Non-parabolic isothermal oxidation kinetics of low pressure plasma sprayed MCrAlY bond coat

Bang-Yan Zhang, Guan-Jun Yang*, Cheng-Xin Li, Chang-Jiu Li

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, China

*: Corresponding author: Prof. Guan-Jun Yang

State Key Laboratory for Mechanical Behavior of Materials

School of Materials Science and Engineering

Xi'an Jiaotong University

Xi'an, Shaanxi, 710049, P. R. China

Tel.: ++86-29-82660970

Fax: ++86-29-83237910

E-mail: ygj@mail.xjtu.edu.cn

Abstract

The non-parabolic isothermal oxidation kinetics of low pressure plasma sprayed MCrAlY bond coat was investigated. To qualitatively explain the abnormal growth phenomenon of thermally grown oxides (TGO), the changes that occurred to their microstructure during the oxidation process were studied. Based on these observations, a modified model was developed to understand and quantitatively predict the non-parabolic oxidation and growth kinetics of TGO. This modified model, which fits well with experimental results, provides a novel method to quantitatively predict the long-term growth behaviour of TGO, and thereby benefits the development of long-life and highly reliable thermal barrier coatings.

Keywords: bond coat, isothermal oxidation kinetics, thermally grown oxide, grain structure, oxygen diffusion rate

1. Introduction

The demand to improve the efficiency in gas turbine in the recent years leads to the increased turbine inlet temperature [1-4]. In this regard, thermal barrier coatings (TBCs) have been widely applied onto the turbine parts that are exposed to the high temperatures, in order to prevent the failure of the superalloy of which they are made [2, 5, 6]. Thermal barrier coatings are generally composed of a thermal insulating ceramic top coating, a MCrAlY or NiAl-based bond coat, and a Ni-based metallic superalloy substrate [5, 7-18]. A layer of thermally grown oxides (TGO) will form at the interface between the bond coat and the top coating during thermal exposure [5, 7-18]. Consequently, TBCs can be regarded as a multi-layers series system composed of the top coating, the TGO layer, and the MCrAlY bond coat. Every layer is of great importance for the service lifetime of the whole TBCs, since cracking and the following spallation might occur in any individual layer.

It has been reported by previous studies that the TGO layer has a significant impact on the lifetime of TBCs [5, 7-9, 19]. For example, a complex strain in the TGO layer will be caused by the increase in the thickness of the TGO layer during its exposure to high-temperatures, or thermal cyclic conditions, which produces much stress near the TGO region, especially in the top coating [7, 20]. The TGO layer is the major source of strain which primarily derives the cracking, delamination and spallation of the top coating from the bond coat surface [5, 7, 14, 21-24]. Therefore, when the thickness of the TGO layer reaches a critical value, the TBCs will experience failure [5, 20, 25]. In addition, it has been observed that during thermal exposure, the residual stress increases as the TGO layer grows, which will accelerate the spallation process of the top coating [4, 5, 7, 20-23]. Therefore, a deeper investigation into the growth behaviour of the TGO layer will provide an important theoretical foundation for understanding and evaluating the lifetime service and long-term reliability behaviour of TBCs.

Lowering the TGO growth rate is of great importance for prolonging the lifetime of TBCs [20]. In TBC systems, a stable, continuous, and slow growing TGO layer is optimal, as it can increase the oxidation resistance of the bond coat. The TGO layer is mainly made up of α -Al₂O₃ and mixed oxides (Cr₂O₃, NiO, and (Ni,Co)(Cr,Al)₂O₄ spinel) [5, 26]. The depletion of Al in bond coat is one of the main reasons for the formation of the mixed oxides [26-29]. The fast growth of the mixed oxides in the TGO layer, which is accompanied by a large volume expansion, can cause the failure of TBCs because it induces cracks in the top coating [30-36]. It has been revealed that the thermal cyclic lifetime of TBCs is inversely proportional to the coverage ratio of mixed oxides in the TGO layer, and that the high coverage of mixed oxides on the bond coat/top coating interface leads to the early spalling of the YSZ coating [34]. Therefore, the lifetime of TBCs can be significantly improved by suppressing or reducing the generation of mixed oxides. In this regard, a TGO layer made up of α -Al₂O₃ is preferred because the oxygen and metal ions have low diffusion coefficients, and the α -Al₂O₃ layers have a high thermal stability [7, 37-42], which result in a low TGO growth rate. It has been proposed that the proper pre-treatment of the bond coat under a low oxygen partial pressure, before the deposition of the top coating, is an effective way to lower the TGO growth rate and suppress the growth of mixed oxides, because a thin and continuous α -Al₂O₃ TGO layer forms on the bond coat surface [40, 43-46]. For instance, it was reported that the pre-oxidation of a MCrAlY bond coat, prior to depositing the top coating, extended the service life of the TBC [43].

