Evaluating Coatings for Current and Future Service

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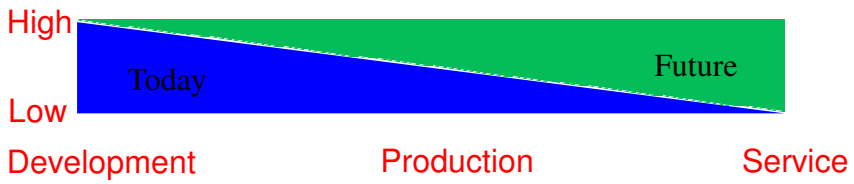
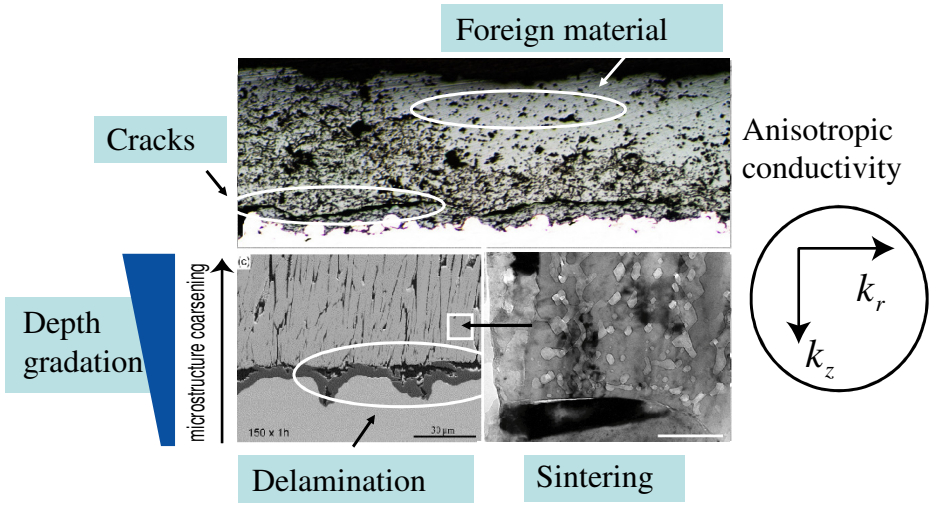
University Turbine System Research Program
(SCIES Project 07-01-SR125)

Use of thermal property measurement to evaluate coatings

- Usage:



Coatings with complex thermal features



Outline

- Phase of Photo-Thermal Emission Analysis (PopTea)
  - Principles
  - Strengths and limitations
- Advances made to the measurement
  - 2D-heat spreading model for thick coatings
  - Subsystem model for coated structures with thin walls
- Advances in characterization of TBCs
  - High temperature evolution of coatings
  - Impact of surface deposits of foreign material
  - Impact of infiltration of foreign material

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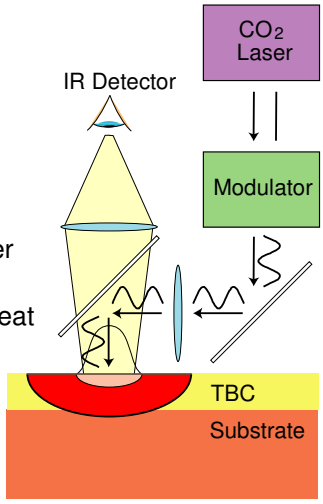
Phase of Photo-Thermal Emission Analysis (PoPTEA)

- What is it?
  - Nondestructive measurement of coating (thermal) properties
- How does it work?
  - Interrogates thermal emission of coating heated with modulated laser
  - Frequency domain
  - Phase of emission dependent on heat transport through coating
  - No sample preparation needed

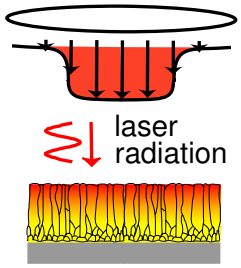


Heat transfer 1-D (thin coat) model

Phase of temperature field has …

1 controlled dependency …

Thermal penetration: (laser frequency) $\ell = \frac{\sqrt{[\alpha]_{coat}/(2\pi f)}}{L}$



3 additional dependencies …

Laser penetration: $\Lambda = \frac{\delta_{opt}}{L}$

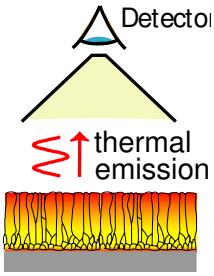
Interface diffusivity contrast: $a_{sub} = \sqrt{\frac{[\alpha]_{sub}}{[\alpha]_{coat}}}$

