Effect of microstructure on early oxidation of MCrAlY coatings

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Corresponding Author: Professor Ping Xiao, PhD

Corresponding Author's Institution: University of Manchester

First Author: Ying Chen, PhD

Order of Authors: Ying Chen, PhD; Xiaofeng Zhao, PhD; Ping Xiao, PhD

Abstract: Two MCrAlY coatings with the same nominal composition, but different microstructures are deposited onto Hastelloy® X superalloy substrates by low pressure plasma spraying (LPPS) and high velocity oxygen fuel (HVOF) spraying, respectively. The early oxidation behaviour of the coatings at 1150 °C is studied. For the LPPS coating with relative coarse grains, the γ and β -phase show different oxidation behaviours: the oxide on the γ phase shows a multi-layer structure, consisting of outer (Ni,Co)(Cr,Al)₂O₄, intermediate (Cr,Al)₂O₃ and inner α -Al₂O₃; the oxidation of the β -phase, however, is characterised by selective oxidation of aluminium and the oxide is composed of a mixture of θ and α -Al₂O₃. For the nanocrystalline HVOF coating, it does not show site-specific oxidation and the oxidation is characterised by formation of an exclusive α -Al₂O₃ scale over the surface. The microstructure-dependent oxidation is quantitatively described from the perspective of oxidation kinetics, with contribution from both lattice and grain boundary diffusion taken into consideration. A critical grain size of the γ phase, below which formation of an exclusive Al₂O₃ scale can be achieved, is predicted and verified. The study gives new insights into oxidation of MCrAlY coatings.

School of Materials
University of Manchester
Manchester
M13 9PL
Tel: 44-161 306 5941
Fax: 44-161 306 3586
Email: ping.xiao@manchester.ac.uk

Ref.: Ms. No. A-18-1526

Effect of microstructure on early oxidation of MCrAlY coatings *Acta Materialia*

Dear Professor Nitin Padture,

Thanks for your efforts to arrange the review of the manuscript and we appreciate the valuable comments given by the reviewers. In this version, we have addressed all of the comments (please see the "responses to reviewers" letter for details) and revisions have been made accordingly (highlighted by red in the revised manuscript). I wish that the revisions are satisfactory for publication of the paper. Please let us know if we need to make more effort in improvement of this paper.

Yours sincerely,

Ying Chen and Ping Xiao

Response to Reviewers

Reviewer #1: Review of Acta Met A-18-1525 Effect of microstructure on early oxidation of MCrAlY coatings by Ying Chen et al.

This paper describes the early oxidation of both an LPPS and HVOF bond coat. The materials is excellently presented in nearly flawless English. In the end the rapid transport of Aluminum by grain boundaries explains nearly all the is observed. Much background is already known and well review in the paper. The paper does an excellent job of putting all the pieces together and extensive experimental results are shown including PLPS (oxide too thin for XRD) SEM and TEM using multiple techniques in the TEM. They then model the results to explain in a semi quantitative way why the results are the way they are. Generally a very nice paper. This reviewer enjoyed reading this well written paper. One caveat is that this reviewer although very familiar with the results in this filed is not an expert on which exact references are most appropriate. The following things can be improved.

1. For less experienced readers they should give the composition and crystal structure of gamma and beta phases.

Reply: We have added a table (**Table 2**) listing the compositions of the β and γ -phase determined by energy dispersive X-ray spectroscopy (see **Table 2** and corresponding text in **Line 11-12, Page 5**) The crystal structures of the γ and β -phases are given in Introduction (**Line 8-9, Page 2**).

2. On page 12 they state that equilibrium imposes strict restrictions on the multi-phase alloy. True but how does this play into the discussed behavior.

Reply: This statement is to stress that the thermodynamic equilibrium in the two-phase NiCoCrAlY coating prevents the interaction of J_{Al}^{γ} , J_{Al}^{β} and J_{Al}^{GB} in the alloy.

We have added this point into the text (**Line 7-8, Page 13**)

3.p. 3 the bond coats were over 200 microns thick. Probably not important given the short heating but typical bond coats are much thinner. If there is a reason for this choice it is worth stating.

Reply: The reason for using a relatively thick coating is to eliminate the effect of substrate/coating interdiffusion on the early oxidation of the coatings.

This statement has been added into the text (**Line 41-43, Page 3**)

4.P.4 It says the samples were heated to 1150C at 200 C/minute and air cooling. At this rate could be a question of will the samples heat fast enough to follow the furnace temperature setting and the question of how fast the

early cooling was. A bit more detail is needed to justify that this heating was achieved in the time specified. Ideally a welded thermocouple on the back of the sample could have proved this.

Reply: The furnace we used for the oxidation experiment had a thermocouple fitted in the centre of the heating chamber and the samples were placed next to the thermocouple. The thermocouple monitored the temperatures around the samples and synchronises the temperature data to the control program, which constantly adjust the input power to meet the temperature setting.

The above description has been added into the text (**Line 15-19, Page 4**).

5. On page line 21 it talks about the buried alpha compensating for the different fluoresce flux by the over lying other oxide. Since the sensitivity ratio is 10. Seems this should be stated as possibly helping but not glossed over like it would somehow luckily attenuate the correct large amount. It seems unlikely that the thin over layer can give 10 X attenuation. This should be more honestly admitted. Such an admission would not seem to undermine any of the main arguments.

Reply: We have added a statement to admit the thin top θ -Al₂O₃ layer is unlike to fully compensate the difference in luminescence intensity between the θ -Al₂O₃ and α -Al₂O₃. Please see **Line 28-30, Page 6**.

6. page 9 line 22 statement should be clearer. What they are saying is that for continuous Alpha formation that the current aluminum replacement needs to be sufficient or more than sufficient to compensate the loss by alumina formation. There is no reason to assume that this is always at the minimum.

Reply: The statement has been revised (**Line 28-29, Page 9**)

7. page 7 they say the formation of theta is 10 times faster than the formation of alpha. Based on what? The measured thicknesses or some reference? Justify the comment.

Reply: The statement is based on the references 37 and 38 cited in the text (**Line 40, Page 7**).

8. page 13, they apparently look at a grain of 700nm such that the alpha alumina forms on the beta and claim that 700 or smaller is needed. However this is a case where the alpha alumina formed. How do they know it would not also form at 900 nm. Seems this is really a lower bound to the upper limit. This needs to be explained what the thinking is here or this admitted as a bound.

Reply: We have added a short explanation of this critical grain size and admitted that it could span a certain range (**Line 34-41, Page 13**)

9. Two corrections of English, on Page 13 line 10 and on page 4 Line 24 in both places the word details is used when the word detail should be used.

Very minor but should be corrected to go with the rest of the perfect English used.

Reply: We have replaced the original words with more detailed words. Please see **Line 27, Page 4** and **Line 21, Page 13**.

Two auxiliary comments for their consideration.

1. One of the TEM images (b) marks Y-rich precipitates. They might note that these are oxygen diffusion paths which if spanning the oxide short circuit the alumina as a diffusion barrier and have caused poor BC performance in some cases.

Reply: At this stage it is difficult to know if the Y-rich precipitates will span the Al_2O_3 layer and how they will affect the performance of the bond coat in long term service based on the early oxidation experiments conducted in this work. We will bear this comment in mind in our future work.

2. The discussion notes that deformation related defects help alpha alumina formation. There is growing evidence that HVOF bond coats outperform even HVOF. HVAF results in even more plastic deformation so the HVOF results can be explained by what they are saying and it may be worth adding this point.

Reply: We have added this point into the text (**Line 7-10, Page 15**).

In summary a very good paper. The most important things to change are in comments 8 and 5. This paper should be easily improved as indicated above and published.

Reviewer #2

Authors have conducted high temperature oxidation behavior at the very early stage focused on microstructures for two different spray processes used MCrAlY coatings.

This article is very important and interesting for understanding fundamental on initial stage of high temperature oxidation of MCrAlYs. However, some revisions are necessary before paper acceptance.

1. Authors applied 1150 deg.C for the high temperature oxidation tests. But in the case of blades of gas turbines or aerospace engines, surface temperature is approximately 900-1000 deg.C. Why authors did choose this temperature?

Reply: Oxidation of MCrAlY at a relatively low temperature (e.g. 900-1000 °C) is significantly slower than that at 1150 °C and a short period of oxidation (e.g. 5 minutes) at 900-1000 °C would produce an

extremely thin oxide layer, which makes it extremely difficult to characterise and analyse. The model study in this work used a slightly higher temperature to avoid this problem, but could still capture the physical essence and provide mechanistic understanding of the early oxidation of the MCrAlY coatings.

