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Pt effect on early stage oxidation behaviour of Pt-diffused γ -Ni/ γ' -Ni₃Al coatings

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Abstract

The early stage oxidation behaviours of γ/γ' -based NiAl coatings with different Pt additions are investigated. It is found that Pt addition can slow down the θ -Al₂O₃ to α -Al₂O₃ transformation. High resolution phase mapping by scanning diffraction analysis shows that α -Al₂O₃ nucleation in the θ -Al₂O₃ scale is inhomogeneous along the coating/scale interface. Spatially resolved PLPS results show a clear correlation between the θ -Al₂O₃ to α -Al₂O₃ transition and the γ or γ' microstructure in the underlying alloy: where Pt stabilises the γ' structure, the suppression of θ -Al₂O₃ to α -Al₂O₃ transition is observed. The slower θ -Al₂O₃ to α -Al₂O₃ transition rate due to Pt addition leads to a lower compressive stress of the stable oxide scale, which contributes to the long term stability of the scale as a result of Pt addition.

Keywords Early stage oxidation; Pt effect; Al₂O₃ phase transformation; ASTAR crystal orientation mapping in TEM

1 Introduction

The Ni-Al-based coating, which is commonly used for oxidation protection of the Ni-base superalloys, is designed to develop a protective Al₂O₃ (thermally grown oxide, TGO) layer during high temperature exposure. This coating fails when the TGO spalls off, which is driven by the increasing TGO strain energy as the oxide thickens. Thus, the lifetime of the coating usually depends on the spallation resistance of the TGO layer. Numerous studies have

reported that the addition of platinum (Pt) can significantly improve TGO spallation resistance of Ni-Al-based alloys or coatings for long-term oxidation at elevated temperatures. For instance, Y. Chen et al. [1] concluded that Pt addition can improve the oxide spallation resistance of the γ/γ' nickel aluminide alloys mainly due to the selective oxidation of aluminium promoted by Pt. P. Y. Hou and V. K. Tolpygo [2] found that 5 - 8 at.% Pt can significantly enhance the oxide spallation resistance of nickel aluminide coatings during cyclic oxidation. They pointed out that Pt can prevent the segregation of impurities (e.g. sulfur) at the oxide/coating interface, resulting in enhanced interfacial adhesion and improved TGO lifetime. Other researchers [3-6] have reported this benefit of Pt caused by other mechanisms such as inhibiting void formation at the coating/oxide interface.

It is widely accepted that for Al_2O_3 -scale forming Ni-Al-based coatings, one (usually θ) or more transient forms of Al_2O_3 initially form during the early stage oxidation, followed by the eventual transformation to stable $\alpha\text{-Al}_2\text{O}_3$ [7-9]. Previous studies have suggested that the early stage oxidation behaviour can affect the prolonged oxidation behaviour of the Ni-Al coating. For example, V. K. Tolpygo and co-workers [10] found that different transient alumina to stable alumina transition rate during early stage oxidation leads to local TGO thickness heterogeneity, which can induce local tensile stresses and is detrimental to TGO lifetime for prolonged oxidation. Therefore, it is important to investigate the early stage oxidation behaviour for a reliable estimation of TGO performance. However, despite the large number of studies about Pt effect on long-term oxidation as mentioned above, only limited attempts [11-14] have focused on the impact of Pt on early stage of oxidation behaviour of Ni-Al alloys or coatings. In addition, some controversial views regarding Pt effect on the early stage $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ transformation have been reported. For instance, J. Jedlinski et al. [12] found that Pt resulted in earlier development of $\alpha\text{-Al}_2\text{O}_3$ (faster θ - to α -alumina transition) for $\beta\text{-NiPtAl}$ alloy at 1100 °C oxidation, whereas Y. Cadoret, et al. [13]

concluded that Pt can slow down θ -Al₂O₃ to α -Al₂O₃ transition by studying the early stage oxidation of Ni₅₀Al₅₀ and Ni₄₀Pt₁₀Al₅₀ alloys at 900 and 1100 °C, respectively. H. Svensson and co-workers [14] concluded that Pt has no effect on this phase transformation by studying the initial oxidation of β -NiPtAl alloys. However, for the Pt-diffused γ -Ni/ γ' -Ni₃Al coating system, little work has been done on the Pt effect on the θ -Al₂O₃ to α -Al₂O₃ transformation. The only related work to the best of our knowledge, suggested that a higher Pt content led to a larger amount of θ -Al₂O₃ in the oxide scale by photo-luminescence piezo-spectroscopy (PLPS) [15]. This indicates a slower θ -Al₂O₃ to α -Al₂O₃ transformation because of Pt addition for this γ/γ' coating system. However, no mechanism has been proposed in their work about this Pt effect on the phase transformation rate, mainly due to the lack of microscopic information about the distribution of the two alumina polytypes and their relation to the coating composition (Pt contents).

In this contribution, the early stage oxidation behaviours of γ/γ' Ni-Al coatings with different Pt additions are studied and compared in terms of TGO microstructure, transient oxide to stable α -Al₂O₃ transformation rate and scale stress evolution, to provide a more comprehensive understanding of Pt effect on the early stage oxidation of this coating. Moreover, in order to explore the mechanism of Pt effect on alumina phase transition, the phase mapping of the alumina polytypes (transient θ -Al₂O₃ and stable α -Al₂O₃) in the scale during the early stage was conducted by the ASTAR (NanoMEGAS) automated crystal orientation mapping on transmission electron microscopy (TEM) [16]. This technique offers significantly improved lateral spatial resolution over the recently developed transmission electron backscatter diffraction (t-EBSD) [17], which enables the diffraction pattern indexed phase mapping of both θ -Al₂O₃ and α -Al₂O₃ during early stage oxidation for the first time, to the best of our knowledge. A new transformation mechanism has been proposed based on

these results to explain the different transformation rate observed on coatings with different Pt contents.

2 Experimental procedures

2.1 Sample preparation and thermal treatment

CMSX-4 single crystal Ni-based superalloy (Rolls-Royce plc) was used as substrates throughout this study. The as-received superalloy bars were cut into buttons (20 mm diameter and 3 mm height) using a SiC cutting blade in a precision cut-off machine (Accutom 5, Struers). All substrates were ground and polished to 1 μm finish and then washed in acetone before Pt electroplating. Three groups of samples (each group contains three button samples) were fabricated, with electroplating time 0 min, 20 min and 50 min, respectively. All electroplated samples were washed in hot distilled water for 0.5h to remove the remaining salts from the electroplating bath. The electroplated Pt layer thickness of each sample was examined by the focus ion beam system (FIB; FEI Quanta 3D). Finally, the substrates with different electroplating time were annealed in vacuum at 1150 $^{\circ}\text{C}$ for 2 h to obtain γ/γ' coatings with different Pt contents.

Isothermal oxidation of γ/γ' coatings with different Pt contents was performed at 1000 $^{\circ}\text{C}$ (or 1050 $^{\circ}\text{C}$ for crystal orientation analysis samples, in order to avoid the formation of Ni-oxides and simplify the index process) in an automated rig (CMTM) in laboratory air. The samples were oxidized for different periods of time up to 30 min, followed by air quenching.

