Effects of breakaway oxidation on local stresses in thermal barrier coatings

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Abstract

It is known that fast-growing non-alumina scales in thermal barrier coating (TBC) systems tend to form at features where aluminium depletion is enhanced due to a high surface-area to volume ratio, a phenomenon known as breakaway oxidation. In this work, the influence of breakaway oxidation around protuberances in an MCrAlY bond coat in a TBC system during isothermal oxidation and after cooling is quantified numerically. A finite element approach is used which incorporates elastic, plastic and creep deformation of the bond coat and thermally grown oxide (TGO) and, importantly, the volumetric strains associated with oxide formation during the isothermal exposure. It is shown how volumetric strains which develop during breakaway oxidation can result in the formation of significant (>0.5 GPa) out-of-plane tensile stresses within the yttria-stabilized zirconia top coat at the oxidation temperature. These stresses are located along the flanks of the bond coat protuberances in locations where sub-critical cracks have previously been reported. The magnitude of the stresses increases with bond coat surface roughness, after the initiation of breakaway oxidation and after cooling. Results are also presented for the normal tractions across both TGO interfaces, and the influence of breakaway oxidation on these is discussed. © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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1. Introduction

Thermal barrier coating (TBC) systems are widely used in aerospace and land-based gas turbines to improve the performance and efficiency of the engine. A typical TBC system consists of an yttria-partially stabilized zirconia (YSZ) top coat and an aluminium-rich intermediate metallic layer or bond coat (BC). One function of the bond coat is to provide a protective layer of thermally grown oxide (TGO) – designed to be α-alumina – to the TBC system. It has been shown in recent finite element (FE) analyses [1] that the volume increase resulting from the growth of the alumina TGO can develop substantial out-of-plane stresses within the YSZ at the oxidation temperature. These stresses tend to be at a maximum at the flanks of BC protuberances and, as will be discussed later, are associated with a non-uniform upward displacement of the top coat resulting from TGO formation. These high-stress locations also correspond to regions where sub-critical cracks form within the YSZ top coat, suggesting that their formation could occur at the test temperature [1].

In previous work [1–3], the calculation of stresses has been undertaken using FE methods with a model which takes into account not only the increasing volumetric strains at temperature associated with growth of the TGO but also creep and plasticity within the BC and TGO and, if appropriate, sintering of the YSZ. The same general approach will be used in the present study, but the key objective will be to examine the effect of chemical failure and localized breakaway oxidation of the BC on stress development within the TBC system. On the basis

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of the earlier studies, it is anticipated that the non-uniform development of fast-growing oxides at the BC surface will lead to large out-of-plane tensile stresses within the YSZ. It has not been possible, experimentally, to determine the magnitude of any such stresses, although a linkage between the onset of breakaway oxidation, cracks and TBC failure has been reported in other work [4–9]. Photoluminescence techniques have been successful in determining the magnitude of stresses in alumina layers, but such an approach cannot be applied to assess stresses associated with non-alumina oxides [7]. The purpose of the present study is to use the FE approach in a first attempt at quantifying the magnitude and location of out-of-plane stresses associated with localized breakaway oxidation of the BC. It will be recognized that fast-growing non-alumina breakaway oxides will tend to form at features where aluminium depletion is enhanced because of a high surface-area to volume ratio. These may be diffusionally isolated regions (“diffusion cells”) [6] or may be BC surface protuberances [5]. It is this latter case which will be examined in detail in this paper for a TBC system consisting of an air-plasma-sprayed YSZ top coat and an underlying MCrAlY bond coat.

2. Oxidation characteristics

2.1. Oxidation kinetics

Oxidation protection of the TBC system is obtained through the formation of a continuous \( \alpha \)-alumina layer on the BC surface. This is taken to thicken parabolically with time at a similar rate to the mid-range behaviour for alumina growth on diverse alumina-forming alloys as compiled by Hindam and Whittle [10]. At 1100 °C, the alumina thickness, \( h_1 \), within the present model is then given as:

\[
h_1 = 5.72 \times 10^{-9} t^{0.5}
\]

where exposure time, \( t \), is in seconds and \( h_1 \) is in metres.

