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Effect of microstructure of a NiCoCrAlY coating fabricated by high-velocity air fuel on the isothermal oxidation

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Abstract

The effect of grain size, dislocations and porosity of a NiCoCrAlY coating fabricated by high-velocity air fuel on the isothermal oxidation behavior is studied. To understand this effect, the microstructure of coating, the chemistry and microstructure of thermally grown oxides (TGO), the phase transformation of alumina, the oxidation rate, and the TGO stress are investigated. It is demonstrated in this study that the oxidation and spallation resistance of TGO are predominantly determined by the porosity rather than grain size and dislocation for the long term oxidation, although the fine γ -grains and dislocation can facilitate the earlier establishment of α -Al₂O₃ scale.

Keywords: NiCoCrAlY; Grain size; Dislocation; Porosity; Oxidation.

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1. Introduction

MCrAlY (M=Ni, Co or both) coatings are widely employed as bond coat materials for thermal barrier coatings, or protective coatings for many demanded applications (e.g. aeroengine and power generation gas turbines) due to its exceptional oxidation and corrosion resistance at elevated temperature[1-4]. The oxidation resistance of these coatings rely on the capability to develop a mechanically stable, slow growing, adherent alumina-based thermally grown oxides (TGO) over the coating surface upon exposure to high temperatures[5, 6].

The MCrAlY coatings are typically fabricated by atmospheric plasma spray (APS), low pressure plasma spray (LPPS) and vacuum plasma spraying (VPS). For the APS sprayed MCrAlY coating, the intrinsic imperfections (e.g. pores and internal oxides) in the underlying coating always enhance the depletion of aluminum. When the content of aluminum is lower than the critical level of alumina nucleation, the spinel (e.g. $(\text{Co,Ni})(\text{Cr,Al})_2\text{O}_4$) and breakaway oxides will develop in the TGO and thus induce failure of coatings [7-11]. The industrial applications are limited for the MCrAlY coating fabricated by LPPS and VPS due to the high cost, although the coating shows a better oxidation resistance performance in comparison to APS coating [7]. To lower the cost and fabricate a high-performance MCrAlY coating, high-velocity oxygen fuel (HVOF) technique is employed to fabricate the MCrAlY coatings. The oxidation behavior of HVOF-sprayed MCrAlY coatings has been extensively studied in the previous investigations [12-14]. The recently developed HVAF technique has attracted constantly increased attention as a potential replacement of HVOF [15]. The in-situ oxidation can be significantly reduced during spraying by replacing pure oxygen in HVOF with air in the HVAF process, except for the lower cost [16, 17]. The lower in-flight particle temperature, higher particle velocity in the flame, and greater control of the process compared with HVOF can lead to the minimal particle phase transformation and higher coating densification [17]. Thus the HVAF technique is likely to be more appropriate for fabricating high-performance MCrAlY coatings with both lower porosity and lower oxygen content compared with the HVOF. At present, only a few

investigations to report the oxidation behavior of HVAF-sprayed MCrAlY coatings. It is reported by Luo et.al [6] that the HVAF-sprayed NiCoCrAlY coating shows a better oxidation resistance at 1150 °C than APS, which is attributed to the dense microstructure of coating. Zhang et.al [18] investigates the effect of surface treatment on the growth of transient alumina in the initial oxidation stage at 1000 °C for the HVAF-sprayed NiCoCrAlY coating. However, the effect of intrinsic microstructure (grain size and porosity) on the oxidation behavior of HVAF-sprayed MCrAlY coatings remains unclear. Understanding on this point could help develop a high-performance MCrAlY coating.

In the present work, the objective is to provide detailed characterization and mechanistic understanding of the isothermal oxidation of HVAF-sprayed NiCoCrAlY coating, with a focus on the effect of the microstructure (grain size and porosity) of the coatings. For comparison, other two types of HVAF-sprayed coatings with larger grain size and lower porosity prepared by subsequent vacuum heat treatment and spark plasma sintering treatment are also studied. The isothermal oxidation test was carried out at 1150 °C in laboratory air. Both microstructure, phase transformation of alumina scale, oxidation rate, the residual stress, and the failure mechanism of TGO for these coatings are systematically investigated.

2. Experimental procedure

2.1. Material and sample preparation

Nickel-based Hastelloy® X polycrystalline superalloy was used as the substrate material, which was grit blasted and ultrasonically cleaned in acetone prior to deposition. . The M3™-HVAF spraying system (Uniquecoat, Oilville, VA, USA) was employed to fabricate the NiCoCrAlY coating. Three types of coatings were designed, namely the **HVAF coating** (prepared by HVAF), **HVAF-V coating** (prepared by HVAF and followed by 4 h vacuum heat treatment at 1100 °C in vacuum ($\leq 10^{-5}$ Pa)) and **HVAF-S coating** (prepared by HVAF and followed by spark plasma sintering treatment

at 1050 °C for 10 min under a pressure of 50 MPa in vacuum ($\leq 10^{-5}$ Pa), with a heating rate of 100 °C/min). Table 1 shows the nominal compositions of the commercially available NiCoCrAlY powder (Amdry 365-2, Sulzer Metco) and the Hastelloy® X superalloy substrate. The whole spraying process of HVOF coating was conducted at atmosphere environment and detailed spraying parameters for the HVOF process are summarized in Table 2.

Table 1. Nominal composition of Hastelloy® X substrate and NiCoCrAlY powder

Material	Element (wt %)									
	Ni	Co	Cr	Al	Y	Fe	Mo	W	C	Mn
Hastelloy® X	47	1.5	22	/	/	18	9	0.6	0.1	1*
NiCoCrAlY	47.5	23	17	12	0.5	/	/	/	/	/

Table 2. Spray parameters employed in the HVOF process

Spraying parameters	HVOF
Spray distance (mm)	180
Spray speed (mm/s)	2000
Powder rate (g/min)	100
Primary gas (L/min)	78
Secondary gas (L/min)	22.5

2.2. Isothermal oxidation

The deposited samples were cut into $10 \times 10 \times 5$ mm³ rectangle plates. To eliminate the effect of surface roughness, all the coatings were mechanically ground down to similar thickness (~200 µm), with final polishing of 0.05 µm using standard metallographic approaches and thoroughly cleaned with acetone prior to oxidation. The isothermal oxidation experiment was performed at 1150 °C in a chamber furnace at atmosphere environment for duration ranging from 1 to 100 h. The samples were removed from furnace after a required exposure time, air-cooled outside the furnace at room

temperature for approximately 15 min.

2.3. Characterization

X-ray diffraction (XRD, Ultimo IV, Riau, Japan) measurements at 30 kV with Cu K α radiation were employed 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 microstructure and chemical composition of coatings and thermally grown oxides layer were executed by Scanning electron microscopy (SEM, FEI Nova Nano 230, Netherlands) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford Instruments). To reveal the grain microstructure of the HVOF coating in greater details, thin lamellae of the coating were prepared by a focused ion beam (FIB, GAIA3, Tescan, Czech Republic) and were analysed using a scanning transmission electron microscope (STEM, TALOS F200X, FEI, USA) equipped with an energy dispersive X-ray spectroscopy (EDS, XIS Ultra DLD, Kratos, Japan) system. The details of STEM sample preparation can be found elsewhere [5]. The grain sizes of the γ and β -grains in the HVOF coating were determined by five SEM micrographs with a magnification of $30000\times$ in conjunction with the TEM analysis using Image J software (National Institutes of Health, USA). The grain sizes in the HVOF-V and HVOF-S coatings were measured using the SEM micrographs combined with FIB etching (FIB-SEM) [19]. The photoluminescence piezospectroscopy (PLPS) was employed to characterize the phase transformation of alumina and residual stress in thermally grown oxides layer using a confocal Raman microprobe (LabRAM HR, Horiba Jobin Yvon, France) with a 532 nm Nd:YAG laser. The spectra were fitted using a mixed Gaussian-Lorentzian function (Labspec software) to obtain the peak positions. The residual stress was calculated based on the peak shift using the spalled TGO debris as stress free reference.

