

An Evaluation of Thermal Barrier Coated Specimens Exposed to Long-term Ageing Tests

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ABSTRACT

Specimens coated with thermal barrier systems were exposed to long-term ageing tests and their behaviour monitored using piezospectroscopy in a non-destructive manner to determine the residual stress in the thermally grown oxide (TGO) layer that forms under the thermal barrier coating. An investigation of these specimens was carried out using destructive evaluation methods (mostly by examination of metallographically prepared cross-sections) in order to validate the observations made using the non-destructive piezospectroscopic method.

In general, for electron beam physical vapour deposition thermal barrier coatings (EB-PVD TBCs) the changes in stress state observed in plan were substantiated in cross-section, although the act of preparing the cross-section changed the stress state in the TGO. For air plasma sprayed (APS) TBCs systems, however, there was little change in stress of the TGO when examined in plan, while similar stresses to those observed for the EB-PVD TBC was found in the cross-section examination. The effect of internal scattering of the laser light by cracks and pores in the APS systems such that the TBC was no longer transparent to the laser light is believed to be responsible for these observations. It was also demonstrated that scattering of the laser light occurred in the cross-section and fluorescence was observed in the TBC that originated in the TGO, and thus great care should be exercised when using the piezospectroscopic method to examine specimens in cross-section.

When the alumina layer began to fail increased levels of chromium were observed and this altered both the peak position and intensity of the fluorescence peaks. This effect should be considered when interpreting the spectra.

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1 INTRODUCTION

This report describes the characterization of thermally aged thermal barrier coating (TBC) systems that had been previously inspected using the non-destructive piezospectroscopic method. The objective of this work was to determine whether or not the changes observed in the spectra produced by piezospectroscopy could be validated using a detailed microstructural evaluation of the specimens.

1.1 PIEZOSPECTROSCOPY

The properties of the thermally growth oxide (TGO) that forms between the TBC and bondcoat during deposition and more extensively during service are believed to strongly influence adhesion in the TBC system [1]. In most cases the TGO is alumina. Piezospectroscopy [2] was used in which Cr^{3+} ions normally present in small amounts in the thermally grown α -alumina fluoresce when suitably excited. In α -alumina the R-line fluorescence is split into a doublet (R_1 , R_2) by crystal field effects. The frequency, ν , of these lines shift with stress, thereby allowing the residual stress in the layer to be determined. Of the two lines, it has been found that the R_2 line has a more linear pressure dependence and is also more isotropic for the different crystallographic orientations [3]. Hence, the stress measurements reported have been primarily based on measurements of R_2 . For polycrystalline materials where the sample volume probed is large compared with the grain size the frequency shift, $\Delta\nu$, of the R_2 line is given by:

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

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

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

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

The method will also detect other alumina phases through the appearance of peaks associated with these phases. The presence of the metastable θ -phase has been observed by this technique [4].

Formation of alumina at high temperature has been extensively studied [5-7] and it has been shown that growth proceeds through γ , δ , θ and finally α -alumina. The growth rates of the metastable phases are greater than the stable high temperature α -alumina phase. It is generally agreed that θ -alumina transforms to α -alumina in a few hours at 1000 °C, although this time maybe modified by the presence of impurities in the alumina. If Ti ions are present, the θ -form can transform to α -alumina more quickly [5], conversely, when larger ions such as Zr, Hf or La are present the θ -form is stabilized for longer periods [6]. The literature reports conflicting results for the influence of Y where it may encourage [5] or inhibit [6] transformation of θ -alumina. But in no case was θ -alumina found at times greater than 50 h at 1000°C.

2 EXPERIMENTAL

2.1 COATINGS

Coatings were deposited on IN738 and CMSX4 substrates. The bulk of the work on piezospectroscopy was with 5 TBC systems as listed below. Pt aluminized (RT22LT) and MCrAlY (Sicoat 2453) bondcoats were used with both electron beam physical vapour deposited (EB-PVD) and air plasma sprayed (APS) TBC. The following systems were investigated:

CMSX4/RT22LT/EB-PVD
CMSX4/2453/EB-PVD
IN783/2453/EB-PVD
CMSX4/2453/APS
IN738/2453/APS

The EB-PVD TBC was supplied by Chromalloy UK, the APS TBC by Plasma and Thermal, Sicoat 2453 by Siemens, and RT22LT also by Chromalloy UK. Rolls Royce and Alstom Power provided the substrate alloys. All coating systems were tested after receiving the appropriate heat treatment.

2.2 AGEING EXPERIMENTS

All coatings were evaluated in the as-received and aged conditions. In all cases samples were aged by heating in air. The TBC coatings with a RT22LT bondcoat were aged at 1100 °C, whilst those with Sicoat 2453 bondcoat were aged at 1000 °C. Isothermal and cyclic ageing tests were used. For the cyclic tests two different cycles were used:

- i) “slow” cool cycle which consisted of heating and cooling samples at 100 °C h⁻¹ in which the time at temperature was varied but was generally 100 h or more. These tests were for up to 4000 h for the MCrAlY bondcoats and 1800 h for the Pt aluminized bondcoats.
- 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 samples 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 1800 h for the MCrAlY and 480 h for the Pt aluminized bondcoats.

2.3 CHARACTERIZATION

After the completion of the ageing tests samples were photographed using optical microscopy, cross-sectioned and metallographically prepared for further examination using an optical microscope and scanning electron microscope (SEM). Some work using the piezospectroscopic method was also carried out on the prepared cross-sections to determine whether there was a correlation between the in-plan and cross-section data.

3 RESULTS and DISCUSSION

3. OPTICAL MICROSCOPY

Photographs of the 12 mm disc specimens after the 4000 h ageing treatment at 1000 °C are shown in Figure 1. In three of the cases it is clear that a circular pattern developed, and as will be demonstrated later (Figures 3 and 4) this pattern is reflected in the stress maps measured by the piezospectroscopic method.

