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# INVESTIGATION OF THE MICROSTRUCTURE OF PLATINUM-MODIFIED ALUMINIDE COATINGS

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## Abstract

*The high temperature performance of Pt-modified aluminide coatings is directly related to their composition and microstructure. In this work, several of the factors that control such features are investigated on a single crystal Ni base superalloy. It will be shown that the bi-phase PtAl<sub>2</sub> + (Ni,Pt)Al composition is more prone to occur at higher Pt surface concentrations, lower temperatures and shorter aluminising treatments. The alloying elements also seem to play a role in the achievement of either a single or a bi-phase structure. Finally, the incorporation of different elements to the Pt/Al coatings brings about shifting of the X-ray peaks, which in turn may indicate the presence of residual stresses.*

Keywords: single crystal nickel superalloy, out-of-pack platinum-modified aluminide coatings, single phase.

## 1.- INTRODUCTION

The use of Pt-modified aluminium diffusion coatings as oxidation resistant coatings [1] or as bond coats for thermal barrier coatings (TBCs) [2] has been frequently cited to exhibit better high temperature stability than the pure aluminide coatings [3], especially under cyclic loads [4]. In essence, platinum helps to create an aluminium reservoir to develop a protective alumina scale [5]. Although various mechanisms have been proposed, the beneficial effects of Pt are still a matter of controversy. Originally, it was thought that Pt hindered Al inward diffusion [1] and outward diffusion of the refractory elements contained in the superalloy [e.g. 6,7]. More recent studies have shown that the observed influences of Pt additions typically include (a) reduction in void growth along the scale/metal interface, (b) modification of the scale/substrate morphology and (c) mitigation of detrimental effects of sulphur segregation [8,9], especially in

the grit blasted condition [10]. Moreover, when used as a bond coat, the rumpling phenomenon needs to be critically considered. Rumpling was earlier reported to originate from differences between the thermal expansion coefficients and mechanical properties between the coating and the substrate [11]. Recent studies on Pt-NiAl systems have clearly demonstrated that rumpling in fact results from the volume changes associated to the non-reversible  $\beta$  to  $\gamma'$  transformation owing to interdiffusion of elements between the substrate and the coating [12-14]. Overall, the thermal stability of the coatings is a critical factor affecting its performance and this in turn, depends on their composition and microstructure. Therefore, in this work it is intended to provide more insight into the understanding of different process parameters on the control of Pt-modified aluminide coatings produced by single step out-of-pack processes without subsequent heat treatments.

## **2.- EXPERIMENTAL PROCEDURE**

A single crystal superalloy (Ni-9Co-6.5Cr-6W-6.5Ta-5Al-1Ti-0.6Mo, wt%) was cut into 2 mm thick discs and grit blasted prior to electrodeposition of a nominal 5  $\mu\text{m}$  thick Pt layer. Different (or no) diffusion treatments were then undertaken under vacuum at 1050 and 1075° C. Then, the samples were vapour aluminised using a low activity process at 1050 and 1075° C without any further annealing, i.e. in a single step process. Characterisation of the coated specimens was carried out by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy coupled to energy dispersive spectrometry (SEM/EDS) and electron probe microanalysis (EPMA).

## **3.- RESULTS AND DISCUSSION**

### **3.1.- Platinum diffused coatings**

Figure 1 (a) shows the typical morphology of the Pt coatings after diffusion annealing at 1050°C for 5 h. The original surface of the substrate can be identified by the more contrasted spots normally surrounding pores and/or particles. Al enrichment was revealed on such particles by X-ray maps, indicating that the particles may result from the originally blasted surface, as typically observed in other studies [15,16].

Figure 1 (b) represents the Pt profiles across the coatings. It can be observed that the Pt concentration flattens out from the outer surface with increasing annealing time. Also, a sharp increase in thickness can be observed to occur after the first diffusion hour but the extended treatments do not lead to a parabolic growth of the layer. A parabolic trend would be typical the

result of a solid state diffusion process across a single phase. However, various phases seem to develop and evolve with time. Indeed, as depicted in Figure 1(a) an irregular diffusion front does occur in the main diffused layer. Only the areas with lower Pt contents closer to the substrate show a relatively planar interface in agreement with the interdiffusion rates calculated by Karunaratne and Reed [17]. These authors also showed that the interdiffusion coefficients of Ta and Re diffusion in Ni are higher than those of Pt and W at temperatures higher than 1000° C. However, no particular increase in these refractory elements has been found across the diffused layer. According to the X-ray maps, only Cr and Co seem to be associated to Ni in the darker regions of Figure 1 (a) indicating the presence of a  $\gamma$  phase whereas the brightest zones i.e. the Pt-rich phases, contain more aluminium, thus indicating the genesis of  $Pt_xAl_y$  phases. On the contrary, at the diffused layer / substrate interface, refractory element enrichment takes place, especially Ta, which agrees with the observations of Karunaratne and Reed [17]. In Table 1 the main results are summarised.

