

An Evaluation of Tests for the Adhesion of Thermal Barrier Coatings

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ABSTRACT

The results of different test procedures to measure adhesion of thermal barrier coatings (TBCs) are compared. Two TBC types have been studied as a function of time at temperatures up to 1100 °C. The tests evaluated were the transverse scratch test, indentation, tensile straining and piezospectroscopy to determine the residual stress of the thermally grown oxide (TGO). Generally, EB-PVD coatings were more responsive to the different test methods with failure generally occurring at the bondcoat/TGO interface, but only in the case of transverse scratching could quantitative values of interfacial strength be obtained. Piezospectroscopy to determine the residual stress in the TGO offers promise for the non-destructive evaluation of the spallation resistance. It was also observed that metastable θ -alumina developed during ageing, suggesting that areas of disbond had occurred. Maps relating residual stress to θ -alumina formation have been generated showing the heterogeneous nature of bonding at the TGO/TBC interface. TBC systems with Pt aluminide and MCrAlY bond coats were aged for periods up to 4000 h in cyclic tests without initiation of spallation of the TBC. Spectra from these samples have been obtained at various stages during the ageing cycles and changes interpreted. The piezospectroscopic method has also been applied to turbine blade both in the used and unused condition. For the used blade deposits present interfered with measurement and attempts made to remove these deposits had limited success.

1 INTRODUCTION

Thermal barrier coatings (TBCs) are widely used on combustors, blades and vanes in heat engines for improving efficiency by allowing higher operating temperatures; yttria stabilised zirconia is the most widely used material. Two types of TBC are commonly used, electron beam physical vapour deposition (EB-PVD) and air plasma sprayed (APS); the former has a columnar grain structure while the latter consists of “splats” typical of material produced during plasma spraying [1,2]. Recently their application has been extended to rotating parts, in particular to gas turbine engine blades. Here the continued performance of the coating system is critical for the design of the engine, and thus any loss of coating by spallation would represent a major problem. In most designs the blade is first coated with a corrosion resistant layer that also acts to bond the TBC to the blade material and is known as a bondcoat. During deposition of the TBC, the substrate and bondcoat are generally heated such that a thin ($< 1 \mu\text{m}$) alumina layer grows due to oxidation of the bondcoat, and it is this alumina layer that promotes bonding between the TBC and the coated substrate. The performance of gas turbine engines is increasingly dependent on the TBC systems and is therefore “design critical”.

During exposure at high temperature the alumina layer (also known as the thermally grown oxide or TGO) continues to grow, and in the case of the EB-PVD TBC it is believed that spallation usually occurs at the alumina/bondcoat interface [3]. Spallation of alumina scales has been related to accumulation of trace impurities, particularly sulphur, at the bondcoat/TGO interface [4,5] or to build-up of residual stress in the alumina layer [6]. For the APS system, spallation of the TBC is generally through cohesive failure within the TBC layer.

Whilst there are numerous methods for the measurement of adhesion, many are simple ranking tests and fail to yield design parameters of use to engineers. Tests which are capable of producing quantitative data fall into two classes; those which can only be carried out in well equipped laboratories, often with complex sample geometry, and “engineering tests” which require relatively simple samples and instruments. Examples of the former are the bulge [7] and cantilever tests [8]. For the latter, the pull test [9], tensile testing [10], indentation [11] and transverse scratch testing [12] which, respectively, determine the interfacial tensile strength, interfacial shear strength, interfacial fracture toughness and, by application of a finite element model, the interfacial tensile strength. It is evident that most of these tests yield different measures of the interfacial strength, and at present there is no simple method to relate one property to another. In addition, the piezospectroscopic technique of using fluorescence to measure residual stress in alumina scales grown on superalloys and coatings [13-15] has been used, and is of particular interest for investigation of TBC coating systems since the TBC is transparent to the incident laser light used. Thus, it is possible to measure the residual stress in the TGO that forms beneath the TBC in a non-destructive manner.

This report discusses progress made in the DTI funded project “Behaviour of coatings used in gas turbines for protection against corrosion and thermal loads” in the programme Degradation of Materials in Aggressive Environments (DME). The project involved a study of some engineering tests (tensile bending, indentation and the transverse scratch test) as well as piezospectroscopy.

2 MATERIALS

Coatings were deposited on IN738 and CMSX4 substrates. Initial work was carried out on MCrAlY bondcoats and APS TBCs supplied by Plasma and Thermal, and Pt aluminised (RT22LT) and EB-PVD TBCs by Chromalloy UK as well as various TBC systems by Rolls Royce. The bulk of the work on piezospectroscopy was with 5 TBC systems as listed below. Pt aluminised (RT22LT) and MCrAlY (Sicoat 2453) bondcoats were used with both electron beam physical vapour deposited (EB-PVD) and air plasma sprayed (APS) thermal barrier coatings (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. In addition, some used and unused turbine blades were supplied by industrial partners.

Samples sizes for the different tests were as follows:

- i) Tensile tests using 4 point bending, 50 x 10 x 2.2 mm
- ii) Transverse scratch tests, 15 mm dia x ~2 mm
6.75 mm dia x variable length
- iii) Indentation, end regions of the 4-point bend samples
- iv) Piezospectroscopy, 12.5 mm dia x ~2 mm thick

3 AGEING EXPERIMENTS

All coatings were evaluated in the as-received and aged conditions. In all cases samples were aged by heating in air. All TBC coatings with a RT22LT bondcoat were aged at 1100 °C, and those with Sicoat 2453 bondcoat were aged at 1000 °C. For some of the initial tests with the MCrAlY bondcoat ageing was also carried out at 1100 °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.
- 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 5 seconds.

4 TENSILE TESTING

Tensile tests were carried out using four-point bend tests at room temperature and at 800 °C. For the room temperature tests, strains up to about 4.5% were possible, whereas at 800°C the maximum strain that could be imposed was 2% due to the constraints of working within a furnace. The tensile strain imposed, ε , was calculated using the following relationship:

$$\varepsilon = \frac{3fd}{u(3s - 4u)} \quad \text{Eq 1.}$$

where f is the cross head speed mm / s, t is the time in seconds, d is the testpiece thickness, u is the distance between the outer and inner rollers and s is the distance between the outer rollers (all dimensions are in mm).

Tensile straining, either uniaxially or in flexure, causes cracking of the coating to occur. As straining is continued the crack density increases and reaches a maximum at the point of spallation. The maximum crack density can be used, with appropriate models, to derive the interfacial shear strength [10,17,16]. One simple model [10] that has been extensively used is as follows:

$$\lambda = \frac{\pi d}{\tau_i} \sigma_f \quad \text{Eq 2.}$$

where λ is the crack spacing at the onset of spallation, d the coating thickness, τ_i the interfacial shear stress and σ_f the fracture stress.

In the current work, attempts were made to utilise this method for TBCs and Figure 1 shows micrographs of unaged and aged RT22LT bondcoat with an EB-PVD coating after tensile straining at room temperature using four-point bending. The unaged sample developed a series of parallel tensile cracks with a spacing of about 250 μm without spallation of the TBC (Figure 1a), whereas the sample isothermally aged for 100 h at 1100 °C spalled after straining to 1.7% (Figure 1b). When observed in cross-section the cracks were found to extend into the RT22LT bondcoat and spallation was at the bondcoat / TGO interface (Figure 1c). The crack spacing on the aged sample was about 425 μm . The observed fracture strain was < 0.1%. Assuming an in-plane Young's modulus of 103 GPa by applying a rule of mixtures for the TBC/TGO system (TBC, 90 GPa and TGO, 400 GPa), the interfacial shear stress of the aged TBC system is 153 MPa. Some work at 800 °C was carried out, but non-uniform bending occurred thereby invalidating the test. Uniaxial tensile tests would overcome this problem.

Tests with APS TBCs also yielded tensile cracking, but often the cracking was of an irregular nature such that it was difficult to determine the crack spacing (Figure 2). Spallation did occur in some cases, but because of the uncertainty in determining the crack spacing, estimates of interfacial shear strength could not be made. Table I lists the results of all tests carried out with both the APS and EB-PVD TBC systems.

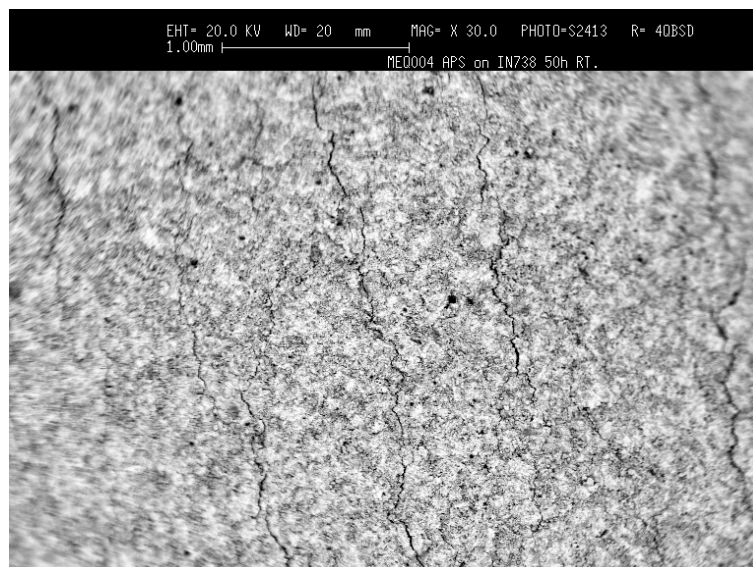
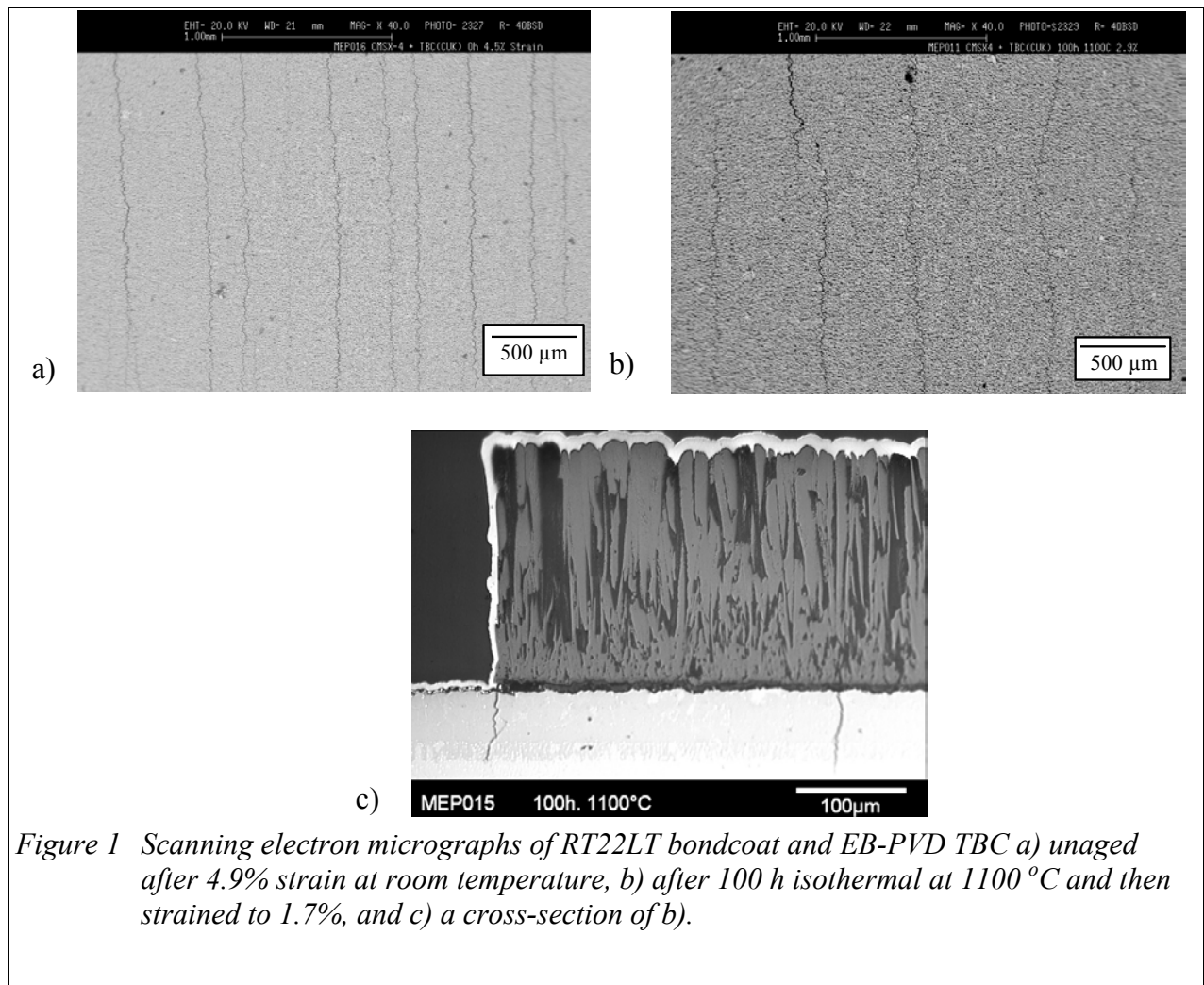


Figure 2 Four point bend test at room temperature of an APS TBC aged for 50 h at 1000 °C

Table I: Tensile tests of TBCs

<i>Coating</i>	<i>Ageing condition</i>	<i>Temperature, °C</i>	<i>Strain, %</i>	<i>Crack spacing, μm</i>	<i>Comments</i>
CMSX4/RT22/EBPVD	as-received	22	3.5	375	No spallation
CMSX4/RT22/EBPVD	as-received	22	4.5	225	No spallation
CMSX4/RT22/EBPVD	as-received	800	2.0	None	No spallation
CMSX4/RT22/EBPVD	as-received	800	2.0	None	No spallation
CMSX4/RT22/EBPVD	1100 °C, 50 h, Air	22	4.0	410	No spallation
CMSX4/RT22/EBPVD	1100 °C, 50 h, Air	22	4.0	405	No spallation
CMSX4/RT22/EBPVD	1100 °C, 50 h, Air	800	1.3	None	No spallation
CMSX4/RT22/EBPVD	1100 °C, 50 h, Air	800	2.0	None	No spallation
CMSX4/RT22/EBPVD	1100 °C, 100 h, Air	22	2.9	515	No spallation
CMSX4/RT22/EBPVD	1100 °C, 100 h, Air	22	1.7	420	TBC Spallation
CMSX4/RT22/EBPVD	1100 °C, 100 h, Air	800	2.0	None	No spallation
CMSX4/RT22/EBPVD	1100 °C, 100 h, Air	800	2.0	None	No spallation
IN738/CoNiCrAlY/APS	none	22	-	None	sample folded
IN738/CoNiCrAlY/APS	none	22	3.5	~500	No spallation
IN738/CoNiCrAlY/APS	none	800	-	None	No spallation
IN738/CoNiCrAlY/APS	none	800	2.0	None	No spallation
IN738/CoNiCrAlY/APS	1100 °C, 50 h, Air	22	4.1	~500	No spallation
IN738/CoNiCrAlY/APS	1100 °C, 50 h, Air	22	3.0	~500	TBC Spallation
IN738/CoNiCrAlY/APS	1100 °C, 50 h, Air	800		None	sample broke
IN738/CoNiCrAlY/APS	1100 °C, 50 h, Air	800		None	sample broke
IN738/CoNiCrAlY/APS	1100 °C, 100 h, Air	22	2.9		No spallation
IN738/CoNiCrAlY/APS	1100 °C, 100 h, Air	22	3.2	~800	TBC Spallation
IN738/CoNiCrAlY/APS	1100 °C, 100 h, Air	800			sample broke
IN738/CoNiCrAlY/APS	1000 °C, 50 h, Air	22			sample broke
IN738/CoNiCrAlY/APS	1000 °C, 100 h, Air	22			sample broke
IN738/CoNiCrAlY/APS	1000 °C, 240 h, Air	22			sample broke
IN738/CoNiCrAlY/APS	1000 °C, 432 h, Air	22			sample broke

This work has indicated that in the case of EBPVD TBCs some useful data could be obtained, and, as will be demonstrated, could be related to data obtained from transverse scratch testing (see Section 6), but the nature of the APS coating made it difficult to discern cracking and crack spacing tended to be somewhat irregular. Many of the samples broke prematurely during the test and this was attributed to porosity in the substrate material.

5 INDENTATION

A Rockwell indentation test has been used to assess adhesion of brittle films on relatively ductile substrates in terms of the extent of delamination around the indent. Recently, Drory and Hutchinson [11] have developed a model to allow quantification in terms of the interfacial toughness. Properties required are the Young's modulus of the coating and substrate, coating Poisson's ratio, and the thickness, residual stress, yield stress and the strain hardening coefficient of the substrate. Tests carried out in the present work at a load of 1500 N with unaged and aged EB-PVD and APS TBC systems indicated that while no delamination occurred, radial cracking was observed (Figure 3). The extent of radial cracking was either unchanged (APS) or, surprisingly, reduced (EB-PVD) with ageing. It is

proposed that the lack of cracking on the aged samples may be related to sintering of the TBC. These observations are of interest, but, since no delamination was observed in the initial tests, there was no basis for the calculation of interfacial toughness.

