THERMAL PROPERTY MEASUREMENTS OF COATINGS

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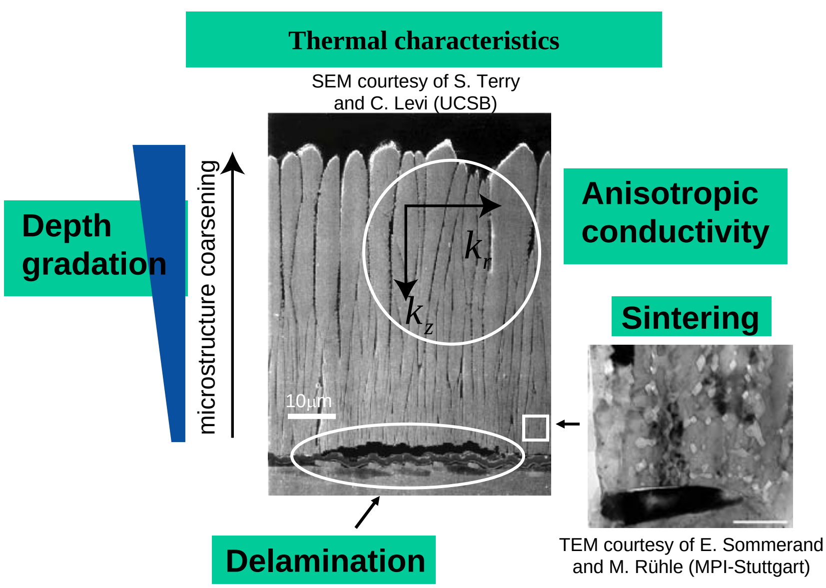


What you will learn about coating thermal property measurements

- Commonality of measurements
- Typical implementations
- UCSB effort

Heat Transport

$$\underbrace{\rho C_p \frac{\partial T}{\partial t}}_{\textbf{Heat accumulation}} = \underbrace{\vec{\nabla}\left(k\,\vec{\nabla} T \right)}_{\textbf{Net transport}} + \underbrace{G}_{\textbf{Heat source}}$$

T = temperature

G = heating source (laser …)

Material properties:

ρC_p = volumetric heat capacity (density x specific heat)

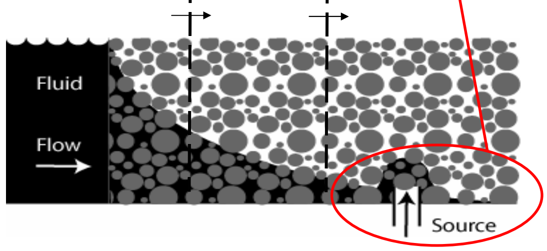
k = thermal conductivity

Heat Transport (2)

Heat accumulation — **Net transport** — **Heat source**

$$\overbrace{\rho C_p \frac{\partial T}{\partial t}}^{\text{Heat accumulation}} = \overbrace{\frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right)}^{\text{Net transport}} + \overbrace{G}^{\text{Heat source}}$$

$$-k\frac{\partial T}{\partial x} \quad \Big| \quad \rho C_p \frac{\partial T}{\partial t} \quad \Big| \quad -k\frac{\partial T}{\partial x}$$



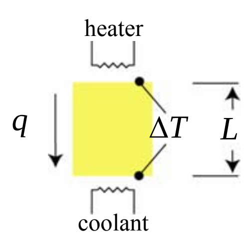
Steady Heat Transport w/o Source

$$\cancel{\rho C_p \frac{\partial T}{\partial t}}^{\,0} = \vec{\nabla}\left(k\vec{\nabla}T\right) + \cancel{G}^{\,0}$$

1-D soln: $$-k\frac{dT}{dx} = q \quad \text{(const. heat flux)}$$

Thermal conductivity measurements based on:

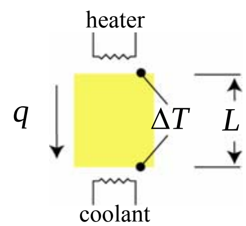
$$k = \frac{q}{\Delta T / L}$$



Steady Heat Transport w/o Source

Thermal conductivity measurements based on:

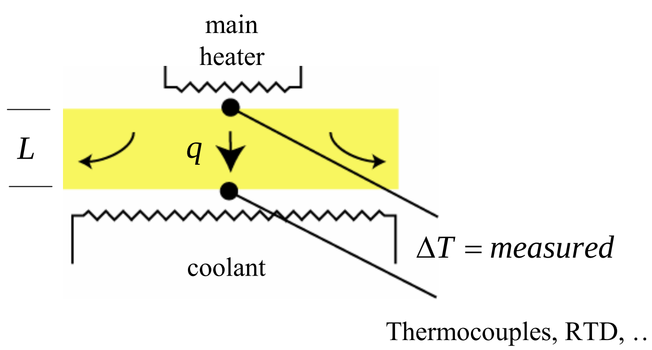
$$k = \frac{q}{\Delta T / L}$$



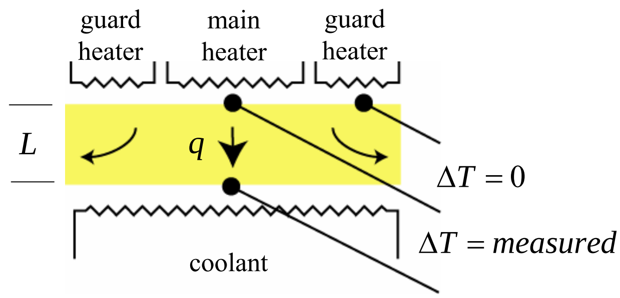
Involves absolute measurements of:

q = heat flux
ΔT = T change (two points of T observation)
L = length

Problem of heat spreading in measurements

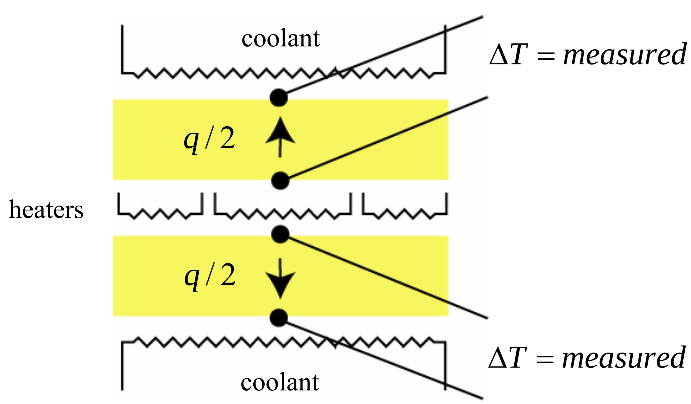


One-sided Guarded Hot Plate (GHP)

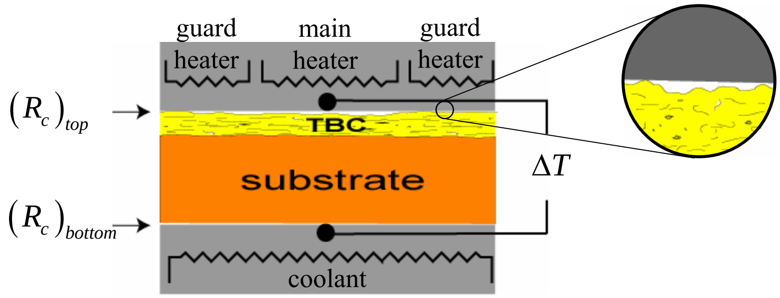


The principle of the GHP is to direct all the heat generated by the main heater to flow axially through the specimen

Two-sided Guarded Hot Plate



GHP Applied to Coatings



$$\frac{\Delta T}{q} = \underbrace{\left(\frac{L}{k}\right)_{COAT}}_{0.0014} + \underbrace{\left(\frac{L}{k}\right)_{SUB}}_{0.00017} + \underbrace{(R_c)_{top} + (R_c)_{bottom}}_{0.00025}$$

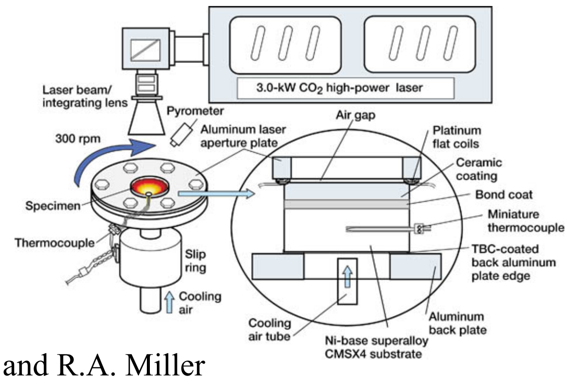
1mm APS coating on 3mm 410 SS substrate
Slifka et. al. J. Thermal Spray Tech. v.7(1) p.43

(in 50 kPa helium ~ 5.75x that of air)

Steady measurements

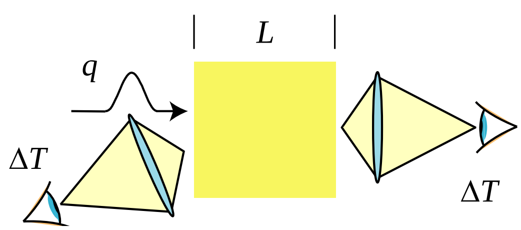
- Two probes for ΔT required (for absolute measurement)
- Magnitude of heat flux needs quantification
- For coatings, the thermal resistance of the coating must be large compared with the substrate and contact resistances

NASA Glenn's *Laser high heat flux rig*



D. Zhu and R.A. Miller

During the test, the ceramic surface and the metal backside temperatures are measured by infrared pyrometers. The metal substrate midpoint temperature can be obtained by an embedded miniature type-K thermocouple.