2.2 Luminescence measurement and data processing

Phase identifications of alumina polytypes as well as measuring residual stresses in oxide scales was carried out at room temperature using PLPS on Renishaw Invia Raman system (RenishawTM, Gloucestershire, UK) with an argon laser source ($\lambda=633\text{ nm}$). The laser spot size was $\sim 5\text{ }\mu\text{m}$. Although according to the subsequent results, some of the oxide scales studied here have a Ni-oxide over-layer above the alumina layer, it was shown by Lipkin and

Clarke [18] that this over-layer do not prevent either the excitation or collection of the fluorescence signal from the Cr^{3+} in alumina scale.

Before each experiment, the spectrometer was calibrated by taking a spectrum from a standard pure silicon sample. Cr^{3+} fluorescence spectra were collected for each measurement with one second acquisition time. Measurements for each sample were taken on a square grid of $200 \times 200 \mu\text{m}$ with a pitch of $20 \mu\text{m}$, thus one map contains 121 measurement points for each sample.

To determine the peak positions in each spectrum, all spectra were deconvoluted in Wire 4.2 software (RenishawTM) with an automatic fitting program by two mixed Gaussian-Lorentzian functions [19]. It is well accepted that the R1 and R2 doublet at $\sim 14400 \text{ cm}^{-1}$ is produced by Cr^{3+} fluorescence in $\alpha\text{-Al}_2\text{O}_3$, and $\theta\text{-Al}_2\text{O}_3$ produces luminescence peaks at $\sim 14546 \text{ cm}^{-1}$ (T1), $\sim 14626 \text{ cm}^{-1}$ (T2) and $\sim 14330 \text{ cm}^{-1}$ (T3) [20], as shown in Fig. 1 a. The relative intensities of the $\alpha\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ luminescence lines provide a semi-quantitative indicator of the $\theta\text{-Al}_2\text{O}_3$ content in the spot area, which is given by [20]:

$$C_{\theta} = \frac{A_{T1} + A_{T2} + A_{T3}}{A_{T1} + A_{T2} + A_{T3} + A_{R1} + A_{R2}} \quad (1)$$

where A_{T1} , A_{T2} and A_{T3} are peak areas for three characteristic peaks of $\theta\text{-Al}_2\text{O}_3$, respectively, and A_{R1} and A_{R2} are peak areas of the characteristic R1 and R2 peaks.

Since the R2 line has a nearly linear dependence on stress, the stress calculation was based on the peak shift of the R2 line with respect to that of the unstrained single crystal sapphire (Fig. 1 b) by [21]:

$$\Delta\nu = 5.07(\text{cm}^{-1}\text{GPa}^{-1})\sigma \quad (2)$$

where $\Delta\nu$ is the frequency shift of the R2 line and σ is the residual stress by assuming an equibiaxial plane stress state in the scale.

2.3 ASTAR automated crystal orientation mapping on TEM

The high resolution phase mapping of the alumina polytypes was performed using the ASTAR automated crystal orientation mapping on TEM (transmission electron microscope, FEI Tecnai, F30) [22], operating at 300 keV. FIB (FEI Quanta 3D) in-situ lift-out technique [23] was used to prepare site-specific specimens for this analysis. Firstly, the electron beam scanned over the area of interest on the FIB sample, and the digital image of diffraction patterns were saved by a high-rate digital camera at each point with a spot size of 5 nm. The crystal information for each phase present in the scanned area was extracted from crystal information files (CIFs) produced from powder diffraction data [24-26]. Theoretical generated patterns (the templates) for each phase were then produced using the pattern generation method by Zaefferer [27]. The acquired experimental patterns were automatically matched with the generated templates by the so-called template matching process [28]. The degree of matching is quantitatively given by the correlation index Q , given by:

$$Q = \frac{\sum_{i=1}^m P(x_i, y_i) T(x_i, y_i)}{\sqrt{\sum_{i=1}^m P^2(x_i, y_i)} \sqrt{\sum_{i=1}^m T^2(x_i, y_i)}} \quad (3)$$

where $P(x, y)$ is the intensity function of a pattern; $T(x, y)$ is the intensity function of the corresponding template; x and y are bounded by the picture width and height respectively.

Furthermore the reliability index assesses the likelihood of the match being unique and is calculated by [28]:

$$R = 100(1 - Q_2/Q_1) \quad (4)$$

where Q_1 and Q_2 stand for the two highest values of the correlation indexes for one pattern.

For a practical point of view, a reliability >15 is considered to be a safe solution.

2.4 Other characterization methods

An optical profilometer (ContourGT, Bruker) was used to examine the surface roughness of the as-fabricated coatings. Scanning electron microscopy (SEM, FEI Quanta 650) and an optical microscope (Olympus BH2-UMA) were used to examine the coating surface microstructure after oxidation. Investigations of cross-sectional microstructure of oxide scales

were conducted by FIB (FEI Quanta 3D). Conventional angular dark field (ADF) images were obtained by TEM (FEI Tecnai, F30) with STEM (scanning transmission electron microscope) detector on the same samples for the orientation mapping in Section 2.3.

3 Results

3.1 Microstructure of the as-fabricated coatings with different Pt contents

Table 1 shows the electroplating time, corresponding Pt layer thickness, average Pt concentration of as-diffused coatings and root mean square roughness (R_q) of the coating surface. 20 min and 50 min electroplating time result in 2 μm and 5 μm Pt, and the corresponding average Pt concentration of the coating is 12.6 at.% and 21.3 at.%, respectively. The root mean square roughness values are almost identical for the two as-diffused coatings, and also very close to that of the uncoated substrate ($\sim 0.45 \mu\text{m}$). The nearly identical roughness values of all samples are prerequisite for the subsequent phase transformation rate analysis, since the surface roughness has a significant effect on the alumina phase transformation in oxide scales [10].

Fig. 2 shows the cross-sectional SEM images of the as-fabricated γ/γ' coatings with 2 μm and 5 μm Pt respectively. The bright phases of the coating are γ' and the dark phases are γ . The coating thickness and the fraction of γ' phase in the coating both increase with increasing Pt contents.

3.2 Transient alumina to stable $\alpha\text{-Al}_2\text{O}_3$ transformation

The alumina phase identification of scales on samples with different Pt additions after short-term oxidation was carried out by PLPS. The spectra taken from different places on each sample were highly reproducible. Therefore, only representative spectra are presented for each sample. Fig. 3 and 4 show the PLPS spectra for all samples after 2 min and 10 min oxidation at 1000 $^\circ\text{C}$ respectively. The characteristic peaks for θ -alumina (if present) and α -alumina were marked in each spectrum, and the semi-quantitative fractions of θ -alumina in

the oxide scale were calculated according to equation (1) based on the average of 10 randomly chosen spectra for each sample.