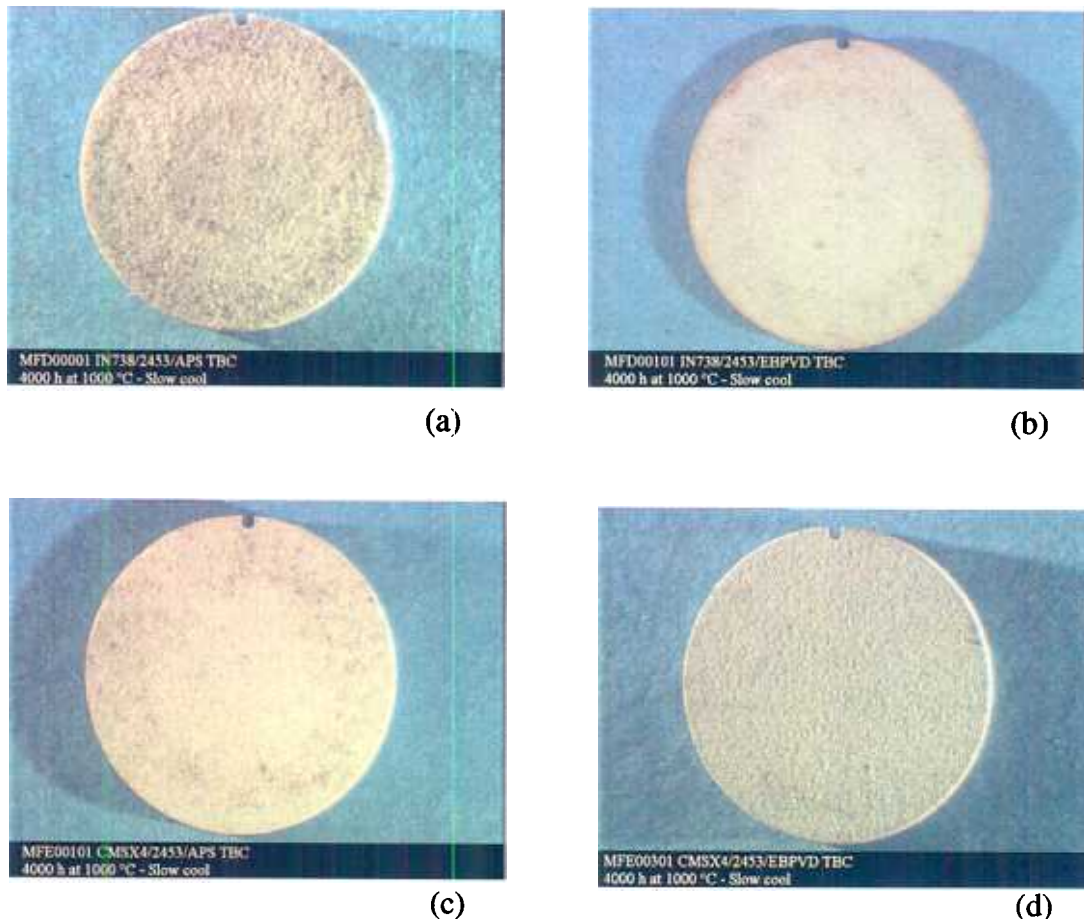


Figure 1 Optical micrograph of specimens with Sicoat 2453 bondcoats after 4000 h ageing at 1000 °C with the slow cool cycle, (a) IN738/APS; (b) IN738/EB-PVD; (c) CMSX4/APS; (d) CMSX4/EB-PVD

Figure 2 shows typical optical micrographs of cross-sections of unaged and aged TBC coating systems with APS and EB-PVD TBCs. It is important to note that the TGO is undulating in the case of the MCrAlY bondcoat and is relatively flat for the Pt aluminized bondcoat.

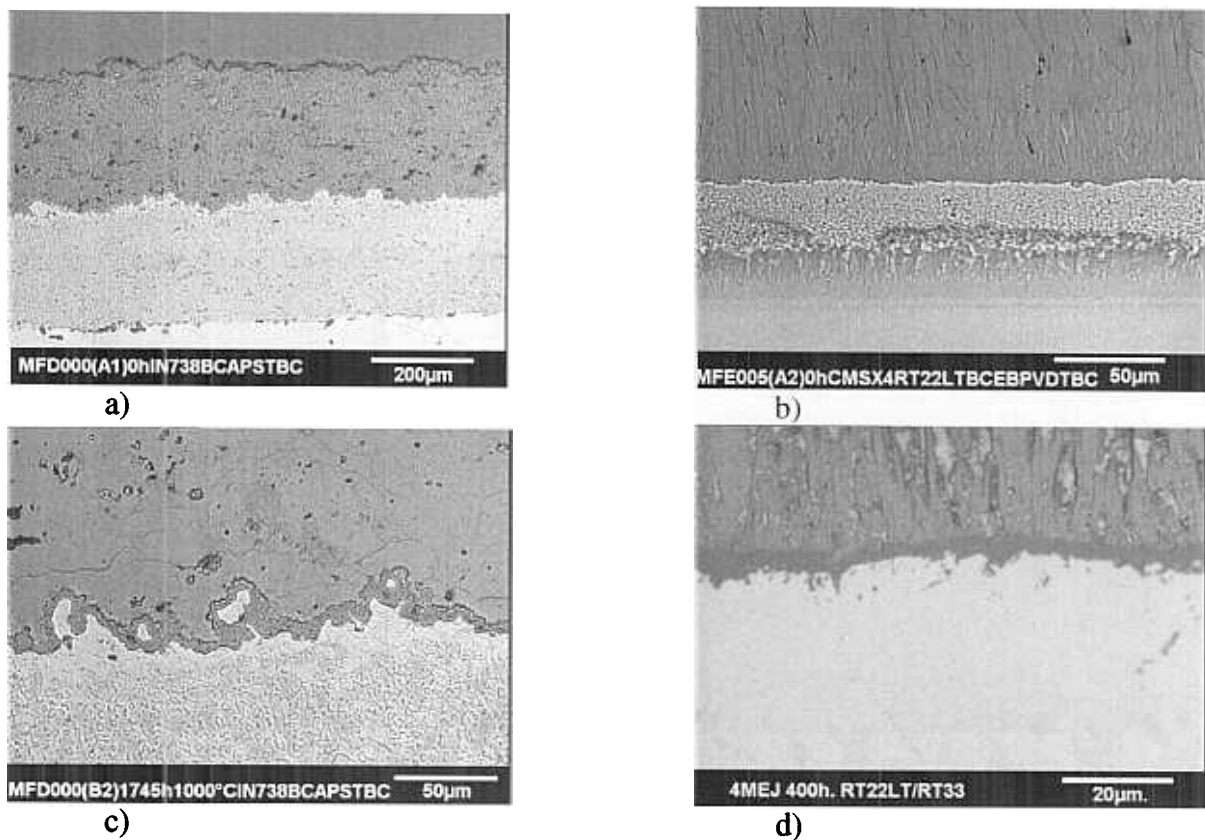


Figure 2 Optical micrographs of polished cross-sections of (a) unaged IN738 substrate MCrAlY bond coat and APS TBC (c) TBC system in (a) after ageing for 1745 h at 1000 °C using a slow cool, (b) unaged CMSX4 substrate Pt aluminide bondcoat and EB-PVD TBC and (d) TBC system in (b) after 400h at 1100 °C using a slow cool.

3.2 IN-PLAN PIEZOSPECTROSCOPY

The results of the piezospectroscopy are described in detail in the NPL Report “An Evaluation of Tests for the Adhesion of Thermal Barrier Coatings”[7], but it is appropriate to report the major conclusions here and to illustrate this with some of the stress maps generated in that work.