Interface effusivity contrast: $\gamma = \sqrt{\frac{[k\rho C]_{sub}}{[k\rho C]_{coat}}}$

2 thermal properties … $[k]_{coat}$, $[\rho C]_{coat}$

Phase detection model (radiation model)

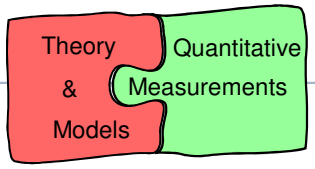
- Optically thin coating ($a_\lambda L$<<1)
  - for interrogation at 5µm



$$\textbf{emmision} = \Sigma_\lambda \underbrace{I_{b,\lambda}(1)}_{\text{from interface}} + 4\underbrace{\int_0^1 I_{b,\lambda}(z)dz}_{\text{from topcoat}}$$

- Phase dependence on one variable:

$$\Sigma_1 = \frac{\varepsilon_{1,\lambda} \leftarrow substrate}{a_\lambda L \underbrace{\leftarrow coating}_{\text{sources of emission}}}$$

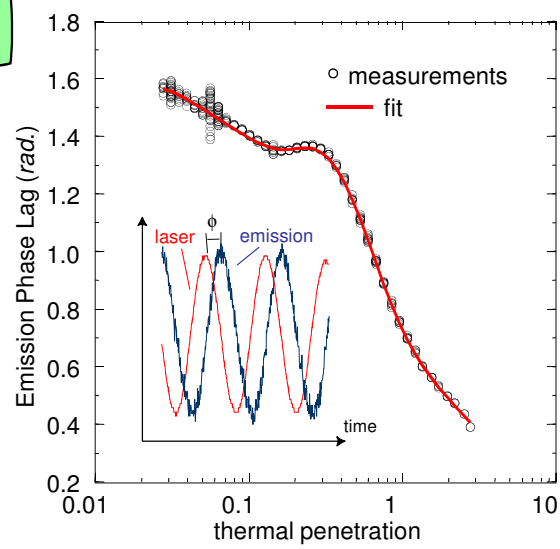


$$\Lambda = \frac{\delta_{opt}}{L}$$

$$a_{sub} = \sqrt{\frac{[\alpha]_{sub}}{[\alpha]_{coat}}}$$

$$\gamma = \sqrt{\frac{[k\rho C]_{sub}}{[k\rho C]_{coat}}}$$

$$\Sigma_1 = \frac{\varepsilon_{1,\lambda}}{a_\lambda L}$$



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PopTea, advantages …

- No calibration of q for laser heating
- Front surface interrogation
- Conductivity and heat capacity measurements possible
- No optical coatings
- Measurements can be done on engine hardware

PopTea, limitations

- Requires substrate backing
  - as a heat sink
  - for thermal contrast (to determine of coating effusivity)
- For *k and ρ Cp* measurements thermal contrast with substrate can not be too large
  (for example aluminum is a bad substrate material)
- Coating thickness is required for thermal property measurements

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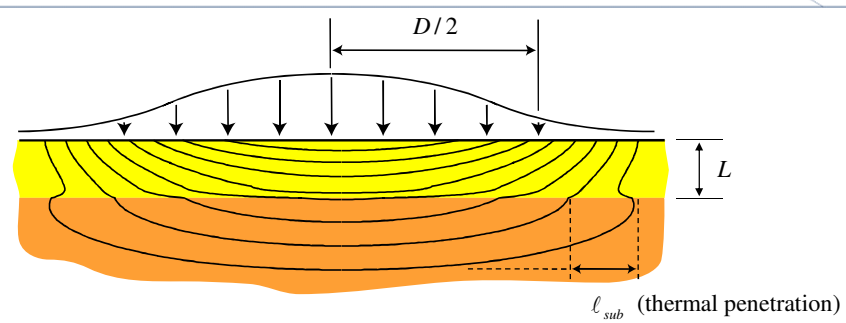
Thick coatings

Condition for 2-D spreading



What is important ? → D / ℓ_{sub} (not D / L)

