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Failure Mechanisms of Calcium Magnesium Aluminium Silicate Affected Thermal Barrier Coatings

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Abstract

Depth profiles of the phase composition of two examples of calcium magnesium aluminium silicate (CMAS) affected thermal barrier coatings (TBCs) from an aero gas turbine engine were obtained using a monochromatic and collimated beam of synchrotron radiation. One TBC was

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deposited by plasma spray and the other by electron beam physical vapour deposition. These examples were complemented with an X-ray diffraction study of mixtures of TBC zirconia powder and sand heated in a furnace. The X-ray diffraction results were compared with electron backscatter images and energy dispersive spectroscopy studies of the cross-sections and mixtures. It was found that when liquid, the CMAS enhances mass transport leading to the densification of the zirconia, which then leads to spalling because of the increased residual stresses generated on cooling. Even without spalling densification will reduce a TBC's ability to thermally insulate. The enhanced mass transport can also lead to destabilisation of the zirconia if yttrium ions preferentially transfer to the liquid or greater stabilisation if calcium or magnesium ions transfer from the liquid to the zirconia. Zircon also precipitates when the zirconium from the TBC reacts with the silicon in the liquid CMAS.

1. Introduction

Thermal barrier coatings (TBCs) consist of a layer of porous ceramic over an oxidation resistant undercoat. TBCs are applied to air cooled components, such as combustion liners and nozzle guide vanes, of modern gas turbine engines. The ceramic layer is the “thermal barrier” as it protects the components from the hot combustion gases. A substantial part of the temperature drop from the hot combustion gases to the cooling air occurs across the ceramic layer, so coated components are substantially cooler than uncoated components. This temperature drop can be translated into increased component durability, higher gas temperatures or both. In turn, higher gas temperatures enable higher engine performance¹. The standard type of ceramic currently used is zirconia stabilised with 7-8wt% of yttria¹.

Interpreting the X-ray diffraction patterns reported in this paper requires reference to the zirconia and yttria phase diagram^{2,3}. At room temperature zirconia alloyed with 7-8wt% of yttria should be a mix of monoclinic and cubic phases of zirconia; however, TBC zirconia is found in a metastable tetragonal state, commonly labelled T' ³. It is expected that the T' phase is formed during the plasma spray coating process because the molten particles in the spray cool rapidly when they strike the metal substrate being coated, and consequently the ions do not have time to redistribute to create the room temperature equilibrium phases of yttrium rich cubic zirconia and

yttrium poor monoclinic zirconia. Although heating at temperatures above 1300°C for 100h can cause diffusion and the formation of equilibrium phases³, the coatings have proved durable in many engines. The alternative coating process, electron beam physical vapour deposition (EB-PVD) also forms a tetragonal zirconia (as shown in section 3.2.2). Pure zirconia is not suitable as thermal barrier because it undergoes a disruptive phase transformation between its monoclinic and tetragonal phases during thermal cycling. It is disruptive because of the difference in unit cell volume between the two phases. The phase diagram suggests that the cubic phase formed from the addition of 17 wt% of yttria (20 mol% $\text{YO}_{1.5}$) would be suitable for TBC applications as this composition remains cubic from 0°C to its melting point at 2700°C – the added yttria “stabilises” the zirconia in its cubic phase. However, the best durability in thermal cycling tests was obtained from the zirconia with 7-8wt% yttria⁴.

Although most modern engines employ TBCs, they can be adversely affected by particles ingested by the engine along with the air it requires for combustion. Two sources of these ingested particles are dust ingested during take-off or landing, and volcanic ash suspended in the air after an eruption. Some particle compositions and sizes melt or soften sufficiently in the hot combustion gases of the engine, so that if they collide with a component they will stick. Successive impacted particles will then build-up deposits. It has been shown that if such deposits build-up on TBCs they can cause parts of the ceramic coating layer to spall^{5, 6}. The deposits identified in the early work⁵ consisted of calcium, magnesium, and aluminium silicates and were therefore labelled CMAS. It is likely that the basic process of particle ingestion, melting and deposition can occur for a wider range of particle compositions than just CMAS. Furthermore, this range of compositions is likely to be wider for newer engines which operate at high temperatures to achieve higher efficiency or thrust. However, rather than invent a new term in this paper we use the label CMAS to describe all deposits on TBCs.

