Highly oxidation resistant and cost effective MCrAlY bond coats prepared by controlled atmosphere heat treatment

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ARTICLE INFO

Keywords:
Thermal barrier coatings
MCrAlY bond coat
Air plasma spraying
Thermally grown oxide
Isothermal oxidation
Controlled atmosphere heat treatment

ABSTRACT

MCrAlY bond coats with high oxidation resistance are essentially important for improving the life-time of thermal barrier coatings (TBCs). In this study, highly oxidation resistant MCrAlY bond coats were prepared by a cost-effective approach involving air plasma spraying (APS) followed by a controlled atmosphere heat treatment (a diffusion treatment performed in a furnace filled with Ar). The results confirmed that a pure α-Al2O3 thermally grown oxide (TGO) was successfully formed on the surface of the heat-treated APS bond coats during isothermal oxidation. The oxidation resistance of the resulting APS bond coats was as high as that of low-pressure plasma sprayed bond coats, which are very expensive. The high oxidation resistance of the APS bond coats fabricated in this study can be attributed to the structural changes of the interface between the splats inside the coating. During the controlled atmosphere heat treatment, the lamellar oxides present between the splats within the as-sprayed APS bond coats converted into isolated oxide particles, and the metal elements could diffuse freely within the coating after the healing of the interface between the lamellar splats. The effect of the changes in the interfacial microstructure of the bond coats on the growth of the TGO was discussed.

1. Introduction

Thermal barrier coatings (TBCs) are widely used in hot components of gas turbine engines used for power generation and aircraft and marine propulsion [1–6]. TBCs are typically composed of an yttria-stabilized zirconia top coat (TC), a MCrAlY bond coat (BC), a thermally grown oxide (TGO) layer, and a nickel- or cobalt-based superalloy substrate (SS) [7–14]. The ceramic top coat is designed to provide thermal insulation, while the MCrAlY bond coat can not only prevent the superalloy substrate from high-temperature oxidation and corrosion by forming a layer of TGO on its surface, but also alleviates the thermal mismatch between the ceramic top coat and the substrate [3,6,15,16].

The typical failure mode of TBCs during both engine service and laboratory testing is the fracture and delamination of the porous ceramic top coat near the irregular bond coat interface [6,17–19]. Although a multitude of phenomena contribute to the degradation of TBCs, it is believed that the growth of TGO is one of the most important factors affecting their service life [6,8,11,17,20,21]. The oxidation resistance of bond coats and the service life of TBCs greatly depend on the ability of the bond coats to produce and maintain a stable, continuous, adherent, and slow growing TGO on their surface [6,17]. It is noteworthy that the TGO layer is not a single-component system. It is composed of a variety of oxides. These oxides can be broadly divided into two categories, namely, the α-Al2O3 and mixed oxides (MO: NiO, Cr2O3, and (Ni,Co)(Cr,Al)2O4 spinel) [6,17,19,22]. A fast growth of the mixed oxides in the TGO layer, which is accompanied by a large volume expansion, can cause the premature spallation failure of TBCs because it induces cracks in the ceramic top coat [19,23–25]. It has been found that the thermal cyclic life-time of TBCs is inversely proportional to the coverage ratio of mixed oxides in the TGO layer, and a high coverage ratio leads to the early spalling of the ceramic top coat [26]. Therefore, the life-time of TBCs can be significantly improved by suppressing the formation and reducing the content of mixed oxides in the TGO layer. In this regard, a TGO layer made up of pure α-Al2O3 is preferred for the reason that the effective diffusion rates of oxygen and metal ions through α-Al2O3 are relatively low and the chemical and thermal stability of α-Al2O3 is relatively high [6,27–29]. From this discussion, it can be concluded that reducing the mixed oxides content and promoting the formation of α-Al2O3 on the surface of bond coats plays an important role in enhancing the oxidation resistance of bond coats and increasing the life-time of TBCs.