On the other hand, it is expected that gas-turbine engine will run at even higher temperatures in future. The study in this work could be also helpful to understanding the early oxidation behaviour of MCrAlY coatings at such temperatures.

2. After "2. Materials and Methods", authors should use "NiCoCrAlY" instead of MCrAlY.

Reply: "MCrAlY" has been replaced by "NiCoCrAlY" throughout the text after "2. Materials and Methods".

3. P.3, L.7: Al₂O₃ --> "l" is subscript notation. Please correct it.

Reply: The above typo has been corrected (**Line 7, Page 3**)

4. Authors applied annealing treatment at 1100deg.C for 2h under 10-5mbar environment for only LPPS coating. Please explain the reason why.

Reply: The reason that post-deposition annealing was applied to LPPS, but not HVOF, was to avoid undesirable grain growth of the nanocrystalline HVOF coating. As the focus of this study is the effect of microstructure on oxidation of the MCrAlY coating, creating two distinct microstructures is essential to our study.

This explanation has been added into the text (**Line 3, Page 4**).

5. Authors used several symbols in section 4. It is better to write up used symbols as "nomenclature".

Reply: A nomenclature has been added into the revised manuscript.

6. P.10, L.26: Authors mentioned "EBSD analysis also shows that the grain boundaries are predominately high-angle grain boundaries and on average a gamma-grain is bordered by five beta-grains and one gamma-grain." How did authors find the five beta-grains and one gamma-grain?

Reply: This finding is determined by image analysis of the EBSD phase-contrast maps (3 in total) of the LPPS coating, in which the contours of over 50 γ -grains and their surrounding grains are analysed.

A short description of these details has been added into **Line 31, Page 10** and **Line 1, Page 11**.

7. P.12, L.6: Authors assigned four different sets of values. How did authors choose these values?

Reply: These values are assigned based on the assumption that the grain boundary diffusion is orders of magnitude faster than lattice diffusion. We believe that the values are qualitatively reasonable, although it is currently not possible to justify these values quantitatively as the lattice and grain boundary diffusion coefficients of aluminium in the NiCoCrAlY bond coat at 1150 °C are not available in the literature. Nevertheless, these values are selected only to provide some examples on how the fast grain boundary diffusion of Al in the coating could affect the selective oxidation of aluminium as a function of grain size.

8. P.15, L.15, Section 4.4: There is no image, no information about microstructure and coating process. And I felt this section is digression. Please consider whether this section is necessary or not.

Reply: We think this section is an extension of our study on MCrAlY coatings and is helpful to understanding the oxidation of the Pt-diffused γ/γ' bond coat. We have added an EBSD image (**Fig.13**), which shows the nanostructured grains in the surface region of a Pt-diffused γ/γ' bond coat, to strength our discussion in this section.

A short description of **Fig.13** is also added into the text (**Line 13-15, Page 16**)

Nanostructured grains

Fig.13. Cross-sectional EBSD inverse pole figure map (RD) of an as-deposited Pt-diffused γ/γ' coating showing the nanostructured grains in the surface region

Effect of microstructure on early oxidation of MCrAlY coatings

Ying Chen¹, Xiaofeng Zhao² and Ping Xiao^{1, 2†}

¹ School of Materials, University of Manchester, Manchester, M13 9PL, UK

² Shanghai Key Laboratory of Advanced High-Temperature Materials and Precision Forming, Shanghai Jiao Tong University, Shanghai, 200240, PR China

Abstract

Two MCrAlY coatings with the same nominal composition, but different microstructures are deposited onto Hastelloy® X superalloy substrates by low-pressure plasma spraying (LPPS) and high velocity oxygen fuel (HVOF) spraying, respectively. The early oxidation behaviour of the coatings at 1150 °C is studied. For the LPPS coating with relative coarse grains, the γ and β -phase show different oxidation behaviours: the oxide on the γ -phase shows a multi-layer structure, consisting of outer $(\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4$, intermediate $(\text{Cr,Al})_2\text{O}_3$ and inner $\alpha\text{-Al}_2\text{O}_3$; the oxidation of the β -phase, however, is characterised by selective oxidation of aluminium and the oxide is composed of a mixture of θ and $\alpha\text{-Al}_2\text{O}_3$. For the nanocrystalline HVOF coating, it does not show site-specific oxidation and the oxidation is characterised by formation of an exclusive $\alpha\text{-Al}_2\text{O}_3$ scale over the surface. The microstructure-dependent oxidation is quantitatively described from the perspective of oxidation kinetics, with contribution from both lattice and grain boundary diffusion taken into consideration. A critical grain size of the γ -phase, below which formation of an exclusive Al_2O_3 scale can be achieved, is predicted and verified. The study gives new insights into oxidation of MCrAlY coatings.

Keywords: MCrAlY; Oxidation; Microstructure

1. Introduction

MCrAlY (M=Ni, Co or a mixture of the two) overlay coatings are widely applied to thermally loaded structures (e.g. gas-turbine blades made of Ni-base superalloys) to protect the components against oxidation and corrosion during service at high temperature [1-4]. The oxidation resistance of these coatings is mainly determined by their chemical compositions, which are carefully engineered to achieve high melting points and capabilities to develop a thermodynamically stable, slow growing, adherent and mechanically robust $\alpha\text{-Al}_2\text{O}_3$ scale over the coating surface upon exposure to high temperatures. The formation of the protective $\alpha\text{-Al}_2\text{O}_3$ scale becomes

[†] Corresponding author: Ping Xiao (p.xiao@manchester.ac.uk).

even more essential when a thermal barrier coating (TBC, typically made of 7-8 wt% yttria stabilised zirconia (YSZ)) is applied on top of the MCrAlY coating, because α -Al₂O₃ is not only an efficient oxygen diffusion barrier, but also thermodynamically compatible with the YSZ TBC (e.g. they do not form interphases and their mutual solubility is very limited) [5], which is critical to the maintenance of the interfacial adhesion upon thermal exposure.

Typical MCrAlY coatings show a two-phase structure: a brittle, Al-rich β -phase (CsCl structure) embedded in a ductile, Al-poor γ -phase matrix (face centred cubic structure). The application of this two-phase structure is to achieve a balance between oxidation resistance and mechanical properties: the β -phase acts as an aluminium reservoir and offers oxidation resistance; the γ -phase improves ductility, thereby reducing the susceptibility of the coatings to brittle cracking induced by thermos-mechanical fatigue [6]. Oxidation of MCrAlY coatings has been extensively studied, and these studies have provided considerable insights into the underlying oxidation mechanisms. However, substantial variations in oxidation kinetics (e.g. whether the growth of the oxide follows a parabolic or subparabolic law [7-10]) and oxide compositions (e.g. whether the oxide scale is composed of predominately Al₂O₃ or a mixture of Al₂O₃ and Ni/Co/Cr- rich oxides [11-13]) have been reported. These discrepancies could be partially explained by the variations in oxidation conditions (e.g. temperatures, environmental oxygen partial pressures [7, 14, 15]), geometrical factors (e.g. surface roughness [16]) and the coating compositions, especially the content of reactive element (e.g. yttrium [8, 17]). However, the facts that for a given oxidation condition MCrAlY coatings with the same composition but different microstructures could differ substantially in oxidation behaviour suggest that composition and oxidation condition alone do not compose the full story [11, 12, 18]. A further complication concerning the oxidation behaviour of the MCrAlY coatings is that the coating has a two-phase structure, in which the individual phase could show different oxidation behaviours, at least during initial stage of the oxidation [11, 19, 20].

It is widely accepted that between 750-1200 °C the growth of α -Al₂O₃ scales is controlled by the concurrent, counter-diffusion of anions (O²⁻) and cations (Al³⁺) along the grain boundaries of the growing oxide [21, 22]. However, the formation of such a continuous, protective α -Al₂O₃ scale is generally preceded by an initially fast oxidation stage associated with severe Al depletion and subsequent formation of the "non-protective" oxides such as NiO, (Ni,Co)(Cr,Al)₂O₄, and Cr₂O₃. [11, 23-28]. The formation of these fast growing, brittle transient oxides is undesirable as they reduce the protectiveness of the scales and undermine the interfacial adhesion [5], especially in the case when YSZ TBCs are applied. During the transient oxidation stage when the multi-component MCrAlY alloy surface is fully exposed to the atmosphere, the resulting oxide composition and microstructure depend on the supply of the metal elements to the surface according to the Wagner's oxidation theory [29, 30]. The diffusion fluxes of the

alloy elements towards the surface, in turn, are not only determined by the composition, but also the microstructure of the underlying metal [31] (e.g. the number of crystallographic defects, such as grain boundaries, which are fast diffusion paths). On the other hand, even under the circumstances when growth of Al_2O_3 is kinetically favoured during the transient oxidation stage, formation of the protective $\alpha\text{-Al}_2\text{O}_3$ is often accompanied with nucleation and growth of metastable Al_2O_3 polymorphs (e.g. $\theta\text{-Al}_2\text{O}_3$) [10, 32, 33]. The metastable Al_2O_3 is less protective, and undergoes a progressive phase transformation to $\alpha\text{-Al}_2\text{O}_3$ during the subsequent oxidation process. This phase transformation causes a disruptive volume shrinkage and tensile stress in the scale, which could compromise the structural integrity of the scale [32]. Nevertheless, the transient oxidation of MCrAlY coatings, especially at the very early stage of the oxidation, has yet to be sufficiently characterised or understood, not to mention a thorough understanding of the relationship between the oxide composition and the underlying coating alloy microstructure.

