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**FACTORS AFFECTING
FLUORESCENCE OF
THERMALLY GROWN OXIDE
IN THE PRESENCE OF A
THERMAL BARRIER
COATING**

**J W Nunn, J P Banks,
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and S R J Saunders**

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Factors Affecting Fluorescence of Thermally Growth Oxide in the Presence of a Thermal Barrier Coating

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ABSTRACT

Adhesion of a thermal barrier coating (TBC) to the bondcoat has been shown to be dependent upon a good bond being maintained between the thermally grown oxide (TGO) and bondcoat. The fluorescence of chromium impurities in the TGO is used as a measure of the residual stress and thus the adherence of the TGO. This non-destructive method is now used to determine the mechanical integrity of the TBC system itself. To better understand this phenomenon the factors affecting the fluorescent signal have been investigated.

The intensity of fluorescent signal is a direct function of the chromium content of the thermally grown oxide (TGO). In some cases where the intensity increases at a rate faster than expected for oxidation of the bondcoat, this may indicate growth of non-protective TGO. The lateral resolution of spectra from TGO without a thermal barrier coating (TBC) present is about 1-3 μm when using a x100 magnification objective. The effect of adding a TBC layer is a degradation of this resolution and further work is required to quantify this. However, it is clear that with APS TBC systems considerable scatter occurs and indeed it is unclear whether the laser light is transmitted through the 300 μm thick APS layer investigated in this work. For EBPVD TBC it is highly likely that the columnar structure may act as a light-pipe to aid transmission through the layer. While it is clear that lateral resolution will be degraded by the presence of the EBPVD layer, it cannot be quantified at present. EBPVD thickness has a marked effect on signal intensity, and it was estimated that the intensity decreases by half for each 20-25 μm additional thickness. For the laser conditions used with this work, approximately 200 μm was the maximum TBC thickness that could be examined to guarantee a reliable fluorescent signal.

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1 INTRODUCTION

This report describes the characterization of thermally aged thermal barrier coating (TBC) systems using the non-destructive piezospectroscopic method. TBC systems consist of a so-called bondcoat that is an oxidation resistant coating that forms a protective alumina oxide scale (the thermally grown oxide or TGO) and the yttria stabilised zirconia TBC. Adhesion of the TBC to the bondcoat has been shown to be dependent upon a good bond being maintained between the TGO and bondcoat [1]. The thermal expansion mismatch between the metallic bondcoat and the alumina TGO is such that at room temperature the TGO is under a large compressive stress (about 3- 4 GPa). Laser excitation of small amounts of Cr^{3+} in the TGO causes fluorescence to occur and the spectral response is pressure (stress) dependent [2]. Thus should the TGO become detached the stress would be reduced and this in turn results in a peak shift in the fluorescent spectrum

The objective of this work was to determine what factors affect the intensity and lateral resolution of the fluorescent signal. In particular the well established [2] peak shift due to changes in the stress state of the TGO would be confirmed, but also a major aim of this work was to investigate the possibility of using changes in the spectral intensity as an additional means of monitoring the performance of the TBC. Factors affecting the intensity and lateral resolution such as TGO thickness, TBC thickness and type have been investigated.

Fluorescence. The use of the fluorescence method, sometimes referred to as piezospectroscopy, is well established [3] and for α -alumina a R-line fluorescence is split into a doublet (R1, R2) by crystal field effects. Of the two lines, it has been found that the R2 line has a more linear pressure dependence and is also more isotropic for the different crystallographic orientations [3]. Hence, the stress determination reported has been primarily based on measurements of R2. For polycrystalline materials in the absence of any out-of-plane stress where the specimen volume probed is large compared with the grain size the frequency shift, $\Delta\nu$, of the R2 line is given by:

$$\Delta\nu = 2.54 (\text{cm}^{-1} \text{ GPa}^{-1}) \sigma \quad (1.)$$

and for the case of a scale with a planar interface which we take to be stressed in only two dimensions, Equation 1 becomes:

$$\Delta\nu = 5.07 (\text{cm}^{-1} \text{ GPa}^{-1}) \sigma_{2D} \quad (2.)$$

where the biaxial stress, σ_{2D} , is taken to be homogeneous.

Curve fitting. The shape and position of the R1/R2 doublet changes with stress, temperature and Cr^{3+} ion concentration, and therefore allows quantitative information on these conditions to be extracted from analysis of the fluorescence spectrum. For a single homogenous stress state at a given temperature a well-defined doublet is observed which requires at least eleven parameters to describe its R1/R2 spectrum. [4]. These are the peak positions of the R1 and R2 line and their separation, the intensities of the R1 and R2 lines and their ratio, the halfwidths of the R1 and R2 lines and their ratio, and the shape of the R1 and R2 lines conventionally expressed as the fraction of Lorentzian versus Gaussian character for each R

line (Figure 1). The behaviour of these parameters has been studied to varying degrees in their response to stress, temperature, and chromium.

The spectra observed from aged TBC systems were not usually similar to the simple doublet observed in single crystal material. Some spectra can be described as being due to two stress states in the material – physically interpreted as being due to bonded (stressed) and de-bonded (unstressed) material. More often, although there may be dominant contributions from two stress states, there is evidence that there may be a distribution of stressed states present. This makes the extraction of quantitative data complicated.

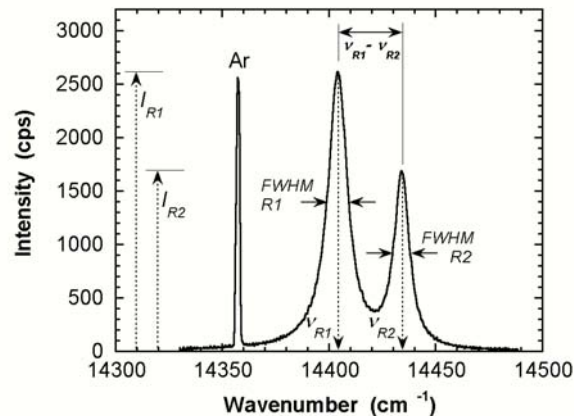


Figure 1: Fluorescence spectrum for Cr doped alumina showing R1 and R2 lines [4]

A procedure was developed to separate the contribution from the different stress states. Each spectrum is considered to consist of an underlying linear baseline (due to background signal and instrumental effects) together with multiple R1/R2 curves. The R1 peak is used to obtain an initial estimate of the parameters for fitting to a single doublet, and the optimisation routine uses a Sequential Quadratic Programming method combined with a line search to find the best-fit parameters subject to constraints on the intensity ratios, halfwidth ratios, R1 and R2 shapes, and R1-R2 separation. If the fit to a single doublet is deemed unsatisfactory, a fit to two doublets is implemented, with the parameters from the fit to a single doublet utilized to obtain an initial estimate of the parameters for the optimisation routine. The appropriateness of the fitting program was compared in an international round-robin [4] and the NPL program was demonstrated to be in agreement with that used by other leading workers in the field. The peak intensity data and stress maps presented later in this report are based on this curve fitting program and the data are presented in terms of the low stress and high stress components of the R2 peak, R2a and R2b, respectively.

Stress maps. Figures 2 and 3 are examples of the type of information that can be obtained by analysis of the changing stress state in the TGO in which MCrAlY specimens were aged at 1000 °C until failure (600 h). The TBC spalled immediately after the specimen was measured. In Figure 2 the high and low stress maps resulting from curve fitting are presented as well as a map showing the intensity ratio R2a/R2b. It can be clearly seen that the top region of the specimen has become less compressively stressed and that in this region the ratio of the low stress signal is much greater than that from the high stressed signal. Figure 3

shows the average stresses over the whole specimen from both the high and low stress maps and in both cases the average stress become less compressive shortly before failure.

