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Effects of the β phase size and shape on the oxidation behavior of NiCoCrAlY coating

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Abstract

The effect of the β phase size and shape on the oxidation behavior of the NiCoCrAlY coating fabricated by laser powder deposition (LPD) was investigated. Thermal cycling experiment performed at 1150 °C indicates that β phase with smaller size and higher aspect ratio (dendritic or disc shape) benefits the exclusive formation of alumina, lower thermally grown oxides (TGO) growth rate and residual stress. The TGO lifetime of the LPD coating is almost a two-fold of that on the coating prepared by high velocity air fuel method, which is attributed to the nanoscale dendritic β phase and dense microstructure.

Key words: A. Metal coating; B. Thermal cycling; C. Selective oxidation; C interfaces .

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1. Introduction

Thermal barrier coatings (TBCs) are commonly deposited on the hot components of gas turbine to provide thermal insulation and, thereby, improve the efficiency and extend the lifetime of the turbine [1]. TBCs typically consist of a yttria-stabilized zirconia (YSZ) top layer, a MCrAlY (M=Ni or NiCo) metallic bond coat which usually consists of the γ/γ' phase and the β -NiAl phase, a superalloy substrate and a thermally grown oxides (TGO) layer which is formed between the top coat and the bond coat after oxidation at elevated temperatures. The durability of the TBCs is the most critical factor for the application. The composition, growth rate, adherence, microstructure and other characteristics of the TGO layer all play a critical role in the durability of TBCs [2, 3]. The premature spallation of the TGO layer is associated with the fast-growing oxides such as NiO, NiCr₂O₄, NiAl₂O₄ and other spinels [4]. Therefore, the formation of a protective and uniform α -Al₂O₃ layer via selective oxidation is desirable due to its low growth rate, low transport rate of other metals and good compatibility with the zirconia [5].

Previous works have shown that the MCrAlY coatings with nano grain size are beneficial for promoting the formation of a uniform α -Al₂O₃ layer and achieving better oxidation resistance [6, 7]. This is thought to be achieved by: (1) enabling faster Al diffusion as a result of more grain boundaries; (2) facilitating the alumina phase transformation from θ to α [8-10]. The MCrAlY coatings with nano grain size are typically fabricated using high velocity oxygen-fuel (HVOF), low pressure plasma spray (LPPS), air plasma spray (APS) and vacuum plasma spray (VPS) with cryomilled feedstock powder [11, 12]. It should be noted that not only the grain size but also the β phase size is reduced down to nanoscale during the milling process. Meanwhile, β phase is the alumina reservoir for the exclusive formation of the Al₂O₃. Therefore, it is of great importance to understand the effect of the size and shape of the β phase on the oxidation behavior. However, up to now, this has not been studied and

well understood. In our previous work, the NiCoCrAlY coating with nanoscale β phase was achieved by laser powder deposition (LPD) method which is proven to promote the formation of alumina and improve oxidation resistance compared with the coatings prepared by conventional methods [13].

In the present work, the objectives are to produce a dense NiCoCrAlY coating with dendritic and nano size β phase by LPD, and to evaluate the effect of the size and shape of the β phase on the oxidation behavior of the coatings. For comparison, the coating with larger phase size prepared by the LPD method and followed by 2 hours vacuum treatment at 1150 °C and coating prepared by high velocity air-fuel (HVOF) were also studied. Particular attention was paid to the effect of size and shape of β phase on the nucleation, phase transformation and growth of the alumina scale. Meanwhile, the residual stress, lifetime and failure behavior of the TGO layer formed on these coatings were characterized and analyzed after thermal cycling tests.

2. Materials and Methods

2.1 Sample preparation

The Nickel-based Hastelloy@X superalloy substrate was grit blasted and ultrasonically cleaned in acetone prior to deposition. Three types of bond coats were designed, namely the LPD coating (prepared by LPD), LPD-V coating (prepared by LPD and followed by 2 hours vacuum treatment at 1150 °C and pressures of $\leq 10^{-5}$ Pa) and HVOF coating (prepared by HVOF). The feedstock was a commercially available NiCoCrAlY powder (Ammdry 365-2, Oerlikon Metco) with the nominal compositions of Ni-23Co-17Cr-12Al-0.49Y in wt%. The deposition procedure for the LPD and HVOF processes can be found in our previous work and will not be repeated here [13].