The objective of this study is to provide detailed characterisation and mechanistic understanding of the early oxidation of two MCrAlY coatings, with a focus on the effect of the microstructure of the coatings. The two MCrAlY coatings used in this work have the same nominal composition but different microstructures, deposited by low-pressure plasma spraying (LPPS) and high velocity oxygen fuel (HVOF) spraying, respectively. LPPS and HVOF are two of the most frequently used thermal spraying techniques to manufacture MCrAlY coatings for industrial applications, and therefore the results in this work should give universal insights into the oxidation behaviour of many MCrAlY coatings during service. Characterisation of oxidation is implemented using correlative microscopy, which links together the observations and analysis from optical microscopy, scanning electron microscopy (SEM) and analytical transmission electron microscopy (TEM). The microstructure-dependent oxidation effects are then described from the perspective of oxidation kinetics, which includes the contribution of both lattice and grain boundary diffusion, to quantitatively illustrate the importance of certain microstructural features of the MCrAlY coatings in governing the transient oxidation behaviour. The analysis of the oxidation of the MCrAlY coatings is further extended to the Pt-diffused γ/γ' bond coat to explain the oxidation of this type of bond coat.

2. Materials and Methods

ANiCoCrAlY coatings were prepared by spraying ANiCoCrAlY powder (Amdry 365-2, Sulzer Metco) onto Hastelloy® X superalloy plates ($55 \times 30 \times 5 \text{ mm}^3$) using HVOF and LPPS, respectively. The thickness of the as-deposited HVOF and LPPS coating is $\sim 230 \text{ }\mu\text{m}$ and $200 \text{ }\mu\text{m}$, respectively. The relatively thick coatings are helpful to eliminating the effect of coating/substrate interfusion on early oxidation of the coatings. Table 1 shows the nominal compositions of the as-sprayed coatings and the Hastelloy® X superalloy

substrate. The LPPS coating was then annealed in a vacuum tube furnace (Carbolite, UK) at 10^{-5} mbar at 1100 °C for 2 h. No post deposition annealing was applied to the HVOF coating to avoid undesirable grain growth. The coated superalloy plates were sliced into square-shape samples (8×8 mm²) using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 10, Struers). Prior to oxidation, the surfaces of the coatings were mechanically polished to a 1 μ m finish. This step produced a similar initial root-mean-square roughness (~ 0.05 μ m) on all samples. Several Vickers micro-hardness indentations were placed into the surfaces as markers and then imaged using an optical microscope (BH2-UMA, Olympus) and SEM (Magellan 400 XHR, FEI). The recorded surface images allowed correlation of the same areas before and after oxidation to study possible site-specific oxidation. Oxidation of the coatings was performed in a CMTM furnace at 1150 °C for 5 minutes in laboratory air, with rapid heating (200 °C/min) and fan-assisted air cooling. The furnace had a thermocouple fitted in the centre of the chamber and the samples were placed next to the thermocouple. The thermocouple monitored the temperatures around the samples and synchronises the temperature data to the control program, which constantly adjust the input power to meet the temperature setting.

After oxidation, the phases present in the thermally grown Al₂O₃ scales were determined using photoluminescence piezospectroscopy (PLPS) on an InViaTM confocal Raman microscope (Renishaw, Gloucestershire, UK) fitted with a He-Ne laser source ($\lambda=633$ nm) according to the methodology described in the references [32]. This technique takes advantage of the high sensitivity of the Cr³⁺ fluorescence, even though the Al₂O₃ scale formed during the early oxidation stage is thin and sometimes buried underneath a duplex (Ni,Co)(Cr,Al)₂O—(Cr,Al)₂O₃transient—oxide layer. Following PLPS measurements, the surfaces of the samples were sputtered with a thin layer of gold and examined using SEM from both top and oblique views to reveal the surface microstructure and topography of the oxides. In order to study the composition and microstructure of the oxides in greater details, cross-sectional thin lamellae of the oxides were prepared by a focused ion beam (FIB, Helios NanoLab 660, FEI) and analysed using a scanning transmission electron microscope (STEM, TecnaiTM G2 200kV, FEI) equipped with an energy dispersive X-ray spectroscopy (EDS, X-MaxN 80T, Oxford Instruments) system. The details of STEM sample preparation can be found elsewhere [34]. But briefly, cross-sectional lamellae were first created by FIB milling through the oxides in the selected regions. The lamellae were then *in-situ* lifted out and welded to a copper grid using a combination of an OmniProbe micromanipulator and a gas injection system fitted in the FIB system, followed by thinning to an electron transparent thickness (< 100 nm). Apart from STEM analysis, the cross-sectional thin lamellae were also analysed using transmission Kikuchi diffraction (TKD) in the Magellan 400 XHR SEM to map the phase distribution over the thickness of the oxides. The transmission geometry adopted in the TKD technique allows a minimum interaction volume between the impinging electrons and the samples being probed, thus

improving the spatial resolution over the conventional electron backscattered diffraction (EBSD). Details of the TKD technique can be found elsewhere [35].

3 Results

3.1 Microstructure of the as-deposited MnNiCoCrAlY coatings

Fig.1 shows the microstructure of the MnNiCoCrAlY coatings deposited by LPPS (Fig.1a) and HVOF (Fig.1b), respectively. Both types of the coatings are dense, homogeneous and exhibit a two-phase microstructure (β and γ). However, their microstructures differ with respect to the grain size of the constituent phases, with the LPPS coating showing much coarser grains than the HVOF coating. The chemical compositions of the β and γ -phase, determined by EDS point analysis, are given in Table 2. The grain size and aspect ratio of the β and γ -phase in the LPPS and HVOF coating, determined by quantitative image analysis, are given in Table 23. Oxide inclusions are hardly seen in either type of the coatings, which indicates that the coating material underwent negligible oxidation during the spraying process. This could be attributed to the low oxygen content during LPPS and the relatively low temperature and high velocity during HVOF, respectively.

3.2 Surface morphology of the oxides

Fig.2 shows the surface morphology and topography of the oxides grown on the LPPS coating. Correlation of the surface microstructure of the same area before and after oxidation shows that the oxides inherit the contours of the underlying metal grains, but the oxides on the β and γ -grains exhibit distinct surface morphologies. The surface of the oxide on the γ -grains shows angular, faceted grains, but the surface of the oxide on the β -grains is characterised by whisker-type grains, which are typical microstructural features of metastable $\theta\text{-Al}_2\text{O}_3$ [32]. Surface topography revealed by the oblique view (Fig.2b) shows that the surface of the oxide on the β -grains is highly uneven, suggesting that the thickness of the oxide may vary substantially even over the surface of a single β -grain. The divergent surface morphologies of the oxides on the β and γ -grains are consistent with the observations reported by Levi et al [20]. The dependence of the oxide morphology on the microstructure of the underlying alloy, however, is not seen on the HVOF MnNiCoCrAlY coating (Fig.3). Instead, the oxide is rather homogeneous with tiny equiaxed grains ($\sim 60\text{-}300\text{ nm}$) densely compacted all over the coating surface.