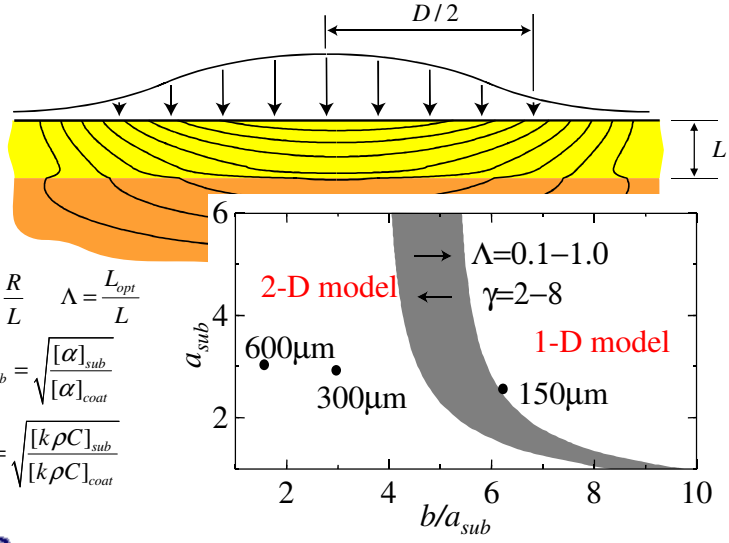
$$\ell_{sub} = \sqrt{\frac{[\alpha]_{sub}}{2\pi f}}$$

← substrate diffusivity

← 1/timescale provided by laser

Thick coatings

Condition for 2-D spreading



$$b = \frac{R}{L} \qquad \Lambda = \frac{L_{opt}}{L}$$

$$a_{sub} = \sqrt{\frac{[\alpha]_{sub}}{[\alpha]_{coat}}}$$

$$\gamma = \sqrt{\frac{[k\rho C]_{sub}}{[k\rho C]_{coat}}}$$

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Differential PopTea measurements

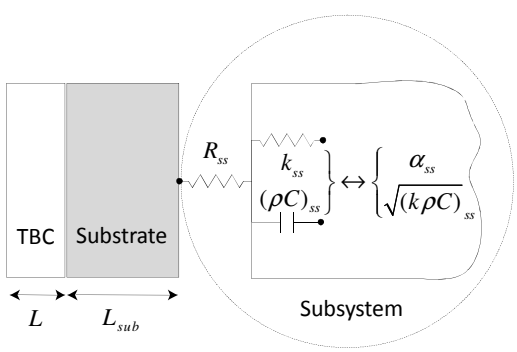
- two measures of thermal penetration
  - one in the coating
  - one in the substrate material

$$\ell_{sub} = \sqrt{\frac{\alpha_{sub}}{\alpha_{coat}}}\,\ell_{coat}$$

- For typical coating-superalloy combinations, this multiplier might range between 2 and 3.
- The assumption of a semi-infinite substrate material requires the substrate material be at least three times as thick and the TBC.

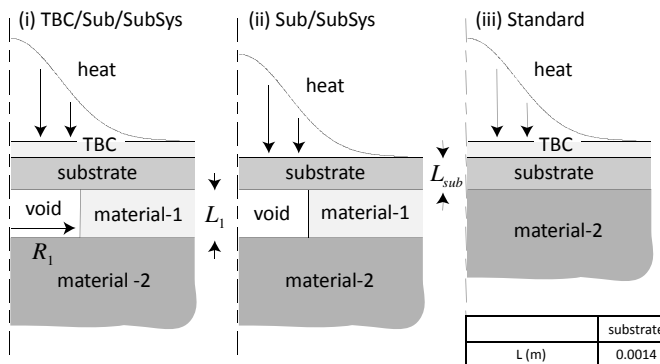
Differential PopTea measurements

- Subsystem model:



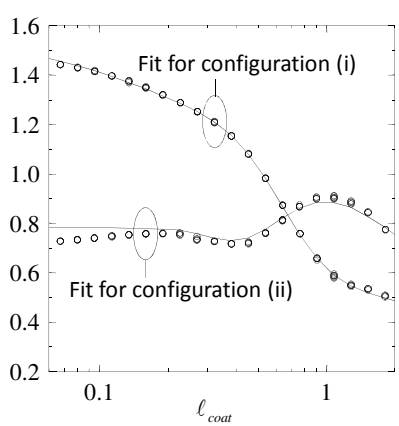
Differential PopTea measurements

Three configurations of the PopTea measurement.