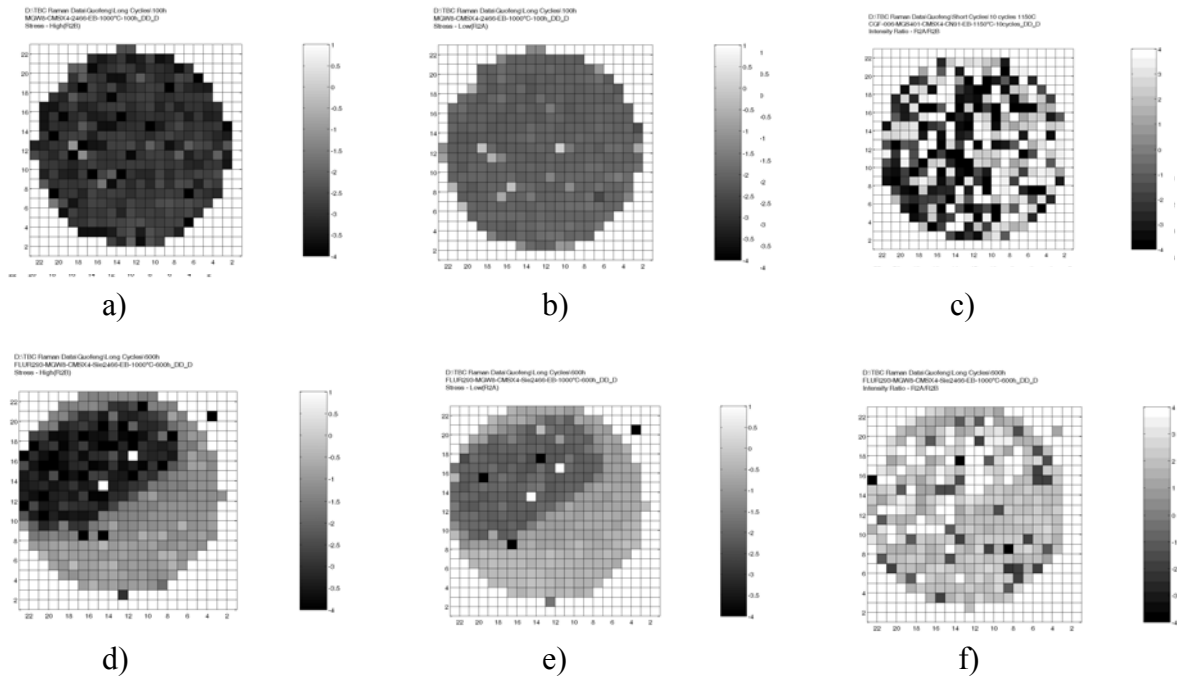
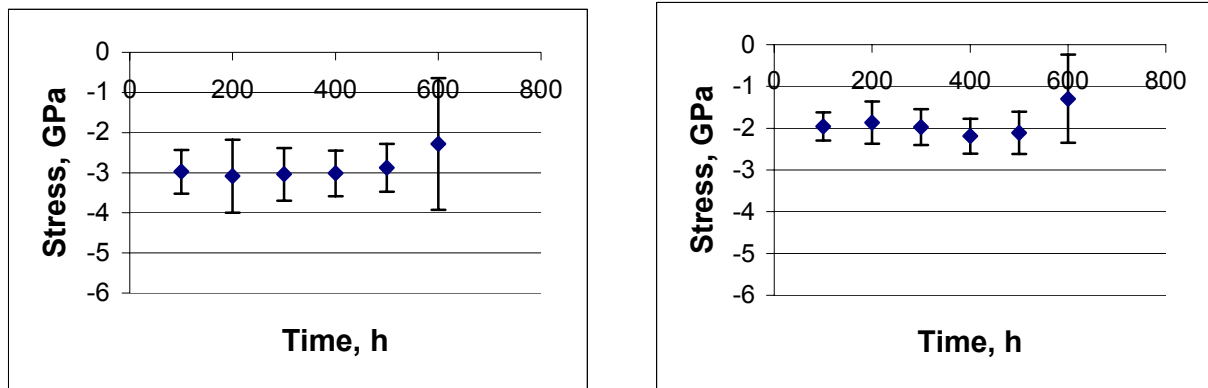


Figure 2: Stress maps for EBPVD/MCrAlY after slow cool ageing tests at 1000 °C for 100 h, (a) R2b (b) R2a (c) R2a/R2b intensity ratio, and after 600 h ageing (d) R2b (e) R2a (f) R2a/R2b intensity ratio, – stress scale black – 4 GPa white + 1 GPa; intensity scale black R2b/R2a = 4 white R2a/R2b = 4.

Figure 3: Mean stress and range of TGO formed on MCrAlY bondcoat during fast ageing



tests at 1000 °C.

The work reported below provides essential information needed to better interpret the stress maps and spectral intensity.

2 EXPERIMENTAL

Coatings. Pt aluminized and MCrAlY bondcoats were deposited on CMSX4 substrates. Both air plasma sprayed (APS) and electron beam physical vapour deposited (EB-PVD) TBCs were used in both cases. All coating systems were tested after receiving the appropriate heat treatment.

Ageing Experiments. All coatings were evaluated in the as-received and aged conditions and were aged by heating in air. The TBC coatings with a Pt aluminide bondcoat were aged at 1150 °C, whilst those with MCrAlY bondcoat were aged at 1000 °C and 1050 °C. Two different cyclic ageing tests were used:

- i) “slow” cool cycle which consisted of heating and cooling specimens at 100 °C h⁻¹ in which the time at temperature was 100 h. These tests were for up to 700 h for the MCrAlY bondcoats. (Some specimens remained intact up to 1900 h)
- ii) “fast” cool cycle which consisted of rapid heating and cooling to temperature with 1 hour holds at temperature; the rapid heating and cooling was uncontrolled and consisted of placing and withdrawing the specimens directly into the hot zone of the furnace. During the cooling phase an additional air blast was used. Cooling to 100 °C was achieved within 80 seconds. These tests were for up to 70 h for the Pt aluminized bondcoats. (Some specimens remained intact up to 200 h)

Characterization. At intervals during the ageing cycles, stress maps were obtained by scanning the surface of each specimen using a 1 mm x 1 mm grid (about 220 spectra were recorded from each specimen). The shift in the R2 peaks was used to determine the changes in stress in the TGO.

Spectral intensity was calibrated in terms of the chromium ion content by preparing Cr-doped alumina compacts sintered at 1600 °C, with chromium concentrations of 3, 42, 120 and 330 ppm. The compacts were about 2 mm thick. The chromium concentration of the alumina compacts and also the TGO was measured by glow discharge mass spectrometry (GDMS).

The effect of differing thickness of the TBC was investigated by taking aged specimens and measuring the intensity of the fluorescent signal as the TBC was progressively thinned by abrading with 280 grade SiC papers. Tapered sections were also prepared to study this effect.

3 RESULTS

3.1 INSTRUMENTAL EFFECTS

3.1.1 Instrument description

The argon ion laser used in this work is normally operated at a power of 62 mW (all lines) which after passing through a plasma filter to remove unwanted radiation lines reduces to 16 mW, and after traversing through beam splitters inside the microscope reduced further to 5.1 mW which actually reached the specimen. The wavelength used was 514 nm. The

typical integration times used in this work are 4 seconds. Figure 4 shows a schematic diagram of the confocal microscope optics in the Dilor_XY spectrometer used in this work. Light from the laser is focussed by lens L_1 to a secondary waist. A pinhole D_1 placed at this focus acts as a spatial filter and removes unwanted light due to incoherent plasma emission and scatter. It also selects the central portion of the focussed laser light, which for a TEM_{00} (transverse electromagnetic) mode ideally has a Gaussian intensity profile. The microscope comprises lenses O_b and L_T . O_b is an infinity-corrected objective with an acceptance cone of semi-angle α which forms a parallel output beam when a point source is placed at the focal point in the focal plane F . This parallel beam is then refocused by the tube lens L_T . The microscope fulfils two rôles with the assistance of the beamsplitter BS: it images the confocal pinhole D_1 onto the specimen (irradiation of the specimen), and collects the backscattered light and images it onto the confocal pinhole D_2 . Lens L_2 then images D_2 onto the entrance slit of the spectrometer. The confocal pinhole D_2 enables the collected signal to be limited to that emanating from a cross-sectional area that may be less than the irradiated area, and also to an axial depth ΔZ .

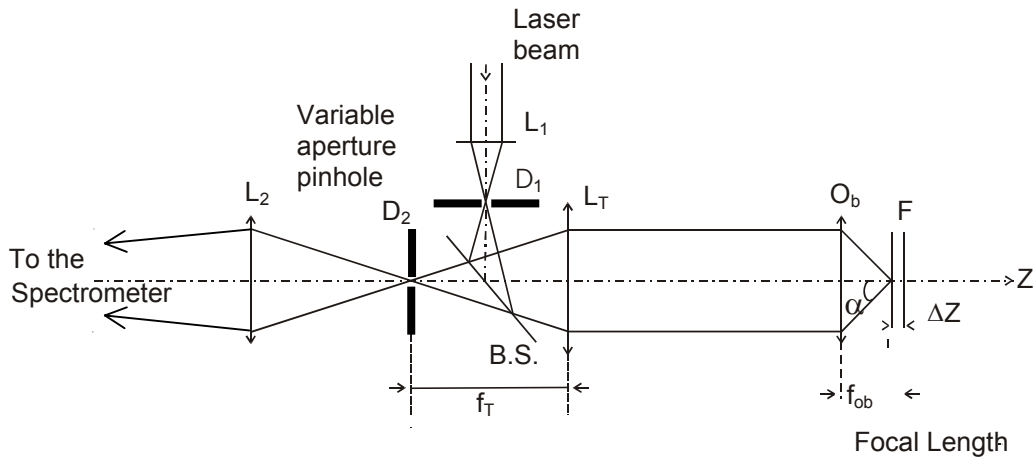


Figure 4: Optical layout of specimen optics

3.1.2 Alignment

In order to focus the irradiating laser spot onto the specimen, diffuse white light from a fibre bundle is imaged onto the specimen while the operator looks at the backscattered light before it is diverted to the confocal pinhole. This is achieved through the use of a flip mirror located between L_T and O_b which directs the light to the eyepiece lenses (not shown in Figure 1). This extended source has a much larger extent than the laser radiation and therefore irradiates a much larger area of the specimen than the laser radiation.