In this study, the non-parabolic oxidation kinetics of the bond coat was investigated. The TGOs oxidation behaviour can be quantitatively revealed by the growth kinetics of the TGO layer. According to the conventional Wagner oxidation theory (the parabolic law), the growth of the TGO layer is controlled by the high temperature diffusion of the elements, and the TGO growth kinetics curves obey

the parabolic law. It has been reported that for a relatively short oxidation time (no more than hundreds of hours), the experimental results of the weight gain and TGO layer thickness are basically in line with the parabolic law [30, 35, 47-51]. In addition, it has been reported by some papers that the weight gain of TBCs that underwent longer oxidation times (more than hundreds of hours) also seemed to be in line with the parabolic law [52-54]. Nevertheless, weight gain changes cannot reflect variations in the TGO structure and make up during the oxidation process, so further research is necessary. The growth behaviour of the TGO layer thickness was considered to be a better way to reflect the structural changes of the TGO. The papers where changes in the TGO layer thickness (including all the oxides) were utilized to research the growth behaviour of TGO also state that the results of experiments carried out with longer oxidation times follow the parabolic law [32, 55]. However, after careful observations, we found that these experimental results seemed to deviate from the parabolic law, which is something that has not been observed up to now. As it has been reported that the oxygen diffusion coefficient of the outer mixed oxides is several orders of magnitude higher than that of the α -Al₂O₃ components [56, 57], the research on the growth behaviour of the TGO layer would benefit if the thickness of the outside mixed oxides is neglected. In this paper, the growth kinetics of the TGO layer thickness (without the mixed oxides) for samples exposed to long oxidation times was carefully studied. Specifically, it was found that the curves of the TGO thickness growth deviated from the parabolic law. This behaviour will be discussed in this paper. Nevertheless, deep and systematic research on the mechanism of the bond coat's non-parabolic oxidation kinetics has never been reported.

In this study, low pressure plasma sprayed (LPPS) bond coat was subjected to pre-oxidation and high temperature isothermal oxidation in air. The long-term growth behaviour of the bond coat was studied, and it was found that the Al₂O₃ TGO growth curve deviated from the parabolic law during the

oxidation process. The reason for the strange TGO growth behaviour, which does not fit well with the conventional Wagner oxidation theory, was examined in the perspective of the oxide grain-structure evolution. Finally, in order to further quantitatively predict the oxidation kinetics, a modified model for the oxide scale growth was developed.

2. Experimental Procedure

The bond coats of a ~ 150 μm thickness were deposited by LPPS using CoNiCrAlY powder in a spherical shape (Amdry 9951, Sulzer-Metco, USA). The spray powder has a mean particle size of ~ 25.9 μm ($d_{10}=12.9$ μm , $d_{90}=38.6$ μm). Nickel-based superalloy Inconel 738 was used as a substrate ($\Phi 25.4$ mm $\times$ 3 mm).

The LPPS system (MF-P 1000 VPS, GTV, Germany) was used to deposit the bond coats. In the LPPS system, a commercial plasma spray gun (F6, 80 kW class, GTV, Germany) was fixed on a six-axis robot (IRB 1600, ABB, Sweden) placed in a 10 m³ vacuum chamber. The LPPS spray conditions are shown in Table 1. During LPPS, high purity argon was chosen as the main gas for spraying and powder feeding gas; high purity hydrogen was used as the auxiliary gas to adjust the arc voltage, and thereby adjust the arc power.

