

## Thermal stability of NiAl and (Ni, Pt)Al coatings on Nimonic 80A alloy at 950°C

M. Reid<sup>a</sup>, M. J. Pomeroy<sup>a,b</sup> and J. Robinson<sup>b</sup>

<sup>a</sup> Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

<sup>b</sup> Department of Materials Science and Technology, University of Limerick, Limerick, Ireland

### Abstract

Specimens of Nimonic 80A alloy have been aluminised or platinum aluminised to form plain NiAl and single phase (Ni, Pt)Al coatings respectively. Specimens of the coated alloys were exposed in air for 188, 375 and 750 hours at a temperature of 950°C. Surfaces of as coated and oxidised specimens were subjected to X-ray diffraction (XRD). Specimens were then sectioned and polished and examined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). After 188 hours, the  $\beta$ -NiAl coating showed slight transformation to  $\gamma'$  (Ni<sub>3</sub>Al). After 275 hours the transformation levels increased, particularly in the areas of the coating adjacent to the alloy substrate. After 750 hours, significant transformation was noted both at the exterior of the coating and in the regions adjacent to the alloy. Similar effects were noted for the Pt modified coating - alloy system, excepting that there was little transformation of the exterior coating layers when no internal oxidation / pitting effect were present. The development of the coating morphologies with exposure time and the differences in morphologies between the NiAl and Pt modified coatings can be explained in terms of Ni egress from the alloy into the coating and Al ingress from the coating to the alloy as the coating and alloy attempt to chemically equilibrate. For the NiAl coating, Ni egress is the major factor causing chemical and morphological change. For the Pt modified coating, initial changes are brought about by Al ingress but then subsequently controlled by Ni egress from the alloy. The absence of a markedly different exterior morphology and composition for the Pt modified coating is due to Pt accelerating subscale diffusion effects and the fact that a  $\gamma'$  zone is unable to form.

**Keywords:** Aluminide coatings, Pt-modified aluminide coatings, equilibration, microstructural change

### Introduction

Typical second and third generation gas turbine alloys typically contain 5wt. % aluminium and the amount of nickel varies between 60 and 70wt. %. The range of stoichiometry  $\beta$ -NiAl coatings at typical turbine operating temperatures is 62 - 78wt. % Ni, 22 - 38wt. % Al. Because of these compositional differences between alloys and coatings, it would be expected that during isothermal exposure at high temperatures (900 to 1150°C) that diffusion will occur such that the coatings and alloys chemically equilibrate. In particular it would be expected that the greater concentration differences for Al would induce more rapid equilibration rates. Some studies of such equilibration effects have been conducted [1, 2, 3] which indicate that such equilibration effects do not just adjust the chemical compositions of the coating but also its microstructure. Thus for example, Basuki et al. [1] were able to show that the microstructural development of a  $\beta$ -NiAl coating on Rene 80H alloy at 1150°C involved homogenisation of the b-coating and the growth of a Ni<sub>3</sub>Al ( $\gamma'$ ) layer at the base of the coating, as well as increased precipitation of carbide and intermetallic phases. Similar reportage by Moretto et al. [2] and Chen & Little [3] also showed that microstructural changes as a result of chemical equilibration could occur on more complex alloys coated with platinum modified  $\beta$ -NiAl coatings, with the latter authors demonstrating the development of  $\gamma'$  regions within the coating due to aluminium loss and Ni gain.

Scrutiny of the microstructures presented in both sets of work does not reveal the development of a  $\gamma'$  zone between the coating and the substrates. However, detailed examination of the concentration profiles given by the relevant papers does not indicate why this should be so.

Aluminium can be lost from the coating because of coating oxidation as well as by diffusion into the alloy substrate. Such losses can also induce changes in coating microstructure as indicated by Young & Gleeson [ref4]. The work reported here was designed to augment the information reviewed above and to make a direct comparison between the microstructural development of NiAl and Pt modified NiAl coatings on a simple Ni - based alloy, Nimonic 80A.

