Thermal diffusivity measurements as a non destructive tool for the microstructural characterisation and the integrity assessment of thermal barrier coatings

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Summary

• Introduction to Thermal Barrier coatings (TBCs)

• Integrity assessment of TBC by thermal diffusivity evaluation

• Microstructural characterisation of TBC by thermal diffusivity evaluation and sintering forecasts

• Through-the-thickness and in-plane thermal diffusivity measurements
The gas turbine
GT Inlet Temperature / GT Efficiency

Temperature

allowable Hot Gas Temperature

Film Cooling

Convective Cooling

Closed-loop Cooling

with TBC

CMC

Allowable Material temperature

IN738

IN939

IN792 DS

1st Gen. SX

2nd Gen. SX

U700


Hipercoat, Stockholm, 2005
The GT hot path components
The thermal barrier coating (TBC)
The material $8\% Y_2O_3+ZrO_2$

- Maximum operating temperature: 1200 °C
- TEC similar to that of substrate ($1 \times 10^{-5}$ vs. $1.2 - 1.3 \times 10^{-5}$)
- High toughness $K_{1c}$ ($9.5 - 10.5$ Mpa m$^{1/2}$)
- Low thermal conductivity ($2.8 - 2.2$ W/mK)
- Coating ~1 W/mK $\leftrightarrow$ 50-170°C
- Coating thickness 100-1000 μm

Fluoritic $AO_2$  
$A +4$
The material $8\% Y_2O_3+ZrO_2$

$$\kappa = \frac{1}{3} C_v \nu \Lambda$$

$$\Lambda \equiv d_i$$

$Y^{+3} \rightarrow Zr^{+4} \rightarrow d_i \downarrow$

Non phonon vibrational modes with $\nu < \nu_{\text{sound}}$
The deposition techniques: APS
The deposition techniques: APS
The deposition techniques: EBPVD
The deposition techniques: EBPVD
Failure mechanisms of TBC

Sintering

TBC

TGO

Bondcoat

Substrate
Failure mechanisms of TBC

- TGO growth
- Thermal fatigue
Non destructive integrity assessment of TBCs Coupons

The objective is to non destructively detect diffuse cracking at the interface between BC and TBC in coupons tested under cyclic oxidation.
Ageing of TBC: sintering

\[(\alpha_0, E_0, H_0, \varphi, \ldots) \quad \Rightarrow \quad (\alpha, E, H, \varphi, \ldots) \Rightarrow (\alpha_0, E_0, H_0, \ldots)\]
Ageing of TBC: cracking at the interface

\[(\alpha_0, \ldots) \implies (T,t) \implies (\alpha, \ldots) < (\alpha_0, \ldots)\]
Integrity assessment: cracks and delaminations

Heat Dirac pulse

The effect of increasing delamination thickness on temperature signal

\[ \frac{l^2}{\alpha} \]

Temperature (a.u.) vs. Time (s)
Crack growth ND detection on samples tested by cyclic oxidation

Superposition of two effects (sintering & cracking) with different relaxation times and magnitudes

↓

No monotonic trend of thermal diffusivity vs. ageing time

↓

Some information about cracking at the interface can be obtained from thermal diffusivity
Crack growth ND detection on samples tested for cyclic oxidation

28 disk shaped samples coated with a APS TBC
  9 thin samples (T1)  254±10 µm
  19 thick samples (T2)  328±9 µm

Porosity 15%
2 hours cycle: 1.5 hour dwell time@1050°C

Average lifetime was estimated on 2+2 samples (T1=1008±12 and T2=880±12 cycles)

Samples have been aged up a fixed percentages of the average lifetime. Thermal diffusivity of each sample was measured in the as sprayed condition and after different aging cycles.
Crack growth ND detection on thermally cycled samples – Thin TBC
Crack growth ND detection on thermally cycled samples – Thick TBC
How to correlate the thermal diffusivity with the damage at the interface?
Modeling of the effect of cracks on TBC thermal diffusivity.
Estimation of cracked interface by 2D-Inversion model