By comparing the data of Table 1, it can be seen that if the diffusion temperature is increased up to 1075° C, short treatments of 1 and 2 hours render the same Pt surface concentrations than at 1050° C for 2 and 3 h, respectively. For the same diffusion time, Ni, Cr and Al incorporation is promoted at the highest temperature. In agreement with our findings, Benoist et al. [18] reported that the superalloy elements Ni, Cr and Al had diffused to the top surface after the diffusion treatments at 1000 and 1100° C of 5 and 10  $\mu$ m thick Pt layers. The concentration profiles were concluded to be very irregular owing to differences in the mean free path of Pt and substrate elements, which may also help in explaining the non-parabolic thickness behaviour of the diffused layer observed in the present study.

### **3.2.- Pt-modified aluminide coatings**

#### ***3.2.1.- Effect of Pt initial coating thickness***

Part of this study examines the role of Pt in the final microstructure of low activity coatings, allowing comparison with the already published results [e.g. 19,20] for high activity coatings. For such purpose, 2.5 and 7  $\mu$ m Pt thick layers have been also deposited and heat treated at 1050 °C for 2, 3 and 4 h. After aluminisation, different microstructures are obtained as shown in Figure 2. It can be observed that as the initial Pt thickness increases and hence, the surface Pt reservoir, a greater volume of precipitates appear at the topmost layers of the coating after aluminisation. According to the XRD patterns, these are identified as  $PtAl_2$  particles (with some

reflections arising from  $\text{Pt}_8\text{Al}_{21}$ ) which precipitate within a  $\beta$ -(Ni,Pt)Al matrix. Krishna et al. [19] reported that only a certain amount of Pt was needed to enhance the Al uptake by about 25%. In the case of 2.5  $\mu\text{m}$  Pt thick layers, the critical amount was established at about 28 wt% Pt.

According to the EDS composition profiles shown in Figure 2, Pt is very diluted in the 2.5  $\mu\text{m}$  thick layers after coating and thus, the single-phase structure can be obtained. For Pt layers thicker than 2.5  $\mu\text{m}$ , the surface Pt concentrations are higher than the above mentioned value of 28 wt% and thus, bi-phase structures are observed. The volume occupied by the  $\text{PtAl}_2$  precipitates seems to depend on the Pt dilution after annealing, which is also related to the heterogeneity of the composition profiles as was shown in Figure 1 (b). Indeed, although Pt is transported inwardly [21] the original richest Pt zones [brighter areas of Figure 1(a)] contained coarser  $\text{PtAl}_2$  particles that require longer times to be diluted in the outwardly growing  $\beta$ -phase.

When the single phase  $\beta$ -(Ni,Pt)Al front climbs towards the outer surface, a great number of precipitates appear, especially Cr, W and Co, which tend to accumulate at the coating grain boundaries, probably by rejection of these elements from the  $\beta$ -phase. Incorporation of refractory elements during Pt/Al coating constitution is a well-known phenomenon that can lead to degradation of the oxidation resistance of the coated superalloy [22]. In high activity pack coatings, Ti, Co and Cr precipitates [15] and Ta and Hf carbides [19] were found to occur depending on the substrate alloy composition. Angenete and Stiller [16] however, found numerous round  $\alpha$ -W precipitates on the outer zone of the coating using an inward type process (high activity), whereas in the outward coating type no precipitates were observed. This may indicate that in the present experimental conditions a pure outward diffusion process has not been established. The presence of Cr may be explained by the fact that the plain  $\beta$ -NiAl phase is only able to dissolve low amounts of Cr [23]. In the case of Pt-plated superalloys, Pt saturation brings about precipitation of PtCr [18], which after longer exposures, i.e. during aluminisation, may evolve releasing Cr into the coating. Although the interdiffusion coefficient of Ta is one order of magnitude higher than that of W at the actual coating temperatures [17], no significant differences between both elements content occur in the outer band, possibly indicating that Pt is more effective in arresting outward diffusion of Ta than that of W.

### ***3.2.2.- Effect of aluminisation temperature and time***

Increasing the testing temperature from 950 up to 1075° C typically dilutes the amount of Pt at the outer surface after coating, although this effect is less pronounced at the highest temperatures. However, even small differences in the Pt content seem to be critical to the formation of single phase (Ni,Pt)Al coatings, which are normally accompanied by a higher content of refractory elements in the interdiffusion layer (Figure 3). This clearly agrees with the enhanced outward diffusion of Ni, Cr and Al with increasing temperature also found after the Pt diffusion treatment (cf. Section 3.1). The resulting concentration of refractory elements then brings about coarsening of the topologically close-packed (TCP) phases at the interdiffusion layer. According to Chen and Little [23] and Rae and Reed [24], these mostly correspond to the  $\mu$  and R phases at 1050 and 1150° C, respectively, on a CMSX-4 substrate and not to a  $\sigma$  phase, which has been reported to hinder Al inward diffusion [23].