3.1.3 Throughput

There are two approaches to modelling the collection efficiency as a function of objective lens numerical aperture (N.A.) where

$$N.A. = n_{air} \sin \alpha$$

and n_{air} is the refractive index of air and α is the maximum cone semi-angle of the objective lens [5]. Assume an infinitely thin planar specimen.

- (i) Assume source of Raman or fluorescence signal is a point which radiates uniformly in all directions. We are concerned with the backscatter that will occur over 2π steradians.

A cone of semi-angle α has an apex solid angle of $2\pi(1 - \cos\alpha) = 4\pi \sin^2 \frac{\alpha}{2}$ steradians, and a lens which subtends this angle at the source will therefore collect this fraction of the total 2π scattered light. This model ignores the fact that the collection and transmittance of extreme rays is less efficient than paraxial rays.

- (ii) A more realistic model is based on the source being a small disk with uniform radiance, i.e. the irradiance has a $\cos \alpha$ fall-off with angle as the angle moves away from normal (0°) to high angle collection. In this case we find that for a lens subtending a semi-angle of α the fraction of light collected scales as $\sin^2 \alpha$. For a finite sized disc a more realistic calculation will need to take account of the irradiance onto the disc, which is most likely to be a truncated Gaussian profile as obtained from a spatially filtered laser beam.

For the following N.A. lenses, these models give the following collection fractions of the total light backscattered over the hemisphere from an opaque surface:

Table I. Theoretical collection efficiencies as a function of N.A.

N.A.	Cone semi-angle (degrees)	Fraction collected	
		Model (i)	Model (ii)
0.5	30	0.13	0.25
0.9	64	0.56	0.81
0.95	72	0.69	0.90

These figures give a feel for the relative collection efficiency as a function of N.A. However, the optics are optimised for a particular N.A. or range of N.A., and the only way of determining the true relative efficiencies is by experiment.

Transparent specimens require this model to be extended to account for the common volume of specimen that is both irradiated and from which signal is collected.

3.1.4 Lateral resolution

In the confocal arrangement, the magnified image of the specimen is projected onto a pinhole of diameter D_1 . The magnification of the microscope, with an infinity-corrected objective, is given by

$$M = \frac{f_t}{f_{ob}}$$

where f_{ob} is the focal length of the objective lens and f_t is the focal length of the tube lens. The stated magnification of the lens objective is normally given for use with a standard tube lens. If the system is properly designed so that all the area of the confocal pinhole is imaged

onto the spectrometer slit, we find that the analysed area, i.e. the lateral resolution, is given by

$$R_{\text{lateral}} = \frac{D_1}{M}$$

Hence for a pinhole of 1.4 mm diameter, and $M=100$, the analysed area will have a diameter of 14 μm , but this may be larger than the irradiated spot.

3.1.5 Axial resolution

Three factors affect the axial resolution, or optical sectioning property, of a confocal arrangement:

- (a) N.A. numerical aperture of objective lens
- (b) M magnification
- (c) D_1 confocal pinhole diameter

$$R_{\text{axial}} \propto \frac{N.A., M}{D_1}$$

The axial resolution is conventionally defined as the FWHM of the signal intensity profile obtained by plotting collected signal intensity versus relative displacement of the specimen along the optical axis.

This approach has been demonstrated using very thin transparent specimens of thickness $\Delta t \ll R_{\text{axial}}$ and with opaque specimens. Figure 5 shows data taken from the Dilor documentation for the Olympus x100 lens which were obtained from measurements on an opaque silicon specimen using 488 nm excitation, i.e. at around 500 nm.

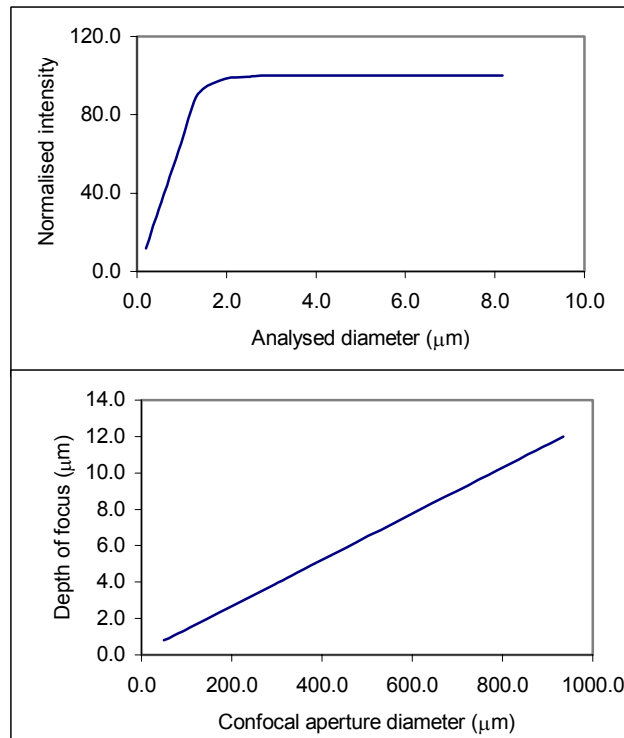


Figure 5: Collection efficiency using x100 Olympus objective [6]

In Figure 5, the two abscissae correspond to each-other and show that the analysed area (lateral resolution) varies with size of confocal pinhole by the constant factor of x100 as predicted. The lower section shows how the measured depth of focus varies with confocal pinhole size, and the upper section shows how the collected signal intensity varies with pinhole size/analysed area.

It can be seen that no gain in signal intensity is obtained for pinhole sizes greater than 250 μm .

The diffraction limit at 500 nm is given by:

$$D_{\min} = \frac{1.22 \lambda}{\text{N.A.}}$$

which gives a value of 0.65 μm for the maximum lateral resolution achievable. From Figure 2 it can be seen that this corresponds to a pinhole aperture of 65 μm , a depth of focus of 1 μm , and a relative collection efficiency of 40%. Measurements of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ fluorescence are made at around 14400 cm^{-1} , i.e. 694 nm. This gives a value of 0.9 μm for the maximum lateral resolution achievable. From Figure 2 this corresponds to a pinhole aperture of 90 μm , a depth of focus of 1.25 μm , and a relative collection efficiency of 57%. However, extrapolating the behaviour of Figure 2 from 500 nm to 694 nm should be taken as indicative only.

3.1.6 TBC specimens

Figure 6 shows the idealised structure of a TBC system. In this case signal is obtained from fluorescence emanating from the few μm thick TGO layer, which may be below 200-300 μm of TBC. The conclusions obtained from measurements of opaque specimens may therefore not hold, and investigations to elucidate the light irradiation and collection involved in this structure are described in later sections of this report.

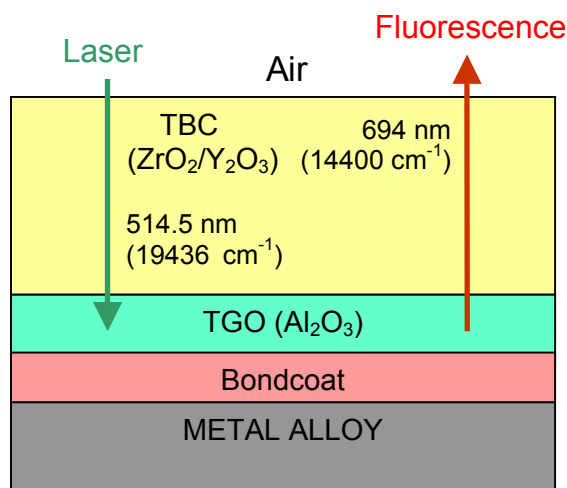


Figure 6: TBC structure (not to scale)

Figure 7a illustrates two idealized extremes where the focus is at the top and bottom of the TBC layer. If the TBC were homogenous one could envisage that the collection efficiency

and lateral resolution could be determined as a function of microscope offset and the thicknesses and refractive indices of the TBC and TGO layers, and related to the characteristics shown in Figure 5. However, the EBPVD TBC is known to be columnar in structure with column diameters of 10 – 20 μm and air gaps separating the columns. These columns may then act as ‘light-pipes’ to transport radiation between the TBC surface and the TGO using total internal reflection. This hypothesis has some support from the observation that the collected fluorescence intensity peaks vary sharply when the focal plane of the objective lies close to the TBC surface.