It is clear that for no Pt addition sample, only stable α -Al₂O₃ can be identified without any signals from θ -Al₂O₃ after just 2 min oxidation at 1000 °C (Fig. 3 a). In other words, θ to α -Al₂O₃ transition finishes within 2 min for samples without Pt. Conversely, a large amount (~55.8 %) of θ -alumina is detected in the scale on 5 μ m Pt coating after 2 min oxidation (Fig. 3 c), and for the coating with 2 μ m Pt, nearly half of the scale consists of θ polymorph (Fig. 3 b). After 10 min oxidation, α -Al₂O₃ gradually prevails in the scale of 2 μ m Pt coating but a weak photoluminescence signal from θ -Al₂O₃ is still detected (Fig. 4 b). And the scale of 5 μ m Pt coating still contains a high content (~ 43.9 %, Fig. 4 c) of θ -Al₂O₃ after 10 min. The θ -Al₂O₃ fractions of all samples during early stage oxidation are summarized in Fig. 5. As can be seen, after 30 min oxidation, the θ -Al₂O₃ to α -Al₂O₃ transformation almost finish on 2 μ m Pt sample (only ~ 5.0 % θ -Al₂O₃), while on 5 μ m Pt coating, ~ 17 % θ -Al₂O₃ was still detected. Clearly, the fraction of θ -Al₂O₃ decreases as increasing the oxidation time during early stage oxidation of the two coatings with Pt addition. Moreover, the more Pt addition results in more θ -Al₂O₃ in the scale, which supports the results in [13, 15, 29]. Hence, it can be concluded that the transient θ -Al₂O₃ to stable α -Al₂O₃ transformation is retarded due to Pt addition for the Pt-diffused γ/γ' coating.

3.3 TGO composition and microstructure evolution

Fig. 6 shows the FIB cross sections of three samples after short-term oxidation at 1000 °C. After 2 min, it can be seen from Fig. 6 a - c that the oxide scale thickness increases as the Pt content increases. This is due to the fact that Pt addition can promote the growth of transient θ -Al₂O₃, as has been confirmed in section 3.2, which grows much faster than the stable α -Al₂O₃. It is worth noting that at this stage, all scales are composed of pure alumina. After 10 min oxidation, however, the oxide scales of no Pt and 2 μ m Pt sample become duplex in

structure: with outer transient oxide (NiO and/or spinel) layer and inner alumina layer (Fig. 6 d and e). As for 5 μm Pt coating with the highest Pt content, the scale still composes of pure alumina after 10 min oxidation, without any Ni-oxides formation (Fig. 6 f).

Fig. 7 shows surface images and FIB cross-sectional images of three samples after 30 min oxidation. The surface of no Pt sample exhibits fine faceted morphology consisting of NiO grains (Fig. 7 a), and larger faceted spinel grains are observed on the 2 μm Pt coating (Fig. 7 b). While the surface of 5 μm Pt coating shows a combination of nodules and blade-like grains (Fig. 7 c). The blade-like morphology is typical for an oxide growth as a result of outward cation diffusion, as expected for the growth of the transient $\theta\text{-Al}_2\text{O}_3$ at the gas/oxide interface in this temperature regime [7, 13]. The blade-like grains are only observed on the surface of 5 μm Pt coating. This is in agreement with the results in Fig. 5, which shows that after 30 min oxidation, $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ transition has almost completed on the no Pt sample and 2 μm Pt coating. As for the cross-sectional microstructure, the oxide scale formed on no Pt sample is multi-layered, consisting of an outer NiO layer, an intermediate spinel layer and an inner alumina layer (Fig. 7 d). The oxide scale on 2 μm Pt coating is similar to that on no Pt sample, but without the outermost NiO layer (Fig. 7 e). The scales on these two samples are not fully dense, and a large number of pores can be observed at the interface of spinel/alumina. The formation of the pores is attributable to the solid-state reaction between NiO and Al_2O_3 , which induces volume contractions and leads to formation of pores [30]. On the other hand, a dense and uniform alumina layer (except for some Cr_2O_3 particles as shown by the arrow in Fig. 7 f) is observed on 5 μm Pt coating. After 30 min oxidation, the oxide scale of no Pt and 2 μm Pt coating is much thicker than that of 5 μm Pt coating because the growth of Ni-oxides is much faster than alumina.

As shown in Fig. 6 and Fig. 7, sufficient Pt addition results in an exclusive alumina TGO layer, compared to samples without Pt (multi-layer TGO structure) or with less Pt addition

(duplex TGO structure). This confirms that Pt can promote alumina growth by inhibiting Ni-oxides growth at very early stage of oxidation.

3.4 TGO growth rate & stress evolution

Fig. 8 is the oxidation time at 1000 °C vs. TGO scale thickness plot of the sample without Pt and with 5 µm Pt, respectively. As can be seen, initially, 5 µm coatings exhibit a faster TGO growth compared to the no Pt sample. This is because within 2 min oxidation, θ -Al₂O₃ to α -Al₂O₃ transition finishes in the scale on no Pt sample (Fig. 3 a) and the TGO only composes of the slow-growing α -Al₂O₃. While fast-growing θ -Al₂O₃ accounts for a large proportion of the scale on 5 µm Pt-diffused γ/γ' coating (Fig. 3 c), which grows much faster.

However, after 30 min oxidation, the average scale thickness of 5 µm Pt sample is only half of that on no Pt sample (Fig. 8). The TGO growth rate of 5 µm Pt sample is significantly reduced due to the phase transformation θ - to α -Al₂O₃, and α -Al₂O₃ gradually becomes dominant in the scale of this sample without any Ni-oxide layer formation (Fig. 5 and Fig. 7 f). But for no Pt sample, the oxide growth rate increases significantly as a result of Ni-oxide layers formation (Fig. 7 d). Therefore, during the early stage of oxidation, Pt firstly increases oxide growth by promoting growth of θ -Al₂O₃, and then it significantly slows down the oxide growth by promoting the selective oxidation of Al and inhibiting the formation of Ni-oxides/spinel. In other words, our study confirmed that Pt has two effects on the oxide scale composition during the early stage oxidation: 1) it can slow down θ - to α -Al₂O₃ phase transformation; 2) Pt can promote the selective oxidation of Al at very early stage of oxidation, in agreement with [11].

The TGO stress evolution of samples without Pt and with the highest Pt content (5 µm) as a function of oxidation time is shown in Fig. 9. After 2 min oxidation, the TGO stresses of the two samples are similar. However, afterwards, the compressive TGO stress of no Pt sample increases significantly from ~ 2.4 GPa (2 min) to ~ 3.8 GPa (30 min), whereas for the 5 µm

Pt sample the compressive stress gradually decreases from ~ 2.2 GPa (2 min) to ~ 1.4 GPa (30 min). This simply implies that Pt addition can reduce the compressive TGO stress during the early stage oxidation of γ/γ' Ni-Al coatings.