Golosnoy et al., Journal of Thermal Spray Technol. 14(2) 2005
How the cracked fraction of interface has been estimated from IA?
Estimation of cracked fraction of interface from IA

Cracks caused by thermal cycling have been supposed to be thicker and sharper than those originated during the spray process.
Estimation of cracked fraction of interface from IA
Estimation of cracked fraction of interface from IA
Estimation of cracked interface by 2D- Inversion model

A good agreement between estimations and SEM is observed.
Estimation of cracked interface by 2D- Inversion model
• The crack thickness has been fixed equal to 3 \( \mu m \) for each sample at each ageing time. When necessary, to zeroing the inversion function, the thickness has been increased up to values of 6 - 11 \( \mu m \) for ageing times close to the end of TBC life.

• For data referring to roughly 50% of TBC life, a crack thickness value intermediate between 3 \( \mu m \) and the maximum value was adopted.
How to avoid the “tuning” effect of the crack thickness in the inversion model?
A figure of merit

Consider the trend of cracked fraction vs. crack thickness and to look for a simple fitting function whose free parameters can be related to the damage at the interface

\[ y = a + \frac{b}{x} \]

\[ r^2 = 0.99795071 \quad DF \quad Adj \quad r^2 = 0.9973652 \quad \text{FitStdErr} = 0.0065762204 \quad Fstat = 3895.7907 \]

\[ a = 0.45304067 \]

\[ b = 0.49346696 \]

A figure of merit

8.0 ± 0.9 \times 10^{-4}

872 cycles

1392 cycles

\text{Alert threshold}

\begin{align*}
T1 & \quad y = 8.47 \times 10^{-4} x + 2.51 \times 10^{-1} \\
R^2 & = 9.03 \times 10^{-1} \\
T2 & \quad y = 6.44 \times 10^{-4} x + 1.93 \times 10^{-1} \\
R^2 & = 9.52 \times 10^{-1}
\end{align*}
Conclusions

• A 2D model has been used for better estimating the cracked fraction of the interface between APS TBC and BC, especially at early stage when there are several short cracks.

• A figure of merit incorporating both cracked fraction and crack thickness was also proposed for ranking the damage and obtaining indications on the failure time.
Microstructural characterisation of APS TBC by thermal diffusivity evaluation and sintering forecasts

The idea

As sprayed TBC

IA SEM

MIP

Thermal diffusivity in gases

Microstructural parameters of as sprayed TBC

Sintering modeling

Comparison with experimental IA, MIP and TD on sintered TBC

Forecast evolution of microstructural parameters with sintering & TD

Thermal diffusivity modeling
Thermal diffusivity in different gases

\[ \alpha_{1p1} \quad \alpha_{2p1} \quad \alpha_{3p1} \quad \alpha_{vp1} \]

\[ \alpha_{1pm} \quad \alpha_{2pm} \quad \alpha_{3pm} \quad \alpha_{npm} \]

Effective crack opening
Aspect ratio of interlamellar pores

Modelling of porous solids

Symmetric models

Asymmetric models

TBC

Asymmetric model
Modelling of porous solids

\[ \frac{k}{k_m} = (1 - f)^x \]

\[ X = \frac{1 - \cos^2 \alpha}{1 - F} + \frac{\cos^2 \alpha}{2F} \]

Modelling of porous solids

Heat flux

$k/k_m$

$f$
Modelling of porous solids - thermal conductivity of gases within pores

\[ k_{bulk} = H_2, \quad Ar, \quad N_2 \]

\[ k_{pores} \neq \]
Modelling of porous solids - thermal conductivity of gases within pores

\[
\Lambda \approx \delta \quad k = \frac{k_{\text{bulk}}}{1 + C \left( \frac{T}{P \delta} \right)}
\]
Modelling of porous solids - thermal conductivity of gases within pores
Modelling of porous solids - thermal conductivity of gases within pores

![Graph showing thermal conductivity as a function of crack thickness for different pressures.](image)
Modelling of porous solids

How is it possible to simultaneously model several types of pores?