3.3 PLPS analysis of the Al_2O_3 scales

Fig.4 shows the PLPS spectra of the Al_2O_3 scales grown on the γ (Fig.4a) and β -grains (Fig.4b) of the LPPS coating, respectively. It should be noted that there are two pre-conditions that allow the PLPS spectra of the Al_2O_3 scales

on different phases to be collected separately with little ambiguity. First, the difference in morphology and thickness between the oxides on the β and γ -grains gives rise to different contrasts of the two types of the areas under the optical microscope. Second, the size of the focused laser spot is in the range of $\sim 3\text{-}5\ \mu\text{m}$, which is comparable to the grain size of the LPPS coating. The PLPS spectra of the Al_2O_3 scales on both β and γ -grains show characteristic R lines (R1 and R2) of $\alpha\text{-Al}_2\text{O}_3$ and T lines (T1 and T2) of $\theta\text{-Al}_2\text{O}_3$, suggesting that the Al_2O_3 scales on β and γ -grains consist of a mixture of θ and $\alpha\text{-Al}_2\text{O}_3$. However, the relative intensities of the T1 and T2 lines collected from the β -grains are substantially higher than those on the γ -grains, suggesting a significantly higher content of $\theta\text{-Al}_2\text{O}_3$ in the Al_2O_3 scales on the β -grains. The higher content of the $\theta\text{-Al}_2\text{O}_3$ on the β -grain is consistent with the previous findings that the β -grain has a large propensity to form $\theta\text{-Al}_2\text{O}_3$ than the γ -grain [20]. To a first approximation, the content of $\theta\text{-Al}_2\text{O}_3$, $c_{\theta\text{-Al}_2\text{O}_3}$, in the Al_2O_3 scale can be estimated by comparing the intensities of the R lines and T lines, given by [36]:

$$c_{\theta\text{-Al}_2\text{O}_3} = \frac{A_{T1} + A_{T2}}{A_{R1} + A_{R2} + A_{T1} + A_{T2}} \quad (1)$$

Where A denotes the areas of the characteristic peaks obtained by fitting the PLPS spectra in WIRETM software (Renishaw, Gloucestershire, UK) by four mixed Gaussian–Lorentzian functions. The calculated $c_{\theta\text{-Al}_2\text{O}_3}$ in the Al_2O_3 scales on the γ and β -grains of the LPPS coating is 3.26% and 50.1%, respectively.

It should be noted that the above calculation is only a qualitative estimation, as it has been reported that the intensity of the $\theta\text{-Al}_2\text{O}_3$ is about 10 times higher than that of the $\alpha\text{-Al}_2\text{O}_3$ [32]. However, the fact that the $\alpha\text{-Al}_2\text{O}_3$ layer is buried underneath the $\theta\text{-Al}_2\text{O}_3$ layer (which will be shown later) means that the intrinsic higher intensity of the $\alpha\text{-Al}_2\text{O}_3$ could be partially cancelled out as the intensity of the laser will decrease as it passes through the $\theta\text{-Al}_2\text{O}_3$ layer before reaching the underlying $\alpha\text{-Al}_2\text{O}_3$ layer. This is expected to decrease the uncertainty of the calculation using Eq (1), although it is unlikely that the thin top $\theta\text{-Al}_2\text{O}_3$ layer could fully compensate the difference in luminescence intensity between $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$.

In contrast with the findings on the LPPS coating, the PLPS spectra of the Al_2O_3 scale on the HVOF coating only show single characteristic R1 and R2 doublet of $\alpha\text{-Al}_2\text{O}_3$ (Fig.5), irrespective of the areas being probed. This suggests that the Al_2O_3 scale on the HVOF coating only contains $\alpha\text{-Al}_2\text{O}_3$ after oxidation.

3.4 TEM analysis of the oxide on the LPPS coating

Fig. 6 shows the TEM analysis of the cross-section of the oxide on the LPPS ~~ANiCo~~CrAlY coating. The oxide on the γ -grain is essentially multilayer, consisting of an outer Ni/Co/Cr-rich layer ($\sim 235\ \text{nm}$ thick), an intermediate

Cr-rich layer (~ 26 nm thick) and an inner Al-rich layer (~ 88 nm thick), as confirmed by the contrast in the STEM annular dark field (STEM-ADF) image (Fig.6a and b) and corresponding EDS mapping (Fig.6d, e, g, and h). Selected area electron diffraction (SAED) conducted on a grain of the outer layer shows the characteristic diffraction pattern of the spinel structure (Fig.6c), suggesting that the outer layer is spinel. SAED analysis of the intermediate Cr-rich and inner Al-rich layer has not been successful due to the extremely fine grains. However, high resolution TEM (HR-TEM) analysis of both the intermediate Cr-rich and inner Al-rich layers reveals a corundum structure, as exemplified in Fig.6f. The combination of the HR-TEM, EDS analysis and PLPS spectra suggests that the Cr-rich and Al-rich layer is mainly α -(Cr,Al)₂O₃ and α -Al₂O₃, respectively. The presence of the overwhelming α -Al₂O₃ in the inner layer is expected, as the growing spinel reduces the oxygen partial pressure at the oxide/metal interface and enables the α -Al₂O₃ to form thermodynamically in preference to its metastable polymorphs (e.g. θ -Al₂O₃). A string of intermittent voids are seen at the interface between the outer spinel and the inner (Cr,Al)₂O₃ layer (Fig.6b). The formation of these interfacial voids is probably induced by the volumetric shrinkage associated with the solid state reactions between the oxides [4]. The total thickness of the oxide is ~ 350 nm.

Unlike the multi-component oxide on the γ -grains, the oxide on the β -grain, however, is comprised of only Al₂O₃, without any indication of the spinel formation seen on the γ -grain, as indicated by the uniform contrast of the oxide (Fig.6a) and EDS analysis. The whisker-type morphology, as observed from the surface in Fig.2, can be also seen from the cross-section. The TKD phase map (Fig.6i) shows that the oxide near the metal/oxide interface is α -Al₂O₃. As a result, the substantial amount of θ -Al₂O₃ detected by PLPS must be in the outer portion of the oxide scale. Attempts have been made to map the distribution of the θ -Al₂O₃ over the thickness of the oxide using TKD. However, these have not been successful, probably due to the small grain size of the θ -Al₂O₃. The oxide shows substantial variation in upward displacement and thickness (ranging from ~ 315 to 585 nm) along the lateral direction. The heterogeneities of the upward displacement and thickness of the oxide are in agreement with the observations of the uneven oxide surface on the β -grains shown in Fig.2b. It is believed that this variation in upward displacement and thickness of the oxide is related to, at least to some extent, the local content of θ -Al₂O₃. As the growth of θ -Al₂O₃ is predominantly controlled by the outward diffusion of aluminium and the growth rate of θ -Al₂O₃ is orders of magnitude higher than that of the α -Al₂O₃ counterpart [37, 38], the oxide is expected to be thinner with smaller outward displacement in the areas where the content of θ -Al₂O₃ is lower. Voids as large as ~ 515 nm in the lateral direction can be seen at the oxide/metal interface or entrapped inside the oxide scale close to the interface (Fig.6a).

It should be noted that the microstructure and composition of the AlNiCoCrAlY coatings during oxidation is dynamic [39, 40], even for the

relatively short oxidation period used in this study. During oxidation, the β -phase near the oxide/metal interface is gradually converted to the γ -phase due to aluminium depletion induced by oxidation. Therefore, the oxide that is grown on the initial β -phase is eventually, at least partially, in contact with a layer of γ -phase after oxidation, regardless of which phase the oxide initially grew on. For example, most of the subsurface regions of the β -grain shown in Fig.6a have been transformed to γ -phase (the brighter contrast), which can be also confirmed by the TKD phase-contrast map in Fig.6i. This phase transformation also makes especially important the correlation of the TEM analysis of the site-specific oxidation with the surface microstructure of the coating before oxidation to identify the relationship between the composition of the oxide and the respective metal phase of the underlying coating. On the other hand, it is also found that the extent of aluminium depletion varies along the lateral direction of the β -grain. For instance, while a small region in the centre of the β -grain remains as the β -phase, the remainder of the grain has been transformed to the γ -phase. This phase transformation becomes more significant as the region of interest moves from the centre of the grain to the grain boundary (Fig.6a). This suggests that diffusion flux of aluminium in the grain boundary region is higher during oxidation.

3.5 TEM analysis of the oxide on the HVOF coating

Fig.7 shows the TEM analysis of the cross-section of the oxide on the HVOF coating. In contrast to the site-specific oxidation seen on the LPPS coating, the composition and microstructure of the oxide on the HVOF coating shows little dependence on the underlying metal phase and consists of exclusive α - Al_2O_3 , as confirmed by a combination of TKD analysis (Fig.7d) as well as previous PLPS analysis (Fig.5). The oxide scale has a fairly uniform thickness (~ 290 nm thick) and homogeneous microstructure along the lateral direction over the entire coating surface (Fig.7a). The microstructure of the Al_2O_3 scale consists of outer equiaxed grains and inner columnar grains. The columnar α - Al_2O_3 form distinctive imprints into the alloy with convex/concave shape edges at the Al_2O_3 grain boundaries. The presence of these columnar grains is a consequence of the inward growth of the α - Al_2O_3 grains [41-43]. Secondary-phase precipitates (the particles with bright contrast marked in Fig.7b) enriched with yttrium are found embedded in the oxide. Apart from forming Y-rich precipitates, EDS mapping (Fig.7c) over a selected area reveals that yttrium segregates to the grain boundaries of the oxide as well as the oxide/metal interface. The segregation of yttrium to the grain boundaries of the Al_2O_3 grains and subsequent formation of the Y-rich particles are not seen in the oxide on the LPPS coating. This difference is expected, as the outward transportation of reactive elements from the underlying alloy to the interface and then to scale grain boundaries will not be realised until a protective, external α - Al_2O_3 scale is fully established [42]. The segregation of yttrium to the growing Al_2O_3 grain boundaries effectively blocks the outward diffusion of aluminium during oxidation and the oxidation becomes

dominated by inward oxygen diffusion, as confirmed by the characteristic columnar grains. The oxide/metal interface is intact, without the presence of the large voids shown in Fig.6a.