Two types of mechanism have been proposed to account for how these deposits damage TBCs. In the first, Mechanism A⁷, a rise in engine temperature (often required for take-off or manoeuvring) causes the CMAS to melt sufficiently to infiltrate the porous ceramic layer of the TBC. After re-cooling the CMAS solidifies again but as it is now inside the ceramic layer, the whole layer has a much greater stiffness than the original porous ceramic layer. Further cooling,

during engine shut-down, then causes this stiffer layer to spall. The residual strains that drive the spallation arise because of the differential shrinkage due to the difference in thermal expansion between the CMAS affected coating and the substrate. After impregnation the residual strains may be similar but the stresses will be larger because the coating is now stiffer. In the second, Mechanism B^{8, 9}, the TBC zirconia interacts chemically with the CMAS deposit and fails because the zirconia is destabilised or its properties are changed by this chemical interaction making it more prone to failure. For example, CMAS affected zirconia changed to a mixture of the original T' tetragonal phase, cubic and a tetragonal phase with different lattice parameters⁹. Initially the zirconia would have been completely in the T' phase.

It is important to note that the much of the CMAS deposits are glasses and will gradually reduce in viscosity rather than have an abrupt melting point^{8, 10}; thus, the rate of infiltration will gradually increase over a range of temperature. The temperature range over which infiltration of TBCs occurs can be as large as 200°C^{8, 10}.

Our goal was to see which CMAS mechanism could account for the failure and degradation we observed in two examples of CMAS affected TBCs from an aero gas turbine engine. The first was a plasma sprayed TBC that acted as an abradable seal, the second, an EB-PVD TBC that protected a turbine aerofoil. The surface temperature of such hot-end components of modern gas turbine engines can reach 1300°C¹¹. These two examples were complemented with a study of mixtures of TBC zirconia powder and sand heated in a furnace.

X-ray diffraction patterns were collected as a function of depth from the CMAS on top of the zirconia layers to the substrate metal, and from the mixtures. The XRD results were compared with electron backscatter images and energy dispersive spectroscopy (EDS) studies of the cross-sections and mixtures. Similar samples have been studied before using electron microscopy (SEM and TEM) and Raman spectroscopy^{8, 12}. The results reported here complement these earlier studies. CMAS has also been shown to affect environmental barrier coatings and this has also been studied with X-ray diffraction¹³.

2. Experimental

Visually the aerofoil TBC was 75% covered with a yellow/brown deposit. The deposits were pronounced at the leading edge and on the high pressure face. The TBC had spalled from the central third of the leading edge. The spalled region was approximately 15x3 mm. Only about 20% of the shroud sample was covered with the yellow/brown deposit. The samples of the shroud and aerofoil were mounted in cold-setting epoxy and cross-sectioned for study in a scanning electron microscope, SEM (JSM-6490LA, JEOL, Japan). After the locations of the CMAS deposits around the cross-sections had been determined, thin 0.3mm slices were cut from the cross-sections with a diamond blade. The slices had to be thin enough to allow a measurable diffraction pattern to be collected in transmission.

Powder samples of the zirconia plasma spray powder (Metco 204 NS, 8wt.% yttria, Oerlikon Metco, Switzerland), sand and zirconia and sand mixtures were heated in air for 4h at 1100°C and 1300°C. The samples were allowed to cool in the furnace before being removed at room temperature. The temperatures and durations of the furnace tests were selected as approximations to the component temperatures and flight durations. The sand was from an air base in the Middle East. Its composition is given in Table 1. As the material was from a natural source its composition varied. The option of transforming the sand into a uniform glass before mixing was rejected as the material ingested by an aircraft engine and deposited on its TBCs was also likely to have similar variation in composition. Variations were also apparent in the CMAS deposits studied here (section 4.5).

Samples were ground in a mortar and pestle before XRD. For XRD sub-samples of these powders were placed in cylindrical holes drilled in a plate and held there by covering the holes with kapton tape. Lanthanum hexaboride (LaB_6) and ceria (CeO_2) XRD standards (660b and 674b respectively, NIST, MD, U.S.A.) were also placed in this plate to enable the position sensitive detectors to be calibrated.