3. Results

3.1. The microstructure of coatings

Fig. 1. The cross-sectional BSE micrographs of (a, d) HVAF, (b, e) HVAF-V and (c, f) HVAF-S coatings.

Fig. 1 shows the cross-sectional microstructure of HVAF, HVAF-V and HVAF-S coatings. As can be seen in Fig.1, all coatings were about 200 μm in thickness and had the same surface roughness. As presented in Fig. 1d, e and f, all coatings exhibit a two-phase microstructure, which comprises the γ-Ni phase (light contrast) and β-NiAl phase (dark contrast)[6]. For HVAF-V and HVAF-S coatings (Fig. 1b and c), the thickness of intermediate inter-diffusion zone (IDZ) at coating/substrate interface is ~5 μm, which indicates an almost same extent of inter-diffusion. Thus the effect of inter-diffusion on the oxidation behavior can be neglected due to thin inter-diffusion layer (~5 μm) and thick coating (~200 μm).

Fig. 2. Surface morphology of the HVAF coating after etching, showing the grain microstructure. The polished samples were etched using a mixture of 50 vol. % HCl, 50 vol. % ethanol with 5 wt. % CuCl₂ dissolved [20].

It should be noted that the microstructures of these coatings shows significant difference in the grain size and porosity. Fig. 2 shows the distribution of γ -grains and β -grains in the HVAF coating. The β -grains are almost equiaxed and the γ -grains are elongated with a large aspect ratio. The grain size of elongated γ -grains is defined by the grain width and aspect ratio [5]. The TEM analysis is employed to further reveal the grain size of γ -grains, as shown in Fig. 3. The distribution of γ -grains and β -grains in the HVAF coating is identified by the elemental mapping. The CoCr enriched grains are γ -grains and Al enriched grain are β -grains, respectively, which is clearly presented in Fig. 3b. The average grain sizes of β -grains and γ -grains in the HVAF coating are about 1.83 μm and 500 nm with a large aspect ratio (range from 1 to 10) in combination with grain distribution in Fig. 2. The formation of fine γ -grains in the HVAF coating can be attributed to the severe cold deformation, which involves extremely low deposition temperature and high flight velocity of particle [5, 16].

Fig. 3. TEM analysis of the HVOF coating: (a, b) bright-field (BF) TEM micrograph and high-angle annular dark-field (HAADF) STEM micrograph, corresponding to EDS maps of, Co, Cr, Al and Y, respectively.

For the HVOF-V and HVOF-S coatings, the grain size increases to several micrometers and almost equiaxed due to the heat treatment (Fig. 1). Thus the high magnification SEM micrographs combined with FIB etching are employed to determine the grain sizes, which are presented in Fig. 4. Although the γ -grains and β -grains are difficult to distinguish after FIB etching, the grain size is uniformly distributed, as shown in Fig. 4a and b. The average grain sizes are about 1.93 μm and 1.75 μm for HVOF-V and HVOF-S coatings, respectively. Additionally, Y enriched precipitates segregates to the grain boundaries for all coatings due to the the low solubility of Y in the NiCoCrAlY (Fig. 2, 3 and 4) [21, 22].

Fig. 4. (a, b) SEM micrographs combined with FIB etching, showing the grain microstructure for HVAF-V and HVAF-S coatings, respectively.

The polished surface morphologies of coatings are presented in Fig. 5 to determine the distribution of pores. Oxide inclusions are hardly detected in either type of coating, which manifests negligible oxidation during the spraying process. For the HVAF coating (Fig. 5a), the pores are distributed at the unmelted particle boundaries and between adjacent particles, which is attributed to insufficient localized plastic deformation during spraying. The microstructure from original particle is retained in the HVAF coating, as the micrograph inserted in Fig. 5a. For the HVAF-V coating, the large-sized pores along unmelted particle boundaries cannot be completely eliminated, although the amount and size of pores are reduced, as shown in Fig. 5b. It is inadvisable to promote the densification of coating by increasing the temperature or time of vacuum heat treatment, which can lead to an intense inter-diffusion between substrate and coating and thereby severely compromise both the oxidation resistance performance of coating and the mechanical properties of substrate [23-25]. Therefore, the spark plasma sintering is employed to realize a higher degree of densification for the HVAF-S coating. Meanwhile, a low degree of inter-diffusion can be controlled due to its capability of fast sintering (Fig. 1c). As shown in Fig. 5c, the HVAF-S coating is fully dense and the pores at the unmelted particle boundaries are hardly seen. The average porosity of

HVAF, HVAF-V, and HVAF-S coatings, determined by image analysis method referring to literature [6, 26], is estimated to be 3.58 %, 1.96 % and 0.16 %, respectively.

Fig. 5. The BSE micrographs of polished surface of (a) HVAF, (b) HVAF-V and (c) HVAF-S coatings.

3.2. TGO spallation resistance

The TGO spallation degree after oxidation from 1 h to 100 h at 1150 °C is plotted in Fig. 6 to evaluate the oxidation performance of these coatings. To determine the ratio of TGO spallation for all coatings after isothermal oxidation, ten 75× magnification BSE micrographs are used to obtain the average spallation ratio of TGO and the error bar is the standard deviation. The low magnification BSE micrographs of TGO surface for three types of coatings after isothermal oxidation at 1150 °C for 50 h, 50 h, and 100 h

are presented in Fig. 7. It can be clearly seen in Fig. 7b, d and f that the spalled section of TGO is shown in white contrast after processing using Image J, so as to further confirm the spallation ratio of TGO. For the HVOF coating, the spalled region can be observed after 25 h oxidation. The spalled area increases as the oxidation time and attains ~32 % of the whole area of the TGO after 100 h oxidation. Luo et al [6] reported similar TGO spallation ratio for the HVOF coating after isothermal oxidation at 1150 °C. For the HVOF-V coating, the distinct TGO spallation (~11 %) is discovered after 25 h oxidation. The detachment of TGO increases dramatically with an increase of the oxidation time and exceeds 50 % after 100 h oxidation. Nevertheless, the TGO formed on the HVOF-S coating is almost intact even after 100 h exposure. It is clearly indicated that the HVOF-S coating exhibits superior spallation resistance, compared with the HVOF and HVOF-V coatings.

Fig. 6. The spallation degree of TGO formed on the coatings as a function of isothermal oxidation time at 1150 °C(The spallation degree is defined by the ratio between spalled area and the whole area of the TGO).

Fig. 7. (a, c and e) BSE micrographs of TGO surface, showing the spallation morphologies of TGO formed on HVAF, HVAF-V and HVAF-S coatings after isothermal oxidation at 1150 °C for 50 h, 50 h, and 100 h, respectively; (b, d and f) processed micrographs of (a, c and e) using Image J, showing the spalled section of TGO in white contrast.

