The Oxide Scale Formation and Evolution on Detonation Gun Sprayed NiCrAlY Coatings during Isothermal Oxidation

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NiCrAlY coatings were prepared by the newly-developed detonation gun spray process. The oxide scale formation and evolution on these coatings during isothermal oxidation in air at 1100°C were investigated. It was found that semi-molten particles, particle debris and pores, are present in the surface layer of the as-sprayed coating. During 100 h oxidation, the particle debris and some semi-molten particles gradually change into oxide mixture consisting of spinel, chromia and nickel oxides. However, after removal of the surface layer of the coating by a grinding treatment, a dense and single-layer $\alpha$-Al$_2$O$_3$ scale forms on the surface of the coating during the oxidation. The mechanisms governing the oxide scale formation and evolution are discussed in terms of atomic diffusion and thermodynamic stability. In addition, thermogravimetric analysis showed that the oxidation rate of the ground NiCrAlY coating at 1100°C is much lower than that of the as-sprayed one. The residual stress in thermally grown oxide scales was investigated using photo-stimulated luminescence spectroscopy.

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1. Introduction

Thermal barrier coatings (TBCs) are generally comprised of a thermally insulating ceramic top coat and a MCrAlY (where M = Ni, Co, or both) bond coat. The MCrAlY bond coat plays an important role in protecting the underlying alloy substrate against high temperature oxidation and providing better adhesion of the top coat to the substrate.\textsuperscript{1) The MCrAlY coating is generally fabricated by low pressure plasma spray (LPPS), vacuum plasma spray (VPS) or air plasma spray (APS) techniques in industrial practice.\textsuperscript{1–3) However, the recently developed detonation gun spray process offers a competing technology to deposit the MCrAlY coating.\textsuperscript{4–6) Compared with MCrAlY coatings produced by conventional plasma spray processes, the detonation gun sprayed MCrAlY coating has a denser microstructure, improved adhesion to the substrate due to a high particle velocity, and lower energy cost.\textsuperscript{4–6) During high temperature oxidation, a thermally grown oxide (TGO) layer forms on the surface of the MCrAlY coating. The microstructure, growth rate and adherence of this TGO layer determine the durability of TBCs to some extent.\textsuperscript{7,8) A dense $\alpha$-Al$_2$O$_3$ scale is always desirable because it offers excellent protection for the substrate due to its slow growth rate and thermodynamic stability at high temperatures.\textsuperscript{8) Previous studies showed that the deposition method and parameters can affect the composition and the microstructure of the TGO scale significantly.\textsuperscript{9–11) Choi et al.\textsuperscript{9) reported that microstructure inhomogeneities in air plasma sprayed NiCrAlY coatings, such as oxide stringers and improperly flattened zones, accelerate oxide phase evolution process locally. Tang et al.\textsuperscript{10) found that the oxide scale formation on the NiCrAlY coatings can be significantly affected by the degree of oxidation that occurred in the coatings during a high velocity oxygen fuel spray (HVOF) spraying process. Shibata et al.\textsuperscript{11) compared the microstructures and oxidation behaviors of CoNiCrAlY coatings prepared by LPPS, APS and HVOF processes and found that Al concentration in the coating is the predominant parameter in determining the microstructure development during oxidation. As to the newly-developed detonation gun sprayed NiCrAlY coatings, the typical microstructural characteristics of this coating and their influences on the oxide scale formation and evolution during the subsequent thermal exposure have not been studied although Wu and co-worker have optimized spray parameters for depositing TBCs with this process.\textsuperscript{4) In the present study, the NiCrAlY coatings were deposited on a nickel base superalloy substrate using the detonation gun spray process. Then, the oxide scale formation and evolution on the as-sprayed and the post surface treated NiCrAlY coatings during 100 h oxidation in air at 1100°C were investigated. The oxidation resistances of these two coatings and residual stress in the corresponding TGO scales were compared.