The X-ray diffraction (XRD) patterns were collected at the powder diffraction beamline of the Australian Synchrotron¹⁴ using an asymmetric flat plate transmission geometry (Figure 1). The

sample was positioned so that the regions-of-interest identified in the electron microscope could be probed. X-ray diffraction patterns were collected at a series of depths through the TBC by stepping the slice upward in increments of 0.1mm. Similarly, translation of the powder-containing plates produced XRD patterns from the series of powder sub-samples. The X-rays were collimated to provide a beam with a cross-section of 0.1mm (vertical) x 1mm (horizontal). A microstrip X-ray detector¹⁵ (Mythen II) was used for the bulk of the XRD, however, this one dimensional detector missed some of the diffraction lines from the EB-PVD TBC because of its crystal texture. Thus a second synchrotron run, with similar transmission geometry, was made using an area detector (MAR 345, marXperts GmbH, Germany) which could record complete diffraction rings and thereby include the missing lines, although only for d-spacings above 1.6Å. The X-ray wavelength employed, 0.73673Å, was located just below the zirconia K absorption edge, which moderately increased the transparency of the zirconia and increased the sensitivity to the CMAS phases that had penetrated into the TBC.

The diffraction patterns were identified using search/match software (EVA, Bruker, MA, U.S.A.) and the crystallographic open database (COD¹⁶) and analysed using least-square fitting software (TOPAS, Bruker, MA, U.S.A.). The area detector plots were transformed to linear d-spacing plots with freeware (Dioplas¹⁷).

3. Results

The EDS and XRD results are summarised in Tables 1 and 2 respectively.

3.1 Shroud TBC (Atmospheric Plasma Sprayed)

3.1.1 SEM

Figure 2 shows a backscattered electron image of a standard plasma sprayed thermal barrier coating without a CMAS deposit and before any heating. This provides a control with which to compare the images from the shroud TBC.

Figure 3 shows a backscattered electron image of the shroud TBC in cross-section. No deposit could be found. This region was typical of the bulk of the shroud TBC with no deposit visible by eye. Although no such deposit was identified, the top of the zirconia layer (zone a in Figure 3) was found to contain many pockets of CMAS and pores that were partially filled with CMAS (Figure 4, label e). The CMAS was identified by EDS (Table 1 CMAS pocket shroud). The brightness level of this material also suggests that the average atomic number of its constituents is between that of the epoxy and the zirconia. Line scans of the elemental compositions determined by EDS from the epoxy to the bond coat showed a high incidence of CMAS-like material in zone a and much less in zones b and c (zones defined in Figure 3). In many of the pockets and partially filled pores the CMAS followed the surrounding zirconia surface, which was consistent with infiltration by a fluid that then solidified.

It is difficult to determine from EDS if any of the Ca, Mg, Al or Si has been incorporated into the zirconia lattice. X-rays of energies associated with these elements were detected where the zirconia appeared dense; however, the level was small and may have been due to background noise. It was unclear if the small amount of Zr detected in the pocket EDS spectra was from the CMAS or the surrounding zirconia. The whole zirconia layer contained Zr and Y in the ratios expected from the standard TBC zirconia¹ (zirconia with 7 to 8 wt% yttria).

Thick TBCs often have the microstructure shown in zone c, composed of flattened splats and lots of pores and micro-cracks. Thick TBCs are often deposited so that they contain large vertical cracks¹⁸ ((d) in Figure 3). However, the microstructures of zones a and b (Figure 3) are not typical of an as-deposited TBC as shown in Figure 2. The rumpled nature of zone a and the dense nature of zone b require explanation.

3.1.2 XRD

Figure 5 shows four diffraction patterns from the shroud TBC. All showed a tetragonal phase typical of modern TBCs¹. However, the zirconia regions closest to the combustion gases (0.1mm corresponding to region a in Fig. 3 and 0.2mm corresponding to region b in Fig. 3) also contained a cubic phase. The peaks from the cubic phase were much narrower than those from

the tetragonal material. The difference in line widths indicated that either the cubic phase was composed of much larger crystals or that the tetragonal phase included a much larger range of lattice spacing. In the Rietveld fits to the zirconia diffraction peaks the micro-strain model available in TOPAS was required to get a good fit; however, in TBC zirconia the range of lattice spacings were likely to be due to variations in composition (e.g. yttrium concentration).

