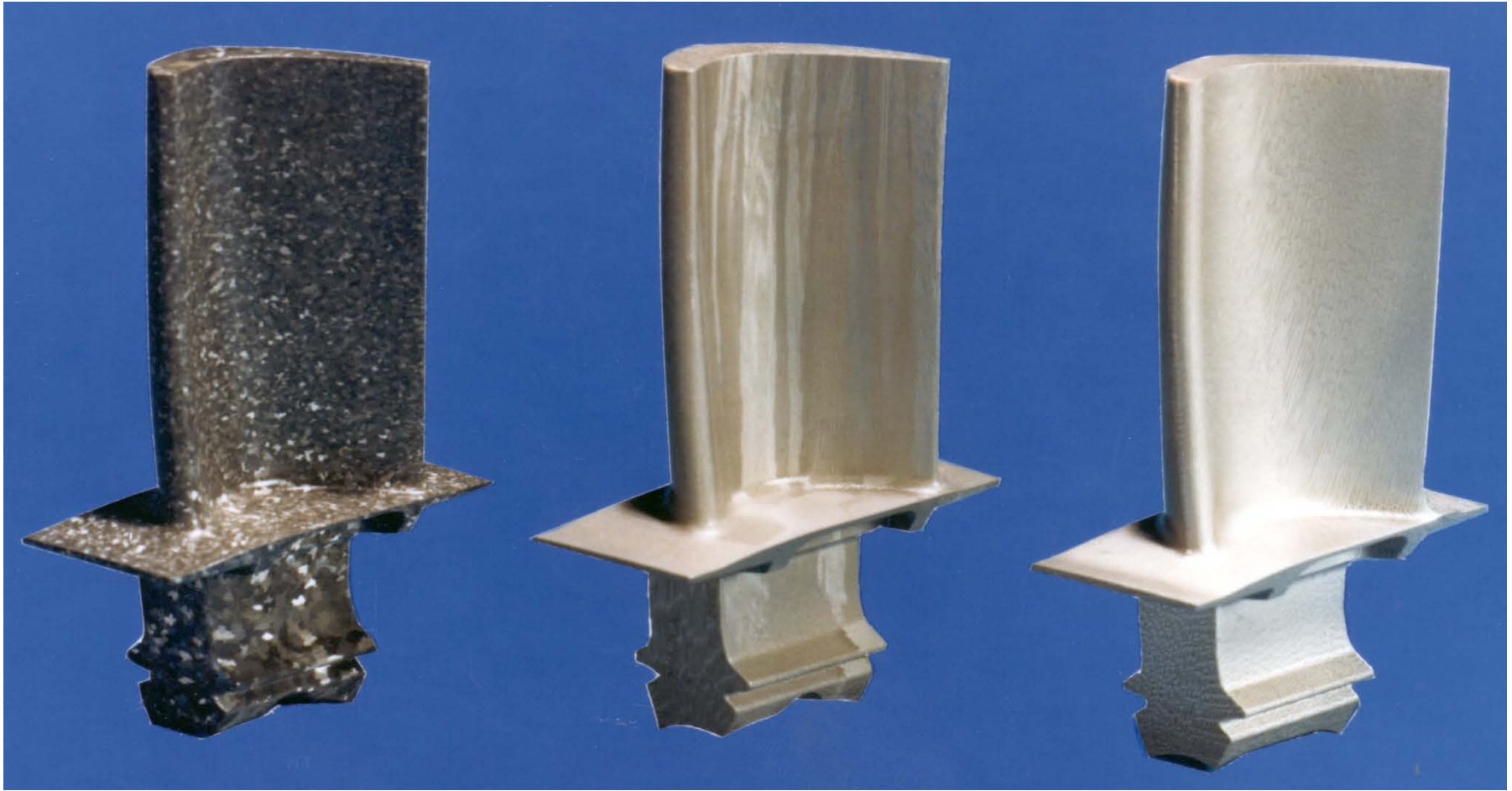
Maximum Service Temperatures of Materials

T4



Current T4 temperature exceeds melting temperature of the superalloys !

Superalloy Turbine Airfoils

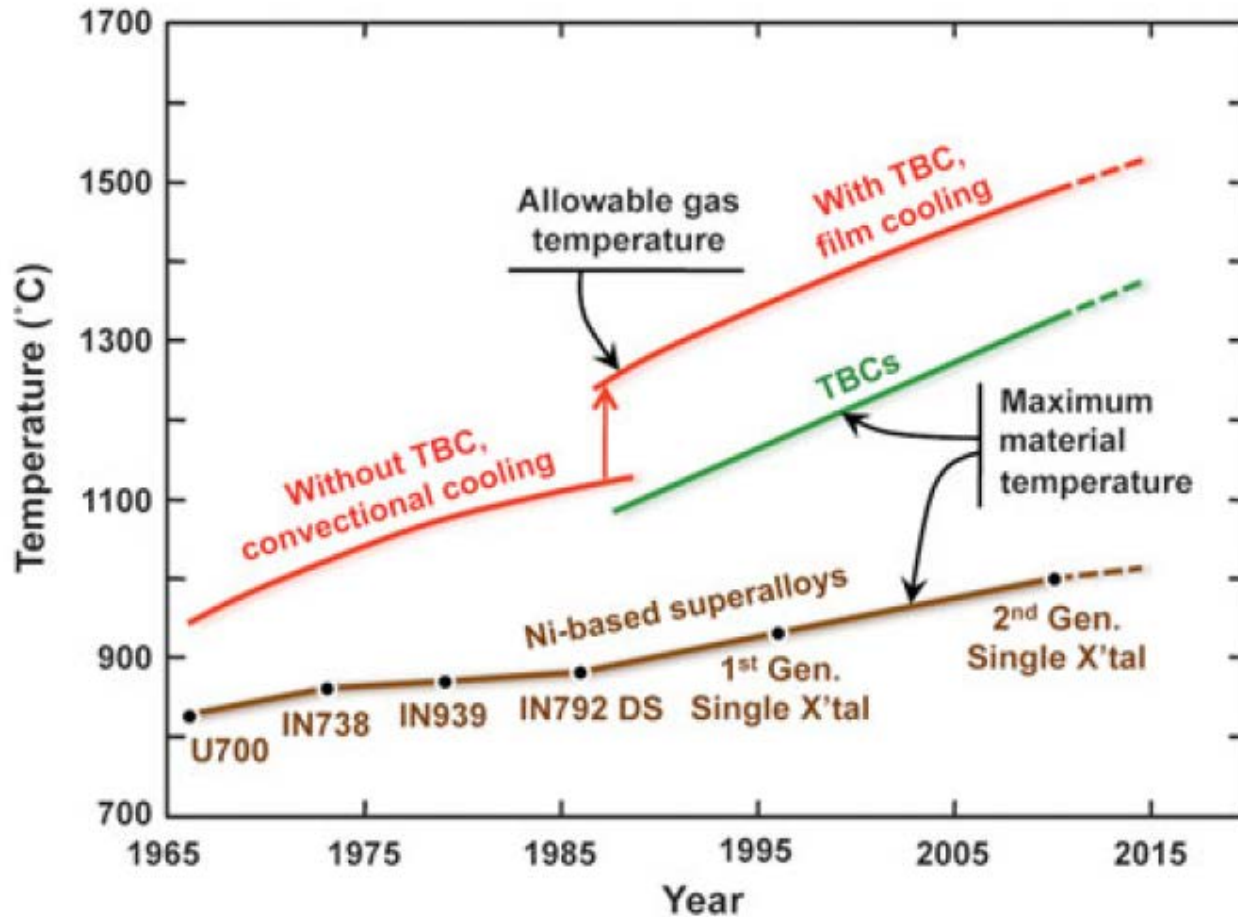


Equiaxed (EQ)

Dir. Sol. (DS)

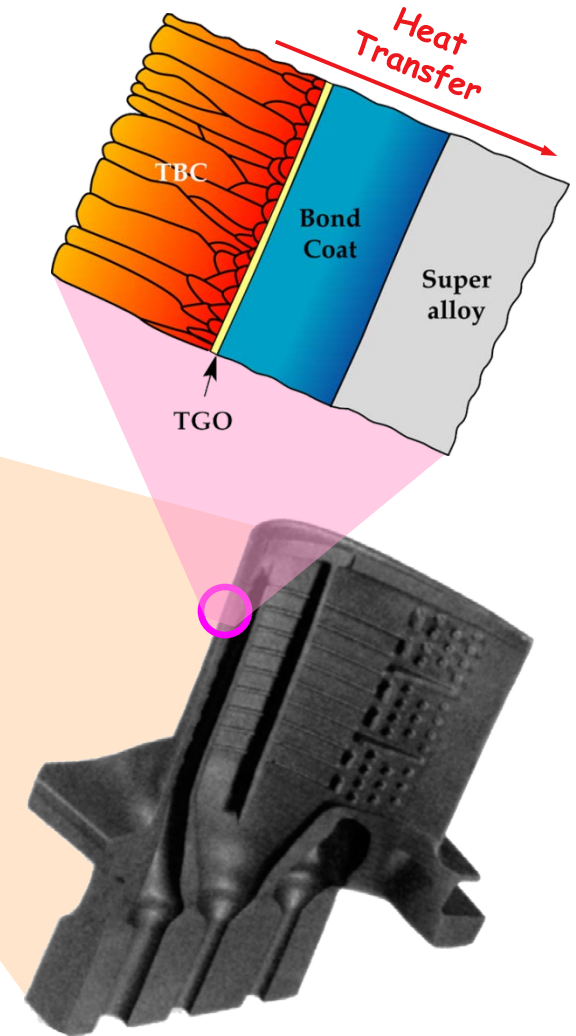
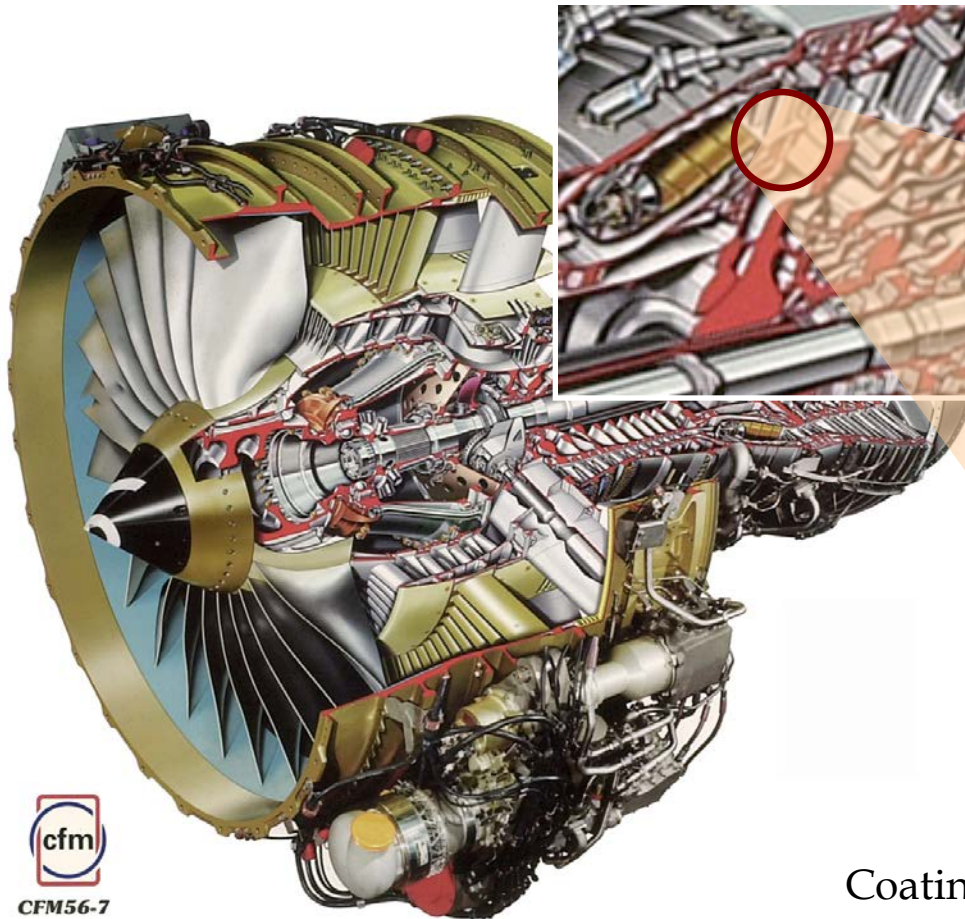
Single Xtal (SX)

Increase in Turbine (T4) Temperatures over Fifty Years



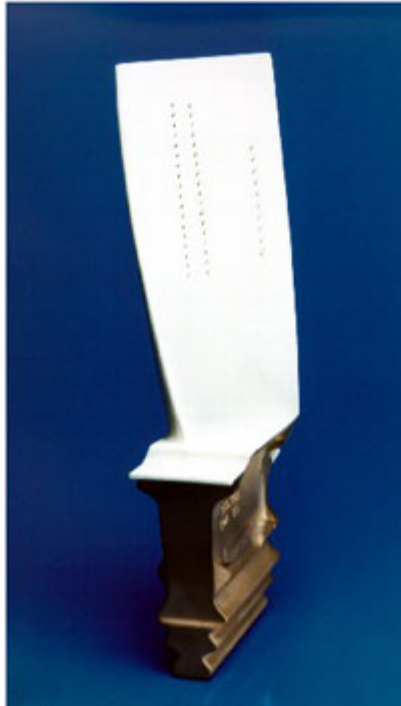
Combination of advances in cooling and materials have enabled
Increases in turbine temperatures and energy efficiencies