## Experimental

Cylindrical specimens of Nimonic 80A alloy approximately 8.4mm in diameter and 15mm long were aluminised and platinum aluminised using standard industrial routes by SIFCO Turbine Components(Co. Cork). The platinum aluminising route was chosen such that single phase (Ni,Pt)Al coatings were obtained. Following cleaning and degreasing, duplicate samples were placed in a muffle furnace for 188, 375 and 750 hours at 950°C. Specimens were placed in cylindrical quartz crucibles in order to collect spalled oxide and prevent any mechanical damage occurring during insertion or removal from the muffle furnace. The composition of the Nimonic 80A alloy is given in Table 1.

Table 1 Nominal composition of Nimonic 80A alloy (wt. %)

Ni	Cr	Al	Ti	Fe	Co
BAL	19.5	1.5	2.6	0.7	0.1

Following exposure, X-ray diffraction (XRD) analysis of the surface layers was carried out using a Philips X'Pert diffractometer using  $\text{CuK}\alpha$  radiation. In addition to phase identification, the X-ray data was used to calculate the unit cell dimension of the  $\beta$ -NiAl or Pt modified  $\beta$ -NiAl coatings after exposure as well as those of as coated specimens. Since no internal standard could be added to calibrate the data obtained, a least squares method was employed to calculate the unit cell parameter. In effect this technique involved computing d spacings for the various h k l reflections for given unit cell dimensions and minimising the square of the errors between observed and measured d spacings. Similar XRD analyses were carried out on as coated samples. When appropriate, a similar technique was employed to calculate the unit cell dimensions of  $\gamma'$  phases. Accuracies of 0.001nm were achieved using this technique. The computed depth of X-ray penetration for the angles of incidence employed ( $\theta = 10$  to  $45^\circ$ ) was 16 $\mu\text{m}$ .

Oxidised and as coated specimens were then sectioned about their midpoint, polished and examined using a JEOL 840 scanning electron microscope (SEM) and selected features were analysed using a PGT IMIX energy dispersive X-ray spectroscopy (EDS) system. It is important to note that the oxide scales formed are not visible in the micrographs presented below since the contrast levels required to make them clear removed the electron contrast effects observed in the coatings. As well as analysing individual features, spectra were collected at 4  $\mu\text{m}$  intervals using a box 15 $\mu\text{m}$  by 2 $\mu\text{m}$  in order to obviate local concentration anomalies associated with point analyses of minor phases and thus give a better overall distribution of elemental concentrations. All analytical data were collected at an accelerating voltage of 20kV, a beam current of 0.26nA and a working distance of 39mm which was fixed by focusing an optical microscope onto the area for analysis. Quantitative analyses were effected using standards developed from spectra acquired for pure Ni, Cr, Ti and Pt and alumina. A standard spectrum was collected from a pure Ni standard under the same beam and geometric conditions prior to every analysis sequence for internal calibration. Using this set of analytical conditions, accuracies of  $\pm 0.3\%$  were achieved and precisions were better than 1%.

## Results

Figure 1 compares typical backscattered electron micrographs of the aluminised and platinum aluminised samples. It is seen that the microstructure of the aluminised Nimonic 80A alloy comprises a dark exterior layer and inner lighter region and then a region comprising dark columnar like features in both the internal layers of the coating as well as within the alloy substrate. Analyses of the exterior layer showed it to contain Ni: Al ratios consistent with a  $\beta$ -NiAl composition and XRD confirmed that the outer dark layer was indeed this phase and had a unit cell dimension of 0.289nm which compares favourably with the 0.288nm value for the lattice parameter given in JCPDS card number 44-1188. The brighter inner layer reflects higher Ni contents and gradual increases in Cr content as the coating - alloy interface is approached. EDS data confirmed that the dark columnar features were  $\alpha$ -Cr, and that they arose either in an aluminide ( $\text{Ni}_3\text{Al}$ ) matrix (in the coating) or an austenitic Ni matrix (in the alloy). The microstructure of the Pt modified NiAl coating is very similar to that described above, excepting that the exterior of the coating has brighter electron contrast due to the average higher atomic number of the phase induced by Pt incorporation. The platinum incorporation also expanded the unit cell parameter of the  $\beta$ -NiAl such that a value of 0.293nm was recorded.