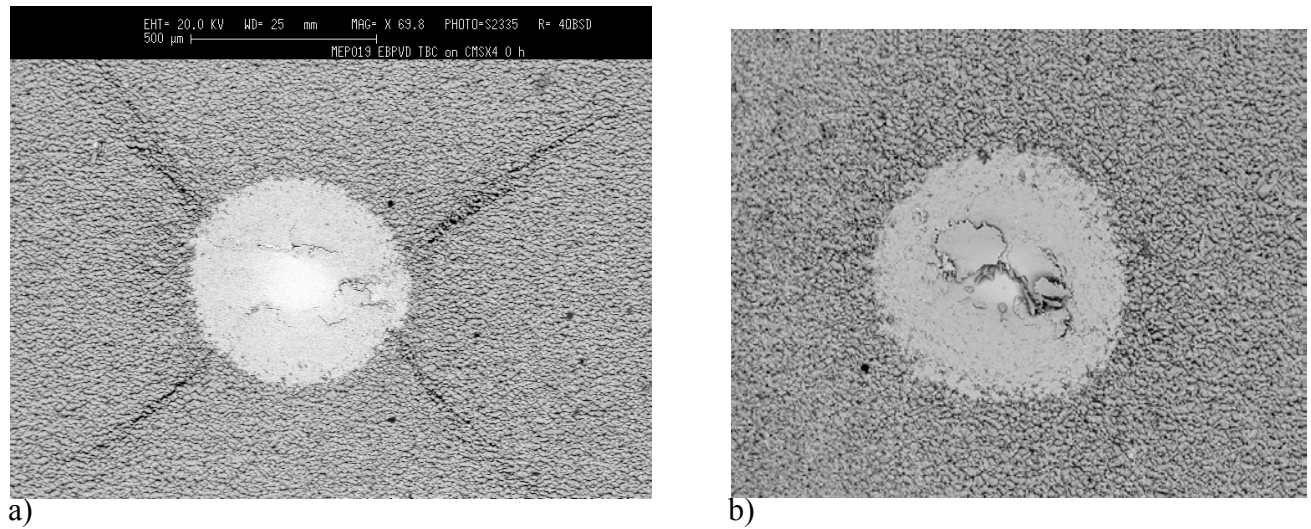
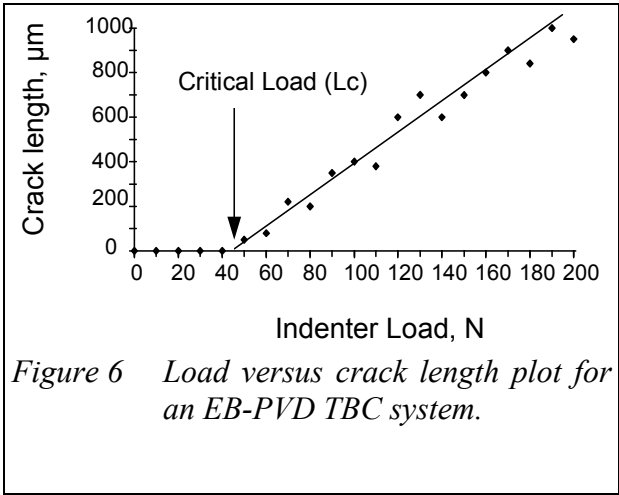
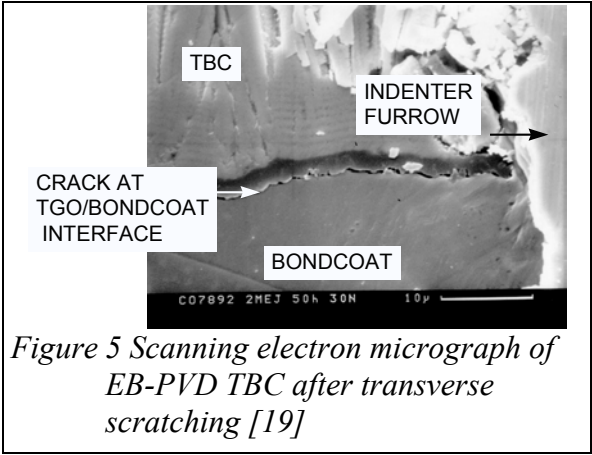
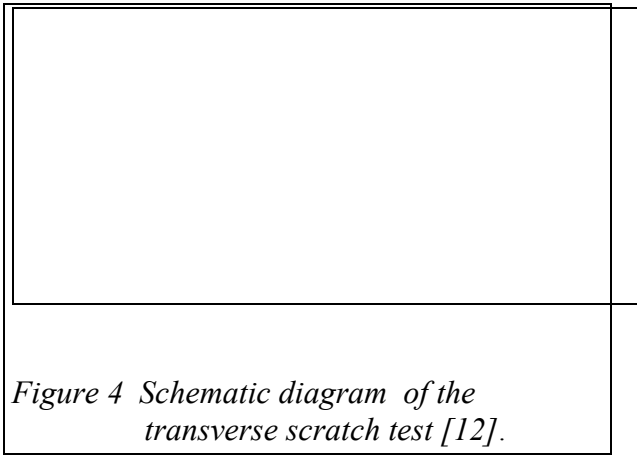


Figure 3 Indentation of an EB-PVD TBC (a) unaged and (b) aged for 200 h at 1100 °C

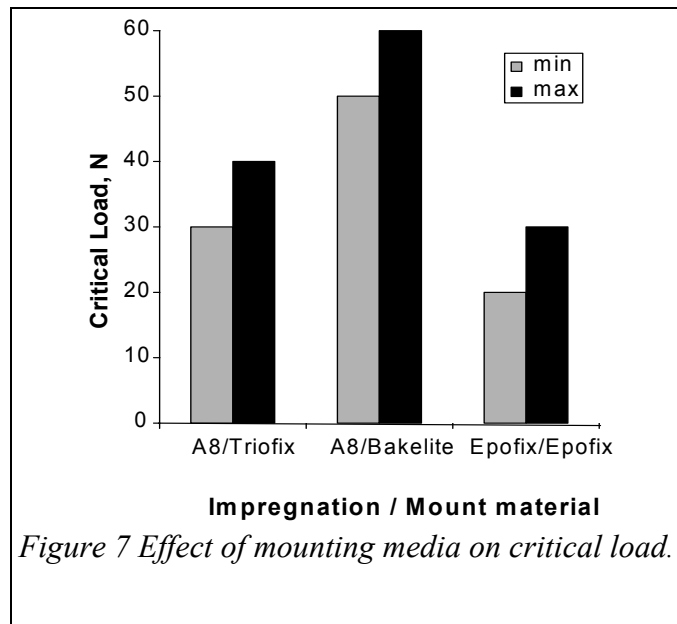
6 TRANSVERSE SCRATCH TEST

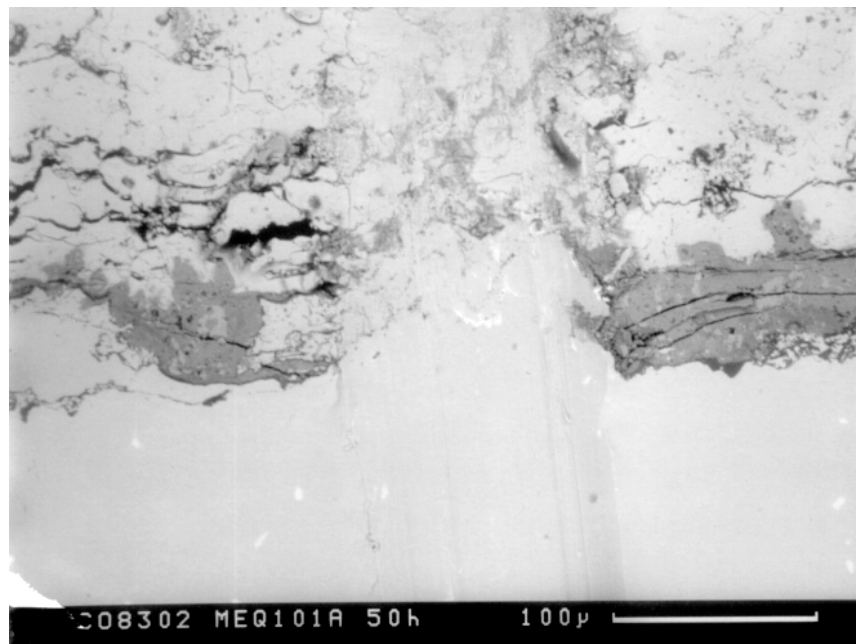
6.1 EXPERIMENTAL APPROACH

The transverse scratch test was developed from the normal scratch test as described by Heavens and Collins [18] used throughout the thin film industry,. The major difference is that the scratch is performed on a cross-section of the sample and the scratch track runs from the substrate out towards the coating causing debonding at the coating/substrate interface, Lopez *et al* [12], Burnett *et al* [19] (Figures 4 and 5). The test is performed several times and measurements of interfacial crack length are made as a function of applied load. These data are then plotted and extrapolated to the point where the crack length would be zero; the critical load, and this value is then used as an index of adhesive strength (Figure 6). Johnstone *et al* [20] tested APS and EB-PVD TBC systems under a range of mounting and polishing conditions. Several factors were found to influence the critical load values, including the radius of curvature of the interface, the degree of surface roughness of the interface between the coating and substrate, and the degree of constraint offered by the mounting media. Testing with various impregnation and mounting media led to a variation in response of the system. The stiffer the mounting media the higher the value of load required for a given crack size and the higher the critical load (Figure 7). The surface roughness inherent in the APS TBC systems led to poor correlation of crack length and load. This was due to the crack not running along the interface but deflecting within the microcracked ceramic structure (Figure 8). This in turn made it difficult to evaluate the true length of the crack in this system.

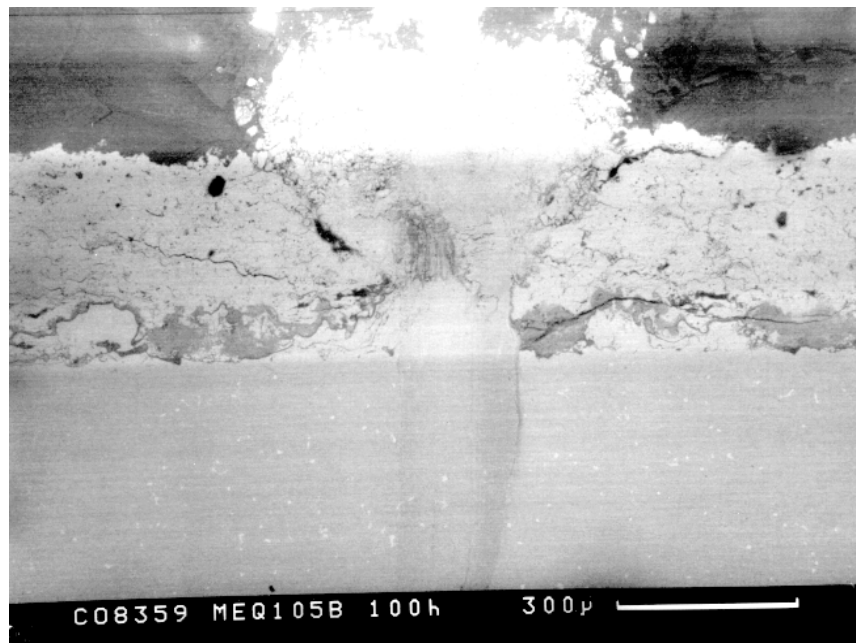


Once a protocol for testing was established [20], the test was applied to EB-PVD TBC's both in the unaged and aged conditions. Figure 9 shows the progressive decrease in the adhesive strength of EB-PVD TBC's on MCrAlY and platinum-aluminide bondcoats, and illustrates the superior high-temperature performance of the MCrAlY-type bondcoat that is in agreement with engine experience [20]. Further work was carried out in collaboration with NPL using the procedure established by Johnstone *et al* [20]. Figure 10 shows the same ranking was found for a series of three TBC systems with different Pt aluminide bondcoat after ageing at 1100 °C for various times, but often the values of critical load were different. This latter observation may not be unexpected since the particular section of interface being assessed could have somewhat different bond strengths (see following section on piezospectroscopy). Additionally, recent work has shown [21] that the critical load in the normal scratch test is very sensitive to the radius of curvature of the diamond indenter used, and since no checks on diamond shape were made in this comparison, further discrepancy might be expected.



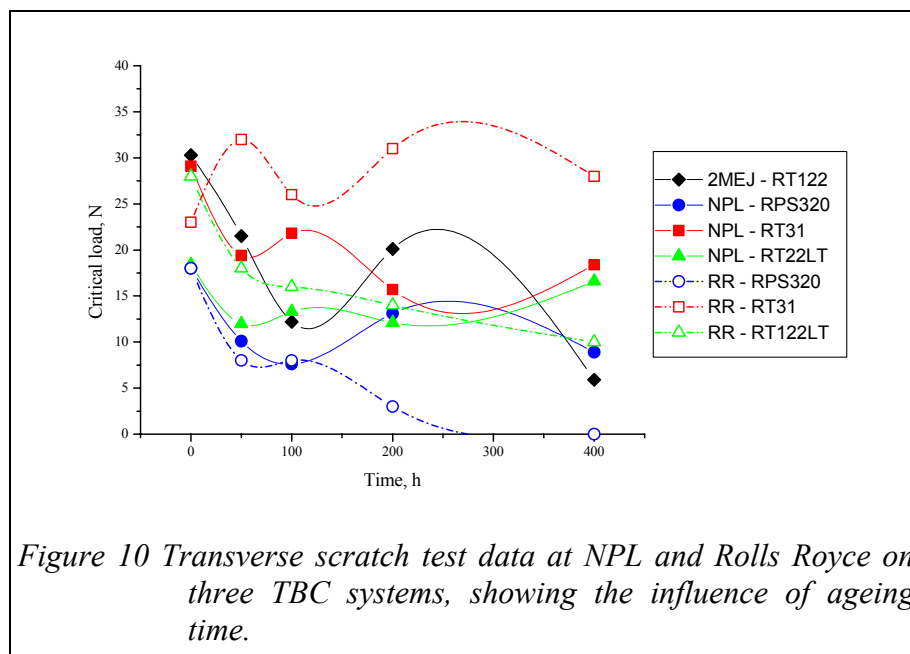
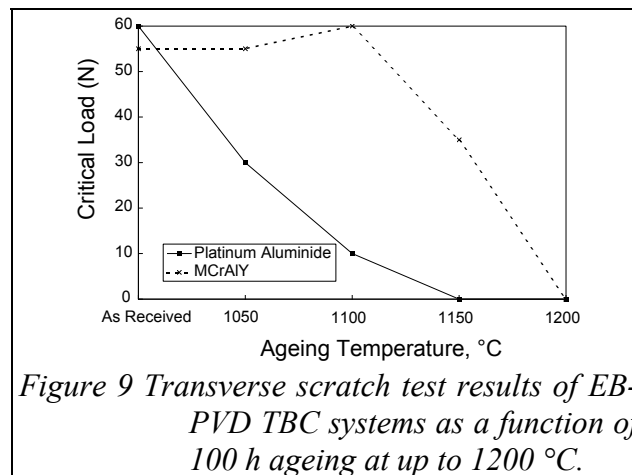


(a)



(b)

Figure 8 Transverse scratches in an APS TBC at different magnifications showing (a) cracking near the TGO/TBC interface, and (b) diagonal cracks running in the TBC



6.2 MODELLING THE TRANSVERSE SCRATCH TEST

The transverse scratch test was modelled by Johnstone *et al* [20] using finite element analysis in an attempt to convert the measured critical load to an adhesive strength and to understand fully the role of curvature of the interface and mounting media stiffness. A DYNA-3D finite element package that is specifically designed for large displacements and plastic work was used for the modelling. The results of the modelling activity showed that although the critical load varied with decreasing radius of curvature (R), the resolved stress across the interface was broadly constant at 400 MPa for an EB-PVD system. This indicates that the critical load was changing due to geometrical effects rather than the adhesive strength changing as a function of R . Importantly it was possible to directly calculate the interfacial strength by inputting the measured critical load derived from the transverse scratch test into

the FE model. Direct validation of this model was possible using the pull test when the TBC system had been sufficiently weakened by ageing. The observed and predicted values of the interfacial strength are shown in Table II. It can be seen that for a measured critical load (L_c) of 5 N there is good agreement in the values of interfacial strength, but at a critical load of 10 N the FE model predicts a larger value. This discrepancy is believed to be due to differences in specimen geometry assumed in the model (6 mm diameter bar) and that used for the pull-off test (flat).

Table II: Comparison of experimental and model values for interfacial strength

Ageing Condition	L_c Value, N	Pull-off Interfacial Strength, MPa	FE Model Interfacial Strength, MPa
49 h at 1100 °C	10	67	105
100 h at 1100 °C	5	53	55
16 h at 1150 °C	10	64	105
49 h at 1150 °C	5	52	55

7 PIEZOSPECTROSCOPY

7.1 BACKGROUND

The properties of the 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 [6]. Piezospectroscopy [13] 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 positions of these lines shift with stress allowing the residual stress in the layer to be determined from the frequency shift. 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 [28]. Hence, the stress measurements reported here 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 shift of the R_2 line is given by:

$$\Delta\nu = 2.54 \text{ (cm}^{-1} \text{ GPa}^{-1}) \sigma \quad \text{Eq. 3.}$$

and for the case of a scale which we take to be stressed in only two dimensions, Equation 3 becomes:

$$\Delta\nu = 5.07 \text{ (cm}^{-1} \text{ GPa}^{-1}) \sigma_{2D} \quad \text{Eq. 4.}$$

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

The method will also detect other alumina phases and the presence of the metastable θ -phase has been observed by this technique [22].

Formation of alumina at high temperature has been extensively studied [23-25] 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 if Ti ions are present, the θ -form can transform to α -alumina more quickly [23] or when larger ions such as Zr, Hf or La are present be stabilised for longer periods [24]. For Y the literature reports conflicting results where it apparently encourages [23] or inhibits [24] transformation of θ -alumina. But in no case was θ -alumina found at times greater than 50 h at 1000°C.