The effects are less marked with increasing coating time as shown in Figure 4. Indeed, the average compositions across the three layers constituting the coatings differ very slightly. Only a 3 wt% difference is found in the refractory elements content in the central layer for longer coating times. This can be explained by the fact that upon the stabilisation of the  $\beta$ -(Ni,Pt)Al phase Cr, W and other refractory elements are expelled from this phase as a result of Ni outward diffusion to the central layers. This clearly indicates that Pt does not impede transport of the base metal as also observed by Benoist et al. [18].

### ***3.2.3.- Effect of Pt annealing treatments***

According to the previous sections, Pt rather than the aluminising treatment plays a key role in controlling the microstructure and composition of the coatings. Therefore, the effect of different diffusion treatments of the as-deposited Pt layers on the aluminisation behaviour has been investigated. The coatings microstructure is shown not to behave linearly, i.e. with increasing diffusion time and/or temperature, the coating does not become systematically more single phase as shown in Figure 5. This may arise from a local redistribution of the elements into the different phases, especially a Pt enrichment in the PtAl<sub>2</sub> particles could be taking place along with an Al enrichment of the  $\beta$ -phase.

The EDS and EPMA microanalyses across the coatings (figure 6) show instabilities in the Pt content in the outer layers in most of the coatings indicating the presence of microprecipitation

of Pt-Al phases, typically PtAl<sub>2</sub>. In Figure 6 the evolution of the Pt content in the transverse section of the coatings is depicted. Clearly, when no diffusion heat treatment is performed, the top layer is exclusively composed of PtAl<sub>2</sub> as inferred by XRD. As the diffusion time increases Pt is diluted from the outermost surface resulting in a more uniform Pt concentration across the coating. However, an incubation time of 4 h seems to be needed for reducing the Pt content at the top surface and extend it further into the substrate. Finally, after 5 h the amount of Pt is reduced by a factor of 1.5 and the depth is fourfold that observed without heat treatment. From the compositions obtained by EPMA, the coatings heat treated between 1 and 3 h at 1050° C should fall in the binary  $\beta$ -(Ni,Pt)Al +  $\zeta$ -PtAl<sub>2</sub> stability field [25]. For longer treatments at the same temperature, the compositions fall within the  $\beta$ -loop of the ternary diagram. However, this is not the observed situation probably because the compositions are very close to the binary field and the alloying elements may partition preferentially to any of the Pt containing phases, thus stabilising either the  $\beta$  or the  $\zeta$  phase and/or may hinder Pt inward diffusion.

Figure 7 shows that incorporation of Pt into the  $\beta$ -NiAl phase brings about strong shifts to lower diffraction angles with respect that of the pure  $\beta$ -NiAl phase ( $2\theta = 44.367^\circ$ ) [7,15]. Incorporation of Pt is known to occur at substitutional sites of Ni in the B2 structure of  $\beta$ -NiAl. Likewise, the PtAl<sub>2</sub> (220) peak is also shifted probably due to incorporation of Ni and/or Cr [26]. It is a well-known phenomenon that the incorporation of a foreign atom into a lattice could induce strains and stresses in such lattice. The stress level is dependent on, among other factors, the size of the incorporated species. In this case, the radii (12-coordinate) of Ni and Pt are 124.0 and 138.5 pm, respectively [27]. Owing to such difference, a significant mismatch is expected to occur in the lattice, thus inducing strains and stresses. However, no linear relationship can be ascribed with the thermal treatment performed to diffuse Pt inwardly, i.e. with its concentration, probably indicating a supplementary effect of some other coarse-sized elements (e.g. W, Ta...). Although this experimental study does not aim at calculating the actual values of strain and stress, Pt seems anyhow to be the main responsible for such feature. For instance, Chen et al. [28] in their studies of a 38.5 wt% Pt containing single phase coating prepared by EB-PVD showed that significant lattice strains were present. Watanabe et al. [29] also calculated the residual stress in a commercial  $\beta$ -(Ni,Pt)Al bond coat and found that this was under tensile stress of about 140 MPa. Therefore, the likely mismatch between the  $\beta$ -(Ni,Pt)Al and the  $\zeta$  PtAl<sub>2</sub> phases might be the responsible for such features.

#### **4.- SUMMARY AND CONCLUSIONS**

The effect of various parameters involved in achieving a given microstructure of Pt-modified aluminide coatings has been investigated in this work. The mechanisms involved are extremely complex owing to the multicomposition of the single crystal superalloy as well as the scarce information on the interdiffusion of Pt for contents higher than 28 wt%, as it is typically found in turbine applications. Overall, it can be summarised that the aluminising temperature plays a more important factor rather than time when platinum-plated and annealed superalloys are considered. The temperature should therefore be controlled to avoid precipitation of secondary harmful phases. It has been confirmed that Al uptake is favoured by the presence of Pt at the outermost layers of the coating using a low activity process. Furthermore, the Pt contents at the outer surface of the coating decreases sharply towards the substrate when longer diffusion treatments are conducted prior to aluminisation. The single-phase structures do not seem to depend exclusively on the amounts of Al, Pt and Ni but also on the participation of alloying elements from the substrate, which, in turn, indicates that Pt does not completely arrest outward diffusion of refractory elements. Finally, the incorporation of Pt to the  $\beta$ -NiAl structure seems to be the responsible for a clear shift of the X-ray peaks to lower diffraction angles although a linear relationship cannot be related to the actual Pt concentration. This indicates that some secondary elements may also play a role in such feature.