3.3. TGO microstructure

Fig.8 shows the optical plan-view micrographs of the TGO formed on all coatings after isothermal oxidation for different time at 1150 °C. For the HVOF and HVOF-V coatings, a considerable ratio of spinel (e.g. $(\text{Co,Ni})(\text{Cr,Al})_2\text{O}_4$) corresponding to the blue colored oxides forms in the TGO after oxidation (e.g. Fig. 8a, b, f and g)[6, 27]. Thus the fraction of spinel in the TGO formed on all coatings as a function of oxidation time is measured by quantitative image analysis, which is summarized in Fig. 9. For the HVOF coating, the ratio of spinel reaches to ~7.1 % after 10 h oxidation and increases to 9.2 % after 25 h oxidation. When the TGO starts to suffer apparent spallation after 50 h oxidation (Fig. 8c), the ratio of spinel declines to ~4.4 %. Additionally, the spinel almost disappear after 100 h oxidation (Fig. 8d). For the HVOF-V coating, the amount of spinel is minor after 10 h oxidation and attains ~5.1% after 25 h oxidation. Similarly, the spinel gradually reduce with the spallation of the TGO after 50 h oxidation (Fig. 8g) and are hardly seen after 100 h oxidation (Fig. 8h). Spinel prefers to form around the pores due to the locally insufficient aluminum supply from the coating [6]. Therefore, the lower amount of spinel for HVOF-V coating can be attributed to the higher degree of densification, as compared with the HVOF coating. Nevertheless, the HVOF-V coating exhibits a higher TGO spallation degree, while the amount of spinel is lower than that for the HVOF coating (Fig. 6 and 9). For the HVOF-S coating, the spinel is hardly detected in TGO even after 100 h oxidation (Fig. 8i-m).

Fig. 8. The optical plan-view micrographs of the TGO formed on HVAF, HVAF-V and HVAF-S coatings after isothermal oxidation at 1150 °C for 10 h, 25h, 50 h and 100 h, respectively.

Fig. 9. The fraction of spinel in the TGO formed on all coatings as a function of isothermal oxidation time at 1150 °C. The error bar shows the standard deviation.

Based on the results displayed in Fig. 6 and 8, the spallation ratio of TGO exhibits obvious difference for the HVAF and HVAF-V coatings after 50 h oxidation. However, for the HVAF-S coating, only minor quantity of spallation of TGO can be observed even after 100 h oxidation (Fig. 6). Therefore, Fig. 10 compares the surface and cross-sectional morphologies for the HVAF, HVAF-V and HVAF-S coatings after isothermal oxidation at 1150 °C for 50 h, 50 h, and 100 h, respectively. For the HVAF coating (Fig. 10a), the internal oxides predominantly grow at unmelted particle boundaries and extend into the coating, which can be also found at TGO/coating interface (Fig. 10b). For the HVAF-V coating (Fig. 10c and d), the presence of internal oxides is still inevitable, in spite of a relatively lower amount of pores in the coating, which can be

attributed to the remaining pores at unmelted particle boundaries (Fig. 5b). However, for the HVOF-S coating (Fig. 10 g and h), no internal oxides can be observed at TGO/coating interface even after 100 h oxidation due to the fully dense microstructure of coating (Fig. 5c). The only interfacial imperfection observed at spalled region is the interface pore, which is probably driven by the Kirkendall effect [20]. Away from the spalled region, the TGO still keeps good adhesion. It is clearly indicated that the pores at unmelted particle boundaries lead to the formation of internal oxides.

The detrimental effect of internal oxides on the oxidation behavior of HVOF and HVOF-V coatings should be noted. As shown in Fig. 10b and e, in these regions of internal oxides, the enhanced Al-depletion zones are observed, which cause localized insufficient aluminum supply from the coatings to form alumina. Thus the spinel will form as a result of depletion of Al and enrichment of Co, Ni and Cr from the underlying coatings, which leads to the breakaway oxidation in the coatings (Fig. 10c and f) [9, 28]. In these regions of no internal oxides, the aluminum is uniformly depleted (Fig. 10b and e). The spinel is brittle and fast growing in comparison to alumina, where the nucleation and propagation of cracks occur easily (Fig. 10f) [8, 9, 29]. Additionally, the spinel mainly consists of $(\text{Co,Ni})(\text{Cr,Al})_2\text{O}_4$ spinel in combination with the EDS result in Fig. 10c1. For the HVOF-S coating (Fig. 10h and i), the uniform and continuous TGO with a smooth TGO/coating interface is observed, where the internal oxidation is completely inhibited.

Fig.10. (a, d, and g) BSE micrographs at spalled regions, showing the surface morphologies of HVAF, HVAF-V and HVAF-S coatings after isothermal oxidation at 1150 °C for 50 h, 50 h, and 100 h, respectively; (b, e, and h) BSE micrographs of cross-section of TGO, giving an overview of the TGO on HVAF, HVAF-V and HVAF-S coatings after isothermal oxidation at 1150 °C for 50 h, 50 h, and 100 h, respectively; (c, f, and i) high magnification BSE micrographs of areas marked by white rectangles in (b, e, and h), showing the cross-sectional microstructure of TGO; (c1) a EDS result of area marked by red crosses in (c), showing the presence of all base metal elements ((Ni + Co):(Cr + Al) $\approx$ 0.5).

Fig. 11 shows the fracture morphologies of TGO after isothermal oxidation at 1150 °C for 25 h. A double-layered TGO structure consisting of an equiaxed outer layer and a columnar inner layer is developed on all coatings. The formation of double layer scale structure results from the concurrent inward oxygen diffusion and outward aluminum diffusion [30-33]. The segregation of reactive element ions (e.g. Y) to the Al₂O₃-based

TGO grain boundaries will inhibit the outward aluminum transport. Thus the dominant growth mechanism of TGO is inward oxygen diffusion along the Al_2O_3 grain boundaries [32, 34-37]. In short, the TGO growth mechanism is same for three types of coatings.

Fig. 11. The fracture section of TGO formed on (a) HVOF, (b) HVOF-V and (c) HVOF-S coatings after isothermal oxidation at 1150 °C for 25 h.

3.4. Oxides growth kinetics

Fig. 12 shows the average thickness of the TGO formed on all coatings as a function of the oxidation time at 1150 °C, which is measured at 50 equidistance points distributed through the cross-sectional area of the TGO divided by the length of interface with a step size of 20 μm. The error bar is the standard deviation of 50 equidistance points. Up to an oxidation time of 25 h, the HVOF coating shows the lowest TGO growth rate. However, the thickness of TGO on the HVOF-S coating is ~2.8 μm after 50 h oxidation, which is lower than that of HVOF coating (~3.2 μm) and HVOF-V coating (~3.8 μm). After 100 h oxidation, the difference of the thickness of TGO become more apparent

(4.1 μm for HVAF coating, 4.8 μm for HVAF-V coating, and 3.5 μm for HVAF-S coating). In general, the HVAF-S coating shows the lowest TGO growth rate for the long-term oxidation (>25 h). Meanwhile, the HVAF-V exhibits the highest TGO growth rate. The reasons for this difference in TGO growth rate for all coatings will be discussed later.

Fig. 12. Kinetics of isothermal oxidation of the HVAF, HVAF-V and HVAF-S coatings at 1150 °C. The horizontal dash line shows the critical thickness of thermally grown oxides (TGO) layer for the propagation of the edge initiated cracks without arrest.

3.5. Phase transformation of TGO in the early stage

Fig. 13. The PLPS spectra of Al_2O_3 scale formed on all coatings after oxidation for: (a) 5 min, (b) 10 min, and (c) 20 min, and (d) shows the evolution of $\theta\text{-Al}_2\text{O}_3$ content with the oxidation time.

Fig. 14. The surface morphologies of TGO formed on the HVAF, HVAF-V, and HVAF-S coatings after isothermal oxidation for 10 min at 1150 °C.