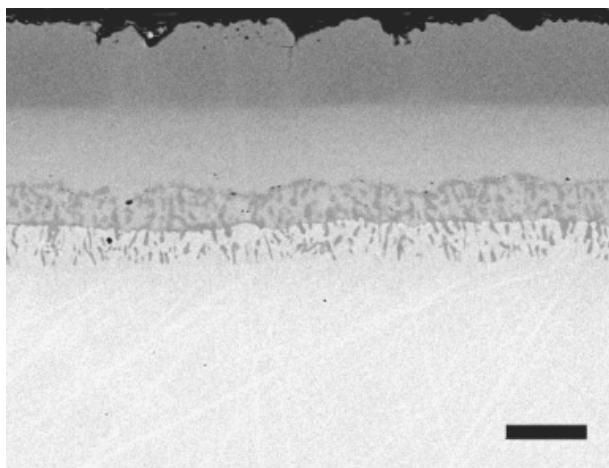


Figure 1a Microstructure of aluminide coated Nimonic 80A alloy (bar = 20 $\mu\text{m}$ )

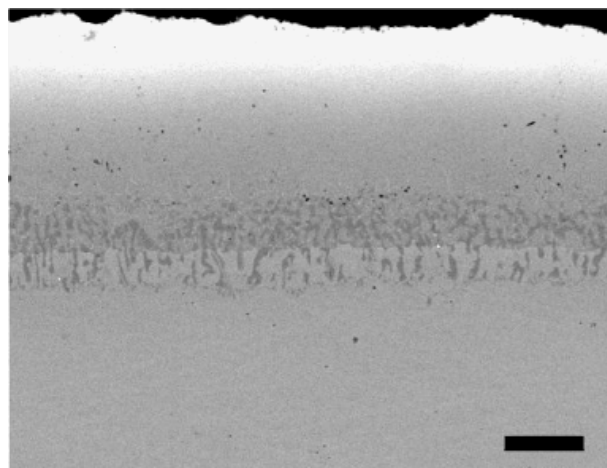


Figure 1b Microstructure of aluminide coated Nimonic 80A alloy (bar = 20 $\mu\text{m}$ )

Following oxidation of the aluminised Nimonic 80A alloy for 188 and 375 hours, XRD analyses showed that the outer 16 $\mu\text{m}$  of coating comprised  $\beta$ -NiAl and that no change in unit cell dimensions had occurred. Some slight traces of  $\gamma'$  phase were also evident. After 750 hours oxidation exposure at 950°C,  $\gamma'$  ( $\text{Ni}_3\text{Al}$ ) was the predominant phase indicating that the Ni:Al ratio had changed significantly between 375 and 750 hours. Similar XRD data was observed for the Pt modified  $\beta$ -NiAl coatings except that the unit cell dimensions of the aluminide phase decreased from 0.293nm to 0.288 nm after 188 and 375 hours before increasing to 0.290nm after 750 hours oxidation exposure. The decrease was due to equilibration of the platinum content of the coating, since after 188 and 375 hours the original significant compositional differences for Pt across the coating became negligible. The increase in unit cell dimension after 750 hours is thought to be due to the Al deficiency of the  $\beta$ -phase after this time. For both coatings,  $\gamma'$  unit cell dimensions were  $0.360 \pm 0.001\text{nm}$ . It is to be noted, that the XRD data was recorded from a surface region where significant internal oxidation / pitting had occurred. As this was not realised until specimens had been cross sectioned, it was not possible to determine phase assemblage by XRD in areas where such oxidation damage had not occurred.