Coated Airfoil Technology



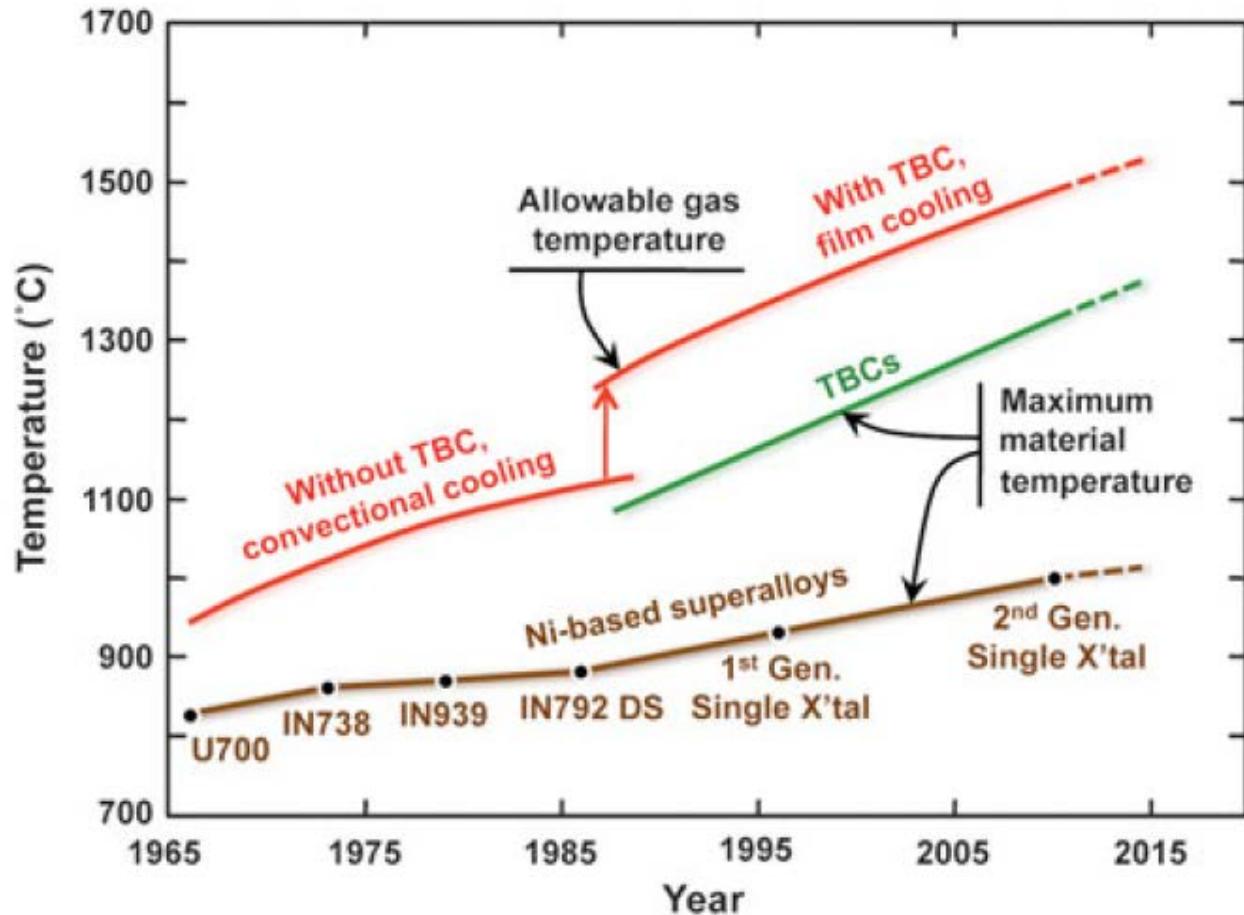
Coatings provide thermal barrier to prevent superalloy blades and vanes melting

Increase in Turbine (T4) Temperatures over Fifty Years



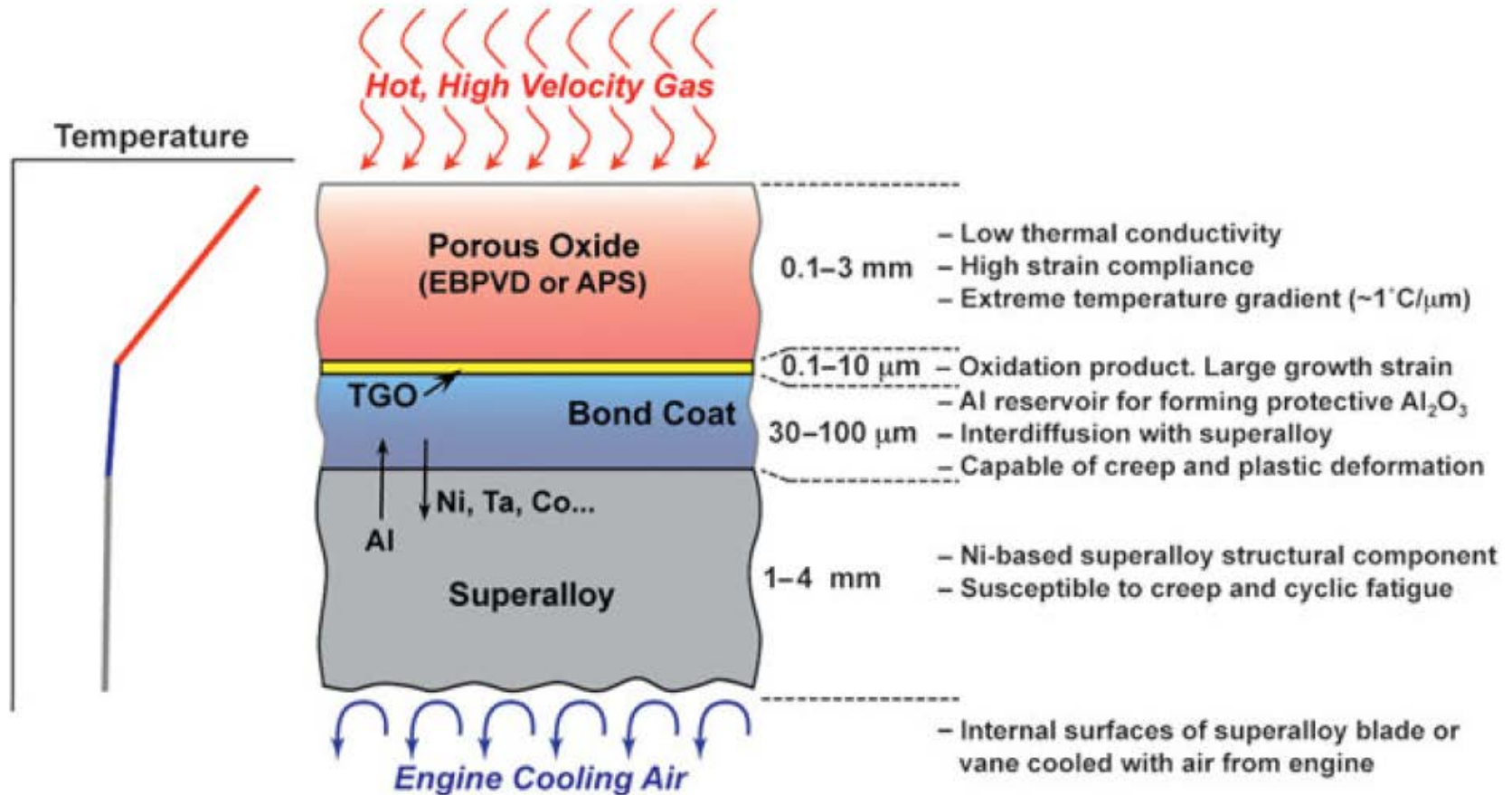
Yttria-stabilized zirconia coatings
~ 150 - 500 micron thick

Thermal gradient
~ 150-200 K/mm



Thermal barrier coatings have enabled a jump in turbine temperatures and energy efficiencies

The Thermal Barrier Coating System



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

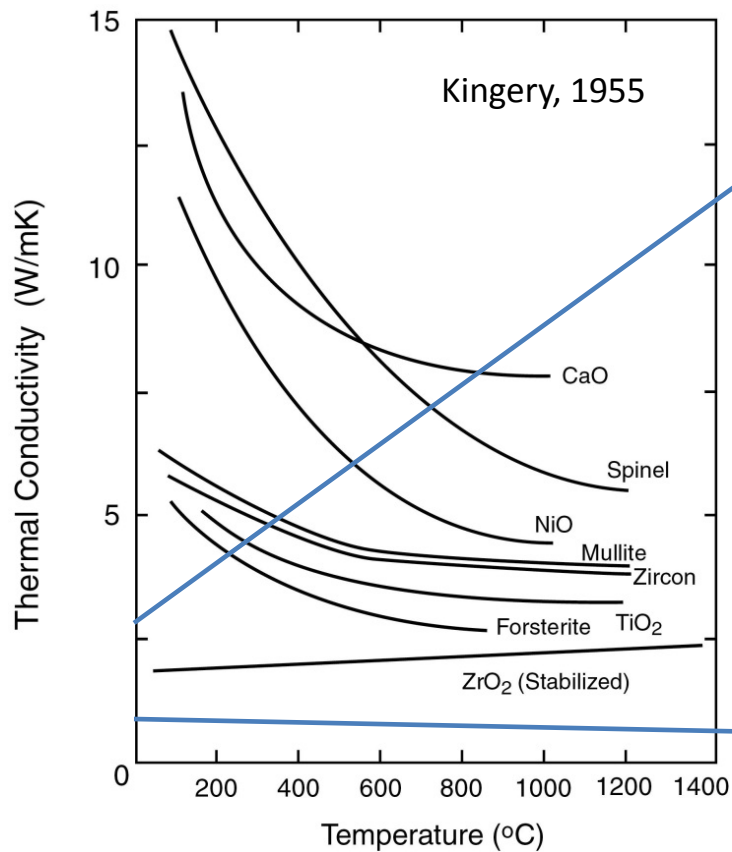
Rationale for Using Zirconia for Thermal Barrier Coatings