2. Experimental Procedures

The substrate material was a nickel base superalloy with a chemical composition of Cr 8.8, Co 9.6, Mo 1.5, W 10.5, Al 5.5, Ti 2.5, Nb 1.0, C 0.18 and Ni balance (mass%). Ni-25Cr-5Al-0.5Y alloy powder (200 to 320 mesh) was used to coat the superalloy plates of $15 \times 10 \times 4$ mm in dimensions by the detonation gun spray process. The spray equipment was an automatic ob-type detonation spray system (Lavrent’ev Institute of Hydrodynamics, Russian Academy of Sciences). The spray parameters have been described elsewhere.\textsuperscript{4) Specimens for oxidation mass gain measurement were sprayed on all six surfaces. The thickness of the as-sprayed NiCrAlY coatings was about 120μm. The oxygen contents in the NiCrAlY powders and corresponding as-
sprayed coatings were determined by a TC-436 Nitrogen/Oxygen determinator. Some as-sprayed coatings were post surface treated by grinding with 1200-grit sandpapers to remove the loose surface layer prior to the isothermal oxidation tests.

The as-sprayed and the ground NiCrAlY coatings were oxidized in air at 1100°C in an electric resistance furnace. Weight measurements were made at varying time intervals during the 100 h oxidation test using a balance with a sensitivity of 0.01 mg. Each weight gain measurement was an average value of three specimens. Before and after the oxidation test, the coatings were examined using the X-ray diffractometer (XRD) and scanning electron microscope (SEM) with an energy-dispersive spectrometer (EDS). The residual stress in the TGO scale was measured by the shift of the photo-stimulated luminescence spectrum from Cr³⁺ incorporated into the TGO scale according to the method described elsewhere. The individual measurement was made at different points on the TGO scale surface and the stress value was determined from an average of 15–20 measurements.

3. Results and Discussion

3.1 Microstructure of the as-sprayed NiCrAlY coating

Figure 1 shows typical microstructures of the as-sprayed NiCrAlY coating on the nickel base superalloy. Due to the high particle velocity in the detonation gun spray process, in the interior of the coating a dense and uniform microstructure was obtained through consecutive and forceful impingements of droplets onto the surface of the specimen, as shown in Fig. 1(a). However, the surface layer of the coating exhibits a rough and loose microstructure because the surface layer is not exposed to the droplet impingements repeatedly during the spraying process as compared with the interior layer (Fig. 1(a) and Fig. 1(b)). Three kinds of typical microstructures, i.e. the semi-molten particles, particle debris and pores, can be observed in the surface layer of the as-sprayed coating, as shown in Fig. 1(b). The particle debris was produced as a result of broken molten or semi-molten particles. It can be seen in Fig. 1(b) that the particle debris contains a large number of pores in its interior, and some semi-molten particles have a weak adherence to the bulk coating below them.

The XRD pattern in Fig. 2 shows that the as-sprayed NiCrAlY coating primarily consists of γ and γ’ phases. The oxides formed on the coating surface during the spraying process cannot be detected by the XRD analysis due to their small amount. However, such oxides can be observed along the particle boundaries of the as-sprayed coating, as shown in Fig. 3(a) and Fig. 3(b). The composition result shown in Fig. 3(b) is an EDS analysis of the oxide stringer in Fig. 3(a). These oxide stringers are sparsely distributed in the coating. The gas analysis shows that the oxygen contents of the original NiCrAlY powder and corresponding as-sprayed coating are 0.028 and 0.25 mass%, respectively. The above results mean that the NiCrAlY coating is only slightly oxidized during the detonation gun spraying process. Tang et al. investigated the influence of the oxygen content in a HVOF sprayed NiCrAlY coating on the composition and microstructure of the oxide scale formed on the coating during the oxidation in air at 1000°C. Their experimental results indicated that with the increase of the oxygen content (from 0.98 to 7.65 mass%) in the as-sprayed coating, the oxides formed on the coating change from dense α-Al₂O₃ to porous NiCr₂O₄ and Cr₂O₃ oxide mixture during the oxidation, and therefore the high oxygen content is harmful to the oxidation resistance of the coating. Accordingly, it can be expected that due to the low oxygen content value (0.25 mass%), the oxygen in the present detonation gun sprayed NiCrAlY coating should have little influence on the oxide scale formation during the oxidation test.
3.2 Oxide scale formation and evolution on the as-sprayed NiCrAlY coating