- *Optical heating* q and *sensing* of ΔT
  - Optical *pump and probe* strategies replace issues of thermal contact resistance with issues of optical penetration
  - Optical coatings can be used to "control" penetration and judicious spectral-wavelength/material selection
  - Particularly attractive if absolute measurements of q and ΔT not required

Measuring ΔT …

- Contact methods
  - Thermocouple, RTD, …
  - ☺ Calibration for absolute ΔT
  - ☹ Interfacial thermal resistances
    - Mechanical finishing
    - Thermal pastes, high k gasses …
- Non-contact methods
  - Optical probes (e.g. pyrometers)
  - ☹ Calibration for absolute ΔT
    - Probe/material combination
  - ☹ Optical penetration
    - Wavelength/material choices
    - Optical coatings

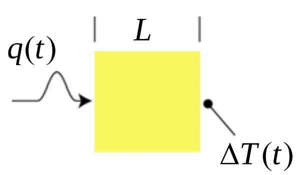
Transient Heat Transport w/o Source

$$\rho C_p \frac{\partial T}{\partial t} = \vec{\nabla}\left(k\vec{\nabla}T\right) + \cancel{G}^{\,0}$$

1-D soln: $\Delta T = f(t, x, \alpha)$ $\quad \alpha = \dfrac{k}{\rho C_p}$

Thermal diffusivity measurements based on:

$$\alpha = f(t, L, \Delta T)$$



Transient Heat Transport w/o Source

Involves absolute measurements of:

t = time

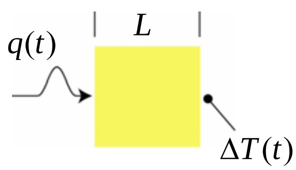
L = length

and … relative measurement of:

ΔT = temperature

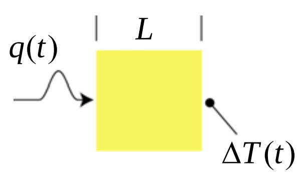
Thermal diffusivity measurements based on:

$$\alpha = f(t, L, \Delta T)$$



Thermal diffusivity measurements based on:

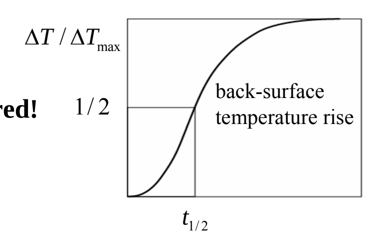
$$\alpha = 1.37 L^2 / (\pi^2 t_{1/2})$$



Involves absolute measurements of:

$t_{1/2}$ = time to half back-surface temperature rise

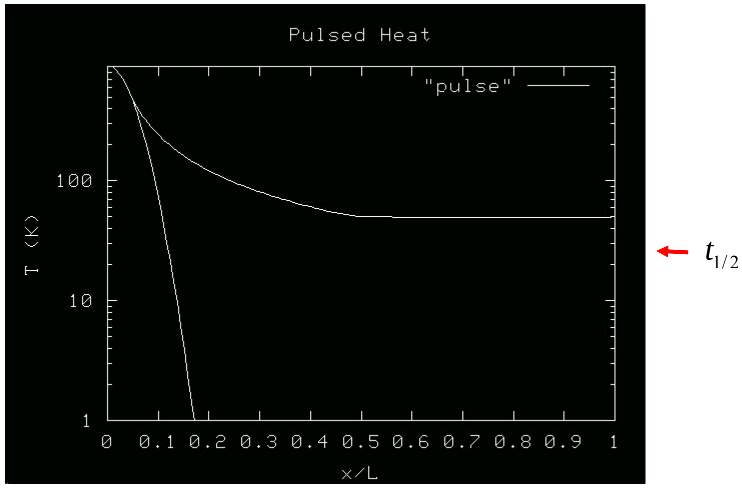
L = length



Detector calibration is not required!

Magnitude of q not required!

Temperature Pulse

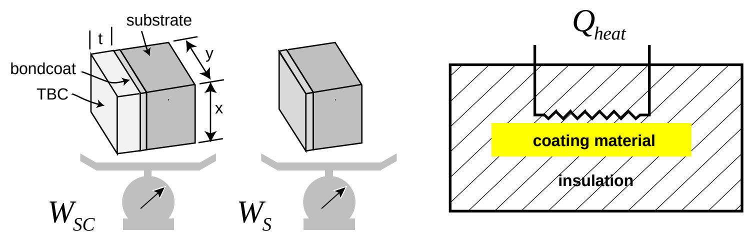


Transient measurements

- One ΔT probe required (for relative measurement)
- ΔT probe *could* be at either front or back surface
  - back surface provides better sensitivity
- Magnitude of heating need not be quantified (for diffusivity measurements)
- A known length scale is required (for diffusivity measurements)

Finding *k* from diffusivity measurements

$$k = \alpha \rho C_p$$



$$\rho = \frac{W_{SC} - W_S}{t \cdot x \cdot y}$$

$$C_p = \frac{Q_{heat}}{m \Delta T}$$

To remember …

- Steady-State measurements
  - ☺ Determines conductivity
  - ☺ Easily quantifications:
    - Length
  - ☹ Difficult quantifications:
    - **Absolute** heat flux
    - **Absolute** temperature change
  - ☹ Two points of T observation
    - Destructive
- Transient measurements
  - ☹ Determines diffusivity (usually, with phase meas.)
  - ☺ Easily quantifications:
    - Length
    - Time
    - **Relative** temperature change
  - ☺ One point T observation
    - *Potentially* nondestructive

Periodic Transient Measurements

- Periodic heating a common strategy. Good for …
  - Signal averaging
  - Thermal penetration depth control
- Involves a quasi- steady state solution to the temperature field

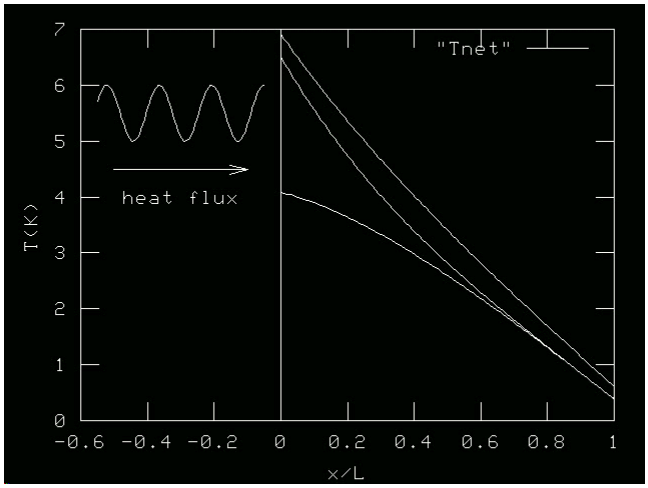
Periodic Heat transfer

$$(I_s + I_t) = -k\frac{\partial T}{\partial r}$$

$$\partial T / \partial t = \alpha \nabla^2 T$$

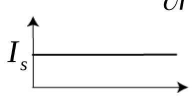
$$T = T_b(?)$$

Transient Temperature



Superposition $T = T_s + T_t$

$$I_s = -k\frac{\partial T_s}{\partial r}$$

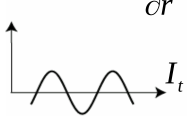


$$\partial T_s / \partial t = \alpha \nabla^2 T_s$$

$$T_s = ?$$

+

$$I_t = -k\frac{\partial T_t}{\partial r}$$



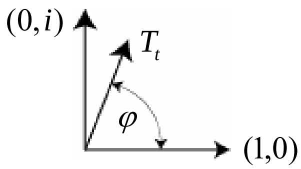
$$\partial T_t / \partial t = \alpha \nabla^2 T_t$$

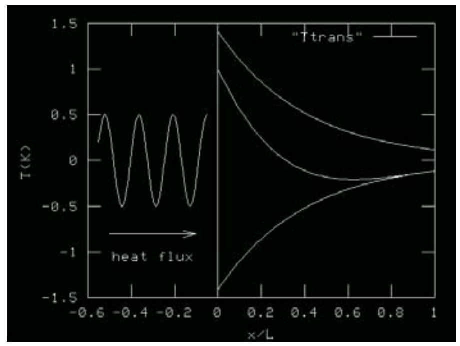
$$T_t = ?$$

The transient temperature field:

Described by:

1) An amplitude
2) A phase

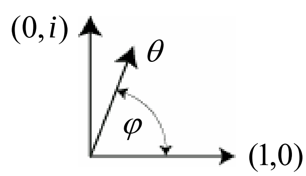




Complex Temperature

$$PDE: \quad \frac{\partial T_t}{\partial t} = \alpha \frac{\partial^2 T_t}{\partial x^2}$$

$$T_t(r,\omega,t) = \mathrm{Re}\{\theta(x,\omega)\exp(i\omega t)\}$$



Transforms governing equation into:

$$ODE: \quad \alpha \frac{\partial^2 \theta}{\partial x^2} - i\omega\theta = 0$$

$\theta(x,\omega)$ is spatial description of the amplitude and phase of the transient temperature field

Analytic Solutions (semi-infinite)

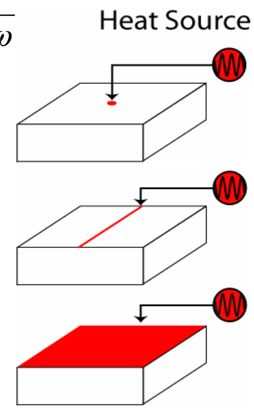
$$p = (1+i)/L_{th}, \quad L_{th} = \sqrt{2\alpha/\omega}$$

$$\theta_{point}(r,\omega) = \frac{P}{2\pi}\frac{\exp(-pr)}{rk}$$

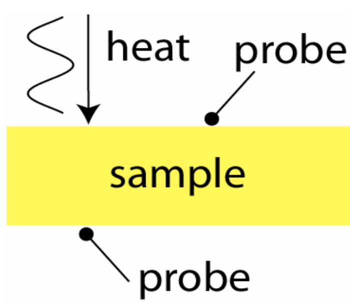
$$\theta_{line}(r,\omega) = \frac{P}{\pi L}\frac{K_o(pr)}{k}$$

$$\theta_{plane}(r,\omega) = \frac{P}{A}\frac{\exp(-pr)}{pk}$$

(P = power, A = area)

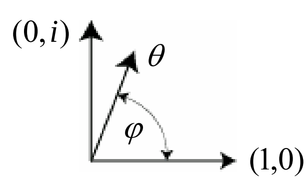


Probing at r ≠ 0



Measurement:

1) **Amplitude**
2) **Phase**

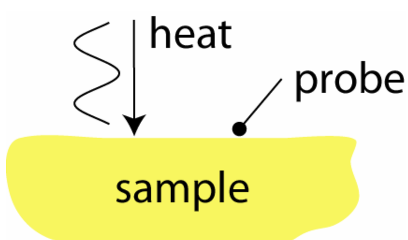


Semi-Infinite Space/Phase Relations

	$G(r,\omega)=\frac{\partial \ln\theta}{\partial \ln r}=\frac{r}{\theta}\frac{\partial\theta}{\partial r}$	$H(r,\omega)=\frac{\partial \ln\theta}{\partial \ln\omega}=\frac{\omega}{\theta}\frac{\partial\theta}{\partial\omega}$
plane	$-pr$	$-0.5(pr+1)$
Line	$-pr\frac{K_1(pr)}{K_o(pr)}$	$-0.5pr\frac{K_1(pr)}{K_o(pr)}$
Point	$-pr-1$	$-0.5-pr$

$$p=(1+i)/L_{th},\quad L_{th}=\sqrt{2\alpha/\omega}$$

Probing at r ≠ 0



$$\theta_{\text{point}}=\frac{P}{2\pi rk}\exp\left(-\frac{(1+i)r}{\sqrt{2\alpha/\omega}}\right)$$

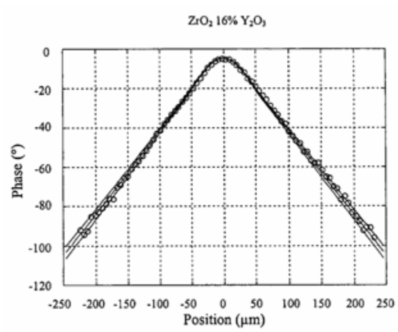
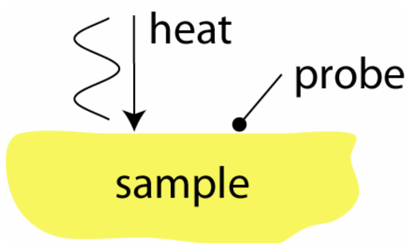


Fig. 1. Experimental phase-shift profile (data points represented by small circles) obtained on a 17.7 mol% $YO_{1.5}$ (16 wt% Y_2O_3) sample at f = 15 Hz. Simulations are shown for α values of 0.77, 0.82, and 0.87 mm^2/s, to indicate precision.

Bisson and Fournier, J. Am. Ceram. Soc. 83(8) 1993
(Laboratoire d'Optique Physique, Paris)

Probing at r $\neq$ 0



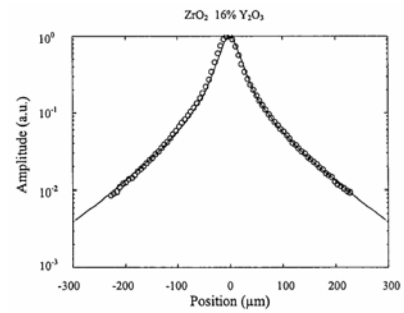
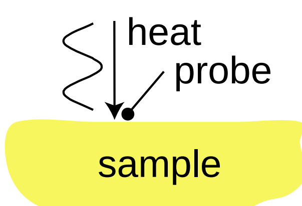


Fig. 2. Experimental amplitude profile (data points represented by small circles) obtained on the same 17.7 mol% $YO_{1.5}$ sample from Fig. 1 at f = 15 Hz, with a simulation for α = 0.82 mm^2/s.

$$\theta_{\text{point}} = \frac{P}{2\pi r k} \exp\left(-\frac{(1+i)r}{\sqrt{2\alpha / \omega}} \right)$$

Bisson and Fournier, J. Am. Ceram. Soc. 83(8) 1993

Probing at r = 0



Measurement:

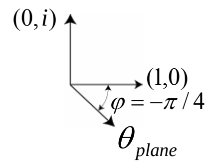
1) Amplitude

Probing at r ≈ 0 (semi-infinite soln.)

$$\theta_{\text{point}}(\omega) = \frac{P}{2\pi}\frac{(1+i)}{\sqrt{2}}k^{-1}\alpha^{-1/2}\omega^{1/2} + C$$

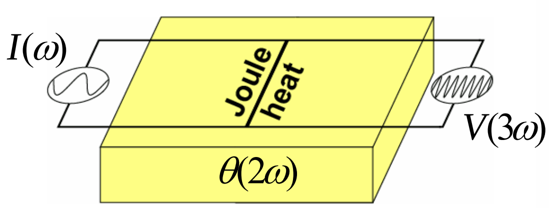
$$\theta_{line}(\omega) = \frac{-P}{2\pi L}k^{-1}\ln\omega + C$$ ⟵ **Notice independence on thermal diffusivity**

$$\theta_{plane}(\omega) = \frac{P}{A}\frac{1-i}{\sqrt{2}}k^{-1}\alpha^{1/2}\omega^{-1/2}$$



Notice: constant phase at r=0 for each case

3-Ω Method



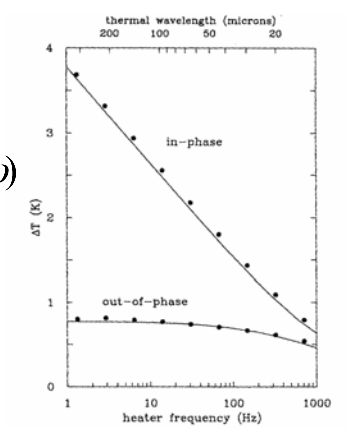
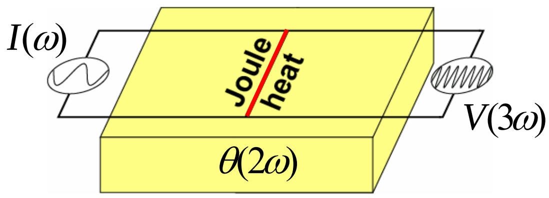


FIG. 6. Example of the temperature oscillations ΔT measured in the 3ω method at $T = 300$ K on a-SiO_2; ΔT has been separated into the amplitude of the in-phase and out-of-phase components. The slope of the in-phase ΔT versus the logarithm of the heater frequency gives the thermal conductivity, $\Lambda = 1.35\times10^{-2}$ W cm^{-1} K^{-1}. The solid lines are Eq. (8) using $\Lambda = 1.35\times10^{-2}$ W cm^{-1} K^{-1}, the measured linewidth $2b = 40$ μm, and the thermal diffusivity (see Ref. 22) of a-SiO_2, $D = 8.3\times10^{-3}$ cm^2 s^{-1}.

