

Degradation of thermal barrier coatings due to thermal cycling up to 1150°C

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The degradation of thermal barrier coatings (TBCs) due to thermal cycling up to 1150°C has been studied. During thermal cycling, the bond coat in the TBCs was oxidised to form an alumina and a mixed oxide layer between the top coat of yttria stabilised zirconia (YSZ) and the bond coat of MCrAlY alloy. The mixed oxide layer mainly consists of α -Cr₂O₃ and (Ni,Co)(Cr,Al)₂O₄ spinel phases, which are formed above the α -alumina layer. Interestingly, the alumina layer gradually disappeared during the oxidation while the content of chromium in the mixed oxide increased with increasing oxidation time. As the oxidation accelerated after the disappearance of the alumina layer, cracks initiated and propagated in the mixed oxide layer near the YSZ. Eventually, the crack propagation induced the spallation of some YSZ top coatings after the 2000 h oxidation.

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1. Introduction

Recently, a lot of research has been directed towards developing superalloy turbine blades capable of operating at higher temperatures. This is because the gas operating temperature is the most important factor in determining the gas turbine engine power and fuel efficiency [1]. At the same time, thermal barrier coatings (TBCs) have been applied to gas turbine blades and vanes in order to increase their operating temperature and in turn to increase the component durability. A typical TBC system is composed of an oxidation-resistant metallic bond coat on the superalloy substrate and a thermal insulating ceramic top coat attached to the bond coat. A yttria stabilised zirconia (YSZ) coating (6–8% Y₂O₃, balance% ZrO₂), produced usually by air plasma spraying (APS), is normally used as a thermal insulator in gas turbine engines. This plasma-sprayed YSZ top coat provides a porous ceramic layer with high strain tolerance and low thermal conductivity. The bond coat consists normally of an MCrAlY (M = Ni and/or Co) alloy produced by either APS or vacuum plasma spraying (VPS). The bond coat provides a rough surface for bonding YSZ and protecting the substrate from oxidation. The oxidation of the TBCs leads to the formation of a continuous protective oxide scale (usually α -Al₂O₃) between the bond and top coats.

As the oxide scale on a metal, referred to as the thermally grown oxide (TGO), grows, internal stresses are built up at the scale/metal interface due to volume changes during oxidation. These stresses further increase because of mismatches in the coefficient of thermal expansion (CTE) among the bond coat, TGO and

YSZ. As a consequence, thermal expansion mismatch strains and interfacial oxide scale growth are the dominant TBC degradation mechanisms, leading to failure of a TBC system by spallation of the YSZ top coat. [2–5]. It has been found [5, 6] that crack initiation and propagation in the TGO layer also caused the failure of TBCs. The degradation of the APS-produced TBCs was studied under isothermal and thermal cycling conditions at 1150°C [5, 7]. It was found that the TGO mainly consisted of α -Al₂O₃ and Ni(Cr,Al)₂O₄ spinel with the α -alumina as a dominant product after oxidation for up to 355 h. The Ni(Cr,Al)₂O₄ spinel was formed between the α -alumina and the YSZ, which was also found in the oxidation of TBCs at temperature below 1100°C [8–12]. Apart from α -Al₂O₃ and Ni(Cr,Al)₂O₄ spinel in the TGO, a thin layer of α -Cr₂O₃ was also found between the bond coat and the α -alumina in some cases [13]. Although there have been extensive studies on the degradation of TBCs and microstructural evolution of TGOs, there has been little study on the relationship among thermal cycle condition, composition change and microstructural evolution of the TGO and failure phenomena of TBCs. The aim of the present work is to examine both the compositional change and microstructural change of the TGO after various thermal cycles and to relate them to the failure of TBCs. In this study, multiple specimens were used for thermal cycling up to 1150°C until failure occurred in some of the TBC specimens. The TGO has been found to evolve differently as compared with previous studies. The transformation from an alumina layer to a porous mixed oxide layer in the TGO was found during thermal