The initial 0.5 h oxidation of the as-sprayed NiCrAlY coating in air at 1100°C results in the formation of a grey oxide layer, as shown in Fig. 4(a) and Fig. 4(b). The EDS line-scan analysis shows that this grey layer contains Ni, Cr, Al and O (Fig. 4(b)). From the XRD spectra in Fig. 5, it can be identified that the grey layer is an oxide mixture consisting of spinel Ni(Cr,Al)₂O₄, Cr₂O₃, NiO and α-Al₂O₃. In addition, it can be noted in Fig. 4(a) that there are significant amounts of grey oxide mixture in the particle debris zone because this zone has a large number of open pores that provide easy penetration paths for the oxygen and the specific surface area for oxidation in this zone is larger. Also, some air might be trapped in the closed pores after coating deposition, leading to subsequent internal oxidation. Furthermore, these pores may hinder the diffusion of Al from the coating interior to the surface, resulting in the local Al-depletion and severe oxidation in the particle debris zone during the oxidation.

A layer of darker oxides under the grey oxide mixture on the semi-molten particles can be seen in Fig. 6(a) and Fig. 6(b). The XRD and EDS line-scan analyses show that the darker oxide scale primarily consists of α-Al₂O₃ (Fig. 5 and Fig. 6(b)). The formation of this duplex oxide scale on the coating can be explained by the Al and O activity near the coating surface. In the initial oxidation stage, in addition to α-Al₂O₃, significant amount of Cr₂O₃ and NiO form on the coating due to a low Al content in the coating and the loose microstructure of the surface layer. Consequently the spinel Ni(Cr,Al)₂O₄ forms via solid phase reactions between the Al₂O₃ (or Cr₂O₃) and NiO oxides.\(^{15,16}\) After the formation of a layer of grey oxide mixture, the oxygen partial pressure at the interface between the metal and the oxide layer decreases to below the equilibrium partial pressure of the Cr₂O₃ and NiO, as a result only the Al₂O₃ forms when sufficient Al is supplied to the oxide layer/metal interface by diffusion from the coating interior. Thus, a dense α-Al₂O₃ subscale forms and grows into a continuous layer below the grey oxide formation during the detonation gun spraying process.
mixture. Similar phenomena have been observed in the HVOF sprayed MCrAlY coatings.\textsuperscript{10,17}

As mentioned above, some semi-molten particles in the surface layer have a weak adherence to the underlying bulk coating and there are some pores in the interface area between the bulk coating and particles (Fig. 1(b)). Therefore, during high temperature oxidation, it is easy for the oxygen to reach these pores, leading to the internal oxidation in this area. As shown in Fig. 6(a), the surface semi-molten particle is partly separated from the bulk coating by the internal oxides in the interface zone. Such a separation may cause severe Al-depletion in the interior of the particle, because the diffusion path for Al from the bulk coating to the particle is blocked by these internal oxides. In addition, it can also be seen in Fig. 6(a) that the particle debris zone has changed completely into the grey oxide mixture after 50 h oxidation due to the fast oxidation of the porous microstructure, and a layer of darker $\alpha$-$\text{Al}_2\text{O}_3$ scale forms below the oxidized particle debris zone.

Further oxidation causes the semi-molten particle to be completely surrounded by the oxides, as shown in Fig. 7(a).

Thus, the interior of the isolated particles gradually becomes Al-depleted. Under this condition, the growth of $\alpha$-$\text{Al}_2\text{O}_3$ begins to slow down at a point during oxidation. Alternatively the Ni and Cr cations outwardly diffuse into the $\alpha$-$\text{Al}_2\text{O}_3$ layer and react with the inward diffusing oxygen near the interface between the $\alpha$-$\text{Al}_2\text{O}_3$ and the grey oxide mixture, then the newly formed NiO reacts with the $\alpha$-$\text{Al}_2\text{O}_3$ (or newly formed $\text{Cr}_2\text{O}_3$) to produce the spinel Ni(Cr,Al)$_2$O$_4$.\textsuperscript{18–20} In the meantime, less fresh $\alpha$-$\text{Al}_2\text{O}_3$ forms with oxidation time at the alumina/alloy interface due to Al-depletion in the particle interior. As a result, the whole isolated particle changes into the grey oxide mixture gradually, as shown in Fig. 7(b). EDS analysis demonstrated that Ni and Cr contents of the unoxidized particle interior in Fig. 7(b) were 88.56 and 11.44 mass\%, respectively, while Al in this region could not be detected by the EDS method. This composition agrees well with the above drawn conclusion. Teratani \textit{et al.}\textsuperscript{21} investigated the oxidation behavior of the unmelted CoNiCrAlY particle on LPPS CoNiCrAlY bond coat and its effect on the mechanical behavior of top coat. They found that the formation of multiple oxides in the unmelted CoNiCrAlY particle causes local fracture of top coat. Therefore, for the detonation gun sprayed TBCs, such severe oxidation of the semi-molten NiCrAlY particle should be avoided to increase the lifetime of TBCs.