2.2 Thermal cycling treatment

Prior to thermal cycling experiment, all the specimens were cut into $10 \times 10 \times 3 \text{ mm}^3$ plates. Then, all the coatings were mechanically ground down to $150 \text{ }\mu\text{m}$ in thickness, polished to a $0.1 \text{ }\mu\text{m}$ finish, and thoroughly cleaned with acetone. Several Vickers micro-hardness indentations were applied at the coating surfaces to act as markers. The thermal cycling experiment was carried out between room temperature and $1150 \text{ }^\circ\text{C}$ in a chamber furnace under ambient atmosphere. Each cycle consisted of a fast heat-up stage from room temperature to $1150 \text{ }^\circ\text{C}$, dwell time of 50 min, and 10 min fan-assisted air quenching after removing the specimens from the furnace.

2.3. Characterization method

X-ray diffraction (XRD, Ultimo IV, Riau, Japan) measurements at 30 kV with $\text{Cu } K_\alpha$ radiation were conducted to study the phase composition of the coatings. The spectra were collected in the 2θ range of $20 \sim 80^\circ$ with a step size of 0.02° , and a scanning speed of $0.5^\circ/\text{min}$. The morphology, microstructure and element distribution of the coatings before and after thermal cycling were characterized by scanning electron microscopy (SEM, FEI Quanta 200, Netherlands) equipped with energy dispersive spectroscopy (EDS). The radius, length and volume fraction of the β phase were quantified by image analysis using Image J software (National Institutes of Health, USA). At least five images with a magnification of $5000\times$ for each sample were measured. The surface roughness of the samples was characterized using optical profilometer (ZegageTM, Zygo, USA). The photoluminescence piezospectroscopy (PLPS) was employed to characterize the stress distribution using a confocal Raman microprobe (LabRAM HR, Horiba Jobin Yvon, France) with a 532 nm Nd:YAG laser. The position of each peak was evaluated through a deconvolution process using the commercial Labspec peak fitting software (Labspec, Horiba Jobin Yvon, France).

The residual stress was calculated based on the peak shift using a stress-free reference recorded from the unstrained sapphire.

3 Results

3.1 Microstructure of the as-deposited samples

Fig. 1 shows the surface microstructures of the LPD, LPD-V and HVOF coatings. The thickness of all the coatings is about 150 μm and the surface roughness is approximately 0.1 μm . The coatings prepared by LPD (shown in Fig. 1a and b) exhibit a dense microstructure and are free of cracks and oxide inclusions. For the HVOF coating, a small number of internal oxides stringers, pores and cracks occur around the unmelted particle boundaries. All types of coatings are characterized by two phases. The bright zone corresponds to the Al-poor γ/γ' matrix phase, while the gray zone corresponds to the Al-rich β phase. These two phases are also confirmed by the XRD analysis.

Fig. 1. The polished surface of the as-deposited (a) LPD coating, (b) LPD-V coating and (c) HVOF coating.

It should be noted that the size and shape of the β phase in these three types of coatings are strikingly different. The β phase in the as-deposited LPD coating is characterized by a “multimodal structure”, in which some regions (marked Region A in Fig. 1a) exhibit a dendritic microstructure with the radius r in nanoscale and a high aspect ratio (defined as the ratio between the length and radius l/r of the β phase), while the other regions (marked Region B in Fig. 1a) present a larger β phase size and much smaller aspect ratio. This “multimodal structure” is associated with the depositing process of the LPD coating which was prepared by overlapping of the scans (overlapping ratio of 25%). This leads to remelting and resolidification of the coating within the overlaid area, resulting in the increase of the grain size. The LPD-V coating shows a larger β phase due to the high-temperature vacuum treatment, and also exhibits two distinguishable regions corresponding to the “multimodal structure” in the as-deposited LPD coating. For the HVAF coating, the β phase is characterized by a spherical shape.