It is well established that NiCoCrAlY coating primarily forms α -Al₂O₃ during oxidation, but transient alumina, particularly θ -Al₂O₃ is always found in the early oxidation stage [5, 20]. The phase transformation rate of θ -Al₂O₃ to α -Al₂O₃ has a non-negligible contribution to the overall TGO growth rate, due to the much faster growth rate of θ -Al₂O₃ than α -Al₂O₃ [20]. Thus the PLPS spectra are collected to identify the composition and evolution of transient alumina in the early time [20, 38]. Fig. 13 shows the PLPS spectra of transient alumina and the evolution of θ -Al₂O₃ with the oxidation time. The peaks near the frequencies of 14,402 cm⁻¹ and 14,432 cm⁻¹ belong to α -Al₂O₃, and the peaks near the frequencies of 14,575 cm⁻¹ and 14,645 cm⁻¹ stand for θ -Al₂O₃. The content of θ -Al₂O₃, C_θ , in the Al₂O₃ scale can be roughly estimated using the following relationship [20, 38]:

$$C_\theta = \frac{A_{14575} + A_{14645}}{A_{14402} + A_{14432} + A_{14575} + A_{14645}} \quad (1)$$

where A denotes the area of characteristic peaks and the subscript represents the peak frequency.

After 5 min oxidation, both θ -Al₂O₃ and α -Al₂O₃ are formed on the HVAF-V and HVAF-S coatings. It should be noted that the content of θ -Al₂O₃ for the HVAF-V coating (18.9 %) is significantly higher than that for the HVAF-S coating (7.1 %). However, no θ -Al₂O₃ is detected for the HVAF coating. After 10 min oxidation, about 7.9 % θ -Al₂O₃ remains on the HVAF-V coating, while for the HVAF and HVAF-S coatings, there is almost no θ -Al₂O₃. When the oxidation time increases to 20 min, no θ -Al₂O₃ is detected on the either sample. Based on the above, the phase transformation rate of θ to α -Al₂O₃ in the early stage is in the order: HVAF > HVAF-S > HVAF-V.

Fig. 14 shows the distribution of θ -Al₂O₃ and α -Al₂O₃ in TGO for three types of coatings after 10 min at 1150 °C. As shown in Fig. 14b, the blade-like morphology on the outer surface of TGO for the HVAF-V coating is observed, which indicates the presence of a considerable amount of θ -Al₂O₃ [39]. For the HVAF-S coating (Fig. 14c), the TGO mainly consists of α -Al₂O₃. Only minor quantity of θ -Al₂O₃ can be seen, which is hardly detected by PLPS technique due to the low content of θ -Al₂O₃ (Fig. 13b). For the HVAF coating (Fig. 14a), the TGO comprises α -Al₂O₃ and no θ -Al₂O₃

can be found. These results agree well with the PLPS spectra presented in Fig. 13b and d.

3.6. TGO stress

Fig. 15. The residual stress of TGO formed on all coatings as a function of isothermal oxidation time at 1150 °C. Each data point represented by solid symbol in this graph is measured from separate samples and represents the average value of 625 measurements. The error bar shows the standard deviation of 625 measurements.

The driving force for TGO delamination derives from the residual stress in TGO, which comes from the thermal mismatch stress and the growth stress [20, 40]. As presented in Fig. 8 and 10, much spinel ((e.g. (Co,Ni)(Cr,Al)₂O₄)) forms in the TGO, where the cracks nucleation and propagation occur easily due to the high brittleness and low

adherence of spinel in comparison to alumina and stress concentration induced by locally rapid volume expansion. [9, 41, 42]. However, away from the spinel, the TGO predominantly consists of $\alpha\text{-Al}_2\text{O}_3$ phase. To evaluate the driving force for TGO delamination, the TGO residual stress around and away from the spinel is respectively determined by PLPS technique [20, 43]. Assuming the TGO/coating interface is flat, the residual stress σ in the TGO refers to the equi-biaxial stress, which can be calculated by the equation [20, 44, 45]:

$$\Delta\nu=5.07\sigma \quad (2)$$

where $\Delta\nu$ is peak shift of R2 line and the peak shift is obtained using the spalled TGO debris as stress free reference. Fig. 15 shows the evolution of residual stress in the TGO away from spinel as a function of oxidation time at 1150 °C. As presented in the Fig. 6, the ratio of TGO spallation exceeds 20 % after 50 h oxidation for the HVAF coating and after 25h oxidation for HVAF-V coating, which is defined as failed. Thus the value of residual stress for these samples is not recorded. Two significant features can be found in the Fig. 15. First, the initial rapid decline in the residual stress is observed for the all coatings, which is probably attributed to the stress relaxation mechanism (e.g. creep or plastic deformations) [46, 47]. Second, the residual stress remains at a stable level (~ 4.5 GPa) after 10 h oxidation for HVAF-S coating. However, the residual stress shows gradually decrease after 10 h oxidation for the HVAF and HVAF-V coatings. It should be specially noted that the HVAF-V coating exhibits a faster decrease in the residual stress, as compared with the HVAF coating. Based on the above analysis, the stability of residual stress for all coatings can be ranked as following: HVAF-S > HVAF > HVAF-V.

It is clearly exhibited in Fig. 8 and 10 that the spallation tends to initiate from spinel zones in the TGO formed on the HVAF and HVAF-V coatings. To map the distribution of residual stress around the spinel, PLPS measurements are conducted a grid of $100 \times 100 \mu\text{m}$ with a step size of $2 \mu\text{m}$. Fig. 16 shows the distribution of TGO stress around the spinel after 25 h oxidation. For the HVAF coating (Fig. 16a and b) and HVAF-V coating (Fig. 16c and d), the residual stress relaxation around the spinel can be clearly observed, which is probably induced by the nucleation and propagation of

interfacial cracks. For the HVAF-S coating (Fig. 16e and f), the distribution of residual stress is relatively uniform due to the absence of spinel. In addition, the level of residual stress corresponding to the color scale in Fig. 16f is in agreement with the level (~ 4.5 GPa) presented in Fig. 15. It is demonstrated that the spinel imperfection in the TGO plays a crucial role in the initiation of TGO spallation [48-50]. The HVAF-S coating obtains a uniform $\alpha\text{-Al}_2\text{O}_3$ scale after long term oxidation, which is beneficial to maintaining a good interfacial adhesion.

Fig. 16. The optic micrographs and corresponding distribution of the residual stress around the spinel in the TGO formed on the (a, b) HVAF coating, (c, d) HVAF-V coating and (e, f) HVAF-S coating.

4. Discussion

4.1. Effect of coating microstructure on the phase transformation of aluminum oxide

As presented in Section 3.5, a different phase transformation rate of alumina for the three types of coating is observed in Fig. 13. The HVAF coating shows the fastest phase transformation rate of θ -Al₂O₃ to α -Al₂O₃, while HVAF-V coating shows the slowest transformation rate.