Table 1

LPPS conditions

Parameters	Value
Arc current (A)	620
Arc voltage (V)	72

Plasma gas (Ar) flow (L·min ⁻¹)	40
Plasma gas (H ₂) flow (L·min ⁻¹)	8
Powder feeding gas (Ar) flow (L·min ⁻¹)	2
Powder feedrate (g·min ⁻¹)	19
Chamber pressure (kPa)	15
Spray distance (mm)	160

The as-sprayed bond coats were subjected to a pre-oxidation treatment conducted in Ar (4 h at 1000 °C and 4 h at 1080 °C, P(O₂) < 3 Pa). This pre-oxidation treatment can form a continuous α -Al₂O₃ oxide scale on the bond coat surface to suppress inward diffusion of oxygen and outward diffusion of cation during the subsequent isothermal oxidation in air. The pre-oxidation with high temperature and low oxygen partial pressure could make the deposited splats have a good metallurgical bonding through the high temperature diffusion, which would enhance elemental diffusion between each deposited splat to supply sufficient Al for the TGO growth on the bond coat surface during the subsequent oxidation [58]. After the pre-treatment, the bond coats were subjected to isothermal oxidation, for different durations, at 1000 °C in air.

The crystalline structure of the TGO layer was characterized by X-ray diffraction analysis (XRD, D8advance 3.0, Bruker, Germany). The microstructure of the coatings and the TGO layer was examined with a field emission scanning electron microscope (SEM, MIRA 3 LMH, TESCAN, Czech Republic) equipped with the energy dispersive spectrometer (EDS, Aztec EDS + EBSD, Oxford Instruments, United Kingdom). The thicknesses of Al₂O₃ TGO that underwent different heat treatments were measured along the local normal direction on the cross-sectional images of the bond coat, using

the ImageJ software, to obtain the Al_2O_3 TGO growth curves. Ni-electroless plating was used to deposit a layer of Ni on the pre-oxidized bond coat surface, in order to protect the TGO scale from spalling off during the cutting and polishing of the pre-oxidized samples. For the same aforementioned reasons, to protect the TGO scale to observe the TGO cross sectional structures with isothermal oxidation, after their pre-oxidation, a thin 8YSZ (8 wt% yttria-stabilized zirconia, 204B-NS, Sulzer-Metco, USA) top coating was deposited on the bond coat surface by a commercial plasma spray system (APS, GP-80, Jiujiang, China). In order to precisely examine the grain size of the Al_2O_3 TGO layer, a bending and collecting approach was developed to obtain the exact grain size diameter at the interface between the TGO layer and the alloy matrix of the bond coat. First, the coatings (bond coat and TGO) were spalled from the substrates. Secondly, the TGO side of the coatings was pasted to a conductive tape, and then the coatings were bended into two pieces; some TGO chippings stuck on the conductive tape. Thus, the rear side of the TGO next to the bond coat could be observed by SEM. Then the oxide grain size and grain boundary density (grain boundary length per unit area, μm^{-1}) could be obtained from the SEM images of the spalled TGO layer.

3. Results and Discussion

3.1. TGO crystalline structure after isothermal oxidation

Fig. 1 shows the XRD patterns of the coatings after undergoing isothermal oxidation in air for different durations. The figure shows that after the pre-treatment, $\alpha\text{-Al}_2\text{O}_3$ is the main component of the oxide scale on the bond coat surface. Hence, the growth of the TGO layer during isothermal oxidation is actually the growth process of the Al_2O_3 scale. In addition, after 50 h, a small fraction of mixed

oxides was observed on the TGO surface, which seemed to thicken very slowly with prolonged oxidation durations.

Fig. 1. XRD patterns of **bond** coatings after isothermal oxidation in air for different durations.

3.2. Surface morphology of coatings that underwent isothermal oxidation for different durations

The surface morphologies of bond coats that underwent isothermal oxidation for different durations are shown in Fig. 2. It can be observed that the surface morphology of the bond coat changed little after the isothermal oxidation for all durations. The bond coat presents a rough surface morphology due to the random stacking of splats. On the coating surface, there are many convexities, which have a size (dozens of micrometres) comparable to the size of the feedstock powder. The convexities resulted from the semi-molten particles. From Fig. 2, some granular splashed particles, with sizes ranging from sub-micrometres to several micrometres, much smaller than the feedstock powder, can also be

observed. These small particles were produced by the impact of splashing liquid droplets on the deposited surface [58, 59]. The semi-molten particles and splashed particles contributed to the surface roughness of the as-sprayed bond coats.