\[ k = \frac{1}{2} \left\{ \Phi \left( \Psi \left( k_m, \frac{f_1}{1-f_2} \right), f_2 \right) + \Psi \left( \Phi \left( k_m, \frac{f_2}{1-f_1} \right), f_1 \right) \right\} \]
The samples - YPSZ APS TBC

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Thickness [μm]</th>
<th>Shape</th>
<th>Size [mm]</th>
<th>Heat treated</th>
<th>Characterised by</th>
</tr>
</thead>
<tbody>
<tr>
<td>WD1</td>
<td>427±16</td>
<td>disk</td>
<td>9.81</td>
<td>Y</td>
<td>Thermal diffusivity and SEM</td>
</tr>
<tr>
<td>WD2</td>
<td>416±15</td>
<td>disk</td>
<td>9.81</td>
<td>Y</td>
<td>Thermal diffusivity and SEM</td>
</tr>
<tr>
<td>WD3</td>
<td>400±21</td>
<td>disk</td>
<td>9.81</td>
<td>Y</td>
<td>Thermal diffusivity and SEM</td>
</tr>
<tr>
<td>WD4</td>
<td>414±13</td>
<td>Square</td>
<td>20</td>
<td>N</td>
<td>SEM</td>
</tr>
<tr>
<td>WD6</td>
<td>n.a.</td>
<td>Rectangular</td>
<td>10 X40</td>
<td>N</td>
<td>Hg intrusion Porosimetry</td>
</tr>
<tr>
<td>WD7</td>
<td>n.a.</td>
<td>Rectangular</td>
<td>10 X40</td>
<td>N</td>
<td>Hg intrusion Porosimetry</td>
</tr>
<tr>
<td>WD8</td>
<td>n.a.</td>
<td>Rectangular</td>
<td>10 X40</td>
<td>Y</td>
<td>Hg intrusion Porosimetry</td>
</tr>
<tr>
<td>WD9</td>
<td>n.a.</td>
<td>Rectangular</td>
<td>10 X40</td>
<td>Y</td>
<td>Hg intrusion Porosimetry</td>
</tr>
</tbody>
</table>

As sprayed

Heat treated 200 h @1250°C
The samples - YPSZ APS TBC

Vertical intra-lamellar cracks
The samples - YPSZ APS TBC

Horizontal inter-lamellar pores
Vertical intra-lamellar cracks
Globular pores
IA characterisation

Elongation (e>3) and orientation criteria

- Overall porosity
- Lamellar pores with symmetry axis parallel to the thickness
- Lamellar pores with symmetry axis perpendicular to the thickness
- Lamellar pores with symmetry axis elsewhere oriented
- Spherical pores

Comparison between As sprayed and Heat treated conditions.
Experimental thermal diffusivity data
Experimental thermal diffusivity data
Input of the inversion code

As lamellar porosity parallel oriented to the heat flux plays the major role in reducing the thermal diffusivity, starting from the IA volumetric fractions, in the inversion code, porosity has been divided into two classes: parallel inter-lamellar pores and spheres.

Inter-lamellar parallel=true inter-lamellar parallel+1/3 elsewhere oriented lamellar

Spheres=True spheres+2/3 elsewhere oriented lamellar+ vertical intra-lamellar cracks.

\[
\begin{align*}
4.1\% & \quad 1\% \\
6.15\% & \quad 2\% \\
5.1\%+8.7\% & =13.8\%
\end{align*}
\]

7 equations for each sample (vacuum, three gases, two pressures)

Average crack thickness and aspect ratio
Output of the inversion code

WDS1 as Sprayed
- \( a/c = 1/38 \)
- Specific surface area: \( 1.82 \cdot 10^6 \, \text{m}^2/\text{m}^3 \)
- Porosity 13.8
- \( 0.088 \pm 0.005 \, \mu\text{m} \)

WDS2 as Sprayed
- \( a/c = 1/37 \)
- Specific surface area: \( 1.0 \cdot 10^6 \, \text{m}^2/\text{m}^3 \)
- Porosity 13.1
- \( 0.163 \pm 0.008 \, \mu\text{m} \)