In general, the results indicate that while clear effects of increased ageing were found for the EB-PVD TBC coating systems (Figure 3), no such effects were found for the APS TBC systems (Figure 4). Furthermore, for the APS TBCs the area of sample from which no spectra were generated (white areas in the maps) increased with increased ageing time. A recent publication by Schlichting *et al* [8] has suggested that APS TBC may contain trace impurities of alumina that may fluoresce and thus mask the stress changes in the TGO. It is also claimed that pores and cracks in the APS TBC cause the system to be opaque to the laser light. This latter effect could account for the loss of spectra with increased ageing of the APS TBC coatings. It is thus possible that measurements made in this work with the APS TBC systems were not related to changes in the residual stress of the TGO.

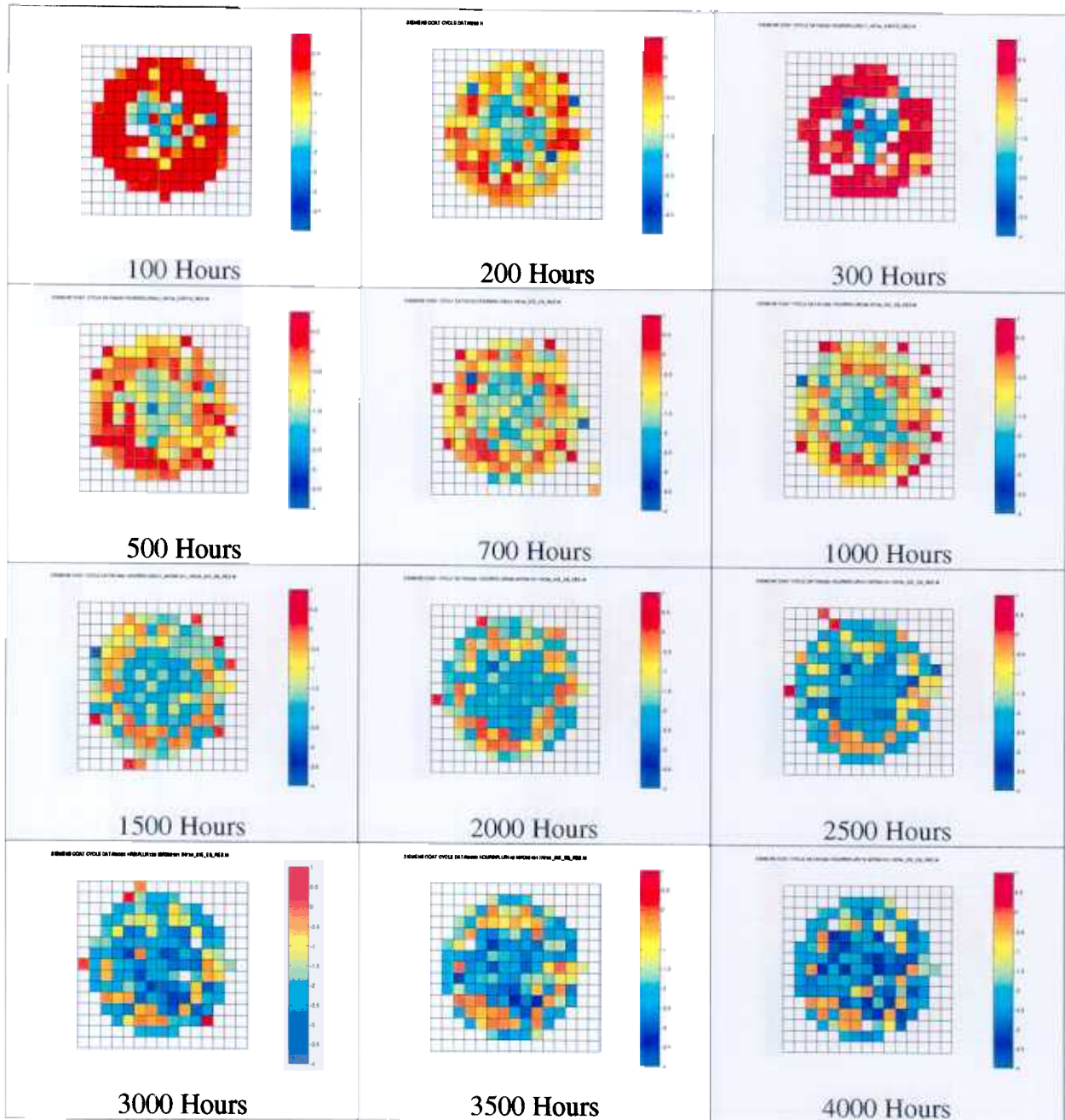


Figure 3 Stress maps for IN738/2453/EBPVD 12 mm diameter discs during ageing for 4000 h at 1000 °C - slow cooling (stress scale indicated by colours; red close to zero, blue 4-5 GPa compressive). Each square represents 1 mm spacing for the spectra.