#### **5.- ACKNOWLEDGEMENTS**

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**Table 1.- Main features of the platinum coating after the different diffusion heat treatments (NB: average EDS wt% compositions at the top surface rounded to the nearest integer).**

<b>T, ° C</b>	<b>Time, h</b>	<b>Thickness, μm</b>	<b>Pt, wt%</b>	<b>Ni, wt%</b>	<b>Co, wt%</b>	<b>Cr, wt%</b>	<b>Al, wt%</b>
as-deposited		5	100	--	--	--	--
1050	1	23	54	24	2	2	2
1050	2	24	49	25	6	5	2
1050	3	26	47	24	4	4	3
1050	4	25	48	26	4	4	3
1050	5	26	42	29	6	5	2
1075	1	24	49	26	3	2	4
1075	2	26	47	27	6	7	3

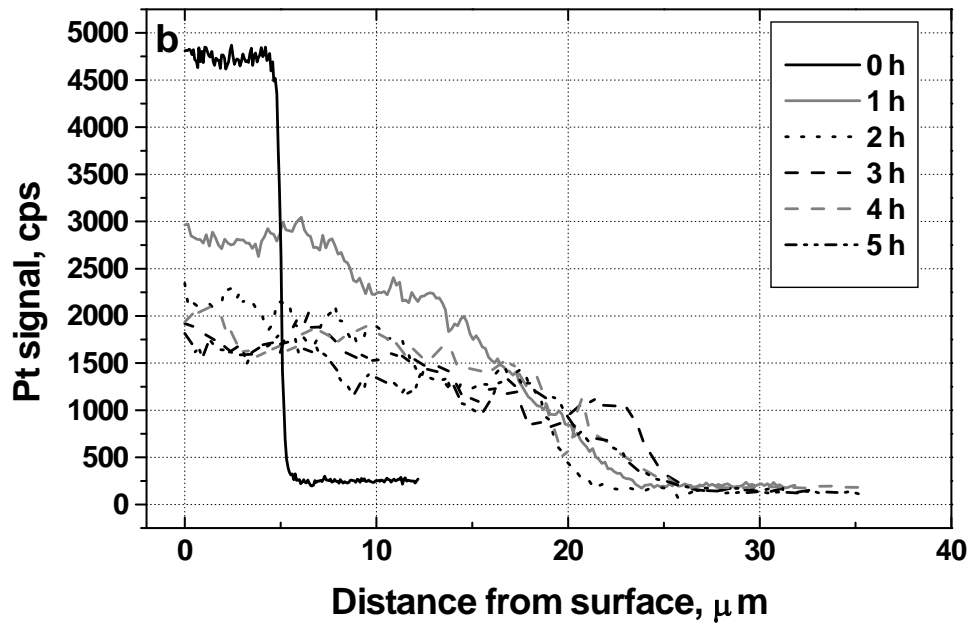
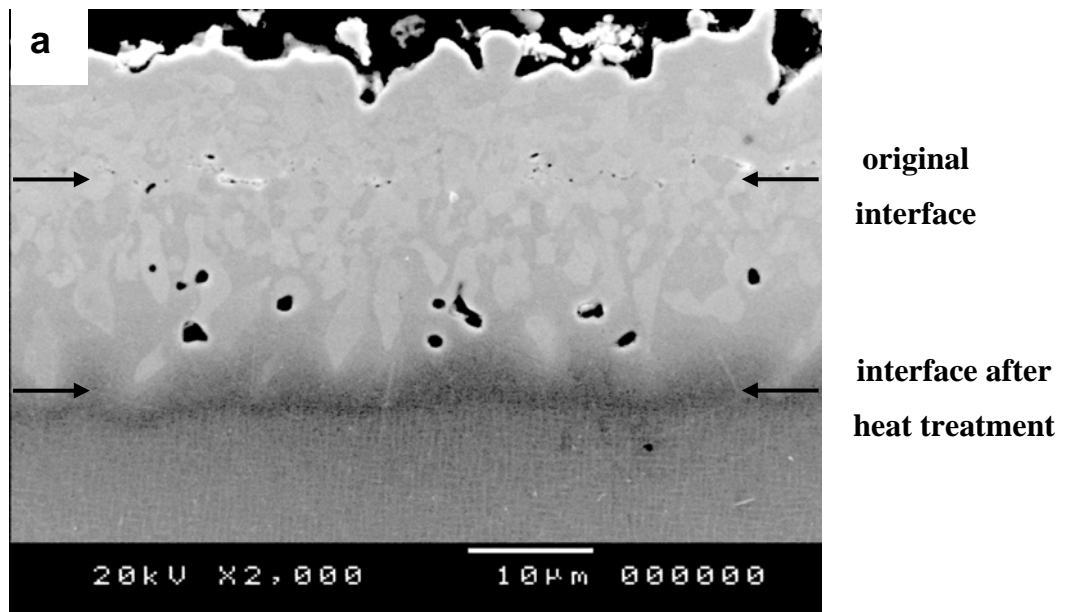


Figure 1.- (a) Typical Pt layer morphology after diffusion treatment (in this figure at  $1050^\circ$  for 5 h) and (b) the standardless Pt line profiles.