It was difficult to fit the patterns containing both the tetragonal and the cubic phases via Rietveld analysis, as the cubic peaks in different parts of the pattern did not correspond to exactly the same cubic cell dimension. This was probably caused by a lack of cubic crystals within the X-ray beam. The lack of crystals was in turn caused by their large size; the cubic material being used-up in a few large crystals rather than being dispersed among many small crystals. In contrast, the tetragonal peaks are more consistent as well as being broader which is symptomatic of the tetragonal material being composed of many small crystals.

In summary, nearly all of the diffraction peaks can be accounted for with phases of zirconia with the exception of a few weak peaks. The absence of diffraction from the CMAS-like phases observed in region a (Figure 3 and 4) suggest that these phases were X-ray amorphous.

The standard 7wt% yttria form of zirconia used for most TBCs is tetragonal after deposition by plasma spraying³. It is therefore likely that the cubic phase observed in regions (a) and (b) formed when the Mg or Ca ions from the CMAS diffused into the zirconia. The cubic phase was observed where the concentration of penetrated Mg and Ca was large, and disappeared when the concentration fell. Both Mg and Ca were used to stabilise zirconia in TBCs prior to the widespread adoption of Y¹⁹.

3.2 Aerofoil TBC (EB-PVD)

3.2.1 SEM

A pristine EB-PVD TBC coating was examined by SEM to provide a comparison to the aerofoil TBC. An image of the tips of the columns obtained using back scattered electrons is shown in

Figure 6. This provides a control with which to compare the images from the aerofoil TBC in Figures 7 and 8. The as-deposited zirconia columns contained many fine pores which were arranged in a series of intersecting lines producing a feather-like pattern.

Figure 7 shows the aerofoil TBC at the leading edge. It shows that in contrast to the shroud TBC, the aerofoil TBC did have a substantial 0.07mm thick deposit of CMAS at the leading edge. The composition is similar to the CMAS in the shroud pockets but with more Mg and 1at% Ti (Table 1). The Si and Ca were also present in the top 0.1mm of the zirconia layer together with Zr, Y and O. The bulk of the zirconia layer contained the Zr, Y and O expected from standard TBC zirconia¹. The deposit was not uniform in thickness around the leading edge. Towards the area of spalled TBC, the CMAS layer became discontinuous. The zirconia layer also became thinner and denser towards the spalled area. The transition occurred over 1mm.

Figure 8 shows the interface between the CMAS and the zirconia layer at a higher magnification. The contrast has been altered from Figure 7 to highlight the phase present on the top of the zirconia columns (A) and within the pockets (B). The contrast with backscattered electrons also shows that the CMAS was not uniform and contained regions of different composition (D and E).

The extra phase (A) is patchy; some sits on the tops of the columns and some in the CMAS. The brightness level of the extra phase sits between the brighter zirconia and the duller CMAS. This suggests that the extra phase contains elements from both the CMAS and the zirconia. EDS (Table 1 Zircon layer) of the extra phase on the surface (A) suggested that it was zircon, ZrSiO_4 . As the brightness of some of the pockets (B) was the same as the extra surface phase (A) they were also identified as zircon. The brightness and EDS of other pockets suggested they were filled with CMAS (Table 1 CMAS in aerofoil pockets). However, because the sizes of many of these CMAS pockets were less than the spatial resolution of EDS (about 5 μm), the Zr and Y contributions may have been from the surrounding zirconia.

Compared to the pristine EB-PVD TBC shown in Figure 6 the aerofoil zirconia contained fewer but larger pores and larger blocks of apparently dense zirconia. Many of the aerofoil pores were

filled with the extra phase and were therefore pockets rather than pores. On examining the degree of densification around the aerofoil cross-section it appeared to be greatest at the leading edge and penetrate deepest in the spalled region.

3.2.2 XRD

To enable the textured pattern of the EB-PVD zirconia to be captured the area detector was employed. Figure 9 shows the diffraction rings from the middle of the zirconia layer. A gap in the second diffraction ring is labelled which the strip detector missed.