7.2 RESULTS AND DISCUSSION

7.2.1 Initial investigations

Some initial work was carried out with a CMSX4/RT22/EB-PVD TBC system after isothermal ageing for 100 h at 1100 °C. Fluorescence spectra were obtained using 488 nm Ar⁺ laser radiation from a Coherent Innova 90-5 laser which was focussed onto the sample using an Olympus microscope confocally coupled to a Dilor XY spectrometer; the probed area was approximately 30 μ m in diameter. The spectra obtained in the R₁ R₂ region were frequently broad and indistinct (Figure 11) although four ‘peaks’ could usually be identified, and may be interpreted as being due to unstressed and stressed components. Deconvolution of the measured R₁ R₂ spectra was therefore attempted by curve-fitting four Voigt curves in this region using a commercial package [29]. Deconvolution of the spectra and mapping the residual stress obtained using equation (3) over relatively large regions indicated that wide variations in residual stress occurred on the same sample. The precision with which the position of these four Voigt components could be determined from the fitting routines was estimated to be approximately ± 2 cm⁻¹, which translates to an uncertainty in the stress values of ± 0.4 GPa. Determination of the band positions is less sensitive to noise and the appropriateness of the fitting functions used than the other parameters of band height and halfwidth; however, further work needs to be done to determine them with greater reliability. Finally, θ -alumina was also found on some parts of a sample after exposure for 100 h at 1100 °C (Figure 11).

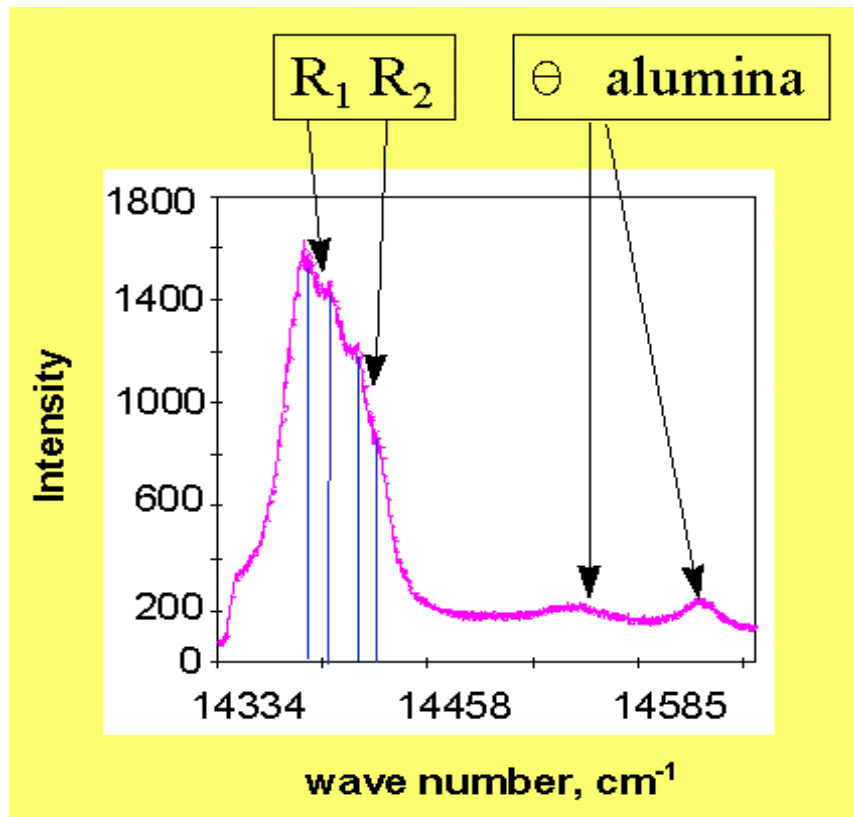


Figure 11 Spectra from a point on boxed area shown in Figure 12. The spectra indicates splitting of the R_1 and R_2 peaks due to at least two stress states and the presence of θ alumina.

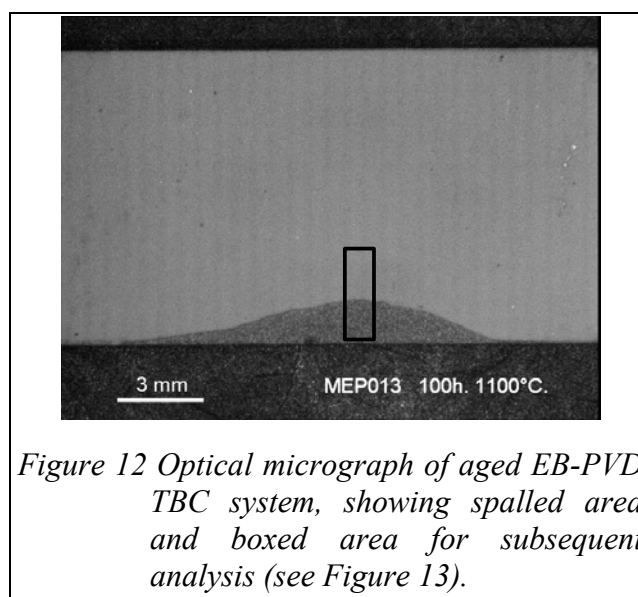


Figure 12 Optical micrograph of aged EB-PVD TBC system, showing spalled area and boxed area for subsequent analysis (see Figure 13).

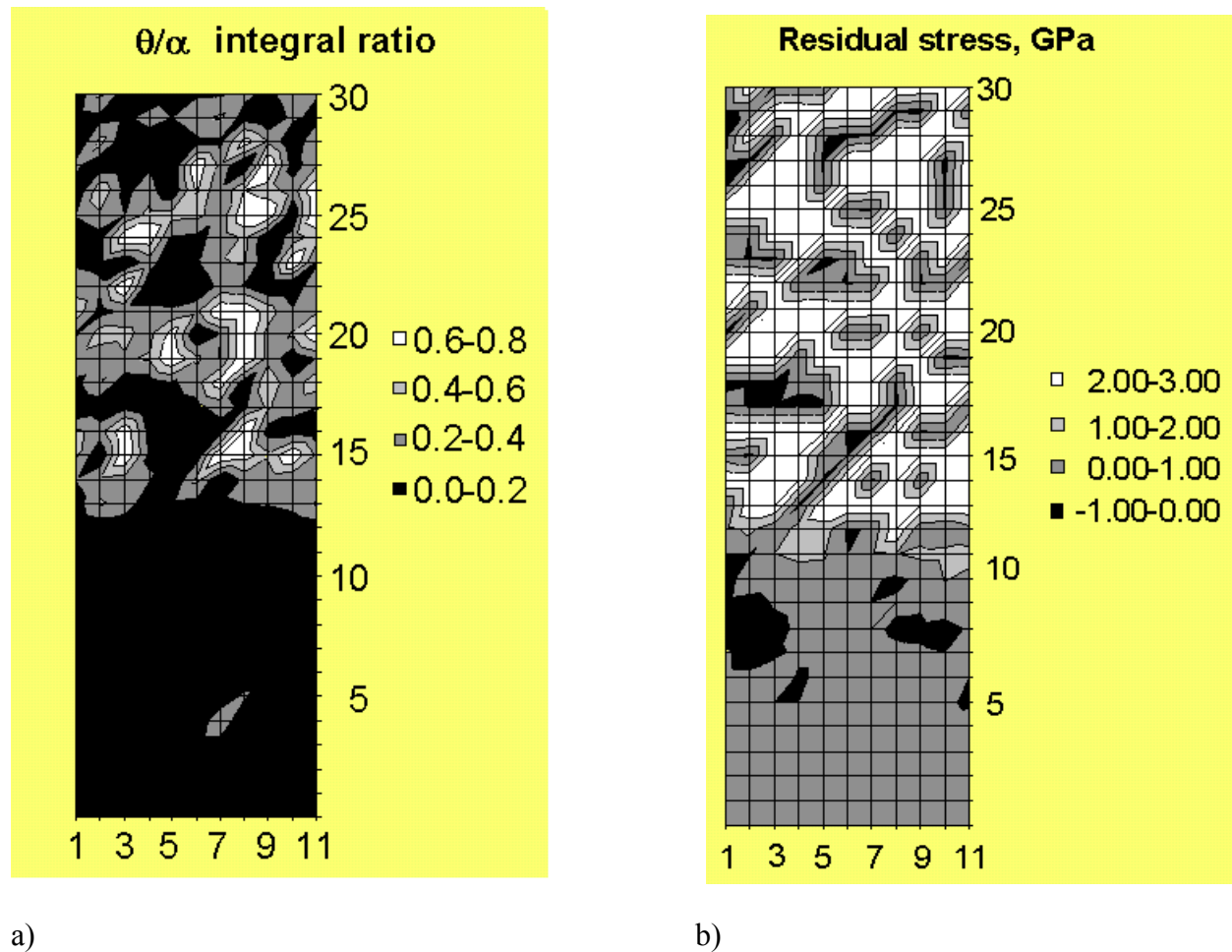


Figure 13 a) Relative distribution of α -alumina and θ -alumina in the boxed area shown in Figure 12, and (b) the residual stress from the same area

Particular interest was focussed on obtaining a more detailed understanding of some of these observations. Figure 12 is an optical micrograph of a sample showing a region from which the zirconia layer had spalled. A high resolution study of an area including some spalled and non-spalled regions was made using a spot size of about 5 μm . Figure 13a shows a map of the relative amounts of θ - to α -alumina based upon the integrated areas of the θ - and α -bands for the area marked by a box in Figure 12. Figure 13b shows the residual stress variation in the α -alumina using the R_2 shifts for the same area. Several points are of interest. Firstly, it can be seen that there is essentially no θ -alumina in the spalled region; secondly, θ -alumina is present in the TGO in regions where the TBC is still adherent. Thirdly, the occurrence of θ -alumina is frequently associated with splitting of the R_1/R_2 peak shapes as shown in Figure 11, and if these spectra are deconvoluted then θ -alumina appears to be correlated with regions of high residual stress in the TGO. Finally the levels of residual stress in the spalled area are lower than expected if the region had spalled at 1100 $^{\circ}\text{C}$. Note that the θ/α ratio is arbitrary since reliable values for the relative cross-sections of the α - and θ -bands are not available. However, given the previously described uncertainty in determining band half widths and heights, it was not possible to use the deconvoluted α -phase spectra to obtain a reliable ratio of 'stressed' to 'unstressed' volumes of alumina.

It is known that if the stress in the α -alumina exceeds a critical value spallation will occur and in so doing a stress free state is produced. Many workers have observed this experimentally using piezospectroscopy. In this case we propose the following interpretation for the occurrence of θ -alumina and the altered stress state in α -alumina. The stress in the α -alumina exceeded the critical value leading to local detachment of the TGO although complete spallation did not occur since the TGO was restrained by the TBC layer. Most probably these events occurred during the final cooling cycle. In the detached region, alumina re-growth occurred at the bondcoat/TGO interface at some intermediate temperature leading to θ -alumina formation. The resultant spectra were from an area which included both attached (stressed) and detached (unstressed) α -alumina and the newly formed θ -alumina. Thus α -alumina is present in two stress states as indicated by the fluorescence spectra, and the existence of θ -alumina correlated with the presence of a high residual stress in the α -alumina. An alternative explanation may be that the shape of the R_1/R_2 bands arises from altered crystal symmetry associated with the transformation of θ - to α -alumina (θ -alumina has a larger molar volume than α -alumina). The presence of four identifiable components suggests that two dominant local symmetries are present. While the former explanation is more generally accepted, concern about the size of the locally detached regions ($> 5 \mu\text{m}$) and the assumptions used in calculation of the residual stress in the TGO warrant consideration of the alternative explanation involving altered crystal symmetries.

The low values of residual stress in the region where the TBC spalled indicate either the alumina has spalled or is delaminated in such a way as to reduce stress. Furthermore, the maximum values of residual stress found under the adherent TBC are less than expected based upon a biaxial thermo-elastic stress due to thermal expansion coefficient mismatch (about 4.4 GPa). Consideration of triaxial stresses would reduce the residual stress as would surface roughness effects [27]. However there is some concern about the applicability of Equation 3 when probing areas of a few microns, since the premise is that a large number of randomly oriented grains are sampled, and at this lateral resolution this assumption may not be valid.

7.2.2 Long-term ageing tests

Following this initial study which indicated the promise of piezospectroscopy as an NDE tool that could be used to predict failure of the TBC system, a more systematic investigation was carried out in which the effect of changing the substrate (IN738 and CMSX4) and TBC type (APS or EB-PVD) while maintaining the same bondcoat (Sicoat 2453) was studied. Also included in this work was a Pt aluminide/EB-PVD system. All samples were examined in the as-received and aged conditions. Ageing was carried out for times up to 4000 h.

Residual stress maps were obtained by collecting spectra at 1 mm intervals over the surface of the TBC system. For the specimens used in this work 225 spectra were collected from each sample. A MATLAB[®] program was written which carried out an automatic fit to the spectra to determine the shift in the R_1 and R_2 peak positions. The spectra were fitted to a Lorentzian equation using a Levenberg-Marquardt minimization method with the following theoretical and empirical constraints applied in order to yield a good fit.

- i) Initial guesses at R_1 and R_2 peak positions were made
- ii) R_1 area was 30 times the peak height
- iii) R_2 area was 20 times the peak height

- iv) R_1 width was initially 20 wavenumbers
- v) R_2 width was initially 17 wavenumbers
- vi) R_1 peak centre was initialised at 14395 wavenumbers
- vii) R_2 peak centre was initialised at 14425 wavenumbers
- viii) A linear fit was then applied and the presence of spectra indicated by a negative slope
- ix) Spectra with a maximum intensity of 100 counts were ignored
- x) a Lorentzian fit was then applied
- xi) R_2 was also a higher wavenumber than R_1
- xii) R_1 and R_2 areas were always greater 100
- xiii) R_1 width was finally fixed to be between 5 and 100
- xv) R_2 width was finally fixed to be between 5 and 80
- xvi) R_1 always had a greater width than R_2

Where a fit using this procedure was not possible, the regions are indicated as white areas in the resultants maps. In general, for the spectra generated from EB-PVD TBC coating systems good fits were possible, but many more examples of failure to meet the fitting criteria listed above were found for the APS TBC systems. In most of these cases, the fit was not possible because the intensity was too low (less than 100 counts). An example of the spectral fitting software output is shown in Figure 14. The blue line represents the experimentally measured spectrum and the red is the fitted curve. As can be seen a good fit was obtained in this case. The map is generated using each spectrum obtained on the sample with the grid representing the 1 mm matrix. Note that although the laser light is focussed to about 5 μm diameter spot the extent of scattering through the TBC is not known, although there are indications that the area of the TGO irradiated could be at least a factor of ten greater. Thus the central 50 μm of the grid is the region generating the spectrum. The two maps shown are for R_1 and R_2 peaks with the colour scale showing residual stress values from +1 GPa (dark red) to -4 GPa (dark blue). It will be noted that, in general, R_1 spectra have a slightly more negative residual stress value than R_2 ; the R_2 value is believed to be the representative value and thus in subsequent maps only R_2 is shown.

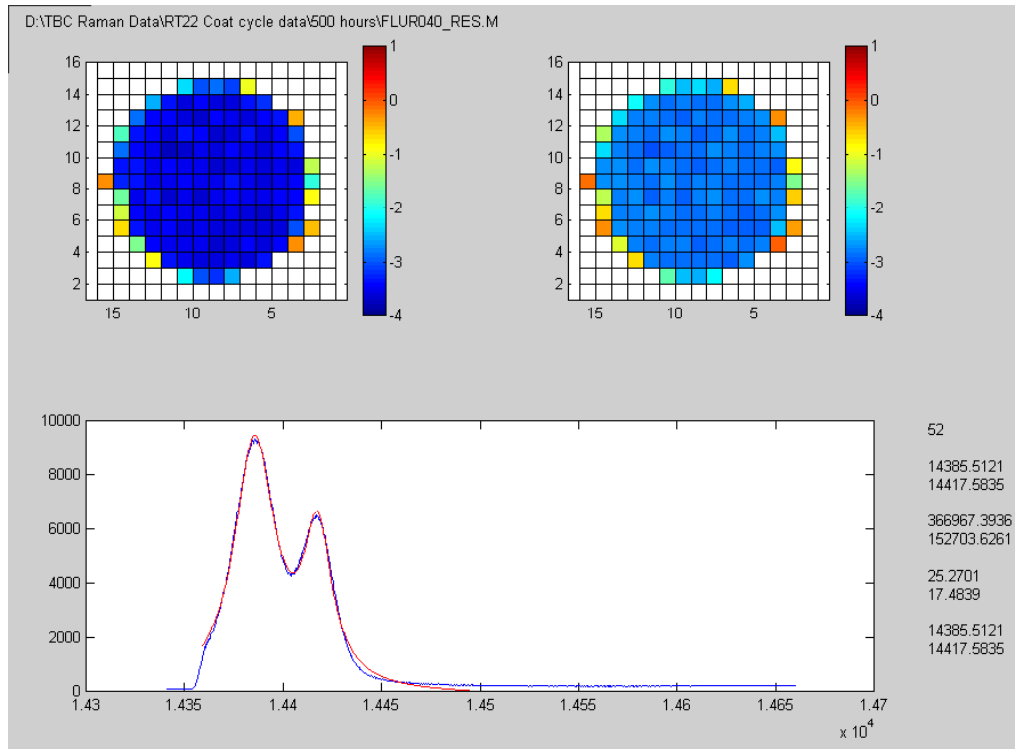


Figure 14 *Output from spectral fitting software showing the experimental spectrum and the fit (bottom) and (top) stress maps generated from the R_1 and R_2 peaks.*



Figure 15 *Optical micrograph of a typical test sample for the piezospectroscopic investigation showing relocation notch.*