Table 2 shows the EDS results from the surface of the coatings after isothermal oxidation in air for different durations. Similar results with the XRD analysis were obtained from Table 2. From Table 2, it can be found that Al_2O_3 remained the sole component until the isothermal oxidation duration was 25 h. When the isothermal oxidation duration was 50 h, the mixed oxides began to appear in the oxide scale. And the content of mixed oxides increased as the oxidation time went on. When the oxidation duration was 600 h, only mixed oxides could be detected, which means that the mixed oxides have grown to be the continuous layer on the outside of the Al_2O_3 scale.

Fig. 2. Surface morphology of the coatings after isothermal oxidation in air for different durations. (a) Pre-oxidized, (b) 16 h, (c) 25 h, (d) 50 h, (e) 100 h, (f) 600 h.

Table 2

EDS results from the surface of the coatings after isothermal oxidation in air for different durations

Durations	O (at.%)	Al (at.%)	Cr (at.%)	Co (at.%)	Ni (at.%)	Y (at.%)
Pre-oxidized	55.07	44.25	0.04	0.14	0.50	0.00
16 h	55.09	44.38	0.03	0.00	0.51	0.00
25 h	55.54	43.88	0.04	0.18	0.35	0.00
50 h	54.64	44.17	0.24	0.15	0.80	0.00
100 h	55.36	42.93	0.50	0.61	0.60	0.00
600 h	50.68	30.29	3.12	2.89	13.03	0.00

3.3. TGO growth kinetics during isothermal oxidation

In order to reveal the TGO microstructure, the cross sections of TGO layers that underwent isothermal oxidation for different durations, were observed; the images are shown in Fig. 3. **Similar**

results with the XRD analysis and the EDS analysis (Table 2) from the surface of the coatings were obtained from the TGO cross sectional microstructure. Fig. 3 reveals that, during isothermal oxidation, a uniform dark layer remained the major component of the TGO layer found on the surface of the bond coat. In addition, Fig. 3d shows that after isothermal oxidation for 50 h, a small fraction of light area formed on the outside surface of the dark layer. The EDS results (Fig. 4) of the points marked in Fig. 3d show that the light area and the dark layer are mixed oxides and α -Al₂O₃, respectively. The appearance of mixed oxides could be attributed to the unexpected oxidation of small splashed particles during the bond coat deposition [58]. The TGO has presented a bi-layered structure (mixed oxides outside, and Al₂O₃ inside) after a 600 h isothermal oxidation (Fig. 3f), which could be clearly observed in Fig. 5 (EDS mappings of the TGO shown in Fig. 3f). This might be attributed to the continuity of the small mixed oxides on the TGO surface. Nevertheless, the thickness of mixed oxides was very small, less than 1/5 the thickness of the uniform α -Al₂O₃ scale.

Fig. 3. Cross sectional microstructure of the TGO underwent isothermal oxidation for different durations. (a) Pre-oxidized, (b) 16 h, (c) 25 h, (d) 50 h, (e) 100 h, (f) 600 h.

Fig. 4. EDS results of the points marked in Fig. 3d. (a) Point 1, (b) point 2.

Fig. 5. EDS element mappings of the TGO cross section shown in Fig. 3f.

To quantitatively reveal the growth kinetics of the TGO layer, the TGO layer thicknesses of bond coats oxidized for up to 100 h were obtained, as shown in Fig. 6. The scattered points were well fitted with a straight line, revealing that the TGO thickness presented a good parabolic relationship with the oxidation duration. This means that the TGO growth kinetics of the coatings with short oxidation durations can be well described by the conventional Wagner theory of oxidation, using the following equation [60-64]:

$$\delta^2 = 2k't \quad (1)$$

where δ is the Al_2O_3 TGO thickness, k' is the oxidation rate constant, and t is the oxidation duration. By taking the differential of Eq. 1, the Al_2O_3 TGO growth rate (oxidation rate, $\frac{d\delta}{dt}$) can be gotten, as follows:

$$\frac{d\delta}{dt} = \frac{k'}{\delta} \quad (2)$$

The above equation (Eq. 2) reveals that the Al_2O_3 TGO growth rate is inversely proportional to the Al_2O_3 TGO thickness, as k' is a constant according to the conventional Wagner oxidation theory.