It has been extensively reported that the phase transformation rate of alumina can be affected by surface roughness, reactive elements doping (e.g. Y, Hf, and Zr), crystallographic defects (grain sizes and dislocations) [5, 20, 51, 52]. The effect of surface roughness and reactive elements doping is negligible, due to the polishing and same doping of reactive element Y before oxidation. It has been reported that the refinement of grain size to nanoscale can facilitate the earlier establishment of α -Al₂O₃, which is induced by the significantly increased grain boundary density [53, 54]. The NiCoCrAlY coating typically comprises of γ -Ni and β -NiAl phases. The β phase is rich in Al and thereby favors the formation of α -Al₂O₃ scale. Thus the exclusive nucleation and formation of α -Al₂O₃ scale will be controlled by the oxidation of the γ -phase. It has been reported by Chen et.al [5] that the nano-sized γ -grains (<700 nm) in the HVOF-sprayed NiCoCrAlY coating can promote the formation of exclusive α -Al₂O₃. In addition, the γ -grain with an elongated shape is also beneficial to the formation of exclusive α -Al₂O₃ [5]. As presented in Fig. 2 and 3, the grain size of elongated γ -grains in the HVAF coating is about 500 nm (<700 nm). For the HVAF-V and HVAF-S coatings, the γ -grains coarsen to order of magnitudes of several micrometers and almost become equiaxed. On the other hand, it is also reported that the formation of dislocations in the HVOF coating can increase the number of nucleation sites of α -Al₂O₃ [5, 55]. The spray particles in a plastic state rather than in a melted state strike onto substrate, due to the extremely high velocity and relatively low temperature in the HVOF spraying [56]. Thus the dislocations come from the “cold deformation” upon

impact with the substrate. Fig. 17 shows a bright-field TEM image (Fig. 17a) of the HVOF coating and the corresponding diffraction pattern (Fig. 17b) of a β -grain. It can be clearly seen that the diffraction spots are elongated and diffuse, which is attributed to the distortions of the lattice associated with the presence of the large number of the dislocations. Thus the dislocations are also present in NiCoCrAlY coating fabricated by HVOF which uses lower deposition temperatures and involves more cold deformation of the particles than HVOF [16]. Based on the analysis above, the fastest phase transformation rate of θ -Al₂O₃ to α -Al₂O₃ for the HVOF coating can be attributed to the fine grain sizes (Fig. 2 and 3) and more dislocations (Fig. 17). Both HVOF-V coating (1100 °C, 4 h) and HVOF-S coating (1050 °C, 10 min, 50 MPa) are heat treated. For the HVOF-V coating, the dislocations may disappear due to the high heat treatment temperature and long time. However, for the HVOF-S coating, it is likely that the dislocations are not completely disappear due to the fast sintering capacity of SPS technique (relatively lower temperature and shorter time). Since the grain sizes are basically equal for the HVOF-V and HVOF-S coatings (Fig. 4), the faster phase transformation rate of θ -Al₂O₃ to α -Al₂O₃ may be induced by the remaining dislocations in the HVOF-S coating in comparison to the HVOF-V coating.

Fig. 17. TEM analysis of the HVOF coating: (a) bright-field image, showing the presence of the larger number of dislocations and (b) diffraction pattern of the β -grain marked with “D” in Fig. 17a. The diffraction spots are elongated and diffuse.

4.2. Effect of coating microstructure on TGO growth rate

As presented in Section 3.4, the HVOF-S coating shows the lowest TGO thickness after 25 h oxidation. However, up to an oxidation time of 25 h, the HVOF coating exhibits the lowest TGO thickness. In addition, the TGO thickness for HVOF-V coating is always maximal for the whole oxidation stage. In the present work, the growth of TGO is primarily affected by the transformation rate of alumina and the porosity (pores). The contribution of θ - Al_2O_3 content in Al_2O_3 scale to overall TGO thickness cannot be neglected, due to about an order of magnitude higher growth rate of θ - Al_2O_3 than α - Al_2O_3 [20, 51]. Moreover, the θ - Al_2O_3 can favor the nucleation and growth of spinel, thereby further thickening the TGO, resulting from the porous microstructure of θ - Al_2O_3 [5, 57]. Once the α - Al_2O_3 scale is completely transformed, the pores in the coating will play a predominant role on the overall increase of TGO thickness. First, the localized insufficient aluminum supply from the coating leads to the formation of spinel around the pores, due to the increased infiltration paths for the diffusion of other metal elements (Fig. 10b and e) [7]. It is also reported by Evans and Taylor [9] that the internally formed oxides in the coatings provide the diffusion barriers preventing the supply of aluminum from the coatings, resulting in the formation of spinel and breakaway oxides. Then the spinel and breakaway oxides grows at an intrinsically much higher rate than the protective α - Al_2O_3 , which further thicken the TGO [7, 9-11]. For instance, the parabolic rate constant for NiO scale growing in air at 1100 °C is typically three orders of magnitude higher than that of the protective α - Al_2O_3 [41]. For the HVOF-V coating, the relatively high temperature and long time during the vacuum heat treatment might lead to the formation of nano-sized alumina scale surrounding the unmelted particle boundaries. Then this alumina scale hinders the diffusion of aluminum from the unmelted particle and thereby causes severely internal oxidation around the unmelted particle boundaries (Fig. 10d and e). Therefore, the higher TGO growth rate for the HVOF-V coating can be attributed to the higher θ - Al_2O_3 content in Al_2O_3 scale and severe internal oxidation, in comparison to other two types of coatings (Fig. 10 and 13). Two important features in Fig. 12 should be noted. First, the TGO thickness for the

HVAF coating is lower compared with the HVAF-S coating by the first 25 h. This result primarily comes from the contribution of the lower θ -Al₂O₃ content in Al₂O₃ scale for the HVAF coating. Second, the difference in TGO thickness is constantly reduced between HVAF and HVAF-S coatings up to an oxidation time of 25 h. Furthermore, the TGO thickness for HVAF coating exceeds that of HVAF-S coating after 25 h oxidation. The Al concentration is sufficient to nucleate alumina in the early stage for the HVAF coating. However, the aluminum concentration in the HVAF coating declines quickly due to the continuous TGO growth and severe internal oxidation (Fig. 10a and b). Then the spinel forms in the Al-depletion zones, which results in the fast TGO growth (Fig. 10b and c). For the HVAF-S coating, a higher θ -Al₂O₃ content in Al₂O₃ scale leads to a higher TGO thickness in the early oxidation stage compared with the HVAF coating, but the HVAF-S coating shows the lowest TGO growth rate for the long-term oxidation due to the dense microstructure of coating. In other words, the porosity plays a predominant role on the oxidation resistance rather than grain size for the long-term oxidation.

4.3. Effect of coating microstructure on residual stress in TGO

Fig. 15 shows the residual stress in TGO for the HVAF-S coating remains stable (~4.5 GPa) for the long-term oxidation. However, for the HVAF and HVAF-V coatings, the residual stress in TGO keeps constant decline until the failure of TGO. As presented in Fig. 10, the severe internal oxidation is found at the TGO/coating interface for HVAF and HVAF-V coatings. The localized volume expansion at interface due to severe internal oxidation easily leads to the stress concentration and thereby initiates the interfacial cracks [48]. The formation of interfacial cracks can release the residual stress in TGO. Thus the continuous decrease in the residual stress with the oxidation time for HVAF and HVAF-V coatings could be attributed to the nucleation and propagation of interfacial cracks. The faster decrease in the TGO residual stress for HVAF-V coating in comparison to HVAF coating could be attributed to more severe interface separation. It is clearly presented in Fig. 16 that the stress relaxation always occurs surrounding the

spinel, which causes a non-uniform and unstable stress distribution in TGO. As discussed in Section 4.2, the spinel is brittle and fast growing [7]. Localized volume expansion in TGO induced by the fast growth of spinel introduce significant stress concentration, which makes TGO fracture easily. Therefore, spallation of TGO initiates from these spinel zones, as indicated by micrographs in the Fig. 8 and 10. For the HVOF-S coating, the high, stable and uniformly distributed residual stress in TGO clearly indicates the mechanical stability of the TGO [8, 10], which can be supported by the good interface adhesion (Fig. 10) and superior spallation resistance of TGO (Fig. 6).