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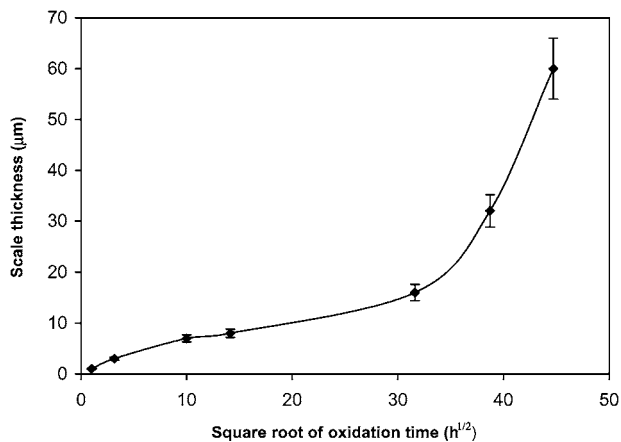


Figure 1 Scale thickness vs. oxidation time for the TBC coated sample oxidised in air at 1150°C.

cycling. The crack formation in the TGO was found to lead to the failure of TBCs due to the spallation of YSZ top coat.

2. Experimental procedure

Samples in size of 10 mm × 10 mm × 20 mm were prepared by APS for both bond coat (~150 µm thick) and top coat (~250 µm thick) on Haynes-230 superalloy plates (conducted in Sermatch Ltd. Lincoln, UK). Chemical composition of the Haynes-230 superalloy in wt% is 22Cr, 14W, 3Fe, 2Mo, 0.02La, 0.015B, and 0.1C with the nickel balanced. Chemical composition of the bond coat in wt% is 21Cr, 8Al, 38.5Co, 32Ni, and 0.5Y. The YSZ contains 8 wt% Y₂O₃ and 92 wt% ZrO₂. The samples were oxidised in air at 1150°C for 1, 10, 100, 200, 1000, 1500 and 2000 h, respectively, with thermal