The radius, aspect ratio and volume fraction of β phase in these three types of coatings were quantitatively determined using image analysis as summarized in Table 1. The lower β phase volume fraction in the LPD coating could be related to inadequate precipitation of the β phase due to the rapid directional solidification and the local inter-diffusion between the substrate and the coatings during the LPD process [12]. The average size of the β phase of the HVAF coating is between the average size of the region A and region B in the LPD-V coating, but it exhibits a much lower aspect ratio.

Table. 1. The average radius, aspect ratio and volume fraction of the β phase in LPD, LPD-V and HVAF coatings.

		Radius r (μm)	Aspect ratio l/r	Volume fraction (%)
LPD coating	Region A	0.17 ± 0.05	87.55 ± 43.86	43.09
	Region B	0.49 ± 0.14	1.87 ± 0.82	
LPD-V coating	Region A	0.58 ± 0.17	15.96 ± 9.83	54.52
	Region B	3.19 ± 1.1	2.83 ± 1.7	
HVAF coating		1.33 ± 0.22		65.79

3.2. Surface morphology of the oxides

Surface morphologies of the as-deposited LPD, LPD-V and HVAF coatings, and the corresponding morphologies of the oxides formed after oxidation at 1150 °C for 20 min are shown in Fig. 2. The nucleation and formation of the oxides on these three types of coatings show distinctive features. A continuous alumina layer is formed on the surface of the LPD coating in both the A and B regions. However, for the LPD-V coating, the oxides on the region A is dense and uniform, but the alumina on the region B is discontinuous and inherits the contours of the underlying β phase. The blue-colored oxides corresponding to spinels are formed on the γ/γ' phase in region B [14]. For the HVAF coating, distinct blue spinel grains scatter around the defects (i.e., pores and cracks). It has been reported that the grain size has a significant effect on the selective oxidation of alumina when the grain size is less than 200 nm [15]. However, the grain size for these three coatings is in the order of several micrometers as revealed by surface etching using a solution of 100 mL HCl, 100 mL alcohol and 5 g CuCl_2 . Therefore, the influence of nano grain size on the oxidation behavior is thought to be negligible in the present work. Meanwhile, the residual stress in the different coatings was not considered due to the low yielding stress of the MCrAlY coating (soft at a

temperature over 900 °C) [16]. It can be concluded that β phase size has a significant influence on the nucleation of the alumina. Meanwhile, the small dendritic β phase and dense microstructure are beneficial for the formation of a uniform and continuous alumina layer at the early stages of oxidation.

Fig. 2. Optical images of the (a, d) LPD, (b, e) LPD-V and (c, f) HVAF coatings before (top) and after (bottom) oxidation at 1150 °C for 20 min. The boundaries of A and B regions are delineated with red dash line for clarity.

The difference in the oxides nucleation and growth caused by β phase can be clearly seen on the LPD-V coating, which exhibits a distinguished multimodal structure (large β phase in region B and small in region A) and the phase size is distributed in large range. Meanwhile, it can separate the effect of the β phase from the influence of the defects, element distribution and diffusion difference in different samples. To evaluate the oxidation behavior, the thermal cycling experiment at 1150 °C was carried out. Fig. 3 shows the surface of the as-deposited LPD-V coating and profilometer images recorded at the same region after 50 thermal cycles. The brighter areas in the Fig. 3b indicates that the TGO on region B is much thicker than that on region A. As seen based on the inset of Fig. 3b, the difference of the TGO thickness between regions A and B is about 2 μ m. The thickness difference of the TGO on these two

areas could be attributed to the larger size of β phases in region B, which prefers the formation of fast-growing spinel proved in Fig. 2e.

Fig. 3. Optical images of (a) the as-polished surface of the LPD-V coating and (b) the profilometer images for the same region after 50 thermal cycles. The inset shows the height profile of the white line.

3.3. Phase of the TGO layer

The PLPS measurements were conducted to characterize the phase of alumina on these three types of coatings after oxidation at 1150 °C for 20 min. The results are shown in Fig. 4. The PLPS spectra of the LPD and LPD-V coatings present the characteristic peaks of α -Al₂O₃, indicating the predominant α -Al₂O₃ in the TGO layer. While for the HVOF coating, the spectrum shows the peaks of both θ -Al₂O₃ and α -Al₂O₃, suggesting a mixture of these two phases in the TGO layer. More than 50 points were inspected on each coating, illustrating that the results are robust and reliable. These results indicate that the phase transformation (θ - α) of the alumina is not significantly determined by the size of β phase or nano grain size, but more dependent on the fabrication methods.