WDS3 as Sprayed
- \( a/c = 1/37 \)
- Specific surface area: \( 1.0 \cdot 10^6 \, \text{m}^2/\text{m}^3 \)
- Porosity 14.4
- \( 0.163 \pm 0.008 \, \mu\text{m} \)
Input for the sintering code

Bruggeman Model

Translation

Cipitria Model

The Cipitria’s sintering code

Surface and grain boundary diffusion, together with grain boundary migration

Grain boundary diffusion, leading to through-thickness shrinkage (reduction in $r_s, h$),

Surface diffusion contributes to pore spheroidization, i.e. reduces $z_s$, causing the half-height of the pore ($h-z_s$) to increase, and increases $r_b$.

Grain boundary migration causes an increase in lateral (in-plane) grain size, $g$, and hence a reduction in $N_s$
The Cipitria’s sintering code

**Grain boundary diffusion**
(reduction in \(a\) and induced increase in \(x_b\))

**Surface diffusion**
spheroidization of microcracks, i.e. reduces \(y_c\), which promotes opening of the microcracks \((a-y_c)\) increases), and increases \(x_b\).

(plus interchange of \(x\) & \(y\) → orthogonal set of microcracks)
IA characterisation
Output of the inversion and sintering codes

WDS1 heat treated

- $a/c=1/38$
- $a/c=1/22$
- $a/c=1/6$

Specific surface area: $1.82 \times 10^6$ m$^2$/m$^3$
Specific surface area: $1.76 \times 10^6$ m$^2$/m$^3$
Specific surface area: $0.39 \times 10^6$ m$^2$/m$^3$
Specific surface area: $0.58 \times 10^6$ m$^2$/m$^3$

WDS3 heat treated

- $a/c=1/37$
- $a/c=1/25$
- $a/c=1/14$

Specific surface area: $0.55 \times 10^6$ m$^2$/m$^3$
Specific surface area: $0.55 \times 10^6$ m$^2$/m$^3$
Specific surface area: $0.55 \times 10^6$ m$^2$/m$^3$
Specific surface area: $0.55 \times 10^6$ m$^2$/m$^3$

Porosity 10.1
Porosity 8.8
Porosity 13.8
Porosity 12.0
Porosity 10.8
MIP characterisation
MIP characterisation

As sprayed

Heat treated
MIP characterisation

![Graph showing MIP characterisation results.](image-url)

- **As sprayed**
- **Heat treated**

**Pore diameter**
- Average overall porosity
- 2 - 100 µm
- 0.5 - 2 µm
- 0.04 - 0.5 µm
- 0.01 - 0.04 µm

**Volumetric fraction [%]**
- Values vary across different pore diameters.
Output of the inversion and sintering codes and MIP

WDS1 heat treated

- $a/c=1/38$
- $a/c=1/22$
- $a/c=1/6$

Specific surface area: $1.82 \cdot 10^6 \text{ m}^2/\text{m}^3$

Specific surface area: $0.39 \cdot 10^6 \text{ m}^2/\text{m}^3$
Specific surface area: $0.58 \cdot 10^6 \text{ m}^2/\text{m}^3$
Specific surface area: $0.70 \cdot 10^6 \text{ m}^2/\text{m}^3$

Porosity 10.1
Porosity 8.8
Porosity 13.5

0.088$\pm$0.005 $\mu$m
0.37$\pm$0.05 $\mu$m
0.26$\pm$0.05 $\mu$m

WDS3 heat treated

- $a/c=1/37$
- $a/c=1/25$
- $a/c=1/14$

Specific surface area: $0.55 \cdot 10^6 \text{ m}^2/\text{m}^3$

Specific surface area: $0.55 \cdot 10^6 \text{ m}^2/\text{m}^3$
Specific surface area: $0.57 \cdot 10^6 \text{ m}^2/\text{m}^3$
Specific surface area: $0.70 \cdot 10^6 \text{ m}^2/\text{m}^3$