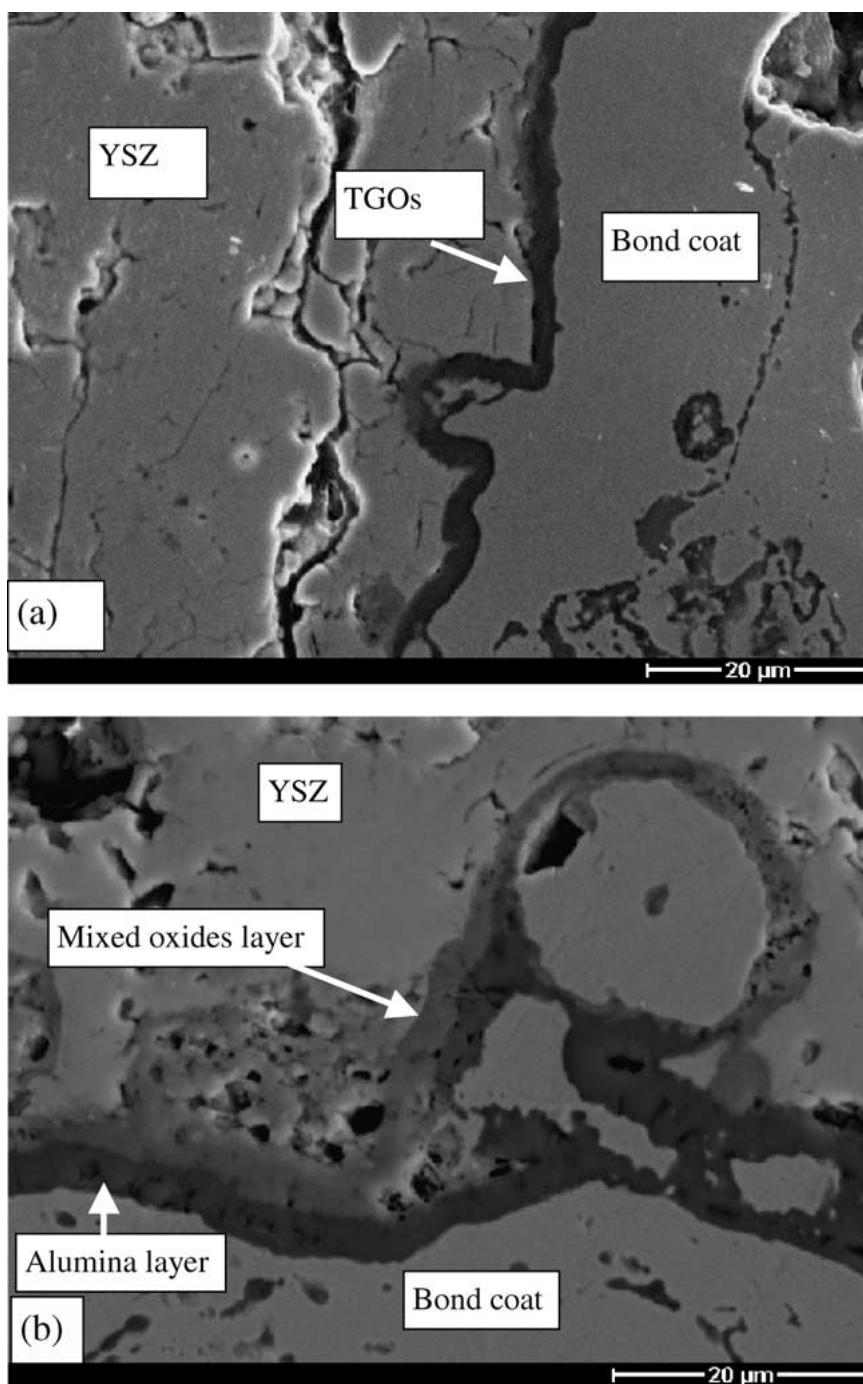


Figure 2 Scanning electron micrographs showing the cross sections of the samples oxidised in air at 1150°C for (a) 10 h, (b) 100 h, (c) 1000 h and (d) 2000 h. (Continued.)

cycles. In the thermal cycling, the samples were cooled and heated at a rate of 10°C/min. Six thermal cycles were carried out for the 2000 h-oxidised samples with dwell periods of 100 h (cycles 1 and 2), 300 h (cycle 3) and 500 h (cycles 4, 5 and 6), respectively. Five thermal cycles were carried out for the 1500 hr-oxidised samples with dwell periods of 100 h (cycles 1 and 2), 300 hr (cycle 3), and 500 hr (cycles 4, and 5), respectively. Four thermal cycles were carried out for the 1000 hr-oxidised samples with dwell periods as 100 hr (cycles 1 and 2), 300 (cycle 3) and 500 hr (cycle 4), respectively. Two thermal cycles were carried out for the 200 h-oxidised samples with dwell periods of 100 hr. One thermal cycle was carried out for the 100 and 10 hr-oxidised samples. Three samples were used for each oxidation condition.

A J840 scanning electron microscope equipped with an energy dispersive X-ray (EDX) microanalyzer was employed to evaluate the TBCs. Crystal structures of oxide scales were determined using X-ray diffraction.

3. Results

The oxidation kinetics of TBCs was determined by measuring the thickness of the TGO as a function of the square root of oxidation time (Fig. 1). Although oxidation was performed with various thermal cycles, the oxidation rate still followed the parabolic law during the oxidation for up to 1000 hrs. In this stage, the TGO was protective because its growth rate was quite low. However, further oxidation led to a substantial increase in the TGO growth rate, although it appeared that the