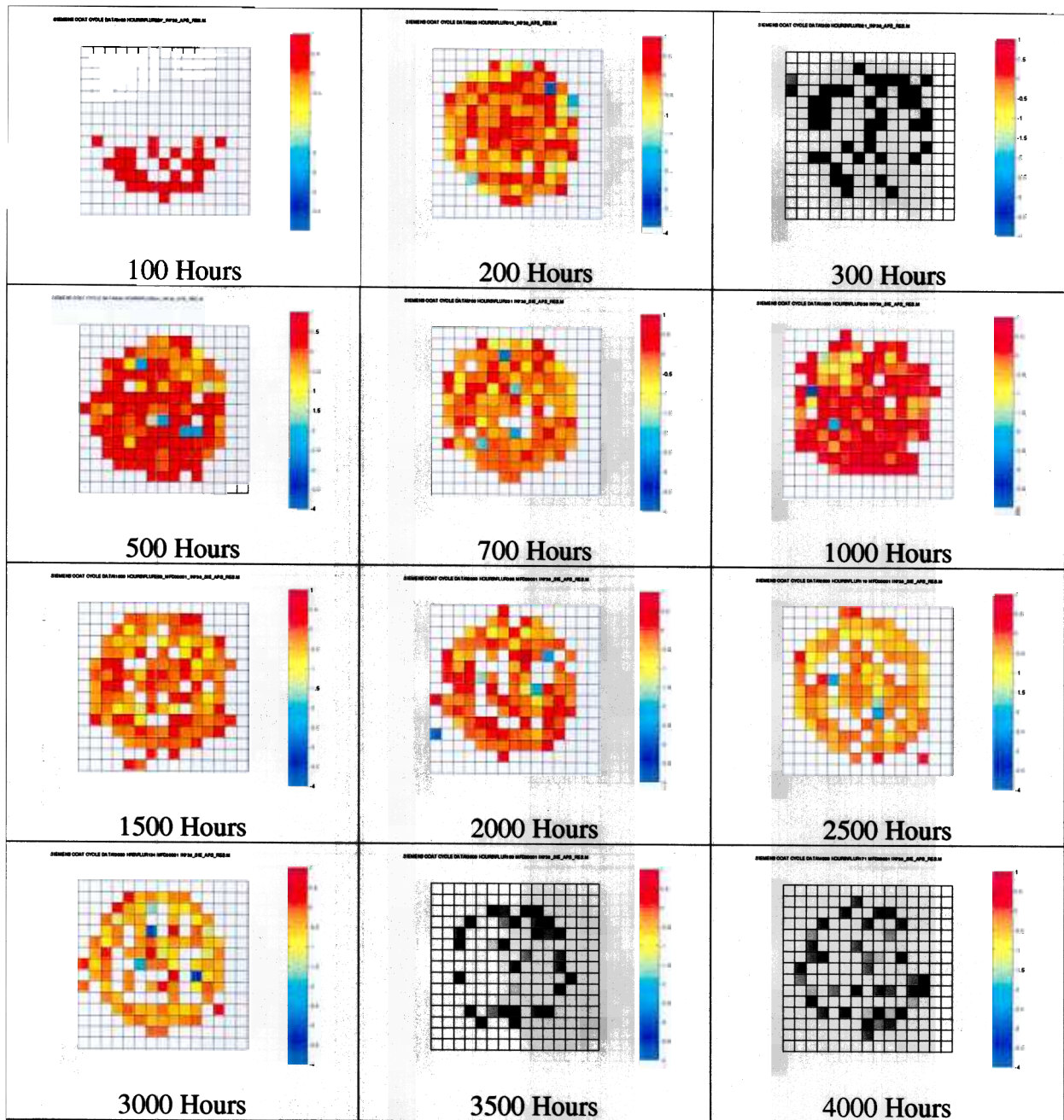


Figure 4 Stress maps for IN738/2453/APS 12 mm diameter discs during ageing for 4000 h at 1000 °C - slow cooling (stress scale indicated by colours; red close to zero, blue 4-5 GPa compressive). Each square represents 1 mm spacing for the spectra.

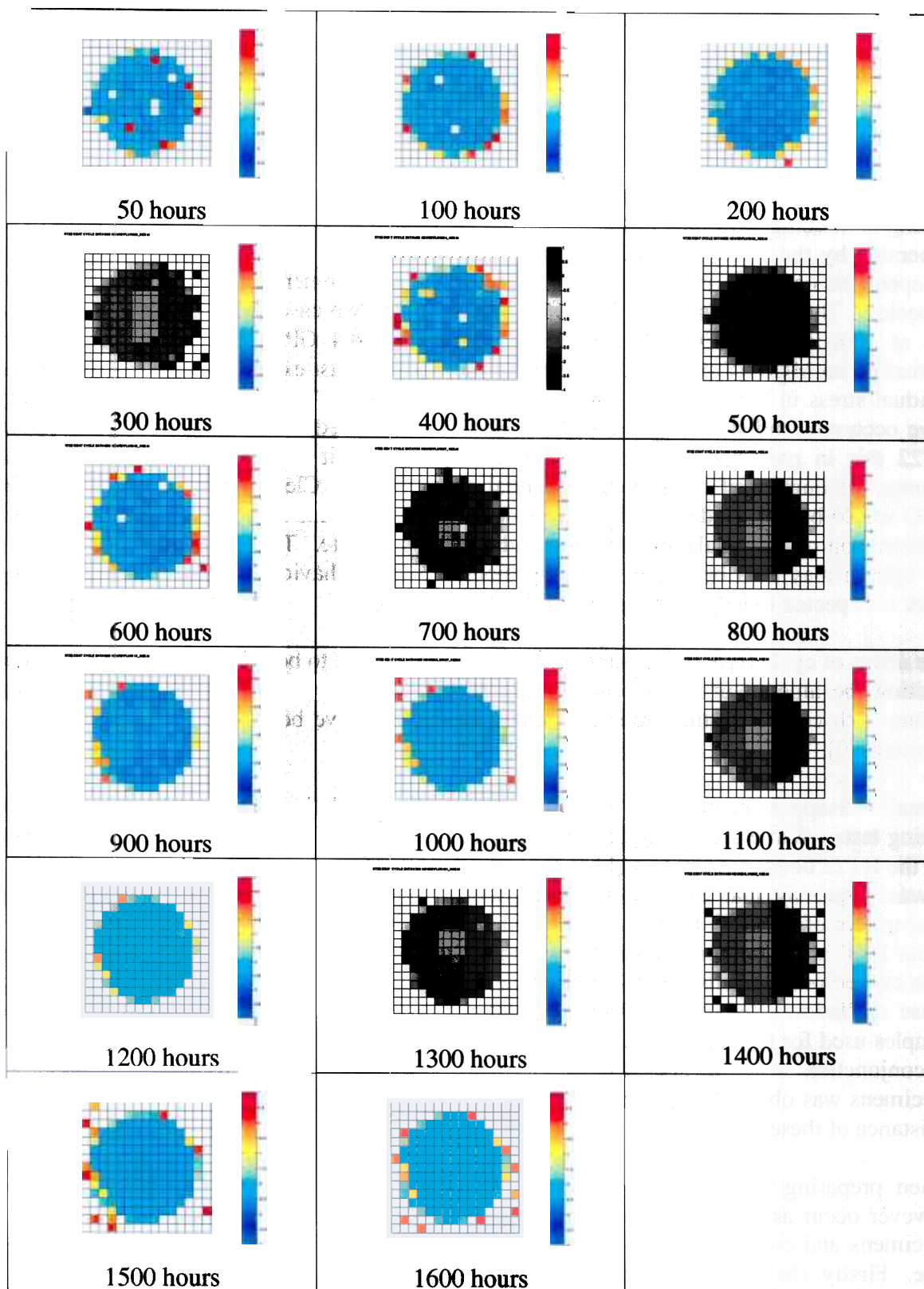


Figure 5 Stress maps for CMSX4/RT22/EBPVD 12 mm diameter discs during ageing for 1600 h at 1100 °C - slow cooling (stress scale indicated by colours; red close to zero, blue 4-5 GPa compressive). Each square represents 1 mm spacing for the spectra.

Considering now the observations in the EB-PVD TBC systems, the greater variation in stress levels in the TGO on the Sicoat 2453 bondcoat (Figure 3) compared with the RT22 bondcoat (Figure 5) can be explained by the fact that the TGO formed in the Sicoat system is undulating whereas that on the RT22 is flat (see Figure 2). Clarke *et al* [4] have argued that stress varies between the peaks and valleys of such an undulating structure, with more tensile values found at the peaks and more compressive values in the valleys.