3.5 Automated crystal orientation mapping with TEM

Fig. 10 and 11 show the results of conventional ADF-STEM and crystal orientation mapping on TEM of samples with 2 μm Pt coating and 5 μm Pt coating respectively after 10 min oxidation at 1050 $^{\circ}\text{C}$. ADF-STEM allows the overall structure (coating-alumina-platinum capping layer) to be determined. However, the similarity in composition of the different alumina polytypes in the scale means that these cannot be determined by the ADF-STEM contrast. Instead scanning diffraction analysis was used to identify the polytypes and the crystal orientation of the alumina at a high spatial resolution (~ 5 nm). TEM diffraction patterns were recorded in a raster scan across the sample and then compared to libraries of templates generated for the different crystal structures present in the sample. From the analysis, maps of the $\theta\text{-Al}_2\text{O}_3$ (indicated by green pixels in Fig. 10 and 11) and $\alpha\text{-Al}_2\text{O}_3$ (indicated by red pixels) could be obtained. These phase maps were overlaid on phase reliability maps (see Eq. 4) to allow grain details of the underlying coating to be shown. The general effect of platinum slowing down θ to α transformation appears to be borne out by this analysis, by inspecting the proportion of $\alpha\text{-Al}_2\text{O}_3$, which was higher in Figure 10 b compared to Figure 11 b. This is in agreement with the results in Section 3.2.

The spatial distribution of θ and $\alpha\text{-Al}_2\text{O}_3$ in the scale can be seen in the maps. Generally, both maps (Fig. 10 b and Fig. 11 b) reveal a fine level of detail with grains as small as ~ 10 nm in the inner region of the scale, while large columnar grains (100 - 200 nm) typically exists in the outer region of the scale. This is consistent with a previous study on NiAl alloy by bright field TEM imaging [14]. Importantly there is variation in the distribution of the different polytypes along the surface of the coating. By inspecting individual grains which

can be distinguished by the greyscale contrast in the phase reliability map (e. g. the regions ‘A’ and ‘B’ in Figure 10 b are distinct grains), there are regions where α -Al₂O₃ has formed at the coating surface, while at others θ -Al₂O₃ is present. Looking further across the scale, it is clear that some regions have not transformed from θ to α as there are columnar grains of θ -Al₂O₃ extending across the entire scale thickness. These observations suggest that the θ -Al₂O₃ to α -Al₂O₃ transformation rate is inhomogeneous along the coating/oxide interface and related to the underlying coating grains.

3.6 PLPS studies on Ni-Al-Pt alloy samples

From PLPS macroscopic results (Section 3.2), we conclude that higher Pt content results in slower θ -Al₂O₃ to α -Al₂O₃ transition. However, the mechanism of this Pt effect is still unclear. Given the absence of any strong crystallographic coherency between the alumina grains (near the coating surface) and the coating grains (Appendix. A), it is therefore important to investigate the effect of the local platinum distribution in the coating since the inhomogeneous distribution of platinum near the surface of the coating could result in the inhomogeneous nucleation of α -Al₂O₃, as confirmed in Section 3.5.

To validate the above assumption, a direct method is to examine the coating grains individually to determine their phase structure and correlate this to the oxide phase grown on each grain during the early stage oxidation of Pt-diffused γ/γ' coatings. Nevertheless, there are problems with this method. Primarily, the alumina growth results in the depletion of aluminium in the coating and hence the γ' to γ phase transition can take place. Thus the TEM samples did not retain any of the original γ/γ' phase distribution even for very short oxidation exposure. Furthermore, the optical microscopy was also unable to distinguish the underlying γ' or γ phase from the oxide surface of these coatings.

In order to circumvent these problems, the early stage oxidation behaviour of Ni-Al-Pt alloy with γ/γ' microstructure was studied. Y. Chen et al. [1] have shown that this alloy

maintains phase contrast of γ' and γ phase under optical microscope on the oxide surface after up to 4 h oxidation at 1150 °C. In addition, γ' to γ phase transformation is prevented during the early stage oxidation due to a sufficient aluminium source in the underlying alloy allowing the ordered γ' phase to exist even after aluminium depletion. Hence, it is possible to study the early stage oxidation of this alloy by PLPS with relation to the underlying alloy phase structure to verify the above assumption.

Ni-20Al-xPt (x= 0, 10, 20 at.%) alloys with γ/γ' microstructure were investigated. The optical surface images of as-received alloys are shown in Fig. 12. The bright areas in Fig. 12 a - c represent γ' and the dark dendritic areas consist of tiny γ' blocks embedded in the γ network-structure channels (Fig. 12 d). With increasing Pt content, the dendrites become narrower and the phase fraction ratio of γ' to γ increases.

The oxides grown on γ' and γ/γ' region, respectively, were studied by PLPS to analyse the phase after short time exposure at 1050 °C. The results of three alloys are shown in Fig. 13-15, respectively. The γ' and γ/γ' region can be easily distinguished after oxidation for all alloys. As the Pt content increases, the θ -Al₂O₃ fraction also rises, no matter which region (γ' or γ/γ') is detected. This also confirms Pt effect on retarding θ -Al₂O₃ to α -Al₂O₃ transformation. For Ni-20Al alloys, the average θ -Al₂O₃ fraction of γ' regions (5 measurements on random locations) is ~ 21.8 % after 2 min oxidation (Fig. 13 b), while θ -Al₂O₃ fraction of γ/γ' regions at this stage is 14.9 % (Fig. 13 c), which is 31.6 % lower than that on γ' areas. After 10 min, the average θ -Al₂O₃ fraction of γ' areas for Ni-20Al is ~ 9.2 % (Fig. 13 e), whereas very weak θ -Al₂O₃ signal can be detected on γ/γ' areas (Fig. 13 f). The results of Ni-20Al-10Pt and Ni-20Al-20Pt alloys also show the same trend. For instance, after 2 min, θ -Al₂O₃ fraction of γ/γ' areas of Ni-20Al-10Pt (53.4 %, Fig. 14 c) is 30.9 % lower than that on γ' areas (77.7 %, Fig. 14 b). And for Ni-20Al-20Pt alloy after 10 min oxidation, θ -Al₂O₃ fraction of γ/γ' areas is 35.8 % lower than that on γ' areas (Fig. 15 e and f). From Fig. 13 - 15, it can be

concluded that θ -Al₂O₃ fraction of γ/γ' areas is significantly lower than that on γ' areas for three alloys throughout the early stage oxidation, which coincides with our assumption that γ phase can promote θ -Al₂O₃ to α -Al₂O₃ transformation, resulting in a lower θ -Al₂O₃ fraction of γ/γ' regions. In other words, these results support that γ grains near the coating/oxide interface promote the transformation from θ -Al₂O₃ to α -Al₂O₃ while γ' grains retard it.