- 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

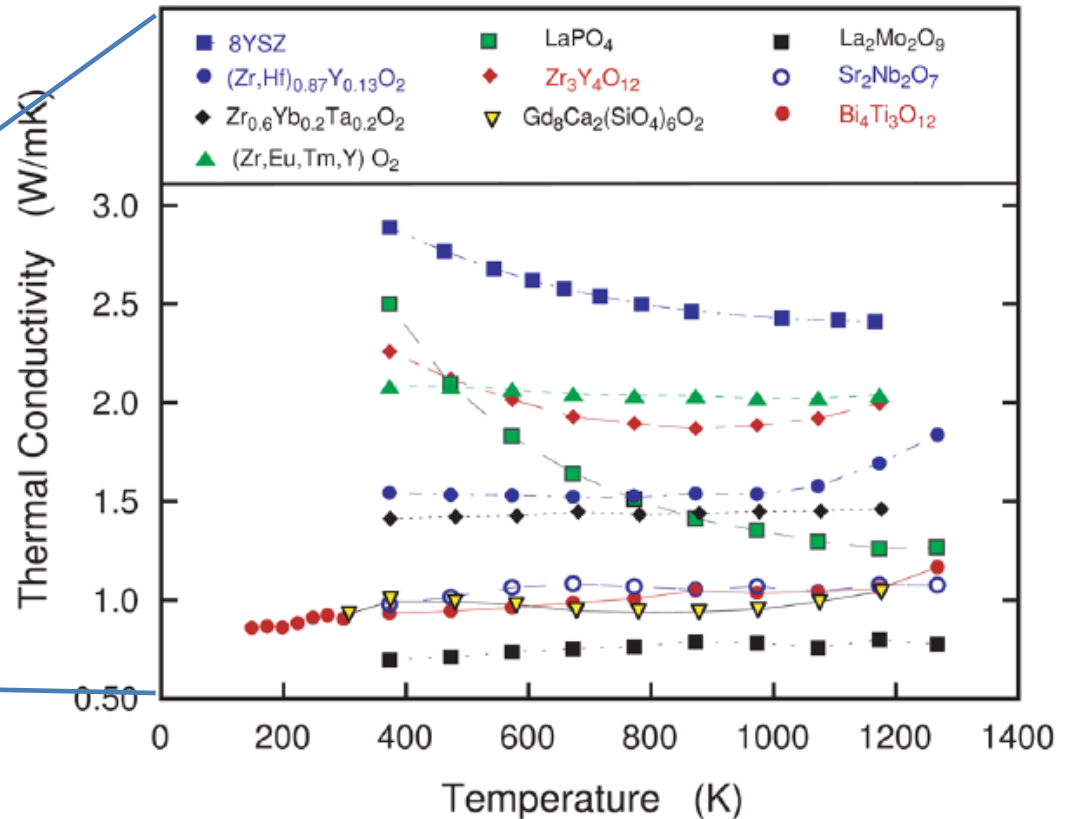
Some Requirements for a TBC

- ❑ 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

Alternative Oxides --- Thermal Conductivity



Newly identified low conductivity oxides

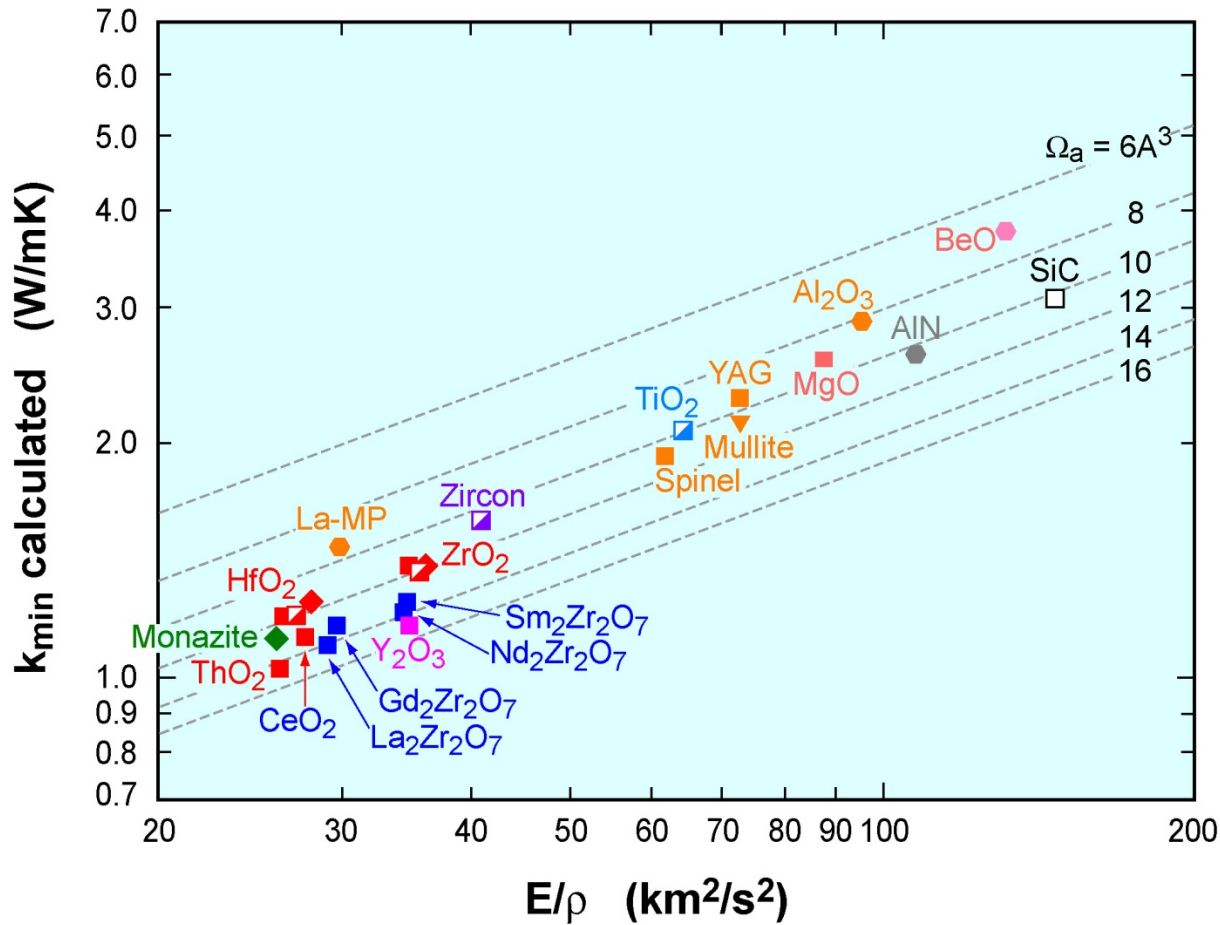


At high temperatures, conductivity always asymptotes to minimum value, K_{\min}

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

NB. Data shown from fully dense materials so no porosity contribution

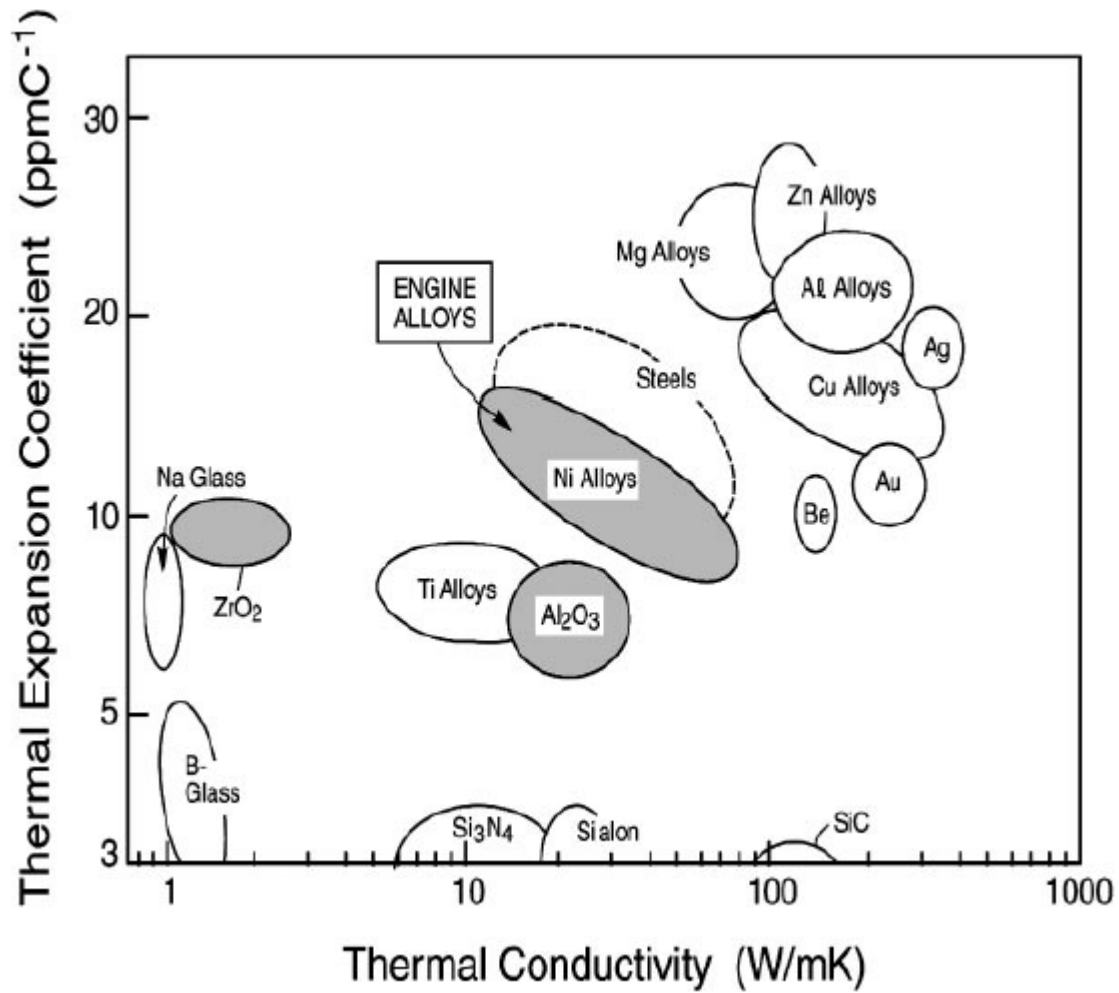
High-Temperature Thermal Conductivity Scaling



$$\kappa_{\min} = k_B v_m \Lambda_{\min} \rightarrow 0.87 k_B \bar{\Omega}_a^{-2/3} (E/\rho)^{1/2}$$

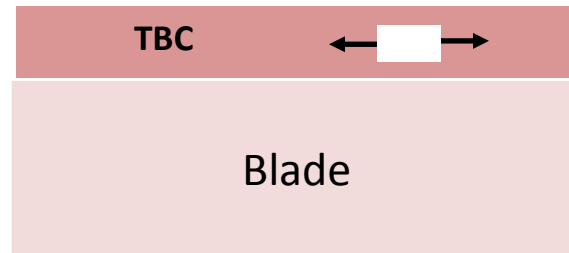
$$\bar{\Omega}_a = [M / (m \rho N_A)]$$

Thermal Expansion Mismatches



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



Mismatch strain in coating:

$$\varepsilon_{\Delta T} = \Delta \alpha \Delta T$$

Elastic strain energy in coating:
$$U_{elastic} = \frac{\sigma^2 h}{2 E_{coat}} = \frac{E_{coat}^2 \varepsilon_{\Delta T}^2 h}{2} = \frac{h (\Delta \alpha \Delta T)^2 E_{coat}^2}{2}$$

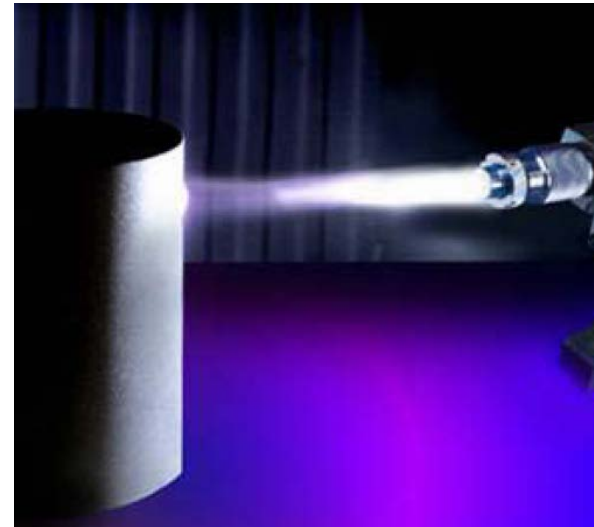
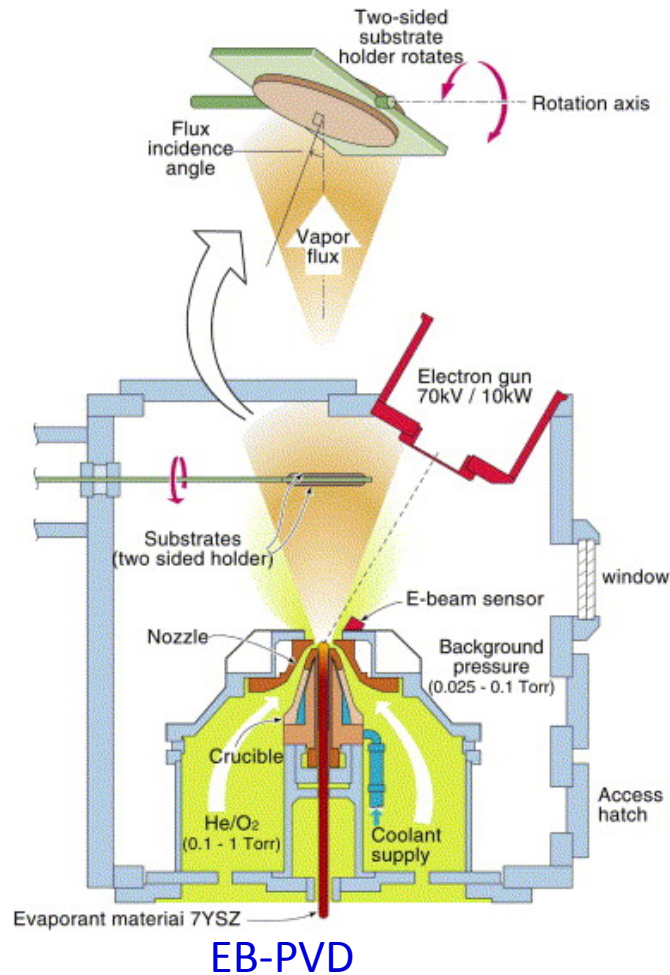
Condition for failure: strain energy release rate, $G >$ fracture toughness of interface, Γ

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

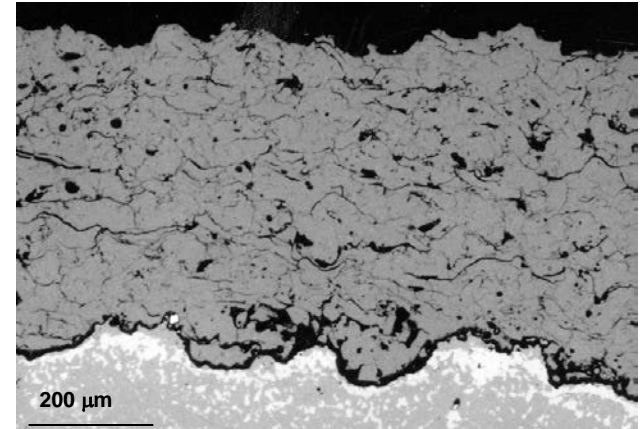
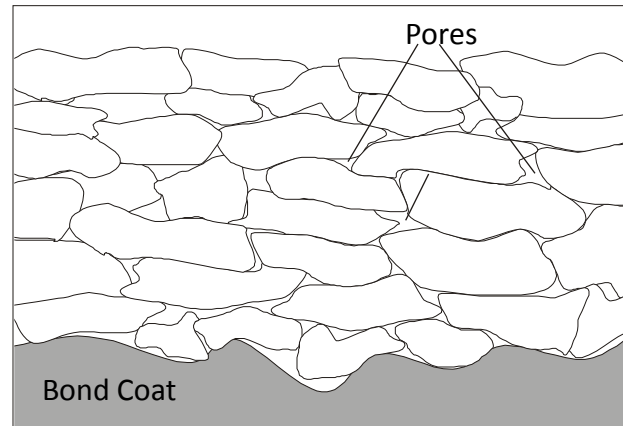