The continuing growth of the alumina layer will deplete the underlying BC of Al as a result of the selective oxidation, but depletion can also occur by interdiffusion with the alloy substrate. In the present study, however, the latter will not be significant because it is the local depletion within BC protuberances that is of interest. This will become important relatively early in life because of the high surface-to-volume ratio at the protuberance and the limited ability to resupply from the Al reservoir within the bulk of the coating [5]. A consequence of this localized depletion is that the protuberance can become at risk of premature chemical failure and the formation of non-protective oxides. A clear example of this process, taken from the work of Hsueh et al. [11], is shown in Fig. 1. The dotted region in this figure will be used as the basis for the FE model used in the present study.

The principles by which severe depletion of the selectively oxidized element can result in chemical failure and the formation of non-protective oxides have been described elsewhere [12]. In the most extreme case, when depletion is essentially complete, it can become thermodynamically possible for other alloy elements to be oxidized underneath the protective oxide. This process has been termed intrinsic chemical failure [12], and has been shown to occur in NiCrAlY coatings [13] and other alumina-forming alloys [14]. Chemical failure can also arise, however, when Al depletion has reached the stage when local rehealing of a mechanically damaged alumina layer is not possible. This process of mechanically induced chemical failure (MICF) [12] will again result in the rapid growth of non-protective oxides. For present purposes, it will be assumed that chemical failure occurs by MICF and that the non-protective oxide formed is NiCr\(_2\)O\(_4\). In practice, substitution of Ni with Co or Cr with Al may occur, but these details do not affect the principles considered here.

Fig. 1. An example of the formation of non-protective oxides resulting from chemical failure at bond coat protuberances in a MCrAlY/APS-YSZ system [11].
This non-protective oxide, of thickness $h_2$, starts to form at the apex of the protuberance after an exposure period, $t_b$, at which protective conditions break down. The oxide is porous [11,13] and is, accordingly, assumed to grow at a constant rate to give a total oxide thickness, $h_{\text{total}}$, at the apex of the protuberance of

$$h_{\text{total}} = h_1^{\text{apex}} + h_2^{\text{apex}} \quad (2)$$

The bounding conditions on and values of $h_1^{\text{apex}}$ and $h_2^{\text{apex}}$ are:

$$h_1^{\text{apex}} = 5.72 \times 10^{-9} t^{0.5}, \quad 0 \leq t < t_b \quad (3)$$

$$h_2^{\text{apex}} = 2.78 \times 10^{-11}(t - t_b), \quad t \geq t_b \quad (4)$$

where exposure time, $t$, is in seconds and oxide thickness in metres. The linear rate constant for the growth of the post-breakaway oxide is less well established than that for the growth of a protective alumina layer (Eq. (1)). The value used here is consistent with limited oxide thickness results reported in the literature [5,11,13]. Similarly, the value used for $t_b$ of $3.6 \times 10^5$ s (100 h) at $1100 \, ^\circ$C is obtained from the results of Niranathumpong et al. [13].

Using Eqs. (3) and (4), the increase in oxide thickness at the apex of the protuberance with exposure time at $1100 \, ^\circ$C is shown in Fig. 2. It is this dependence that is used within the FE model. The temperature dependence of the elastic properties of the protuberance is given as:

$$h_2^{\text{valley}} = 2.78 \times 10^{-12}(t - t_b), \quad t \geq t_b \quad (7)$$

i.e. the growth rate is an order of magnitude slower than at the apex of the protuberance where breakaway oxidation has occurred. In actuality, the TGO in the valley regions will continue to grow protectively and parabolically over the course of the maximum exposure considered here (200 h/1100 °C). The assumption of a breakaway condition initiated at the same value of $t_b$ as for the apex region is a device to speed up the computation process by facilitating a linear extrapolation of oxide thickness around the protuberance. Generally, for the values used in Eqs. (6) and (7), this assumption of a breakaway condition but with a subsequent relatively low linear rate constant leads to errors in the estimate of oxide thickness in the valleys of <10%.