4 Discussion

4.1 Pt effect on the θ -Al₂O₃ to α -Al₂O₃ transformation

Platinum addition has been shown to alter the transformation dynamics of θ -Al₂O₃ to α -Al₂O₃ [12, 13]. However, the precise mechanism for this is still unclear. The results in this article suggest that one effect of platinum is the local variation in the nucleation of α -Al₂O₃ in the scale. This alters the conventional model of oxide transformation on these coatings. According to Hayashi and Gleeson [31], α -Al₂O₃ nucleates uniformly along the coating/oxide interface, leading to a duplex layered structure of the oxide scale, as shown schematically in Fig. 16 a. However, in this study, γ grains near the interface promote α -Al₂O₃ nucleation while γ' grains retard this transformation (Fig. 16 b and c). Under this circumstance, we can explain why Pt addition slow down this transformation and the non-uniform distribution of α -Al₂O₃ along the interface. The θ -Al₂O₃ to α -Al₂O₃ transformation is accelerated on coatings with lower Pt content due to more γ grains near the coating/oxide interface (Fig. 16 b). Conversely, for coatings with higher Pt content, this transformation is retarded because of the higher γ' phase to γ phase fraction ratio near the coating/oxide interface (Fig. 16 c). Then, the early α nuclei on γ grains grow toward the gas/oxide interface and finally grow into large grains, while α -Al₂O₃ nucleation happens later on γ' grains, which is consistent with the microstructural observations in Fig. 10 b and Fig. 11 b. A previous study suggested that β grains of NiCrAlY coatings have a large tendency to form θ -Al₂O₃ than the γ grains [32], which seems to be supportive to our mechanism considering that both γ' and β phase contain

more aluminium than the γ phase because aluminium diffusion might affect the θ to α transformation rate [13].

Through the use of spatially resolved PLPS measurements on the NiPtAl alloys with γ/γ' structure, it was possible to show that where Pt stabilises the γ' structure in nickel the suppression of the θ -Al₂O₃ to α -Al₂O₃ transition was seen. This offers a validation for the proposed new model in Fig. 16. In the absence of significant crystallographic coherence between the alumina grains (both α and θ) and the coating (Appendix A), it is concluded that the original distribution of γ/γ' in the coating (associated with the local Pt content) directly determines the phases present in the oxide scale. This study combined with other studies on MCrAlY coatings [32, 33] can provide a thorough understanding of the relationship between the oxide phase/composition and the underlying coating microstructure.

In search of the reason(s) why the alumina phase transformation is retarded on the γ' phase region, firstly, as a noble metal, Pt is non-reactive and does not form any oxide during oxidation of the coatings. There is also no evidence that Pt can diffuse into the lattice of Al₂O₃ or segregate to the grain boundaries of Al₂O₃ in the literature. Therefore, it is very unlikely that the retarded θ to α transformation on the γ' region is caused by the direct chemical interaction between Pt and Al₂O₃.

On the other hand, since Pt strongly partitions into γ' , the γ and γ' phase have different lattice parameters and corresponding interplanar spacing (d-spacing) [34]. This would affect the epitaxial strain in the θ -Al₂O₃ at the very initial stage of oxidation. A low d-spacing mismatch between θ -Al₂O₃ and the underlying metal phase is expected to favour the formation of θ -Al₂O₃ due to the low energy barrier, thus slowing down the θ to α phase transformation. For this reason, we propose that a possible reason for the retarded θ to α transformation on the γ' regions is the lower minimum d-spacing mismatch between θ -Al₂O₃ and γ' phase.

To support this argument, the possible orientation relationships in terms of minimum interplanar spacing (d-spacing) mismatch between $\theta\text{-Al}_2\text{O}_3$ and two coating phases (γ' and γ) were investigated. In order to find the possible orientation relationships between $\theta\text{-Al}_2\text{O}_3$ and original γ' (and γ) phases, the transmission diffraction data including the d-spacing values for γ' , γ and $\theta\text{-Al}_2\text{O}_3$ phase were generated by SingleCrystal TM software with the basic lattice parameters for each phase [26, 34] as input. Note that the lattice parameters for γ' and γ were measured at 1000°C in [34], while the lattice parameters for $\theta\text{-Al}_2\text{O}_3$ was measured at room temperatures [26]. Thus the d-spacing values of $\theta\text{-Al}_2\text{O}_3$ have been multiplied by a factor of $(1+\alpha_{\text{Al}_2\text{O}_3}\Delta T)$, where $\alpha_{\text{Al}_2\text{O}_3}$ is the coefficient of thermal expansion of alumina ($\sim 8 \text{ ppm } ^\circ\text{C}^{-1}$) and ΔT is the temperature drop between the oxidation temperature and room temperature ($\sim 1000^\circ\text{C}$). Table 2 gives the data for the two Ni-based coating phases (γ' and γ) and $\theta\text{-Al}_2\text{O}_3$ including the low-index (hkl) planes and the corresponding d-spacing values. The d-spacing mismatch between planes of $\theta\text{-Al}_2\text{O}_3$ and the corresponding γ' (or γ) plane with closest d-spacing matching is defined as:

$$\varepsilon = \frac{d_{hkl}^\theta - d_{h'k'l'}^{\gamma'}}{d_{hkl}^{\gamma'}}$$

As can be seen from Table 2, in the case of 11 low-index planes of γ' (or γ), there is a clear d-spacing mismatch advantage which favours the coherent growth of $\theta\text{-Al}_2\text{O}_3$ on the γ' region by working through the γ' (or γ) planes as follows:

3 of the 11 low-index planes do not have a close match to the planes of $\theta\text{-Al}_2\text{O}_3$ (these planes are (111), (221) and (222)). As for the remaining 8 planes, 6 of them have a d-spacing mismatch (strain, ε) below 1% between $\theta\text{-Al}_2\text{O}_3$ and γ' (with the other two exhibiting a strain up to 1.3%). On the contrary, for the γ planes, only three of them have a strain below 1% and the others show a much higher strain (2 - 2.5%) than that for the γ' phase. 1% has been chosen as a reasonable threshold for the elastic limit of alumina [7] beyond which the coherency is likely to fail. Hence, there are many more possible coherent orientations

between $\theta\text{-Al}_2\text{O}_3$ and γ' for a given surface facet of the metal substrate. This accounts for the strong tendency for the growth of $\theta\text{-Al}_2\text{O}_3$ on the γ' phase region, rather than the γ phase.

In order to explain why the phase transformation from $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ is further delayed on alloys with higher Pt contents (Figs. 3 - 5 and Figs. 13 - 15), additional comparison of d-spacing mismatch for Ni-20Al, Ni-20Al-10Pt and Ni-20Al-20Pt alloys was carried out. Table 3 lists the low-index (hkl) planes and the corresponding d-spacing values of the γ' and γ phase for the three alloys. The d-spacing values of $\theta\text{-Al}_2\text{O}_3$ can be found in Table 2. The d-spacing values for γ' and γ are generated by SingleCrystal TM software with the basic lattice parameters of the three Ni-Al alloys [1] as input. (The lattice parameters for the Ni-20Al-20Pt alloy was obtained by extrapolating the data of Fig. 1 b in [1].) Note that the lattice parameters for the three alloys were measured at room temperatures in [1], thus the d-spacing values of the three alloys have been multiplied by a factor of $(1+\alpha_{\text{Ni}}\Delta T)$, where α_{Ni} is the coefficient of thermal expansion (CTE) of Ni-based alloys ($\sim 14 \text{ ppm}^\circ\text{C}^{-1}$; strictly speaking, γ' and γ have different CTEs. But previously work [34] has shown the difference is very minor, therefore is neglected in calculation) and ΔT is the temperature drop between the oxidation temperature and room temperature ($\sim 1000^\circ\text{C}$). Then the d-spacing mismatch between planes of $\theta\text{-Al}_2\text{O}_3$ and the corresponding γ' (or γ) planes with closest d-spacing matching is calculated as strain in Table 3. As can be seen from Table 3, in the case of 11 low-index planes of γ' (or γ), there is a clear d-spacing mismatch advantage which favours the coherent growth of $\theta\text{-Al}_2\text{O}_3$ on alloys with higher Pt contents, as elaborated as follows.