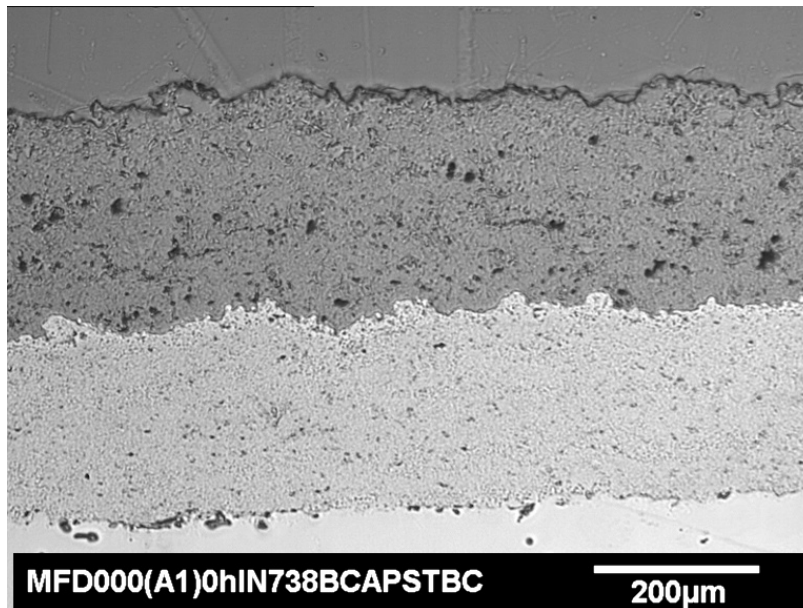


Figure 16 *Optical micrograph of a polished cross-section of an IN738 substrate with a MCrAlY bondcoat and an APS TBC in the “as-received” condition.*

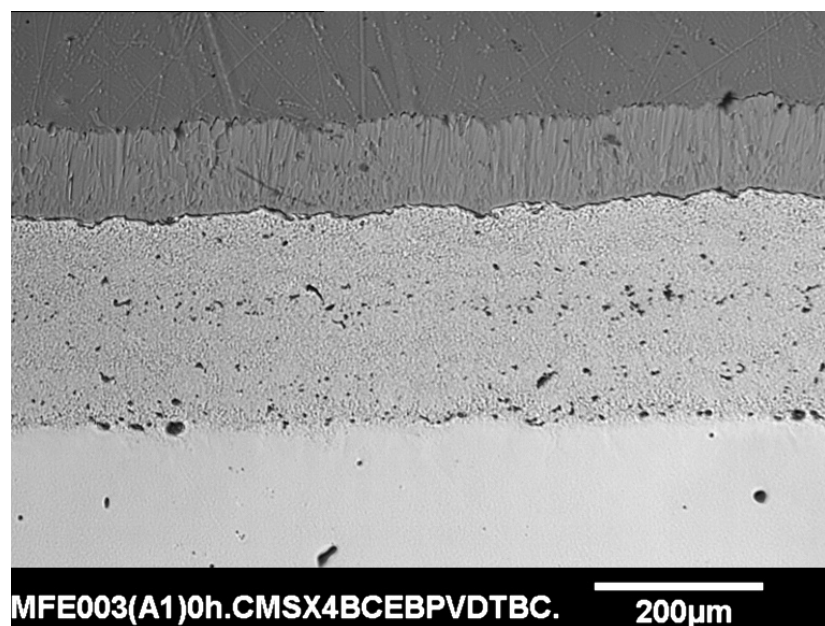


Figure 17 *Optical micrograph of a polished cross-section of a CMSX4 substrate with a MCrAlY bondcoat and an EB-PVD TBC in the “as-received” condition*

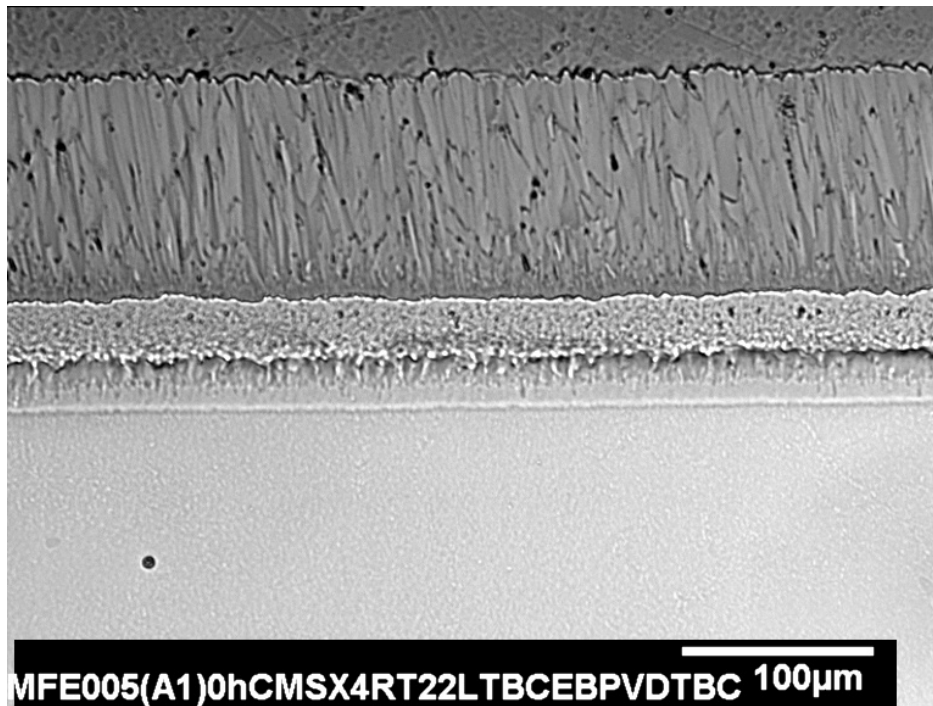


Figure 18 Optical micrograph of a polished cross-section of a CMSX4 substrate with a RT22 bondcoat and an EB-PVD TBC in the “as-received” condition

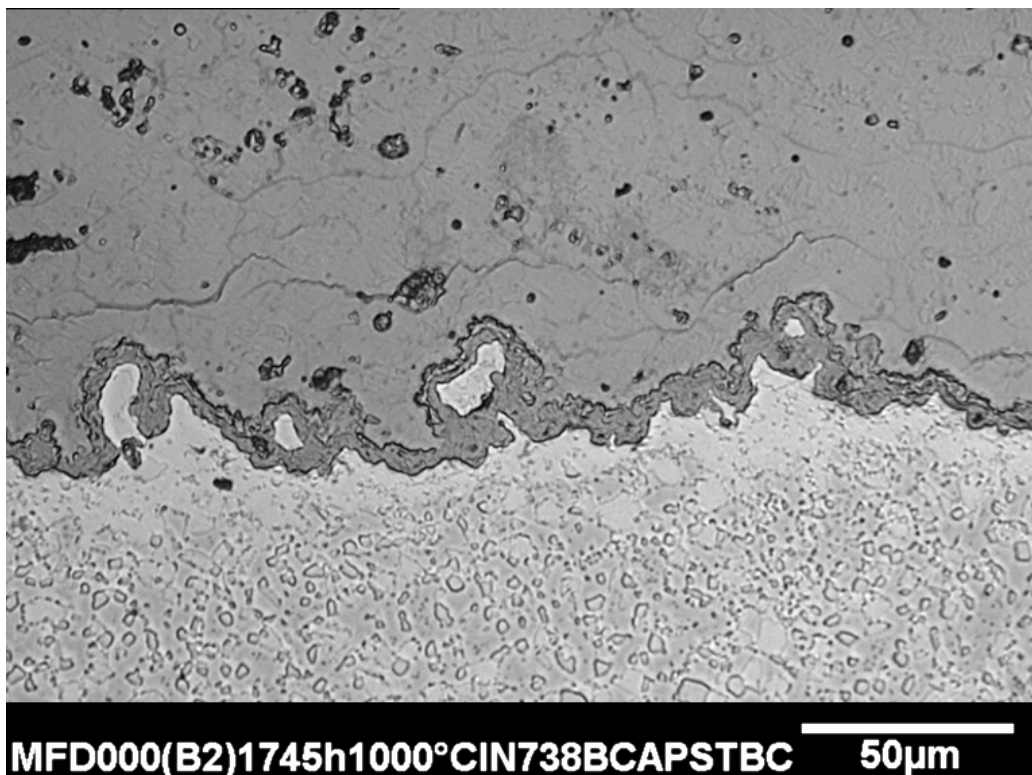


Figure 19 Optical micrograph of a polished cross-section of an IN738 substrate with a MCrAlY bondcoat and an APS after 1735 h ageing at 1000 °C.

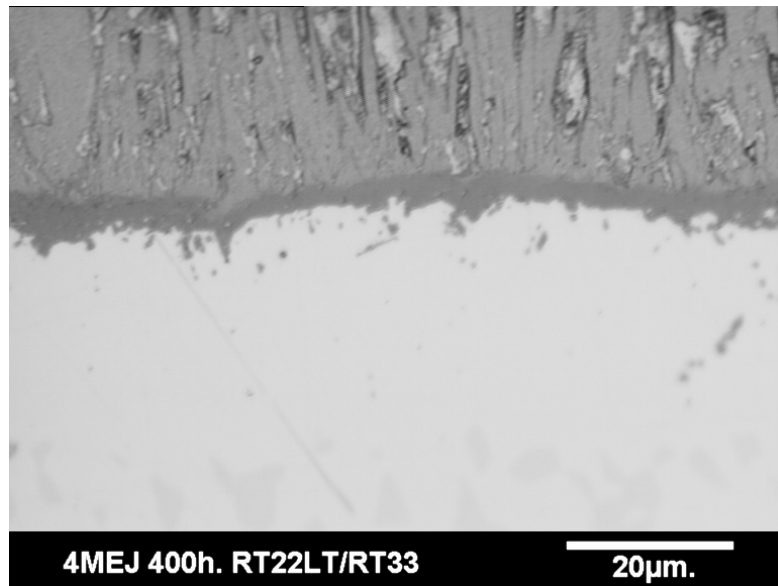


Figure 20 *Optical micrograph of a polished cross-section of a CMSX4 substrate with a RT22 bondcoat and an EB-PVD TBC after 400 h at 1100 °C.*

Figure 15 is a micrograph of the sample shape used showing a notch that was used for relocation. Figures 16 - 18 show cross-sections of some of the as-received samples (IN738/2453/APS, CMSX4/2453/EB-PVD and CMSX4/RT22/EB-PVD, respectively). It will be seen that the Sicoat 2453 was about 220-250 μm thick, the APS about 250 μm and the EB-PVD about 100 μm . Figures 19 and 20 are cross-sections through aged samples showing the TGO that developed on Sicoat 2453 and RT22 respectively.

It was planned to age the samples until spallation occurred and monitor the samples exposed to cyclic tests at intermediate times, so that changes in the TGO residual stress could be related to the ultimate failure of the TBC system. In almost all cases no spallation was observed, nevertheless changes in residual stress were found for the five different systems as a function of ageing cycle.

Figures 21 – 30 show the residual stress maps generated for the specimens listed above in the various ageing tests. Examination of these Figures leads to the following observations.

For the Sicoat 2453 bondcoat:

- i) The compressive residual stress in the TGO in coating systems with EB-PVD TBCs was always higher than that found in the APS TBC systems (cf Figures 21, 25 with 23, 27);
- ii) For the EB-PVD TBCs the compressive residual stress in the TGO was lower when the fast cooling cycle was used compared with the slow cool cycle (cf Figures 21, 25 with 22, 26);
- iii) Again for the EB-PVD TBC systems, stresses were slightly lower with an IN738 substrate than CMSX4 (cf Figures 21 with 25);

- iv) Stress increased with increasing exposure for the EB-PVD TBC systems for both types of cooling cycles while no clear increase was found for the APS TBC systems (cf Figures 21, 22, 25, 26 with 23, 24, 27, 28);
- v) Increased areas of samples with the APS TBC systems yield no spectra with increasing ageing times (Figures 23, 27);
- vi) The stress was found to vary over the surface of the sample for all types of sample (Figures 21-28).

For the RT22 bondcoat (note, only one systems was examined – CMSX4/RT22/EB-PVD):

- i) Compared with the Sicoat 2453 bondcoat system, the stress in the TGO formed on RT22 was more uniform over the sample surface (cf Figures 29, 30 with 21-28);
- ii) Fast cooling cycles resulted in more areas with lower stress (cf Figure 29 with 30);
- iii) A small area of the sample exposed to the slow cool cycle spalled after about 500 h (see Figure 31), and that edge of that sample (7-8 o'clock) continued to show reduced residual stress values for the duration of the test (Figure 29).

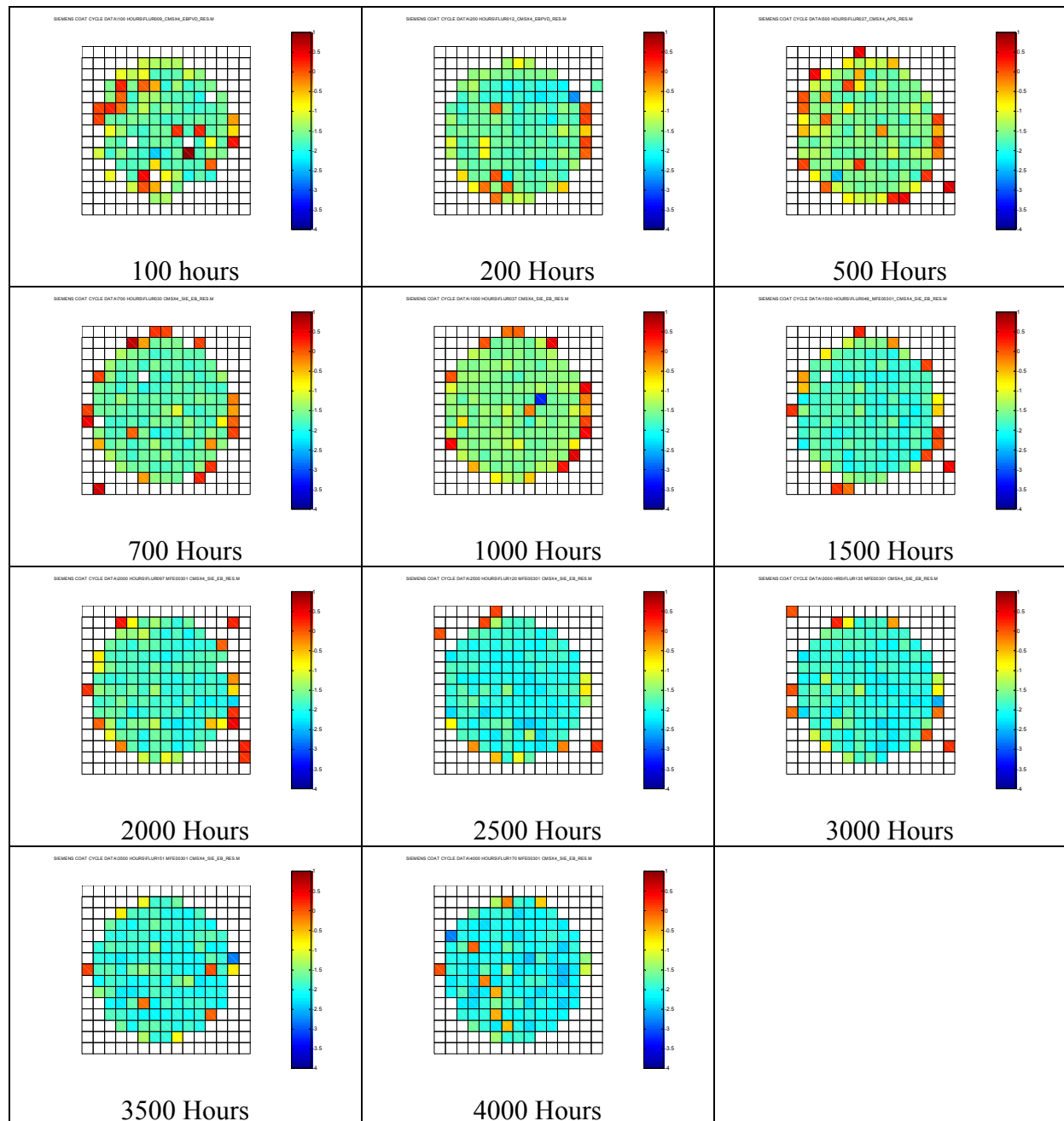


Figure 21 Stress maps for CMSX4/2453/EBPVD during ageing for 4000 h - slow cooling