2.2. Pilling–Bedworth ratios

As discussed in some depth in a previous paper [1], the Pilling–Bedworth ratio, $\phi$, for the formation of the protective layer of $\alpha$-alumina on the BC surface is taken as 1.28, which is the same value as for the oxidation of the pure metal. After breakaway, however, the oxide formed will be complex, with varying quantities of Cr, Ni and possibly Co [13]. For present purposes, it will be assumed, without much loss of generality, that the oxide formed is NiCr$_2$O$_4$. The overall reaction for the formation of this spinel can be expressed as in (A) below and can be considered to arise by direct conversion of the Al-depleted bond coat.

$$\text{Ni} + 2\text{Cr} + 2\text{O}_2 \rightarrow \text{NiCr}_2\text{O}_4 \quad (A)$$

The ratio, $\phi$, for this reaction can be calculated using molar volumes, $V_i$, as:

$$\phi = \frac{V_{\text{NiCr}_2\text{O}_4}}{V_{\text{Ni}} + 2V_{\text{Cr}}}$$

where the subscripts indicate the molar volume of that particular species. Established values [15] of the molar volumes are

$$V_{\text{Ni}} = 6.6 \, \text{cm}^3; \quad V_{\text{Cr}} = 7.2 \, \text{cm}^3; \quad V_{\text{NiCr}_2\text{O}_4} = 43.0 \, \text{cm}^3$$

Using these in Eq. (8) gives a value for the volume change ratio, $\phi$, of 2.05, and it is this which is used in the computations when calculating the volumetric strain produced during breakaway oxidation.

3. Physical and mechanical properties

The MCrAIY bond coat considered in this work is treated as an isotropic material that is capable of deforming elastically, plastically and by creep. All modes are considered within the FE model. The temperature dependence of the elastic properties of the bond coat is shown in Table 1 and that of its yield strength in Table 2 [16].

The creep behaviour of the bond coat is described by
where \( A_{bc} = 13.27 \text{ s}^{-1} (\text{MPa} \text{ m} \text{ s}^{-1})^{-1} \), \( n_{bc} = 4.09 \), \( Q_{bc} = 263,000 \text{ J} \text{ mol}^{-1} \), \( R = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1} \). The creep strain rate, \( \dot{e}_{bc} \), has units of \( s^{-1} \), \( \sigma_{bc} \) of MPa and \( \theta \) of °C.

The protective oxide (\( \alpha \)-alumina) is also assumed to be an isotropic and homogeneous material with elastic properties at various temperatures as given in Table 3.

Spectrum of the \( \alpha \)-alumina layer is described by Eq. (10), which was obtained previously [18] from the experimental results of Lin and Becher [19]:

\[
\dot{e}_{\text{ox}} = A_{\text{ox}} \exp \left[ -\frac{Q_{\text{ox}}}{R(\theta + 273)} \right] \sigma_{\text{ox}}^{n_{\text{ox}}} \tag{10}
\]

Here, \( A_{\text{ox}} = 6800 \text{ s}^{-1} (\text{MPa} \text{ m} \text{ s}^{-1})^{-1} \), \( n_{\text{ox}} = 2.3 \) and \( Q_{\text{ox}} = 424,000 \text{ J} \text{ mol}^{-1} \).

The YSZ top coat is also assumed to have isotropic elastic properties as listed in Table 4. The values are appropriate for a plasma sprayed layer or a densified electron beam–physical vapor deposition (EB-PVD) variant.