Air Plasma Spraying (APS) is the most commonly used technique for the deposition of industrial MCrAlY bond coats [30,31]. Unlike the costly thermal spraying processes, APS is carried out at atmospheric
pressure, and is thus cost-effective [31]. In addition, APS bond coats are typically deposited by melted and semi-melted spraying droplets, which make the surface of the bond coats rough and suitable for adhering to plasma-sprayed ceramic top coats [30,32]. However, the spraying powders used in the APS process are prone to oxidation in the high-temperature flame flow. This increases the oxide content of the resulting bond coats. The low momentum of the sprayed powders also makes the bond coats porous [30,33]. It has been reported that the APS bond coats with a high content of original oxides and pores can easily form the mixed-oxide TGO layer on their surface [31]. Since the growth rate of mixed oxides is high, the cheap air plasma-sprayed MCrAlY bond coats usually show a low oxidation resistance at high temperatures.

Low-pressure plasma spraying (LPPS, also known as vacuum plasma spraying) is used to prepare high-performance MCrAlY bond coats with low oxide and pore contents [31,34]. Since LPPS is carried out in vacuum, the risks of oxidation and air entrapment during the deposition are significantly low. Generally, the TGO growth rate of LPPS bond coats is significantly lower than that of APS bond coats [31,35]. However, owing to high equipment cost, the LPPS process is expensive as compared to APS. In addition, LPPS requires time-consuming evacuation process and flooding cycles, which reduce the deposition efficiency of the process. Furthermore, the online process control by optical diagnostic means such as the substrate and in-flight particles pyrometry is difficult in a vacuum chamber. Thus, despite the higher oxidation resistance of LPPS bond coats, the higher cost and lower efficiency of the LPPS method limit its application for the preparation of MCrAlY bond coats.

In this study, the oxidation resistance of APS MCrAlY bond coats was improved by subjecting them to a controlled atmosphere heat treatment. After the heat treatment, the APS bond coats showed an oxidation resistance comparable to that of LPPS bond coats. To know the reason for the improved oxidation resistance of the heat-treated APS bond coat, the interfacial microstructure of the coating, composition of the TGO layer, and TGO growth rate during the isothermal oxidation were examined. Finally, the effect of the changes in the interfacial microstructure of the bond coats on the growth of the TGO layer was discussed.

Table 1
Spraying parameters.

<table>
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<th>Parameters</th>
<th>Value</th>
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<td>Arc current (A)</td>
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</tr>
<tr>
<td>Arc voltage (V)</td>
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<tr>
<td>Primary plasma gas (Ar/slpm)</td>
<td>30</td>
</tr>
<tr>
<td>Primary plasma gas (H2/slpm)</td>
<td>2</td>
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<tr>
<td>Powder feed gas (Ar/slpm)</td>
<td>5</td>
</tr>
<tr>
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<td>35</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>100</td>
</tr>
<tr>
<td>Traverse speed of torch (mm/s)</td>
<td>800</td>
</tr>
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![SEM images of the CoNiCrAlY feedstock powder: (a) surface morphology; (b) cross-sectional morphology; (c), (d) EDS results of (b).](image)

Fig. 1. SEM images of the CoNiCrAlY feedstock powder: (a) surface morphology; (b) cross-sectional morphology; (c), (d) EDS results of (b).
2. Experimental procedures

2.1. Experimental materials

Nickel-based superalloy IN738 (ø25.4 mm × 3 mm) was used as the substrate. The nominal composition (at.%) of this superalloy was Ni-16.59Cr-7.75Co-7.01Al-3.66Ti-0.75W-0.97Mo-0.54Ta-0.48Nb-0.75C-0.05Zr-4.95B. Prior to the coating deposition, some substrates were ultrasonically cleaned with acetone and then grit-blasted with alumina grit to improve the adherence of the coating. The other substrates were polished to observe the microstructure at the interface between them and the coating. Commercial CoNiCrAlY powder (Amdry 9951, Oerlikon Metco, Switzerland) with a nominal composition (at.%) of Co-29.16Ni-21.81Cr-15.93Al-0.32Y was used as the feedstock powder. The CoNiCrAlY powder particles were spherical, and the average particle size was 26 μm (d_{10} = 13 μm and d_{90} = 39 μm). The surface and cross-sectional morphologies as well as the electron diffraction X-ray spectrometry (EDS) results of the feedstock powder are shown in Fig. 1. As can be observed from Fig. 1(b), the CoNiCrAlY powder consisted of both the γ-Ni matrix and β-NiAl phases [36]. The dendritic crystals belonged to the γ phase (Point 1), while the interdendritic area corresponded to the β phase (Point 2).