According to the conventional Wagner oxidation theory, the oxidation kinetics during longer oxidation times should also follow the straight-line behaviour observed in Fig. 6. However, the results (Fig. 7) show that the points for longer oxidation durations diverged from the straight lines shown in Fig. 6, and that the Al_2O_3 TGO growth rate gradually decreased for longer oxidation times. In short, it was observed that Al_2O_3 TGO had different oxidation rate constants during an oxidation treatment of 1000 h, which is a behaviour that does not fit well with the conventional Wagner oxidation theory, i.e. parabolic function.

The dominant growth mechanism of Al_2O_3 TGO on the MCrAlY bond coat can be regarded as the diffusion of oxygen from the outside surface of the TGO, into the interface between the TGO and the alloy matrix of the bond coat [37, 60, 61, 65-68]. For the bi-layered TGO found on the bond coat surface of the samples that underwent long isothermal oxidation times, the oxygen diffusion to the inside went through the mixed oxides and the $\alpha\text{-Al}_2\text{O}_3$ scale. It has been reported that the oxygen diffusion coefficient in mixed oxides is much higher than that in $\alpha\text{-Al}_2\text{O}_3$ by several orders of magnitude [56, 57], and the mixed oxides layer can be neglected when considering the growth of TGO via oxygen diffusion [37, 56, 57, 69]. Hence, in this study, the mixed oxides were excluded when calculating the TGO layer thickness to better understand the growth behaviour of the Al_2O_3 scale.

It has been widely reported that the k' value of the Al_2O_3 TGO layer is directly proportional to the inward diffusion rate of oxygen during the isothermal oxidation [60, 61, 67-70]. Thus, the oxygen diffusion in the Al_2O_3 TGO layer was brought to the forefront of this research. For the oxygen diffusion in the oxide scale that covered the bond coat surface, the grain boundaries and the bulk crystalline

grains are the main diffusion routes [37, 60, 61, 65, 67-73]. Since the grain boundary is the interface between two grains with different crystalline orientations, the grain boundary is actually a layer of irregularly arranged atoms [74, 75]. Therefore, there are more large voids in a grain boundary, than in bulk crystalline grains, which allow the atoms to diffuse more easily. It has been reported that the oxygen diffusion coefficient through the α - Al_2O_3 grain boundaries is about three orders of magnitude larger than that through α - Al_2O_3 bulk crystalline grains [71]. As a result, for the α - Al_2O_3 scales, except those with ultra-large size grains or even single crystals, the dominant diffusion route should be through grain boundaries. Therefore, it is necessary to analyse the grain boundary diffusion behaviour.

Fig. 6. Al_2O_3 TGO growth kinetics curve for the first 100 hours of high-temperature oxidation.

Fig. 7. Al_2O_3 TGO growth kinetics curve for long oxidation durations of up to 1000 h.

3.4. Microstructure evolution of Al_2O_3 TGO during isothermal oxidation

In order to reveal the essential reason of the non-parabolic relationship between the TGO layer thickness and oxidation duration, the grain structure of the Al_2O_3 TGO layer located on the surface of the bond coats was examined. Fig. 8 shows the fractured cross-sectional microstructure of a TGO layer formed on the surface of a bond coat that underwent the isothermal oxidation for 50 h. From Fig. 8, it can be seen that the Al_2O_3 grains present columnar structures that grow inward in the direction perpendicular to the bond coat's surface. The inward growth of the Al_2O_3 grains resulted from the inward oxygen diffusion in the oxide grain boundaries [37, 61, 68, 70, 72]. It can also be seen that the lateral size of Al_2O_3 grains at the TGO/bond coat interface increased gradually in the TGO growth direction. This change was caused by some small grains that grow slowly and merged into larger adjacent ones having faster growth rate. This will increase the grain size and decrease the grain boundary for oxygen diffusion in the TGO layer, and thereby gradually decrease the diffusion coefficient of O during the oxidation [27, 37, 61, 68, 70]. Consequently, a lower experimental TGO

thickness was observed for long-term oxidations, for example a 1000 h oxidation, than the parabola fitting of TGO thickness grain coarsening.