### 4. The finite element model

Representative YSZ–TGO interfacial regions (e.g. as shown in Fig. 1) were identified as two-dimensional periodic unit cells for the coupled oxidation–stress analysis. Appropriate periodic and symmetry boundary conditions were defined in the FE model. The oxidation, physical and mechanical properties of the materials within the TBC system and used within the model have been described in earlier sections. Three aspect ratios (\( b/a \) in Fig. 1) were used in this study in order to investigate the influence of this ratio on the magnitude of stresses near the TGO layer. It has been shown elsewhere [2] that increasing BC surface roughness will increase out-of-plane stresses in the interfacial region when the TGO remains protective. The present study will examine the joint effects of surface roughness and breakaway oxidation. The mean volumetric strain, \( e_T \), arising as a result of the oxidation of the bond coat is given as \( \dot{e}n(\phi) \), where the ratio of volume increase on oxide formation, \( \phi \), is 1.28 during protective oxidation and 2.05 during breakaway (Section 2.2).

The partitioning of this volumetric strain in the directions normal and tangential to the TGO surface were the same as that deduced by Huntz et al. [20]. Within the model, oxide growth occurred during the isothermal exposure periods of either 100 or 200 h at 1100 °C. After this exposure, a final cooling transient to 25 °C took place.

Fig. 3 shows the finite element mesh and the boundary conditions used when the aspect ratio (\( b/a \)) was 0.25. The initial thicknesses of the BC and YSZ layers were 50 and 200 \( \mu \text{m} \), respectively. The FE mesh consisted of about 8274 quadratic generalized plane strain elements with full integration. The displacement of the periodic plane (Fig. 3) in the \( x_1 \) direction is calculated according to the coefficient of thermal expansion of the alloy substrate, the temperature change and the width of the unit cell [17].

### 5. Results and discussion

#### 5.1. Stress development during isothermal exposure

The FE predictions of the oxide thickness that formed around a BC protuberance within the computer model after 200 h at 1100 °C are shown in Fig. 4. Here, the protective alumina layer (the "primary TGO") formed during the first 100 h to produce a uniform layer across the BC surface. The breakaway or "secondary TGO" formed over the period 100–200 h and was thickest at the apex of the protuberance (Section 2.1). As required, the total oxide thickness was ~13 \( \mu \text{m} \) at this location, but was ~4 \( \mu \text{m} \) in the valley regions remote from the protuberance. This demonstrated that the outer layers of the bond coat had been successfully converted to the oxide phase at differing rates around the protuberance whilst accommodating the nonlinear variation of the associated strains.

These volumetric strains, associated with the growth of the TGO during the exposure period (Section 2.2), produced stresses within the TBC system at the oxidation temperature. Examples of the distribution and magnitude of the out-of-plane, \( \sigma_{23} \), stress at 1100 °C after 200 h oxidation at this temperature for two aspect ratios of the protuberance are shown in Fig. 5.

The immediate feature to note from Fig. 5 is that out-of-plane tensile stresses develop at temperature within the...
YSZ top coat at locations on the flanks of the BC protuberance. The magnitude of the stresses increases with the aspect ratio, showing a maximum of \( \sim 200 \) MPa for a relatively flat surface \((b/a = 0.25)\) but reaching values as high as 650 MPa for the rougher BC surface \((b/a = 1.0)\). For comparison, this maximum value was only \( \sim 150 \) MPa after 100 h oxidation and with protective alumina formation. This is similar to the value predicted previously [1] for the same bond coat geometry in a TBC system consisting of a Pt-aluminide BC and EB-PVD YPS top coat.

The mechanism for this stress development will be discussed shortly, but it is first worth noting that isothermal oxidation also develops normal stresses, \( \sigma_n \), across the two TGO interfaces at the oxidation temperature. The variation of these tractions with the ratio \( X_1/(a + c) \) (see Fig. 1), for the three aspect ratios used, after 200 h oxidation at 1100 °C is shown in Fig. 6a for the YSZ/TGO interface. Not unexpectedly, at the apex of the protuberance, \( \sigma_n \), is compressive due to the reaction of the YSZ top coat to the upward jacking of the breakaway oxide in this region. These compressive normal stresses at the apex increase with BC roughness from \( \sim 450 \) MPa for \( b/a = 0.25 \) to \( \sim 900 \) MPa for \( b/a = 1.0 \). They reduce with distance away from the apex of the protuberance and are essentially zero along the flat region between the protuberances. In contrast, the TGO/BC interface experiences only a small out-of-plane stress (±20 MPa) at temperature (Fig. 6b) even after breakaway oxidation has occurred. It seems unlikely that tensile crack damage at this interface will develop at the oxidation temperature.