Firstly, for each alloy, the number of planes which have a d-spacing mismatch below 1% (1% has been chosen as explained above) between $\theta\text{-Al}_2\text{O}_3$ and γ' is higher than that between $\theta\text{-Al}_2\text{O}_3$ and γ , as shown by the last row of Table 3. This is consistent with the findings in Table 2. For the Ni-20Al alloy, 4 of the 11 low-index planes do not have a close match to the planes of $\theta\text{-Al}_2\text{O}_3$. While for the other two alloys, only three planes do not match with those

of θ -Al₂O₃. Moreover, as shown by the last row of Table 3, the number of planes which have a d-spacing mismatch below 1% between θ -Al₂O₃ and γ' (or γ) increases with increasing Pt contents. Hence, there are more possible coherent orientations between θ -Al₂O₃ and the alloy with increasing Pt contents. This strongly supports the experimental results in this work: the θ -Al₂O₃ to α -Al₂O₃ transformation is retarded on alloys/coatings with higher Pt contents.

It should be noted that the above discussion is not contradictory to the results in Appendix A which have suggested no strongly preferred orientation relationships between the Al₂O₃ grains (both α and θ) and the metal substrate. This is because Appendix A presents the results after a period time of oxidation, during which most of the original γ' phase in the surface region is transformed to γ phase. This is no longer subject to the same strain considerations as discussed above.

It is worth pointing out that in addition to Pt, some alloying elements in CMSX-4 substrates can also affect the transient to stable Al₂O₃ transformation. For example, Cr is known to partition to the γ phase of the coating and can accelerate the transient to stable Al₂O₃ transformation by formation of Cr₂O₃ in the initial oxidation stage [7]. This seems to be supportive to our findings that the θ -Al₂O₃ to α -Al₂O₃ transformation is faster on the γ phase.

4.2 Pt effect on TGO composition & stress

The benefit of Pt for promoting exclusive alumina growth and inhibiting Ni-oxide growth, as already discussed in previous publications [1, 4, 11, 35], can be ascribed to two reasons. Firstly, Pt is inert and does not react with oxygen at temperatures up to 1200 °C. But it has strong preference of replacing Ni site in the ordered L1₂ structure of γ' , resulting in an increase of the Al:Ni atom ratio with increasing Pt content on a given crystallographic plane containing both Al and Ni. This increment of Al:Ni ratio would kinetically favour the formation of alumina in preference to NiO on that plane, when considering only the reacting constituents, Al and Ni [11]. Secondly, the enrichment of Pt in the subsurface of the Pt-

containing coatings during the early stage oxidation also contributes to this Pt benefit [36]. This enrichment not only favours the formation of alumina as stated in the first aspect, it can also decrease the chemical activity of Al (a_{Al}) at the oxide/coating interface. The decrease of a_{Al} would, in turn, facilitate the diffusion flux of Al from the inner part of the coating to the oxide/coating interface [35], thus providing a sufficient and consistent Al source for alumina growth.

Reduction of the TGO compressive stress of Pt-containing coatings during early stage oxidation can be explained by the slower transformation from transient alumina to stable α - Al_2O_3 . Firstly, the slower transformation rate due to presence of Pt allows for an extended stress relaxation process, which is due to the tensile stresses generated by the large volume shrinkage (~10 %) associated with the transformation from the monoclinic θ phase to the hexagonal α phase with higher density [10, 13, 37]. This tensile stress relaxation can lead to significant reductions of TGO compressive stress [38, 39]. Secondly, the increase ratio of θ/α in the oxide scale in the presence of Pt may lower the growth stress since θ - Al_2O_3 is more plastic than α - Al_2O_3 [13], which also contributes to the lower stress of higher Pt coatings.

4.3 Early stage oxidation effect on prolonged oxidation performance

As mentioned above, Pt additions can significantly promote the growth of metastable θ - Al_2O_3 , which is less protective than the stable α - Al_2O_3 . Moreover, the growth rate of θ - Al_2O_3 is about an order of magnitude higher than α - Al_2O_3 [40]. An extended lifetime of less protective and faster growing θ - Al_2O_3 due to Pt addition seems disadvantageous to the scale spallation resistance at first sight. However, the long term oxidation investigations of coatings used in this study (Appendix B) shows that coatings with highest Pt contents still presented the longest TGO lifetime, despite the extended lifetime of the θ - Al_2O_3 scale. Although the reasons for this phenomenon remain to be clarified, the fact that Pt inhibits detrimental Ni-

oxide formation at early stage of oxidation (Fig. 7) can partially explain the extended lifetime of Pt-containing coatings.

In addition to the TGO lifetime, the early stage oxidation can also affect the scale morphology and stress evolution during the prolonged oxidation. It is found that the slower θ to α transition rate during early stage oxidation caused by Pt addition can result in a different oxide morphology and low compressive stress of the stable scale, compared to coatings without Pt (Appendix C). This stress reduction can also contribute to the longer TGO lifetime of Pt-containing coatings, as reported elsewhere [13].

5 Conclusions

Pt addition has three effects on the early stage oxidation of γ/γ' -based Ni-Al coatings: 1) retard θ -Al₂O₃ to α -Al₂O₃ transformation thus extending transient θ -Al₂O₃ lifetime; 2) promote the growth of alumina and inhibit the growth of Ni-oxides; 3) significantly reduce the TGO stress during the early stage of oxidation. Crystal orientation mapping results show that the nucleation of α -Al₂O₃ is inhomogeneous along the oxide/coating interface and might be related to the variation of coating compositions due to Pt additions. Spatially resolved PLPS study of Ni-Pt-Al alloy (with γ/γ' microstructure) shows that where Pt stabilises the γ' structure in nickel, the suppression of θ -Al₂O₃ to α -Al₂O₃ transition is observed. Based on these findings, a new mechanism has been proposed to explain this Pt effect on θ -Al₂O₃ to α -Al₂O₃ transformation: γ grains near the coating/oxide interface promote α -Al₂O₃ nucleation while γ' grains retard this transformation.

Appendix A. Coating/alumina orientation analysis

Two interface regions of the specimen in Fig. 11 (white rectangles in Fig. 11) were investigated to explore the possibility of coherent relationships affecting the phase transformation in the TGO scale. Through a non-negative matrix factorisation (NMF) decomposition [41], representative diffraction patterns for different phases were isolated at

the interface region, which also gave a general idea of their location in the sample. Therefore, phase maps that were complementary to the ASTAR analysis can be built and compared. Fig. A1 and A2 exhibit the results for Region 1 and 2.