$$\theta_{line}(\omega) = \frac{-P}{2\pi L}k^{-1}\ln\omega + C$$

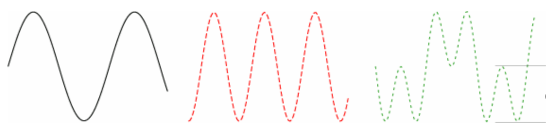
Cahill D.G. Rev. Sci. Instrum. 61(2) 802

3-Ω Method



$$V = IR \approx I\theta$$

$I(\omega)$ $\quad$ $\theta(2\omega) \propto I^2$ $\quad$ $V(3\omega) \propto I\theta - I$



$\propto \theta(2\omega)$

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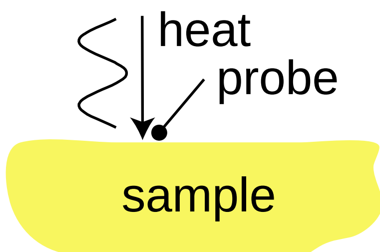
Probing at r = 0



Why is there no phase information for probe $r = 0$ location?

No length scale for thermal diffusion to interact with!

Moving probe introduces a length scale $r \neq 0$

Can coatings be measured using phase at $r = 0$?

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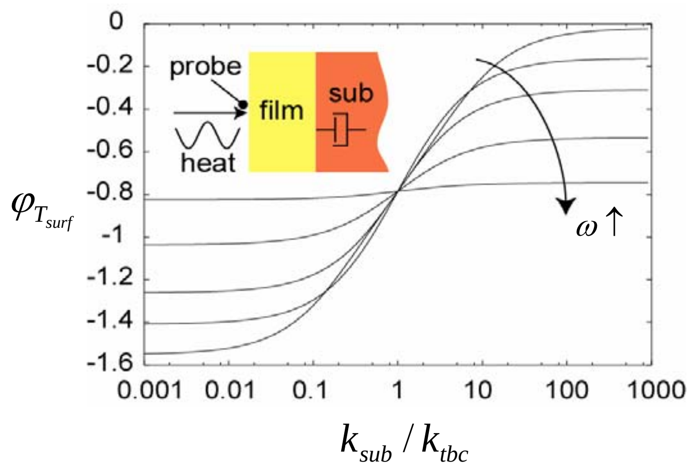
Coating thickness: adds needed length scale



Design of a *Nonintrusive* measurement for coating thermal properties

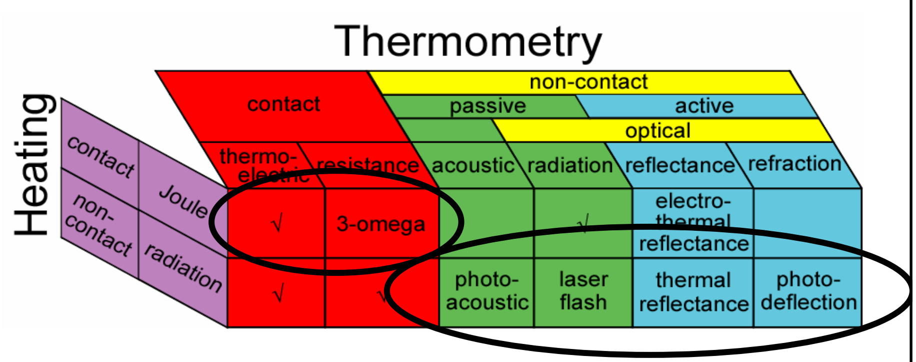
Methods differentiated by:

1) Invasiveness
2) Desired thermal properties
3) Sample geometry
4) Heating method/geometry
5) Thermometry

Design of a *Nonintrusive* measurement for coating thermal properties

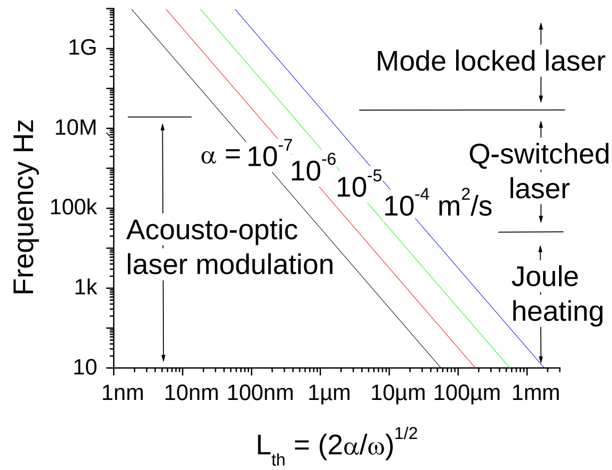
- Steady-state heat transfer unsuitable
  - requires two point temperature measurement
- Transient heat transfer preferred
  - One point temperature measurement (at surface)
- Contact ΔT probes (typically) unsuitable
  - Interference with heating
  - Calibration not needed for diffusivity measurements
- Optical heating typical
  - Magnitude of heating not needed for diffusivity measurements
- Periodic heating
  - Signal averaging
  - Thermal penetration depth control

Design of a *Nonintrusive* measurement for coating thermal properties

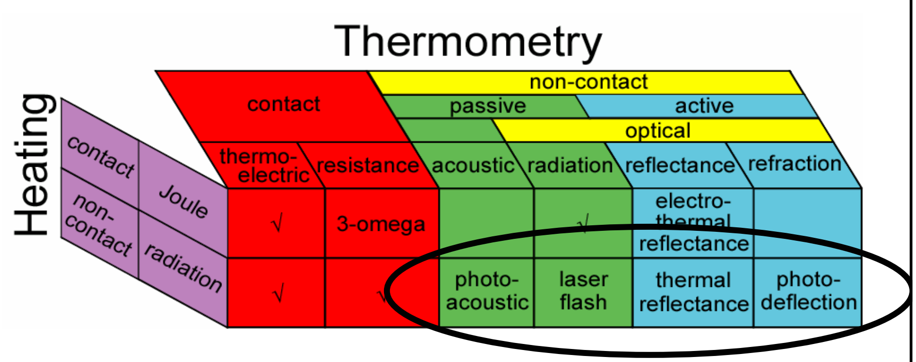


intrusive **nonintrusive**

Heat Sources

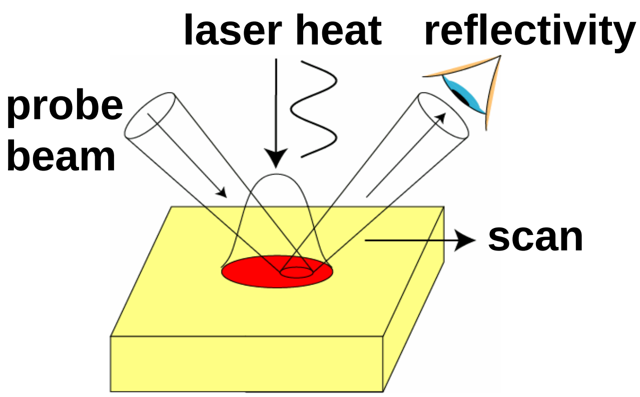


Nonintrusive Thermometry



nonintrusive

Photo-thermal Reflectance



Reflectance temperature coefficient

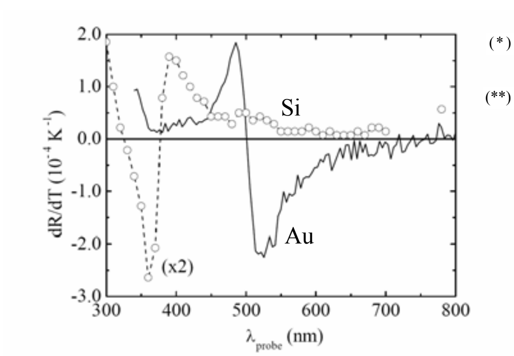


Fig. 1: Reflectance temperature coefficient, as a function of wavelength, for Au (solid line) * and crystalline silicon (circles) * *.

(*) N. Cella at ESPCI-Paris.