Fig. 4. PLPS spectra of the TGO scale on the LPD, LPD-V and HVAF coatings after oxidation at 1150 °C for 20 min.

Fig. 5 shows the XRD patterns of the oxides formed on the three types of coatings after 10 thermal cycles. The TGO layer on both of the HVAF coating and the LPD-V coating exhibits spinel phase. In contrast, TGO layer on the LPD coating is primarily composed of α - Al_2O_3 . This is consistent with the results shown in Fig. 2; that is, the blue-colored spinel phase can be found on the surface of the HVAF and LPD coatings, whereas the oxide layer on the LPD coating is homogenous.

Fig. 5. XRD patterns of the HVOF, LPD-V and LPD coatings after 10 thermal cycles at 1150 °C.

3.4. Spallation resistance

The thermal cycling tests were carried out at 1150 °C to evaluate the TGO spallation resistance of these three types of coatings. The surface of the TGO layer was checked by an optical microscope after every ten thermal cycles. The specimens were considered as failed as soon as any spallation of the TGO layer was detected. The thermal cycling results show that the TGO layer failed after 50, 80 and 90 thermal cycles for the HVOF, LPD-V and LPD coatings, respectively. The TGO layer on the LPD coating possesses the longest lifetime, which is slightly longer than that on the LPD-V coating, but almost two times longer than that on the HVOF coating. The average spallation degree (defined as the spalled area of the TGO layer to the total area of the specimen) of these three types of coatings after failure were measured using the Image J software as shown in the Fig. 6. The spallation degree of the HVOF coating was much higher than that of the coatings prepared by LPD. This is related to

the difference in defect density and failure modes which will be explained in the Discussion section.

Fig. 6. The spallation degree of the HVOF, LPD-V and LPD coatings after 50, 80 and 90 thermal cycles at 1150 °C, respectively. The scale bar shows the standard deviation.

3.5. Sectional microstructure after failure

Fig. 7 shows the fractured cross-sectional images of the TGO layer on the HVOF, LPD-V and LPD coatings when the TGO layer began to detach. For all the coatings, the TGO layer is characterized by a typical duplex layer microstructure. As confirmed by EDS analysis, the coarse outer layer contains a mixed oxides of Ni, Cr and Co. The inner layer is predominantly composed of α -Al₂O₃. It is worth mentioning that the outer TGO layer on the HVOF coating is more porous than that on the coatings prepared by LPD. This can be attributed to the formation of porous spinel and the volume shrinkage caused by the alumina phase transformation from θ to α at the early stages of oxidation. Meanwhile, a large amount of pores could be found at the interface of the outer and inner layers on the HVOF and LPD-V coatings, which could be a result of the volume contraction due to the solid reaction between the Al₂O₃ and NiO [17].

Fig. 7. SEM images of the TGO layer on the (a) HVOF, (b) LPD-V and (c) LPD coatings after 50, 80 and 90 thermal cycles at 1150 °C, respectively.

Fig. 8 presents the cross-sectional images and the corresponding EDS elemental mapping of the HVOF, LPD-V and LPD coatings after 50, 80 and 90 thermal cycles at 1150 °C, respectively. An electro-deposited Ni layer was added on the surface to protect the TGO layer during the polishing process. It could be noted that internal oxidation formed in the HVOF coating along the unmelted particle boundaries. Meanwhile, many cracks occurred in the TGO layer (Fig. 8 a) on the HVOF coating which could be related to the formation of the low-toughness and porous spinel phase. For the LPD and LPD-V coating, a dense and uniform TGO layer is formed and none of the internal oxidation was found. Based on the EDS results, the TGO layer on the LPD is predominately α -Al₂O₃ and a small amount of spinel was found on the surface of the LPD-V coating, while Cr and Ni are contained in the TGO layer of the HVOF coating (as spinel phase).

Fig. 8. The cross-sectional images and the EDS elemental mapping of the (a)HVOF, (b)LPD-V and (c)LPD coating after 50, 80 and 90 thermal cycles at 1150 °C, respectively.