4.4. Understanding the TGO Spallation

Based on the discussion above, different spallation patterns can be found for three types of coatings. For the HVOF and HVOF-V coatings, the spallation of TGO first initiates from the spinel zones and subsequently spreads all over the surface of coatings upon cooling with the increased oxidation time (Fig. 8 and 10). For the HVOF coating, only minor quantity of detachment of TGO occurs after 100 h oxidation. Therefore, the following section devotes to discuss the failure behavior for all coatings.

It is well documented that two competing failure mechanisms consisting of edge and buckling driven delamination interact for a compressed film system [48, 58]. When films subject to an equi-biaxial compressive stress state, the elastic strain energy stored in TGO. The associated energy release rate G in the TGO is expressed as [48, 59]:

$$G = \frac{1 - \nu_{ox}^2}{2E_{ox}} \sigma^2 h_{ox} \quad (3)$$

where σ , h_{ox} , E_{ox} , and ν_{ox} are the residual stress, thickness, Young's modulus and Poisson's ration of the TGO layer, respectively.

Assuming the coating fails by edge driven delamination. The size of interfacial cracks to initiate an edge delamination is generally on the order of several TGO thicknesses. For a film system in compression, the interfacial crack belongs to model II[48]. Under the idealized assumption that frictional sliding plays a negligible role on the

consumption of energy stored in TGO. Therefore, when the energy release rate G exceeds the interfacial toughness of mode II Γ_i^{II} , the critical TGO thickness for the edge delamination without arrest is [48, 58, 59] :

$$h_{ox}^c = \frac{2E_{ox}\Gamma_i^{\text{II}}}{(1-\nu_{ox}^2)\sigma^2} \quad (4)$$

with $E_{ox} = 380 \text{ GPa}$ [60], $\nu_{ox} = 0.25$ [60], $\sigma = 4.5 \text{ GPa}$ (Fig. 14) and $\Gamma_i^{\text{II}} = 80 \text{ J/m}^2$ [61], the estimated critical TGO thickness is about $3.2 \text{ }\mu\text{m}$.

If the coating fails by buckling driven delamination, buckling delamination occurs when length of pre-existing interfacial crack exceeds the critical width of detached film d_c [48, 62]:

$$d_c = \sqrt{\frac{\pi^2 E_{ox} h_{ox}^2}{3(1-\nu_{ox}^2)\sigma}} \quad (5)$$

The estimated critical width of detached TGO is about 17 times of TGO thickness.

Based on the above analysis for the failure mechanisms of TGO, the edge delamination plays a predominant role on the TGO failure when TGO thickness exceeds the critical thickness. For the HVAF coating, the detachment of TGO first occurs in the weak area where spinel forms, as shown in Fig. 8 and 10. Then the detached area creates new edge for edge delamination. Thus the TGO suffer severe spallation (oxidation for 100 h) (Fig. 6), while TGO thickness exceeds the critical thickness ($3.2 \text{ }\mu\text{m}$). This result is quite well consistent with the estimated critical thickness, which is presented in Fig. 12. When the TGO thickness is lower than critical thickness, the localized spallation of TGO occurs around the spinel (oxidation for 50 h) (Fig. 8). For HVAF-V coating, the amount of spinel in TGO is lower in comparison to HVAF coating (Fig. 9), but the TGO thickness exceeds the critical thickness in the earlier time (oxidation for 50 h) (Fig. 12). At this moment, the significant spallation of TGO starts to occur (Fig. 6). These results indicates that once the new edge is created and the TGO thickness exceeds the critical thickness, the edge driven failure of TGO will lead to severe TGO spallation. Therefore, the HVAF-V coating shows a much higher spallation degree of TGO after oxidation for 50 h ($\sim 31 \%$), compared with the HVAF coating ($\sim 10 \%$). For the HVAF-S coating, the

TGO suggests a buckling delamination mode of failure due to the growth of uniform TGO and good interface adhesion (Fig. 10h and i). The calculated critical width of detached area by equation (5) is about 59.9 μm in a 3.5 μm thick TGO (oxidation for 100 h). This width is very close to minimum width of the spalled area (50~120 μm) observed in Fig. 10g. In other words, the detachment of TGO occurs, only when the length of pre-existing interfacial crack exceeds 59.9 μm (17 times of TGO thickness). Since the interface pore is only microstructural imperfection at the spalled interface (Fig. 10g), the pore might be the nucleation site of initial interfacial crack. However, the pore is hardly detected away from the spalled area (Fig. 10h). Thus the nucleation and propagation interfacial crack are well suppressed by the good interface adhesion and low TGO growth rate for the HVAF-S coating.

In general, the superior spallation resistance of TGO for the HVAF-S coating can be attributed to the uniform, continuous and slowly growing TGO layer and good interface adhesion, which result from the fully dense and uniform microstructure of coating.

5. Conclusions

In this study, the effect of grain size, dislocations and porosity of a NiCoCrAlY coating fabricated by high-velocity air fuel (HVAF) on the isothermal oxidation behavior is systematically investigated and compared with those fabricated by HVAF coating after vacuum heat treatment (HVAF-V) and HVAF coating after spark plasma sintering (SPS) treatment (HVAF-S). The following conclusions can be drawn:

1. The intrinsic defects in the as-sprayed HVAF coating are the pores without internal oxides, which involve extremely low deposition temperature and high flight velocity of particle. The porosity in the HVAF coating is estimated to be 3.58 %. For the HVAF-V coating, the porosity is reduced to ~1.96 %. However, the pores at the unmelted particle boundary cannot be completely eliminated after vacuum heat treatment. The HVAF-S coating shows a fully dense microstructure with a porosity of ~ 0.16 %, which can be attributed to the capability of fast sintering of SPS.
2. The fine grain size of γ -grains and dislocations in the HVAF coating can facilitate

the earlier establishment of α -Al₂O₃ in the early time, which is beneficial to lowering the TGO growth rate. For the HVAF-V and HVAF-S coatings, the transformation rate of θ -Al₂O₃ to α -Al₂O₃ is lowered due to the grain growth and dislocations recovery.

3. The porosity plays a predominant role on the TGO growth rate for the long-term oxidation. Additionally, the contribution of grain size and dislocations in the coatings to the TGO growth rate can be counteracted by that of porosity with the increased oxidation time.
4. The formation of spinel in the TGO and severe internal oxidation can be observed for the HVAF and HVAF-V coatings due to the relatively high porosity. However, the TGO predominantly consists of alumina and no internal oxidation is found for the HVAF-S coating, which benefit from the fully dense microstructure.
5. The isothermal oxidation tests at 1150 °C demonstrate that the HVAF-S coating shows a much better oxidation and spallation resistance of TGO, compared with the HVAF and HVAF-V coatings. The spinel and internal oxidation are detrimental to the stability of TGO.
6. The stability and uniformity of residual stress in TGO for the HVAF-S coating for the long-term oxidation indicates a good interface adhesion between TGO and coating. The constantly decrease in the residual stress in TGO with the oxidation time for HVAF and HVAF-V coatings manifest a weak interface adhesion. Furthermore, the distribution of residual stress around the spinel shows that the stress relaxation prefers to occur in this zone by the nucleation and propagation of cracks.

In summary, vacuum heat treatment cannot completely eliminate the pores at the unmelted particle boundaries in the HVAF coating and instead increases the grain size. Thus the internal oxidation is still inevitable after thermal exposure. Additionally, the increased grain size will delay the transformation of θ -Al₂O₃ to α -Al₂O₃. The spark plasma sintering is a promising method to fully densify the microstructure of coating with a low oxygen content (e.g. HVAF). Perhaps the porosity of HVAF coating can be reduced by regulating the spray parameter and size distribution of spray particles.