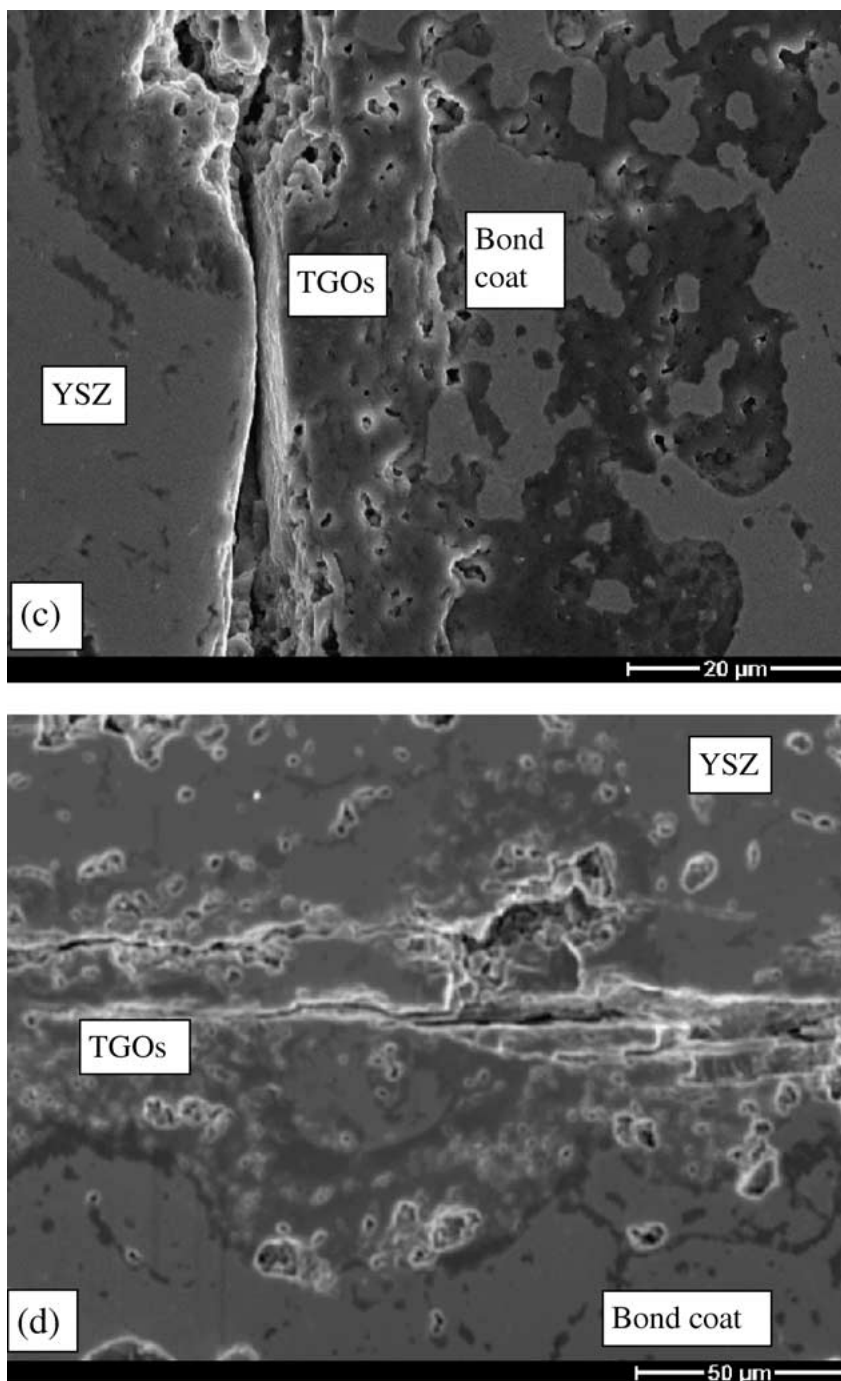


Figure 2 (Continued.)

oxidation rate still followed the parabolic law with a higher oxidation rate constant. As a result, catastrophic oxidation occurred, leading to a dramatic increase in the thickness of the TGO.

Cross sections of TBCs are presented in Fig. 2. Obviously, the TGO evolved during high temperature exposure. For the 10 h-oxidised sample, the dark-coloured layer between YSZ and bond coat is very dense with a very little amount of grey-coloured oxide attached to the YSZ (see Fig. 2a). For the 100 h-oxidised sample, the dark layer became more porous than that in the 10 h-oxidised sample (Fig. 2b). Also, there was a grey layer of oxide present between the dark layer and the YSZ (Fig. 2b). After 1000 h oxidation, the dark layer almost disappeared while the porous grey layer became dominant (Fig. 2c and d). In addition, cracks were formed in the TGO, which might be caused during thermal cycling. The formation of grey layers and cracks in the TGO should be the reason for the growth rate of the TGO to increase considerably after 1000 h oxidation. The crack formation has also led to oxygen penetration through the TGO and the internal oxidation in the bond coat where some dark oxides were formed. For the TBC specimens oxidised for 2000 hrs during thermal cycles, the spallation of TBCs occurred with a third of the specimens showed visible cracks in the TBCs. The remaining third of the specimens still appeared intact.