2.2. Coating deposition

The CoNiCrAlY bond coats with a thickness of 200 μm were deposited on the surface of the substrate using a commercial APS system (APS, GP-80, Jiujiang, China). The spraying parameters are listed in Table 1. For the coating deposition, high purity argon (Ar ≥ 99.999%) was used for plasma spraying and powder feeding. High purity hydrogen (H₂ ≥ 99.999%) was used as the auxiliary gas to adjust the arc voltage, and hence the arc power.

2.3. Controlled atmosphere heat treatment and isothermal oxidation test

Some of the as-sprayed bond coats were subjected to a controlled atmosphere heat treatment in the presence of Ar (10 h at 1100 °C, P(Ar) ≥ 1 × 10⁵ Pa, P(O₂) < 0.001 Pa) in an industrial vacuum furnace (SBF 966H, EXEMOO, China). The reason for employing these heat-treatment conditions are as follows. High-purity argon was blown into the furnace at a pressure slightly above the standard atmospheric pressure to prevent atmospheric oxygen from entering into the furnace during the heat treatment. This reduced the oxygen content of the furnace, thereby preventing the oxidation of the coating during the heat treatment. Compared to other oxygen-reducing approaches (such as employing Ar-H₂ or high vacuum), filling the furnace with argon is relatively safe and inexpensive. Since the heat treatment of thermally sprayed MCrAlY bond coats is generally carried out at 1100 °C [37–39], we also carried out the heat treatment of the APS CoNiCrAlY bond coats at 1100 °C. The results showed that this heat treatment (at 1100 °C with low oxygen partial pressure) when carried out for longer durations (10 h) significantly changed the internal microstructure of the as-
sprayed bond coats. Finally, the heat-treated and non-heat-treated (as-sprayed bond coats) bond coats were subjected to isothermal oxidation for different durations (4, 25, 100, 200, and 400 h) at 1000 °C in air in a muffle furnace.

2.4. Microstructural characterization

In order to characterize the microstructure and composition of the bond coats as well as the TGO layer, a field emission scanning electron microscope (SEM, MIRA 3 LMH, TESCAN, Czech Republic) equipped with EDS (Aztec, Oxford Instruments, United Kingdom) was employed to generate secondary electron (SE) images, backscattered electron (BSE) images, and EDS test data. In addition, X-ray diffraction (XRD, D8advance 3.0, Bruker, Germany) was employed to characterize the crystalline structure of the TGO layer. All the samples were analyzed in the 2θ range 20–80° at a step size of 0.1°. The oxide and pore contents of the bond coats as well as the thickness of the TGO layers subjected to isothermal oxidation for different durations were measured by Image Tool software using the micrographs taken from the cross-sections of the tested samples. In order to protect the TGO scale from spalling off during the cutting and polishing of the tested samples, Ni-electroless plating was employed to deposit a layer of Ni on the bond coat surface.

Fig. 3. Lamellar inter-splat oxides and pores of the as-sprayed CoNiCrAlY bond coats: (a) SE image; (b) oxides; (c) pores.