Figure 10 shows the corresponding linearised plots of intensity versus d-spacing obtained by integrating about the azimuthal angle Ψ shown in Figure 9. This plot shows that the EB-PVD zirconia (mid TBC) was in the T' phase which is usual for TBCs. Figure 10 also shows XRD data from the border region where the X-ray beam sampled both the zirconia and the CMAS (border). Here the bulk of the zirconia was still T' but a little monoclinic was also observed. The main diffracting CMAS phase was identified as diopside, a phase that can incorporate a range of different ions including those identified in the CMAS by EDS. Again some of the CMAS may have been amorphous and therefore did not produce a diffraction pattern.

3.3 Furnace Heated Powder Samples

3.3.1 XRD

The plots in Figure 11 show that the heating of the zirconia powder alone produced little or no change. No zircon was detected (no peaks at 2.64 and 2.51 Å). Heating of the sand did produce changes in the XRD patterns, however, there were no distinct diffraction peaks from the heated or unheated sand in the regions shown in Figures 11 or 12 (2.66 to 2.48 Å).

Figure 12 shows the results from the heated mixture (red and green) together with the unheated pure zirconia powder (black) as a reference. The zirconia changed little on heating with the sand at 1100°C 1h. However, the 1300°C 4h diffraction pattern was different from the other two. It

appears that the original tetragonal zirconia had been transformed into monoclinic zirconia and zircon (ZrSiO_4). The formation of monoclinic zirconia indicates the removal of Y from much of the zirconia; however, this does not appear to be a redistribution of Y within the zirconia as no cubic zirconia has formed to maintain the balance – cubic zirconia forms when the Y concentration is high. The formation of monoclinic zirconia therefore suggests that Y has diffused into the molten sand. This expectation will be checked by EDS in the next section.

Larger portions of the collected diffraction patterns were fitted using Rietveld analysis to assess the proportions of the different phases (Table 2). Broadly, the results of the table suggest that on heating to 1100°C the calcite and muscovite melted and solidified as amorphous material, but the quartz and the zirconia remained crystalline and solid. It also appears that the stabilising elements in the zirconia become more evenly distributed with an increase in the fraction of the zirconia that was tetragonal and a decrease in the fraction of cubic. Then on heating to 1300°C the fraction of crystalline quartz decreases suggesting that some of it melted and solidified on cooling as amorphous material. However, heating at 1300°C has also enabled zircon to form and made monoclinic the dominant zirconia phase (89% of the zirconia). It should be noted that reference to the melting points of pure phases (e.g. calcite and quartz) may be misleading. The sand phases were unlikely to be pure and this lack of purity, and eutectics with other components within the sand, may have reduced their melting points.

3.3.2 SEM

A backscattered electron image of the mixture heated at 1300°C for 4h is shown in Figure 13. After heating, the whole sample had become fused together as the phases that had been molten at 1300°C solidified; however, the sample had been ground prior to the collection of the XRD patterns. The SEM image therefore shows the fragments of the fused mixture after grinding. In particular, Figure 13 shows a shard (dark grey), in which were embedded regular shapes (light grey). Within these shapes were agglomerated particles (white). The EDS of the regions labelled 1 to 3 are shown in Table 1 (Shards 1, 2 and 3). The bulk of the shard (1) was identified as the solidified CMAS into which some of the Zr and Y had diffused. It is likely that the diffusion occurred during heating while the CMAS was molten. The EDS and XRD results in section 3.3.1

identified the shapes (2) as zircon. The agglomerated particles (3) were identified by EDS as the remnants of the zirconia powder.

The initial Y: Zr ratio in the zirconia powder was 1:9, thus the high 1:1 Y:Zr ratio in the CMAS (Shard 1) and the low 1:40 Y:Zr ratio in the remnant zirconia (Shard 3) suggested that Y entered the CMAS more readily than Zr. This explains the formation of the monoclinic zirconia reported in section 3.3.1. However, this explanation does require the amount of Zr consumed in forming the observed zircon to be small.