APS

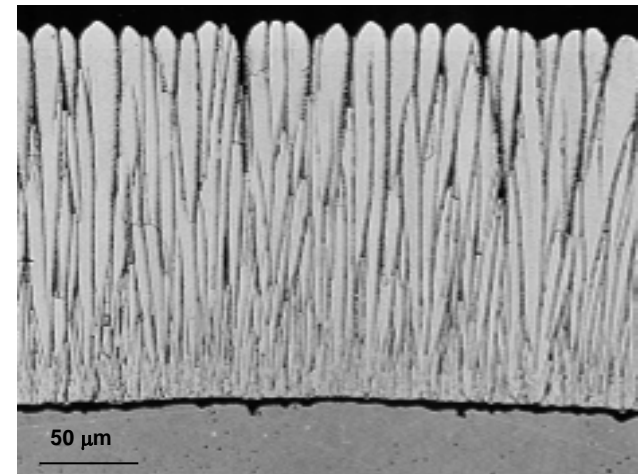
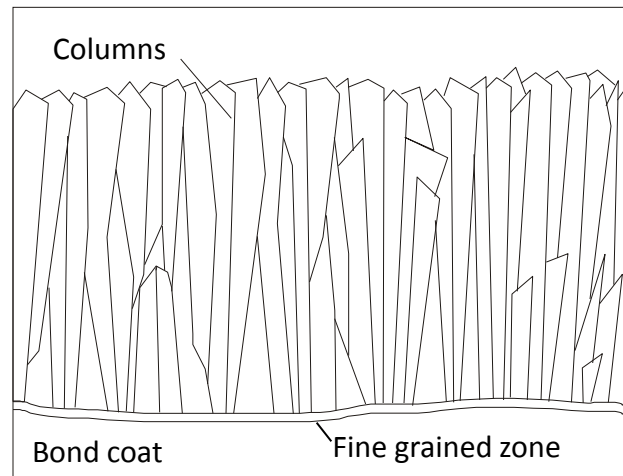
Deposition of Thermal Barrier Coatings

- Deposition methods for introducing porosity for strain compliance

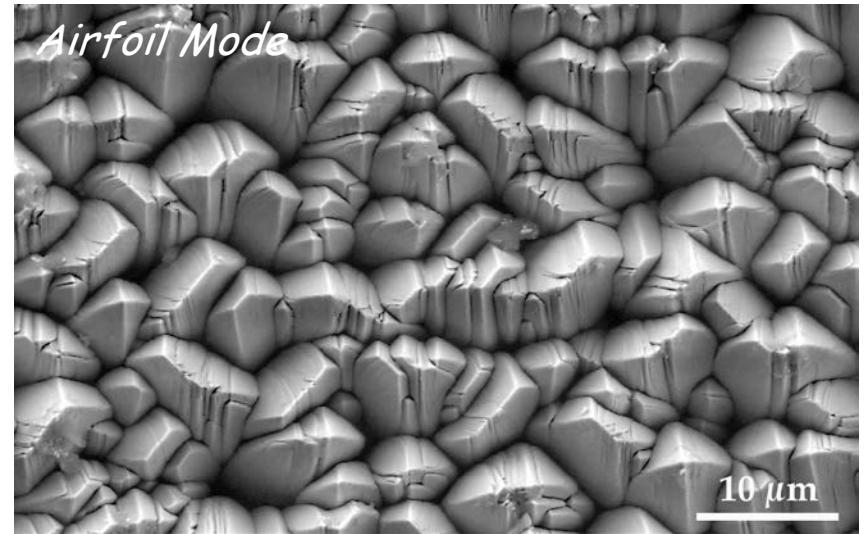
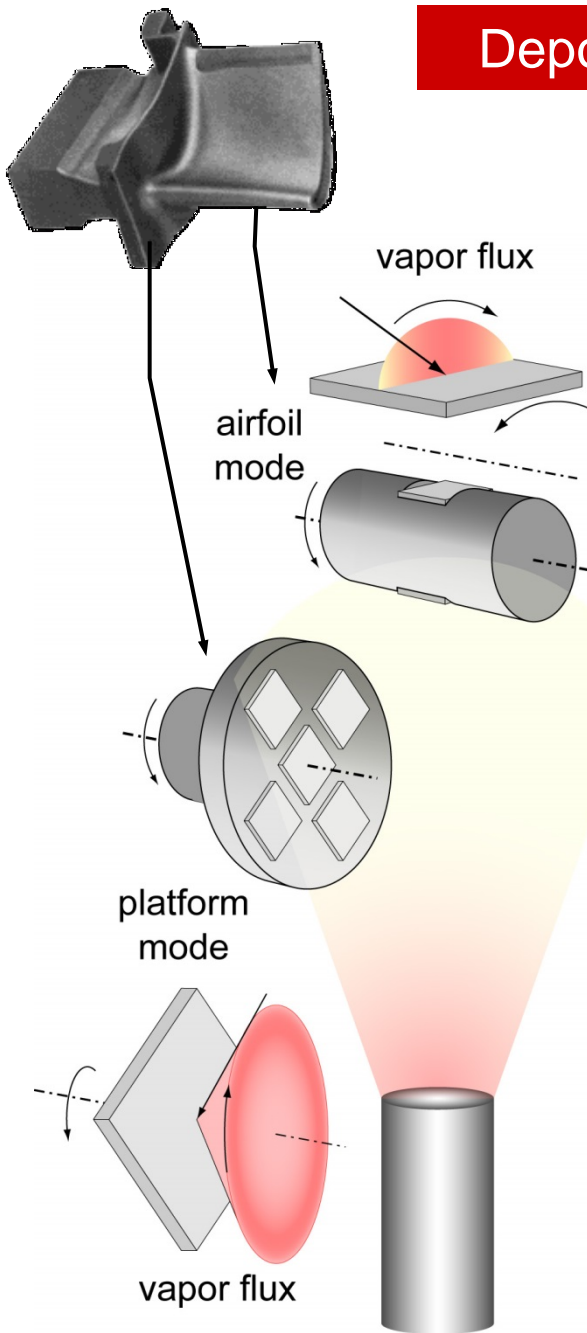
APS
(Atmospheric
Plasma
Sprayed)



EB-PVD
(Electon Beam -
Physical Vapor
Deposited)



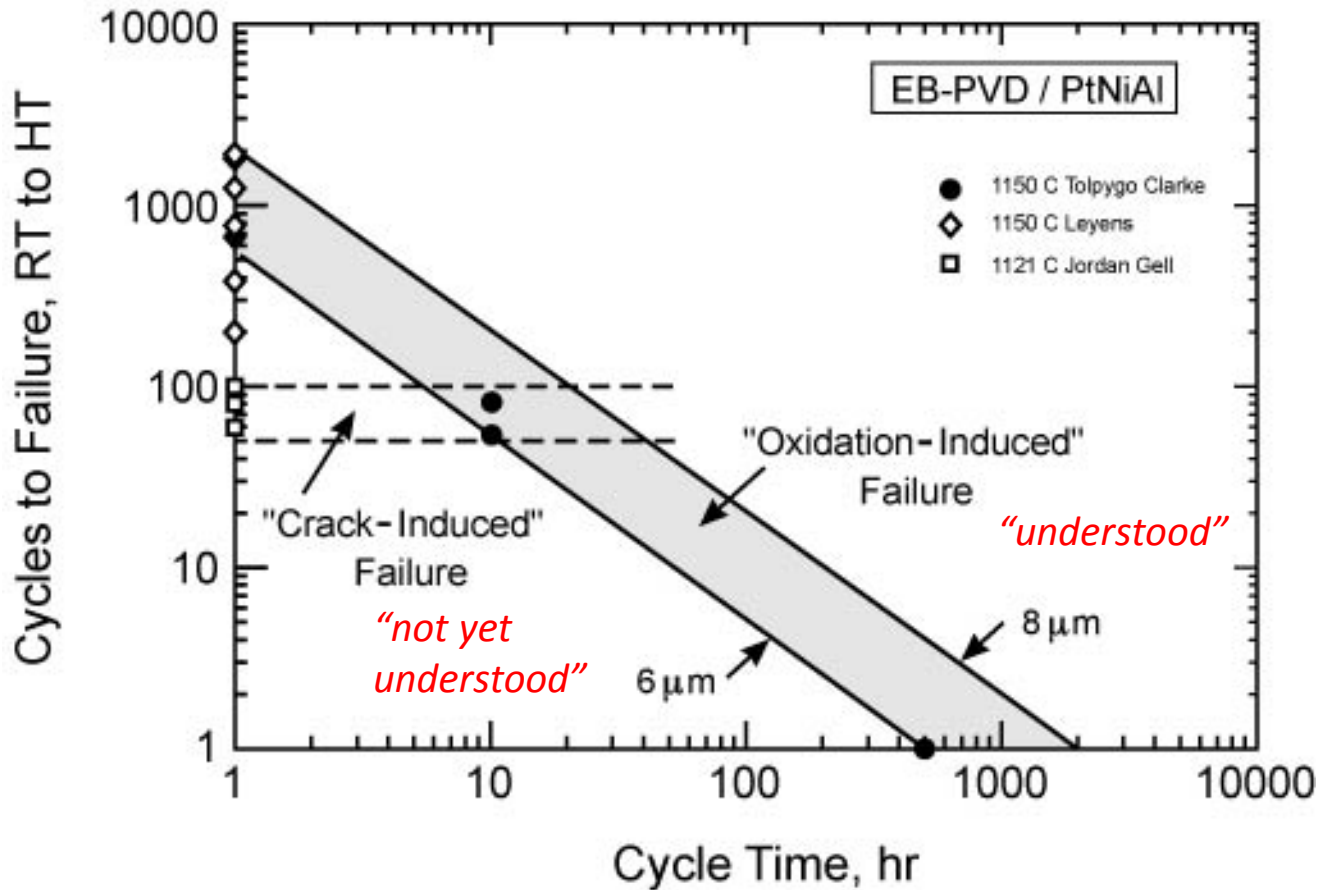
Deposition Effects on Microstructure



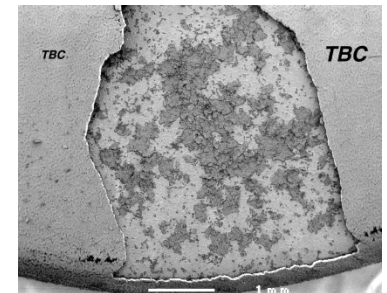
Assuring Thermomechanical Reliability – Prime Reliance