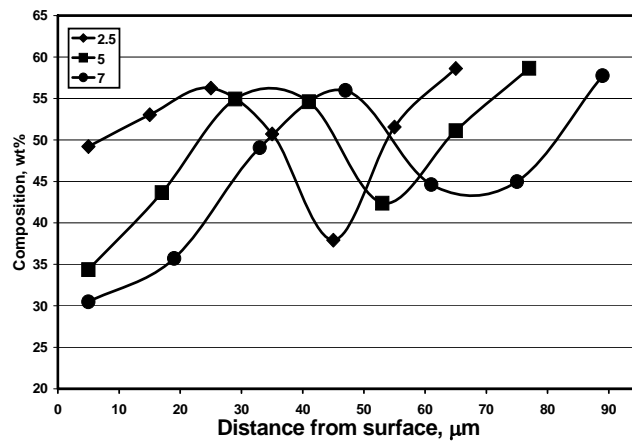
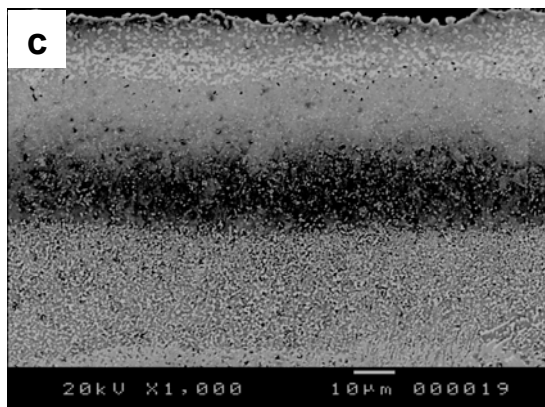
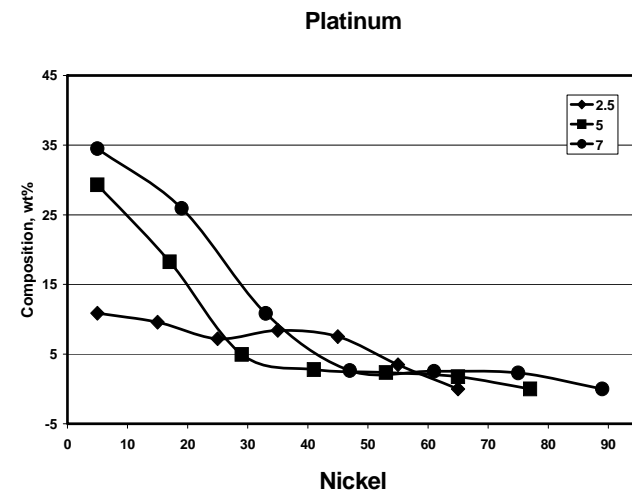
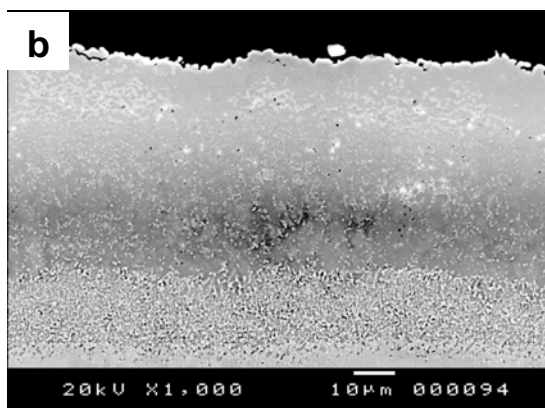