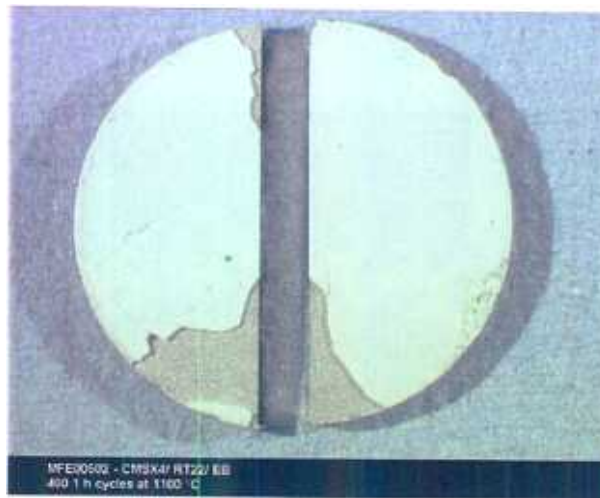
The slow development of stress in the TGO formed on Sicoat 2453 over long periods during ageing is in contrast to the almost immediate attainment of a stable stress state for the TGO generated by the RT22 bondcoat. Stress generation due to thermal expansion mismatch is independent of oxide thickness [9] so that stress development over time would not be expected. The maximum stress levels measured for the two cases where ageing was carried out at 1000 and 1100°C was calculated as -3.5 and -4.4 GPa, respectively for alumina formation on MCrAlY coatings. Thus some mechanism must exist for initially lowering the residual stress in the Sicoat bondcoat. During the slow cool cycles some stress relief may have occurred, and since the Sicoat 2453 would be expected to be less creep resistant than RT22 this in part may explain the difference, although it is difficult to understand the eventual attainment of the expected residual stress values. Clearly the TBC on top of the TGO would be expected to modify stress development and this may be more marked with a combination of an undulating structure and a weak substrate. The slow growth of stress in the system may then be due to sintering modifying the behaviour of the TBC. Modelling work is expected to help clarify some of these issues.

The effect of cycle type on the stress distribution is believed to be due to higher cooling rates limiting the amount of stress relief during cooling to such an extent that local spallation occurs with complete stress relief. These observations have been well documented in the literature [9].

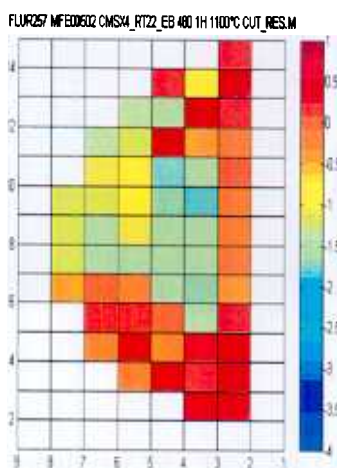
A major disappointment in this work was the lack of spallation observed in the long term ageing tests. While the ageing temperatures were somewhat lower than those normally used for the RT22 bondcoat systems (1135 °C is used to induce spallation in a few hundred hours) it was surprising that even after almost 2000 h the samples remained intact: an ageing temperature of 1000 °C for the Sicoat 2453 samples was expected to induce spallation after about 1500 h. A further consideration is that rapid heating and cooling is normally used in tests carried out by Rolls Royce for example, but in this work even the fast cooling cycle did cause spallation after nearly 500 h exposure. One possible explanation could be that the samples used for this work were somewhat thinner than normal in order to use thermography in conjunction with the laser flash to monitor local scale detachment. Bowing of these specimens was observed which could have contributed to the better than expected spallation resistance of these samples.

When preparing the samples for cross-sectioning, considerable spalling of the TBC did however occur as indicated in Figure 6a. Fluorescence spectra were obtained from the cut specimens and compared with the original (Figures 6b and c), and there are two points of note. Firstly, the spalled area now has a very low stress whereas that part of the specimen that retained the TBC has a higher stress than that from which the TBC spalled. Secondly, the stress in the region still covered by the TBC is lower than when first measured. These observations would appear to validate the general view that low values of TGO residual stress are related to spallation of the TBC, and that possibly cutting the sample led to general stress

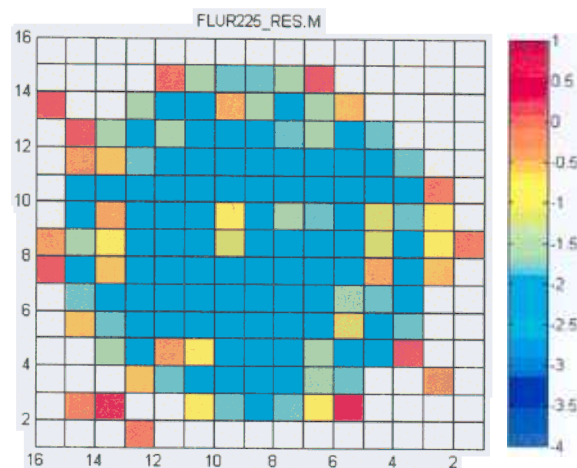
relief. Thus care should be taken when looking at the absolute values of stress determined from polished cross-sections.



(a)



(b)



(c)

Figure 6 (a) Optical micrograph of CMSX4/RT22LT/EB-PVD TBC after ageing for 480 h in the fast cool cycle at 1100 °C and then cutting, (b) stress map from the left-hand half of the specimen and (c) the stress measured before cutting.

3.3 CROSS-SECTION PIEZOSPECTROSCOPY AND DIGIMAPS

A relatively simple method of validation of the in-plan piezospectroscopic measurements is to carry out similar measurements on the cross-sections. It is accepted that cutting and metallographic preparation will alter the stress state of the oxide, but it is believed that such changes are relatively small and will not mask major changes that might exist between the in-plan and cross-section results. Furthermore use of the SEM and energy dispersive analysis

allows generation of element distribution maps (digimaps), so that the composition of the TGO layer can be determined.

Figure 7 shows typical digimaps of the TGO and confirms that an aluminium-rich compound was present (alumina).