4. Discussion

4.1 Summary of Failure and Degradation

The small amount of TBC lost from the aerofoil leading edge will have reduced the thermal protection of the aerofoil locally. However, densification was more widespread in both the aerofoil and shroud TBC. For the aerofoil this densification will reduce the degree of thermal insulation, increase the temperature of the underlying nickel superalloy and accelerate damage from creep. In the shroud TBC the densification may increase the cohesive strength of the coating. This would reduce its ability to abrade in small pieces as required for an abradable seal. Instead the delamination of large flakes may occur. Therefore both the spalling and densification observed were forms of TBC degradation. We now consider which mechanism or mechanisms caused them.

4.2 Mechanisms

The analysis of shroud, aerofoil and powder samples provided evidence in support of both failure mechanisms A and B^{7,8,9}. In support of mechanism A (infiltration, solidification, differential thermal contraction stresses, spalling) infiltration was observed in all three samples; and TBC spalling had occurred from the aerofoil sample. In support of mechanism B (reaction, destabilisation of the zirconia, spalling) the formation of zircon was observed in both the powder and aerofoil samples; cubic zirconia was observed in the shroud; and monoclinic zirconia was

observed in the aerofoil sample and in the 1300°C mixed powder sample. However, all three samples also showed different behaviour. No zircon or monoclinic zirconia was observed in the shroud. Furthermore, the shroud and aerofoil samples both showed a general decrease in effects with depth through the TBC layer. In summary, the evidence suggests that both mechanisms can affect the durability of TBCs, but they are active under different conditions and that the different samples, and furthermore different regions of the aerofoil and shroud samples, endured different conditions. It is proposed that four parameters account for the observations: temperature, temperature gradient with depth, solubility and concentration ratios.

In regard to mechanism A, although it was clear that CMAS phases had infiltrated both the aerofoil TBC and the hollow spheres of zirconia in the powder experiment, it was also clear that the next step was not simple solidification. Comparison of the as-deposited plasma sprayed and EB-PVD zirconia (Figures 2 and 6) with the plasma sprayed (Figures 3 and 4) and EB-PVD (Figures 7 and 8) zirconia that had been subject to CMAS attack showed that the CMAS did not just infiltrate the existing pore networks and then solidify within these networks on cooling. In both cases the distribution of the CMAS (or zircon) did not follow the network of pores shown in either as-deposited material but was instead concentrated into fewer larger pockets. It appears that after the CMAS penetrated the initial pore networks, the zirconia densified, collecting the fluid CMAS into the remaining pores as shown in the schematic of Figure 14.

The probable driving force for the densification is the reduction of the total surface energy of the air/zirconia or melt/zirconia interfaces. Similar driving forces account for precipitate coarsening and grain growth. When the microstructures of the as-deposited zirconia layers (Figures 2 and 6) are compared to those from the shroud and aerofoil (Figures 3, 4, 7 and 8), the comparison shows that the reduction in surface area, and hence total surface energy, was large. However, as the expected TBC temperatures in the engines (1600K)¹¹ are much less than the melting point of zirconia (2970K)² a slow rate of densification was expected. To step ions or vacancies through the lattice of a material, or along surfaces, rapidly enough to cause densification or sintering usually requires temperatures around 2/3 times the melting point of a material in kelvin²⁰.

To explain the unexpectedly rapid densification it is proposed that the molten CMAS provides a path for the rapid transport of the zirconia or zircon elements (Zr, O, Y, Ca, Mg, Si), thereby accelerating the movement of elements from energetically unfavourable sites to energetically favourable ones. Thus the molten CMAS dissolves the zirconia elements (Zr and Y) from small promontories or crystals of zirconia and then adds (Zr, Y, O, Ca or Mg) to the larger zirconia crystals or precipitates out Zr, Si and O onto existing zirconia surfaces to form zircon¹¹.

The proposed mechanism for failure (mechanism C) is then a mixture of mechanisms A and B where the sequence of steps is: infiltration, dissolution, densification and precipitation, followed by spalling on cooling.