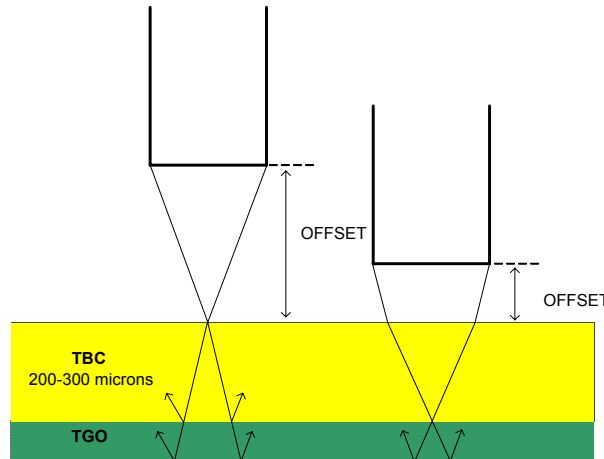


Figure 7a: Measurement geometries

The column diameter stated above is large compared with the wavelength of radiation involved and the use of geometrical optics allows a valid analysis of the light-piping qualities of the TBC columns.

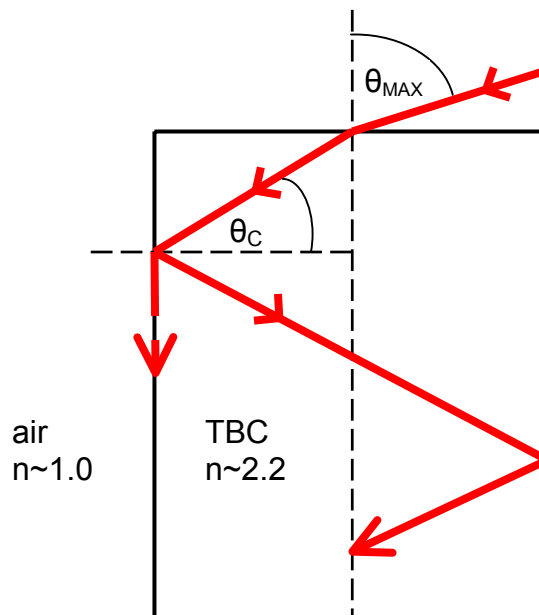


Figure 7b: Reflection in a light-pipe

The critical angle θ_C specifies the minimum angle of incidence within the light-pipe at which total internal reflection will take place:

$$\sin \theta_C = \frac{n_{\text{air}}}{n_{\text{TBC}}}$$

This is shown in Figure 7b, where the ray along the TBC/air boundary shows refraction at 90° . In turn, θ_{max} specifies the angle of incidence from air onto the TBC light-pipe which corresponds to the θ_C :

$$\frac{\sin \theta_{\text{max}}}{\sin(90 - \theta_C)} = \frac{n_{\text{TBC}}}{n_{\text{air}}}$$

θ_{max} therefore defines the N.A. of the fibre, and it can be shown that:

$$\text{N.A.} = \sqrt{(n_{\text{TGO}}^2 - n_{\text{air}}^2)}$$

If we take $n_{\text{TBC}} \sim 2.2$ which is typical for yttria-stabilised cubic zirconia [6], we find the following:

$$\theta_C = 27^\circ; (90 - \theta_C) = 63^\circ.$$

Since $(90 - \theta_C)$ exceeds the critical angle, using the principle of reversibility we can immediately see that $\theta_{\text{max}} = 90^\circ$ and $\text{N.A.} = 1$ (θ_{max} cannot exceed 90° , nor can N.A. exceed 1 in air).

Hence light incident at any angle onto the TBC light-pipes will be transported to the TGO interface. Similarly, light incident at any angle onto the TBC light-pipe at the TGO interface will be transported by the light-pipe back to the surface if $n_{\text{TGO}} < 1.96$ (typically $n_{\text{TGO}} = 1.75$).

We therefore note that the TBC columns should be very efficient light pipes, and accept light from all N.A. objectives, regardless of the orientation of the light pipe axis with respect to the optical axis. This is noteworthy, since the tops of the TBC columns are of angular conical shape rather than being flat. The returning backscattered light may couple out of the TBC column into a larger solid angle than that of the objective lens, and hence the collection efficiency will be a function of objective N.A. and TBC column orientation.

As reported later, it is observed that the collected fluorescence signal falls off rapidly with TBC thickness. The following lists some possible explanations, but may not be exhaustive:

- (i) The columns are not completely surrounded by air, but may butt up against other TBC columns, leading to the light leaking and spreading as in a homogenous layer;
- (ii) The air gaps become filled with debris, providing a lower index mismatch and allowing light to leak out;

- (iii) The columns do not have perfect ‘walls’, and these flaws provide sites for light scatter out of the columns;
- (iv) The columns are themselves not simple, but may bifurcate, leading to spread.

In order to further understand how significant is the light-pipe aspect to light transport within the TBC layer, further calculations and experiments are required. We note also that the air-gap/TBC columnar structure is similar to the ‘holey’ fibre structure where the cladding consists of an array of air holes that run the length of the fibre and combine wavelength-scale features with a high refractive index contrast (glass-air). These are under further consideration at the time of writing.

3.2 SPECTRAL INTENSITY AND CHROMIUM CONTENT OF THE TGO

Oxidation of Pt Aluminide. The oxidation kinetics of the Pt aluminide bondcoat was studied at 1050 °C and 1150 °C in air. Fracture sections were prepared and the oxide thickness measured in a scanning electron microscope (SEM). Figure 8 shows a parabolic plot of the data obtained after oxidation at 1050 °C and it can be seen that approximately linear relationship was obtained; similar kinetics were found at 1150 °C. Some of the oxide scales formed during this investigation were also analysed by GDMS and the chromium concentrations observed were 7500 ppm after 375 h at 1050 °C and 6000 ppm after 120 h at 1150 °C.

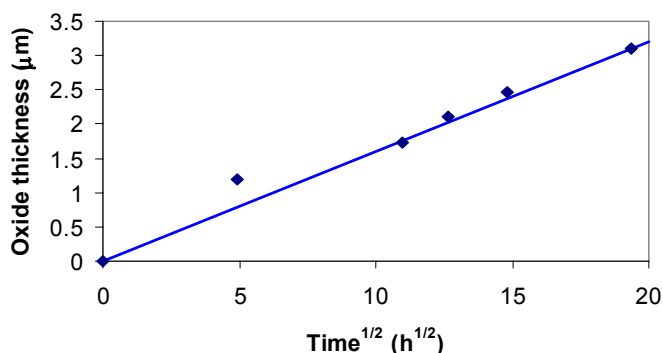


Figure 8: Oxidation kinetics of Pt aluminide coating at 1050 °C

Spallation of TBC coated specimens. The EBPVD TBC coated Pt Aluminide spalled after 70 h exposure at 1150 °C in the fast cycling ageing tests whereas the TBC coated MCrAlY spalled after 200 h at 1050 °C and 600 h at 1000 °C. It was noteworthy that in both cases spallation occurred after standing for some time at room temperature.

Spectral Intensity. The spectral intensity of the Cr doped alumina pellets was measured, and Figure 9 shows a linear relationship was observed between intensity and Cr concentration as would have been expected. The 42 ppm Cr –doped alumina pellet was progressively thinned to 20 μm and the spectral intensity measured. As can be seen from Figure 10, a reduction in intensity was only observed after thinning to 100 μm. From this information and knowing the density of the pellet (82% of bulk alumina) and the cone angle (72°) of the illuminating laser light, it was possible to calculate the number of Cr ions contributing to the signal. These values were compared with the Cr content of the TGO and a

reasonable agreement was found. This result gave confidence that, at least in the absence of TBC, the Cr content of the TGO could be monitored using the fluorescence signal. The intensity and integral of the R2 peaks (R2a and R2b) obtained from the fluorescence spectra of the TGO formed on the Pt aluminide was plotted as a function of oxidation time. The log/log plot showed that the intensity and peak integrals obeyed the same relationship with a slope of approximately 0.4 (Figure 11). This is a similar relationship as was observed for the oxide thickness as a function of time (Figure 8). Consider now the intensity time relationship observed on the aged EBPVD/Pt aluminide system shown in Figure 12, where after an initial rapid period of oxidation, a linear increase in intensity with exposure time was observed. This would suggest that either the oxidation kinetics had changed or that the Cr concentration in the oxide scale was increasing with increasing exposure, but in either case the scale was becoming less protective with increasing time.