- 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

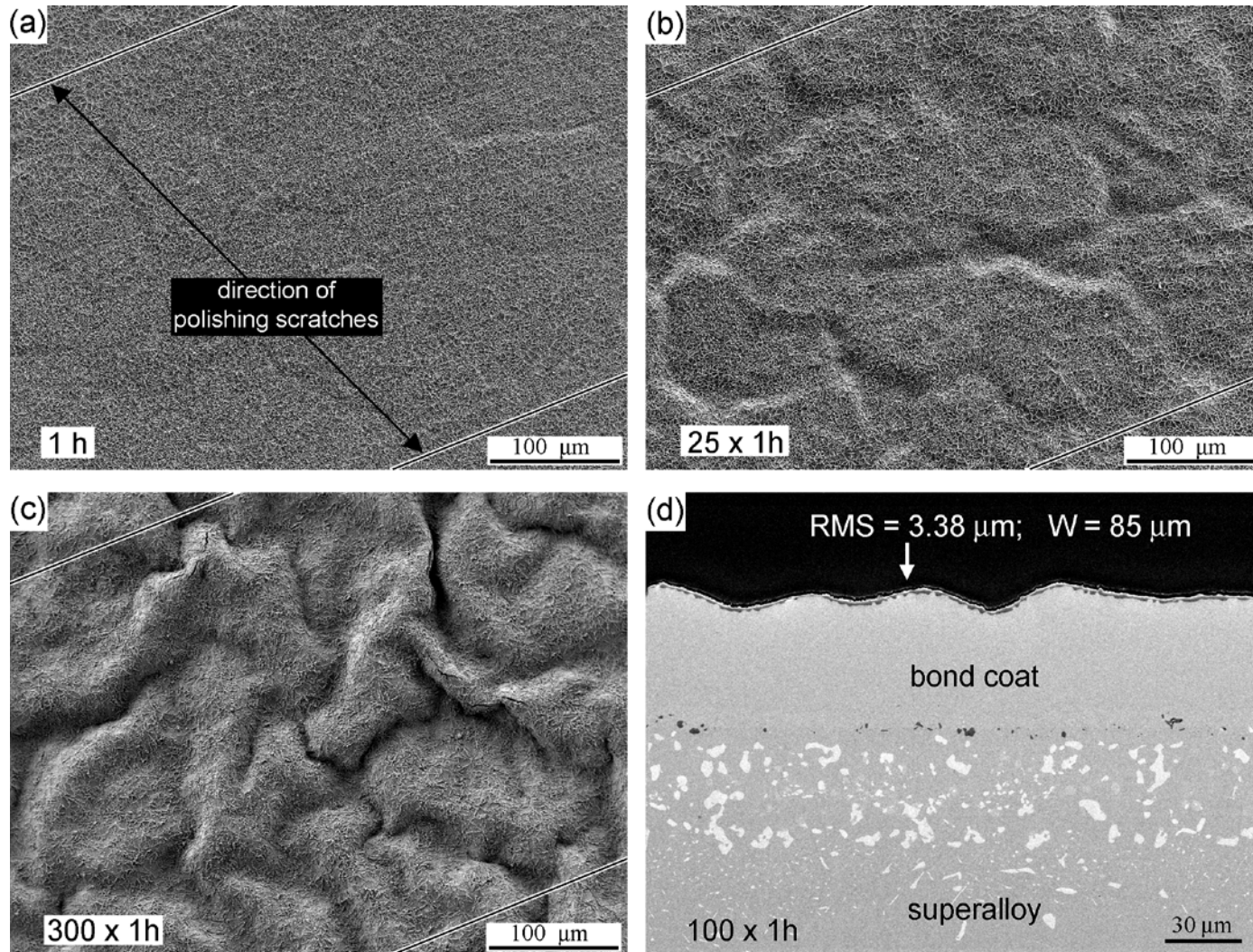


Failure typically by TBC buckling/spallation



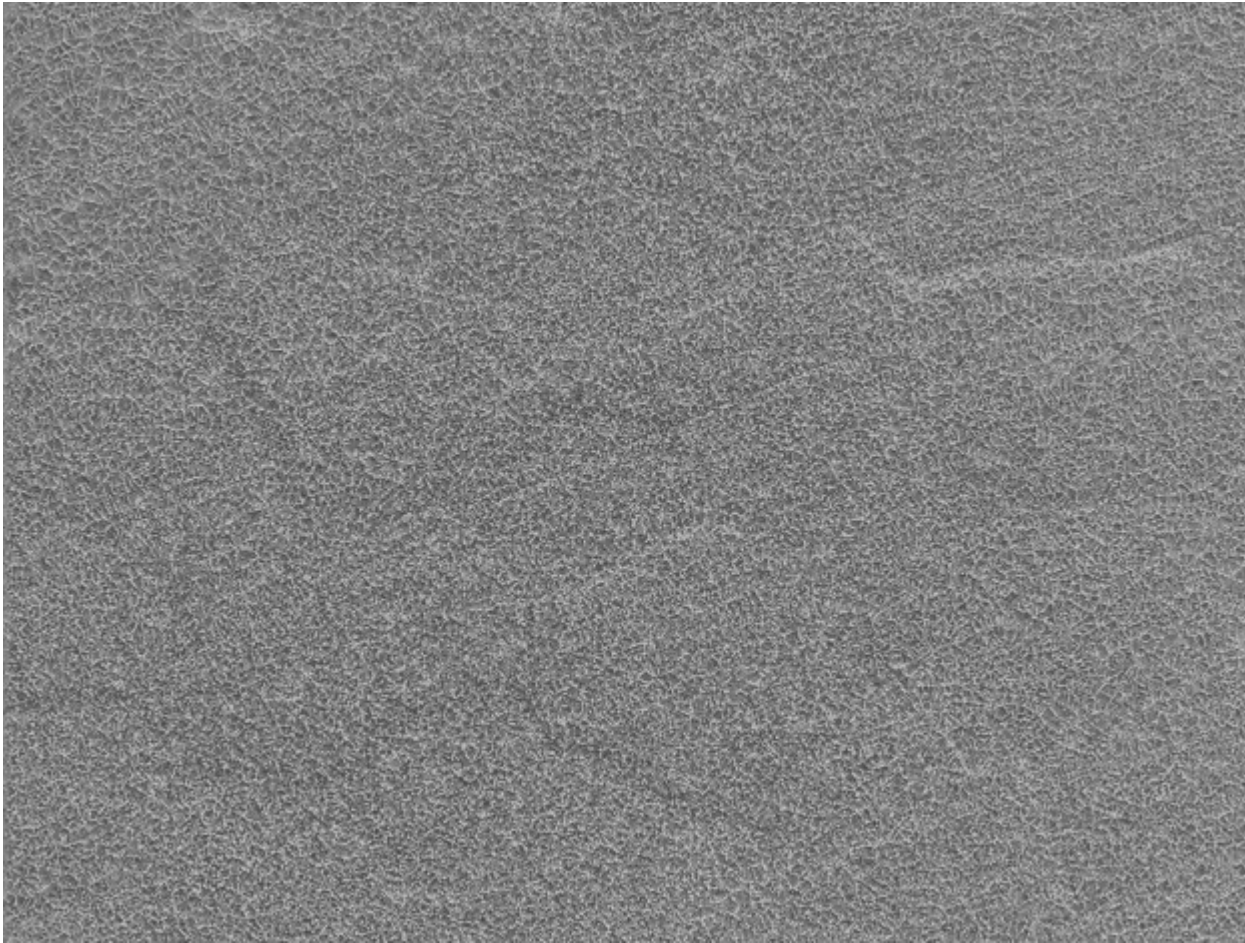
Effect of Thermal Cycling on Bond Coat

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

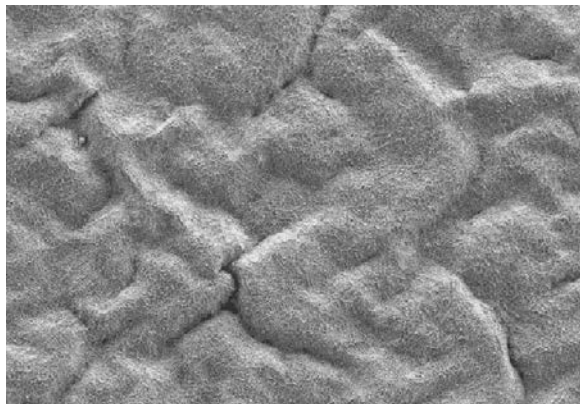


Thermal Cycling Instability

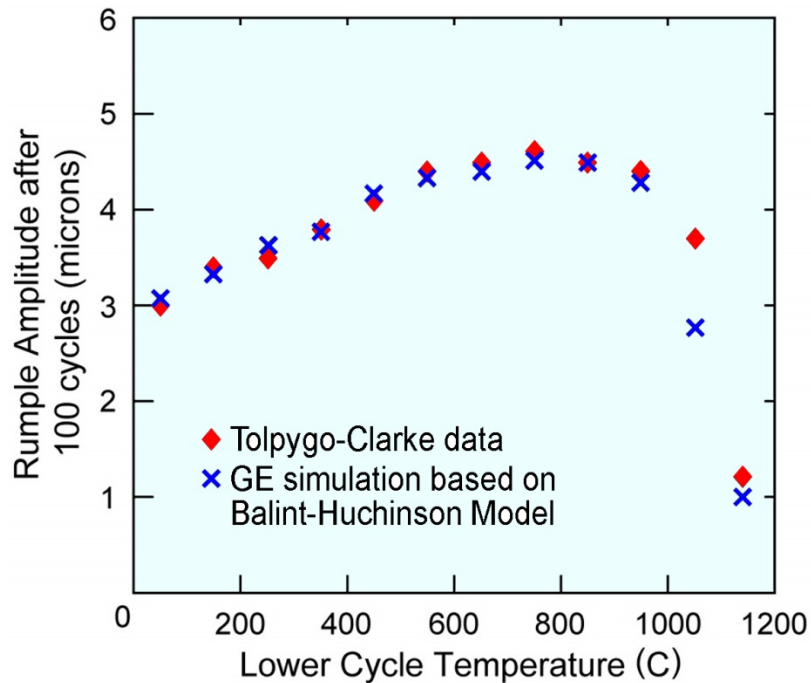
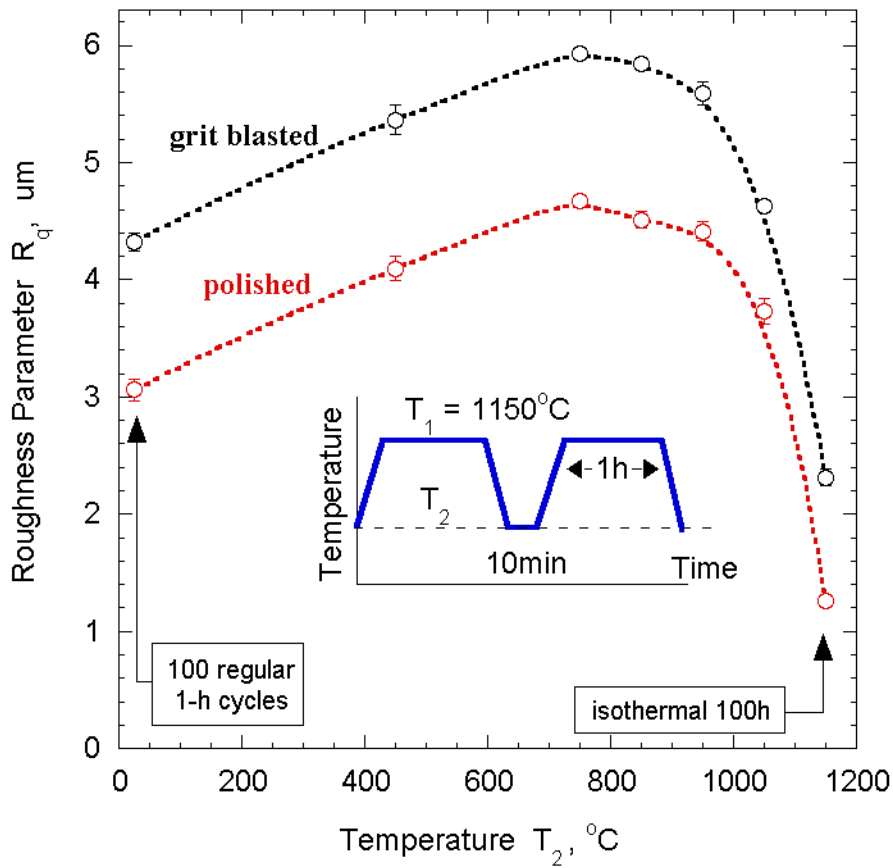
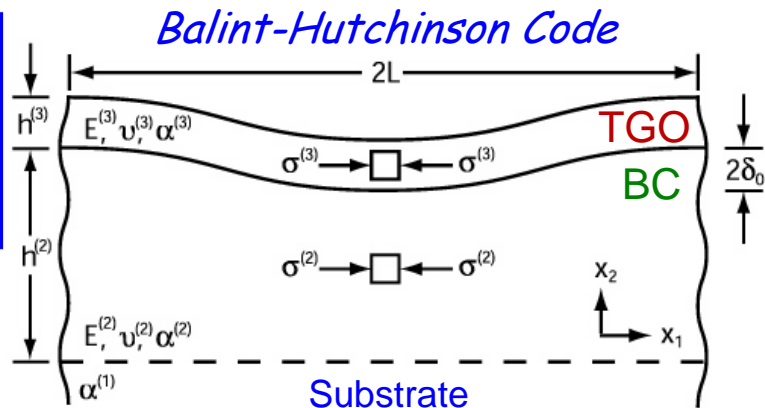
Life of TBC is often limited by morphological instability (“rumpling”) of the metal bond coat on thermal cycling causing incompatibilities with TBC. More stable alloys needed