XRD was conducted on the oxide surface exposed by the complete spallation of the YSZ top coat. The XRD pattern is shown in Fig. 3, indicating that there exist $(\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4$ spinel, $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Cr}_2\text{O}_3$, and YSZ phases. The elemental information for different oxide layers was determined by EDX microanalysis (Fig. 4). The microanalysis in conjunction with the XRD results demonstrates that the dark oxide is predominantly comprised of $\alpha\text{-Al}_2\text{O}_3$ in the samples oxidised for less than 1000 hours whereas $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ are the major phases of the dark oxide in the samples oxidised for more than 1000 hours. In addition, the content of $\alpha\text{-Cr}_2\text{O}_3$ in the dark oxide increased with increasing oxidation time. The grey layer of oxides mainly contains Al, Cr, Ni and Co. For the oxidation less than 1000 hours, the levels of Al, Cr, and Ni in the grey layer do not change apparently, but they change

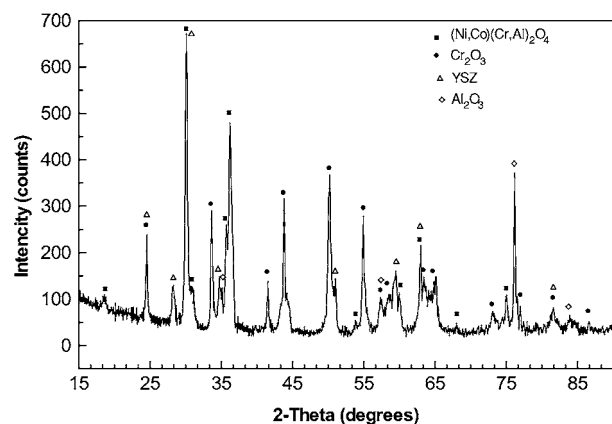


Figure 3 X-ray diffraction pattern for the exposed oxide scales attached to the bond coat for the samples oxidised in air at 1150°C for 2000 h.

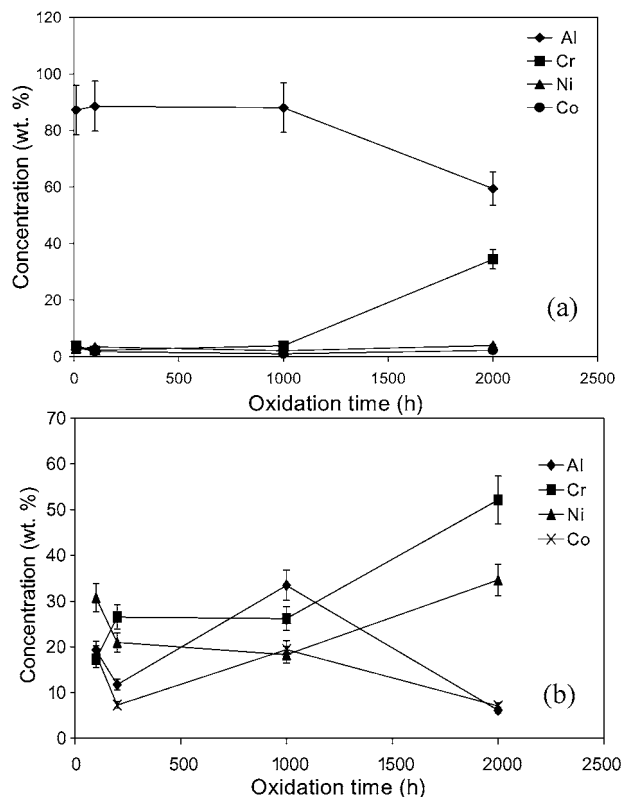


Figure 4 EDX microanalysis for (a) the dark oxide layer and (b) the grey oxide layer in the samples oxidised in air at 1150°C for different periods.

considerably when the oxidation time is longer than 1000 hours with the Cr and Ni level increasing and the Al level decreasing (Fig. 4). Therefore, the grey oxide in the TGO consists of $(\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4$ spinel, $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ before the 1000 hr oxidation, and $(\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4$ spinel and $\alpha\text{-Cr}_2\text{O}_3$ after the 1000 h oxidation. The YSZ detected by XRD should be the top coat attached to the TGO after spallation.