(**) G. E. Jellison Jr., F. A. Modine, Phys. Rev. B **27** (12), 7466

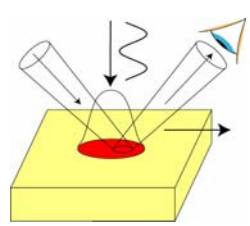
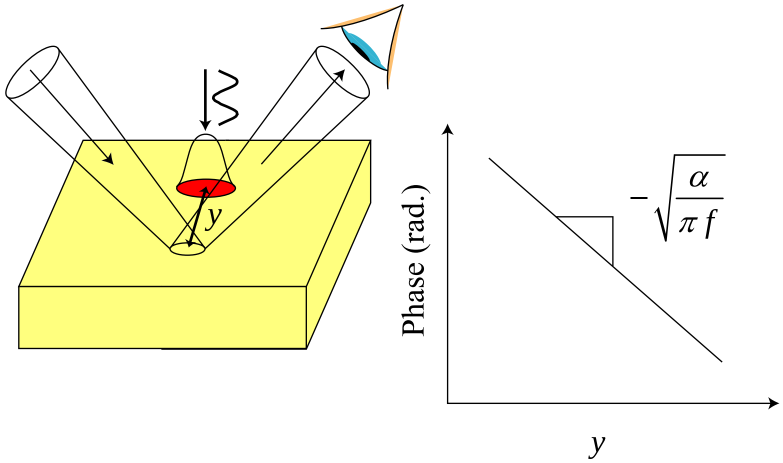
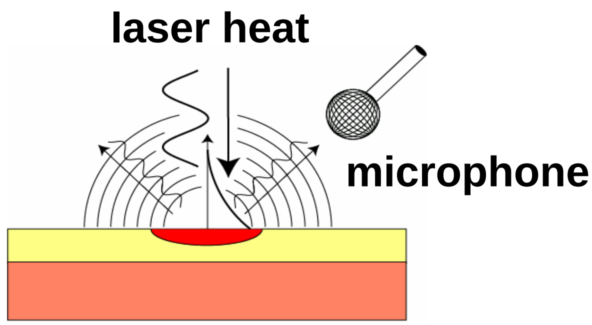


Photo-thermal Reflectance

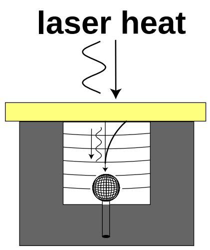


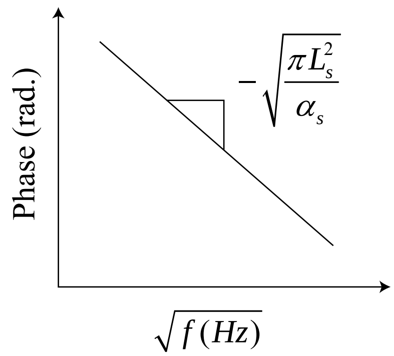
Photoacoustic



A. Rosencwaig and A. Gersho, Bell Laboratories

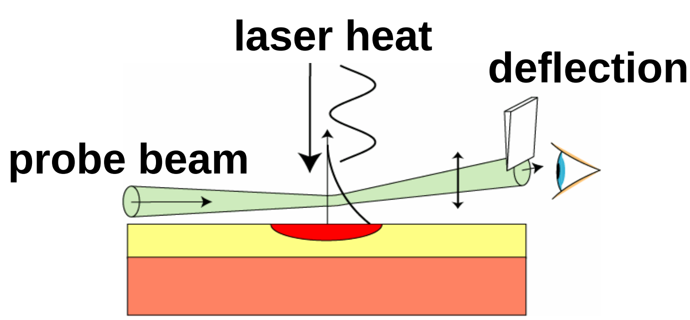
Photoacoustic





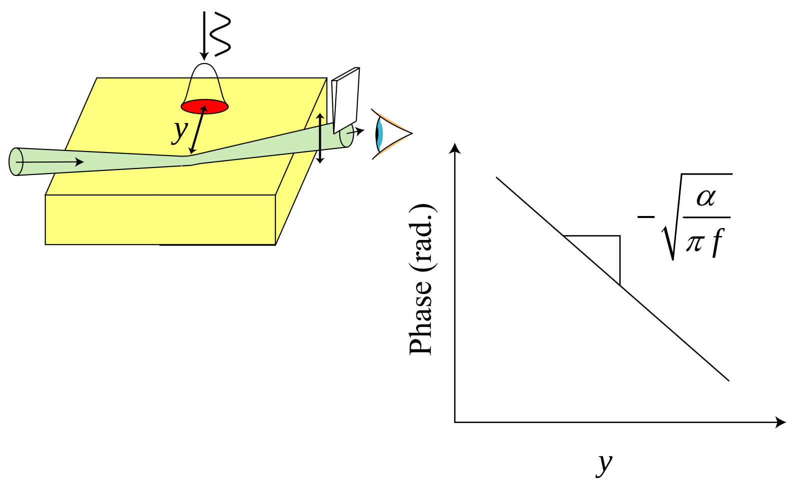
$$P \cong \frac{\gamma P_o I_o (\alpha_g \alpha_s)^{1/2} \exp\left[i\left(\omega t - \pi/2\right)\right]}{2\pi L_g T_o k_s f \sinh\left(\frac{L_s(1+i)}{\sqrt{\alpha_s/\pi f}}\right)}$$

Photodeflection (mirage effect)

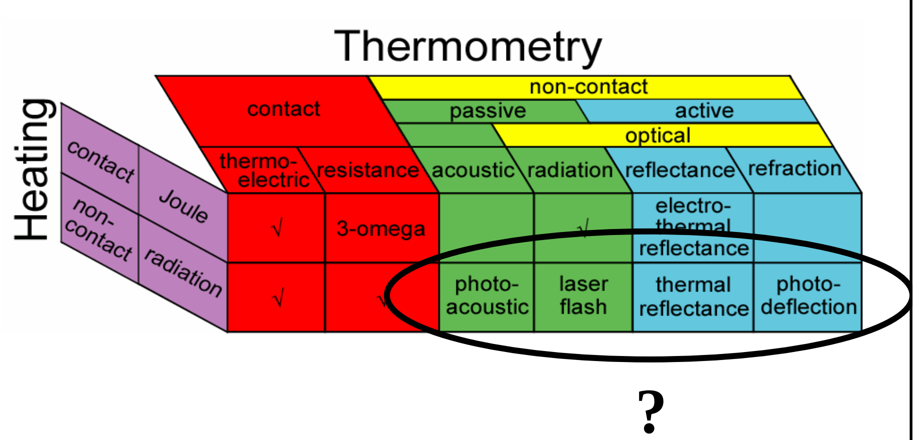


A.C. Boccara, D. Fournier and J. Badoz,
Laboratoire d'Optique Physique

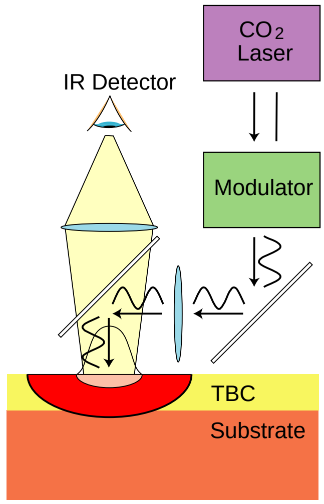
Photodeflection



What is suitable for TBCs?

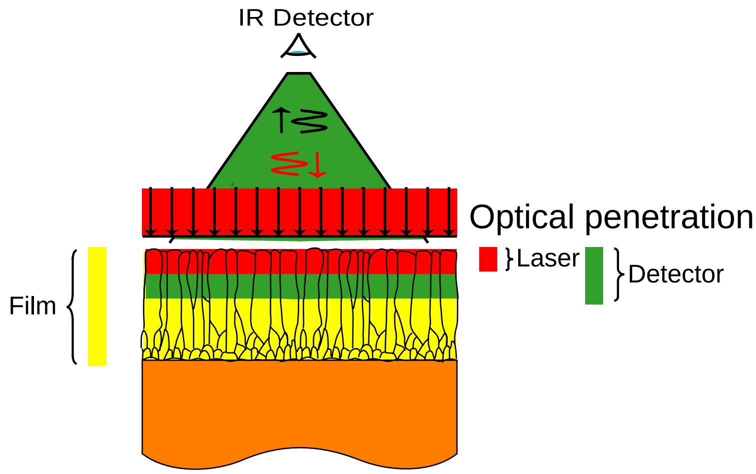


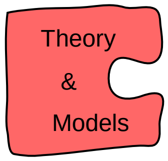
UCSB Effort: Phase of Thermal Emission Spectroscopy



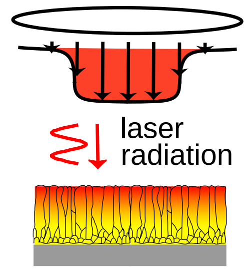
- What is it?
  - Nondestructive measurement of coating properties
- How does it work?
  - Interrogate thermal emission of coating heated with modulated laser
  - Phase of emission dependent on heat transport through coating
- Main difference?
  - Interrogates temperature field inside coating

2D measurement





Heat transfer model



Phase of temperature field has 3 (or 4) dependencies:

Laser penetration: $\Lambda \equiv \frac{L_{opt}}{L}$

Thermal penetration: $\ell = \sqrt{[\alpha_z]_{coat}/\omega}\,/\,L$

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

Interface resistance: $B_i \equiv \frac{L/k}{R_c}$

1D Soln. with optical penetration

$$\tilde{\theta}_{1D} \equiv \frac{\tilde{T}_{1D}}{L\tilde{I}_o/[k_z]_{film}} = \ell\,\frac{\tilde{\zeta}_{1D}(z) - (\Lambda/\ell)\exp\left(-\frac{z/\ell}{\Lambda/\ell}\right)}{1 - i(\Lambda/\ell)^2}$$

$$\tilde{\zeta}_{1D}(z) \equiv \frac{\tilde{F}_{1D}\cosh\left(\sqrt{i}\,z/\ell\right) - \sinh\left(\sqrt{i}\,z/\ell\right)}{\sqrt{i}}$$

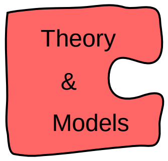
$$\tilde{F}_{1D} \equiv \frac{1+\gamma\tanh(\sqrt{i}/\ell)}{\gamma + \tanh(\sqrt{i}/\ell)} \qquad \gamma \equiv \sqrt{\frac{[k_z\rho C]_{sub}}{[k_z\rho C]_{film}}}$$

$\ell \equiv \frac{\sqrt{[\alpha_z]_{film}/\omega}}{L}$ Axial diffusion vs. film thickness

$\frac{z}{\ell} =$ Probe depth vs. axial diffusion

$\gamma =$ Interface effusivity

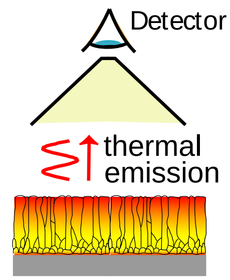
$\frac{\Lambda}{\ell} = \frac{\delta_{opt}}{\sqrt{[\alpha_z]_{film}/\omega}}$ Optical penetration vs. axial diffusion



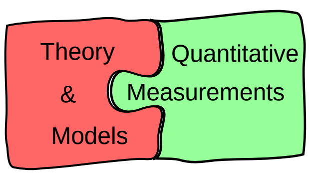
Simplified radiation model

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

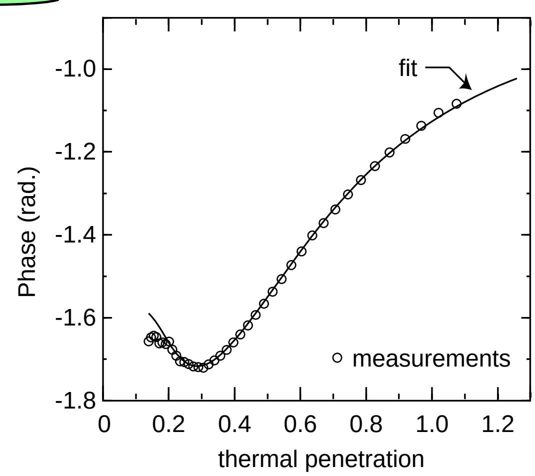
$$\textbf{\textit{emmision}} = \Sigma_\lambda \underbrace{I_{b,\lambda}(1)}_{\text{from interface}} + 4\underbrace{\int_0^1 I_{b,\lambda}(z)dz}_{\text{from topcoat}}$$

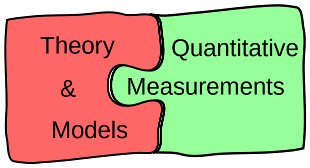


- Phase dependence on one variable: $\Sigma_\lambda = \varepsilon_{1,\lambda} / a_\lambda L$
  (independent of scattering!)