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

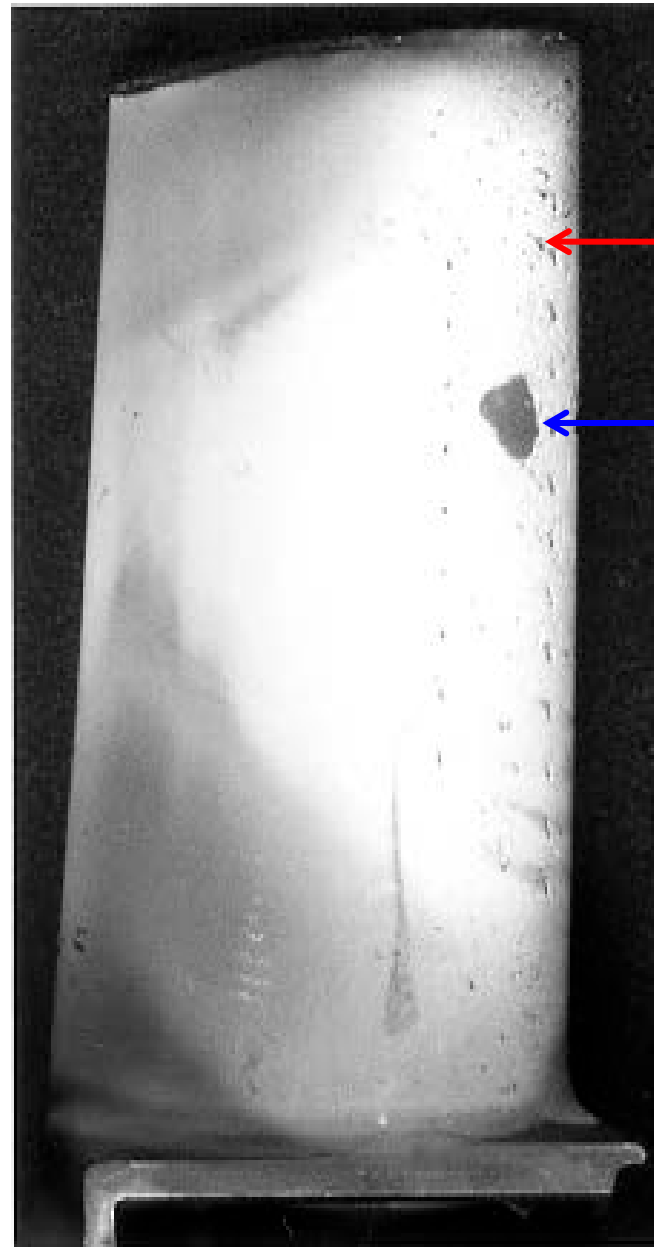


Mechanics Model Validation



Impact Resistance Requires High Fracture Toughness

1820 engine cycles

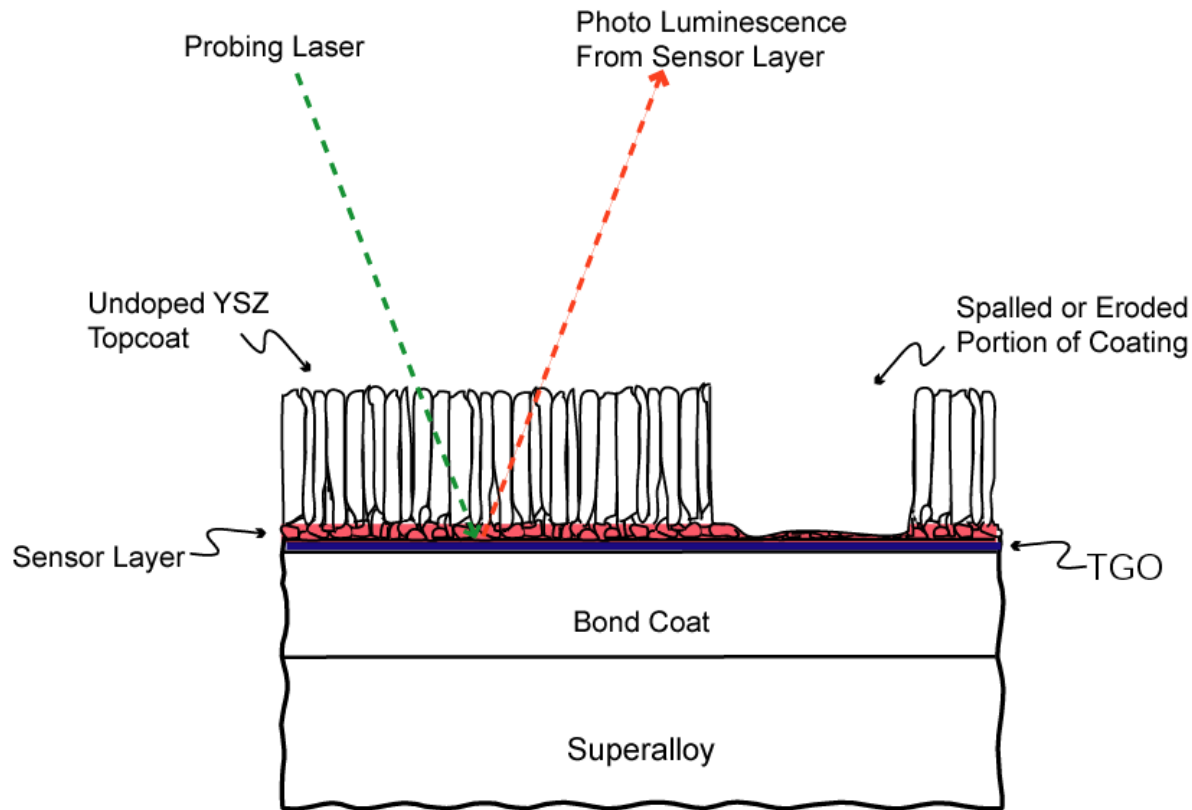


Impact
Damage

TBC
spallation

Luminescence Based Temperature and Damage Sensor

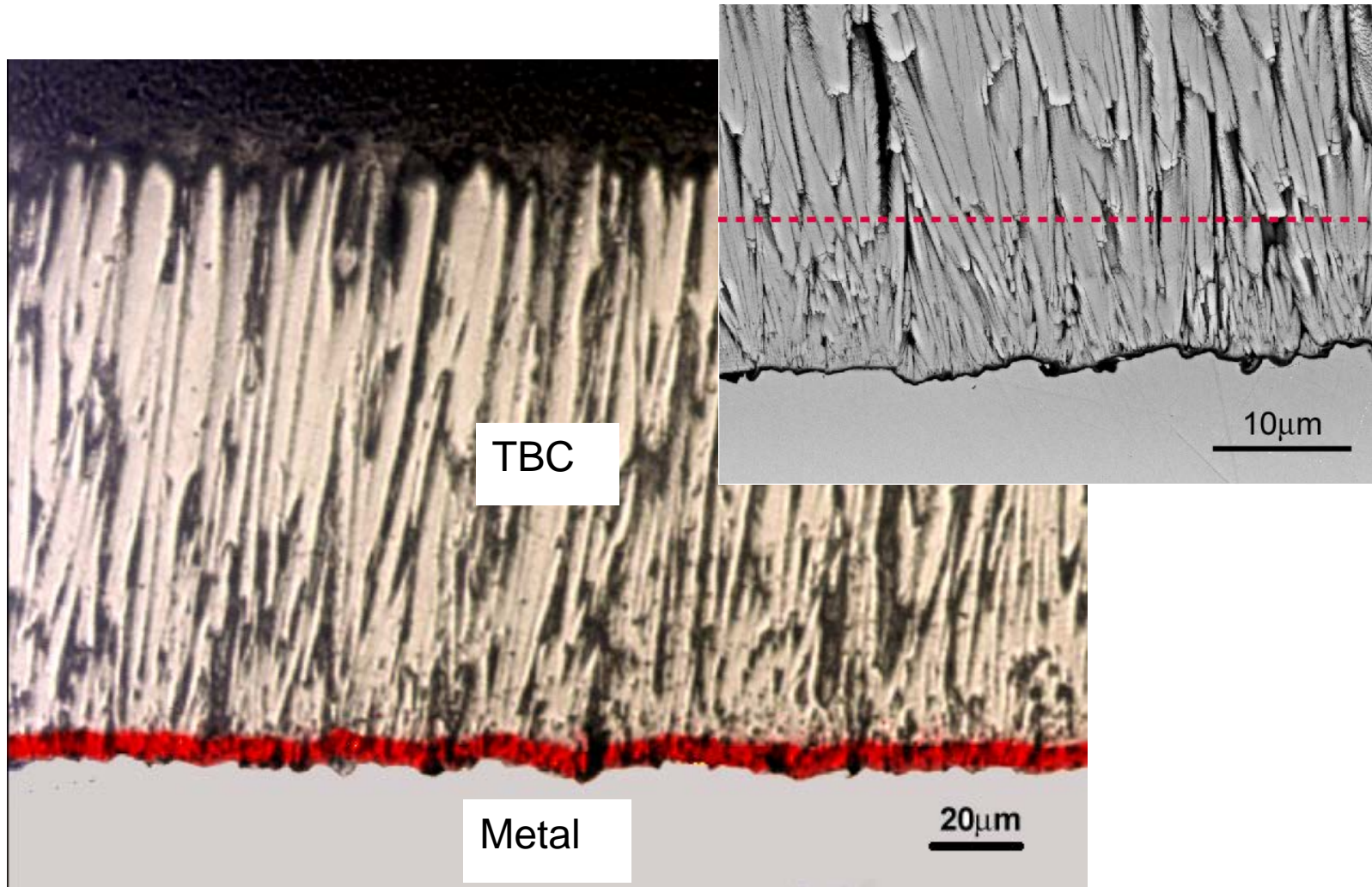
Non-contact method



- 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

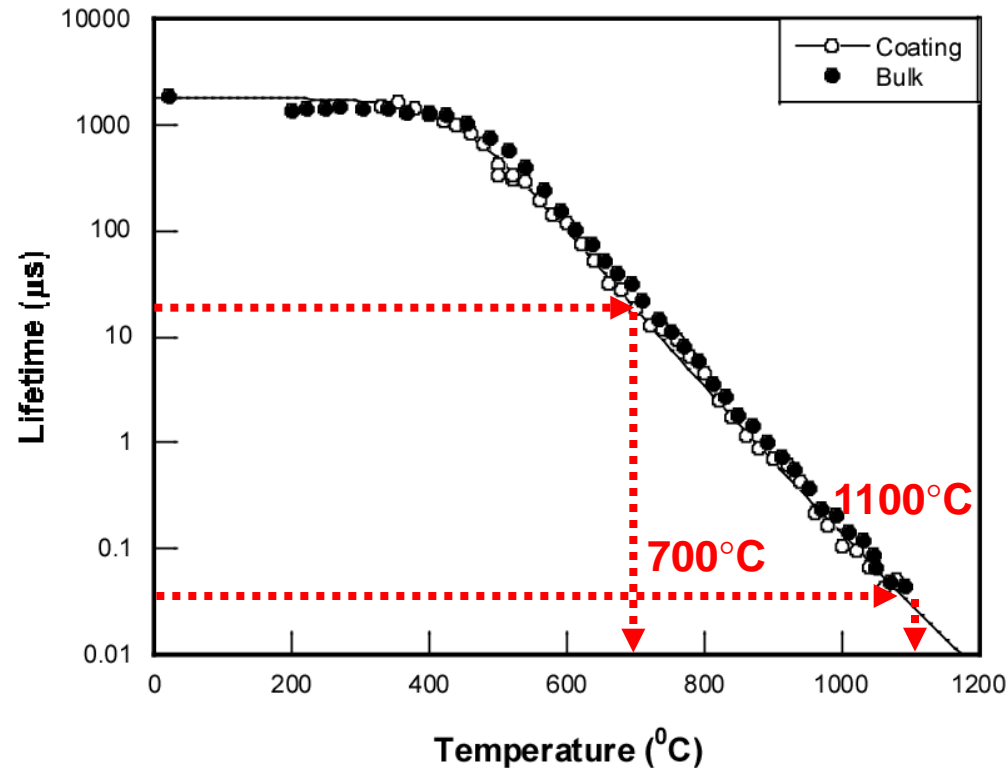
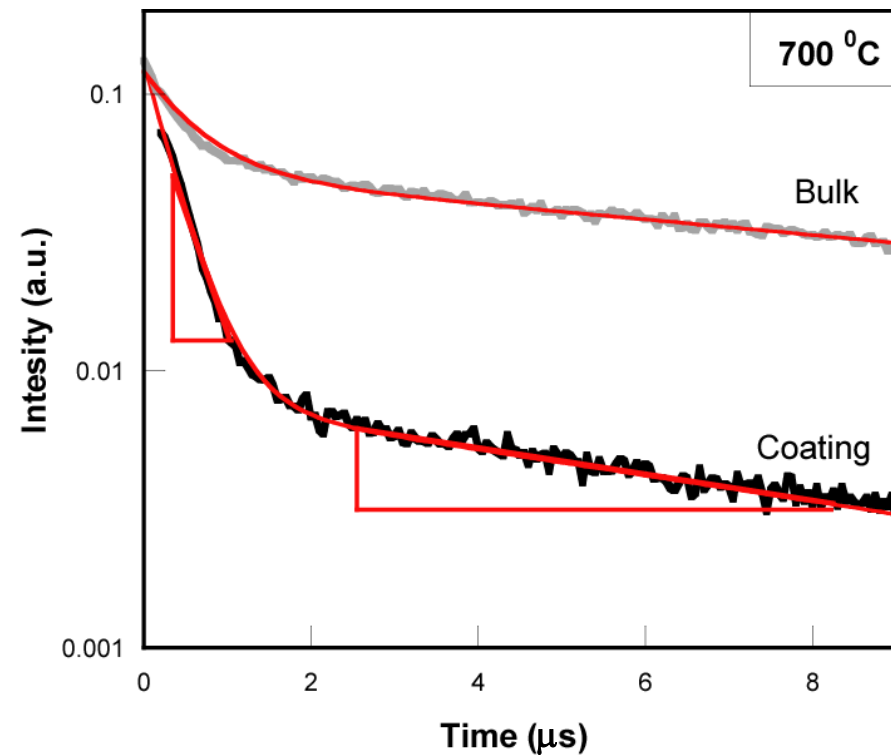
Example: Eu Doped TBC Sensor Layer



Superimposition of white light and UV luminescence images

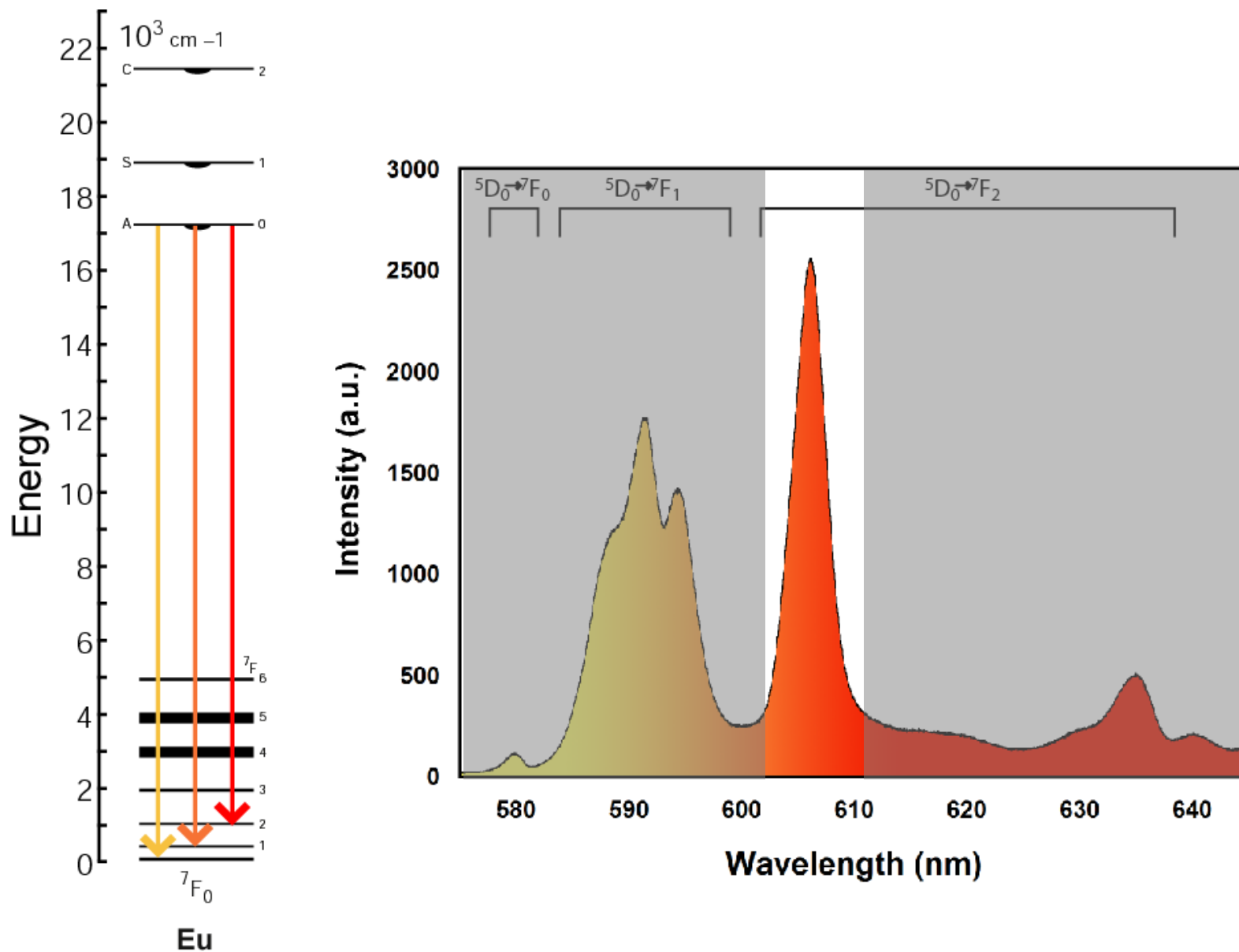
Temperature Sensing Using Luminescence Lifetimes