3.6. Stress evolution of the oxides

The average stress of the TGO layer was measured based on the luminescence shift of α - Al_2O_3 using PLPS method, as shown in Fig. 9. Each data point in Fig. 9 is the average of more than 200 points with a step size of 3 μm and the error bar shows the standard deviation. It can be seen that the residual stress of the TGO layer on the HVOF coating increases with the number of cycles until fail. However, the residual stress of the TGO layer on the LPD and LPD-V coatings show a distinctly different trend, especially during the first 30 thermal cycles. The average stress on the LPD-V coating increases only slightly during the first 30 thermal cycles. On the contrary, for the LPD coating, the TGO stress is much higher at the beginning and decreases during the first 30 thermal cycles. This could be related to the discontinuous alumina nucleation at the initial stage which make the stress relaxation more easier. In

general, the TGO stress of the LPD coating is much higher than that of the LPD-V coating. In addition, TGO stress obviously decreases when detachment occurs.

Fig. 9. The average residual stress of the TGO layer as a function of the thermal cycles.

The high sensitivity of PLPS in combination with the high spatial resolution of the optical microscope enabled us to locate at the area marked with Vicker's indentations and characterize the stress of the oxides with a spatial precision in the order of a few micrometers [10]. The contour of stress on the surface of LPD-V coating after 50 thermal cycles is shown in Fig. 10. It can be seen that for region B which is characterized by larger β phase, the values of the stress are much higher. This is reasonable due to the formation of the fast-growing spinel within this region (as shown in Fig. 3).

Fig. 10. Optical image of (a) the as-deposited LPD-V coating and (b) the stress distribution of the same area after 50 thermal cycles.

4. Discussion

4.1. Effect of size and shape of β phase on the nucleation of alumina

The results presented in this study confirm that the size and shape of the β phase have a significant effect on the nucleation and exclusive formation of the alumina. For the LPD coating, nano scale β phase with high aspect ratio promotes the formation of a continuous α - Al_2O_3 layer. While for the HVAF and LPD-V coatings with larger β phases, the spinel phase is formed. Meanwhile, the TGO growth rate on the larger β phase is much higher than on the smaller one, as presented in Fig. 3b. A uniform, low growth rate α - Al_2O_3 layer is critical for the stability of the TGO layer. Therefore, the mechanisms of how the size and shape of the β phase affect the exclusive formation of the α - Al_2O_3 will be discussed here in detail.

The NiCoCrAlY coating typically consists of γ/γ' and β phases. The β phase is rich in Al and favors the formation of α - Al_2O_3 . Therefore, the exclusive nucleation and formation of α - Al_2O_3 layer will be controlled by the oxidation of the γ/γ' phase. The formation of the α - Al_2O_3 on the γ/γ' phase could be achieved when the Al concentration N_{Al}^{γ} in the γ/γ' phase exceeds a critical value which is related to the diffusion of Al in the β phase. The N_{Al}^{γ} could be written as[18]:

$$N_{\text{Al}}^{\gamma} \geq N_{\text{Al}(\text{min})}^{\gamma} \zeta(\eta) \quad (1)$$

with

$$N_{\text{Al}(\text{min})}^{\gamma} = \frac{V_c}{V_{\text{ox}}} \sqrt{\frac{\pi K_p}{\tilde{D}}} \quad (2)$$

where V_c and V_{ox} are the molar volume of the NiCoCrAlY coating and α - Al_2O_3 , respectively.

K_p is the parabolic rate constant of α - Al_2O_3 in cm^2/sec . $\tilde{D}$ is the interdiffusion coefficient of

Al in the γ/γ' phase. $N_{\text{Al}(\text{min})}^{\gamma'}$ is the critical Al concentration for the single γ/γ' phase to form an exclusive alumina layer [19]. Substituting with appropriate values ($V_c=7.0 \text{ cm}^3/\text{mol}$, $V_{\text{ox}}=25.6 \text{ cm}^3/\text{mol}$, $\tilde{D}=1.21 \times 10^{-11} \text{ cm}^2/\text{s}$ and $K_p=9 \times 10^{-13} \text{ cm}^2/\text{s}$) [20-23], the calculated critical Al concentration $N_{\text{Al}(\text{min})}^{\gamma'}$ is about 13.2% (mole fraction), which is in good agreement with the reported values in the literature [23].