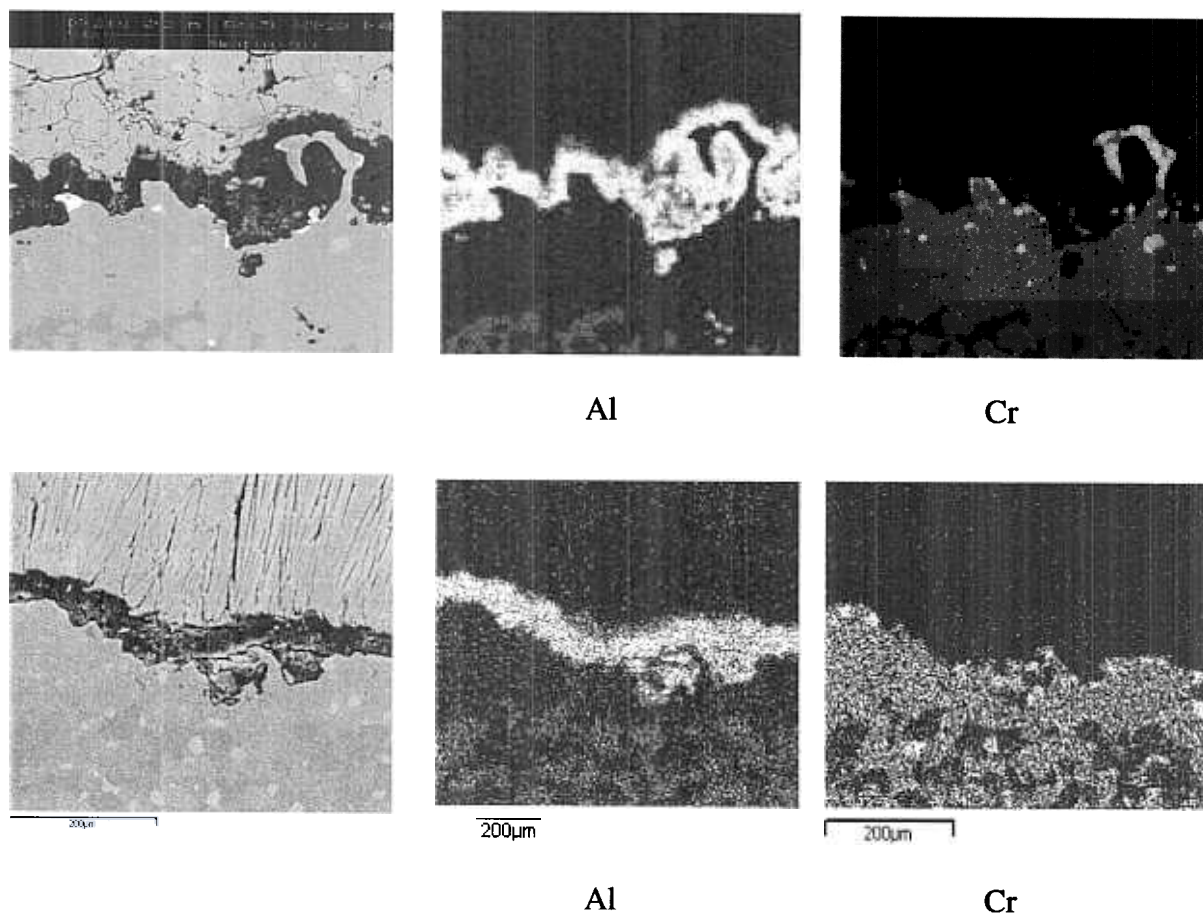


Figure 7 Secondary electron image of TGO formed on (a) MCrAlY/APS system and (b) MCrAlY/EB-PVD system

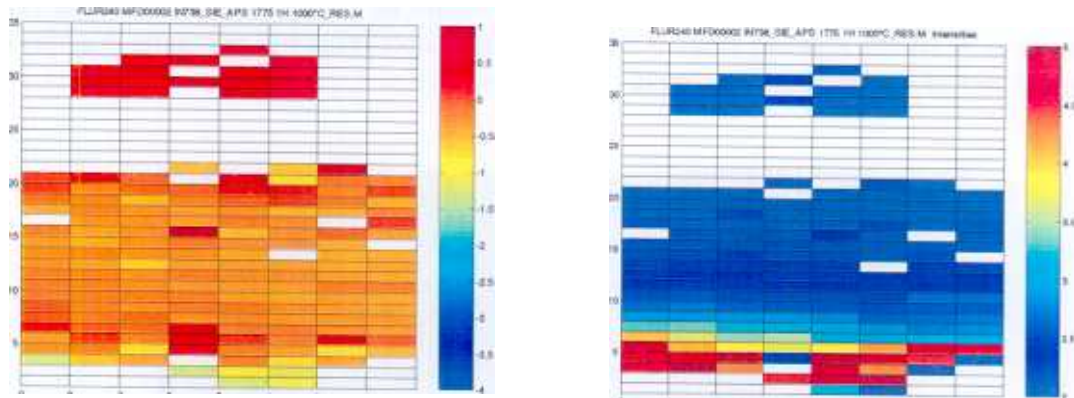


Figure 8 (a) Residual stress map from a polished cross-section of the IN738/2453/APS systems after ageing for 1785 h in the fast cool cycle, and (b) the associated intensity map of the fluorescence signal. The spectra were collected from a $10 \times 10 \mu\text{m}$ grid. The TGO layer is at the bottom of each map and its location is indicated by the high intensity (red/brown) region

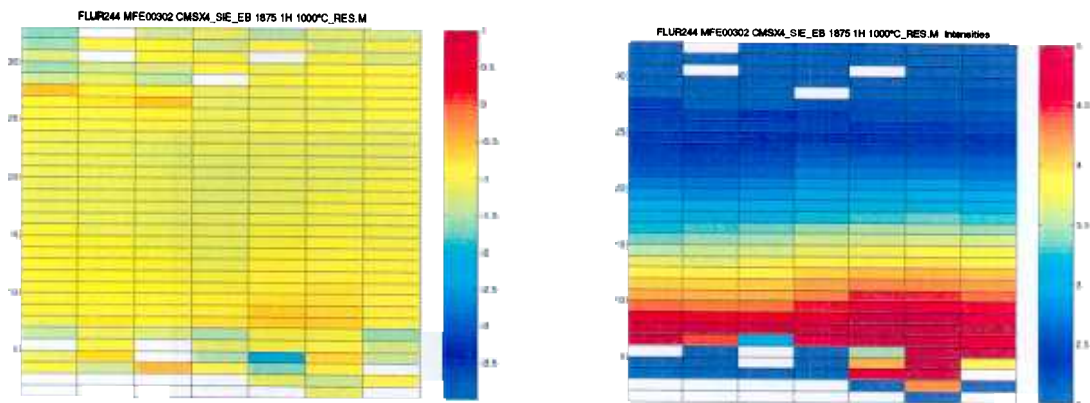


Figure 9 (a) Residual stress map from a polished cross-section of the CMSX4/2453/EB-PVD systems after ageing for 1875 h in the fast cool cycle, and (b) the associated intensity map of the fluorescence signal. The spectra were collected from a $10 \times 6 \mu\text{m}$ grid. The TGO layer is at the bottom of each map and its location is indicated by the high intensity (brown) region

Figures 8 and 9 show stress maps from cross-sections of APS and EB-PVD systems, respectively, after the ageing tests and should be compared with similar maps shown in Figures 3 and 4. It will be observed that the stress is highest where the TGO is present, but in the case of the APS coating the stress level is higher than that observed in the in-plan tests, while for the EB-PVD systems the stress in the TGO is lower in the cross-section than when measured in-plan. This provides confirmation of two effects. Firstly, as mentioned previously, preparation of the cross-section would be expected to change (lower) the stress, and indeed this is what was observed when comparing the results of the measurements on the EB-PVD TBC systems. Secondly, the higher stress found on the APS TBC system confirms the view expressed in the literature that internal scattering of the laser beam is preventing interrogation of the TGO and that any fluorescence is being generated within the TBC [8]. Micrographs of the APS system in the as received and aged state are shown in Figure 10 and

show that the structure is highly cracked and that this cracking appears to have increased with ageing. The presence of this fractured structure would be expected to reduce and probably eliminate any signal coming from the TGO system and probably accounts for the almost complete loss of signal after long ageing times as shown in Figure 3.