Porosity 12.0
Porosity 10.8
Porosity 12.2

0.163$\pm$0.008 $\mu$m
0.22$\pm$0.05 $\mu$m
0.30$\pm$0.05 $\mu$m
Thermal diffusivity estimations

WDS1

WDS3

Time [h]
Thermal diffusivity [m²/s]

air
vacuum
Conclusive remarks

✓ A good agreement between the experimental estimations of **specific surface area** by MIP, Inversion code and Sintering model has been found

✓ The effective **crack opening** estimated by the inversion code is in good agreement with sintering model and IA

✓ **Aspect ratios increase** as estimated by inversion code only partially agrees with that forecasted by the sintering code

✓ **Porosity drop** as measured by MIP resulted smaller than that observed by IA and forecasted by sintering model

✓ **Thermal diffusivity** forecasts in "good" agreement with experimental results for one heat treated sample. A bimodal fine pore distribution could be a possible explanation for the overestimation of thermal diffusivity for sample 1

✓ Thermal diffusivity measurements using different gases and pressures coupled with IA seems to be a useful technique to obtain microstructural parameters to be used as input for the sintering model
Through-the-thickness and in-plane thermal diffusivity measurements
In-plane thermal diffusivity

\[
\frac{\Theta(k, z, t)}{\Theta(k = 0, z, t)} = \frac{F(k)}{F(k = 0)} e^{-\alpha_p k^2 t}
\]

For slab or semi-infinite body, the spatial Fourier Transform $\Theta$ of the in-plane temperature field, decays exponentially in time once normalized by its continuous component. Hence, taking the logarithm of the ratio, it is possible to obtain the in-plane diffusivity from the slope of the fitting straight line.

Laser thermography

Laser thermography - in-plane thermal diffusivity

Laser thermography - in-plane thermal diffusivity

Elastic modulus measured by three point bending test

\[
\sigma = \frac{\pm Fl}{4L} \quad \gamma \quad \delta = \frac{Fl^3}{48EI}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>In-depth thermal diffusivity ([10^{-7} \text{ m}^2 \text{ s}^{-1}])</th>
<th>In depth thermal conductivity ([\text{W/ mK}])</th>
<th>In-plane thermal diffusivity ([10^{-7} \text{ m}^2 \text{ s}^{-1}])</th>
<th>In-plane thermal conductivity ([\text{W/ mK}])</th>
<th>In-plane elastic modulus E ([\text{GPa}])</th>
<th>Simulated in-depth Thermal diffusivity ([10^{-7} \text{ m}^2 \text{ s}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.6(\pm)0.3</td>
<td>0.8</td>
<td>5.1(\pm)0.4</td>
<td>1.1</td>
<td>9.5(\pm)0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>B</td>
<td>3.9(\pm)0.4</td>
<td>0.9</td>
<td>5.1(\pm)0.4</td>
<td>1.2</td>
<td>11.4(\pm)1.5</td>
<td>3.9</td>
</tr>
<tr>
<td>C</td>
<td>6.3(\pm)0.1</td>
<td>1.6</td>
<td>6.4(\pm)0.2</td>
<td>1.6</td>
<td>1.8(\pm)1.5</td>
<td>6.7</td>
</tr>
</tbody>
</table>
In the literature several correlations between mechanical and thermo-physical properties of heterogeneous solids have been proposed. It is worth comparing in our case the *in-plane* thermal diffusivity and the *in-plane* elastic modulus of the three samples.

\[
\frac{\alpha_{pA}}{\alpha_{pB}} \equiv \frac{E_A}{E_B}
\]

\[
\frac{\alpha_{pA}}{\alpha_{pC}} \equiv \frac{\alpha_{pB}}{\alpha_{pC}} \ll \frac{E_A}{E_C} \equiv \frac{E_B}{E_C}
\]

The assumptions underneath the cross correlation models usually the porosity is supposed to be some orders of magnitude smaller than the typical TBC thickness. In the case of vertical cracks crossing most of TBC thickness this is not true anymore.
Thank you for your kind attention!