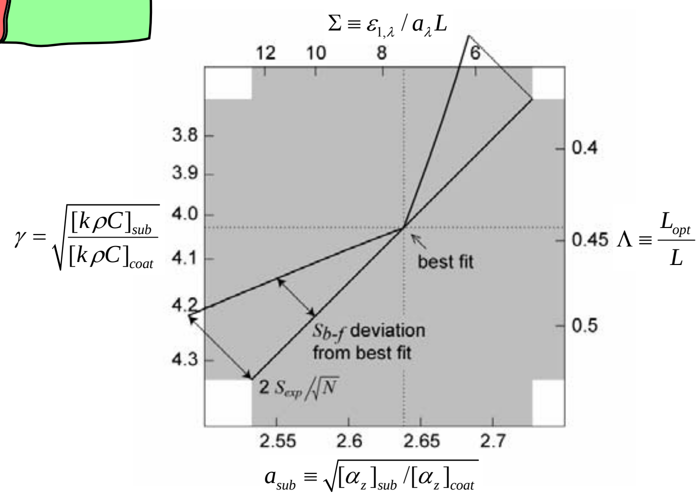


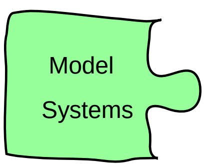
Fitting measurements



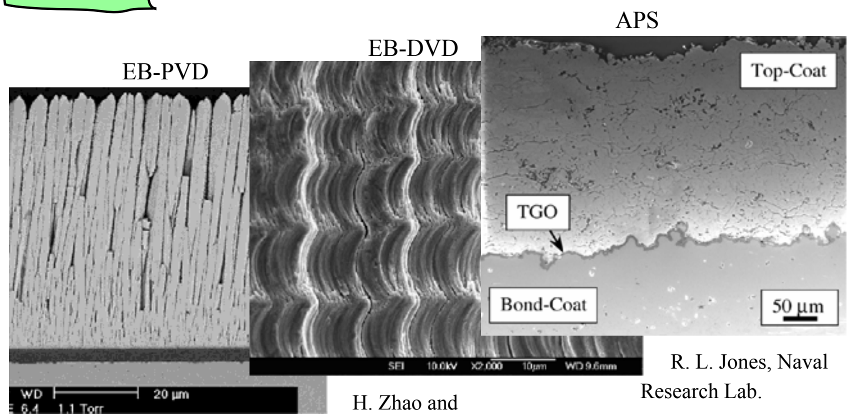


Fitting measurements





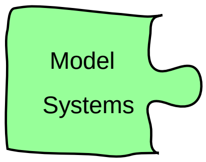
Measurements of as-deposited coatings



N. R. Rebollo and C. Levi, UCSB

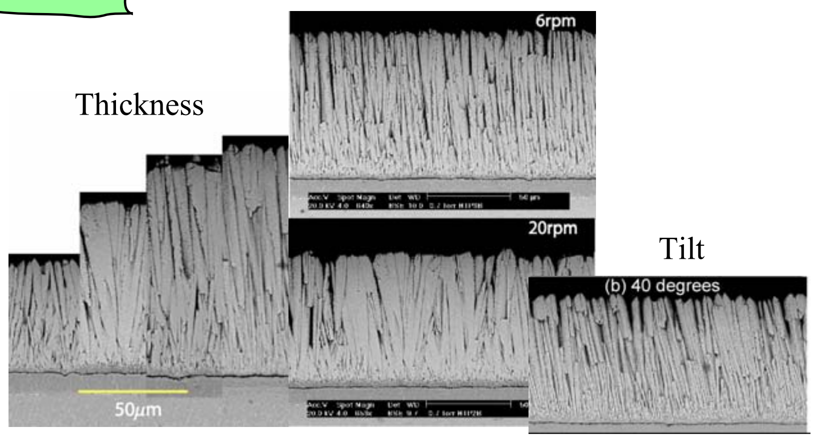
H. Zhao and H. Wadley, U. Virginia

R. L. Jones, Naval Research Lab.



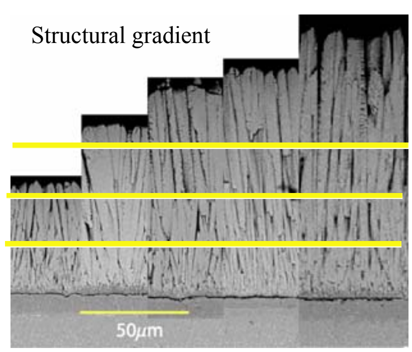
Effect of Deposition Process

Rotation rate

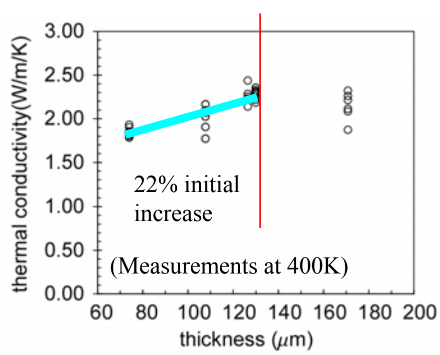


K. J. Lawson and J. Nicholls, Cranfield University, UK

EB-PVD coating thickness

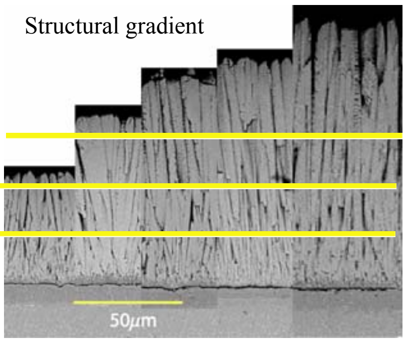


Thermal conductivity

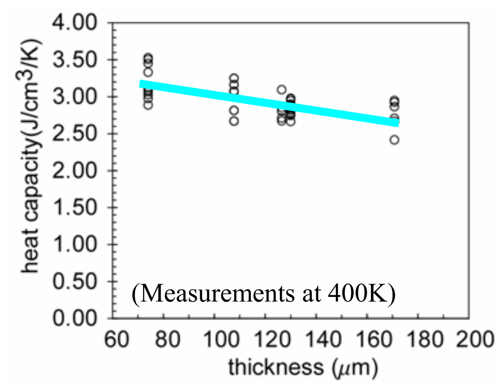


SEM courtesy of K. J. Lawson and J. Nicholls, Cranfield University, UK

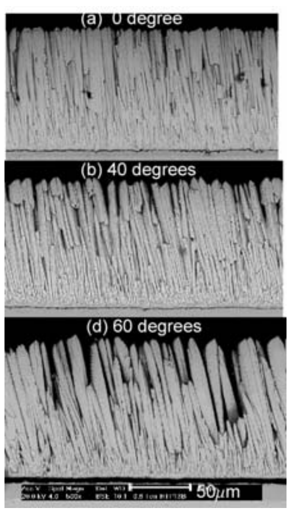
EB-PVD coating thickness

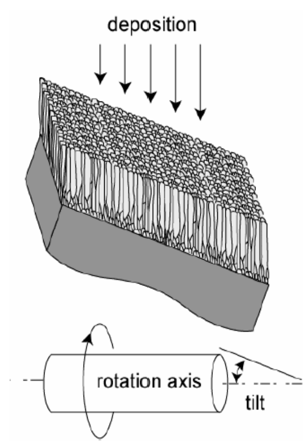


Heat capacity



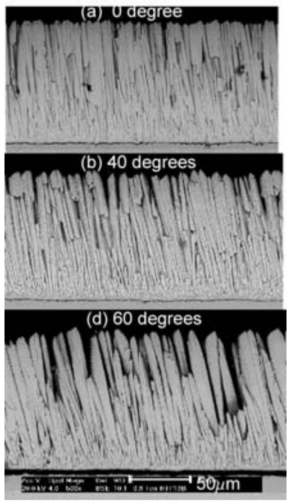
EB-PVD deposition tilt



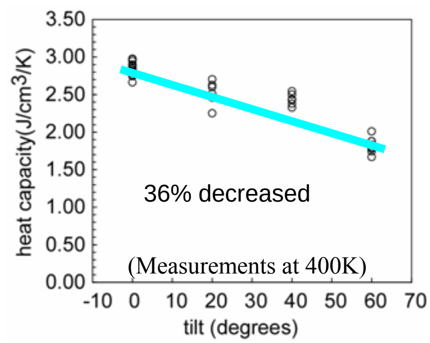


SEM courtesy of K. J. Lawson and J. Nicholls, Cranfield University, UK

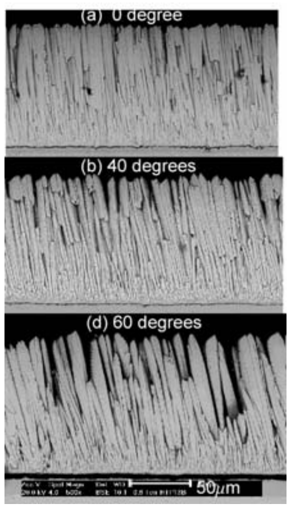
EB-PVD deposition tilt



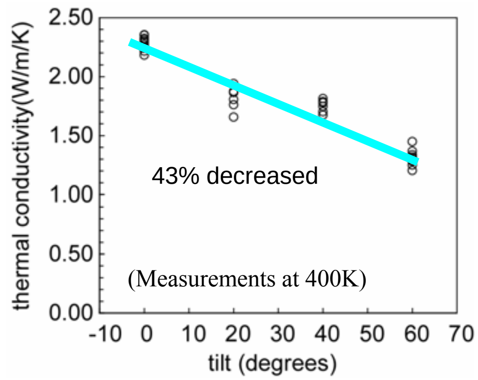
Heat capacity



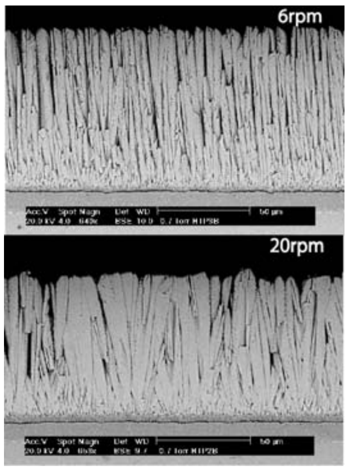
EB-PVD deposition tilt

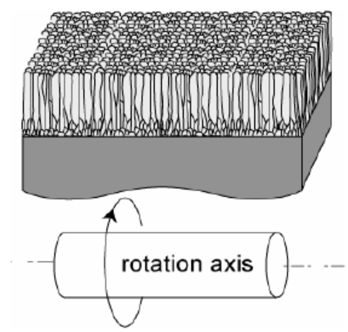


Thermal conductivity



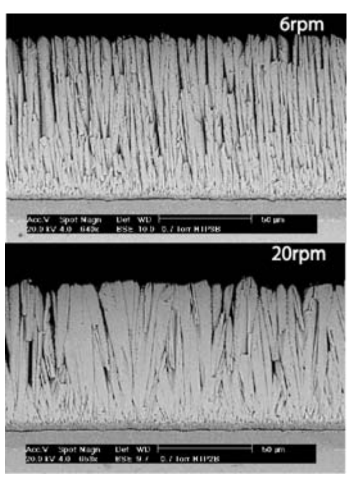
EB-PVD rotation rate



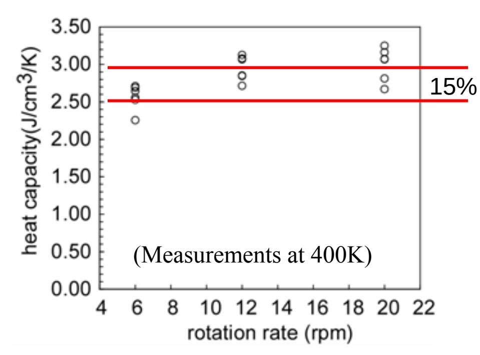


SEM courtesy of K. J. Lawson and J. Nicholls, Cranfield University, UK

EB-PVD rotation rate

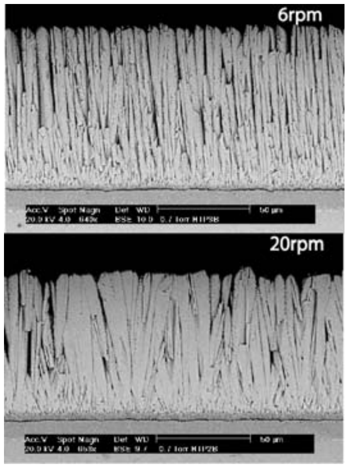


Heat capacity

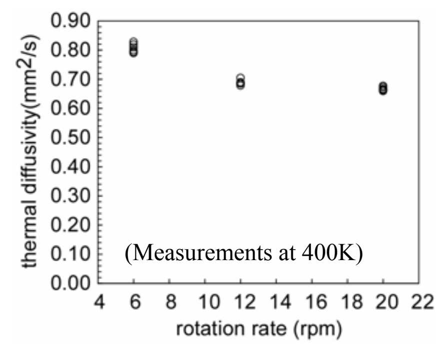


More "solid" microstructure forms at high rotational speeds -----larger column diameters, less branching [*U. Schulz, et al, 1997*]

EB-PVD rotation rate



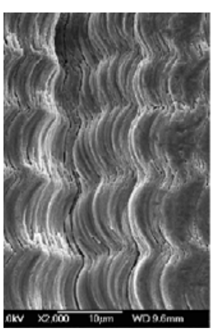
Thermal diffusivity



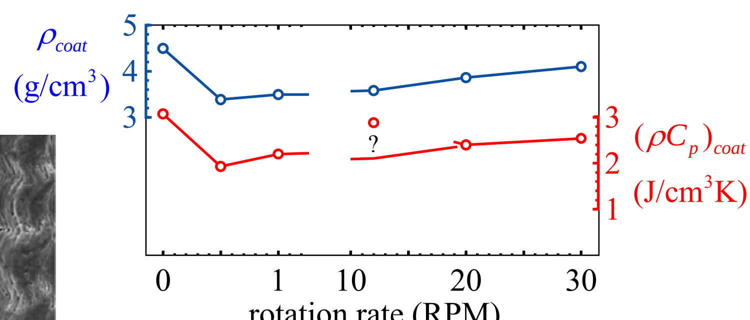
(Apposing trends in diffusivity and density null change in thermal conductivity with rotation rate)