The following evidence supports the role of the molten CMAS in dissolving, transporting, and depositing elements:

1. The creation of zircon in the aerofoil and the 1300°C mixed powder samples – confirmed by XRD, SEM and EDS.
2. The presence of Y and Zr in the solidified CMAS in the 1300°C mixed powder sample.
3. The formation of monoclinic zirconia in the 1300°C mixed powder and aerofoil sample which indicates the diffusion of Y from the zirconia into the CMAS.
4. The formation of the cubic phase in the shroud sample which suggests the diffusion of Mg or Ca into the zirconia.

4.3 Densification, Elastic Energy, Residual Stresses and Spalling

Similar mechanisms for spallation have previously been proposed^{8,9}. In earlier work on CMAS⁸ and on the generation of residual strains without CMAS^{21,22} the elastic energy and stress available for driving a delamination crack on cooling were calculated. The calculations assumed that TBC/substrate bi-material system will elastically relax when held at high temperatures for long times. They showed that the available energy depended on the effective stiffness or elastic modulus of the coating. Denser coatings would then be more prone to failure. Assuming the degree of contraction is determined by the thick substrate rather than the coating, then the energy stored in the coating per unit width (J) after cooling is given approximately by Equation 1.

$$J = 0.5 E_c (\Delta\alpha \Delta T)^2 h \quad (1)$$

Where E_c is the elastic modulus of the coating,

$\Delta\alpha$ is the difference between the thermal expansion coefficients of the coating and the substrate,

ΔT is the temperature drop, and

h is the thickness of the coating.

Then if the coating's average modulus increases because of the intrinsic densification of the zirconia or because it now contains stiffer CMAS material, then the energy available for the propagation of a delamination crack will have increased. Infiltration by CMAS is also likely to increase J by increasing $\Delta\alpha$. It should be noted that the type of failure depends on the direction of the stresses generated as well as the amount of elastic energy available. Thus the spalling of the zirconia at the leading edge of the aerofoil can be explained by the generation of compressive in-plane stresses during cooling. The combination of the high curvature at the edge and the in-plane compressive stress created a radial stress component that pulled the zirconia layer away from the aerofoil.

4.4 Phase Changes

As well as spalling on thermal cycling because of the increase in the stiffness of the zirconia layer⁸, the formation of monoclinic zirconia and cubic zirconia is also a concern for TBC durability. The removal of stabiliser from the zirconia to form monoclinic could be important because of the 7.6% unit cell volume change between monoclinic and tetragonal during thermal cycling.. In contrast, the addition of extra stabiliser is unlikely to be as important as suggested in the literature⁹ because of the unit cell volume change in transforming from tetragonal to cubic is only 0.2%. The unit cell volumes were calculated using the crystallographic data from COD¹⁶.

While monoclinic zirconia was found in the mixed powder heated to 1300°C (Fig. 12) and in the aerofoil TBC (Fig. 10 border), cubic zirconia was found in the shroud TBC (Fig. 5). This difference may be due to a higher concentration of Mg or Ca within the CMAS that initially deposited on the shroud TBC.

4.5 Variations in CMAS composition

The backscattered electron image of Figure 8 showed that the CMAS layer on the surface of the aerofoil was inhomogeneous. This may have arisen during interaction with the TBC; however, it could also be a relic of the variation in composition between the ingested particles. Different parts and phases of the CMAS may have infiltrated at different temperatures and had different viscosities. They may have also reacted differently. An artificial homogenous CMAS¹³ may not mimic such a range of behaviour. Experiments with a range of compositions could capture this.

5. Conclusions

Although mechanism A accounted for the spalling of the TBC observed by eye at the leading edge of the aerofoil, it did not account for the intrinsic densification of the zirconia seen with microscopy in both the aerofoil and shroud TBCs. We proposed mechanism C, where mass transport is enhanced by the liquid (or low viscosity) CMAS that penetrates the pores in the TBC, to account for the accelerated densification of the zirconia. The enhanced transport is also the basis of Mechanism B where it accounts for the formation of monoclinic and cubic zirconia, and zircon. For example, if the liquid CMAS contains magnesium and calcium ions it is possible for these to transfer into the zirconia to enhance stabilisation. Irrespective of any spallation the densification of both the aerofoil and shroud TBCs are degradation. Densification reduces both a coating's ability to thermal insulate and to act as an abradable seal.