	substrate	material-1	material-2
L (m)	0.0014	0.003	---
k (W/m²/K)	9.8	180	15
rCp (J/kg/K)	3.6 x10⁶	2.4 x10⁶	3.8 x10⁶
R1 (m)	---	0.0033	---

Differential PopTea measurements



Measurement results

	dPopTea (a) & (b)	PopTea (c)
α (m²/s)	2.75 x10⁻⁷	2.78 x10⁻⁷
k (W/m²/K)	0.810	0.885
ρC (J/kg/K)	2.95 x10⁶	3.19 x10⁶

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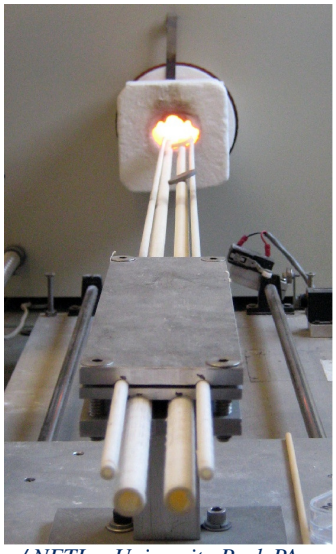
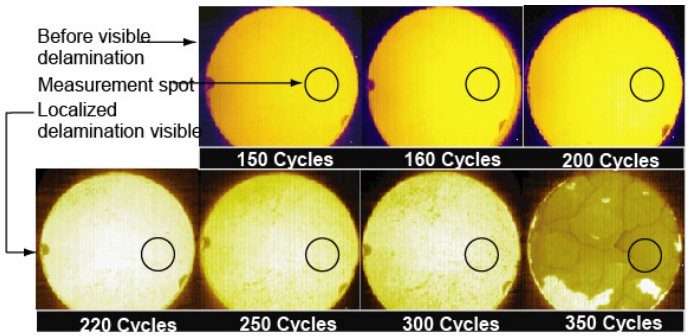
High temperature evolution of coatings

- How do coating thermal properties change with high temperature exposure?

- 7YSZ EB-PVD TBCs deposited on platinum-modified nickel-aluminide coated single crystal superalloys provided by Howmet Corporation
- Thermal cycling between room temperature and 1150 C until failure.
- Each cycle consisted of a 1-h exposure and 10-min cooling to room temperature. Heating and cooling rates ~ 200 C/min.

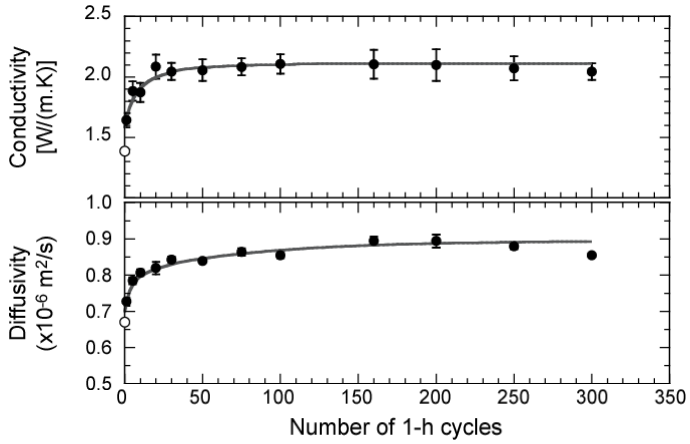


Various stages of thermal cycling



- Infrared camera images showing progression of interface delamination

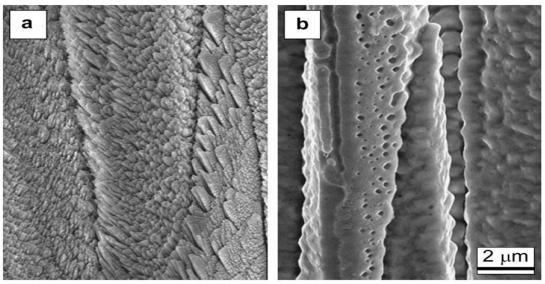
Evolution of thermal properties



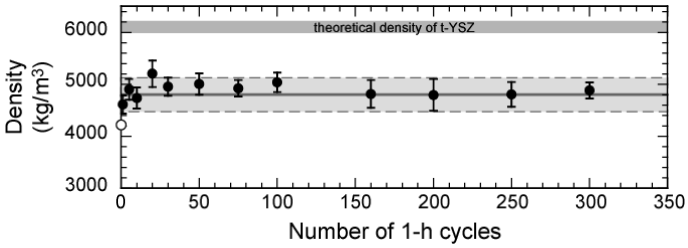
- Catastrophic spallation of the coating was preceded by a small (apparent) drop in the coating thermal conductivity/diffusivity.