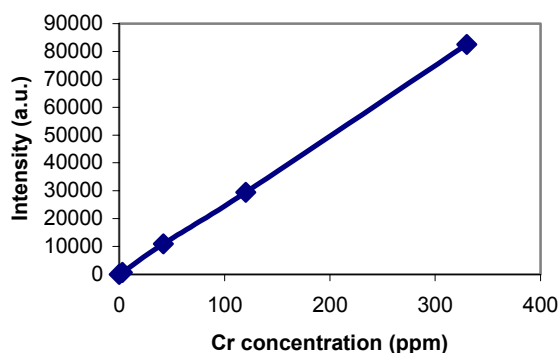


Figure 9: Fluorescence intensity of R2 peaks for Cr-doped pellets

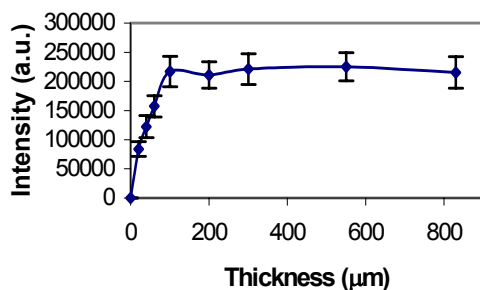


Figure 10: Fluorescence intensity of R2 peaks for 42 ppm Cr in alumina as a function of pellet thickness

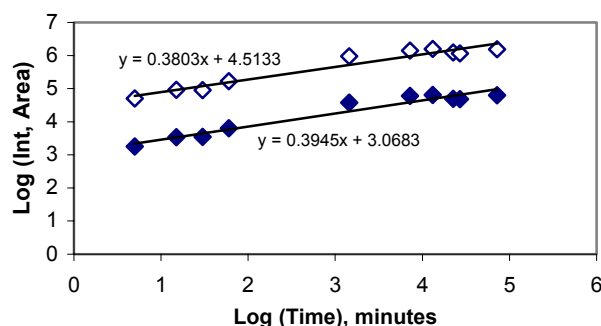


Figure 11: R2 fluorescence intensity/area as a function of exposure time for alumina formation on Pt aluminide bondcoat at 1050 °C, open symbols integral R2, closed symbols intensity

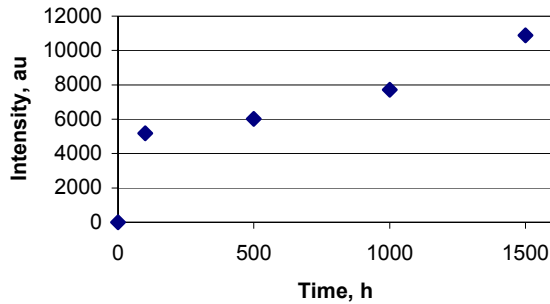


Figure 12: R2 fluorescence intensity for a EBPVD/Pt aluminide TBC system after extended aging at 1050 °C

3.3 SPECTRAL INTENSITY AND TBC THICKNESS

Specimens of EB PVD and APS TBC were firstly aged in order to obtain a sufficient fluorescent signal from the TGO. Both specimens were then mounted at a very shallow angle and then polished back in order to obtain a gradually increasing thickness of TBC as shown in Figure 13 where the numbers represent different portions of the specimen. Region 5 is the TBC being studied in this case.

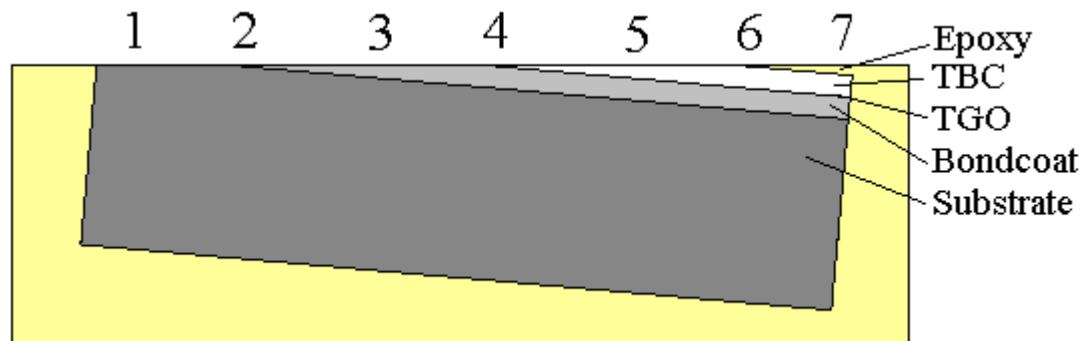


Figure 13: Schematic diagram of a taper section of TBC coated specimen

Scans originating in region 1 and moving on through to point 6 were obtained. The thickness of TBC above the TGO could be calculated from the position and knowledge of the angle by which the specimen was tilted before polishing.

3.3.1 EBPVD TBC:

Figure 14 shows the way in which the detected fluorescent varied as the tapered specimen was scanned from position 3 through to 5 of Figure 13. The abscissa has been scaled to actual displacement through the cross-section for ease of interpretation. Notice how from approximately the 90 μm position onwards the collected signal strength decayed as a function of the TBC thickness.

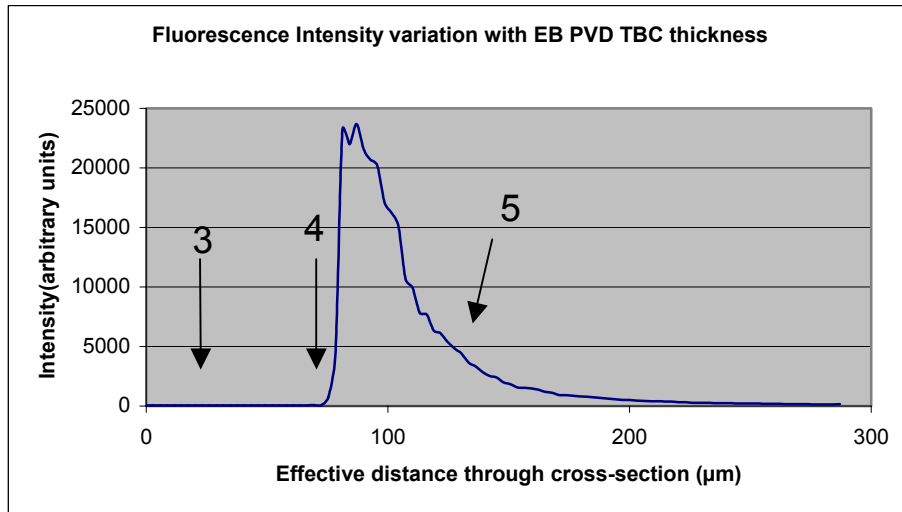


Figure 14: Fluorescent signal intensity across taper section of an EBPVD TBC coated system aged at 1150 °C.

Fitting an exponential function to the right hand side of the intensity profile in Figure 16 we find that the expression:

$$I = k \cdot e^{-t/25}$$

where I is the intensity, k a constant and t is the TBC thickness

is a good fit to the data (Figure 15). Put differently, approximately 20 μm of EBPVD TBC is enough to halve the fluorescence signal.

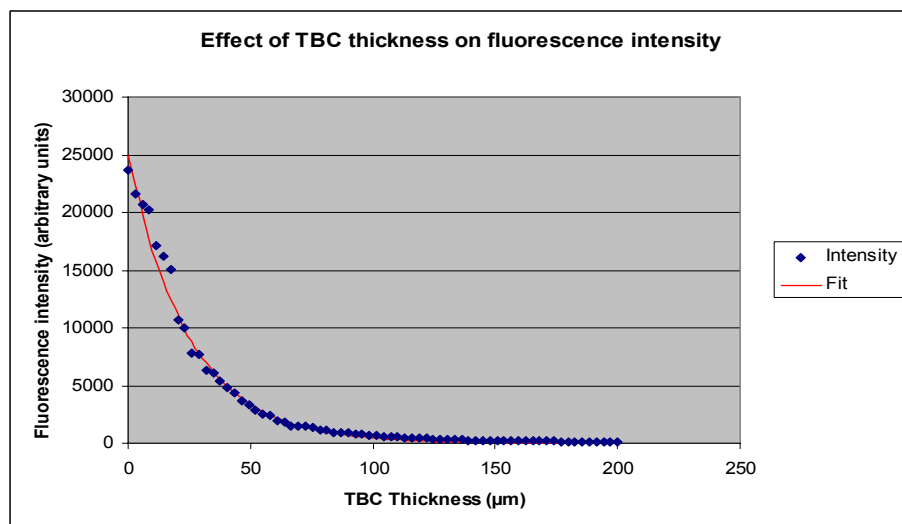


Figure 15: Fluorescent signal intensity of an EBPVD TBC coated system aged at 1150 °C fitted to an exponential function.

In order to gain additional confidence in the result, another aged EBPVD TBC specimen was studied. After each intensity measurement was made, the thickness of the TBC was reduced by abrading with 280 grade SiC papers. The result is shown in Figure 16. The best exponential fit to this sparser data was:

$$I = k \cdot e^{-t/20}$$

which is in fair agreement to that observed before. It confirms that the TBC extinguishes the signal intensity with a ‘half intensity’ thickness of approximately 20 μm .