4. Discussion

The findings in this work show that for a given composition, the microstructure of the **ANiCo**CrAlY coating has a substantial impact on its oxidation behaviour. For the LPPS coating with relative coarse grains, the γ and β -phase show different oxidation behaviours. Oxidation of the γ -phase is manifested by formation of a multilayer oxide structure (the sequence of the oxides from the gas/oxide to oxide/metal interface is determined by their thermodynamic stability, with the less protective spinel on top and the most thermodynamic stable α -Al₂O₃ in contact with the metal). The oxidation of the β -phase, however, is controlled by selective oxidation of aluminium and subsequent formation of the oxide consisting of a mixture of θ and α -Al₂O₃. The oxidation of the nanocrystalline HVOF coating, on the other hand, is characterised by exclusive formation of an α -Al₂O₃ scale all over the surface, without any dependence of oxide composition on the underlying metal phases. These findings suggest that refinement of the **ANiCo**CrAlY coating grain structure promotes the selective oxidation of aluminium on the γ -phase and the formation of protective α -Al₂O₃ over both the β and γ -phase, which in turn reduces the overall oxide growth rate and enhances oxidation resistance of the coating. The mechanistic interpretations of these findings will be explored in the following sections.

4.1 Effect of coating microstructure on selective oxidation of aluminium

In theory, growth of exclusive Al₂O₃ on the γ -phase will only occur if the following two criteria are met: first, an external Al₂O₃ scale is originally developed on the γ -phase; second, following the establishment of the original Al₂O₃ scale, the diffusion supply of aluminium towards the interface must be sufficiently rapid or more than sufficient to compensate the instantaneous loss of the aluminium consumed during oxidation in order to maintain the growth of the exclusive Al₂O₃.

According to Wagner's criterion, the minimum concentration of aluminium in the γ -phase to originally develop an external Al₂O₃ scale on the γ -phase, $N_{Al(min)}^\gamma$, is given by [30]:

$$N_{Al(min)}^\gamma = \left(\frac{\pi g N_O^\gamma D_O^\gamma V_m^\gamma}{3 D_{Al}^\gamma V_m^{Al_2O_3}} \right)^{\frac{1}{2}} \quad (2)$$

Where g is a constant; V_m^γ and $V_m^{Al_2O_3}$ is the molar volume of the γ -phase and Al₂O₃, respectively; $N_O^\gamma D_O^\gamma$ is the oxygen permeability in the γ -phase; D_{Al}^γ is the diffusion coefficient of aluminium in the γ -phase.

Once the initial external Al_2O_3 scale is established, the minimum concentration of aluminium in the γ -phase, $N'_{\text{Al}(\min)}^{\gamma}$, to maintain the growth of exclusive Al_2O_3 is given by [29]:

$$N'_{\text{Al}(\min)}^{\gamma} = \frac{V_m^{\gamma}}{V_m^{\text{Al}_2\text{O}_3}} \left(\frac{\pi k_p^{\text{Al}_2\text{O}_3}}{D_{\text{Al}}^{\gamma}} \right)^{\frac{1}{2}} \quad (3)$$

where $k_p^{\text{Al}_2\text{O}_3}$ is the parabolic rate constant of Al_2O_3 .

It should be noted that Eqs (2) and (3) are derived based on single-phase alloy and they are in principle not applicable to multiphase alloys. However, the observations in Fig.6 suggest that for a relatively short time of oxidation the γ and β -phase are oxidised independently and their interaction is, therefore, believed to be minimal. As a result, Eqs (2) and (3) could be still reasonable approximations for the γ -phase at the initial oxidation stage.

For a polycrystalline aggregate, the overall diffusion flux of a solute is the sum of the fluxes through the bulk lattice and grain boundary. As a result, D_{Al}^{γ} can be written as:

$$D_{\text{Al}}^{\gamma} = D_{\text{Al}}^L(1 - f) + D_{\text{Al}}^{GB}f \quad (4)$$

Where D_{Al}^L and D_{Al}^{GB} are diffusion coefficients of aluminium through the lattice and along the grain boundary, respectively. f is the ratio of the area of the grain boundary, given by:

$$f = \frac{2\delta}{d} \quad (5)$$

Where δ is the grain boundary thickness (~ 0.6 nm for nickel alloys [44]) and d is the grain size.

Mathematical description of D_{Al}^{GB} requires quantitative data on the geometry of the γ -grains and the types of the grain boundaries (Apart from misorientation angles, in a two-phase AlNiCoCrAlY coating a γ -grain can be bordered by either β -grains (γ/β grain boundaries) or γ -grains (γ/γ grain boundaries). In order to extract these data, EBSD was performed on both coatings and the results of the LPPS coating are shown in Fig.8 (EBSD indexing of the HVOF coating was not successful, and the reason will be discussed later). The EBSD analysis shows that most of the γ -grains and β -grains show equiaxed morphology parallel to the surface, which is in agreement with the quantitative image analysis reported in Table.32. Furthermore, the EBSD analysis also shows that the grain boundaries are predominately high-angle grain boundaries and on average a γ -grain is bordered by five β -grains and one γ -grain (based on image analysis of over 50 γ -grains and

1 | their surrounding grains; the twin boundaries inside the γ -grains are not
 2 considered). Therefore, D_{Al}^{GB} can be expressed as:

$$D_{Al}^{GB} = \frac{1}{6}D_{Al}^{\gamma\gamma} + \frac{5}{6}D_{Al}^{\gamma\beta} \quad (6)$$

3 Where $D_{Al}^{\gamma\gamma}$ and $D_{Al}^{\gamma\beta}$ are diffusion coefficients of aluminium along the γ/γ and
 4 γ/β grain boundaries.

5 Combine Eqs (2-6), we have:

$$N_{Al(min)}^{\gamma} = \left(\frac{\pi g N_O^{\gamma} D_O^{\gamma} V_m^{\gamma}}{3 \left[D_{Al}^L \left(1 - \frac{2\delta}{d} \right) + \left(\frac{1}{6} D_{Al}^{\gamma\gamma} + \frac{5}{6} D_{Al}^{\gamma\beta} \right) \frac{2\delta}{d} \right] V_m^{Al_2O_3}} \right)^{\frac{1}{2}} \quad (7)$$

$$N_{Al(min)}^{\gamma} = \frac{V_m^{\gamma}}{V_m^{Al_2O_3}} \left(\frac{\pi k_p^{Al_2O_3}}{D_{Al}^L \left(1 - \frac{2\delta}{d} \right) + \left(\frac{1}{6} D_{Al}^{\gamma\gamma} + \frac{5}{6} D_{Al}^{\gamma\beta} \right) \frac{2\delta}{d}} \right)^{\frac{1}{2}} \quad (8)$$

6 $N_{Al(min)}^{\gamma}$ and $N_{Al(min)}^{\gamma'}$ can be then normalised as:

$$\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}} = \frac{\left(\frac{\pi g N_O^{\gamma} D_O^{\gamma} V_m^{\gamma}}{3 \left[D_{Al}^L \left(1 - \frac{2\delta}{d} \right) + \left(\frac{1}{6} D_{Al}^{\gamma\gamma} + \frac{5}{6} D_{Al}^{\gamma\beta} \right) \frac{2\delta}{d} \right] V_m^{Al_2O_3}} \right)^{\frac{1}{2}}}{\left(\frac{\pi g N_O^{\gamma} D_O^{\gamma} V_m^{\gamma}}{3 D_{Al}^L V_m^{Al_2O_3}} \right)^{\frac{1}{2}}} \quad (9)$$

$$\frac{N_{Al(min)}^{\gamma'}}{N_{Al(min)}^{\gamma L}} = \frac{\frac{V_m^{\gamma}}{V_m^{Al_2O_3}} \left(\frac{\pi k_p^{Al_2O_3}}{D_{Al}^L \left(1 - \frac{2\delta}{d} \right) + \left(\frac{1}{6} D_{Al}^{\gamma\gamma} + \frac{5}{6} D_{Al}^{\gamma\beta} \right) \frac{2\delta}{d}} \right)^{\frac{1}{2}}}{\frac{V_m^{\gamma}}{V_m^{Al_2O_3}} \left(\frac{\pi k_p^{Al_2O_3}}{D_{Al}^L} \right)^{\frac{1}{2}}} \quad (10)$$

7 Where $N_{Al(min)}^{\gamma L}$ and $N_{Al(min)}^{\gamma' L}$ represent the minimum concentration of
 8 aluminium to originally develop an exclusive Al_2O_3 layer and maintain the
 9 subsequent growth of exclusive Al_2O_3 , respectively, when only lattice diffusion
 10 of aluminium is involved (e.g. in case of a single-crystal γ -alloy).