Figure 2 shows the development of coating morphologies with time at 950°C for the aluminide coating. It is clear that the coating morphology changed after 188 hours such that a uniform contrast coating arises at the surface which is undercut by a bright phase of the order of 5µm thick. In addition, two columns of similar thickness and backscattered electron contrast can be seen to extend through the coating to differing depths. After 375 hours, the undercut layer has slightly increased in thickness and channels of this phase extend through the coating thickness (see figure 2b). EDS analyses of the undercut layer and the channels were consistent with  $\gamma'$  compositions (76.0 at.% Ni, 0.2 at.% Co, 18.5 at.% Al, 2.1 at.% Ti and 3.1 at.% Cr). The compositions of the outer layers were consistent with the  $\beta$ -NiAl phase observed using XRD. After 750 hours (figure 2c) the bright layer adjacent to the alloy had grown in thickness from about 8µm to 20µm and a layer of similar electron contrast some 5 to 8µm thick had developed at the surface of the coating. Between these layers a layer of dark electron contrast was observed. EDS analyses indicated that the exterior and interior layers had compositions consistent with a  $\gamma' + \gamma$  (austenitic nickel) phase assemblage whilst the dark layer was of a composition consistent with a  $\gamma' + \beta$ -NiAl phase assemblage where the  $\beta$  content was small. The XRD observations that after 750 hours  $\gamma'$  was effectively the only phase present confirm the quantitative analytical interpretation of the outer coating morphology.

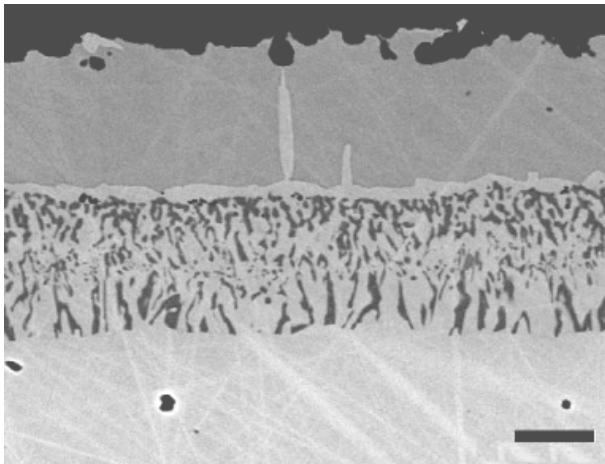


Figure 2a Microstructure of aluminide coated Nimonic 80A alloy after 188 hours at 950°C (bar = 20µm)

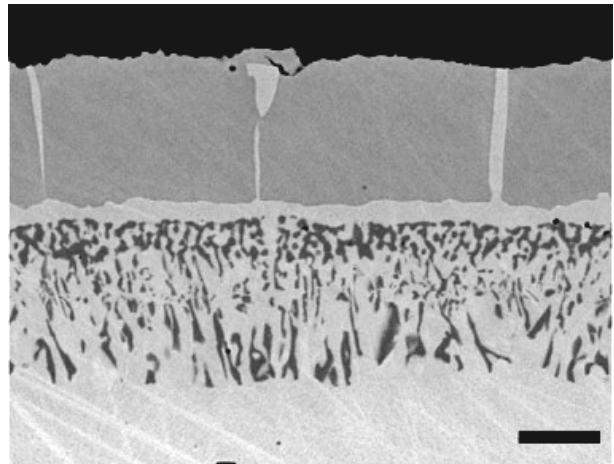


Figure 2b Microstructure of aluminide coated Nimonic 80A alloy after 375 hours at 950°C (bar = 20µm)

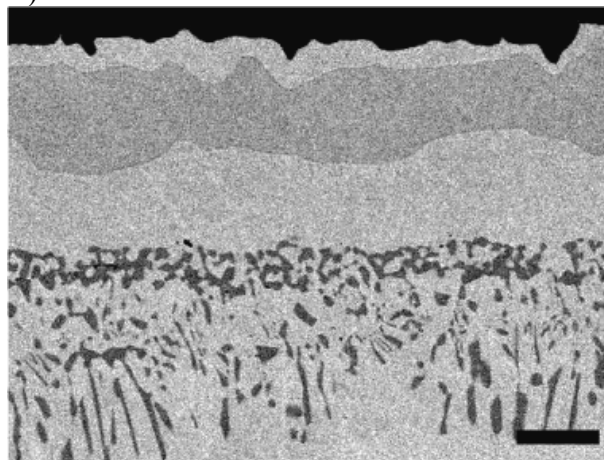


Figure 2c Microstructure of aluminide coated Nimonic 80A alloy after 750 hours at 950°C (bar = 20µm)