Evolution of thermal properties

- Evolution of thermal properties
  - Morphology of as-deposited condition (a) and after 350 1 h cycles at 1150C (b).

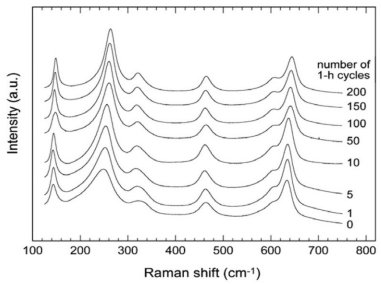


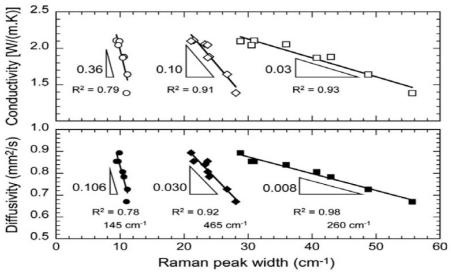
Evolution of thermal properties



- No significant change in density with heat treatment
- Implies changes in the thermal diffusivity / conductive result from changes in pore geometry (not volume fraction)

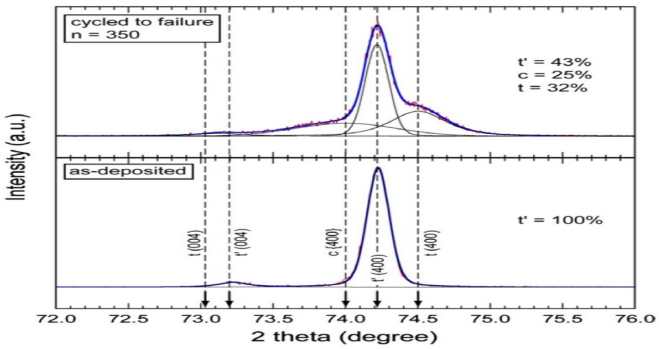
Evolution of thermal properties





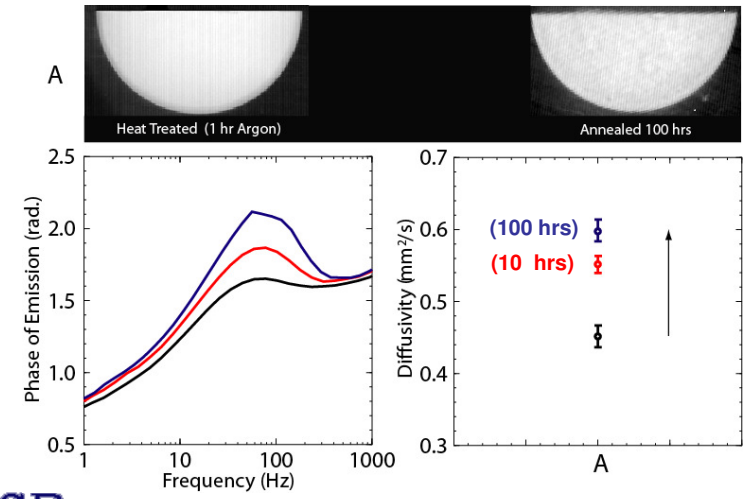
- The width of the Raman bands correlates with both thermal diffusivity and thermal conductivity.
  - suggests the increase in thermal conductivity may also be influenced by a decreased in phonon scattering by defects

Evolution of thermal properties



- X-ray diffraction shows 25% of the coating had transformed to the cubic phase
  - Taking $k_{tetragonal}$ = 3.0 W/m/K and k_{cubic} = 2.6 W/m/K, the bulk conductivity of this mixture (75% tetragonal + 25% cubic zirconia) is calculated to be 2.9 W/m/K.