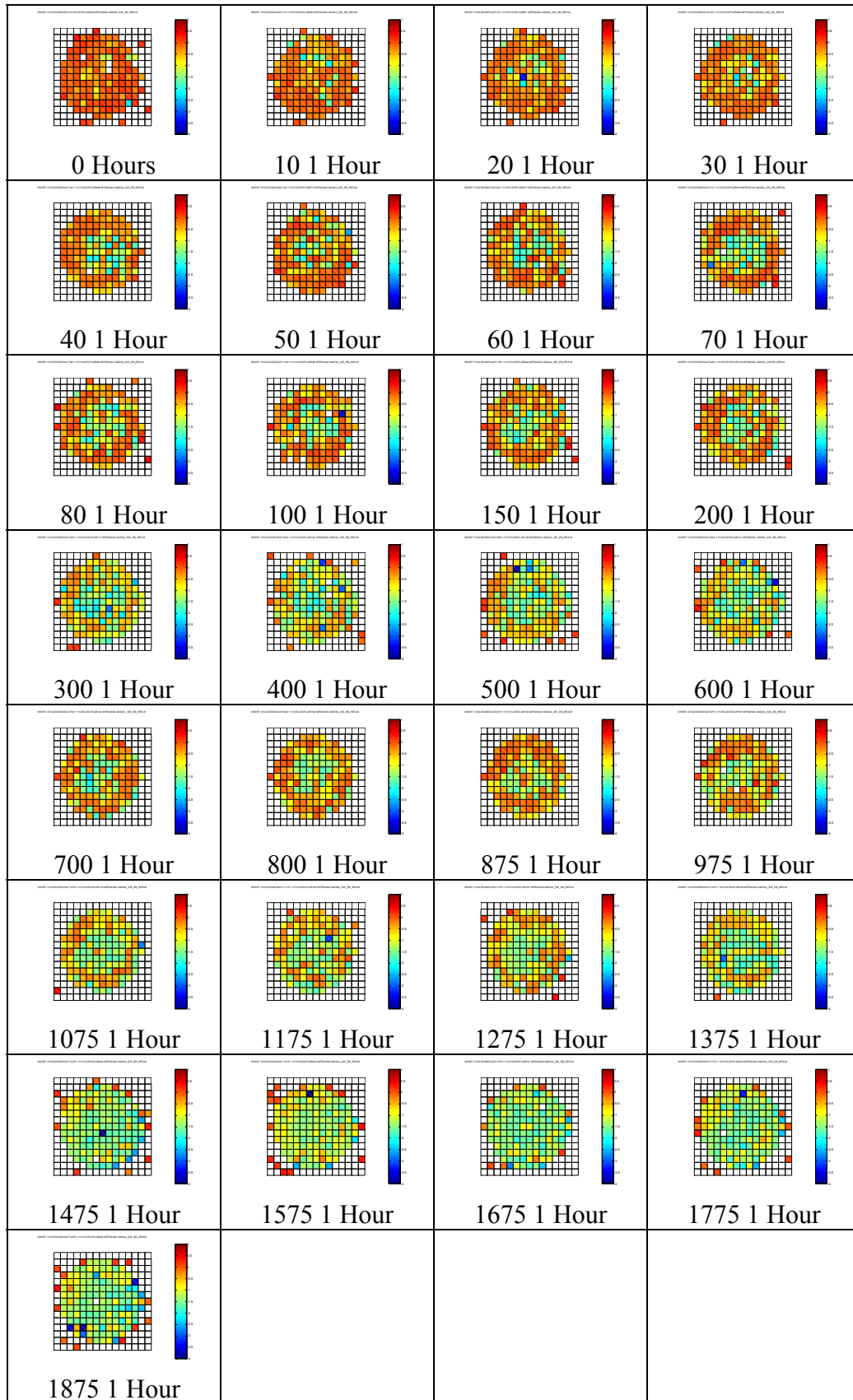


Figure 22 Stress maps for CMSX4/2453/EBPVD during ageing for 1875 h -fast cooling

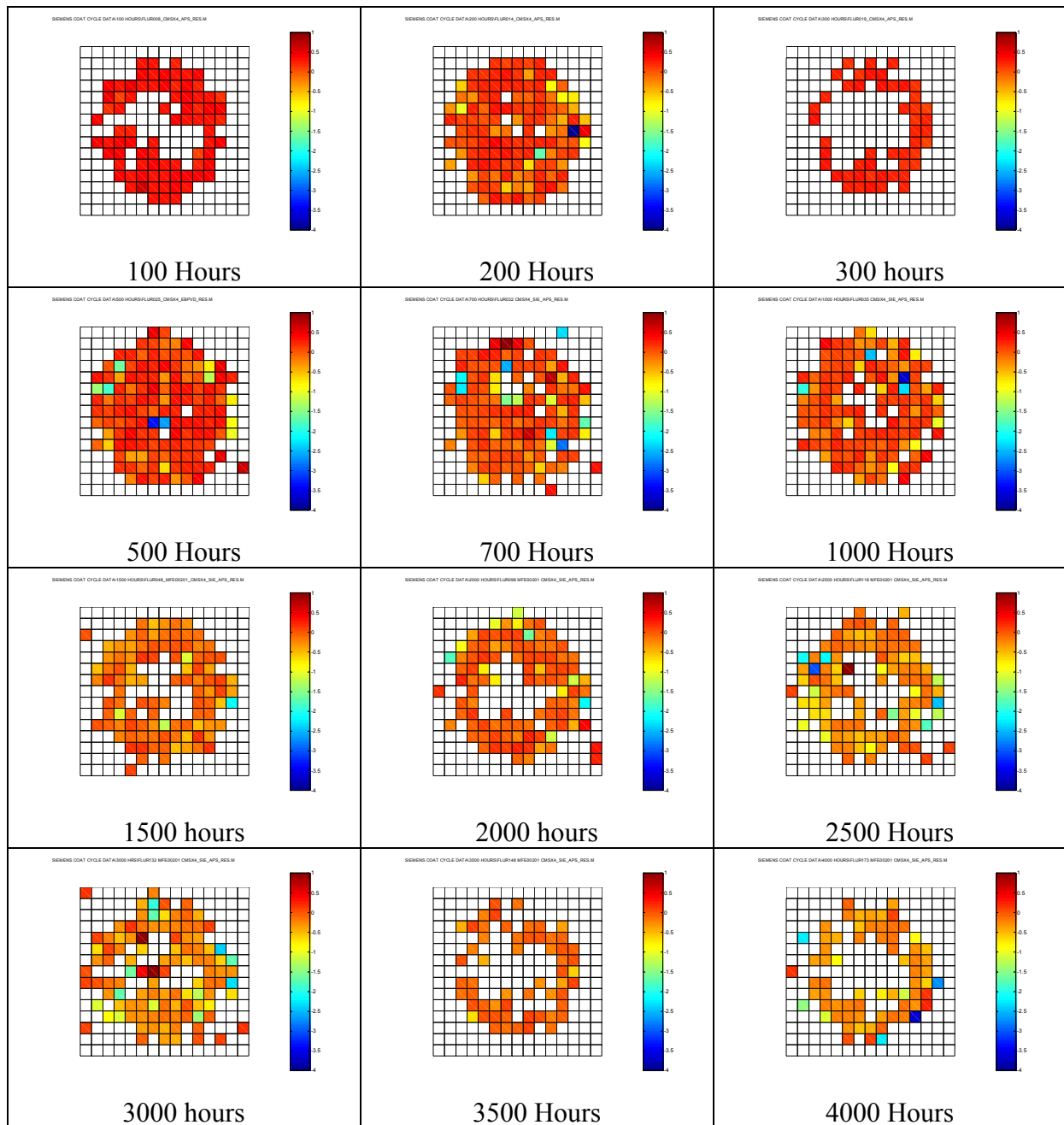


Figure 23 Stress maps for CMSX4/2453/APS during ageing for 4000 h - slow cooling

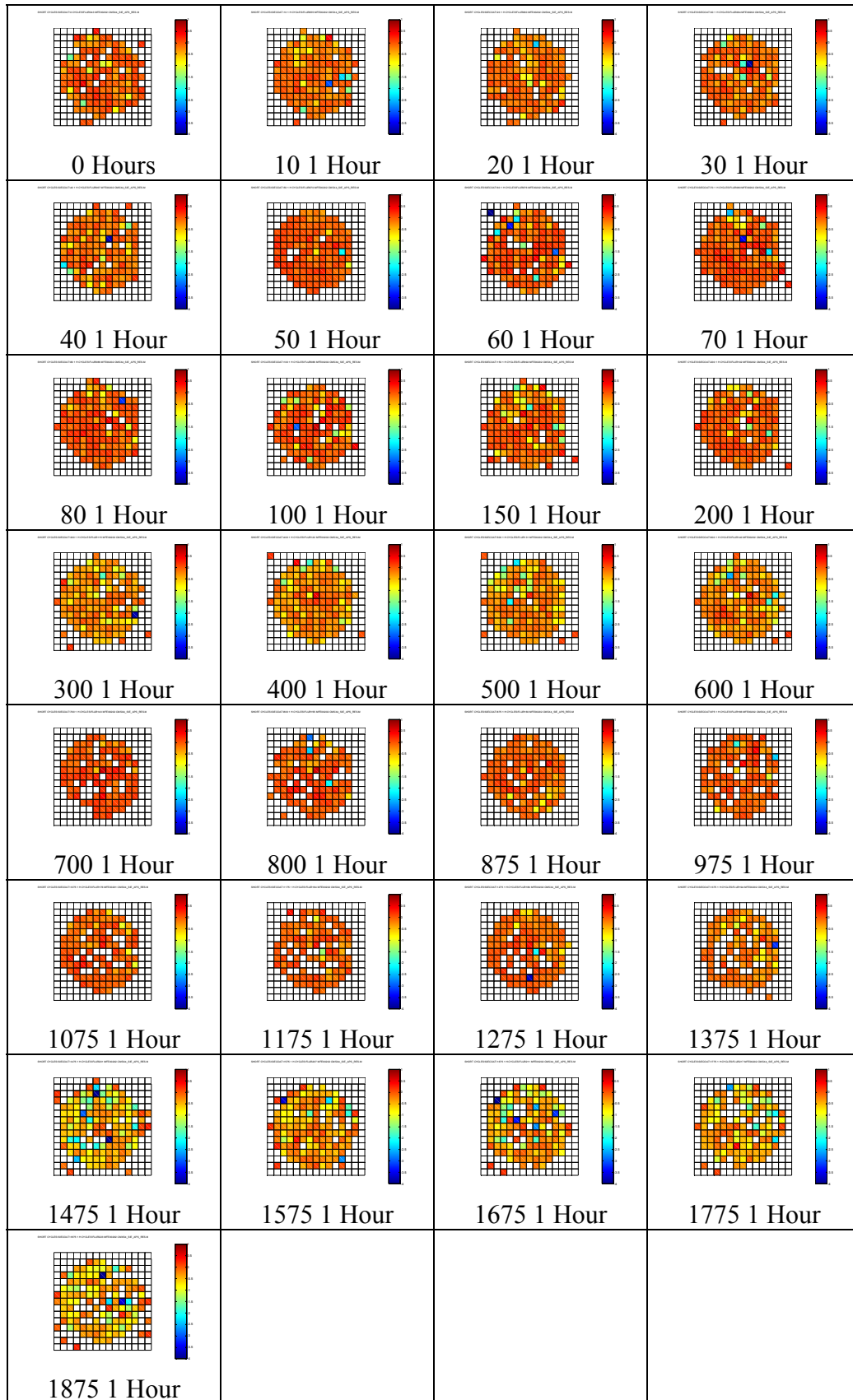


Figure 24 Stress maps for CMSX4/2453/APS during ageing for 1875 h - fast cooling

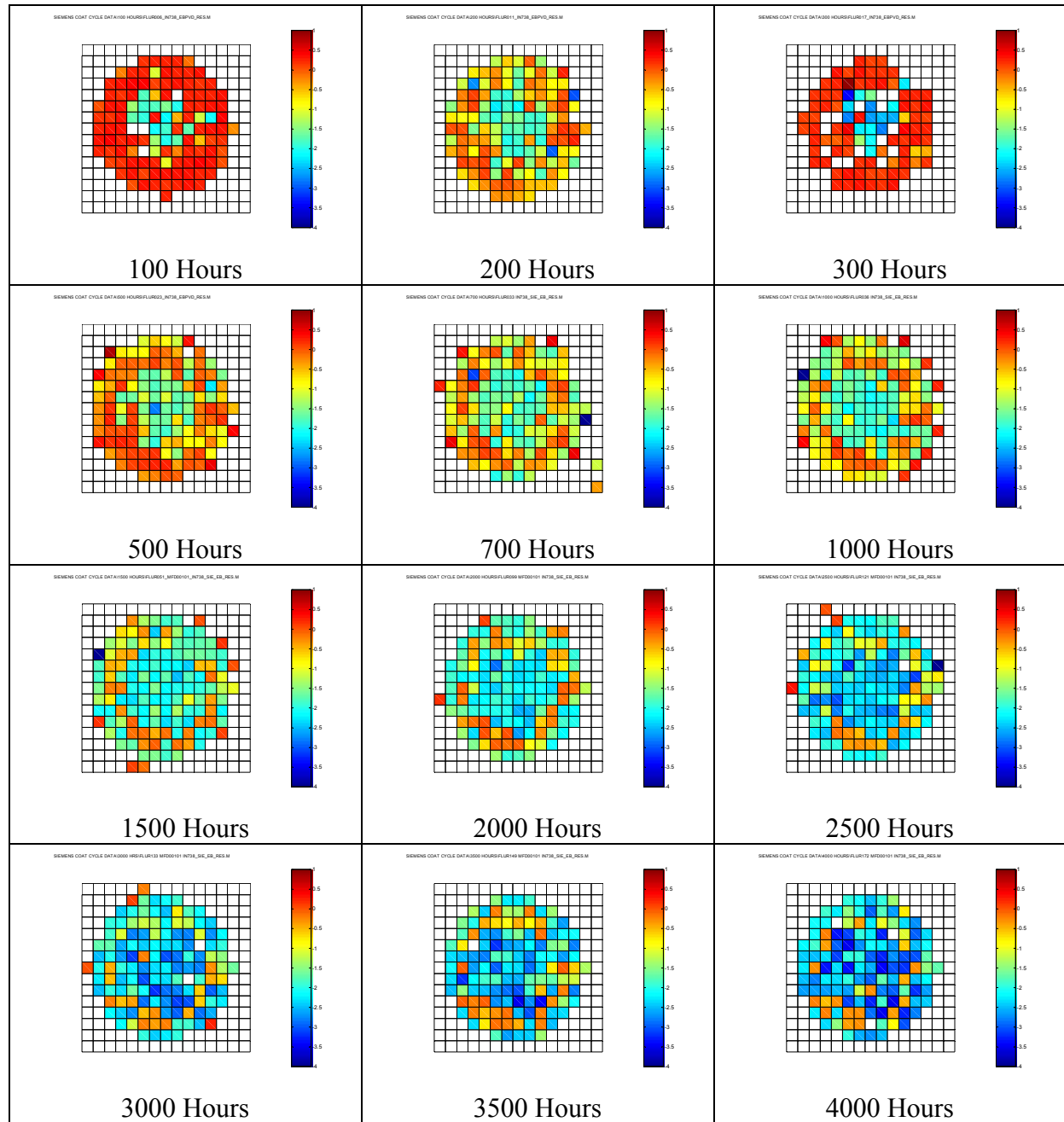


Figure 25 Stress maps for IN738/2453/EBPVD during ageing for 4000 h - slow cooling

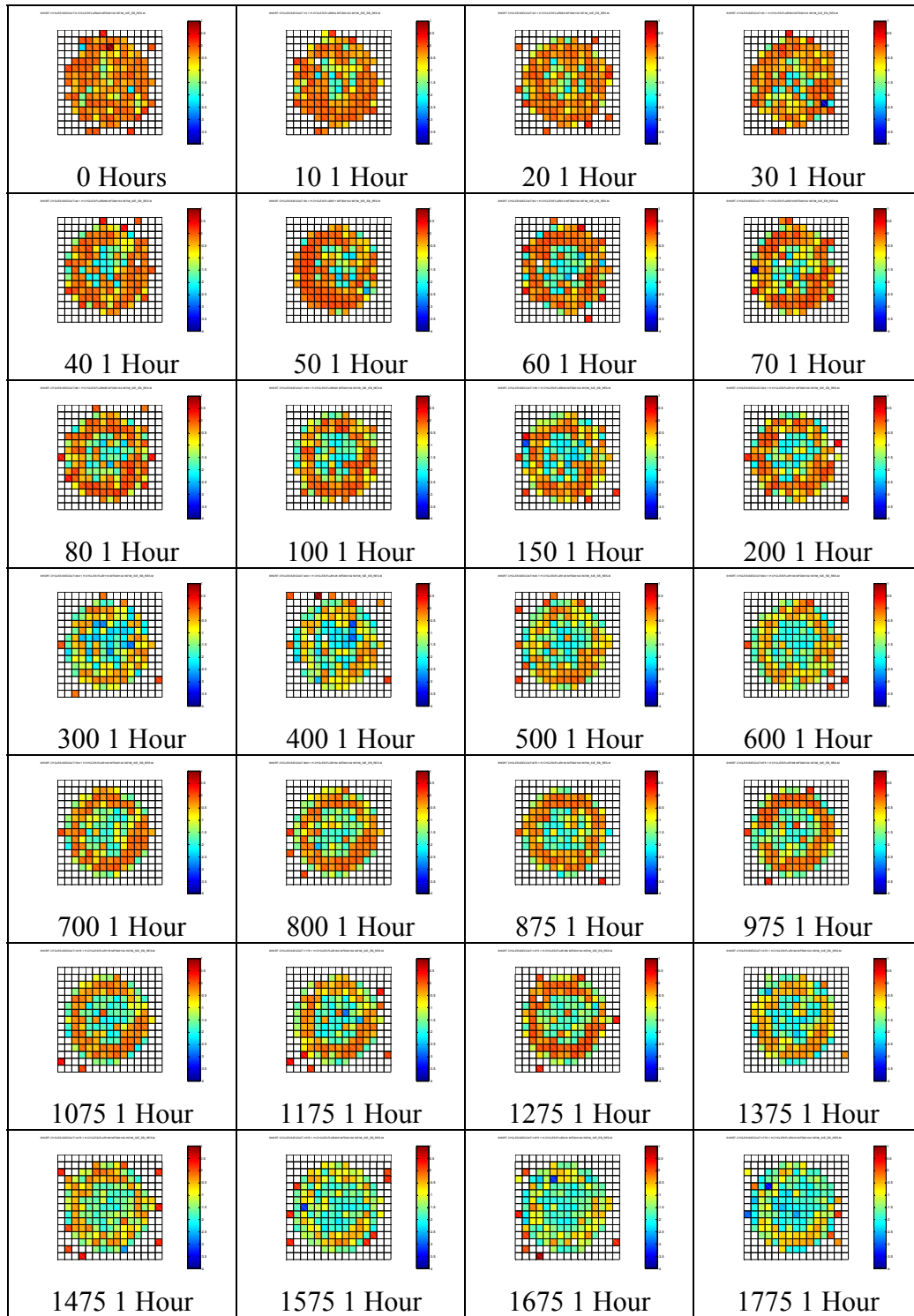


Figure 26 Stress maps for IN738/2453/EBPVD during ageing for 1775 h -fast cooling