Two different morphological developments of the Pt modified single phase NiAl coatings with time at 950°C occurred. One morphological development involved the development of a duplex layer coating with an outer bright layer and an inner darker layer above the diffusion zone as displayed in Figure 3. The other involved the development of an island like morphology with bright electron contrast islands within a darker matrix (see figure 4). The layer like morphology was associated with surface oxidation only, whilst the island like morphology arose when significant internal and pitting oxidation occurred. For the layer like morphology, it can be seen from figure 3 that as time increases, the thickness of the brighter external layer decreases. EDS analyses of the bright external layers showed that after 188 and 375 the Ni : Al ratios were consistent with a  $\beta$ -rich  $\beta + \gamma'$  phase assemblage. After 750 hours at 950°C, the analyses indicated that a  $\gamma'$  rich  $\beta + \gamma'$  phase assemblage could be expected. For all times, the inner darker layers gave compositional data which was consistent with a  $\gamma'$  phase assemblage.

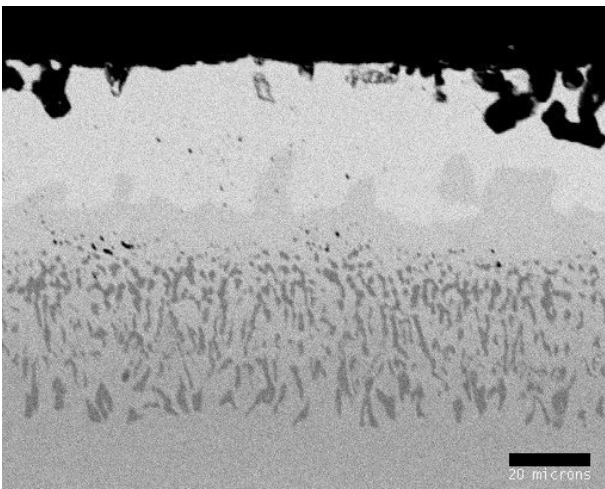


Figure 3a Microstructure of Pt modified aluminide coated Nimonic 80A alloy after 375 hours at 950°C (bar = 20 $\mu$ m)

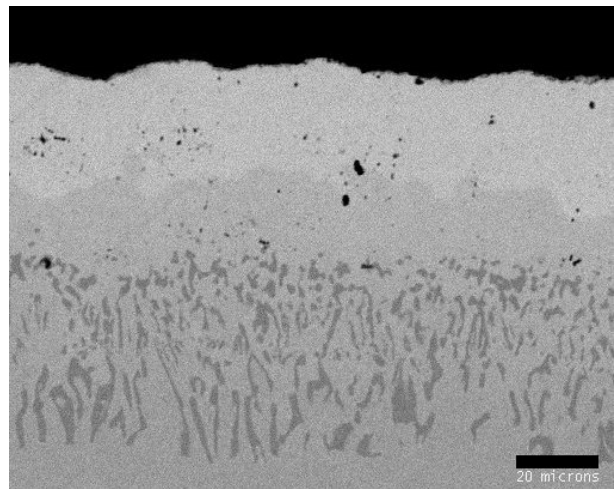


Figure 3b Microstructure of Pt modified aluminide coated Nimonic 80A alloy after 750 hours at 950°C (bar = 20 $\mu$ m)