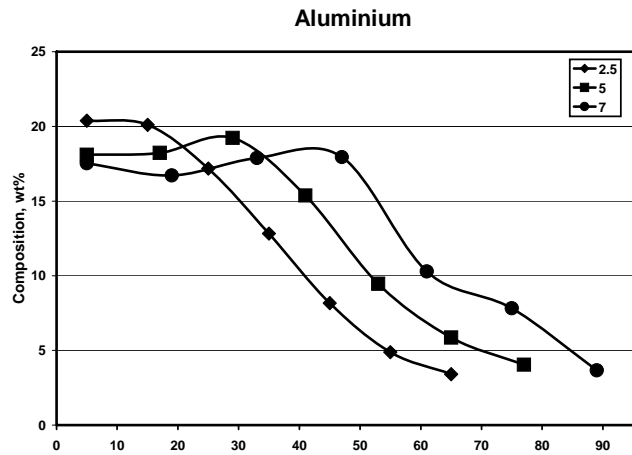
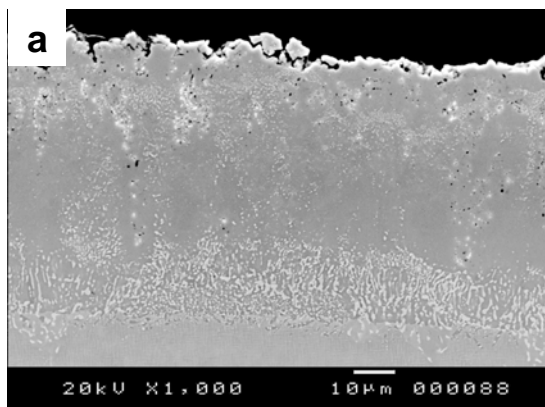
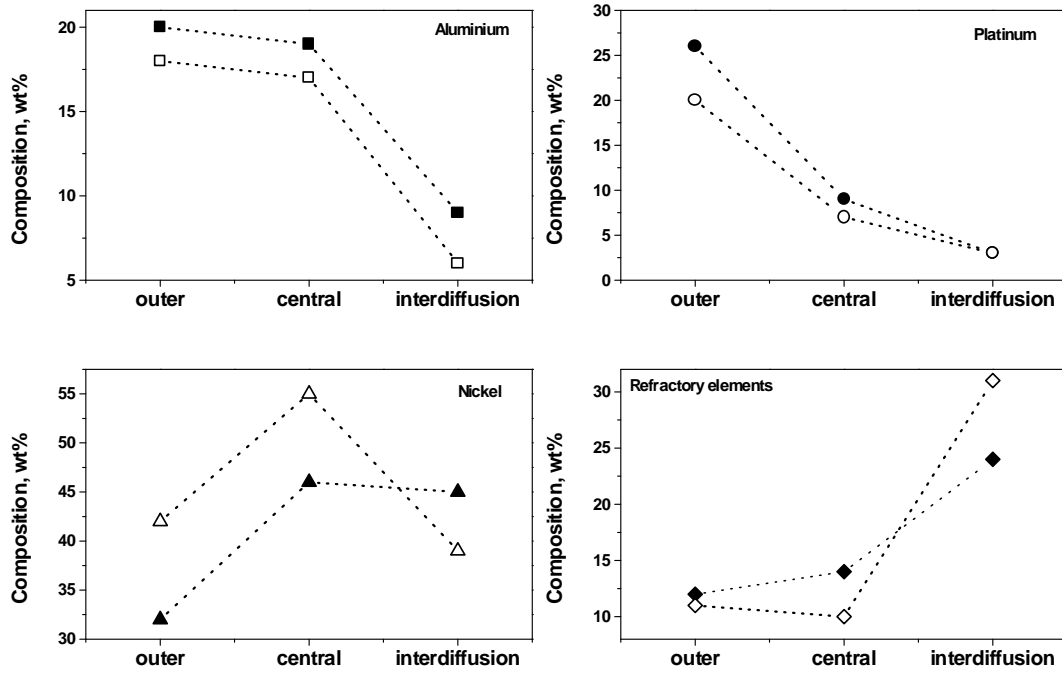
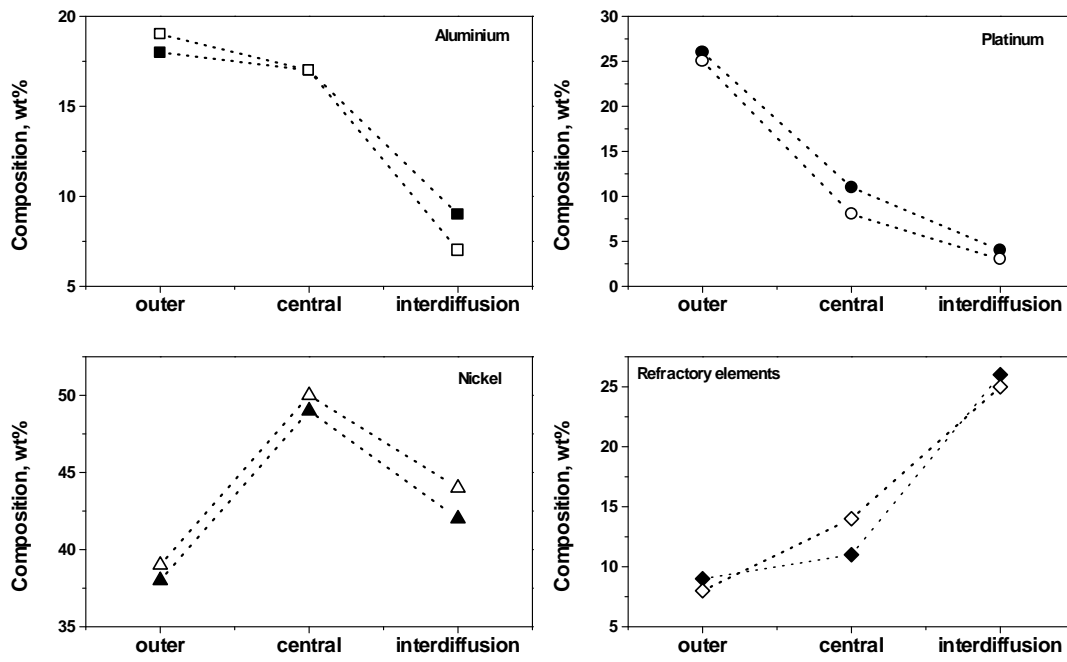