10 micron sensor layer on EB-PVD coating

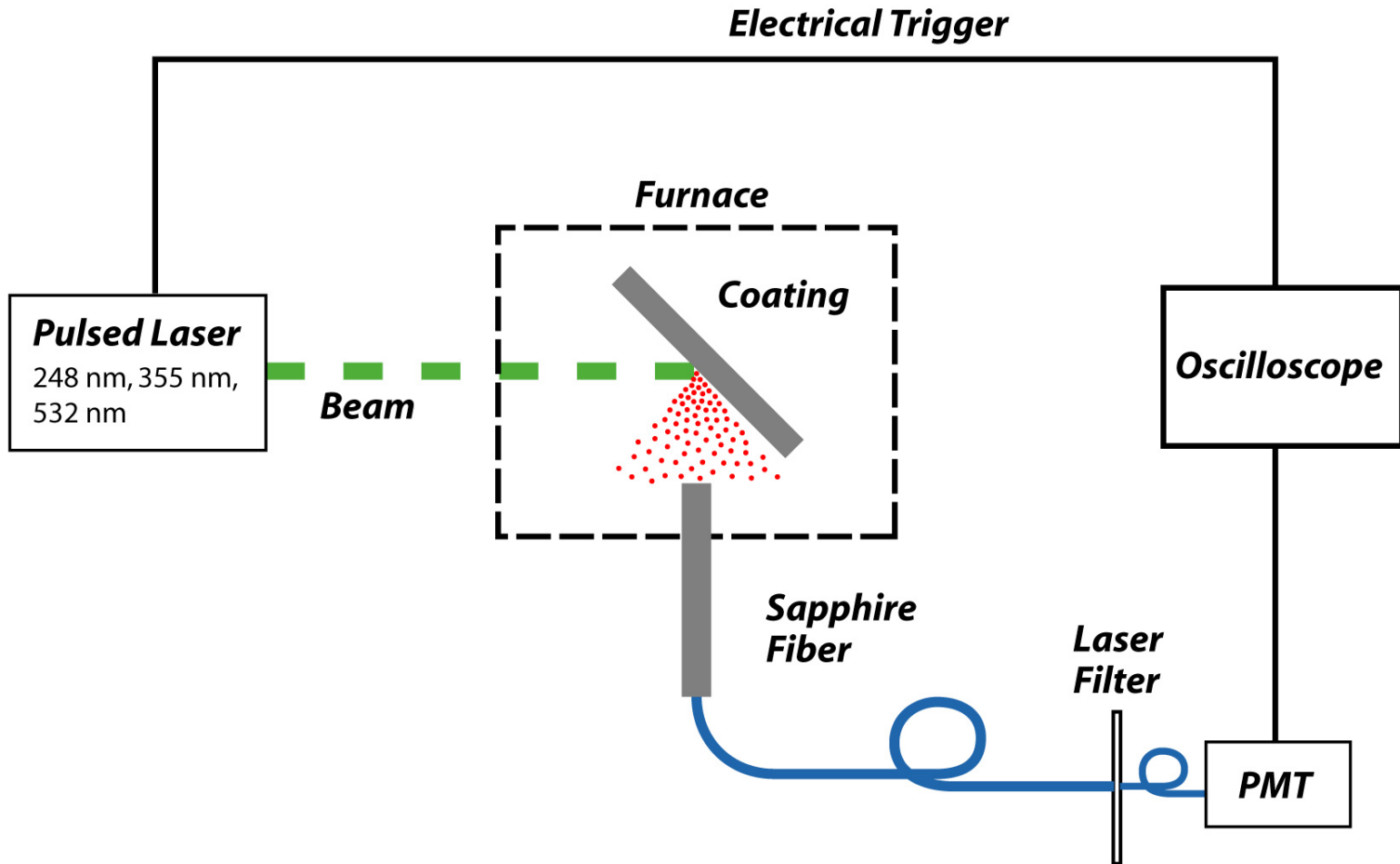


Calibration of luminescence lifetime provides basis for temperature measurements on engine components

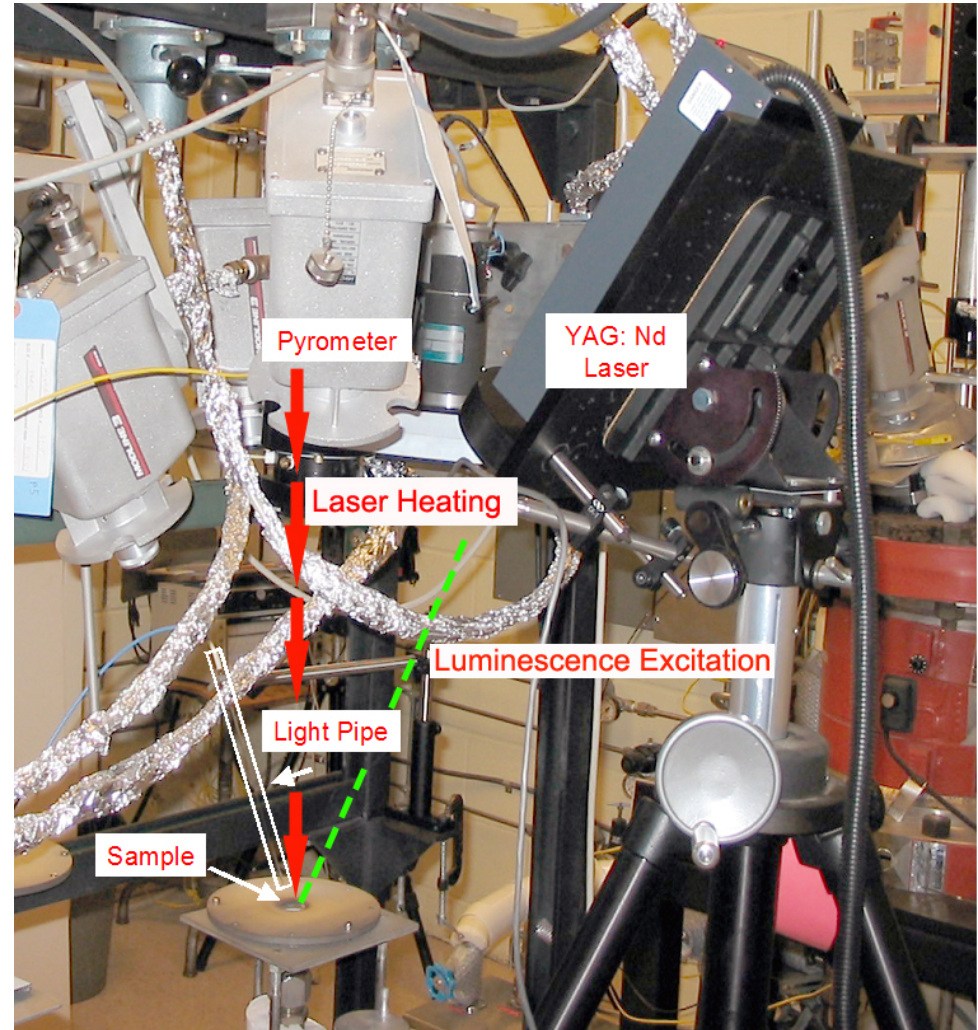
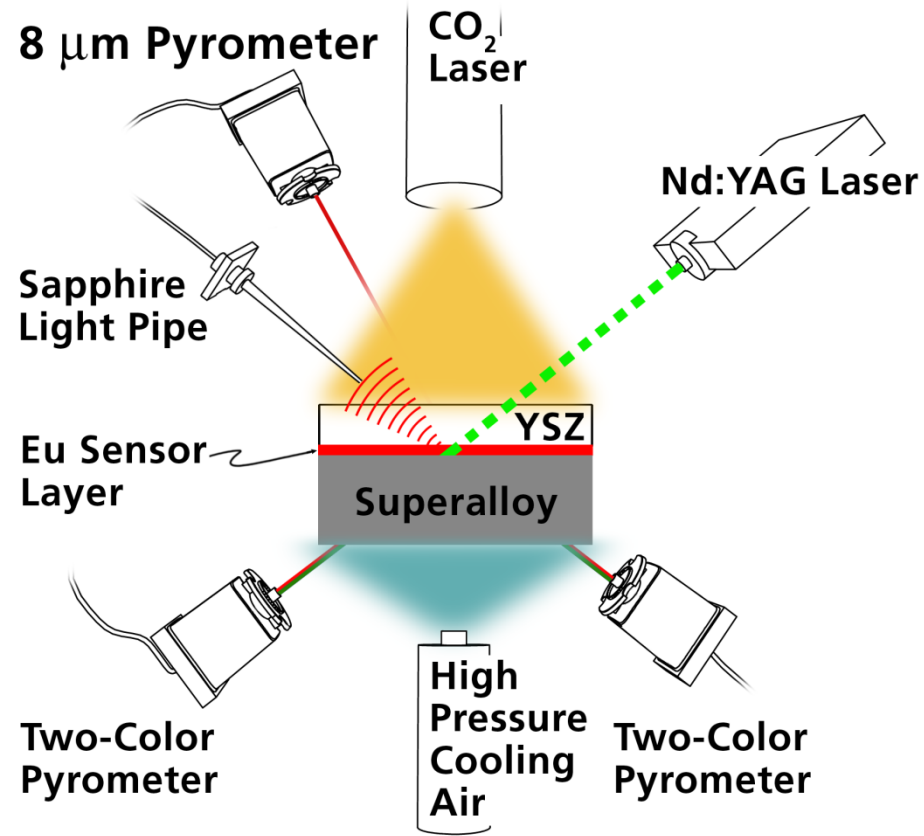
Major Luminescence Transitions in Eu^{3+} doped YSZ