11 Eqs 9 and 10 can be simplified as:

$$\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}} = \frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}} = \frac{1}{\left[1 + \left(\frac{D_{Al}^{\gamma\gamma} + 5D_{Al}^{\gamma\beta}}{6D_{Al}^L} - 1\right) \frac{2\delta}{d}\right]^{\frac{1}{2}}} \quad (11)$$

Eq (11) shows that $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$ and $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$ share the same mathematical description. As a result, only the relationship between $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$ and the grain size, d , is discussed in the following section, as the same relationship applies to $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$.

According to Eq (11), for a given $\frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L}$ and $\frac{D_{Al}^{\gamma\beta}}{D_{Al}^L}$ the relationship between $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$ and d can be predicted. Although quantitative relationship between $D_{Al}^{\gamma\gamma}$, $D_{Al}^{\gamma\beta}$ and D_{Al}^L are not known, it is reasonable to assume that $D_{Al}^{\gamma\gamma}$ and $D_{Al}^{\gamma\beta}$ are orders of magnitudes higher than D_{Al}^L ($D_{Al}^{\gamma\beta} \gg D_{Al}^L$ and $D_{Al}^{\gamma\gamma} \gg D_{Al}^L$). Fig.9 gives four examples of the evolution of $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma L}}$ as a function of d , where $\frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L}$ and $\frac{D_{Al}^{\gamma\beta}}{D_{Al}^L}$ are assigned four different sets of values ($\frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L} = 100, \frac{D_{Al}^{\gamma\beta}}{D_{Al}^L} = 200; \frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L} = 200, \frac{D_{Al}^{\gamma\beta}}{D_{Al}^L} = 100; \frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L} = 100, \frac{D_{Al}^{\gamma\beta}}{D_{Al}^L} = 1000$ and $\frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L} = 1000, \frac{D_{Al}^{\gamma\beta}}{D_{Al}^L} = 100$). It is seen that in all cases $N_{Al(min)}^{\gamma}$ decreases with decreasing d and this effect becomes more significant when d drops to the nanoscale. In case of $\frac{D_{Al}^{\gamma\gamma}}{D_{Al}^L} = 100$ and $\frac{D_{Al}^{\gamma\beta}}{D_{Al}^L} = 1000$, the $N_{Al(min)}^{\gamma}$ in the HVOF coating is approximately half of that in the LPPS coating. In sum, the transition from formation of Al_2O_3 along with $(Ni,Co)(Cr,Al)_2O_4$ and $(Cr,Al)_2O_3$ on the γ -phase in the coarse-grain LPPS coating to selective oxidation of aluminium on the γ -phase in the nanocrystalline HVOF coating suggests that the grain boundaries of the underlying alloy play an important role in selective oxidation of aluminium. The fast diffusion paths provided by grain boundaries effectively increase the diffusion flux of aluminium to the γ -phase surface. Refinement of the grain size to nanoscale significantly increases the grain boundary density and the contribution of grain boundary diffusion to the total aluminium flux reaching the metal surface, which lowers the threshold of the aluminium concentration in the γ -phase to form an exclusive Al_2O_3 scale.

4.2 Critical grain size of the γ -phase to form exclusive Al_2O_3

While it has been shown that decreasing grain size of the $AlNiCoCrAlY$ coating promotes selective oxidation of aluminium on the γ -phase, the critical grain size, below which oxidation of the γ -phase will transform to growth of exclusive Al_2O_3 , remains to be determined, at least for the

oxidation temperature used in this study. The schematic illustration of this critical grain size, d_c , is given in Fig.10. Here we consider three types of aluminium diffusion fluxes towards the surface: diffusion through the γ -lattice, J_{Al}^{γ} , diffusion through the β -lattice, J_{Al}^{β} and diffusion along the γ/β boundary, J_{Al}^{GB} , in the order of $J_{Al}^{\gamma} < J_{Al}^{\beta} < J_{Al}^{GB}$ (thermodynamic equilibrium in a multi-phase alloy (e.g. the two-phase ~~AA~~NiCoCrAlY alloy) imposes strict restriction on diffusion of metal components between different phases, which prevents the interaction of J_{Al}^{γ} , J_{Al}^{β} and J_{Al}^{GB} in the alloy). The resulting profile of the instantaneous aluminium flux reaching the surface and corresponding oxide microstructure are also superimposed in Fig.10. If the minimum flux of aluminium required forming exclusive Al_2O_3 is defined as J_{Al}^{min} , we will have $J_{Al}^{\gamma} < J_{Al}^{min} < J_{Al}^{\beta} < J_{Al}^{GB}$, as our observations have shown that oxidation of the β -phase is characterised by selective oxidation of aluminium, but oxidation of the γ -phase is featured by growth of Al_2O_3 , $(Ni,Co)(Cr,Al)_2O_4$ and $(Cr,Al)_2O_3$. As the aluminium flux over the coating surface is expected to be continuous, there must exist a segment with a length of $\frac{d_c}{2}$, bounded by the γ/β boundary and the intersection between the aluminium flux profile and J_{Al}^{min} , still having an aluminium flux higher than J_{Al}^{min} . In this region, formation of exclusive Al_2O_3 is still possible even the region is within the γ -phase. In an extreme scenario when the grain size of γ -phase is decreased to d_c or below, the formation of $(Ni,Co)(Cr,Al)_2O_4$ and $(Cr,Al)_2O_3$ Ni/Co/Cr-rich transient oxides could be completely inhibited.

To confirm the prediction above, the composition of the oxide across the γ/β boundary region shown in Fig.6a is examined in details, and the corresponding EDS analysis is shown in Fig.11. It is found that unlike the multilayer nature of the oxide formed in the inner part of the γ -grain far away from the grain boundary, the oxide in the vicinity of the grain boundary (~ 350 nm in the lateral direction) is free of base metal elements (e.g. Ni and Co, Fig11b and c), suggesting that the oxide in this region is Al_2O_3 . This region corresponds to the segment with a length of $\frac{d_c}{2}$ shown in Fig.10. This also predicts that when the grain size is reduced to 700 nm, there will be no Ni/Co/Cr-rich transient oxides formed on the γ -phase. The prediction is in good agreement with our observations of the nanocrystalline HVOF coating showing formation of exclusive Al_2O_3 all over the surface. It should be noted that the prediction $d_c \approx 700$ nm is made based on the analysis of the specific γ/β -grain and γ/β boundary shown in Fig.11. In reality, d_c may span a certain range as J_{Al}^{β} , J_{Al}^{γ} and J_{Al}^{GB} could depend on many factors (e.g. crystallographic orientation of γ/β -grain, grain boundary misorientation, grain boundary composition and the type of Al_2O_3 developed (θ or α - Al_2O_3)), which may nevertheless vary from grain to grain and boundary to boundary in the NiCoCrAlY coatings.

Strictly speaking, the discussion above only considers the scenario when the γ -grains are equiaxed. When the grain geometry deviates from equiaxed morphology, it is less useful to predict the oxide composition simply using the grain size given by Fig.10, without taking the shape factor of the grain into account. For grains with elongated surface shape (aspect ratios much larger than 1), as long as the widths of the grains are no larger than d_c , formation of exclusive Al_2O_3 is still expected even though the length or grain size could be larger than d_c . The implication here is that for a given grain size, elongated γ -grains are more effective than equiaxed grains to form exclusive Al_2O_3 . Therefore, apart from the nanoscale grain size, the presence of the large amount of the long, narrow γ -grains in the HVOF coating further promotes the formation of exclusive Al_2O_3 even though the lengths of the grains, and sometimes the grain size, are larger than d_c .