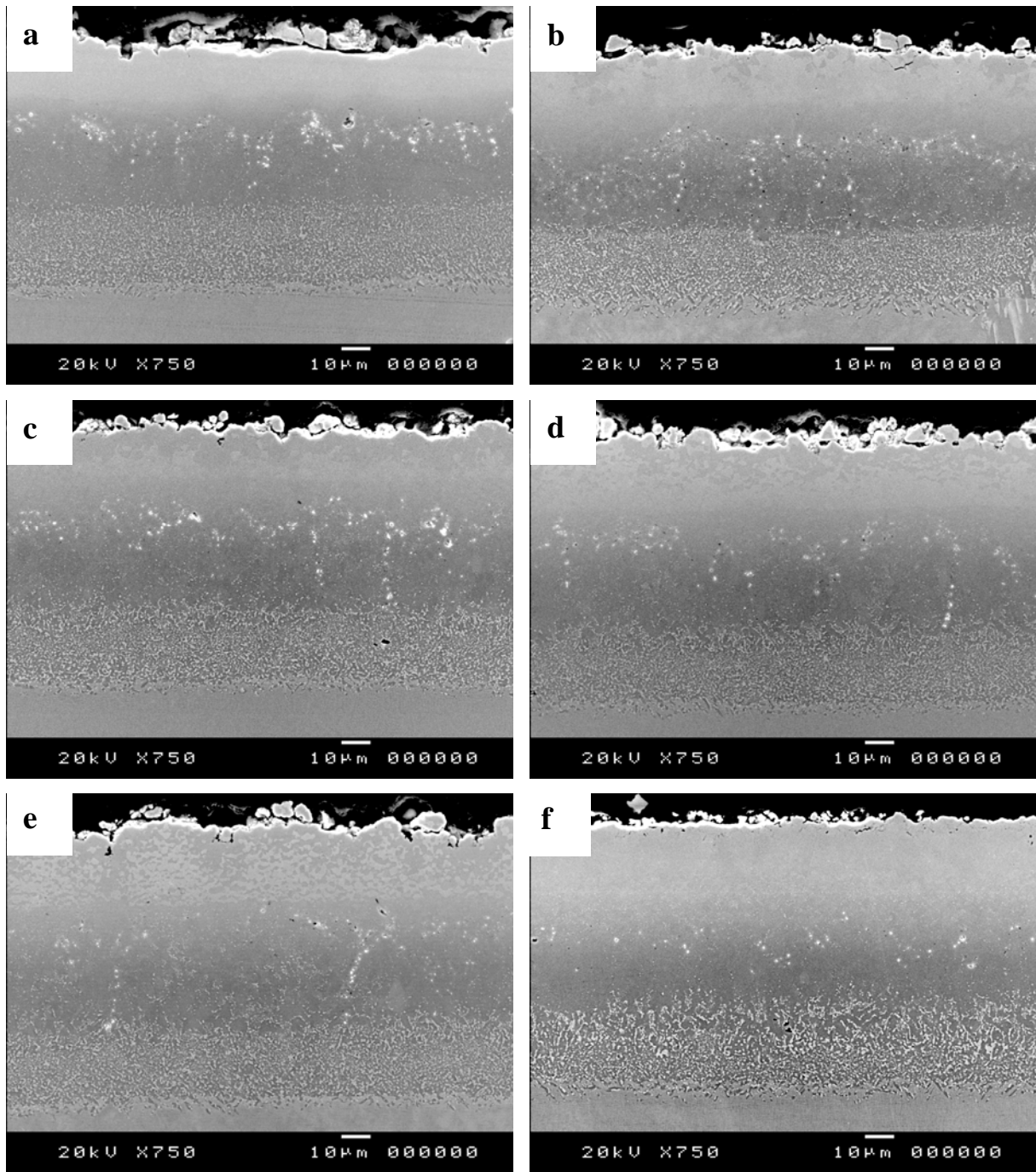
Figure 2.- Coating microstructure after aluminisation at 1050° C for 8 h of (a) 2.5, (b) 5 and (c) 7 μm thick Pt-plated substrates (all annealed at 1050° C for 2 h) and their corresponding Al, Pt and Ni EDS composition profiles.