Luminescence Decay Measurement System

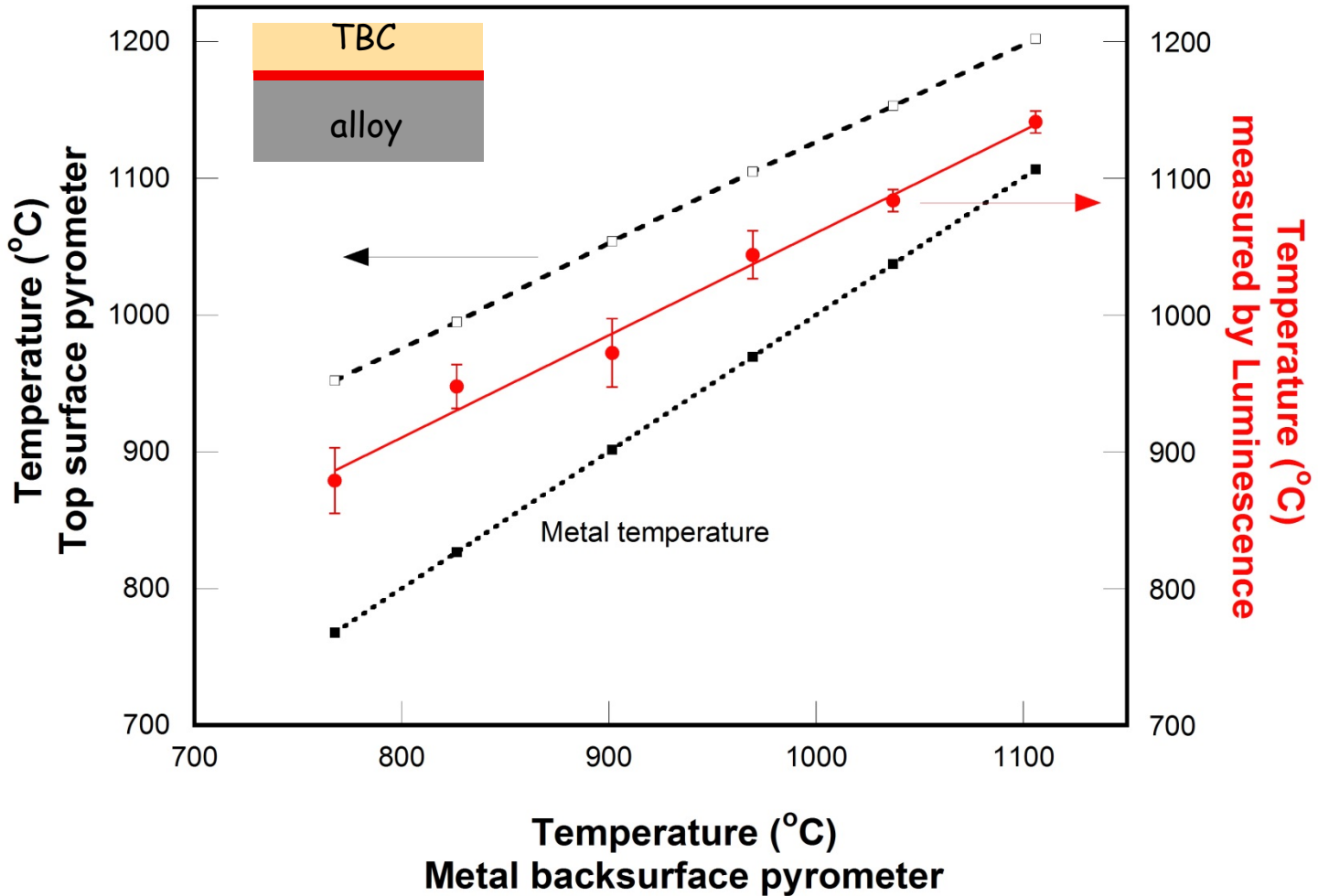


TBC Interface Temperature in a Thermal Gradient

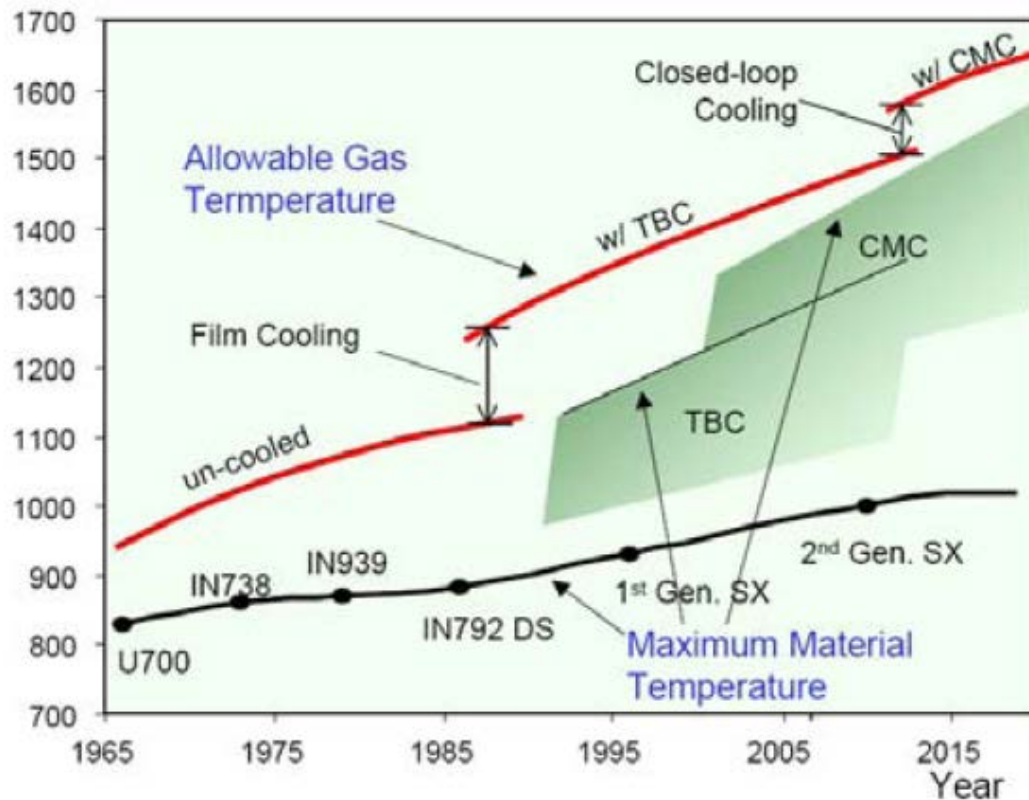


TBC Interface Temperature in a Thermal Gradient

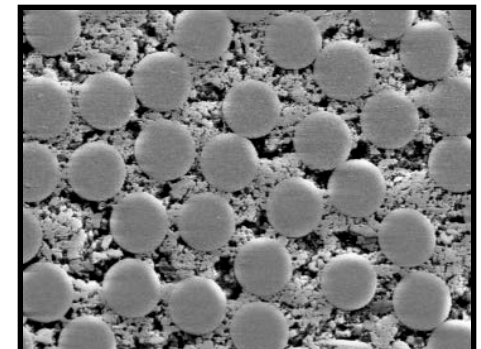
TBC thickness: 146 μm



The Next Materials Frontier: Ceramic Matrix Composites

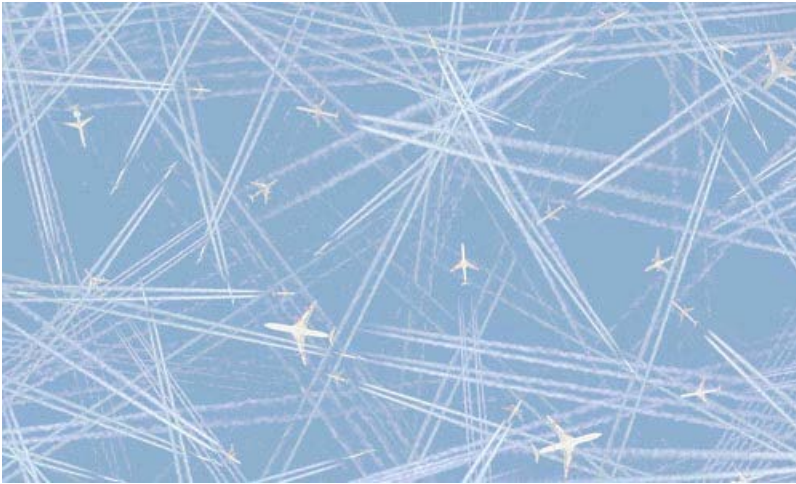


- High temperature capability
- High corrosion resistance
- Toughening mechanisms:
 - Microcracking
 - Fiber pull out
 - Crack bridging
- 90% cooling air reduction
- Reduced emissions



Future Limits To Gas Turbines: Unresolved Challenges

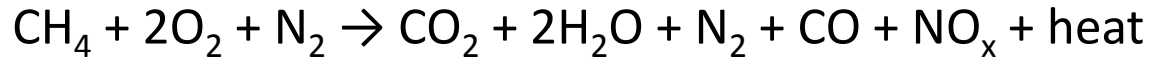
- Atmospheric pollution from engine exhausts
 - Chemical reactions produce NO_x -- will limit max combustion temperature



- 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

Combustion Creates NO_x Pollution

Combustion Reaction



Zeldovich Mechanism for NO_x Formation

- The chemical reactions that lead to thermal NO_x formation are:

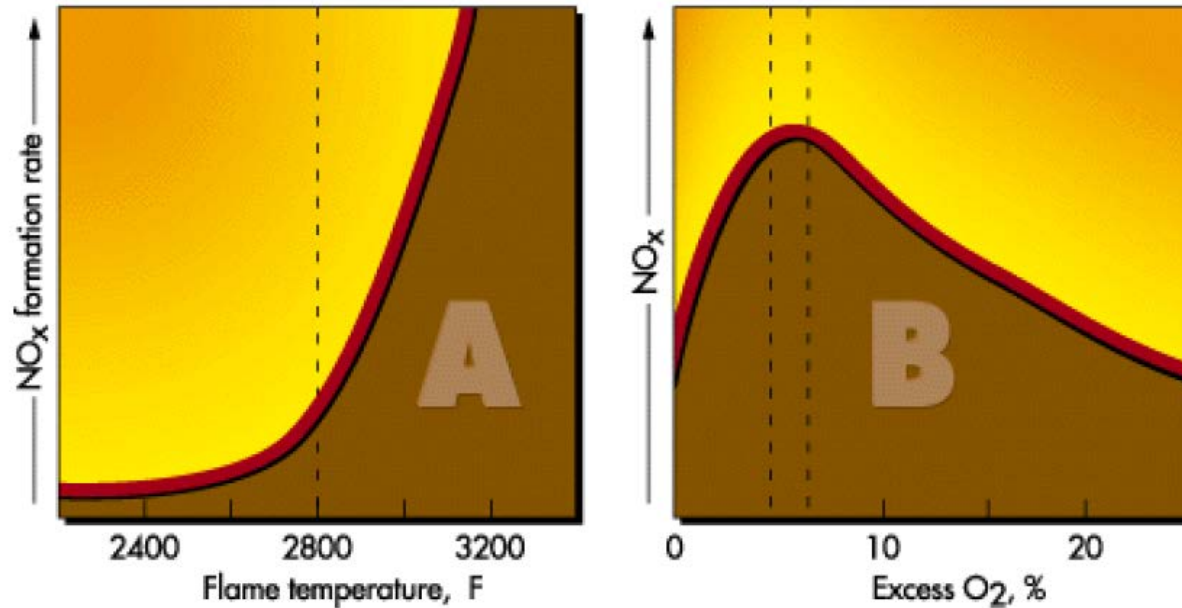


- In the first reaction di-nitrogen is attacked by O to form NO and a nitrogen radical
- The nitrogen radical then attacks O₂ to form another NO and regenerates the oxygen radical
- The overall reaction is given by, $\text{N}_2 + \text{O}_2 \leftrightarrow 2(\text{NO})$
-

Highly endothermic: $\Delta H_f = +90.4 \text{ kJ/mol}$

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

NO_x Emissions Depend on Combustion Temperature



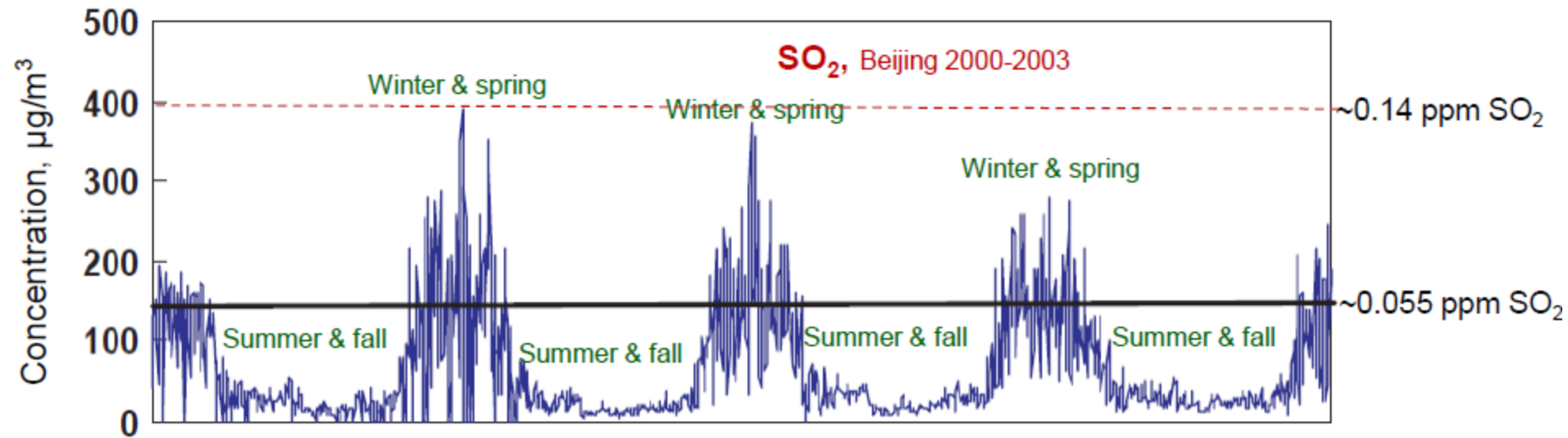
Wikipedia

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

Aerospace turbines might need their own high-temperature catalytic convertor

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.



SO₂ Corrosion Resistance

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.

Source: R. Sokhi, *World Atlas of Atmospheric Pollution*, Anthem Press, New York, 2008



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

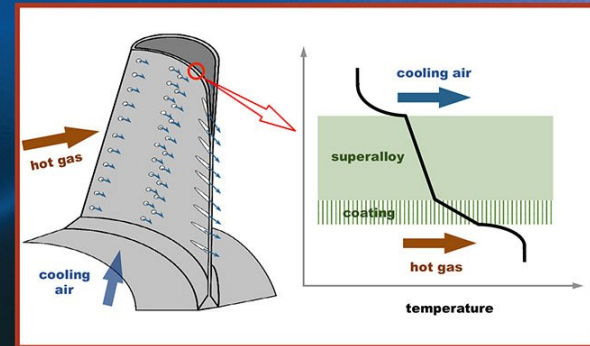
Want to Know More ?



clarke@seas.harvard.edu

Turbine Aerodynamics, Heat Transfer, Materials, and Mechanics

Edited by
Tom I-P. Shih
Vigor Yang



PROGRESS IN ASTRONAUTICS AND AERONAUTICS

Timothy C. Lieuwen, Editor-in-Chief
Volume 243