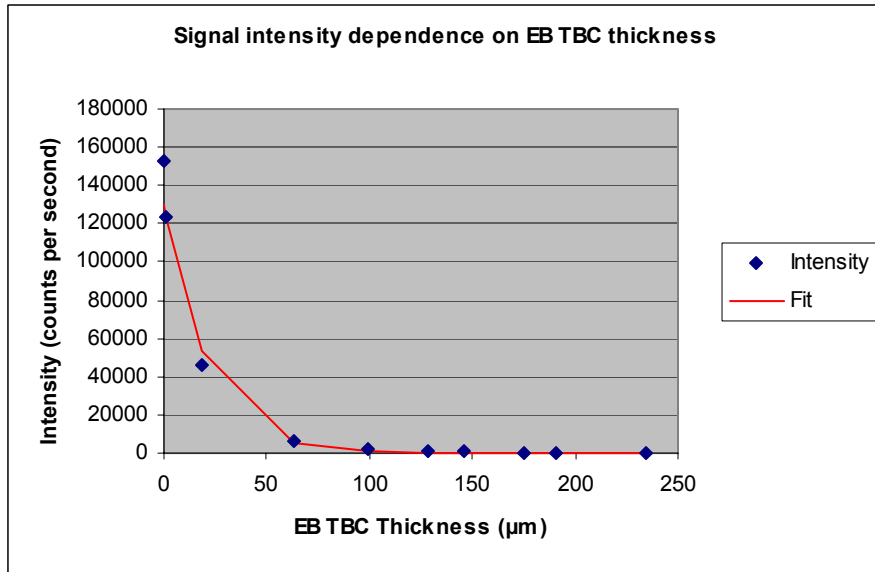


Figure 16: Fluorescent signal intensity of an EB TBC coated system aged at 1150 °C as a function of TBC thickness (TBC progressively thinned by abrading).

3.3.2 APS TBC:

APS TBC specimens were prepared following the same two techniques as used for the EBPVD TBC described above. The results are shown in Figures 17 and 18, respectively.

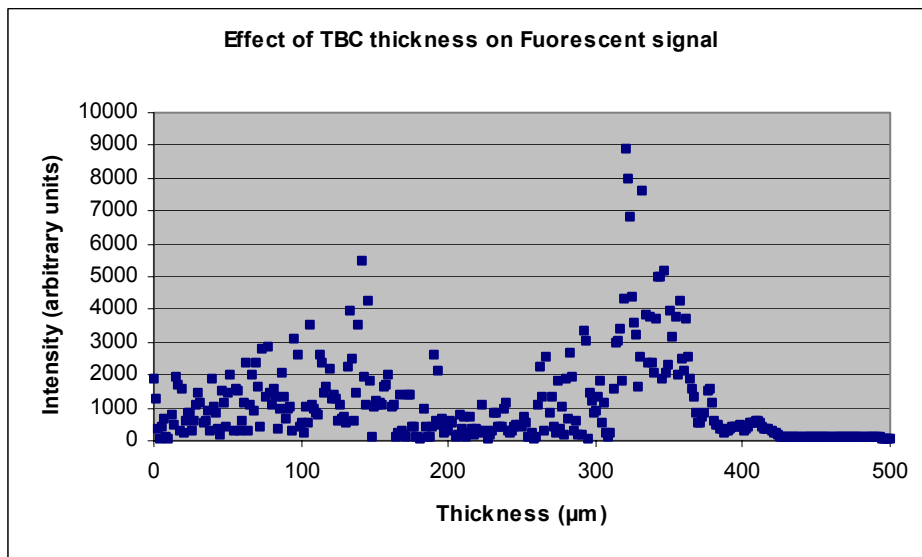


Figure 17: Fluorescent signal intensity across a taper section of an APS TBC coated system aged at 1000 °C

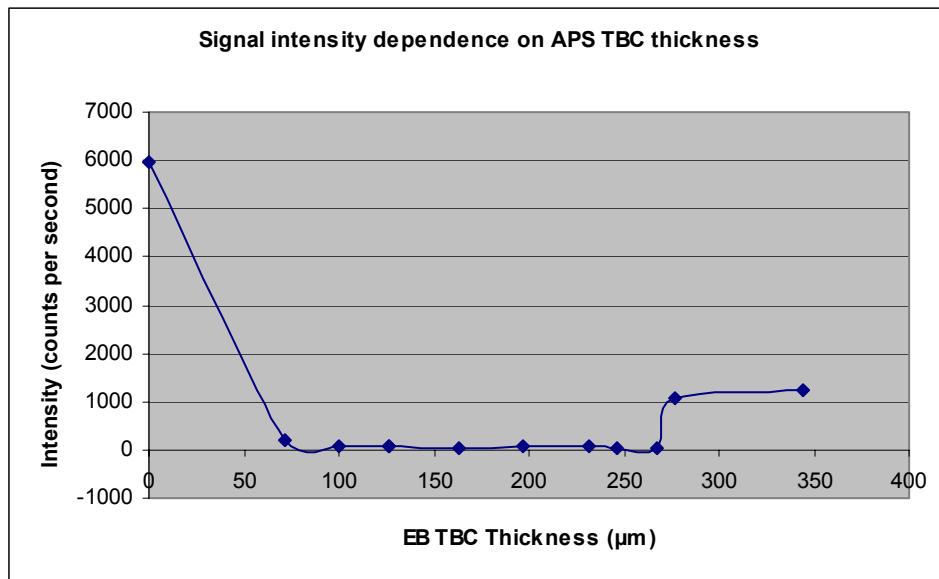


Figure 18 Fluorescent signal intensity of an APS TBC coated aged at 1000 °C system as a function of TBC thickness (TBC progressively thinned by abrading).

The results are very different to those obtained for EBPVD TBC. It is clear that the APS TBC is very inhomogeneous in its transmittance, and it also seems to indicate that the uppermost 60 or 70 μm of TBC may contain some material which also fluoresces in addition to the TGO at the substrate/TBC interface. Trying to fit any form of mathematical expression to the transmittance of APS TBC is clearly meaningless.

3.4 SPECTRAL INTENSITY AND DEFOCUS

The intensity of fluorescence collected by the microscope is also dependent on focus. Figure 19 shows how the collected intensity varied with focus position for 3 different magnification objectives. The signal intensity has been normalised in order to separate the depth of focus effect from effects due to area of illumination and collection efficiency. Generally the signal level obtained with the x100 objective was approximately 4 times larger than that obtained with the x10 objective. Notice that the intensity was maximum when the microscope was focussed directly on the surface of the specimen. If the focus was altered in either direction, the collected signal decreased. The rate at which the signal decreased with defocus was greater for larger magnifications. Figure 19 shows that when using x100 magnification it is necessary to keep the focus of the microscope well monitored. This poses some limitations on the study of curved surfaces. These results were obtained when collecting fluorescent signal from a failed specimen where the TBC had already spalled off. The focus dependence may be somewhat different with TBC present.

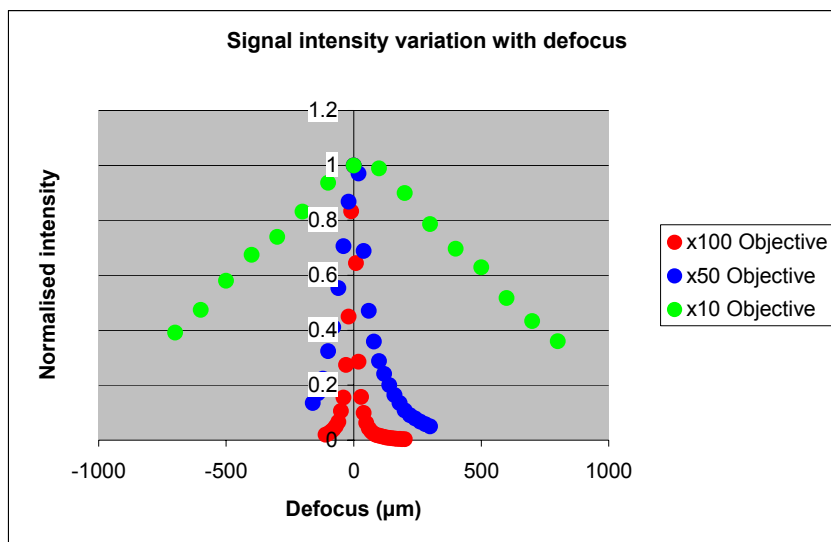


Figure 19: *R2 peak intensity as a function of microscope objective*

3.5 EFFECT OF TBC ON LATERAL RESOLUTION OF FLUORESCENCE SIGNAL

Lateral resolution of the fluorescence signal is primarily limited by the presence of the TBC rather than by any limitations inherent to the microscope itself. The argon ion laser used to excite the fluorescence is focused down by the microscope x100 objective to a spot which is approximately 1 μm in diameter at the top surface of the TBC. When imaging a 3 μm thick layer of TGO in cross-section (in the absence of any TBC) the resolution achieved is as good as 1 or 2 μm . It can be adjusted to some degree by changing the pinhole diameter of the confocal microscope. Figure 20 shows the intensity profiles obtained along 30 μm long scans over the 3 μm thick TGO with different pinhole settings.

Notice that the signal strength decreases as the pinhole size is reduced. In practice the pinhole is left at setting 13 (arbitrary units) in order to obtain the best possible signal strength. Thus the lateral resolution achievable in this work when only TGO was present is as good as 3 micrometres.