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References

- [1] N.P. Padture, M. Gell, E.H. Jordan, Thermal barrier coatings for gas-turbine engine applications, *Science*, 296 (2002) 280-284.
- [2] A.G. Evans, D.R. Mumm, J.W. Hutchinson, G.H. Meier, F.S. Pettit, Mechanisms controlling the durability of thermal barrier coatings, *Progress in Materials Science*, 46 (2001) 505-553.
- [3] G.W. Goward, Progress in coatings for gas turbine airfoils, *Surface and Coatings Technology*, 108-109 (1998) 73-79.
- [4] J.T. DeMasi-Marcin, D.K. Gupta, Protective coatings in the gas turbine engine, *Surface and Coatings Technology*, 68-69 (1994) 1-9.
- [5] Y. Chen, X. Zhao, P. Xiao, Effect of microstructure on early oxidation of MCrAlY coatings, *Acta Materialia*, 159 (2018) 150-162.
- [6] L. Luo, X. Shan, Z. Zou, C. Zhao, X. Wang, A. Zhang, X. Zhao, F. Guo, P. Xiao, A high performance NiCoCrAlY bond coat manufactured using laser powder deposition, *Corrosion Science*, 126 (2017) 356-365.
- [7] Y. Li, C.-J. Li, G.-J. Yang, L.-K. Xing, Thermal fatigue behavior of thermal barrier coatings with the MCrAlY bond coats by cold spraying and low-pressure plasma spraying, *Surface and Coatings Technology*, 205 (2010) 2225-2233.
- [8] E.P. Busso, H.E. Evans, Z.Q. Qian, M.P. Taylor, Effects of breakaway oxidation on local stresses in thermal barrier coatings, *Acta Materialia*, 58 (2010) 1242-1251.
- [9] H.E. Evans, M.P. Taylor, Diffusion Cells and Chemical Failure of MCrAlY Bond Coats in Thermal-Barrier Coating Systems, *Oxidation of Metals*, 55 (2001) 17-34.
- [10] V.K. Tolpygo, D.R. Clarke, K.S. Murphy, Oxidation-induced failure of EB-PVD thermal barrier coatings, *Surface and Coatings Technology*, 146-147 (2001) 124-131.

- [11] P. Niranatlumpong, C.B. Ponton, H.E. Evans, The Failure of Protective Oxides on Plasma-Sprayed NiCrAlY Overlay Coatings, *Oxidation of Metals*, 53 (2000) 241-258.
- [12] Y. Han, Z. Zhu, B. Zhang, Y. Chu, Y. Zhang, J. Fan, Effects of process parameters of vacuum pre-oxidation on the microstructural evolution of CoCrAlY coating deposited by HVOF, *Journal of Alloys and Compounds*, 735 (2018) 547-559.
- [13] W. Brandl, G. Marginean, D. Maghet, D. Utu, Effects of specimen treatment and surface preparation on the isothermal oxidation behaviour of the HVOF-sprayed MCrAlY coatings, *Surface and Coatings Technology*, 188-189 (2004) 20-26.
- [14] W. Brandl, D. Toma, H.J. Grabke, The characteristics of alumina scales formed on HVOF-sprayed MCrAlY coatings, *Surface and Coatings Technology*, 108-109 (1998) 10-15.
- [15] E. Sadeghimeresht, N. Markocsan, P. Nylén, Microstructural characteristics and corrosion behavior of HVAF- and HVOF-sprayed Fe-based coatings, *Surface and Coatings Technology*, 318 (2017) 365-373.
- [16] R.Q. Guo, C. Zhang, Q. Chen, Y. Yang, N. Li, L. Liu, Study of structure and corrosion resistance of Fe-based amorphous coatings prepared by HVAF and HVOF, *Corrosion Science*, 53 (2011) 2351-2356.
- [17] E. Sadeghimeresht, N. Markocsan, P. Nylén, Microstructural and electrochemical characterization of Ni-based bi-layer coatings produced by the HVAF process, *Surface and Coatings Technology*, 304 (2016) 606-619.
- [18] P. Zhang, E. Sadeghimeresht, S. Chen, X.-H. Li, N. Markocsan, S. Joshi, W. Chen, I.A. Buyanova, R.L. Peng, Effects of surface finish on the initial oxidation of HVAF-sprayed NiCoCrAlY coatings, *Surface and Coatings Technology*, 364 (2019) 43-56.
- [19] T. Sui, B. Song, J. Dluhos, L. Lu, A.M. Korsunsky, Nanoscale chemical mapping of Li-ion battery cathode material by FIB-SEM and TOF-SIMS multi-modal microscopy, *Nano Energy*, 17 (2015) 254-260.
- [20] C. Zhao, Y. Zhou, Z. Zou, L. Luo, X. Zhao, F. Guo, P. Xiao, Effect of alloyed Lu, Hf and Cr on the oxidation and spallation behavior of NiAl, *Corrosion Science*, 126 (2017) 334-343.
- [21] T.J. Nijdam, W.G. Sloof, Effect of Y Distribution on the Oxidation Kinetics of

NiCoCrAlY Bond Coat Alloys, *Oxidation of Metals*, 69 (2007) 1-12.

[22] J. Lu, Y. Chen, C. Zhao, H. Zhang, L. Luo, B. Xu, X. Zhao, F. Guo, P. Xiao, Significantly improving the oxidation and spallation resistance of a MCrAlY alloy by controlling the distribution of yttrium, *Corrosion Science*, 153 (2019) 178-190.

[23] J. Shi, H.Q. Li, M.Q. Wan, H.L. Wang, X. Wang, High temperature oxidation and inter-diffusion behavior of electroplated Ni–Re diffusion barriers between NiCoCrAlY coating and orthorhombic-Ti₂AlNb alloy, *Corrosion Science*, 102 (2016) 200-208.

[24] O. Knotek, E. Lugscheider, F. Löffler, W. Beele, Diffusion barrier coatings with active bonding, designed for gas turbine blades, *Surface and Coatings Technology*, 68-69 (1994) 22-26.

[25] H. Peng, H. Guo, J. He, S. Gong, Cyclic oxidation and diffusion barrier behaviors of oxides dispersed NiCoCrAlY coatings, *Journal of Alloys and Compounds*, 502 (2010) 411-416.

[26] S. Deshpande, A. Kulkarni, S. Sampath, H. Herman, Application of image analysis for characterization of porosity in thermal spray coatings and correlation with small angle neutron scattering, *Surface and Coatings Technology*, 187 (2004) 6-16.

[27] K.P. Trumble, M. Rühle, The thermodynamics of spinel interphase formation at diffusion-bonded Ni/Al₂O₃ interfaces, *Acta Metallurgica et Materialia*, 39 (1991) 1915-1924.

[28] R.G. Wellman, A. Scrivani, G. Rizzi, A. Weisenburger, F.H. Tenailleau, J.R. Nicholls, Pulsed electron beam treatment of MCrAlY bondcoats for EB PVD TBC systems part 2 of 2: Cyclic oxidation of the coatings, *Surface and Coatings Technology*, 202 (2007) 709-713.

[29] E.A.G. Shillington, D.R. Clarke, Spalling failure of a thermal barrier coating associated with aluminum depletion in the bond-coat, *Acta Materialia*, 47 (1999) 1297-1305.