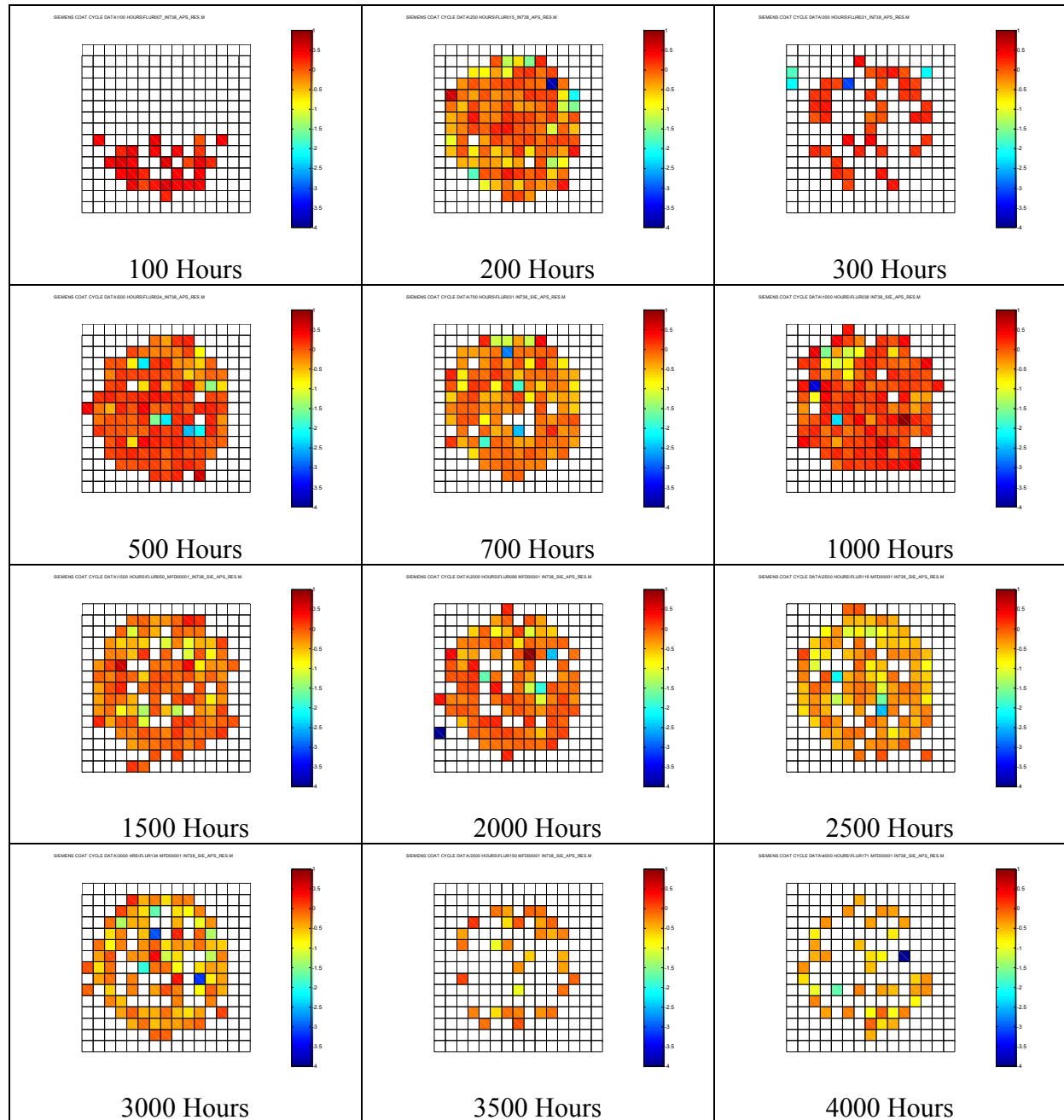


Figure 27 Stress maps for IN738/2453/APS during ageing for 4000 h - slow cooling

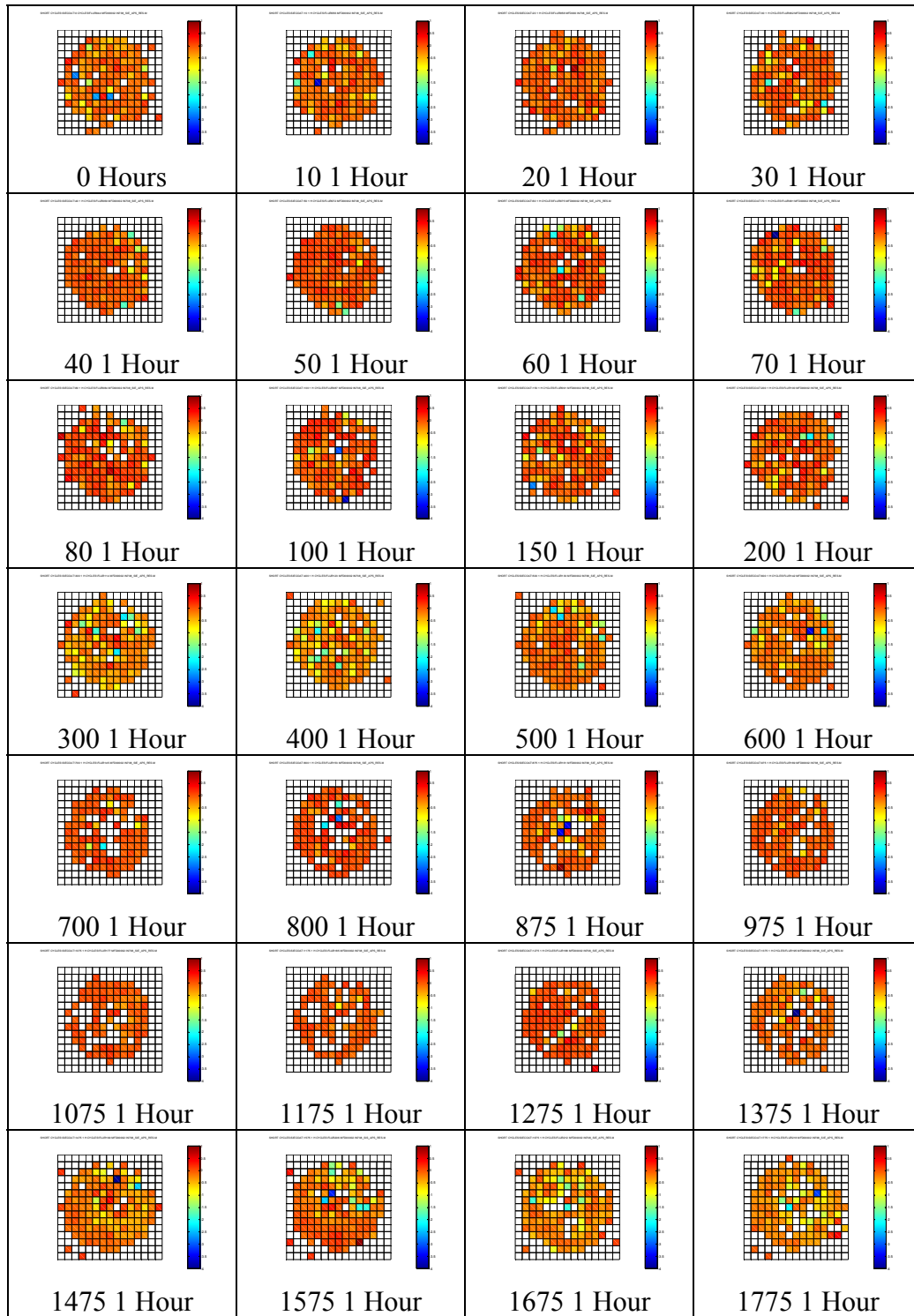


Figure 28 Stress maps for IN738/2453/APS during ageing for 1775 h - fast cooling

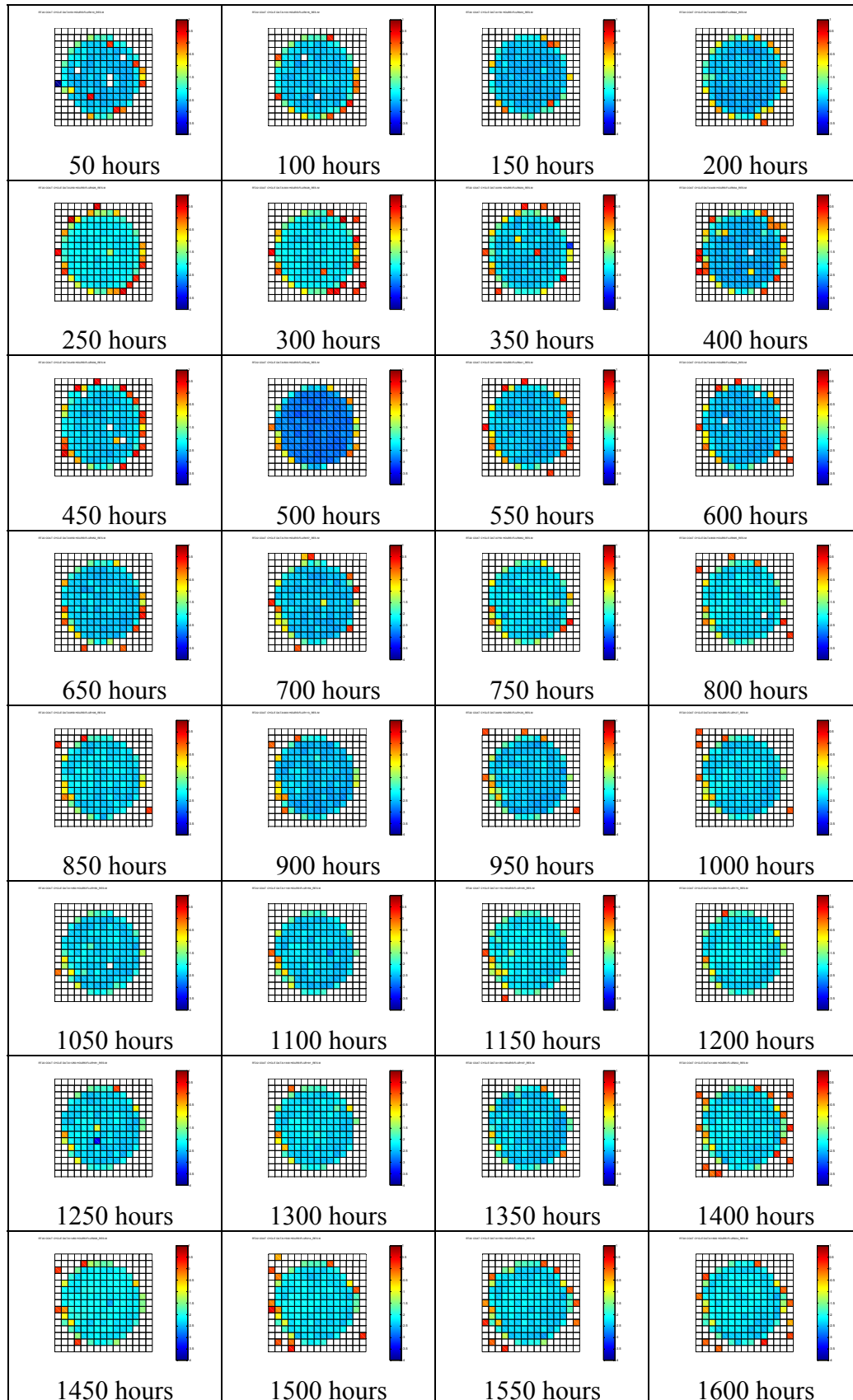


Figure 29 Stress maps for CMSX4/RT22/EBPVD during ageing for 1600 h - slow cooling

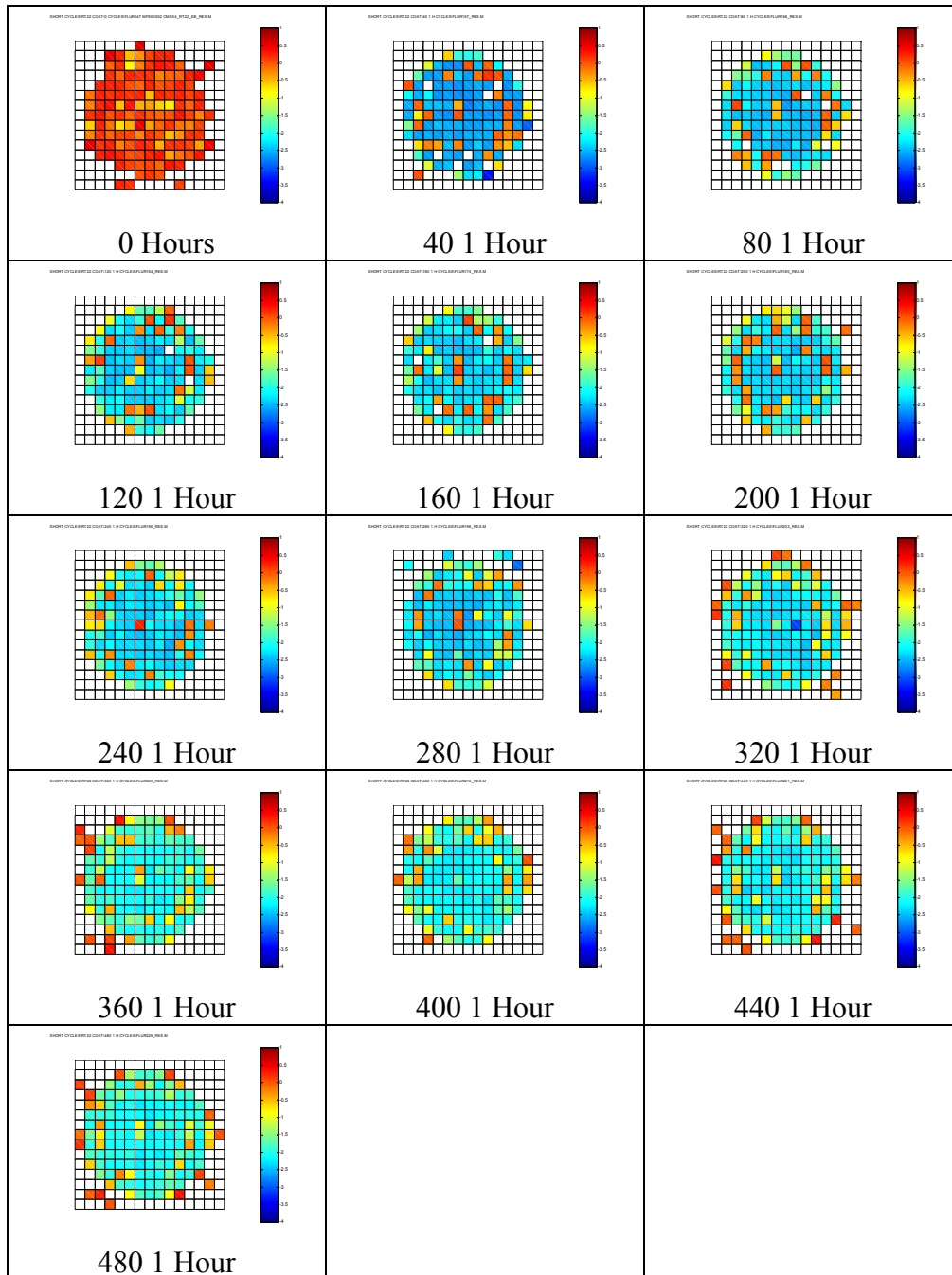


Figure 30 Stress maps for CMSX4/RT22/EBPVD during ageing for 480 h - fast cooling



Figure 31 *Optical micrograph of CMSX4/RT22/EB-PVD aged for 650 h at 1100 °C with the slow cool cycle*

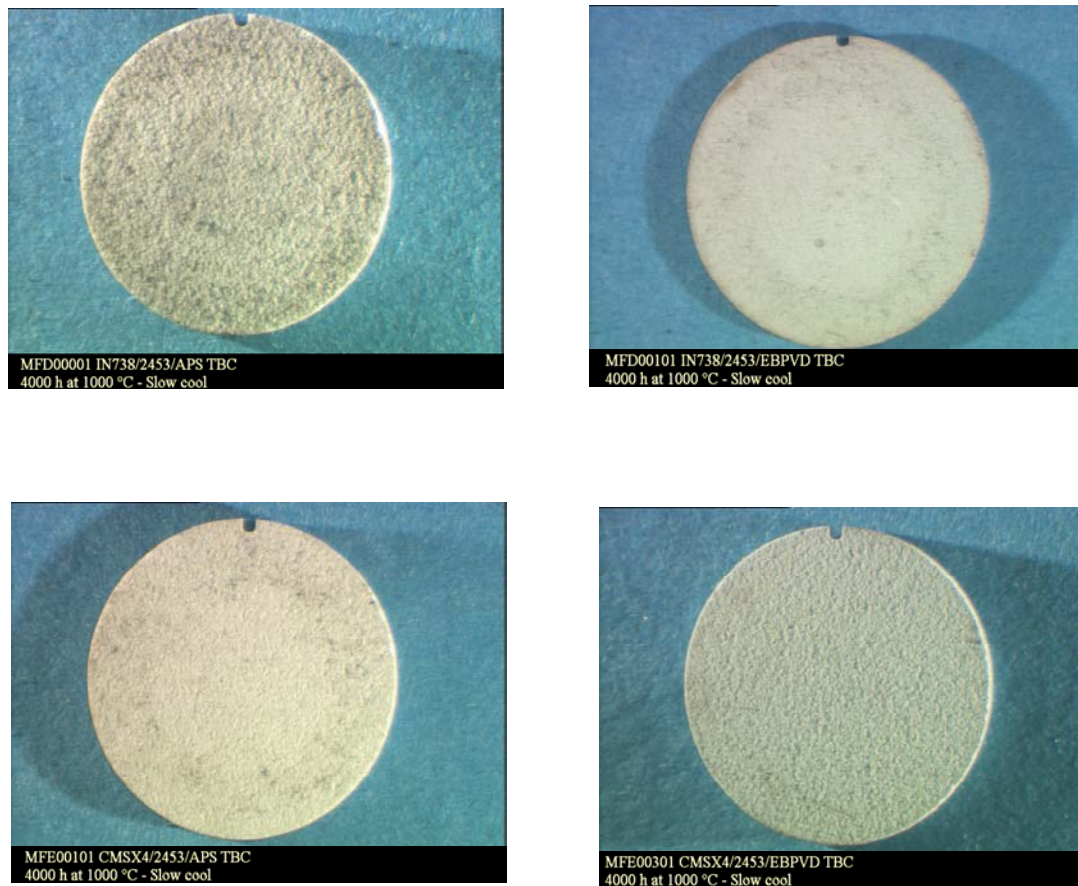


Figure 32 Optical micrograph of samples with Sicoat 2453 bondcoats after 4000 h ageing at 1000 °C with the slow cool cycle, top left IN738.APS; top right IN738/EB-PVD; bottom left CMSX4/APS; bottom right CMSX4/EB-PVD

In general, these results indicate that while clear effects of increased ageing were found for the EB-PVD TBC coating systems, no such effects were found for the APS TBC systems. Furthermore, for the APS TBCs the area of sample from which no spectra were generated increased with increased ageing time. A recent publication by Schlichting *et al* [30] 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 are not related to changes in the residual stress of the TGO, and further work is required to clarify these observations.