Longer, 1 mm, scans starting on the metal, covering the TGO, the entire TBC, and ending on the epoxy resin were also obtained in order to investigate the degradation of resolution which might be expected due to the fact that the TGO is not located in the focus plane of the microscope. Figure 23 shows the intensity profile obtained when focusing directly on cross section of the specimen

Figure 24 shows how the resolution of the intensity profile has degraded when the microscope is defocused by an amount equivalent to the thickness of the TBC. In this case the resolution has been degraded to approximately 140 μm purely by defocus.

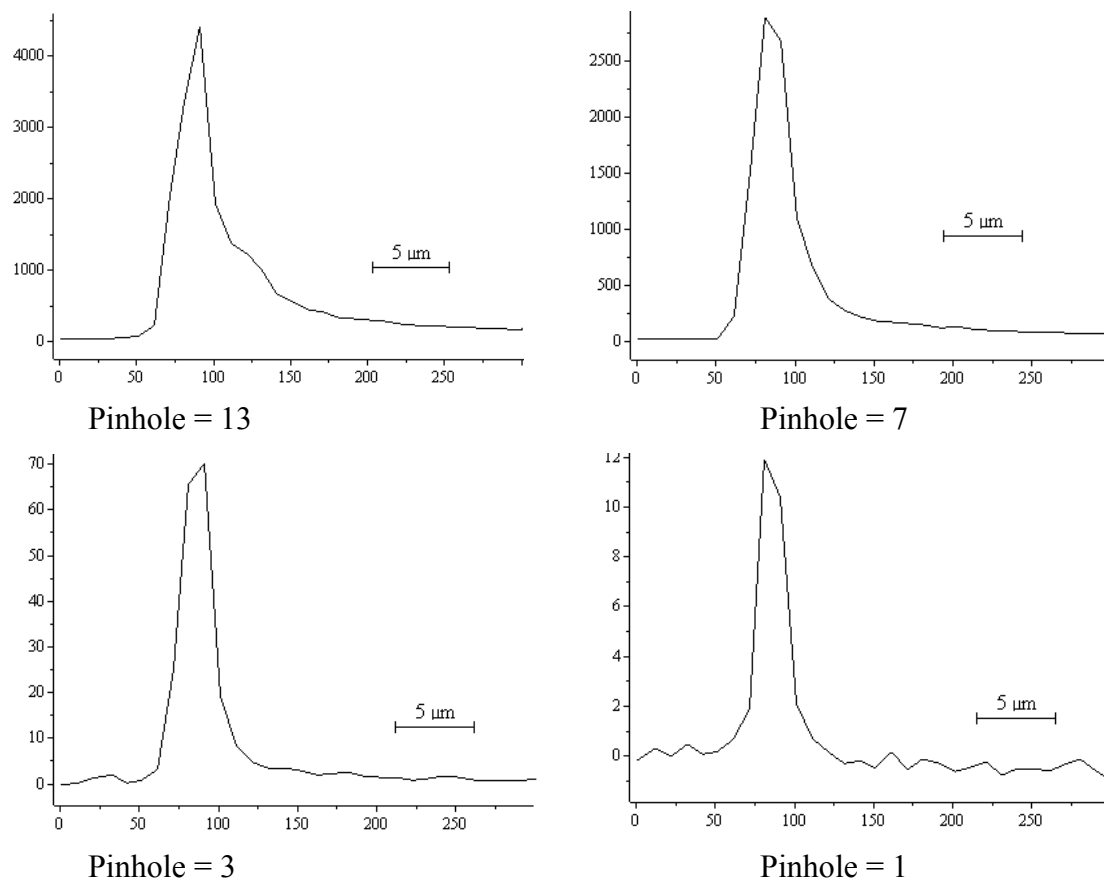


Figure 20: Effect of pinhole size on lateral resolution – scan across 3 μm thick TGO cross-section

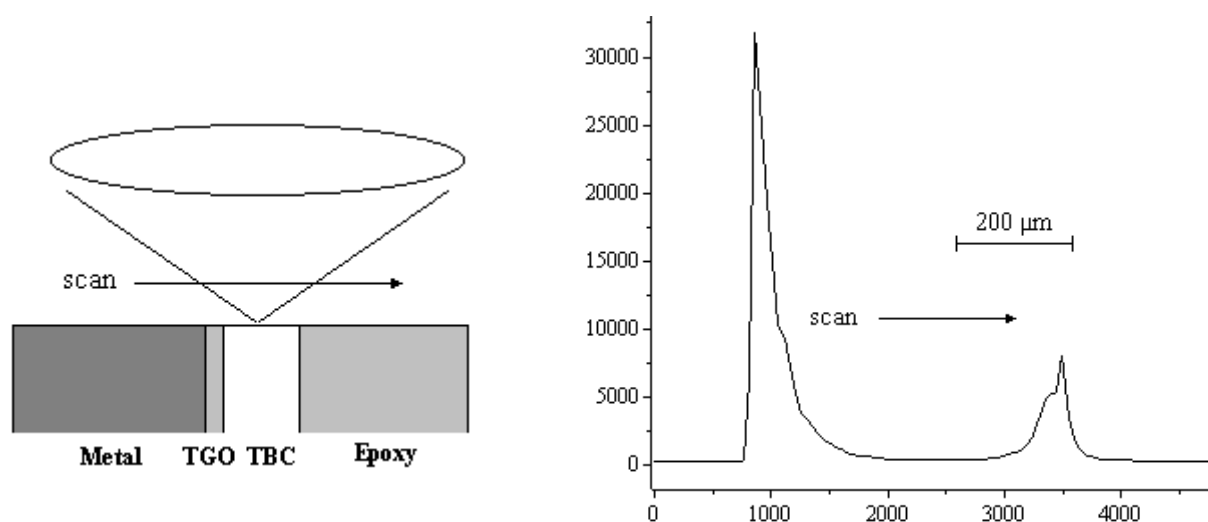


Figure 21: Schematic diagram of scan across cross-section of an EB TBC system, and the resultant fluorescent signal with focus at plane of specimen.

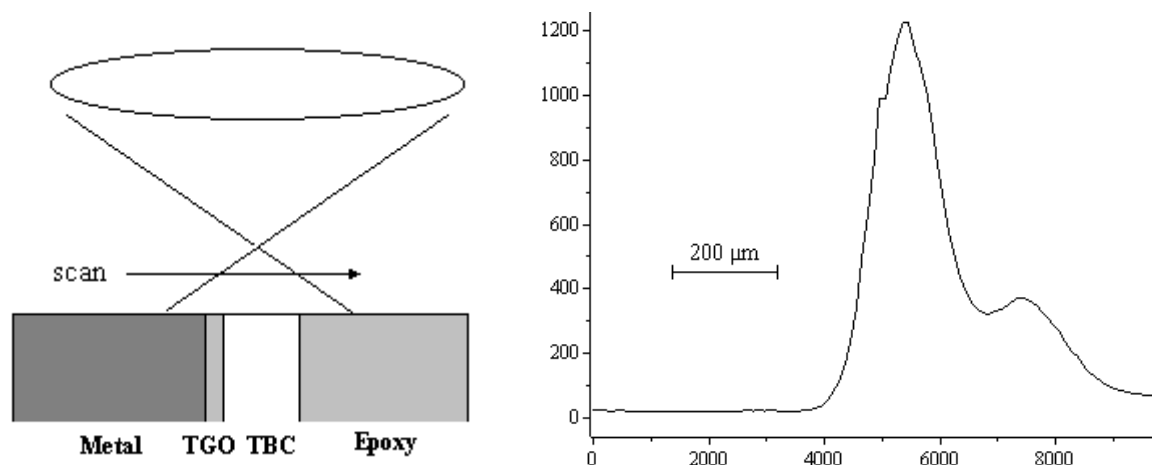


Figure 22: Schematic diagram of scan across cross-section of an EB TBC system, and the resultant fluorescent signal with focus 200 μm above plan of specimen

A test was made inserting free-standing EBPVD TBC between the objective and the cross-sectioned specimen shown in Figures 21 and 22. However, the free standing EBPVD TBC which had spalled off another specimen already had a TGO attached to it. When scanning over the cross-section, the signal obtained was simply that of the TGO attached to the free-standing EBPVD TBC. An attempt was made to remove the TGO from the free-standing EBPVD TBC using abrasive papers, but it was found that the EBPVD TBC simply fractured into many small pieces. It was possible to remove the TGO from APS TBC, but when this was placed above the cross-sectioned material shown in Figures 21 and 22 the signal obtained showed that there was sufficient alumina contaminating the APS TBC to completely mask any signal that might have come from the cross-sectioned TGO layer beneath it. In order to carry out this work properly alumina free EBPVD and APS TBC is required.