Fig. 4. Cross-sectional microstructure of the interface between the as-sprayed CoNiCrAlY bond coats and the superalloy substrate: (a) BSE image; (b) EDS results of (a).
3. Results and discussion

3.1. Lamellar inter-splat oxides and pores of the as-sprayed coating

Fig. 2 shows the cross-sectional microstructure of the as-sprayed CoNiCrAlY bond coats. The high-magnification BSE image of Fig. 2(a) shows that the as-sprayed splats consisted of only one phase unlike the feedstock powder in which two phases coexisted (Fig. 1(b)). In the phase of the as-sprayed splats, the content of the metal elements was substantially the same as that in the nominal composition of the powder (only the content of Al decreased slightly from 15.9 to 12.4 at.%) (Fig. 2(b)). This indicates that the β phase of the feedstock powder
Fig. 7. Cross-sectional microstructure of the CoNiCrAlY bond coats after the isothermal oxidation for different durations: (a), (b) 4 h; (c), (d) 100 h; (e), (f) 400 h; (a), (c), (e) non-heat-treated bond coats; (b), (d), (f) heat-treated bond coats.

Fig. 8. Oxide and pore contents of the CoNiCrAlY bond coats after the isothermal oxidation for different durations: (a) oxide content; (b) pore content.
dissolved into its $\gamma$ phase during the coating deposition process. In addition, the $\beta$ phase could not precipitate out from the $\gamma$ phase during the rapid solidification of the melt splat. The reduction in the Al content of the as-sprayed splats indicates that Al was selectively oxidized during the coating deposition process.

Fig. 2(a) also shows that a large number of lamellar alumina films existed in the coating. These alumina films were relatively continuous and smooth and most of them existed between the adjacent splats. It is worth noting that the adjacent splats were not completely in contact with each other. It can be clearly seen from the high-magnification SE image of Fig. 3(a) that lamellar pores existed between some of the adjacent splats. The amounts of the lamellar inter-splat oxides and...
 pores of the as-sprayed bond coats (Fig. 3(b) and (c)) could be calculated by adjusting the threshold of the SE image (Fig. 3(a)) in Image Tool software. The statistical results showed that the oxide and pore contents of the as-sprayed bond coat were 6.53 ± 0.37% and 0.46 ± 0.03%, respectively. Since these lamellar oxides and pores were present between the adjacent splats, the metal phases of the splats were mostly isolated from each other (Figs. 2(a) and 3(a)).

Fig. 4(a) shows the cross-sectional microstructure of the interface between the as-sprayed CoNiCrAlY bond coats and the superalloy substrate. A small part of the interface between the splat wrapped by a layer of alumina film and the substrate showed close contact. However, at most of the points, lamellar pores were present between the as-sprayed coating and the substrate. The EDS line analysis results (Fig. 4(b)) showed that the Ni, Co, Cr, Al, Ti, W, Mo, and Ta contents were different on both sides of the coating-substrate interface. On the coating side, the Co, Cr, and Al contents were higher, while the Ni, Ti, W, Mo, and Ta contents were higher on the substrate side. This difference is consistent with the nominal element contents of the powder and substrate. This implies that there was no significant diffusion of elements between the as-sprayed coating and the substrate because of the presence of lamellar oxides and pores.

3.2. Dispersed spherical oxides of the heat-treated coating

Fig. 5 shows the cross-sectional microstructure of the controlled atmosphere heat-treated CoNiCrAlY bond coats. After the heat treatment, the β phase precipitated from the supersaturated γ phase. In addition, the morphology of the lamellae of films between the adjacent splats changed significantly. These originally smooth alumina films transformed into spherical particles with discontinuous distribution. The statistical results for the pore content of the bond coats showed that after the heat treatment, the lamellar pores in the coating decreased from 0.46 ± 0.03% (as-sprayed state) to 0.05 ± 0.01%. This significant reduction in the pore content indicates that the lamellar pores present between the adjacent splats in the as-sprayed coating closed after the heat treatment. As shown in Fig. 5(a), as a result of the closure of the pores and the morphological changes of the oxide films, the metal phases of the adjacent splats came in contact with each other.