$\xi(\eta)$ is related to the size and shape of the β phase. $\eta=\tilde{D}t/l$, is the distribution function. l is the diffusion distance of the Al in the β phase to the interface of metallic coating and the TGO layer. The distribution function of η over the coating/TGO interface is equivalent to the average η over a semi-infinite straight line with randomly distributed particles on it. Therefore, the $\xi(\eta)$ can be written in terms of a parameter z as [24]:

$$\xi(z)=\left[1+\sum_{n=1}^{\infty} z \exp\left(-\frac{z^2}{(4n)^2}\right) \int_{\frac{z}{4n^2}}^{\infty} \exp(-n^2 y^2) dy\right]^{-1} \quad (3)$$

with

$$z=P_L \sqrt{\tilde{D}t} \quad (4)$$

where y is the auxiliary variable; n is positive integer. Microstructure parameter P_L is the number of intercepts by the β phase in the alloy per unit length of a linear probe. It could be noted that the $\xi(z)$ is not only a function of the P_L but also a function of oxidation time t , as plotted in Fig. 11, indicating that the $\xi(z)$ decreases with the increase of t . This means that the Al concentration at the surface may not satisfy the requirement for the exclusive formation of the alumina at the initial stage, but it can be satisfied after a certain time. This could explain the formation of the dense and columnar alumina layer on both of the LPD and LPD-V coating after long term oxidation as shown in Fig. 8.

Fig. 11. The $\xi(z)$ as a function of the oxidation time t and microstructure parameter P_L .

Meanwhile, the $\xi(z)$ decreases with the increase of P_L . P_L is determined by the shape, volume fraction f and size of the β phase, which can be written as[24]:

$$P_L = \begin{cases} \frac{3f}{2r} & \text{(spherical shape with a radius } r) \\ \frac{3f}{a} & \text{(cubic shape with side length } a) \\ \frac{l+r}{lr}f & \text{(cylindrical shape with a radius } r \text{ and a length } l) \end{cases} \quad (5)$$

To clarify, the effectiveness of the different shape could be introduced, which is defined as the increase in P_L by increasing the volume fraction of the for a given initial β phase volume and can be written as [24]:

$$EFF. = \frac{1}{\sqrt[3]{V_0}} \frac{dP_L}{df} = \begin{cases} 3.22 & \text{Sphere} \\ 4.0 & \text{Cubic} \\ 1.84 \sqrt[3]{\frac{l}{r} \left[\frac{r}{l} + \frac{3}{2} \right]} & \text{Cylinder} \end{cases} \quad (6)$$

The effectiveness of these three different shapes as a function of the aspect ratio l/r is plotted in Fig. 12. It suggests that the effectiveness of the cylinder shape is much higher than that of the spherical and cubic shape. The increased effectiveness means a decrease in the minimum

Al concentration required for the exclusive formation of the alumina. Therefore, the cylinder (dendritic) shape is superior to that of the spherical and cubic shape. Meanwhile, increasing the aspect ratio ($\gg 1$) or decreasing it ($\ll 1$) of the cylinder phase could significantly improve the effectiveness. That's to say that modifying the shape or the aspect ratio of the β phase could be an effective method to optimize the TGO layer.

Fig. 12. The effectiveness of the β phase with different shapes as a function of the aspect ratio l/r .

The minimum Al concentrations in the γ/γ' phase required for the exclusive formation of alumina as a function of time are calculated based on the equations 1-5 and plotted in Fig. 13. The Al concentration N_{Al} on the surface of the γ/γ' phase on the as-deposited coatings measured by the EDS are superimposed in this figure. The N_{Al} of the γ/γ' phase in the LPD coating is slightly higher than that of the LPD-V and HVOF coatings which could be attributed to the inadequate precipitation of the β phase during the fast resolidification process. When N_{Al} is smaller than the minimum Al concentration N_{Al}^* at $t=0$ s, the formation of the mixed oxides is inevitable. However, the size and shape of the β phase determine the time needed for reaching the parabolic oxidation state and the necessarily minimum Al

concentration. More specifically, β phase with smaller size and higher aspect ratio, such as in the region A of the LPD coating, will suffer a shorter transient oxidation stage and require a lower Al concentration in the γ/γ' phase in the parabolic oxidation stage. As the oxidation time increases, the interfacial Al concentration N_{Al} will decrease. The benefit of a smaller and cylindrical β phase for the exclusive formation of alumina will be more apparent.