Isothermal aging at 1150 C



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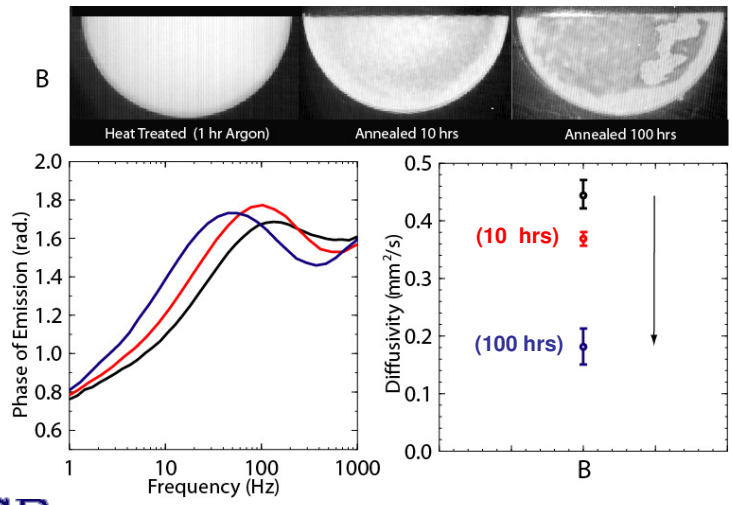
Isothermal aging at 1150 C



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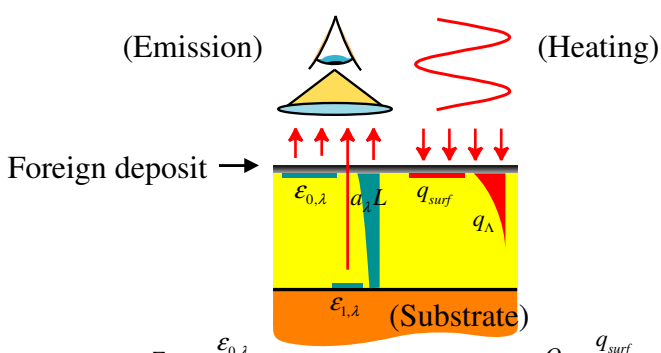
Foreign surface deposits

New Optical Model

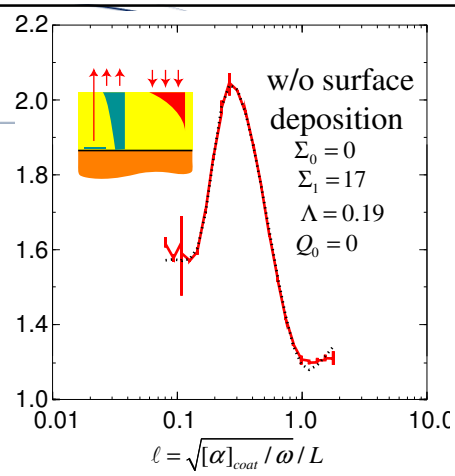


$$\Sigma_{0,\lambda} = \frac{\varepsilon_{0,\lambda}}{a_\lambda L} \qquad Q_0 = \frac{q_{surf}}{q_\Lambda}$$

$$\Sigma_{1,\lambda} = \frac{\varepsilon_{1,\lambda}}{a_\lambda L} \qquad \Lambda = \frac{L_{opt}}{L}$$

Foreign surface deposits

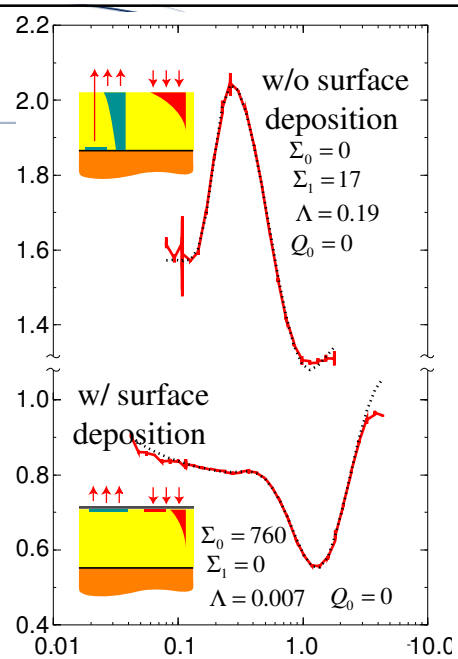
Test specimen:
7YSZ EB-PVD ~150 µm on nickel-based superalloy