For Region 1, a small region of θ -Al₂O₃ close to the nickel-alumina interface (the upper phase map in Fig. A1) can be seen. The diffraction patterns for these θ -Al₂O₃ have partial coherency with the underlying nickel (overlapping reflections as shown by the upper diffraction pattern image). Indexing the remainder of the region, it was found that the majority of the alumina has transformed to α -Al₂O₃ (lower phase map in Fig. A1). By overlaying these diffraction patterns, both θ -Al₂O₃ and α -Al₂O₃ in this region have no strong orientation relationship with the nickel substrate, as shown by the lower diffraction pattern image.

There is a twinned area in the middle of the nickel in Region 2 (Fig. A2, twin boundaries are indicated). Similar to Region 1, a small coherent θ -Al₂O₃ region near the surface of nickel is observed. In addition, the coherency is more prominent in the twinned region than the outer twin region (as the greater coincidence in the diffraction pattern from the inner-twin suggests). Importantly, both α grains and large θ grains that form further out from the interface layer exhibit little or no coherency with the substrate, as indicated by the lower diffraction patterns in Fig. A2.

Overall, θ -Al₂O₃ always nucleates partial-coherently along the nickel surface whereas with continued growth this transforms into incoherent α -Al₂O₃, with no obvious relationship to the underlying nickel orientation. This suggests that the nickel substrate orientation has no effect on θ to α -Al₂O₃ phase transformation.

Appendix B. Prolonged oxidation lifetime of coatings with different Pt additions

Fig. B1 shows the optical images of three coatings with different Pt additions after prolonged oxidation. For no Pt sample, local TGO spallation occurs after 50 h (bright areas in

Fig. B1 a), and spallation is observed nearly all over the surface after 200 h (Fig. B1 c). In contrast, the 5 μm Pt coating scale remains intact up to 200 h oxidation (Fig. B1 e).

Appendix C. Early stage oxidation effect on the stable scale morphology & stress

The TGO stress evolution of no Pt sample and 5 μm Pt coating after prolonged oxidation is shown in Fig. C1. The TGO stress of 5 μm Pt coating is lower than that of no Pt sample, until the TGO spallation on Pt sample which causes a significant drop of stress (Fig. C1 a). Moreover, there are two stages of stress evolution of 5 μm Pt coatings. During Stage I (up to 10 h), the TGO stress remains at a low level (~ 3.5 GPa) compared to no Pt coatings. After 10 h (Stage II), the stress shows a significant rise (~ 4.5 GPa). Due to Pt addition, the growth of $\theta\text{-Al}_2\text{O}_3$ is extended and thus numerous blade-like $\theta\text{-Al}_2\text{O}_3$ forms on the surface of 5 μm Pt coating during early stage oxidation. These blade-like $\theta\text{-Al}_2\text{O}_3$ grains totally transform into stable $\alpha\text{-Al}_2\text{O}_3$ and sustain their blade-like shape after phase transformation on the surface of the stable scale (Fig. C1 b, after 5 h oxidation). These blade-like oxides, being less constrained by the underlying coating, can cause the R peaks of $\alpha\text{-Al}_2\text{O}_3$ in PLPS spectrum shift to much higher frequencies, resulting in lower TGO stresses. In this case, it should be assured that the scale is intact, because any crack would give similar stress-free signals, which has been ruled out by the microstructural study of the oxide scale. While for the no Pt sample, since θ to α transformation is much faster, no blade-like oxide remains on the stable scale. Therefore the TGO stress of this sample is higher until TGO spalls. It is noticed that the blade-like oxides on the stable scale of 5 μm Pt coating become smoother with oxidation time (Fig. C1 c) as a result of surface diffusion driven by a reduction of surface energy, which causes a slight rise of stress during the Stage I. Eventually, these blade-like oxides on the surface evaporate after prolonged exposure at high temperatures (Fig. C1 d), thus leading to a significant rise of the TGO stress.

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Fig.1 a) Luminescence spectrum showing characteristic peaks for θ - Al_2O_3 and α - Al_2O_3 of an oxide scale; b) R peaks of an α - Al_2O_3 scale on a Pt-diffused γ/γ' coating after isothermal oxidation at 1100 °C for 1 h. For comparison, the spectrum from a stress-free, polycrystalline alumina is shown by the red line.

Fig. 2 Cross-sectional SEM images of as-diffused samples: a) 2 μm Pt coating; b) 5 μm Pt coating.

Fig. 3 Typical luminescence spectrum of a) 0 Pt, b) 2 μm Pt and c) 5 μm Pt samples after 2 min oxidation at 1000 °C.

Fig. 4 Luminescence spectrum of a) 0 Pt, b) 2 μm Pt and c) 5 μm Pt samples after 10 min oxidation at 1000 °C.

Fig. 5 Fraction profiles of θ - Al_2O_3 as a function of oxidation time.

Fig. 6 a) - c): FIB/SEM cross-sectional images after 2 min oxidation; d) - f): FIB/SEM cross-sectional images after 10 min oxidation at 1000 °C of no Pt sample, 2 μ m Pt coating and 5 μ m Pt coating, respectively.

Fig. 7 a) - c): SEM surface images; d) - f): FIB/SEM cross-sectional images of no Pt sample, 2 μm Pt coating and 5 μm Pt coating after 30 min oxidation at 1000 °C.

Fig.8 Oxide scale thickness evolution of no Pt sample and 5 μm Pt sample as a function of oxidation time.

Fig. 9 The TGO stress evolution of no Pt sample and 5 μm Pt sample as a function of oxidation time.

Fig. 10 a) ADF STEM image of 2 μm Pt sample after oxidation at 1050 $^{\circ}\text{C}$ for 10 min; b) combined phase map and phase reliability map obtained from automated crystal orientation mapping in TEM, taken from the red box region in a). Green colour: $\theta\text{-Al}_2\text{O}_3$; red colour: $\alpha\text{-Al}_2\text{O}_3$.

Fig. 11 a) ADF STEM image of 5 μm Pt sample after oxidation at 1050 $^{\circ}\text{C}$ for 10 min; b) combined phase map and phase reliability taken from the red box region in a). Green colour: $\theta\text{-Al}_2\text{O}_3$; red colour: $\alpha\text{-Al}_2\text{O}_3$.

Fig. 12 Microstructure of the as-received a) Ni-20Al, b) Ni-20Al-10Pt, c) and d) Ni-20Al-20Pt alloy. The inset in d) shows the magnified morphology of the tiny γ channels in the γ/γ' region.

Fig. 13 a) and d): the optical image; b) c) e) and f): PLPS spectra taken from different phase regions of Ni-20Al alloy after oxidation at 1050 °C for 2 min and 10 min, respectively.