Considering now the observations in the EB-PVD TBC systems, the greater variation in stress levels in the TGO on the Sicoat 2453 bondcoat compared with the RT22 bondcoat can be explained by the fact that the TGO formed in the Sicoat system is undulating whereas that on the RT22 is flat (see Figures 19 and 20). Clarke *et al* [27] 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 [31] 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 now in progress would be 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 [31].

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 for the RT22 bondcoat systems (1135 °C is normally 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. Figure 32 is an optical micrograph of the

samples With Sicoat 2453 bondcoats after 4000 h ageing at 1000 °C with the slow cool cycle where it can be seen in some cases that circular patterns have developed, and indeed similar patterns are observed in the some of the residual stress maps. It is possible that bowing of the samples occurred which could have contributed to the better than expected spallation resistance of these samples.

7.2.3 TBC coated blades

7.2.3.1 Results

Industrial partners in this project supplied used and unused blades as part of the evaluation of the use of piezospectroscopy. Both of the used blades had significant amounts of deposit present on the sample and in these cases spectra were obtained in the “as-received” state as well as after slight abrasion using an alumina grinding wheel to remove the deposits. In one case an EB-PVD system was supplied, while the other was APS. The used EB-PVD TBC system had been in service for about 7000 equivalent operating hours and no information was available about the exposure conditions for the APS TBC coated blade.

The size of the components being studied required somewhat different optical arrangements compared with work described above on test samples. For the blades the spot size was approximately an order of magnitude greater than that used for the test samples so that the spectra were generated from an area of about 300 μm diameter. The used blades had deposits on some parts of the surface, and spectra were obtained from these blades both before and after “cleaning” with light abrasion with an alumina grinding wheel.

Considering first the spectra from the APS TBC coated blade that are shown schematically in Figures 33-38. For the unused blade only a few of the locations investigated on both the convex and concave surfaces yielded spectra which were of low intensity and generally the stress was close to 0 GPa (Figures 33-34). The used blade was covered with a heavy deposit on the convex surface and none of the areas investigated yielded a spectra except a point on the trailing edge where an intense spectrum was observed which corresponded to a relatively low stress of -0.86 GPa (Figure 35). For the concave surface less deposit was present and more spectra observed, again however the values of stress were close to 0 GPa (Figure 36). After abrasion with the alumina grinding wheel, almost all the areas examined yielded spectra, although the intensity was low in many cases. The convex surface tended to have stress values of about -0.5 GPa or less (Figure 37), while somewhat higher values were observed on the concave surface (Figure 38). These results are considered further in section 7.2.3.2.

For the EB-PVD TBC coated blades the corresponding information is shown in Figures 39-44. Figure 39 is an optical micrograph of sections cut through the blade showing the stress distribution and spectral intensity on both concave and convex surfaces of an unused blade. High intensity spectra were always observed with stress values at about -2.0 GPa except at the rounded part of the convex surface where the stress was reduced to -0.37 GPa. Because of the small size of this part of the blade, it was possible to use the normal imaging and thus high spatial resolution (5 μm) could be achieved. A 5 x 5 matrix from a flat part on the convex surface near the trailing edge was examined using 5 μm steps and Figure 40 shows a stress map and corresponding spectral intensity. It is noteworthy that over this very small area there were large changes in both intensity (up to 3 orders of magnitude) and stress which

varied from close to zero for most of the surface but some areas had a stress of about -1.5 GPa.

For the used EB-PVD TBC coated blade which also had significant amounts of deposit present, generally high intensity spectra were observed where the deposit was thin with stress values between -0.4 -1.77 GPa for the corresponding positions on the concave and convex surfaces (Figures 41 and 43). When these areas were abraded to remove the deposit, spectral intensity was generally reduced and stress values were about -0.4 GPa for most areas (Figures 42 and 44).

For the EB-PVD TBC coated unused blade, an additional study was carried out using the high spatial resolution imaging to determine whether any significant effects of curvature on stress could be observed. Figure 45 shows spectra from near the leading edge (highly curved) and near the trailing edge (almost flat), and it can be seen that on the flat region stress values were the same on both the concave and convex surfaces. For the concave surface near the leading edge two stress states were found, a higher one which corresponded to that found on surface near the trailing edge and a lower value which was the same as that found on the convex surface at the leading edge. It was also of interest to note that spectra from the convex surfaces were lower in intensity than those from the concave surface.

7.2.3.2 General conclusions

The piezospectroscopy method is able to measure fluorescence spectra on TBC coated blades, but as with the test samples there appears to be a significant difference between the EB-PVD and APS systems. Generally higher stress values were found with EB-PVD TBCs in both the used and unused states. This may be related to the proposed contamination of TBC powder [29] discussed earlier. Further work on these blades is clearly warranted and will be carried out in the new DTI funded programme at NPL. Some early results of this new programme have indicated a further complication. In the case of long-term exposures diffusion effects have been observed such that fluorescence of the TBC has been observed in cross-sections of the long-term aged samples. This fluorescence was strongest near the TGO/TBC interface, and was increased with increasing ageing time.

Deposits clearly influenced the observed behaviour, often preventing observation of spectra. This was not always the case, however, and work is required to determine whether components of the deposit fluoresce or whether the signal was indeed generated by the TGO. Attempts to remove the deposit using abrasion certainly changed both the observed stress state and signal intensity, but the method used may have introduced alumina impurities from the grinding wheel or may have been too severe penetrating both the TBC and TGO. Clearly more work is required to fully interpret these observations.

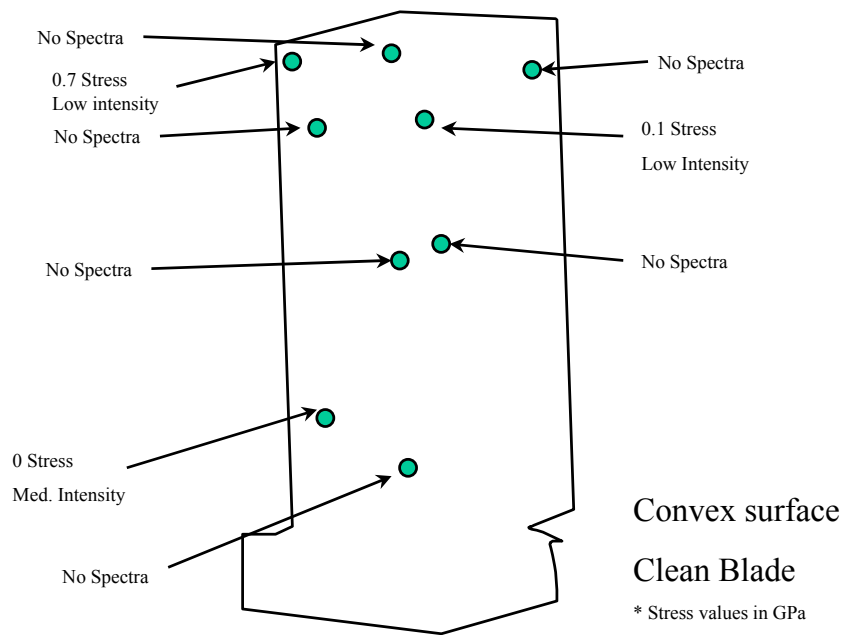


Figure 33 Schematic diagram of stress distribution and spectral intensity at various locations on an unused APS TBC coated blade – convex surface

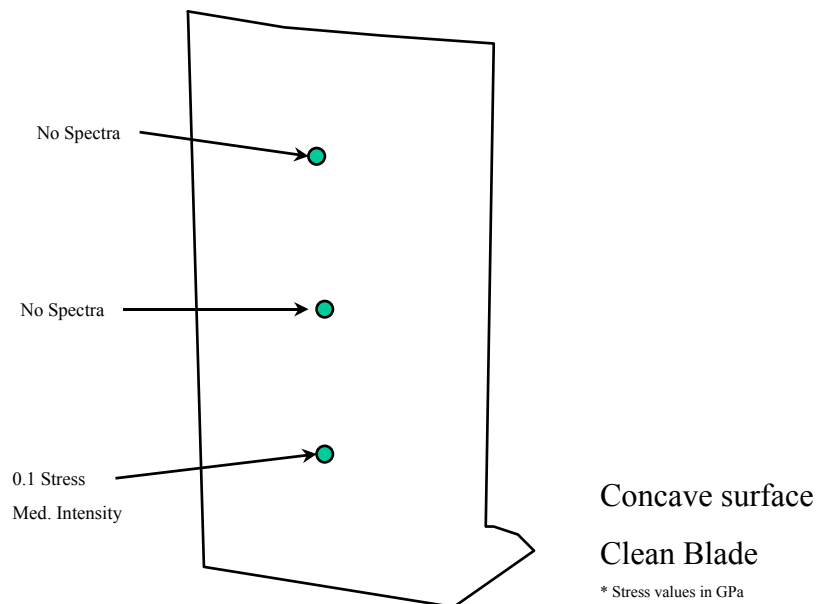


Figure 34 Schematic diagram of stress distribution and spectral intensity at various locations on an unused APS TBC coated blade – concave surface

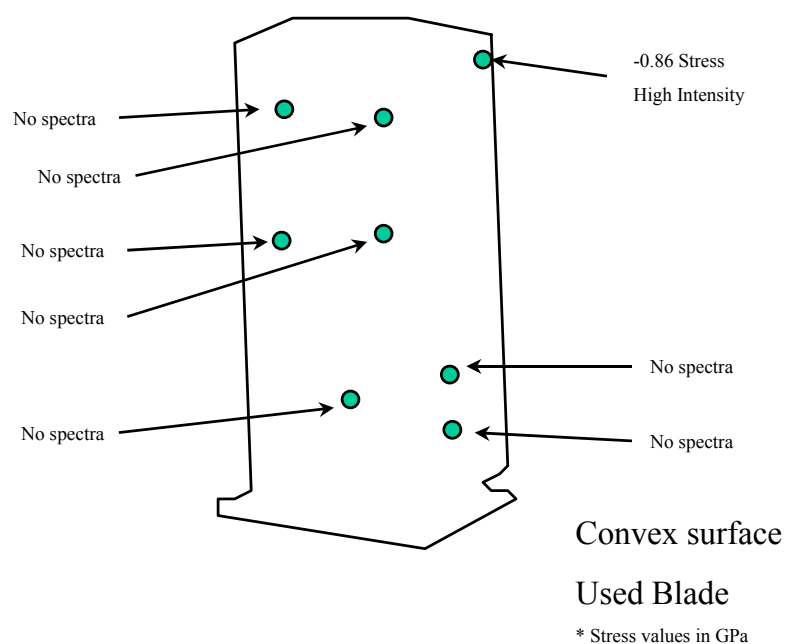


Figure 35 Schematic diagram of stress distribution and spectral intensity at various locations on a used APS TBC coated blade – convex surface

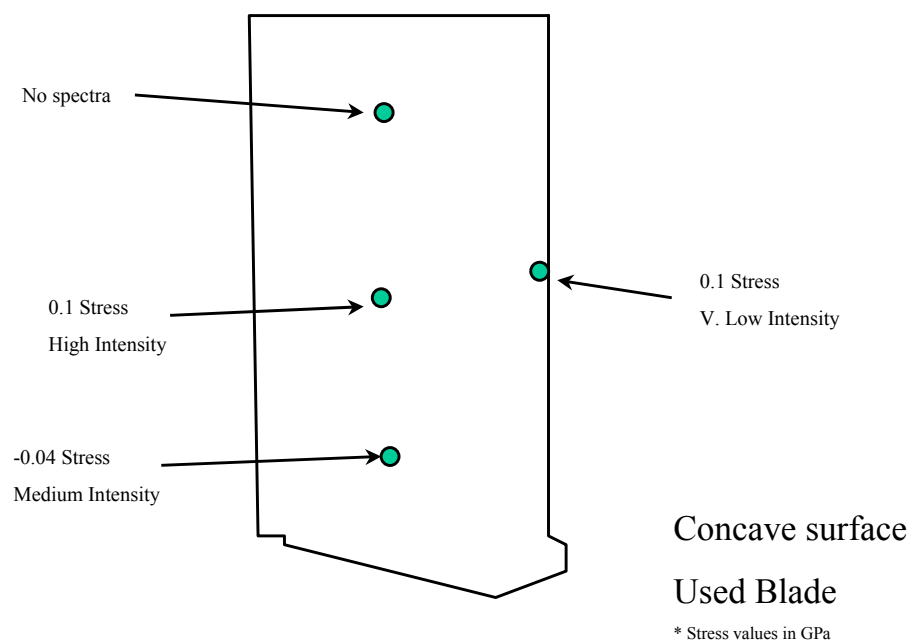


Figure 36 Schematic diagram of stress distribution and spectral intensity at various locations on a used APS TBC coated blade – concave surface

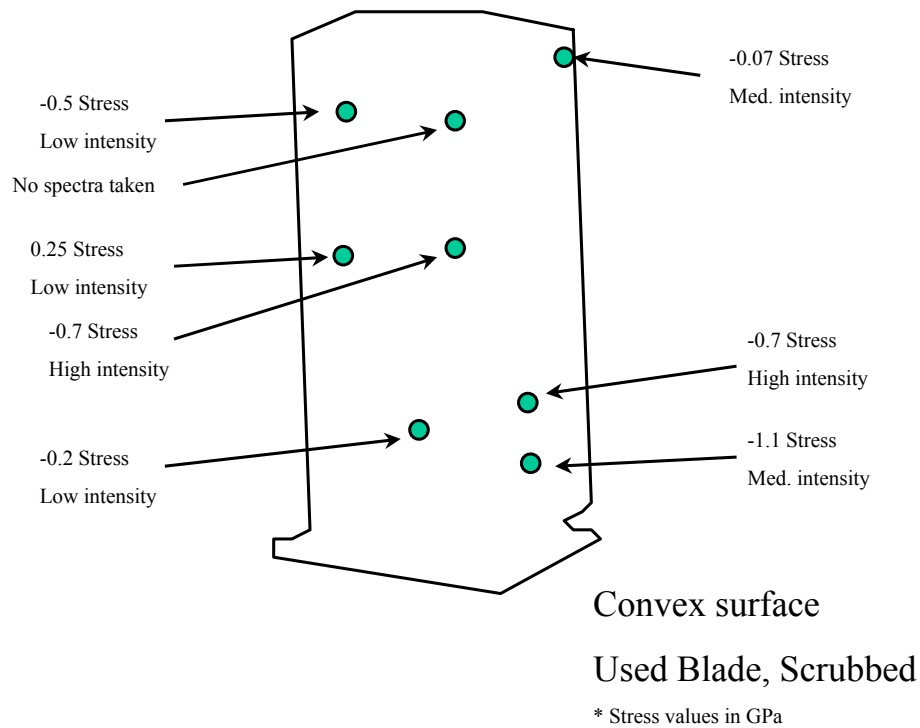


Figure 37 *Schematic diagram of stress distribution and spectral intensity at various locations on a used APS TBC coated blade – convex surface after abrasion to remove deposits*

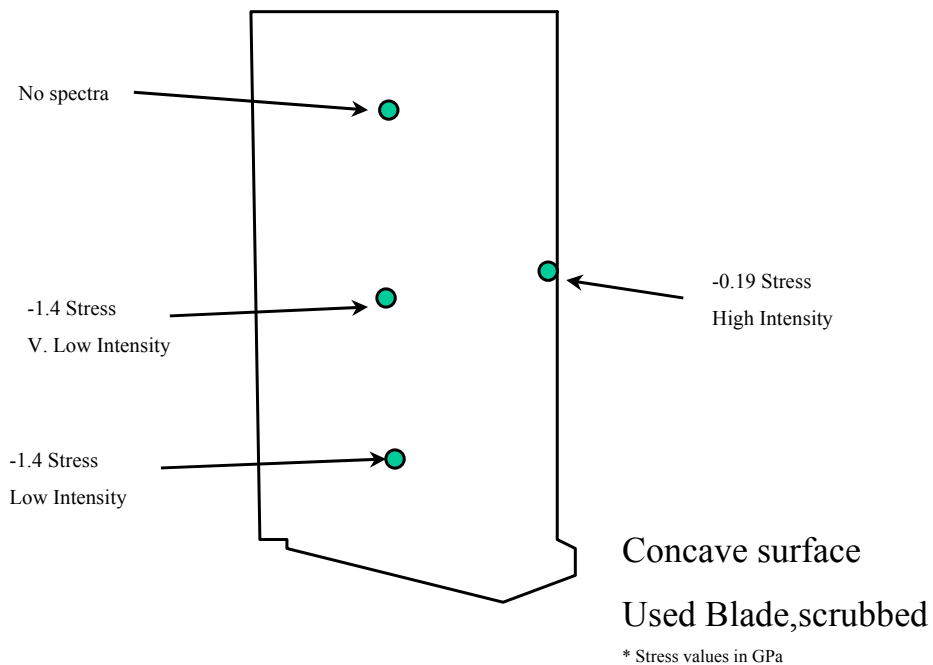


Figure 38 *Schematic diagram of stress distribution and spectral intensity at various locations on a used APS TBC coated blade – concave surface after abrasion to remove deposits*