Fig. 13. The minimum Al concentration in the γ/γ' phase required for the exclusive formation of alumina as a function of diffusion time.

The minimum Al concentration gives only a necessary but not a sufficient condition for the formation of the protecting alumina layer [19]. In addition to the Al concentration in the γ/γ' phase and the size and shape of the β phase, there are many other factors that control the exclusive formation of alumina for the NiCoCrAlY coating, which are: (1) grain size, which affects the diffusion coefficient and, thus, determines the $N_{Al(min)}^{\gamma}$; (2) defects such as pores, cracks and surface roughness, which leads to enhanced aluminum depletion and, therefore, internal oxidation and formation of the spinel.

4.2. Phase transformation of alumina

The current work also shows that the phase of the alumina formed at the initial oxidation stage on these three types of coatings are different. The alumina formed on the LPD and LPD-V coatings is primary α phase after 20 min oxidation at 1150 °C, while the alumina on the HVOF coating is a mixture of the α and θ phase shown in Fig. 4. This indicates that the alumina phase transformation is much faster on the LPD and LPD-V coatings than on the HVOF coating. Since the growth rate of the θ -Al₂O₃ is about an order of magnitude higher than α -Al₂O₃, the TGO layer is expected to be thicker on the HVOF coating [10]. Meanwhile, the density of the θ -Al₂O₃ is 13% smaller than the α -Al₂O₃ and the alumina phase transformation is accompanied by a disruptive volume shrinkage, resulting in cracks and porosity [9]. Therefore, this porous layer allows the upward diffusion of other ions such as Ni and Cr, leading to the formation of the spinel phases [9]. This indicates that earlier transformation is beneficial for the stability of the TGO layer.

It has been reported in the literature that the factors that could promote the Al₂O₃ phase transformation are the surface roughness (e.g., scratches), nano grain size, alumina oxide dispersions as a result of the cryomilling process and Fe ion [10, 25, 26]. Due to the fact that the surface of all the coatings has been polished down to 0.1 μ m finishes before oxidation, the difference caused by surface roughness in the present work could be negligible. Meanwhile, the coatings studied here were prepared without a cryomilling process and the grain size is not in nanoscale. The possible reason for the promoted transition of the alumina on the LPD and LPD-V coatings could be the Fe ions which diffuse into the bond coat layer during the LPD process due to the local inter-diffusion between the coating and substrate²⁴. It has been proved that the adding of Fe₂O₃ could significantly reduce the transformation temperature and result in orders of magnitude decrease in time required for complete transformation of α -Al₂O₃ [27]. In addition to the α -Al₂O₃ nuclei, the Fe ions can also be

considered as the underlying reason for the facilitated the alumina phase transformation in the nanostructured NiCoCrAlY coating when the cryomilled powder is used as the feedstock [28]. Because the stainless steel balls are usually used as milling media during the cryomilling process, the incorporation of Fe ions into the coating would be inevitable. As a result, the facilitated alumina phase transformation could be not due to the nano grain size or phase as reported in the literature but due to the contamination of Fe ions during the fabrication process.

4.3. Spallation behavior

Based on Fig. 6, it can be noted that the LPD coating exhibits the longest lifetime which is slightly higher than that of the LPD-V coating, but almost two times of the HVOF coating. The TGO layer on the HVOF coating fails through large scale delamination after thermal cycling and exhibits a high spallation degree. Meanwhile, the TGO on the coatings prepared by LPD shows small scale delamination and exhibits a much lower spallation degree. The reason for the improved spallation resistance of the LPD coating will be discussed as follows. Due to the fact that the surface of the coatings was polished down to a 0.1 μm finish, the interface of the TGO and bond coat could be assumed to be flat. The energy release rate of the TGO layer under compression could be calculated by [29]:

$$G = \frac{\sigma^2 h_{ox}(1 - \nu_{ox})}{2E_{ox}} \quad (7)$$

where the σ , h_{ox} , ν_{ox} and E_{ox} are the residual stress, thickness, Poisson's ration and Young's modulus of the TGO layer, respectively. The interfacial cracks will initiate when the energy release rate exceeds the interfacial toughness. The TGO thickness and residual stress affect the stability of the TGO layer.