4.3 Comparison of the microstructures the Al_2O_3 scales on the β -phases

The current work has also shown that while oxidation of the β -phase in both LPPS and HVOF coatings is characterised by selective oxidation of aluminium, the phase compositions and microstructure of the Al_2O_3 scales are rather different. The oxide formed on the β -grains of the LPPS coating consists of a mixture of θ ($\sim 50.1\%$) and α - Al_2O_3 , while the oxide formed on the β -grains of the HVOF coating is exclusive α - Al_2O_3 . This suggests that the microstructure of the HVOF coating is also beneficial to the earlier establishment of an α - Al_2O_3 scale.

In theory, α - Al_2O_3 originates from two sources: one is the phase transformation from the metastable Al_2O_3 precursors; the other is from direct nucleation of α - Al_2O_3 and subsequent grain growth. While the effect of the microstructure on the former is not clear (it is actually difficult to determine if metastable Al_2O_3 indeed formed on the HVOF coating), it has been known that processing methods that introduce defects to the metal substrates (e.g. grain refinement and cold work) could provide more heterogeneous nucleation sites for oxides [23, 42]. The high-density grain boundaries in the nanocrystalline HVOF coating increases the number of sites available for heterogeneous nucleation of α - Al_2O_3 and, therefore, facilitate earlier establishment of an α - Al_2O_3 scale. On the other hand, while both LPPS and HVOF involve using thermal/kinetic energy to strike particles onto the substrate, the extremely high velocity and relatively low temperature (e.g. spray particles in a plastic rather than a melted state) using in the HVOF spraying means that the particles undergo more "cold deformation" upon impact with the substrate [45]. Apart from grain refinement, the severe plastic deformation at relative low temperature is likely to introduce more crystallographic defects (e.g. dislocations) into the deposited coatings and therefore provide more heterogeneous nucleation sites for α - Al_2O_3 . Fig.12 shows a bright-field TEM image (Fig.12a) of the as-deposited HVOF coating and the corresponding diffraction pattern (Fig.12b) of a β -grain. 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. The significant cold work also causes the Kikuchi patterns of the HVOF coating to be diffuse and unsuccessful EBSD indexing. In sum, it is suggested that the large number of the crystallographic defects, including grain boundaries and dislocations, in the HVOF coating promotes the preferable nucleation of the α -Al₂O₃ and shortens the transient oxidation period. It is expected that the similar effect is also present in NiCoCrAlY coatings deposited by high velocity air fuel (HVOF) spraying which uses lower deposition temperatures and involves more cold deformation of the particles than HVOF [46].

Another difference in oxidation behaviour of the β -phase between the LPPS and HVOF coating is that while there are large voids at the interface between the oxide and the β -phase in the LPPS coating, the oxide/metal interface in the HVOF coating is intact. It is known that voids could form at the oxide/metal interface during selective oxidation of the Ni-rich β -NiAl based alloys and coatings [47]. Experimental and theoretical analyses have shown that the intrinsic mechanisms for formation of these interfacial voids are associated with vacancy injection (the Kirkendall effect) and their subsequent coalescence due to the non-reciprocal diffusion of the metallic elements in the multicomponent alloys [47, 48] (e.g. the differential diffusion of nickel and aluminium in Ni-rich β -NiAl at 1150 °C, in which inward diffusion of nickel is more than three times faster than the outward diffusion of aluminium [49]). For the ~~M~~NiCoCrAlY coatings studied in this work, the smaller grain size of the nanocrystalline HVOF coating allows a greater diffusion flux of aluminium from the alloy to the surface, which effectively mitigates the Kirkendall effect and the propensity of subsequent void formation at the interface. Furthermore, the slower oxidation rate and the inward oxide growth mechanism of the β -phase on the HVOF coating, which resulted from earlier establishment of a protective α -Al₂O₃ scale and subsequent segregation of yttrium at the growing oxide grain boundaries, also helps to prevent vacancy condensation at the oxide/metal interface [19]. In addition, the segregation of the yttrium to the oxide/metal interface in the HVOF coating diminishes the driving force for detrimental impurity segregation (e.g. sulphur) at the oxide/metal interface and prevents vacancies from rapid coalescence [42]. Once formed, some of the interfacial voids could be undercut by the subsequently formed oxide around the peripheries of the voids and then entrapped inside the oxide [50], resulting in the formation of the voids inside the bottom part of the oxide on the β -phase in the LPPS coating.

4.4 Implication to oxidation of Pt-diffused γ/γ' bond coats

The findings in this work also provide insights into understanding the oxidation of the Pt-diffused γ/γ' bond coat [51, 52]. This type of bond coat consists of an Al/Pt-poor γ -phase matrix and Al/Pt-rich γ' -precipitates. Representative chemical compositions of the γ and γ' -phase in the coating surface region

reported by Zhao et al are given in Table.43 [52]. The relatively low concentration of aluminium (8.2 at.%) and platinum (11.8 at.%) in the γ -phase is believed insufficient to form an exclusive Al_2O_3 scale. This argument can be supported by the facts that formation of Ni-rich transient oxides (e.g. spinel) have been found on bulk Ni-Al-Pt alloys with even higher aluminium and platinum concentrations than those of the γ -phase in the coating counterparts [53, 54]. However, the Pt-diffused γ/γ' bond coat is generally reported to have good oxidation resistance by forming a pure and adherent Al_2O_3 scale over the coating surface [52, 55, 56]. This paradox is attributed to the intrinsic difference in microstructure between the Pt-diffused γ/γ' bond coats and the bulk alloys. The Pt-diffused γ/γ' bond coat, especially its surface region, is characterised by the presence of numerous fine, nanoscale γ' precipitates dispersed in the γ -matrix [51, 57]. Fig.13 shows an EBSD inverse pole figure map of an as-deposited Pt-diffused γ/γ' bond coat, in which nanostructured grains are clearly seen in the surface region of the coating. This unique microstructure is associated with the Pt-diffusion induced recrystallisation and subsequent precipitation process during the fabrication of the coating [51]. The great number of grain/phase boundaries provides numerous fast diffusion paths of aluminium at the initial stage of the oxidation and therefore benefits the establishment of an exclusive Al_2O_3 scale. The Ni-Pt-Al alloys used in the literature for oxidation study, on the other hand, are generally fabricated by arc melting and featured by coarse grains up to millimetres in diameter [53, 54]. Therefore, the contribution of fast aluminium diffusion along the alloy grain boundary to the overall oxidation of the alloy is negligible and the resulting diffusion flux of aluminium is therefore not sufficient to form exclusive Al_2O_3 .

5. Conclusions

The early oxidation behaviour of a HVOF and LPPS AlNiCoCrAlY coating at 1150 °C has been studied. The following conclusions can be drawn from this work.

1. The LPPS coating with relatively coarse-grains shows site-specific oxidation behaviour. The oxide on the γ -phase shows a multi-layer structure, consisting of outer $(\text{Ni,Co})(\text{Cr,Al})_2\text{O}_4$, intermediate $(\text{Cr,Al})_2\text{O}_3$ and inner $\alpha\text{-Al}_2\text{O}_3$. The oxide on the β -phase is composed of a mixture of θ and $\alpha\text{-Al}_2\text{O}_3$.
2. The nanocrystalline HVOF coating shows formation of an exclusive $\alpha\text{-Al}_2\text{O}_3$ scale all over the surface, without any dependence of oxide composition on the underlying metal phases.
3. Refinement of the AlNiCoCrAlY coating microstructure promotes the selective oxidation of aluminium on the γ -phase. This effect is associated with the fast diffusion of aluminium along the γ/β grain boundaries, which contributes to a significant amount of the diffusion flux of aluminium in the nanocrystalline HVOF coating and therefore

- 1 reduces the threshold of the aluminium content in the γ -phase to form
2 exclusive Al_2O_3 .
- 3 4. It is predicated that oxidation of the γ -phase would transform from
4 growth of Al_2O_3 along with $(\text{Ni},\text{Co})(\text{Cr},\text{Al})_2\text{O}_4$ and $(\text{Cr},\text{Al})_2\text{O}_3$ to selective
5 oxidation of aluminium when the size of the γ -grain is reduced to
6 700 nm, provided that the grain is equiaxed. An elongated shape of
7 the γ -grain is beneficial to the formation of exclusive Al_2O_3 .
- 8 5. The large amount of the crystallographic defects, including grains
9 boundaries and dislocations, in the HVOF coating increases the
10 number of sites available for heterogeneous nucleation of α - Al_2O_3 and,
11 therefore, facilitate earlier establishment of an α - Al_2O_3 scale. Formation
12 of interface voids are inhibited in the HVOF coating, which is attributed
13 to the small grain size of the coating, early establishment of a
14 protective α - Al_2O_3 and associated segregation of yttrium to the grain
15 boundaries of the growing oxide as well as metal/oxide interface.
- 16 6. The contribution of grain boundaries to aluminium diffusion can be also
17 used to explain the difference in oxidation behaviour between the
18 Pt-diffused γ/γ' bond coats and their alloy counterparts.