Fig. 6(a) shows the cross-sectional microstructure of the interface between the heat-treated CoNiCrAlY bond coats and the superalloy substrate. At the coating-substrate interface, a number of small alumina particles were present. Moreover, in the region between these alumina particles, the metal phases of the splat and the substrate were in contact with each other. The EDS line analysis results (Fig. 6(b)) showed that the Ni, Co, Cr, Al, Ti, W, Mo, and Ta contents on both sides of the coating-substrate interface (within 5 μm depth) changed slowly. Compared to the as-sprayed coating (Fig. 4), the heat-treated coatings showed diffusion of elements between the coating and the substrate. However, it is worth noting that the diffusion of elements during the heat treatment did not cause significant microstructural changes (such as the formation of secondary phases and Kirkendall porosity [40]) near the coating-substrate interface.

3.3. Isothermal oxidation behavior of the non-heat-treated and heat-treated coatings

Fig. 7 shows the cross-sectional microstructures of the CoNiCrAlY bond coats subjected to isothermal oxidation for different durations. It can be clearly seen from Fig. 7(a), (c), and (e) that after the isothermal oxidation, the alumina in the non-heat-treated bond coats showed a lamellar structure and the metal phases of the adjacent splats were still separated by the lamellar alumina film. However, as shown in Fig. 7(b), (d), and (f), the alumina particles in the heat-treated bond coats were spherical in shape with a discontinuous distribution and the metal phases between the adjacent splats were connected to each other. This is consistent with the microstructural observations of the heat-treated bond coats (Fig. 5(a)). It was found that the oxide content in the non-heat-treated bond coats increased gradually with an increase in the isothermal oxidation time. On the other hand, no significant change was observed in the oxide content of the heat-treated bond coats after the isothermal oxidation (Fig. 8(a)). As shown in Fig. 8(b), the pore contents of the isothermally oxidized non-heat-treated and heat-treated bond coats were comparable to those of the as-sprayed bond coats and the non-oxidized heat-treated bond coats, respectively. The pore content showed no significant change with an increase in the isothermal oxidation time. Furthermore, from the high-magnification images we can see that after 400 h of isothermal oxidation, the sput of the non-heat-treated bond coats (Fig. 9(a)) contained only the γ phase, and the Al content (3.0 at.%) in this phase was significantly lower than that of the feedstock powder (10.8 at.%). On the other hand, similar to the case for the non-oxidized heat-treated bond coats (Fig. 5(a)), the sput of the oxidized heat-treated bond coats (Fig. 9(b)) contained a large amount of the β phase. The reduction of the β phase and Al content in the sput of the non-heat-treated bond coats indicates that Al in these bond coats underwent a severe selective oxidation during the isothermal oxidation. In addition, as shown in Fig. 10, the substrate of the non-heat-treated coatings underwent severe oxidation during the isothermal treatment. The substrate of the heat-treated coatings on the other hand, did not oxidize. On the basis of these results, it can be stated that the controlled atmosphere heat treatment significantly inhibited the oxidation of the
bond coats during the isothermal oxidation.

Fig. 11 shows the XRD patterns of the bond coats subjected to isothermal oxidation for different durations. In the case of the non-heat-treated bond coats (Fig. 11(a)), the mixed-oxide \(((\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4\text{ spinel})\) TGO was formed after 4 h of oxidation. On the other hand, in the case of the heat-treated bond coats (Fig. 11(b)), the mixed-oxide TGO was not formed until the isothermal oxidation time reached 400 h. To know the reason behind this phenomenon, the cross-sectional microstructure of the TGO layer was observed.