4. Discussion

There have been [5–13] extensive studies on the degradation of TBC systems at temperatures from 1000 to 1150°C. Previous studies showed that after a long-term oxidation the TGO were composed of $\alpha\text{-Al}_2\text{O}_3$ and spinel while the $\alpha\text{-alumina}$ was a major product. Some study [13] found a thin layer of $\alpha\text{-Cr}_2\text{O}_3$ formed between the bond coat and $\alpha\text{-alumina}$. However, this study indicated that after long-term oxidation at 1150°C the $\alpha\text{-alumina}$ disappeared while the TGO consisted mainly of $\alpha\text{-Cr}_2\text{O}_3$ /spinel mixed oxides so that the protective capability of the TGO was substantially reduced. Experimental results also indicated that the content of Al in the TGO decreased with increasing oxidation time while the content of Cr in the TGO increased with increasing oxidation time. Meanwhile the porosity in the alumina layer increased with increasing oxidation time. These suggest that the alumina layer gradually dissolved into the mixed oxide layer. The stress level usually fluctuated in the TBCs during thermal cycling because of the TGO growth and thermal mismatch among the YSZ, TGO and bond coat [14]. As the number of the thermal cycles after the 1000 hr oxidation increased, the formation of cracks in the TGO

was further promoted. The α -Al₂O₃ layer was formed at the beginning of oxidation. However, the crack formation and the increasing porosity in the TGO might change the oxidation kinetics, i.e., promoting the formation of the mixed oxides, which leads to different oxidation behaviour from previous studies [15, 16]. In addition, when the Al was depleted in the bond coat to a certain extent, the continuous formation of α -Al₂O₃ would terminate. In this case, Cr, Ni, and Co might diffuse to the surface of the α -Al₂O₃ layer to form α -Cr₂O₃ and (Ni,Co)(Cr,Al)₂O₄ spinel. A previous study on the degradation of TBCs at 1150°C suggested that oxygen might penetrate to the bond coat/alumina layer interface to form α -Cr₂O₃ or (Ni,Co)(Cr,Al)₂O₄ spinel between the alumina and bond coat [13]. However, this work showed the formation of mixed oxides between the YSZ top coat and alumina. Further studies need to be carried out to understand the factors controlling microstructural change of the TGO in TBCs during thermal cycling.

Regarding the oxidation kinetics (see Fig. 1), the TGO growth seemed to be controlled by diffusion through the α -alumina when the oxidation time was less than 1000 hours. Assuming that the oxidation from the beginning to 1000 hrs and from 1000 to 2000 hr follows the parabolic law [17],

$$x^2 = k_c t \quad (1)$$

where x is the thickness of the oxide layer, t is the oxidation time, and k_c is the reaction rate coefficient

which is related to the diffusion rate of reacting elements.

According to the experimental data shown in Fig. 1, k_c can be obtained as approximately $9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for oxidation until 1000 hrs and $7 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for oxidation from 1000 to 2000 hrs. The k_c for oxidation until 1000 hrs in this study is very close to that [$(8-12) \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$] obtained from studying the oxidation of the PtAl bond coat at the same temperature, where the alumina layer was formed from oxidation [18]. However, the k_c for oxidation from 1000 to 2000 hrs in this study is much larger than that obtained from oxidation of the PtAl bond coat. This indicates that the oxidation of the MCrAlY alloy bond coat at the early stage is controlled by the diffusion through the alumina layer, while the oxidation at the later stage, where there is no alumina layer present in the TGO, is controlled by diffusion through the mixed oxide layer. The diffusion rate in α -alumina should be much lower than that in the mixed oxides [17, 19].

As indicated in Fig. 2, cracks initiated and propagated in the mixed grey oxides adjacent to the YSZ in parallel with the bond coat surface. The internal stresses created by the oxide formation and growth as well as the thermal expansion mismatch between different materials should be the main reason for this phenomenon [17]. In the samples after long term oxidation, a high porosity appears in the grey mixed oxide layer (Fig. 2), which weakens the mixed oxides. The formation of porosity could be due to the vaporisation of solid Cr₂O₃ into CrO₃ gases at the oxidation temperature (1150°C)