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Figure Captions

Figure 1 Schematic of the X-ray diffraction experiment. The sample slice is colour coded: CMAS deposit (orange), zirconia layer of the TBC (blue), TBC bond coat and substrate metal (green) and epoxy (light grey).

Figure 2 Standard plasma sprayed TBC

Figure 3 Shroud TBC in cross-section imaged using backscattered electrons, showing the rumpled zone (a), the dense zone (b), the normal zone (c), and a large vertical crack in the zirconia layer (d).

Figure 4 The top of the zirconia layer shown in Figure 3 (zone a) imaged using backscattered electrons with brightness and contrast adjusted to show the CMAS in the pores (e).

Figure 5 Diffraction peaks at selected depths below the zirconia/gas interface with crystal structure labels.

Figure 6 Reference image of a pristine EB-PVD TBC coating

Figure 7 Aerofoil TBC in cross-section imaged using backscattered electrons.

Figure 8 Tip of zirconia column from Fig. 7 showing, the extra phase created (A), the pockets (B) and pores (C) within the column tip, and two locations within the CMAS layer with different compositions (D and E).

Figure 9 Diffraction rings imaged with the area detector.

Figure 10 Linearised diffraction patterns from the middle of the zirconia layer (mid TBC) and from the border between the zirconia and the CMAS.

Figure 11 Diffraction patterns from the three controls of zirconia powder not mixed with the sand.

Figure 12 Diffraction patterns from the two samples of zirconia mixed with sand after heating (1100C and 1300C) and the zirconia control sample without heating (RT).

Figure 13 Backscattered electron image of a shard from the 1300°C for 4h zirconia plus sand sample.

Figure 14 A schematic showing an EB-PVD zirconia column BEFORE and AFTER densification.

Tables

Table 1 Composition in Atomic Percentage from EDS

Samples and Locations								
	Sand	CMAS* on top of aerofoil	CMAS* in aerofoil pockets	Zircon* layer	CMAS* pocket shroud	Shard 1 (glass)	Shard 2 (zircon)	Shard 3 (zirconia)

Elements	O	61.6	59.9	64.5	66.6	60.1	62.2	66.7	66.5
	Si	17.6	15.6	6.32	16.3	13.5	21.3	16.2	1.4
	Ca	7.4	9.13	3.15	0.1	12.8	7.8	0	0
	Al	5.35	5.8	4.6	0.2	11.8	3.3	0	0
	Fe	1.43	2.2	0.5	0	0.5	0.7	0	0
	Mg	1.8	6.1	0.2	0	0.5	1.1	0	0
	K	0.7	0	0	0	0	0.5	0	0
	Na	1.6	0	0.1	0	0	0.5	0	0
	Ti	0.2	1	0.3	0	0	0.1	0	0
	S	1.6	0	0	0	0	0	0	0
	P	0.4	0	0	0	0	0	0	0
	Y	0	0	0.7	0.1	0	1.3	0	0.8
	Zr	0	0.3	19.4	16.7	0.8	1.1	17.1	31
	Hf	0	0	0.2	0	0	0	0	0.3

* Average over several locations

Table 2 Rietveld Results, where c, t and m refer to cubic, tetragonal and monoclinic zirconia respectively. The fraction (wt. %) of the total zirconia in each phase is shown in brackets. The COD crystal structure files employed in the Rietveld models are shown in brackets in the following list: cubic zirconia (5000038), tetragonal zirconia (9015117), monoclinic zirconia (1010912), quartz (9010146), calcite (1010928), muscovite (9012886) and zircon (9002554).

Sample	c wt %	t wt %	m wt%	Quartz wt%	Calcite wt%	Mus. wt %	Zircon wt%	Rp (%)	Phases with Preferred Orientation
Sand RT				21.2	67.5	10.4%		17.4	Quartz, Calcite Mus., (< 1 wt%)
Zirconia	28.5	41.5	30.0					13.4	cubic

RT	(28.5)	(41.5)	(30.0)						
Sand plus zirconia 1100°C 4h	2.5 (12.3)	11.4 (56.2)	6.4 (31.5)	78.0	1.8			14.9	quartz
Sand plus zirconia 1300°C 4h	0 (0)	8.0 (10.7)	66.5 (89.3)	19.2			6.25	11.5	Zircon (<1wt%)

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