Fig. 8. The fractured cross-sectional microstructure of a TGO layer that formed on the surface of a bond coat that underwent isothermal oxidation for 50 h in air.

3.5. Generalized 3D model for the TGO growth behaviour

In order to further understand and quantitatively interpret the above abnormal phenomenon, a generalized 3D model of the oxide scale that forms on the surface of the bond coat was developed and a theoretical calculation was performed. In the 3D diagrammatic sketch of the α -Al₂O₃ TGO on the bond coat surface, shown in Fig. 9, the red lines express the grain boundaries of the α -Al₂O₃ TGO. In order to more easily understand and simplify the subsequent calculation, the Al₂O₃ scale is shown underneath the bond coat marked by dashed lines in the upper part of Fig. 9. From Fig. 9 it can be seen that along the TGO growth direction (the direction of increasing z-axis), the grain boundary density decreases as the lateral grain size increases. To quantitatively evaluate the grain boundary in TGO, the grain boundary density was defined as the ratio of the grain boundary area to the unit volume of the

TGO. The grain boundary density changed with the z-axis, since the grain size increased with an increase of TGO growth, as shown in Figs. 8 and 9. The grain boundary density was not homogeneous along the z-axis direction. The oxide scale shown in Fig. 9 is segmented to a great many of very thin and equal-thickness slices along the z-axis direction. As it was assumed that the grain boundary density of a single thin slice was homogeneous, Eq. (2) could be applied to the thin slices. The oxygen diffusion resistance per unit area in the entire Al_2O_3 scale actually was the overlapping result of the slices in series. However, to quantify the TGO growth kinetics, Eq. (2) has to be changed as follows:

$$\frac{d\delta}{dt} = \frac{1}{\frac{\delta}{k'}} \quad (3)$$

where $\frac{\delta}{k'}$ is proportional to the unit resistance of oxygen diffusion through an oxide scale with thickness of δ . For TGO layers with inhomogeneous oxygen diffusion properties along their thicknesses, due to changes in their grain size, and thereby grain boundary density, Eq. (3) has to turn into an integral:

$$\frac{d\delta}{dt} = \frac{1}{\int_0^\delta \frac{1}{f_{k'z}(z)} dz} \quad (4)$$

where $f_{k'z}(z)$ is the oxidation rate constant at the z local region. Then, the oxidation kinetics theory for inhomogeneous TGO can be expressed as,

$$t = \int_{\delta_0}^\delta \left(\int_0^z \frac{1}{f_{k'z}(z)} dz \right) dz \quad (5)$$

where δ_0 is the thickness of the Al_2O_3 scale on the surface of the pre-oxidized bond coat. Because $f_{k'z}(z)$ cannot be a constant, Eq. (5) will not be a parabolic function. Therefore, the Al_2O_3 TGO growth kinetics curves do not fit well into the conventional Wagner oxidation theory, which fits with the above experimental results (Fig. 7).

A further understanding of the TGO growth mechanism can be obtained by the above discussion and calculations. It can be found that the method of predicting the long-time TGO growth behaviour using the short-time parabola TGO growth pattern is improper, and the above discussion about the non-parabolic Al_2O_3 TGO growth behaviour should be utilized to predict the long-time TGO growth behaviour. Meanwhile, it was found that an increase of the initial Al_2O_3 lateral grain size plays an important role in retarding the thickness growth of the TGO layer. Therefore, research on this would benefit the development of long-life and highly reliable TBCs.

Fig. 9. 3D diagrammatic sketch of the $\alpha\text{-Al}_2\text{O}_3$ TGO on the bond coat surface. The red lines express the grain boundaries of the $\alpha\text{-Al}_2\text{O}_3$ TGO.