Foreign surface deposits

Test specimen:
7YSZ EB-PVD ~150 µm on nickel-based superalloy

with ~750nm Pt coating

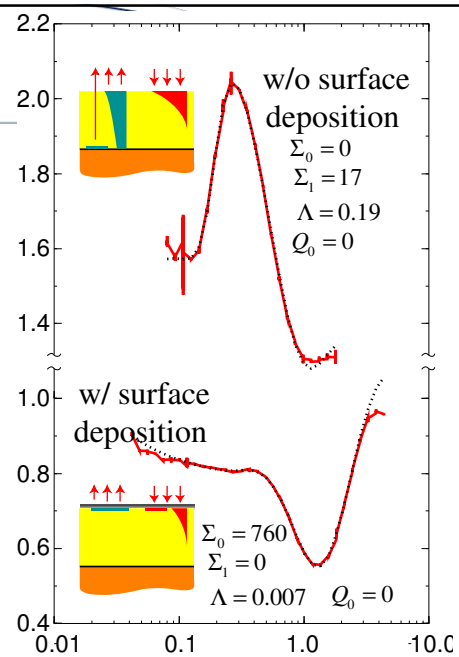


Foreign surface deposits

Test specimen:
7YSZ EB-PVD ~150 µm on nickel-based superalloy

Change in results as a consequence of surface deposit:

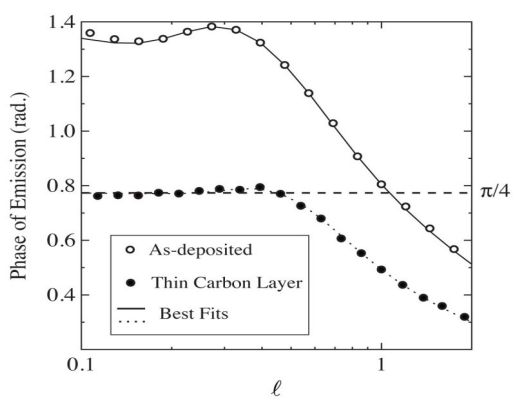
thermal diffusivity: 0%
thermal conductivity: 15%
volume specific heat: 15%



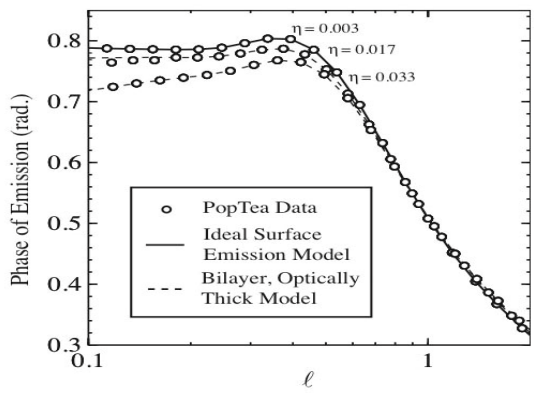
$\ell = \sqrt{[\alpha]_{coat} / \omega} / L$

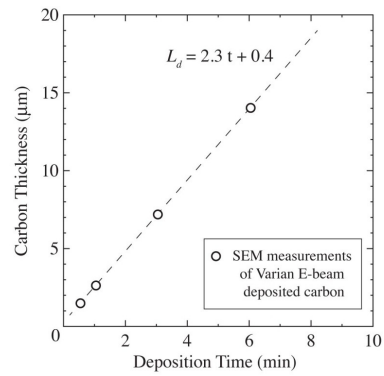
Thin Carbon deposit

Test specimen:
7YSZ APS ~ 300 µm on nickel-based superalloy



Thick Carbon Deposit





Bilayer Model

EBVD Sample						
	PopTea Model				Bilayer Model	
η	0	0.003	0.017	0.033	0.017	0.033
α (× 10^{-7})	3.55	3.52	3.47	3.36	3.54	3.57
k	0.84	0.91	0.99	0.98	0.94	0.93
ρC_p (× 10^{6})	2.36	2.59	2.85	2.91	2.65	2.61

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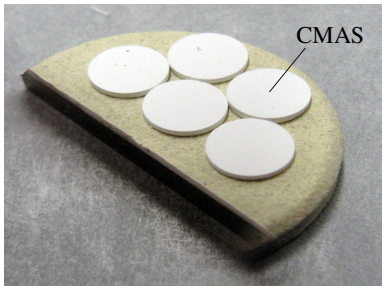
Infiltration of CMAS (Calcium-Magnesium-Aluminum-Silicates)