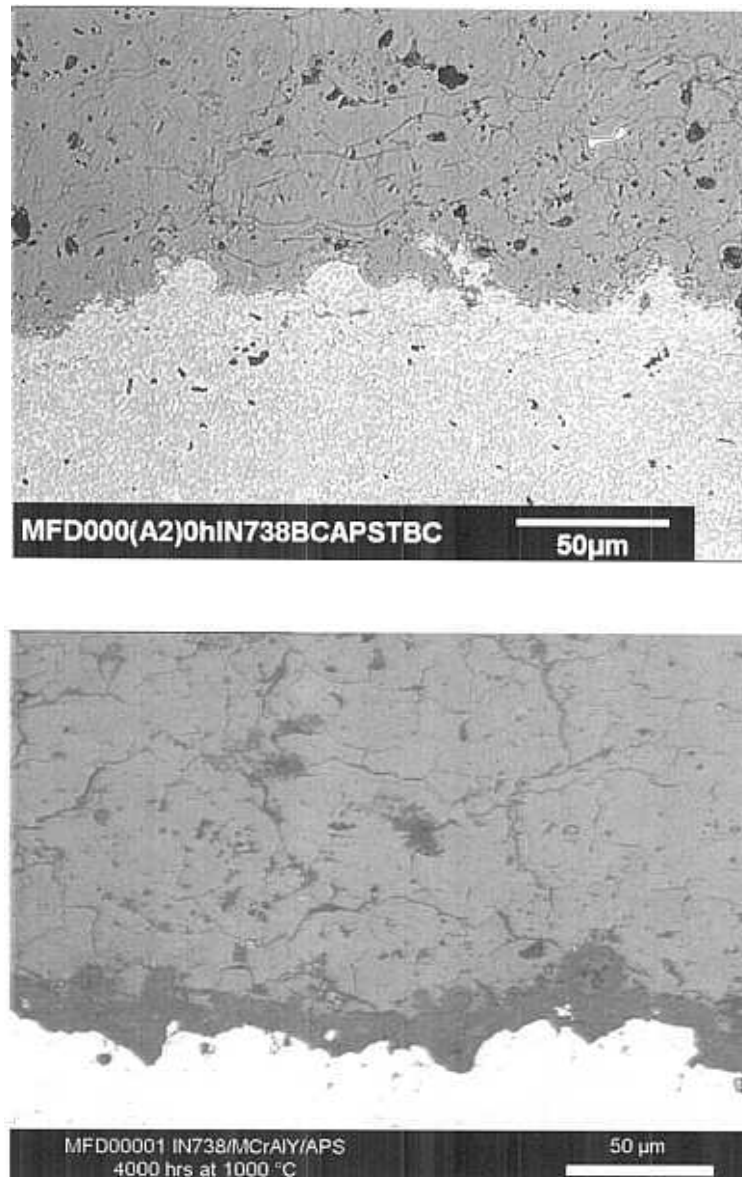


Figure 10 Optical micrographs of cross-section through as-received and aged APS TBC

The origin of fluorescence in the APS TBC systems used in this work is not clear at this junction, since it has been demonstrated that the as received APS TBC did not fluoresce, and that the TGO did not contribute to the fluorescence spectra. There remains the possibility that traces of Cr are being incorporated in the TBC during the ageing process, but it has not been possible to confirm this during this investigation.

Further evidence of internal scattering of the laser light is also shown in Figures 8 and 9, where it can be seen that fluorescence occurs within the TBC layer itself. Furthermore Figures 8 and 9 also show corresponding intensity maps and it can be observed that the fluorescence signal decays rapidly in intensity with increasing distance from the TGO. There is the possibility that the fluorescence is derived from Cr impurities in the TBC itself or that trace amounts of alumina diffused into the TBC during ageing or internal scattering occurred in the TBC. If impurities were responsible for the effect, then a uniform distribution in the TBC would be expected.

To determine whether the fluorescence in the TBC was a diffusion or scattering effect, a piece of free standing EB-PVD TBC was prepared in cross-section and measurements established that no chromium fluorescence was observed. The same specimen was then coated with an alumina adhesive (Cerambond) and again examined in cross-section. Figure 11 shows the intensity of the fluorescence signal as a function of distance from the alumina adhesive. It is clear that even as far as 1 mm from the alumina layer significant fluorescence occurs from a part of the specimen previously shown not to fluoresce (the free standing TBC). It is proposed therefore that the observed fluorescence in the TBC found in cross-section is due to multiple reflections involving the TGO layer where the fluorescence originated.

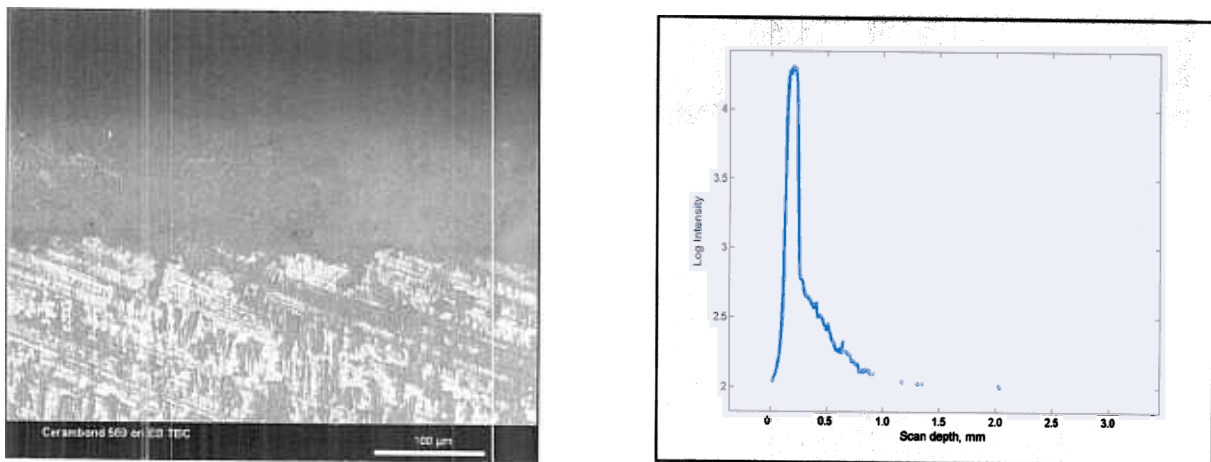
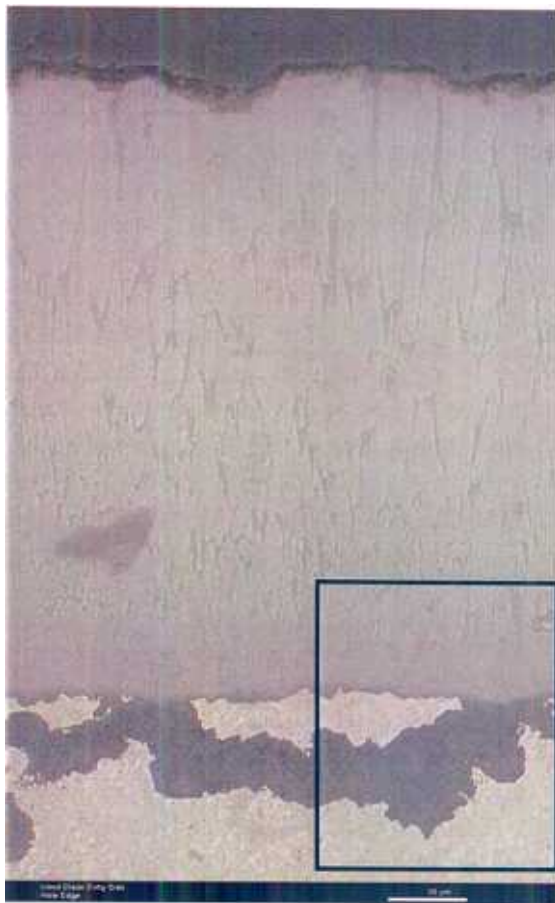