3.6. Quantitative prediction of TGO growth based on grain boundary density examinations

According to the above theoretical deduction, the oxidation rate constant, $f_{k_z}(z)$, is the key factor that affects the TGO growth behaviour. Therefore, the TGO microstructure, especially the Al_2O_3 grain boundary density at the interface of the TGO and the bond coat, is very important for the Al_2O_3

TGO growth behaviour. The grain boundary density can be obtained from the grain size because it is proportional to the reciprocal of the grain size. The Al_2O_3 grain size is a visual physical quantity, which is beneficial for understanding the above theoretical derivation. Thus, obtaining an accurate grain size is very important for analysing the Al_2O_3 TGO growth behaviour, and to verify the above theoretical calculations. However, it is extremely difficult to quantitatively obtain the grain size of this kind of thin TGO layer. It was previously reported that electron backscatter diffraction (EBSD) could be used to analyse the cross sections of TGO to examine their grain size [76-78]. Although the cross sectional analysis can be realized by optimizing the sample preparation approach, the obtained results are not very precise because the cross sections of the cut grains do not always show the maximum diameter of the grains. This deviation would inevitably cause inaccuracies in the prediction. In order to precisely examine the grain size of Al_2O_3 TGO, a bending and collecting approach, which was described detailedly in the experimental section (Section 2), was developed to obtain the microstructure of the rear side of the TGO layer next to the bond coat.

The microstructure of the TGO rear side (at the interface of the TGO and the bond coat), which was spalled from the samples, is partly shown in Fig. 10. From this figure (Fig. 10), it can be observed that the shape of the Al_2O_3 grains at rear side of the TGO layer is polygonal during the oxidation process, although a small fraction of the grains presents an aspect ratio larger than 2. The lateral grain sizes of Al_2O_3 , for samples that underwent different isothermal oxidation durations, were obtained from the SEM pictures of the rear side of the TGO spalled from the samples, and the grain size distribution is shown in Fig. 11. It can be generally seen that the oxide lateral grain size increased with prolonged oxidation times. For the purpose of having a deeper understanding of the influence that the grain structure has on the growth behaviour of the TGO layer, the changes of the average lateral Al_2O_3 grain

sizes, and of the grain boundary distribution at the TGO layer/bond coat interface, were shown in Fig.

12. The results show that the grains at the TGO growth front, i.e. at the TGO layer/bond coat interface, increased gradually with increasing oxidation times due to grain growth and merge, which led to a reduction in the grain boundary density for oxygen diffusion. As discussed above, the decreasing grain boundary density for oxygen diffusion in the TGO will decrease the diffusion coefficient of O during the oxidation. Since the oxidation rate constant (k' , Eq. (1)) is proportional to the oxygen diffusion coefficient, k' will decrease gradually as the oxidation time goes on, which would make the Al_2O_3 scale growth behaviour not fit well with the conventional Wagner oxidation theory, i.e. a parabolic function.

Fig. 10. Comparison between the Al_2O_3 microstructure of the TGO rear side (at the interface of the TGO and the bond coat) that underwent different isothermal oxidation durations. (a) Pre-oxidized, (b) 25 h, (c) 100 h, (d) 200 h, (e) 400 h, (f) 600 h.

Fig. 11. Lateral Al_2O_3 grain size distribution of samples that underwent different isothermal oxidation durations.

Fig. 12. Grain boundary density and Al_2O_3 grain size (next to the BC) changes of samples that underwent different isothermal oxidation durations.

The relationship between the oxidation rate constant $f_{k_z}(z)$ and the TGO thickness can be inferred from the relationship between the grain boundary density and the TGO thickness. The latter one, i.e. the relationship between the grain boundary density and the TGO thickness, can be deduced from the relationship between the oxide grain size and the TGO thickness. Fig. 13 shows the relationship of the TGO thickness with the grain boundary density, and with the Al_2O_3 lateral grain size (next to BC) of the samples with different isothermal oxidation durations. The data of the grain sizes in this figure were fitted by the black curve shown in the figure using the following equation:

$$a(\delta) = 0.41e^{0.5\delta} \quad (6)$$

where $a(\delta)$ is the lateral size of Al_2O_3 grains at the TGO layer/bond coat interface when the TGO thickness is δ . Then, the oxidation rate constant, $f_{k_z}(z)$, can be obtained from Eq. (6), and a TGO

growth kinetics theory can be acquired. However, because the oxide grains in Fig. 10 are not round, the statistical data of the grain size obtained from Fig. 10 inevitably have some errors, which will make the final calculated results have a bigger deviation. Therefore, in order to decrease the deviation, the statistical data of the grain boundary density are directly applied to the theoretical calculation for the TGO growth kinetics, and the grain boundary density data were fitted, shown as the red curve in Fig. 12, using the following equation:

$$\rho(\delta) = 7.7e^{-0.5\delta} \quad (7)$$

where $\rho(\delta)$ is the grain boundary density when the TGO thickness is δ .