The development of out-of-plane stresses towards the base of the top coat at the exposure temperature is a relatively little-recognized effect, even though substantial stresses can arise. They are a feature of a non-planar BC surface.
and result from the strains that need to develop to maintain continuity within the TBC system. These continuity strains arise because the out-of-plane displacement due to oxide growth varies along the rough BC surface. The mechanism can be understood by reference to Fig. 7, which, for simplicity, considers the situation prior to oxide breakaway around the protuberance. From this, it can be appreciated how the out-of-plane displacement rate (along the vertical, \( x_2 \), axis) due to continuing oxidation must vary with location along the horizontal \( x_1 \) axis simply because of the non-planar geometry. At the apex of the protuberance and along the adjacent flat regions, the out-of-plane displacement rate due to the volumetric strains associated with (uniform) TGO growth is \( \dot{g}_n \). This is the maximum displacement rate due to the uniform growth of the \( z \)-alumina layer and occurs in a direction normal to the local BC surface. This normal displacement rate occurs also around the curved surface of the protuberance but the vertical out-of-plane displacement rate, \( \dot{g} \), will now be less than the maximum value, \( \dot{g}_n \). Because of the absence of free space at the TGO/topcoat interface, these displacements will be imposed upon the YSZ top coat.

If the top coat maintains continuity and adherence with the bond coat, out-of-plane tensile strains will need to develop within the top coat, at the oxidation temperature, to accommodate the differences \( (\dot{g}_n - \dot{g}) \) in out-of-plane displacement rates. These continuity strains will tend to be a maximum where the difference \( (\dot{g}_n - \dot{g}) \) is largest. These locations lie along the flanks of protuberances, as shown by the FE calculations (e.g. Fig. 5). As pointed out above, these are also sites where short sub-critical cracks often form within the top coat. An example for a Pt-aluminide bond coat with an EB-PVD YSZ top coat can be found in Ref. [1]. Similar cracks in a TBC system consisting of a MCrAlY bond coat and air-plasma-sprayed YSZ top coat have been reported by Haynes et al. [4] and by Taylor et al. [5]. They have also been found in a TBC system with a Pt-modified MCrAlY bond coat and EB-PVD top coat [21]. It is suggested that such cracks are a
generic feature of the failure process when rough bond coat surfaces are present and may well form during isothermal exposure. It should be noted that these cracks in the top coat are not associated with BC ratcheting resulting from thermal cycling [22] but could act as a precursor for this process.

5.2. Out-of-plane stresses after final cooling

Contour plots of the maximum out-of-plane stress at 25 °C after 200 h exposure at 1100 °C for two values of the roughness parameter \( b/a \) are shown in Fig. 8. Again it is clear that larger stresses are associated with the rougher surface within both the BC and the YSZ top coat. The largest stress values, \( \sim 900 \) MPa, are found within the top coat and along the flanks of the BC protuberance. This is the same location that experiences the maximum out-of-plane stress during isothermal exposure (see Fig. 5), but a further increase in stress, of around 50%, occurs as a result of cooling.

The comparable \( \sigma_{22} \) contour plot after cooling from an exposure period of only 100 h at 1100 °C, i.e. before the onset of breakaway oxidation, is shown in Fig. 9 for \( b/a \) values of 1.0 and 0.5. Even for the rougher BC surface (Fig. 9a), the maximum out-of-plane stress in the YSZ is only 100–200 MPa, which should be compared with the maximum values of \( >910 \) MPa (Fig. 8a) after breakaway oxidation has taken place. For the less-rough surface after cooling from 100 h at 1100 °C (Fig. 9b), maximum out-of-plane stresses in the YSZ are \( <100 \) MPa. Indeed, for these pre-breakaway conditions, the largest out-of-plane stresses after cooling develop in the BC protuberance itself, where maximum values for the roughest surface of up to 500 MPa are predicted (Fig. 9a). The corresponding maximum Mises stress...
stresses in the bond coat were found to be greater than the 0.2% yield stress of the bond coat (see Table 2), so some yielding of the BC has occurred during cooling. However, in practice, these MCrAlY-type coatings have very limited ductilities at low temperatures [23] (say \( \leq 300 \, ^\circ\text{C} \)), so fracture under tensile stressing is more likely than extensive plasticity within this temperature range.