It is suspected that the characteristic columnar structures of the EBPVD TBC can act as a light-pipe channelling the laser light from the focussed spot on the top of the TBC down to the TGO layer beneath. The secondary signal peaks on the right hand of Figures 21 and 22 are located at the TBC-epoxy interface. It may be that laser light launched into the top of the EBPVD TBC may channel towards the left until it reaches the TGO, thus exciting fluorescence which also travels back to the right through the EBPVD TBC columns and then escapes in such a way that the objective can still collect the light. This effect may serve to explain why sometimes sharp signal peaks with a lateral half width of approximately 5 μm (much smaller than we would expect through defocus) may still be obtained even when imaging a plane specimen through an EBPVD TBC.

A second possible explanation for the right hand peaks of Figures 21 and 22 is that the top surface of the EBPVD TBC has become contaminated with alumina dust from the furnace or from other specimens around it. If this contamination were present we would expect a secondary peak near the TBC epoxy interface, and if the contaminations is particulate in nature, we might occasionally observe sharp and spatially well defined signal peaks when imaging a plane specimen through an EBPVD TBC.

Since the signal decays so abruptly with EBPVD TBC thickness (a half extinction thickness of approximately 20 μm), a small contamination which may possess only 0.00049 of the fluorescent material density of the TGO which lies beneath 200 μm of EBPVD TBC may

contribute a signal strength comparable to it. Thus the technique is quite sensitive to any contamination which may possess traces of chromium in it. If surface contamination of particulate was giving rise to fluorescent signals, then it would be expected that these spectra would have close to zero stress.

An alternative way to assess the degree of the spreading of the light as it traverses through the TBC on its way to excite fluorescence in the TGO was also investigated. Images were obtained of the light distribution under a free-standing piece of TBC which had spalled off actual specimens. The experimental arrangement is shown in Figure 23, and results for EBPVD TBC are shown in Figure 24 a,b and those for APS TBC are shown in Figure 25 a,b

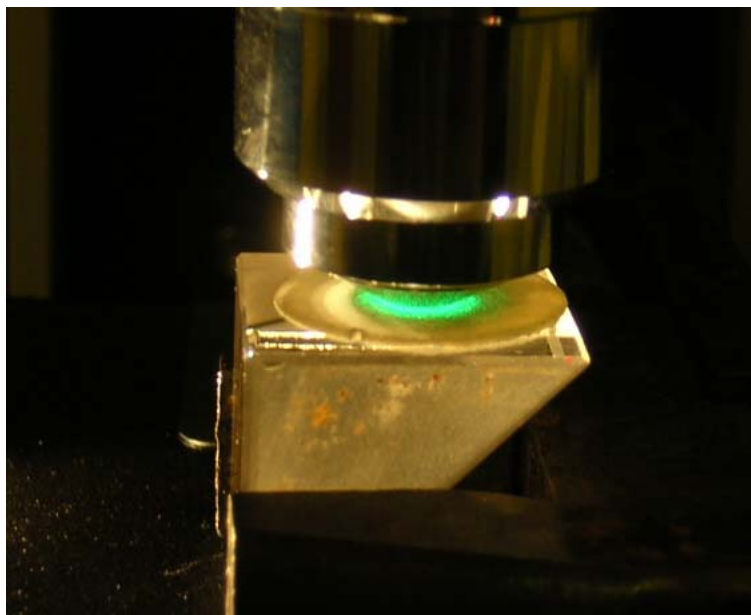
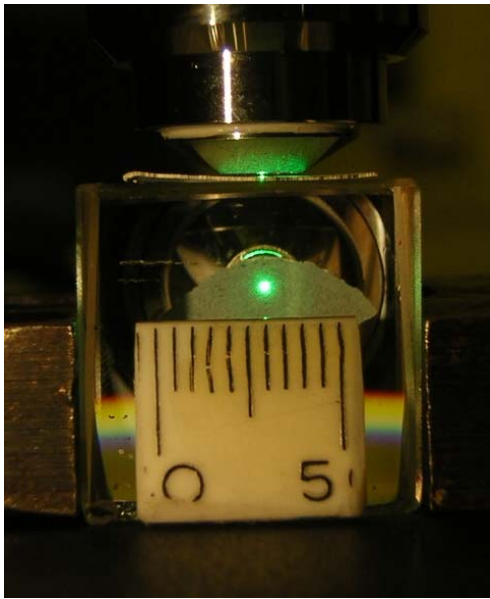


Figure 23: Experimental arrangement showing a piece of APS TBC resting on a 45 degree prism. The light which is transmitted through the TBC can be seen by a camera which is 'looking in' from the lefthand side.

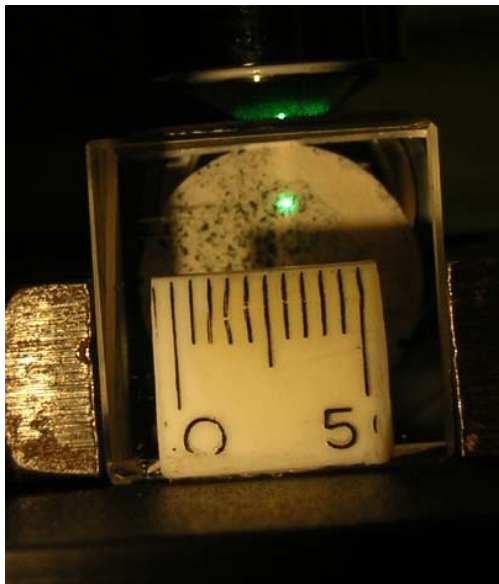


(a)

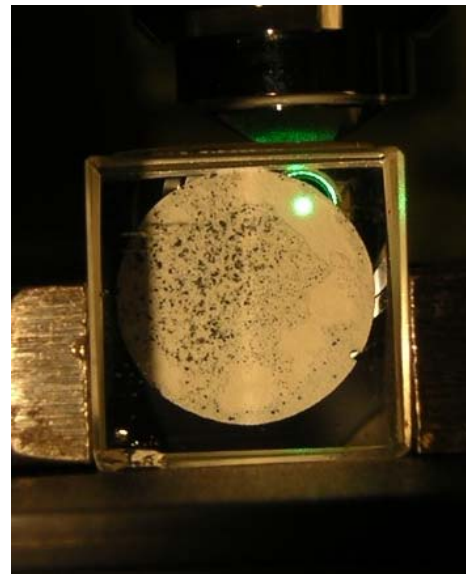


(b)

Figure 24 a,b: Photograph showing the size to which the spot of light has spread after it has traversed through a free standing piece of EBPVD TBC. The images suggest a patch of light with a diameter in the region of 0.5 mm.



(b)



(a)

Figure 25 a,b: Photograph showing the size to which the spot of light has spread after it has traversed through a free standing piece of APS TBC.

As can be seen from Figures 24 and 25, the light spreads out quite considerably as it traverses through the TBC. The spread in the light could be caused by at least two mechanisms:

scattering, and the cone of illumination coming from the high numerical aperture of the objective. It should be noted however, that the resolution may not be as bad as that suggested by these pictures because the fluorescent light originating close to the perimeter of the patch of light has a much smaller probability of being collected by the objective and making its way to the spectrometer. It should also be noted that the sensitivity of the CCD of the camera used to obtain Figures 24 and 25 may not be able to distinguish between a large saturated white level and a very small super-saturated level within it. So the intensely illuminated patch of light may be significantly smaller than that shown in Figures 24 and 25, enabling the lateral resolution to be better than these figures suggest.

4 DISCUSSION AND CONCLUSIONS

The work carried out has demonstrated that the absolute intensity of the fluorescence signal is directly related to the Cr content, and a good correlation was obtained between the amount of Cr in the TGO and calibration artefacts. Furthermore, the intensity was shown to increase approximately parabolically when measuring spectra obtained from alumina after short-term oxidation tests, verifying that monitoring intensity is an effective means of measuring the oxidation kinetics. In one case when a TBC system was exposed for long times the Cr content was observed to increase almost linearly with increasing time, suggesting that the Cr concentration of the alumina was increasing with increasing time, and/or the oxidation rate was departing from the normally protective sub-parabolic kinetics.

The lateral resolution obtainable in the presence of TBC is still not entirely resolved. Almost certainly any signal originating from an APS TBC system which appears to have high lateral resolution is most probably originating from contamination trapped near the surface of the TBC. Work continues to quantify the lateral resolution for EBPVD TBC material, and is dependent upon obtaining alumina-free TBC. Calculations and experiments show the lateral resolution to be 1-3 μm in the absence of TBC.

TBC thickness has a marked effect on the signal intensity. For the conditions used in this work the maximum thickness of EBPVD TBC that could be examined was about 200 μm . Increasing the laser power would probably increase this thickness somewhat, but care would be required to ensure that there were no heating of the TBC since this would contribute to peak shifts. In the case of APS TBC, the coated specimens were at least 300 μm thick and it is unclear whether the lack of signal is simply a function of thickness or is a characteristic of the APS material. However, if the EBPVD TBC acts to some extent as a light-pipe, as hypothesised previously, then it might be expected that only relatively thin APS TBCs might be transparent to laser light.

5 ACKNOWLEDGEMENTS

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