[30] B.A. Pint, Optimization of Reactive-Element Additions to Improve Oxidation Performance of Alumina-Forming Alloys, *Journal of the American Ceramic Society*, 86 (2003) 686-695.

[31] J.A. Nychka, D.R. Clarke, Quantification of Aluminum Outward Diffusion During

Oxidation of FeCrAl Alloys, *Oxidation of Metals*, 63 (2005) 325-352.

[32] D. Naumenko, B.A. Pint, W.J. Quadakkers, Current Thoughts on Reactive Element Effects in Alumina-Forming Systems: In Memory of John Stringer, *Oxidation of Metals*, 86 (2016) 1-43.

[33] A. Kumar, M. Nasrallah, D.L. Douglass, The effect of yttrium and thorium on the oxidation behavior of Ni-Cr-Al alloys, *Oxidation of Metals*, 8 (1974) 227-263.

[34] D. Li, H. Guo, D. Wang, T. Zhang, S. Gong, H. Xu, Cyclic oxidation of β -NiAl with various reactive element dopants at 1200°C, *Corrosion Science*, 66 (2013) 125-135.

[35] B.A. Pint, M. Treska, L.W. Hobbs, The effect of various oxide dispersions on the phase composition and morphology of Al₂O₃ scales grown on β -NiAl, *Oxidation of Metals*, 47 (1997) 1-20.

[36] F.A. Golightly, F.H. Stott, G.C. Wood, The influence of yttrium additions on the oxide-scale adhesion to an iron-chromium-aluminum alloy, *Oxidation of Metals*, 10 (1976) 163-187.

[37] D.G. Lees, On the reasons for the effects of dispersions of stable oxides and additions of reactive elements on the adhesion and growth-mechanisms of chromia and alumina scales-the 'sulfur effect', *Oxidation of Metals*, 27 (1987) 75-81.

[38] X. Wang, G. Lee, A. Atkinson, Investigation of TBCs on turbine blades by photoluminescence piezospectroscopy, *Acta Materialia*, 57 (2009) 182-195.

[39] B. Pint, The oxidation mechanism of θ -Al₂O₃ scales, *Solid State Ionics*, 78 (1995) 99-107.

[40] R.W. Jackson, D.M. Lipkin, T.M. Pollock, Thermal barrier coating adherence to Hf-modified B2 NiAl bond coatings, *Acta Materialia*, 80 (2014) 39-47.

[41] Y. Li, C.-J. Li, Q. Zhang, G.-J. Yang, C.-X. Li, Influence of TGO Composition on the Thermal Shock Lifetime of Thermal Barrier Coatings with Cold-sprayed MCrAlY Bond Coat, *Journal of Thermal Spray Technology*, 19 (2009) 168-177.

[42] V. Teixeira, M. Andritschky, W. Fischer, H.P. Buchkremer, D. Stöver, Effects of deposition temperature and thermal cycling on residual stress state in zirconia-based thermal barrier coatings, *Surface and Coatings Technology*, 120-121 (1999) 103-111.

- [43] L. Qiu, F. Yang, W. Zhang, X. Zhao, P. Xiao, Effect of Al content on the lifetime of thermally grown oxide formed on Ni–Al alloys after isothermal oxidation, *Corrosion Science*, 89 (2014) 13-20.
- [44] Y. Zhou, X. Zhao, C. Zhao, W. Hao, X. Wang, P. Xiao, The oxidation performance for Zr-doped nickel aluminide coating by composite electrodepositing and pack cementation, *Corrosion Science*, 123 (2017) 103-115.
- [45] L. Yang, L. Zheng, H. Guo, The residual stress of oxide scales grown on Ni-Al alloys doped with minor Dy and Y, *Corrosion Science*, 112 (2016) 542-551.
- [46] V.K. Tolpygo, D.R. Clarke, Alumina scale failure resulting from stress relaxation, *Surface and Coatings Technology*, 120-121 (1999) 1-7.
- [47] Y. Chai, C. Lin, Y. Li, Effects of creep-plastic behavior on stress development in TBCs during cooling, *Ceramics International*, 43 (2017) 11627-11634.
- [48] J.W. Hutchinson, M.Y. He, A.G. Evans, The influence of imperfections on the nucleation and propagation of buckling driven delaminations, *Journal of the Mechanics and Physics of Solids*, 48 (2000) 709-734.
- [49] S.-S. Kim, Y.-F. Liu, Y. Kagawa, Evaluation of interfacial mechanical properties under shear loading in EB-PVD TBCs by the pushout method, *Acta Materialia*, 55 (2007) 3771-3781.
- [50] N.M. Yanar, G.H. Meier, F.S. Pettit, The influence of platinum on the failure of EBPVD YSZ TBCs on NiCoCrAlY bond coats, *Scripta Materialia*, 46 (2002) 325-330.
- [51] V.K. Tolpygo, D.R. Clarke, Microstructural study of the theta-alpha transformation in alumina scales formed on nickel-aluminides, *Materials at high temperatures* 17 (2000) 59-70.
- [52] B.A. Pint, Limitations on the Use of Ion Implantation for the Study of the Reactive Element Effect in β -NiAl, *Journal of The Electrochemical Society*, 141 (1994) 2443.
- [53] D. Mercier, B.D. Gauntt, M. Brochu, Thermal stability and oxidation behavior of nanostructured NiCoCrAlY coatings, *Surface and Coatings Technology*, 205 (2011) 4162-4168.
- [54] Q. Zhang, C.-J. Li, C.-X. Li, G.-J. Yang, S.-C. Lui, Study of oxidation behavior of nanostructured NiCrAlY bond coatings deposited by cold spraying, *Surface and*

Coatings Technology, 202 (2008) 3378-3384.

[55] D. Salehi Doolabi, M.R. Rahimpour, M. Alizadeh, S. Pouladi, S.M.M. Hadavi, M.R. Vaezi, Effect of high vacuum heat treatment on microstructure and cyclic oxidation resistance of HVOF-CoNiCrAlY coatings, *Vacuum*, 135 (2017) 22-33.

[56] E. Lugscheider, C. Herbst, L. Zhao, Parameter studies on high-velocity oxy-fuel spraying of MCrAlY coatings, *Surface and Coatings Technology*, 108-109 (1998) 16-23.

[57] C. Kaplin, M. Brochu, Effects of water vapor on high temperature oxidation of cryomilled NiCoCrAlY coatings in air and low-SO₂ environments, *Surface and Coatings Technology*, 205 (2011) 4221-4227.

[58] J.W. Hutchinson, Z. Suo, Mixed Mode Cracking in Layered Materials, *Advances in Applied Mechanics*, 29 (1991) 63-191.

[59] R.T. Wu, K. Kawagishi, H. Harada, R.C. Reed, The retention of thermal barrier coating systems on single-crystal superalloys: Effects of substrate composition, *Acta Materialia*, 56 (2008) 3622-3629.

[60] L.T. Wu, R.T. Wu, X. Zhao, P. Xiao, Microstructure parameters affecting interfacial adhesion of thermal barrier coatings by the EB-PVD method, *Materials Science and Engineering: A*, 594 (2014) 193-202.

[61] T. Xu, S. Faulhaber, C. Mercer, M. Maloney, A. Evans, Observations and analyses of failure mechanisms in thermal barrier systems with two phase bond coats based on NiCoCrAlY, *Acta Materialia*, 52 (2004) 1439-1450.

[62] F. Cao, B. Tryon, C.J. Torbet, T.M. Pollock, Microstructural evolution and failure characteristics of a NiCoCrAlY bond coat in “hot spot” cyclic oxidation, *Acta Materialia*, 57 (2009) 3885-3894.