Independent measurements of ρ_{coat} and $(\rho C)_{coat}$

EB-DVD



SEM Courtesy of H. Zhao and H. Wadley, U. of Virginia



Comparison of two measurements predicts:

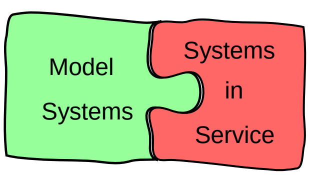
$(C_p)_{coat} \sim 0.6$ J/gK

in contrast to single crystal:

$(C_p)_{bulk} \sim 0.5$ J/gK **(MEVREL, JECS, 2003)**

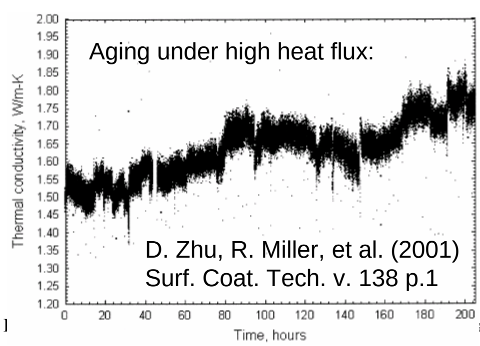
Heath Monitoring of Coatings

- *A quantitative nondestructive measurement of coating thermal protection is not currently employed* on serviceable engine parts
- *Complex physical changes that precede spallation may be monitored by changes in the coating's thermal performance*

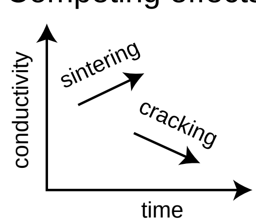


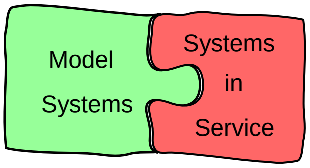
Aging effects

Evolution of
Top-coat
Interface

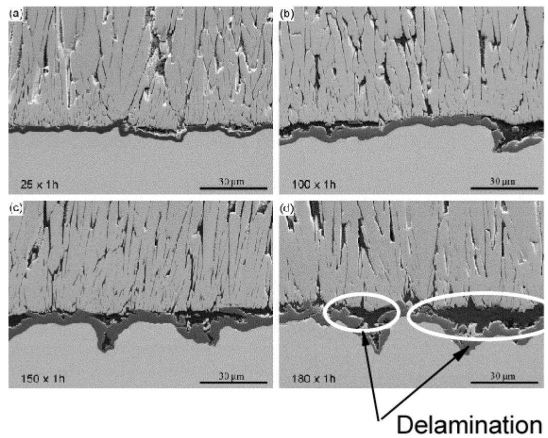


Competing effects:

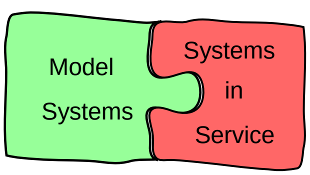




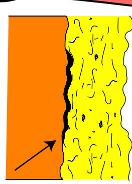
Aging effects



SEM courtesy of V. K. Tolpygo, D. R. Clarke (UCSB) and K. S. Murphy (Howmet)



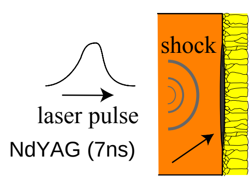
Delamination (model systems)



dissolved
NaCl void

APS, 300um YSZ
NiCoCrAlY bond-coat
IN738 substrate

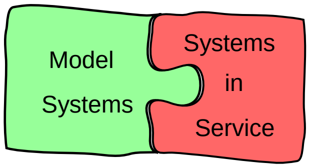
R. Vassen (IWV – Forschungszentrum Jülich)



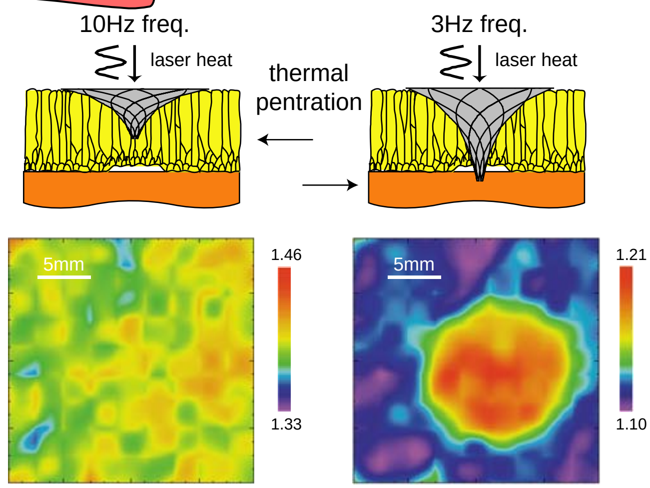
mechanical
delamination

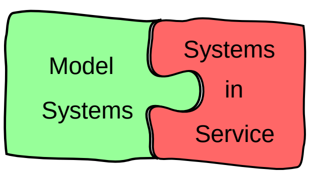
EB-PVD, 90μm YSZ
NiAl bond-coat
CMSX4 substrate

P. Tavernier and D. Clarke (UCSB)

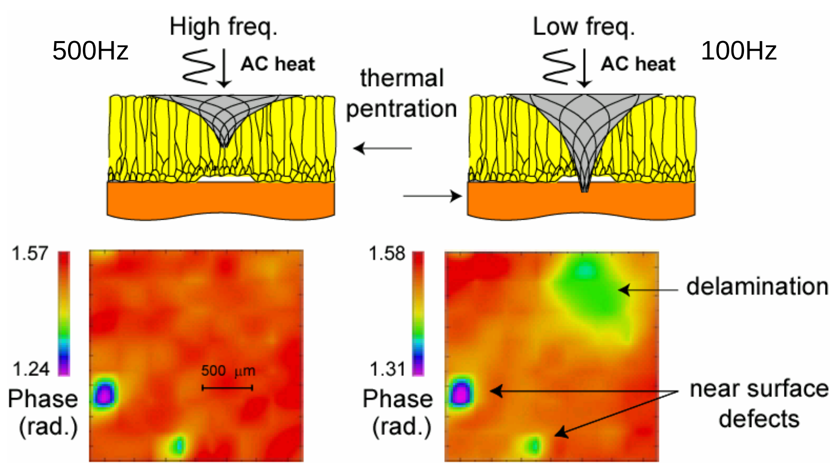


Void underlying “thick” APS coating



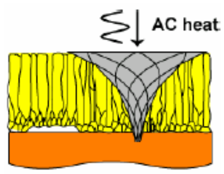


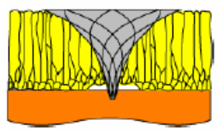
Delamination of “thin” EB-PVD coating



Model Systems | Systems in Service

Influence of delamination

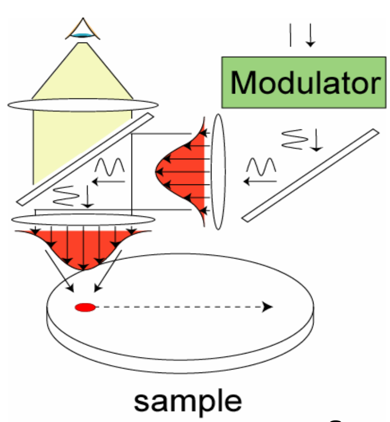


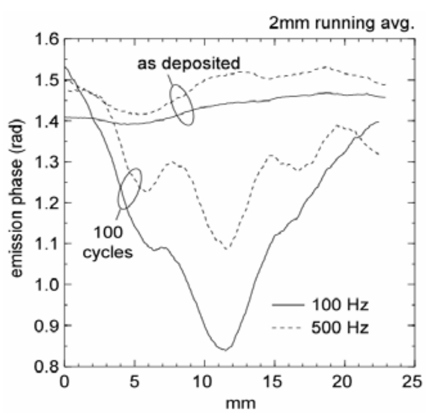


	$[k]_{coat}$ (W/m/K)	$[\rho C]_{coat}$ (J/cm^3/K)	$[\alpha_z]_{coat}$ (mm^2/s)	L_{opt} (μm)	Rc (Kμm^2/W)
Upper diagram	1.25	1.92	0.649	37.9	0.34
Lower diagram	1.37	1.94	0.708	35.1	3.51
Erroneous fitting	1.67	2.25	0.744	41.4	---

Model Systems | Systems in Service

Furnace cycle



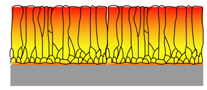


Samples provided by A.G. Evans (UCSB)

Systems in Service

Future issues?

Coatings altered by real service



- Combustion products altering optical properties
- Sintering and CMAS effects on thermal properties
- Differentiating changes at the interface from those within coating
- Optically thick coatings