- What is the impact of CMAS infiltration on thermal properties of coating
- Coating: 300 µm 7% wt. yttria-stabilized zirconia air plasma spray

Composition of CMAS:

Materials	CaO	MgO	Al_2O_3	SiO_2
Mol %	35	10	7	48
Cp (J/kg/K)	806.9	1000.9	864.1	815.4
Cp (J/kg/K)	835			

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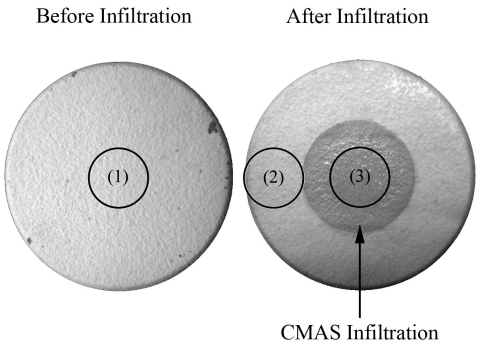

CMAS infiltration:

- CMAS disc 80 µm thick and 1 cm diameter
- Heated to 1300ºC to melt CMAS
- Cooled slowly (2ºC/min) for temperatures below 1000ºC

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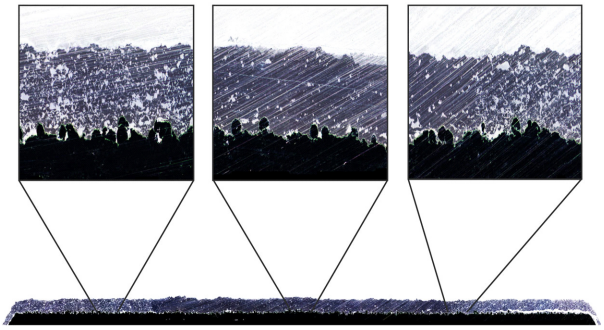

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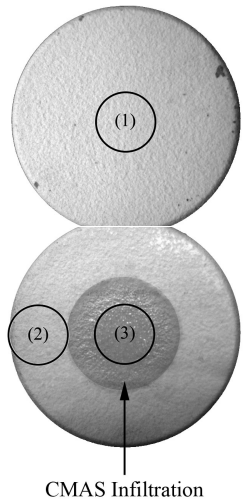
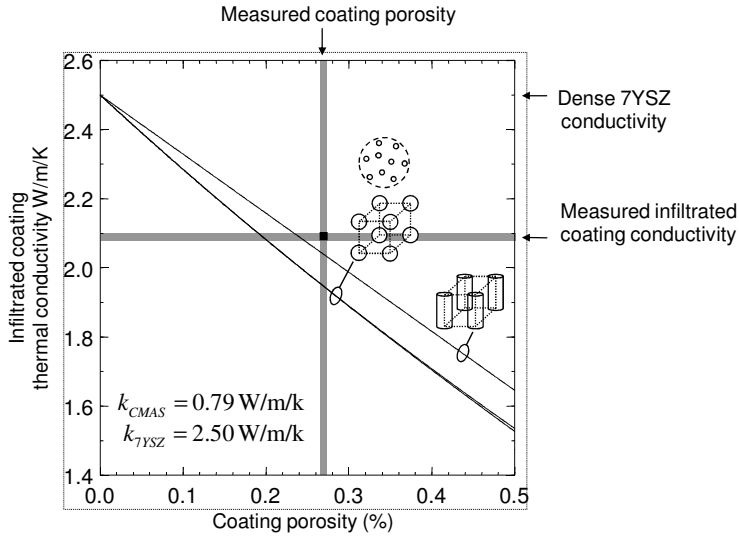


	Measurement (1) *Baseline*	Measurement (2) *Annealed 1300ºC*	Measurement (3) *Infiltrated*
α (m^2/s)	4.46×10^{-7}	4.46×10^{-7}	8.46×10^{-7}
k (W/m/K)	0.91	0.88	2.09
ρC_p ($J/cm^3/K$)	2.04	1.94	2.47
C_p (J/kg/K)	475	475	
ρ (kg/m^3)	4300	4100	
ϕ	**27%**	31%	

Effective medium theory



Conclusion (CMAS)

- Effect of the CMAS infiltration can be measured on thermal barrier coatings
- Thermal conductivity more then doubled
- Heat capacity increased by over 20%
- Effective medium theory suggests through coating connectivity of CMAS is important to the large rise in thermal conductivity

Thanks