Fig. 14 a) and d): the optical image; b) c) e) and f): PLPS spectra taken from different phase regions of Ni-20Al-10Pt alloy after oxidation at 1050 °C for 2 min and 10 min.

Fig. 15 a) and d): the optical image; b) c) e) and f): PLPS spectra taken from different phase regions of Ni-20Al-20Pt alloy after oxidation at 1050 °C for 2 min and 10 min.

a) Previous θ - to α - Al_2O_3 transformation model: α - Al_2O_3 uniformly nucleates at coating/oxide interface

b) New transformation model: γ grains promote α - Al_2O_3 nucleation while γ' grains retard this transition

c)

Fig. 16 a) Previously reported transformation model of α - Al_2O_3 : uniformly nucleate along the interface, resulting in a layered structure of the oxide scale; b) and c) new transformation model in our study which illustrates lower Pt content and higher Pt content coatings, respectively.

Fig. A1 Phase maps and corresponding diffraction pattern images of different phases in Region 1.

Fig. A2 Phase map and corresponding diffraction pattern images in Region 2.

Fig. B1 Optical images of sample surface after different periods of prolonged oxidation at 1050 °C. The bright area is the surface of the underlying metal due to spallation of the TGO.

Fig. C1 a) Residual stress evolution in TGO scale on no Pt sample and 5 μ m Pt coating with oxidation; b) - d) scale surface morphologies of 5 μ m Pt coating after 5h, 10 h and 50 h isothermal oxidation at 1050 $^{\circ}$ C.

Table 1 Electroplating time and corresponding Pt thickness, average Pt concentration and surface roughness

Electroplating time, min	0	20	50
Pt layer thickness, μm	0	2	5
Average Pt content, at. %	0	12.6	21.3
R_q , μm	0.45	0.40	0.48

Table 2 Low-index (hkl) planes and the corresponding d-spacing values of two Ni phases (γ' and γ) and θ -Al₂O₃: the d-spacing mismatch between planes of θ -Al₂O₃ and the corresponding γ' (or γ) plane with closest d-spacing matching is calculated and listed as the strain

θ -Al ₂ O ₃		γ'			γ		
(hkl)	d _{hkl} , Å	(hkl)	d _{hkl} , Å	strain	(hkl)	d _{hkl} , Å	strain
(20 $\bar{1}$)	4.5307	(100)	3.6000	1.30%	(100)	3.5623	0.23%
(201)	3.5542	(110)	2.5456	0.96%	(110)	2.5189	2.03%
(400)	2.8660	(111)	2.0785	-	(111)	2.0567	-
($\bar{1}$ 11)	2.5700	(200)	1.8000	1.17%	(200)	1.7725	2.74%
(111)	2.4497	(210)	1.6100	1.00%	(210)	1.5931	2.14%
(310)	2.3172	(211)	1.4697	0.92%	(211)	1.4543	0.13%
(202)	2.2652	(220)	1.2728	0.96%	(220)	1.2533	2.53%
(311)	2.0298	(221)	1.2000	-	(221)	1.1874	-
($\bar{1}$ 12)	2.0232	(310)	1.1384	0.51%	(310)	1.1265	0.54%
(1 $\bar{1}$ 2)	1.9078	(311)	1.0853	0.009%	(311)	1.0689	1.54%
(003)	1.8211	(222)	1.0329	-	(222)	1.0234	-
($\bar{2}$ 0 $\bar{3}$)	1.6273	d-spacing mismatch between planes of θ -Al ₂ O ₃ and γ' : $\varepsilon = \frac{d_{hkl}^{\theta} - d_{h'k'l'}^{\gamma'}}{d_{hkl}^{\gamma'}}$			d-spacing mismatch between planes of θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{hkl}^{\theta} - d_{h'k'l'}^{\gamma}}{d_{hkl}^{\gamma}}$		
($\bar{1}$ 13)	1.5728						
(113)	1.4909	For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ' : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma'}}{d_{(311)}^{\gamma'}} = 0.009\%$			For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$		
(020)	1.4562						
(220)	1.4113	For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$			For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$		
(221)	1.3475						
(22 $\bar{2}$)	1.2850	For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$			For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$		
(404)	1.1326						
(223)	1.0854	For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$			For example, the d-spacing mismatch between θ -Al ₂ O ₃ and γ : $\varepsilon = \frac{d_{(223)}^{\theta} - d_{(311)}^{\gamma}}{d_{(311)}^{\gamma}} = 1.54\%$		
(024)	0.9962						

*Note: The data for θ -Al₂O₃ is listed as a decreasing order for d-spacing values, and only the d-spacing values which are within the range of γ' and γ phases are listed.

Table 3 Low-index (hkl) planes and the corresponding d-spacing values of two Ni phases (γ' and γ) of three Ni-Al alloys: Ni-20Al, Ni-20Al-10Pt and Ni-20Al-20Pt: the d-spacing mismatch between planes of θ -Al₂O₃ and the corresponding γ' (or γ) plane with closest d-spacing matching is calculated and listed as the strain for the γ' and γ phase, respectively

(hkl)	Ni-20Al		Ni-20Al-10Pt		Ni-20Al-20Pt	
	γ' : d _{hkl} (Å)	γ : d _{hkl} (Å)	γ' : d _{hkl} (Å)	γ : d _{hkl} (Å)	γ' : d _{hkl} (Å)	γ : d _{hkl} (Å)
	strain	strain	strain	strain	strain	strain
(100)	3.5632	3.5415	3.5761	3.5512	3.5949	3.5580
	0.25%	0.36%	0.61%	0.08%	1.10%	0.11%
(110)	2.5196	2.5042	2.5287	2.5111	2.5420	2.5159
	-	-	1.60%	2.34%	1.00%	2.20%
(111)	2.0573	2.0447	2.0647	2.0503	2.0756	2.0542
	1.66%	1.05%	2.00%	1.32%	-	-
(200)	1.7816	1.7622	1.7881	1.7670	1.7975	1.7704
	2.22%	3.30%	-	-	1.30%	2.90%
(210)	1.5935	1.5838	1.5993	1.5891	1.6077	1.5912
	1.30%	1.10%	1.66%	1.01%	0.99%	2.31%
(211)	1.4547	1.4458	1.4599	1.4497	1.4676	1.4525
	0.10%	0.71%	0.25%	0.44%	0.78%	0.25%
(220)	1.2598	1.2460	1.2644	1.2494	1.2710	1.2518
	-	-	1.63%	2.80%	0.86%	2.74%
(221)	1.1877	1.1805	1.1920	1.1837	1.1983	1.1860
	-	-	-	-	-	-
(310)	1.1268	1.1199	1.2874	1.1230	1.1368	1.1251
	0.51%	1.13%	0.19%	0.80%	0.36%	0.67%
(311)	1.0742	1.0627	1.0781	1.0656	1.0838	1.0676
	1.05%	2.14%	0.68%	1.86%	0.15%	1.67%
(222)	1.0223	1.0174	1.0260	1.0202	1.031	1.0222
	-	-	-	-	-	-
Number of strain < 1%	3	2	4	3	6	3