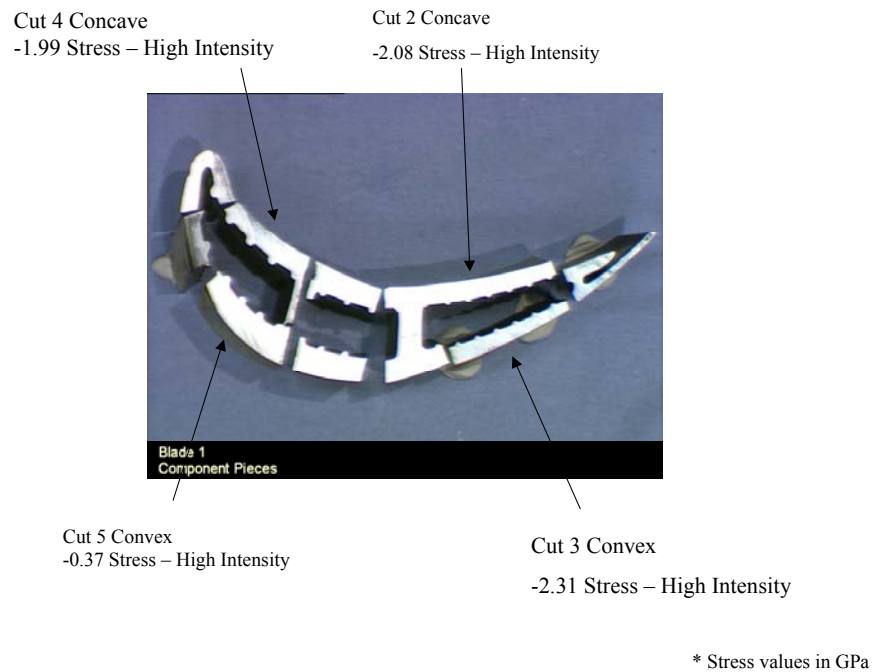


Figure 39 *Optical micrograph of cut sections through an unused EB-PVD TBC coated blade, showing the stress distribution and spectral intensity at various locations*

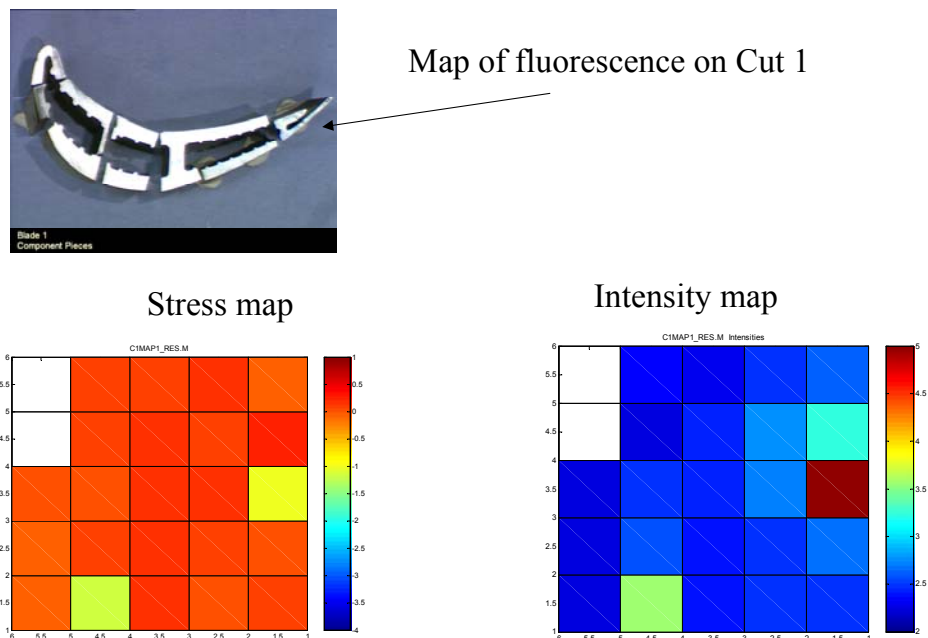


Figure 40 *Optical micrograph of cut sections through an unused EB-PVD TBC coated blade, showing the stress distribution and spectral intensity over a 25 x 25 μm area*

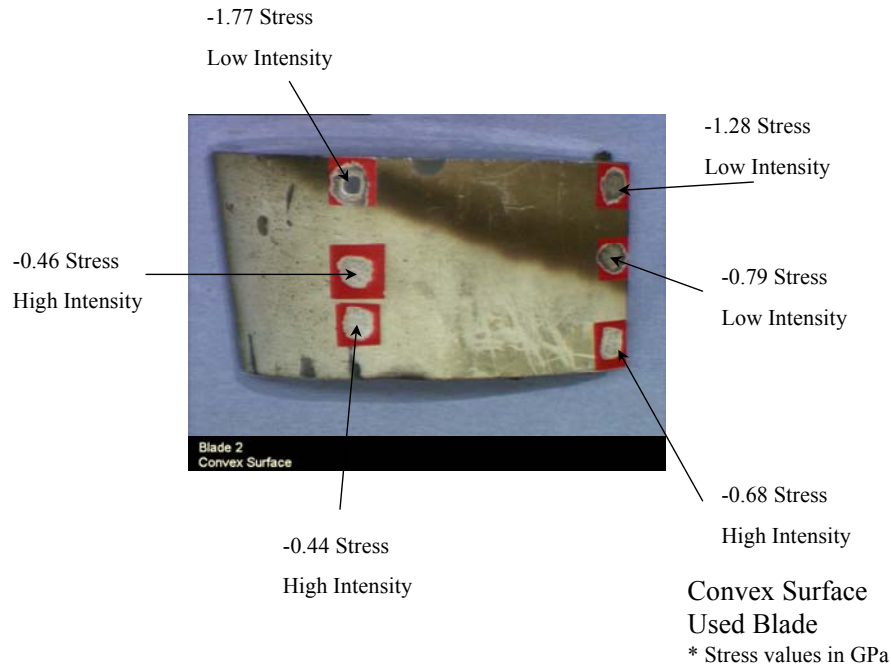


Figure 41 *Optical micrograph of a section of a used EB-PVD TBC coated blade, showing the stress distribution and spectral intensity at various locations – convex surface*

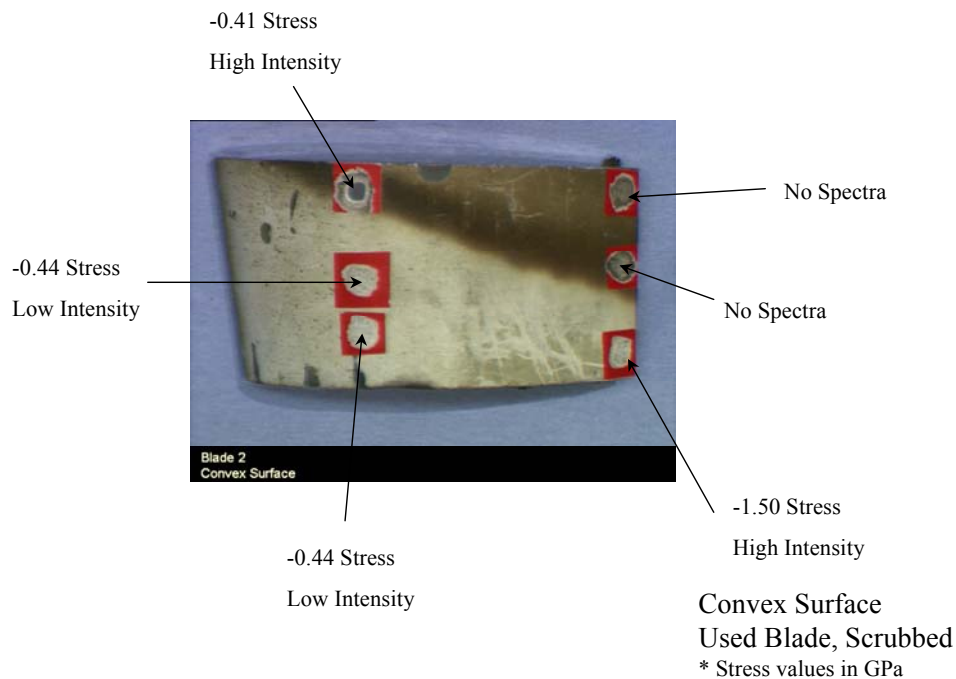


Figure 42 *Optical micrograph of a section of a used EB-PVD TBC coated blade, showing the stress distribution and spectral intensity at various locations – convex surface after removal of deposits*

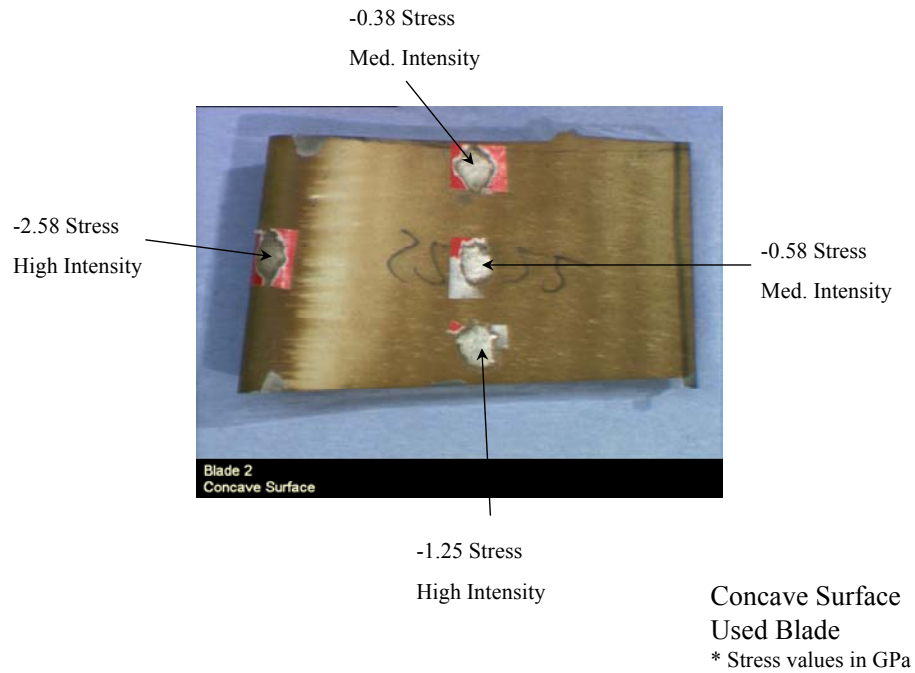


Figure 43 *Optical micrograph of a section of a used EB-PVD TBC coated blade, showing the stress distribution and spectral intensity at various locations – concave surface*

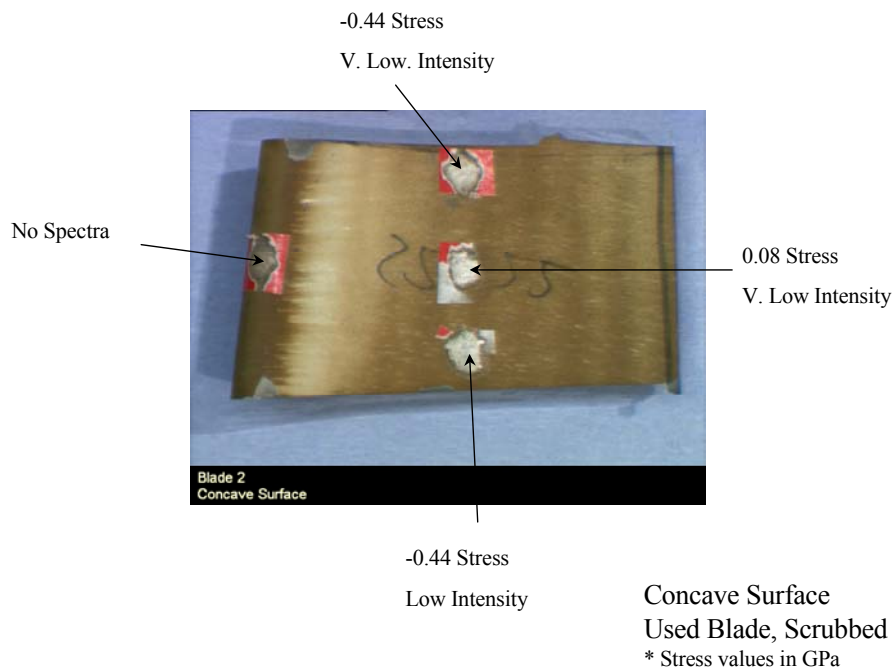
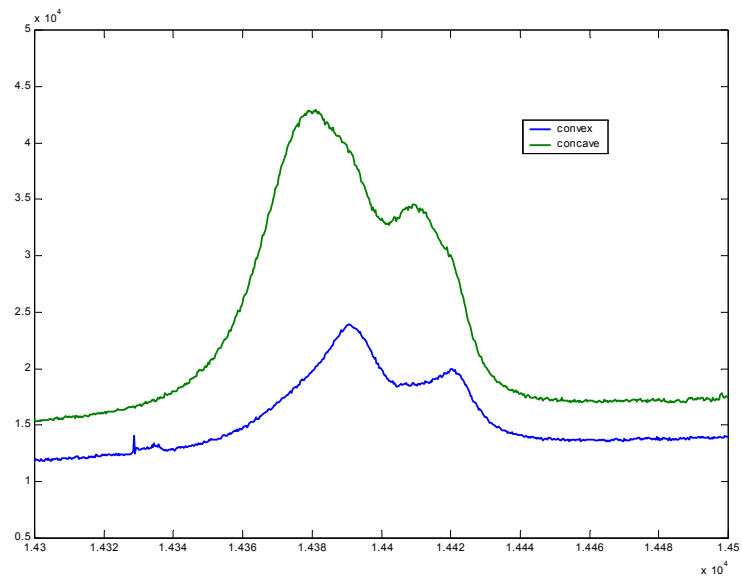
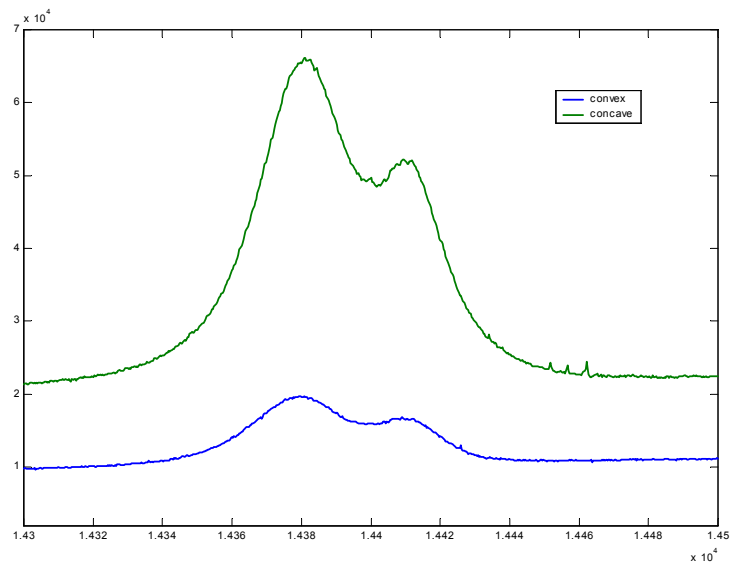


Figure 44 *Optical micrograph of a section of a used EB-PVD TBC coated blade, showing the stress distribution and spectral intensity at various locations – concave surface after removal of deposits*



a)



b)

Figure 45 Spectra from concave (green) and convex (blue) surfaces of an unused EB-PVD TBC coated blade (a) near the leading edge, and 9B0 near the trailing edge

8 SUMMARY

A number of different test methods for evaluation adhesion of TBCs have been evaluated. The transverse scratch test can yield quantitative data on the interfacial strength when coupled with finite element modelling, and simple tensile tests will measure interfacial shear strength if the interface has been somewhat degraded by ageing at high temperature. While not found in this work, it is also believed that indentation under suitable high load conditions could also provide information on the interfacial fracture toughness.

A novel method of looking at adhesion is to use piezospectroscopy in which the residual stress in the TGO can be monitored in a non-destructive manner. There is considerable interest in further development of this method. Use of this technique has indicated that the TGO is somewhat unstable as revealed by the presence of metastable θ -alumina. Possible correlation with high residual stress in the TGO which may promote delamination/spallation has been proposed, but there are a number of unresolved questions concerning the technique that need further investigation.

A long-term ageing study using piezospectroscopy of 5 different systems indicated that APS TBC coated sample behaved differently from the EB-PVB TBC. For the APS systems stress did not build up with increasing time as was found for the EB-PVD TBC systems when a MCrAlY bondcoat was used. Furthermore, the stress distribution over the sample surface with the MCrAlY bondcoat was variable, while for a platinum aluminised bondcoat (RT22) with an EB-PVD TBC stress was quickly established at the expected level from thermal expansion mismatch considerations and was uniform over the sample surface. No further changes occurred through the ageing tests. The lack of build-up of stress in the APS system may be related to lack of transparency of the TBC due to cracks and pores, and or to the presence of alumina impurities derived either from the initial powder used to develop the coating or to inter-diffusion.

In none of the long-term tests was any significant spallation of the TBC observed. It is possible that the ageing temperature was too low to promote spallation in the time available.

The work started in this project will continue in further work at NPL. One of the first tasks in this new work will be to carry out a destructive examination of all the aged TBC coated samples to improve our understanding of the observations described above.

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