Therefore, according to the above discussion, $f_{k'z}(z)$ can be calculated as follows:

$$f_{k'z}(z) = \frac{1}{C} \rho(z) = \frac{7.7e^{-0.5z}}{C} \quad (8)$$

where C is the positive constant related to the material and temperature. The thickness of the Al_2O_3 scale on the surface of the pre-oxidized bond coat is about $0.38 \mu\text{m}$. Then, by combining Eqs. (5) and (8), the TGO thickness growth kinetics, more in tune with the practical experimental data, was obtained as follows:

$$t = \int_{0.38}^{\delta} \left(\int_0^z \frac{1}{f_{k'z}(z)} dz \right) dz = 0.52C(e^{0.5\delta} - 0.5\delta - 1.02) \quad (9)$$

According to the above experimental results, the TGO thickness is about $2.8 \mu\text{m}$ when the isothermal oxidation duration is 600 h. Then, by plugging these data ($\delta = 2.8 \mu\text{m}$ when $t = 600 \text{ h}$) into Eq. (9), the constant C can be obtained ($C=705.6$). Therefore, Eqs. (8) and (9) can be expressed by the following equations:

$$f_{k'z}(z) = \frac{7.7e^{-0.5z}}{705.6} = 0.011e^{-0.5z} \quad (10)$$

$$t = 366.9(e^{0.5\delta} - 0.5\delta - 1.02) \quad (11)$$

Eq. (11) is the theoretical calculated result of the TGO thickness growth kinetics. According to Eq. (11), it can be seen that the TGO growth behaviour does not fit well with the conventional Wagner oxidation theory.

In order to further verify the above discussion and theoretical calculations, Fig. 14 shows the comparison between the experimental results and the theoretical calculated results of the thickness of the Al_2O_3 scale. It was found that the curve of the calculated Al_2O_3 TGO thickness values could fit well with the experimental data. Therefore, the above calculated theoretical results and analysis are reasonable, and the changing oxide grain structure is the key determinant that will affect the TGO growth behaviour.

Fig. 13. The relationship of the TGO thickness with the grain boundary density, and with the Al_2O_3 lateral grain size (next to BC) of the samples with different isothermal oxidation durations.

Fig. 14. Comparison between the experimental and theoretical values obtained using the model in this study.

4. Conclusions

In this study, the non-parabolic isothermal oxidation kinetics of low pressure plasma sprayed MCrAlY bond coat were experimentally investigated, and a modified model was developed to quantitatively predict the TGO growth kinetics. It was found that the Al_2O_3 TGO had different oxidation rate constants during isothermal oxidations of long durations, which did not fit well with the conventional Wagner oxidation theory. For a deeper understanding of the reason for the aforementioned experimental phenomenon, the microstructures (grain structures) of the Al_2O_3 scale on the surface of coatings that had undergone different isothermal oxidation durations were carefully examined. It was found that the columnar oxide grains at the TGO growth front, i.e. at the TGO/bond coat interface, increased gradually as the oxidation time went on, due to grain growth and merge, which led to a reduction in the grain boundary for oxygen diffusion. A decrease in the oxygen diffusion rate would result in the decreasing oxidation rate constant (k'), which would qualitatively explain the above abnormal TGO layer growth phenomenon. To further understand and quantitatively interpret the

above abnormal phenomenon, a generalized 3D model of the oxide scale on the bond coat surface was developed and theoretical calculations were performed. The results of the theoretical calculation showed that the TGO growth behaviour did not fit well with the conventional Wagner oxidation theory. In order to further verify the above discussion and theoretical calculation, the experimental data from this study were applied to the calculation, and a comparison between the experimental results and the theoretical calculated results of the thickness of the Al_2O_3 scale was made. From the comparison, it was found that the above calculated results and analysis are reasonable. This research reveals that the changing oxide grain structure is the dominant determinant factor that affects the TGO growth behaviour. This modified model provides a novel method for the quantitative prediction of the long-term growth behaviour of the TGO layer, and thereby benefits the development of long-life and highly reliable TBCs.

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