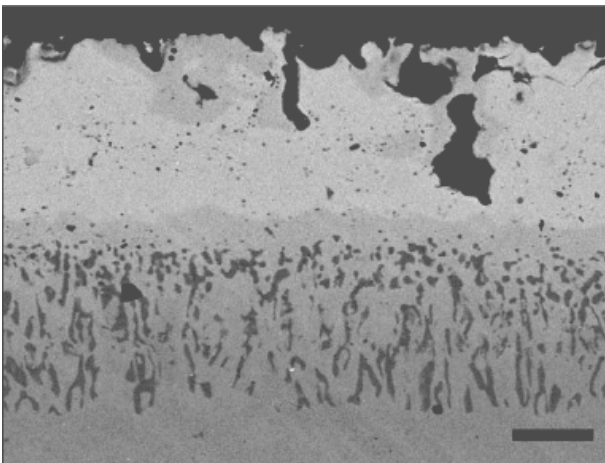


Figure 4a Microstructure of areas of internal oxidation / pitting of Pt modified aluminide coated Nimonic 80A alloy after 375 hours at 950°C (bar = 20 $\mu$ m)

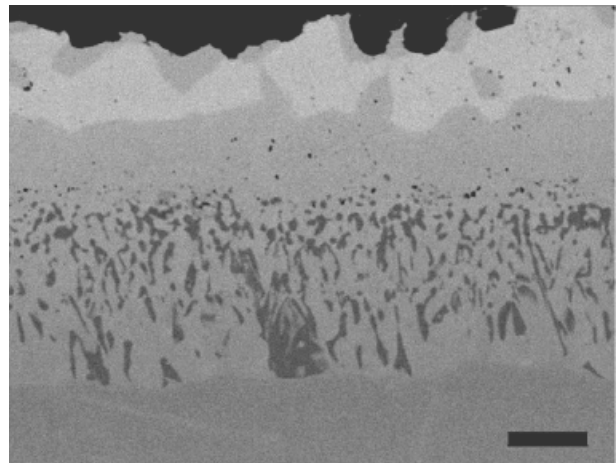


Figure 4b Microstructure of areas of internal oxidation / pitting of Pt modified aluminide coated Nimonic 80A alloy after 750 hours at 950°C (bar = 20 $\mu$ m)

For the internally oxidised and pitted regions, the bright islands shown in Figure 4 had compositions consistent with Pt modified  $\beta$ -NiAl, whilst the darker regions had analyses consistent

with a  $\gamma'$  phase assemblage. The relevant analyses for the 750 hour specimen where an outer dark band, intermediate bright band and inner dark band coating morphology can be seen (figure 4c) is related in the discussion section.

In addition to changes in coating morphology, changes in the thickness and morphology of the dark  $\alpha$ -Cr phase within the diffusion layers also arose. Close examination of Figures 1a, 2a, 2b and 2c clearly shows that the thickness of the diffusion zone increases as time at 950°C increases for the NiAl coating. Comparison of Figures 1b and 3a and 3b show that similar effects arose for the Pt modified coating excepting that the increase in diffusion zone thickness was less in the presence of the coating containing platinum. Analyses of diffusion zone thickness - time data implied a parabolic relationship and using such a correlation the rate of thickening of the diffusion zone beneath the NiAl coating was calculated to be  $2.1 \times 10^{-1} \mu\text{m s}^{-1/2}$  whilst that for the Pt-modified NiAl coating was  $1.6 \times 10^{-1} \mu\text{m s}^{-1/2}$ . Thus, the diffusion zone beneath the NiAl coating grew at a rate about 30% faster than that beneath the Pt modified NiAl coating. The concentration profile data developed from the  $15 \times 2 \mu\text{m}$  area analyses clearly showed that the Ni:Al ratios in the region of the  $\alpha$ -Cr precipitates were consistent with in  $\gamma + \gamma'$  phase assemblage. Furthermore, it was very interesting to note that the average Ni and Al concentrations in the diffusion zone for all specimens (as-coated, isothermally exposed and both coating types) corresponded to those expected from the Ni-Al phase diagram, [ref5] to represent the  $\gamma + \gamma' - \gamma$  phase boundary.