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Nomenclature

A_{R1} PLPS peak area of the R1 peak of α -Al ₂ O ₃	A_{R2} PLPS peak area of the R2 peak of α -Al ₂ O ₃
A_{T1} PLPS peak area of the T1 peak of θ -Al ₂ O ₃	A_{T2} PLPS peak area of the T2 peak of θ -Al ₂ O ₃
$c_{\theta-Al_2O_3}$ content of θ -Al ₂ O ₃	d Grain size
d_c critical grain size of γ to form exclusive Al ₂ O ₃	D_{Al}^{GB} diffusion coefficient of aluminium along the grain boundary
D_{Al}^L diffusion coefficient of aluminium through the γ lattice	D_{Al}^{γ} overall effective diffusion coefficient of aluminium in γ
$D_{Al}^{\gamma\beta}$ diffusion coefficient of aluminium along the γ/β boundary	$D_{Al}^{\gamma\gamma}$ diffusion coefficient of aluminium along the γ/γ boundary
D_O^{γ} diffusion coefficient of oxygen in γ	f ratio of the area of the grain boundary
J_{Al}^{GB} diffusion flux along the γ/β boundary	J_{Al}^{min} the minimum flux of aluminium required forming exclusive Al ₂ O ₃
J_{Al}^{β} diffusion flux through the β -lattice	J_{Al}^{γ} diffusion flux through the γ -lattice
$k_p^{Al_2O_3}$ parabolic rate constant of Al ₂ O ₃	N_O^{γ} solubility of oxygen in γ
$N_{Al(min)}^{\gamma}$ the minimum concentration of aluminium in γ to originally develop an external Al ₂ O ₃ scale	$N_{Al(min)}'^{\gamma}$ the minimum concentration of aluminium in γ to maintain the growth of exclusive Al ₂ O ₃
$N_{Al(min)}^{\gamma L}$ the minimum concentration of aluminium in γ to originally develop an exclusive Al ₂ O ₃ layer when only lattice diffusion of aluminium is involved	$N_{Al(min)}'^{\gamma L}$ the minimum concentration of aluminium in γ to maintain the growth of exclusive Al ₂ O ₃ when only lattice diffusion of aluminium is involved
V_m^{γ} molar volume of γ	$V_m^{Al_2O_3}$ molar volume of Al ₂ O ₃
δ grain boundary thickness	

Fig.1 Microstructure of (a) LPPS and (b) HVOF coatings. The LPPS coating shows coarser grains than the HVOF coating. Both coatings consist of β -phase (grey contrast) and γ -phase (light contrast).

Fig.2 Surface morphology of the LPPS coating after oxidation: (a) top view and (b) oblique view. The coating shows site-specific oxidation. The inset at the top left corner of Fig.2a is an optical image of the same area prior to oxidation, which is used to correlate the morphology of the oxide with the underlying metal phase before oxidation. The metal phases below the oxides are indicated.

Fig.3 Surface morphology of the HVOF coating after oxidation: (a) top view (b) a higher magnification image of the area within the white rectangle in Fig.4a. The coating does not show phase-specific oxidation.

Fig.4 PLPS spectra of the Al_2O_3 scale on (a) γ -phase and (b) β -phase of the LPPS coating surface

Fig.5 PLPS spectra of the Al_2O_3 scale on HVOF coating surface.

Fig.6 TEM analysis of the cross-section of the oxide on the LPPS coating: (a) STEM-ADF image giving an overview of the oxide on the γ and β -phase; the white spots between the protective platinum layer and the oxides are the gold particles sputtered on the surface of the oxide to increase electrical conductivity for SEM and FIB analysis. The β -phase near the oxide/metal interface has been transformed to γ -phase (termed as "newly-formed γ " in the figure) due to Al depletion during oxidation. (b) a high magnification STEM-ADF image of the oxide on the γ -phase, showing the multi-layer nature of the oxide; (c) diffraction pattern of a grain in the outer layer of the oxide on the γ -phase, showing typical spinel structure; (d, e, g and h) EDS mapping over the area in (b) showing the presence of all base metal elements ($(\text{Ni}+\text{Co}):(\text{Cr}+\text{Al}) \approx 0.5$) in the outer layer of the oxide, chromium and aluminium ($\text{Cr}:\text{Al} \approx 1.5$) in the middle layer of the oxide and exclusive aluminium in the inner layer of the oxide; (f) a high-resolution TEM image of the inner layer of the oxide on the γ -phase. The corresponding FFT pattern shows typical corundum structure. (i) TKD phase-contrast map across the oxide/metal interface, showing that the oxide near the metal/oxide interface is $\alpha\text{-Al}_2\text{O}_3$.

Fig.7 TEM analysis of the cross-section of the oxide on the HVOF coating: (a) STEM-ADF image giving an overview of the oxide. The white spots between the protective platinum layer and the oxides are the gold particles sputtered on the surface of the oxide to increase electrical conductivity for SEM and FIB analysis. (b) a high magnification STEM-ADF image showing the presence of the precipitates enriched with yttrium (c) EDS mapping over the area in the black rectangle in Fig.7b showing segregation of yttrium to the oxide grain

boundaries and oxide/metal interface (d) TKD phase-contrast map with red colour representing α -Al₂O₃ and blue colour γ -Ni.

Fig. 8 EBSD analysis of the as-deposited LPPS coating: (a) phase-contrast map and (b) inverse pole figure colour map.

Fig.9 Evolution of $\frac{N_{Al(min)}^{\gamma}}{N_{Al(min)}^{\gamma_L}}$ as a function of the grain size of the γ -phase for four different sets of grain boundary diffusion coefficients. The grain size of the γ -phase in the LPPS and HVOF coating used in this study is also indicated.

Fig.10 Schematic illustration of the aluminium flux to the surface of γ -grain, β -grain and across the β/γ grain boundary during oxidation. The minimum aluminium flux to form exclusive Al₂O₃ is indicated and the corresponding oxide compositions are also superimposed. Due to the higher aluminium flux along the β/γ grain boundary and the continuity of the flux profile over the surface, the oxide within the segments, $\frac{d_c}{2}$, remains exclusive Al₂O₃ even though the regions are within the γ -grain.

Fig.11 TEM analysis of the oxide across the γ/β grain boundary shown in Fig.6a: (a) STEM-ADF image showing morphology and element contrast (b, c) EDS mapping showing distribution of cobalt and nickel over the area within the white rectangle in Fig.11a. The oxide near the γ/β boundary is free of nickel and cobalt, with existence of only aluminium and oxygen.

Fig.12 TEM analysis of the as-deposited HVOF coating: (a) bright-field image showing the presence of the larger number of dislocations (b) diffraction pattern of the β -grain marked with "D" in Fig.12a. The diffraction spots are elongated and diffuse.

Fig.13. Cross-sectional EBSD inverse pole figure map (RD) of an as-deposited Pt-diffused γ/γ' coating showing the nanostructured grains in the surface region

Fig.1

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Fig.2

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Table 1 Chemical compositions (wt. %) of Hastelloy® X superalloy and MCrAlY coating

	Ni	Cr	Co	Al	Y	Fe	Mo	W	C	Mn	Si	B
Hastelloy® X	Bal	22	1.5	/	/	18	9	0.6	0.1	1*	1*	0.008*
MCrAlY	Bal	17	23	12.5	0.45	/	/	/	/	/	/	/

Table.2 Chemical compositions (at. %) of the β and γ -phase determined by EDS point analysis

	Ni	Co	Cr	Al
β	49.51	12.68	8.89	28.92
γ	43.18	23.05	24.51	9.26

Table 32 Grain size and aspect ratio of β and γ -phase in LPPS and HVOF coatings

	LPPS coating		HVOF coating	
	Grain size (μm)	Aspect ratio	Grain size (μm)	Aspect ratio
β	2.68 ± 1.12	1.15 ± 0.13	0.78 ± 0.31	1.27 ± 0.17
γ	2.11 ± 0.85	1.12 ± 0.11	0.31 ± 0.19	1-10

Table 43 Composition of the γ and γ' -phase in the surface region of a Pt-diffused γ/γ' bond coat [51]

	Main elements (at.%)					
	Ni	Al	Pt	Cr	Co	W
γ	61.8	8.2	11.8	9.3	7.4	1.0
γ'	50.3	22.5	23.5	0.9	2.6	/