The variation in the normal tractions across the TGO interfaces after cooling to \( 25 \, ^\circ\text{C} \) following oxidation at \( 1100 \, ^\circ\text{C} \) for 100 h, i.e. prior to breakaway oxidation, is shown in Fig. 10. At the apex of the protuberance, the normal stress across the YSZ/TGO interface remains compressive, but it acquires a maximum tensile value of \( \sim 100 \, \text{MPa} \) along the flank of the protuberance for \( b/a = 1.0 \) (Fig. 10a). In contrast, tensile stresses exist across the TGO/BC interface at the apex after cooling, as can be seen in Fig. 10b. These increase (approximately linearly) with BC surface roughness from \( \sim 110 \, \text{MPa} \) for \( b/a = 0.25 \) to \( \sim 400 \, \text{MPa} \) for \( b/a = 1.0 \).

The corresponding variation of the normal tractions across the TGO interfaces after cooling to \( 25 \, ^\circ\text{C} \) following oxidation at \( 1100 \, ^\circ\text{C} \) for 200 h, i.e. after a period of breakaway oxidation, is shown in Fig. 11. The trends found for cooling prior to breakaway oxidation (Fig. 10) are repeated in that compressive stresses have developed across the YSZ/TGO interface at the apex of the protuberance and tensile stresses across the TGO/BC interface. However, the compressive stresses across the outer TGO interface after breakaway oxidation has occurred are substantially larger (by a factor of \( \geq 6 \)) than those predicted prior to breakaway oxidation. These, again, can be attributed to the reactive stresses developed in the presence of the YSZ top coat. By contrast, the tensile stresses across the TGO/BC interface at the apex are slightly smaller but of similar magnitude to those developed after cooling prior to the initiation of breakaway oxidation.
6. Conclusion

The FE calculations show that the growth of the TGO during isothermal exposure at 1100 °C will generate out-of-plane tensile stresses within the YSZ top coat near the flanks of bond coat (BC) protuberances. The magnitude of these stresses increases with BC surface roughness, specifically with the geometric parameter \( b/a \), and with the nature of the oxide formed. For the roughest bond coat considered here, \( b/a = 1.0 \), maximum out-of-plane stresses within the YSZ of \( \sim 150 \) MPa will have developed at temperature after 100 h oxidation at 1100 °C. Over this period, the protective alumina TGO will have grown to 3.3 \( \mu \)m thickness. Subsequent breakaway oxidation after this period and the formation of faster-growing non-protective oxides around the BC protuberances increases the rate of stress development. For example, an exposure period of 200 h at 1100 °C, leading to a total TGO thickness of \( \sim 13 \) \( \mu \)m, develops a maximum out-of-plane tensile stress within the YSZ of \( \sim 500 \) MPa at the apex of the BC protuberance, which increase with BC roughness. For example, they reach \( \sim 500 \) MPa for \( b/a = 1 \) even after protective oxidation and, at this level, may prejudice the integrity of the TGO/BC interface. Significantly, cooling after a period of breakaway oxidation does not increase the normal tractions at this interface. The inference is that breakaway oxidation will not increase the likelihood of fracture at the TGO/BC interface. In all the cases examined, the normal tractions across the YSZ/TGO interface in the vicinity of the BC protuberance remained compressive both at the oxidation temperature and after cooling.

The FE calculations also show that large (\( \sim 500 \) MPa) out-of-plane tensile stresses can develop within the BC itself at protuberances as a result of cooling after 100 h oxidation at 1100 °C. These stresses may be sufficient to induce transverse cracking of the protuberance since the bond coat ductility can be negligible at room temperature.

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