**Figure 3.- EDS average compositions across the different layers of the coatings obtained after 8 h (N.B. solid symbols = 1000° C, open symbols = 1050° C).**



**Figure 4.- EDS average compositions across the different layers of the coatings obtained at 1050° C (N.B. solid symbols = 6 h, open symbols = 8 h).**



**Figure 5.- SEM cross sections of the Pt-modified coatings after aluminisation at of 5 μm thick Pt layer annealed at 1050° C for (a) no anneal, (b) 1h, (c), 2h (d) 3h, (e) 4h and (f) 5h.**

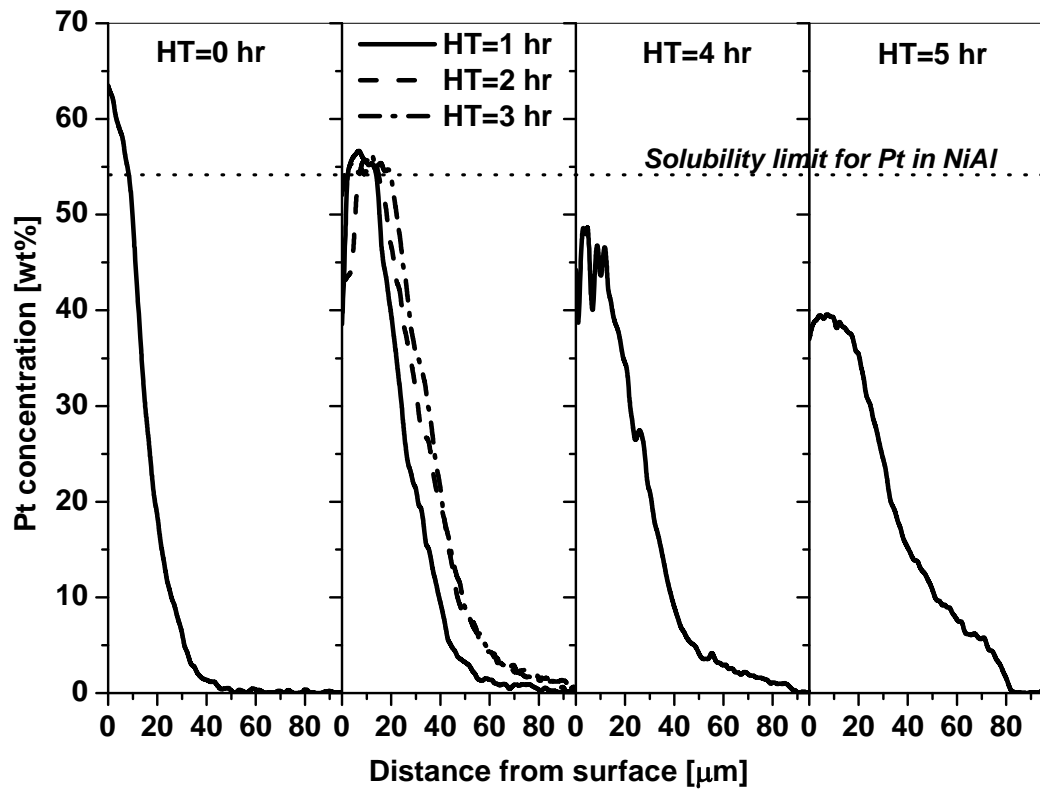
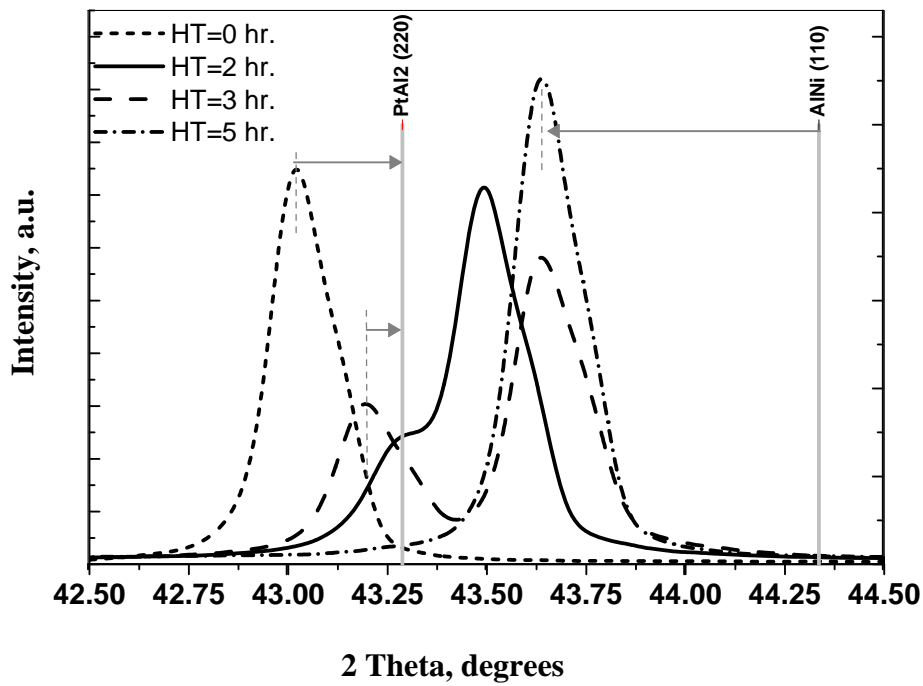


Figure 6.- EPMA profiles across the coatings showing the irregular dilution of a 5 μm Pt with diffusion time after aluminisation.





**Figure 7.- XRD shifts of the NiAl (110) and PtAl<sub>2</sub> (220) reflections, due to presence of Pt in the NiAl and of Ni in the PtAl<sub>2</sub> phases, respectively, as function of heat treatment.**