Figure 11 Optical micrograph of a polished cross-section of the TBC/Cerambond interface, and the associated fluorescence signal intensity across that interface.

The alumina layer formed during ageing may become less protective and one consequence might be that the TGO becomes enriched in chromium. It is unclear how the increasing chromium content would manifest itself in the fluorescence spectra. There is evidence in the literature [10] that the intensity increased up to a maximum at about 1 wt% Cr and thereafter decreased, while there is a linear increase in R_2 shift with increasing chromium content. Thus the effect of build-up of chromium in the TGO layer is of interest, and several cases were observed during examination of the cross-sections of the aged specimens and in an examination of cross-section of used blades. Figure 12 shows an example of the SEM examination of these samples together with the associated residual stress and intensity maps.



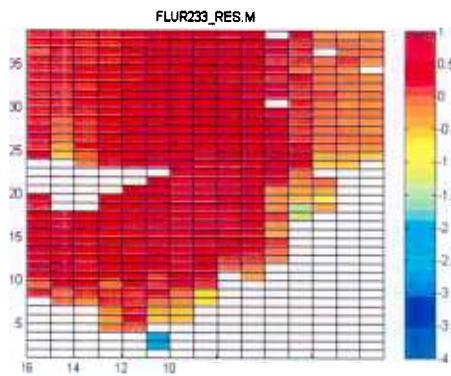
SEI



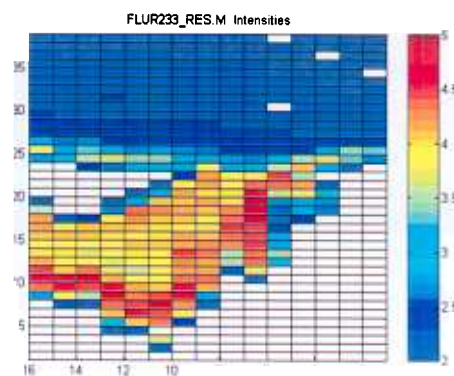
Al



Cr



Stress map



Intensity map

Figure 12 *Scanning electron micrograph of a cross-section of a blade taken from service with the corresponding Al and Cr digimaps and the fluorescent stress map and associated intensity of the boxed area*

The stress map suggests that the TGO has close to zero stress, but care in interpretation is required since the TGO contains significant amounts of chromium as indicated by the digimap. It is also of interest to note that in the region of the TGO where the Cr concentration is high the intensity of the signal has decreased suggesting that the concentration is greater than 1 wt %.

4 SUMMARY AND CONCLUSIONS

- While no spalling of the TBC was observed in the ageing tests, most specimens spalled when first cut. It was observed that the aged specimens were bowed and it is proposed that this bowing may have allowed some stress relief in the TGO, thus inhibiting spallation of the TBC.
- 2 The use of piezospectroscopy in plan to determine residual stress values of the TGO in TBC systems has in large measure been validated for the case when EB-PVD TBCs were used. Examination of metallographic cross-sections has confirmed the presence of aluminium-rich scales, and when piezospectroscopy was used to examine the cross-section a region of high compressive residual stress was found where the TGO was present. When compared with the residual stress maps measured in plan, the stresses in the cross-sectioned specimen were less compressive, but it would be expected that some stress relief would have taken place during cross-sectioning.
 - 3 The in plan piezospectroscopy showed uniform stress in the TGO for Pt aluminized bondcoat systems while the stress distribution was much more varied for the MCrAlY systems. The cross-sections provided an explanation of this behaviour in that the TGO had a rumpled morphology when formed on MCrAlY bondcoats and was almost flat for the Pt aluminized bondcoat and it has been reported that stress redistribution would be expected for the rumpled interface.
 - 4 A similar examination of the APS TBC systems in cross-section using piezospectroscopy also showed a region of relatively high compressive stress associated with the TBC, and this was in contrast to the almost zero stress found when the specimens were examined in plan. It had been reported in the literature that the APS TBC is non transparent to laser light, and these observations support this conclusion.
 - 5 The laser light appears to be scattered by cracks and pores in the APS TBC. Cross-section of the APS TBC in the unaged and aged conditions indicated that cracking increased with ageing, and this would be consistent with the loss of signal from most of the APS TBC specimens subjected to long-term ageing.
 - 6 Fluorescence spectra were also observed in both the EB-PVD and APS TBCs when examined in cross-section. The intensity of the signal decreased almost exponentially with distance from the TGO/TBC interface. It was proposed that this effect could have been the result of the TBC being doped with Cr impurities, diffusion of chromium doped alumina into the TBC during ageing or internal scattering of the laser light. It was concluded that scattering in the cross-section was responsible for this effect.

- 7 It some of the long-term aged specimens chromium levels in the TGO layer were observed to increase, presumably because the alumina layer was becoming less protective with increasing ageing. While it was not possible to completely understand the effects of the increased chromium levels on the fluorescence spectra observed from a study of the specimens in cross-section, the altered chromium levels would be expected to increase intensity of the signal with chromium concentrations up to 1 wt% with further increases in chromium concentration reducing the signal intensity. Some evidence to support this expected trend was found.
- 8 Chromium doping of the alumina is also known to alter peak position toward more tensile values, and a linear relationship with a constant of approximately $1 \text{ cm}^{-1}/\text{wt}\%$ Cr present have been reported in the literature. For the chromium doped TGO layers observed in this work, the apparent stress was close to zero, but if as indicated the chromium concentration was several wt% then caution needs to be exercised when interpreting such data. It was difficult to measure the chromium levels in the less protective TGO layers due to interference from the bondcoat, but if 4-5% were present then this amount to an error in assessment of the residual stress of about 1 GPa.

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