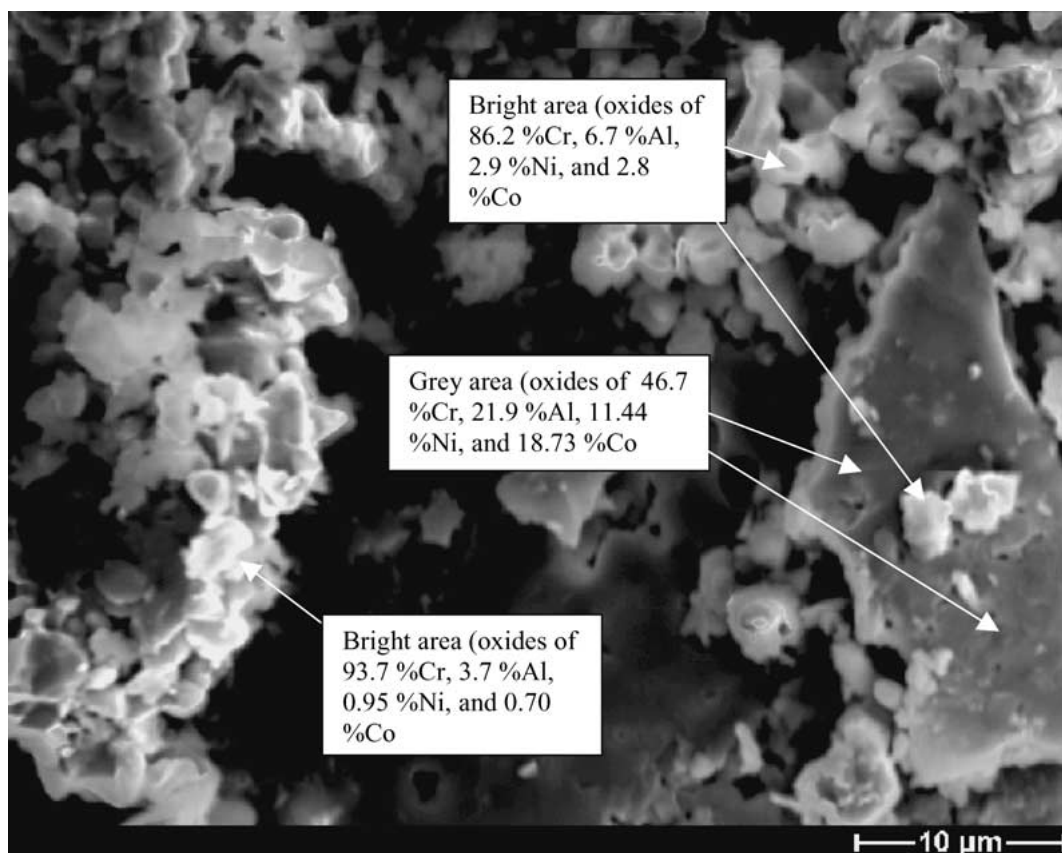


Figure 5 Scanning electron micrograph showing the oxide surface exposed by the spallation of YSZ for the samples oxidised in air at 1150°C for 2000 h.

[20, 21]. EDX microanalysis showed that high concentration of Cr was present at the surface of cracks, suggesting that the Cr₂O₃ might be formed after the initiation of cracking. After the spallation of YSZ top coat, dispersed Cr₂O₃ particles were identified on the top of spinel, further indicating that the Cr₂O₃ was formed after the initiation of cracking (Fig. 5). The continuation of cracking in the porous TGO leads to the spallation of the YSZ top coat.

5. Summary

The high temperature degradation of air plasma sprayed thermal barrier coatings was evaluated. α -alumina was formed initially next to the bond coat. A mixed oxide layer of α -Cr₂O₃ and (Ni,Co)(Cr,Al)₂O₄ spinel were formed next to the YSZ after further oxidation. During the further oxidation, the α -alumina layer gradually disappeared while the mixed oxide layer increased its thickness until the spallation of the YSZ top coat. The content of chromium oxide in the TGO increased with increasing oxidation time while the content of aluminium decreased at the same time. The oxidation kinetics was initially controlled by diffusion through the alumina, then controlled by the diffusion through the mixed oxide. The substantial increase in the oxidation rate and an increase in the number of thermal cycles led to the formation of cracks in the mixed oxides, resulting in the spallation of the TBCs.

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