Fig. 12 shows the cross-sectional microstructure of the TGO layer of the bond coats subjected to isothermal oxidation for different durations. As can be seen from these images, the thickness of the TGO layer increased gradually with an increase in the isothermal oxidation time. It is noteworthy that after 4 h of isothermal oxidation, the TGO layer on the surface of the non-heat-treated bond coat divided into two layers with significantly different contrast. The EDS results shown in Fig. 13(a) revealed that O, Al, Co, and Cr were present in large amounts in the outer TGO layer, while the inner layer consisted mainly of O and Al. This indicates that the outer layer was the mixed-oxide \(((\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4\text{ spinel})\) TGO layer, while the inner layer was \(\alpha\text{-Al}_2\text{O}_3\) TGO. This is consistent with the XRD results shown in Fig. 11(a). In addition, the thickness of the outer mixed-oxide TGO layer of the non-heat-treated bond coats increased gradually with an increase in the isothermal oxidation time. However, the thickness of the inner \(\alpha\text{-Al}_2\text{O}_3\) TGO layer did not change significantly with the isothermal oxidation time. In the case of the heat-treated bond coats, only \(\alpha\text{-Al}_2\text{O}_3\) was present in the TGO layer during the initial stage of isothermal oxidation (Figs. 11(b), 12(b), and 13(b)). The thickness of this \(\alpha\text{-Al}_2\text{O}_3\) TGO layer increased gradually with an increase in the isothermal oxidation treatment time. The mixed-oxide \(((\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4\text{ spinel})\) TGO layer was not observed on the surface of the \(\alpha\text{-Al}_2\text{O}_3\) TGO layer until the isothermal oxidation time reached 400 h (Fig. 12(f)). These results
show that the controlled atmosphere heat treatment significantly inhibited the formation of the mixed-oxide TGO layer on the surface of the bond coats during the isothermal oxidation.

In order to determine the growth rate of TGO, the thickness of the TGO layer on the surface of the bond coats subjected to isothermal oxidation for different durations was measured to obtain the TGO growth curves. The TGO thickness $\delta$ was defined as:

$$\delta = \frac{\sum \text{(cross-sectional TGO area)}}{\sum \text{(cross-sectional length of TGO/BC interface)}}$$  \hspace{1cm} (1)

This approach helped to simplify the complexity arising from the rough surface morphology of the bond coats as well as the heterogeneous growth of TGO especially when mixed oxides were formed on the surface of the bond coats [24]. The relationship between the thickness of the entire TGO layer and the square root of the isothermal oxidation time is shown in Fig. 14. As shown in Fig. 14, the scattered points fitted to a straight line, indicating that the TGO thickness had a good parabolic relationship with the oxidation duration. It is worth noting that the oxidation rate constant of the heat-treated bond coats was 0.14 $\mu$m/h$^{1/2}$, which is comparable to that of LPPS bond coats [35]. However, the non-heat-treated bond coats showed an oxidation rate constant of 0.26 $\mu$m/h$^{1/2}$. The oxidation rate constant of the non-heat-treated bond coats was about twice that of the heat-treated bond coats, indicating that the controlled atmosphere heat treatment significantly reduced the TGO growth rate of the APS bond coats.

### 3.4. Heat treatment reducing the growth rate of TGO

It has been reported that during isothermal oxidation of bond coats, the growth of the TGO layer on their surface can be controlled by adjusting the parameters that govern the TGO composition and structure such as: the (i) partial oxygen pressure, (ii) oxidation temperature, and...
(iii) bond coat composition and microstructure [27, 41, 42]. Since the oxygen content in the surrounding environment and the oxidation temperature were constant during the isothermal oxidation in air, the TGO growth of the heat-treated and non-heat-treated APS bond coats was mainly affected by the microstructure of the coating. Therefore, the effect of the changes in the interfacial microstructure of the bond coats on the growth of the TGO on the surface of the as-sprayed splats was covered with a layer of alumina formed during the coating deposition (Fig. 2). Oxygen first contacted the alumina film during the isothermal oxidation. Previous studies have shown that the growth of alumina is mainly dominated by the inward diffusion of oxygen so that it can diffuse into the interior of splats through the alumina film and react with the metal elements in the splats [43, 44]. Compared to Co, Ni, and Cr, Al has the lowest free energy change of reaction. Hence, the selective oxidation of Al occurred first in the splat [45]. This increased the thickness of the alumina film between the adjacent splats during the isothermal oxidation (Fig. 7). At the same time, because of the inward growth of the alumina film, these lamellar pores between the adjacent splats did not close during the isothermal oxidation. As a result, the oxide content of the bond coats increased gradually with an increase in the isothermal oxidation time. However, the pore content remained unchanged (Fig. 8). The increased thickness of the alumina film also implies that a large amount of Al in the splat was consumed, thus reducing the Al-content within the splats and the β phase content (Fig. 9(a)).