As such, the total oxide scale formation and evolution process on the as-sprayed NiCrAlY coating during high temperature oxidation up to 100 h can be described by four steps as schematically presented in Fig. 8. The as-sprayed
coating has three typical microstructures, i.e., the semi-molten particles, particle debris, and pores (Fig. 8(a)). And the four steps are: (1) Step I, a single layer of grey oxide mixture forms on the coating surface and the internal oxidation occurs in the particle debris zone and pores (Fig. 8(b)); (2) Step II, a darker $\alpha$-$\text{Al}_2\text{O}_3$ subscale develops on the coating surface and the particle debris zone changes completely into grey oxide mixture (Fig. 8(c)); (3) Step III, some semi-molten particles are separated from the bulk coating by the oxides and the interior of these particles suffers severe Al-depletion (Fig. 8(d)); (4) Step IV, due to severe Al-depletion in the isolated particle interior, the whole isolated particles gradually change into grey oxide mixture (Fig. 8(e)).

3.3 Oxide scale formation on the ground NiCrAlY coating

Previous studies showed that other than the spraying process, the surface treatment of the as-sprayed MCrAlY coating also has a significant influence on the formation of TGO scales during the oxidation. For instance, the chromate treatment of the LPPS CoNiCrAlY bond coat can protect the unmelted CoNiCrAlY particles from fully oxidation by promoting the preferential formation of an $\text{Al}_2\text{O}_3$ layer in the early stage of oxidation. Concerning the surface remelting treatments, it has been shown that the pulsed electron beam treated LPPS CoNiCrAlY coating has a strongly enhanced oxidation resistance without spinel formation in the oxide scale. The laser remelting treatment of plasma sprayed NiCrAlY coating brings a homogeneous and dense remelted layer and improves the oxidation resistance of the coating. Regarding mechanical treatment after coating deposition, the study of Guo et al. showed that the shot-peening treatment of EBPVD NiCoCrAlY coating increases the bond strength of the TGO layer. Also, the study of Monceau et al. showed that the grit blasting treatment of modified nickel aluminides bond coat can prevent the TGO from spalling to some extent.

As to the detonation gun sprayed NiCrAlY coating, this coating has a unique microstructure. The surface layer of this coating is rough and loose; however, its interior is dense. Therefore, appropriate surface treatments to remove or modify the loose surface layer may have a significant effect on improving the oxidation resistance of this coating. Hence, in this research, some as-sprayed coatings were post-surface treated by grinding with 1200-grit sandpapers to remove the loose surface layer. As shown in Fig. 9(a), the ground coating has a smooth surface except for some little pits that originate from the subsurface pores. After 10 h oxidation in air at 1100°C, the smooth surface of the ground coating is mostly covered by uniform dark oxides, as shown in Fig. 9(b). In addition, a small amount of grey oxides present on the coating surface (Fig. 9(b)). EDS maps of the oxides in Fig. 9(b) show uniform dark oxides, as shown in Fig. 10. According to the EDS maps in Fig. 10 and the XRD spectrum in Fig. 11, it can be concluded that the dark oxides are $\alpha$-$\text{Al}_2\text{O}_3$. EDS maps (Fig. 10) suggest that the grey oxides are primarily NiO. The cross section SEM images of the oxidized ground coating and EDS line-scan results show that the $\alpha$-$\text{Al}_2\text{O}_3$ scale is dense and primarily has a single-layer structure (Fig. 12(a) and Fig. 12(b)). A duplex oxide scale forms only on the pit surface which was not ground, as shown in Fig. 12(c). The formation of the dense and single-layer $\alpha$-$\text{Al}_2\text{O}_3$ scale on the ground coating can be attributed to two reasons. Firstly, the semi-molten particles, particle debris and pores in the surface layer of the as-sprayed coating are removed by the post surface treatment. Thus, the surface of the coating becomes smooth and dense, which greatly decreases the specific surface area for oxidation and avoids local Al-depletion in the surface layer. Also, the dense microstructure of the ground coating is beneficial to the diffusion of Al from the coating interior to the surface. Secondly, the surface grinding introduced deformation defects near the coating surface, such as dislocations. During the heating and initial oxidation, these dislocations introduced by surface grinding can serve as fast-diffusion paths for the supply of Al to the coating surface and promote the formation of the dense and single-layer $\alpha$-$\text{Al}_2\text{O}_3$ scale.
3.4 Isothermal oxidation kinetics and residual stress in TGO scales