In addition to the elastic strain energy, the failure modes also have a great influence on the TGO stability. For a coating under biaxial compressive stress, failure can occur through edge

initiated delamination or buckling. In our previous work, the prerequisites of the occurrence of these two competing modes have been discussed [13]. For the buckling failure mode, the critical diameter of the interfacial cracks should exceed 24 times of the thickness of the TGO layer. While for the edge delamination mode, the interfacial cracks will propagate without arrest when crack length is several times of the TGO layer and TGO thickness reach 3.4 μm . This indicates that failure through edge delamination is facilitated compared with buckling under the same condition.

Based on the above analysis, the reasons for the inferior lifetime of the HVOF coating could be mentioned as: (1) The residual stress in the TGO layer of the HVOF coating is much higher and increases dramatically with oxidation time. This is related to the larger β phases and higher density of defects such as the cracks and pores which facilitate the formation of spinel. The growth rate of the spinel is almost three order of magnitude higher than that of the alumina, which leads to the increase of the residual stress. (2) Edge delamination mode is preferred due to the existence of the scattered defects. The spinel exhibits low fracture toughness and high growth rate, making the occurrence of cracks much easier. These scattered interfacial cracks are inclined to coalesce which eventually lead to failure through edge delamination. (3) The higher growth rate of the θ - Al_2O_3 and spinel accelerate the thickening of the TGO layer.

For the coatings prepared by the LPD, the defects such as pores and cracks are rarely found on the surface, making the TGO layer prefer to fail through buckling. Meanwhile, the nature of the LPD processing makes the Y^{3+} distribute more finely and homogeneously, which is beneficial for the adherence of the TGO layer to the substrate [30, 31]. These could be the reasons of the better oxidation resistance of the LPD and LPD-V coatings compared with HVOF coating. However, the slightly improved TGO lifetime on the LPD coating over the LPD-V coating could be attributed to the formation of the homogeneous and low growth rate

alumina layer. It was shown in Fig. 2 that the β phase size and distribution determines the formation of the oxides at the early oxidation stages. The smaller β phase size favors the formation of a uniform α -Al₂O₃. The Ni- and Cr- rich oxides are formed on the surface of the γ/γ' phase in the region with larger β phase (region B in the LPD-V coating), leading to the increase of the TGO growth rate and local stress. At the parabolic stage, a dense and uniform inner layer of the alumina formed which favors the stabilization of the interface between TGO and bond coat. It is expected that the uniform and dense alumina layer on the LPD coating could be more desirable for the TBCs application.

5. Conclusions

The NiCoCrAlY coating with dense, defect-free microstructure, nano and dendritic phase distribution was fabricated using laser powder deposition (LPD) method. Particular attention has been focused on the effect of size and shape of the β phase on the oxidation behavior such as the oxides nucleation, phase composition, TGO growth rate and stress distribution. For comparison, the LPD-V coating prepared by the LPD method and followed by 2 hours heat treatment in vacuum and HVOF coatings prepared by high velocity air fuel methods were studied. Based on the results, the following conclusions can be drawn:

- (1) The size and distribution of the β phase determine the nucleation of the alumina at the initial oxidation stages. This phenomenon can be clearly seen on region B in LPD-V coating that the alumina completely inherits the contours of the β phase, while the spinels are formed on the γ/γ' phase.
- (2) The small radius r and high aspect ratio (defined as l/r) of the β phase are beneficial for the exclusive formation of the α -Al₂O₃, lower TGO growth rate and residual stress.
- (3) The TGO layer on the LPD coating shows the longest lifetime, which is almost two fold of that on HVOF coating. In addition to the size and shape of β phase, the failure

modes determined by the defects (e. g., pores and cracks) also play an important role in the TGO spallation resistance.

- (4) The coatings prepared by LPD (including LPD and LPD-V coating) facilitate the alumina transformation from θ to α phase, which is thought to be related to the Fe ions incorporated in the coating during deposition process.

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