In the case of the original α-Al2O3 TGO layer on the surface of the outer splats, oxidation was severe because of its direct exposure to the atmosphere. The continued growth of the original α-Al2O3 TGO layer required a continuous supply of Al. However, a large amount of Al was consumed during the oxidation of the coating. Meanwhile, the lamellar alumina films between the adjacent splats blocked the continuous supply of Al from the internal splats to the outer splats [46]. When the Al supply was not adequate, Co, Ni, and Cr in the splats diffused outward through the original α-Al2O3 TGO and reacted with oxygen to form mixed-oxide TGO [19, 22, 42]. Therefore, the non-heat-treated bond coats formed mixed oxides during the early stages of isothermal oxidation, and the thickness of this mixed-oxide TGO layer increased gradually with an increase in the isothermal oxidation time. On the other hand, the thickness of the original α-Al2O3 TGO layer did not change significantly with the isothermal oxidation time (Fig. 12). On the basis of these results, it can be stated that the lamellar alumina films and pores of the as-sprayed bond coat facilitated the early formation of the mixed-oxide TGO layer during the isothermal oxidation.

Fig. 15(b) shows the schematic diagram of the microstructural changes of the heat-treated bond coats subjected to isothermal oxidation. As shown in Fig. 15(b), the closure of the lamellar pores between the splats of the heat-treated bond coats inhibited the diffusion of atmospheric oxygen into the bond coats. Therefore, the internal structure of the heat-treated coating remained unchanged during the isothermal oxidation (Fig. 9(b)). As a result, the oxide and pore contents of the coatings remained unchanged (Fig. 8). The internal oxide content of the bond coats remained unchanged. This indicates that a large amount of Al was retained in the metal phase of the splats. On the other hand, after the heat treatment, the lamellar alumina films between the adjacent splats in the coating transformed into spherical alumina particles with discontinuous distribution (The transformation of lamellar alumina to spherical alumina particles during heat treatment is caused by alumina film agglomeration. Thompson showed that solid films are usually unstable in the as-deposited state and they agglomerate to form islands when heated to sufficiently high temperatures. This process is driven by surface energy minimization and can occur via surface diffusion well below the melting temperature of a film [47]). Hence, the metal phases of the adjacent splats were in contact with each other (Fig. 5). During the isothermal oxidation process, the presence of a large amount of Al and the elimination of the diffusion barrier for Al resulted in the continuous growth of α-Al2O3 TGO on the surface of the bond coats, thereby inhibiting the formation of the mixed-oxide TGO (Fig. 12). In summary, the closure of the pores as well as the morphological changes of the alumina films in the heat-treated bond coats led to the continuous growth of pure α-Al2O3 TGO on their surface during the isothermal oxidation.

4. Conclusions

1. In the case of the non-heat-treated CoNiCrAlY bond coats, mixed-oxide TGO was formed after 4 h of isothermal oxidation. However, mixed-oxide TGO was not observed in the heat-treated CoNiCrAlY bond coats until the isothermal oxidation time reached up to 400 h.

2. The oxidation rate constant of the non-heat-treated bond coats was 0.26 μm/h1/2, while that of the heat-treated bond coats was 0.14 μm/h1/2 (equivalent to that of LPPS CoNiCrAlY bond coats).

3. During the controlled atmosphere heat treatment, the lamellar pores in the bond coats closed, and the lamellar alumina films between the adjacent splats transformed from smooth alumina films to spherical alumina particles with discontinuous distribution.

4. The closure of the pores as well as the morphological changes of the oxide films in the heat-treated bond coats promoted the continuous growth of pure α-Al2O3 TGO on their surface during the isothermal oxidation.

Fig. 15. Schematic diagram of the microstructural changes of the CoNiCrAlY bond coats during isothermal oxidation: (a) non-heat-treated bond coats; (b) heat-treated bond coats.
This work was supported by the National Science Foundation of China (Grant No. 51671159), the Fundamental Research Funds for the Central Universities, and the National Program for Support of Top-notch Young Professionals.

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