Figure 13 presents the mass gain as a function of oxidation time for the as-sprayed and the ground NiCrAlY coatings at 1100°C. The oxidation kinetics curve of the ground coating shows much lower mass gain than that of the as-sprayed one. The difference in oxidation resistance between the as-sprayed and the ground coatings is due to their different oxidation behaviors. As mentioned previously, these two coatings exhibit different TGO microstructure and composition during high temperature oxidation. For the as-sprayed coating, the extensive growth of grey oxide mixture consisting of spinel Ni(Cr,Al)₂O₄, Cr₂O₃ and NiO leads to a rapid weight gain.²⁷ In addition, some semi-molten particles and particle debris zone in the loose surface layer of the as-sprayed coating are severely oxidized and transformed completely into grey oxide mixture during the subsequent oxidation, which also increases the oxidation rate greatly. In contrast, for the ground coating, due to the removal of the loose surface layer and the introduction of rapid paths for Al diffusion to the surface, a dense, continuous and protective α-Al₂O₃ scale forms on the coating during the oxidation. The formation of this protective α-Al₂O₃ scale leads to a lower oxidation rate for the ground coating.

The evolution of the residual compressive stresses in TGO scales of the as-sprayed and ground NiCrAlY coatings with oxidation time is shown in Fig. 14. It can be seen in Fig. 14 that the residual compressive stress in TGO scales of the ground NiCrAlY coating is much higher than that of the as-sprayed one within 100 h. The difference in stress value between these two coatings can be mainly attributed to two reasons. Firstly, the as-sprayed coating has a much rougher surface than the ground coating, which decreases its compressive stress in TGO scales greatly. The model proposed by Aubry et al.²⁸ showed schematically how a rougher metal surface could allow an easier release and/or an adaptation of the compressive stresses in the oxide layer. Secondly, significant internal oxidation in the as-sprayed coating will introduce compressive stresses in the metal coating and hence tensile stresses in the surface oxide layer, also resulting in the decrease of the compressive stresses in TGO scales of the as-sprayed coating to some extent.

4. Summary

The oxide scale formation and evolution on the detonation gun sprayed NiCrAlY coatings during 100 h oxidation in air at 1100°C were examined. It was found that the as-sprayed coating has a rough and loose surface layer even though its interior is dense. The semi-molten particles, particle debris and pores in the loose surface layer of the coating result in the formation of a grey oxide mixture and impair the oxidation resistance of the detonation gun sprayed NiCrAlY coatings.
After the removal of this loose surface layer by a grinding treatment, a dense, continuous and protective $\alpha$-$\text{Al}_2\text{O}_3$ scale forms on the coating surface during the oxidation. The residual compressive stress in TGO scales of the ground NiCrAlY coating is much higher than that of the as-sprayed one within 100 h oxidation. All these indicate that the loose surface layer of the detonation gun sprayed NiCrAlY coating has a great influence on the oxidation resistance of this coating and residual stress in the corresponding TGO scales. Although the dense interior of this coating is favorable for the formation of a protective $\alpha$-$\text{Al}_2\text{O}_3$ scale, the loose surface layer determines the oxidation resistance of this coating to some extent. Therefore, appropriate surface treatments to remove or modify the loose surface layer may be advisable to improve the oxidation resistance of the detonation gun sprayed NiCrAlY coating.

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