## Discussion

From the results presented above, it is clear that the microstructures of the coatings change with time and that such changes are brought about by either nickel enrichment or aluminium depletion effects which result in the transformation of NiAl to  $\text{Ni}_3\text{Al}$ . The development of coating microstructure with time for the NiAl coating clearly involves two mechanisms one related to oxidation where aluminium usage for scale formation reduces the subscale concentration and the other related to degradation of the NiAl coating by either aluminium ingress into the alloy or nickel egress into the coating or of course both. For the Pt-modified coating Al usage for oxide formation appears not to cause any significant development of a subscale  $\gamma'$  layer unless internal oxidation / pitting occurs. Subscale aluminium concentrations after 750 hours were measured at 19at. % for the NiAl coating and 26at. % for the Pt modified coating. Furthermore, for the latter coating type the 26at. % concentration extended through the coating thickness unlike the NiAl coating where the Al content increased to 29at. %, at a depth of  $16\mu\text{m}$  beneath the scale. These two observations clearly indicate that Al mobility within the subscale regions of the Pt modified coating are higher as proposed by Felten [ref6] and Newcomb and Stobbs [ref7]. However, it is important to realise that diffusion rates in  $\text{Ni}_3\text{Al}$  are two orders of magnitude less than for NiAl (compare [ref8] and [ref9]) and thus the development of a subscale layer having a  $\gamma'$  composition and structure would also result in slow diffusion from the  $\beta$ -NiAl region of the coating some  $16\mu\text{m}$  in from the subscale region. For the Pt modified coating, the likely coating phase assemblage after 750 hours is  $\beta + \gamma'$  and the enhanced diffusion rates associated with the presence of the  $\beta$ -phase as well as phase boundaries would readily explain why no subscale  $\gamma'$  layer forms when platinum is present. An alternative explanation would be that nickel is able to diffuse away from the subscale region more rapidly in the case of the Pt modified coating thus slowing  $\gamma'$  formation. No evidence of this was observed although there were indications of a Pt depletion effect in the subscale regions which, since Pt is most likely to be located on Ni sites in  $\beta$ -NiAl ([ref8]), may have a similar effect. What can be said, is that subscale aluminium depletion effects due to oxidation and slow diffusion cause the morphological changes associated with the exterior regions of the NiAl coating.

The more rapid development of the diffusion zone for the NiAl coating compared to that for the Pt modified coating is also thought to be attributable to Ni and Al countercurrent diffusion. The

occurrence of  $\alpha$ -Cr inclusions in the diffusion layer after coating occurs via the precipitation of Cr from the alloy because Ni loss into the coating or Al enrichment of the alloy. Both effects increase local Al activities and decrease local Ni activities to levels where Cr precipitation is inevitable. Further Ni egress or Al ingress during isothermal exposure exacerbates the situation such that the Cr precipitates grow deeper into the alloy. Since, the rate of growth is greater in the case of the NiAl coating compared to the Pt modified coating, it seems that the 4at. % Pt in the bulk coating decreases the extent to which nickel activities in the diffusion zone are lowered. This occurs most probably as a result of Pt inhibiting Al ingress or Ni egress since the Pt contents of the diffusion zones after 188, 375 and 750 hours were less than 1 at. %. These findings are consistent with previous work [10] and so it can be concluded that Pt reduces the diffusion of Ni from the alloy into the coating or Al from the coating into the alloy or both.

Now that subscale and diffusion zones have been discussed, it is possible to rationalise the development of the coating morphologies between these two structural features. As stated in the results section, the changes to the morphologies relate to the development of a  $\gamma'$  layer at the base of the coating i.e. adjacent to the diffusion zone and this is again due to Ni egress from the alloy, Al ingress from the coating or both effects. As indicated above, Basuki et al. [1], the reason that the chemical equilibration of Rene 80 H alloy with a NiAl coating involves preferential Ni diffusion from the substrate into the coating. This Ni enrichment of the coating induces the development of a  $\gamma'$  layer which undercuts  $\beta$ -NiAl.

In order to attempt to determine if Ni egress or Al ingress controlled the development of the  $\gamma'$  undercut layer, Ni and Al concentration differences between the bulk coating composition and the alloy were plotted against time. The resulting graph is shown in Figure 5 and clearly indicates that the rate of chemical equilibration for aluminium is similar for both coating types.

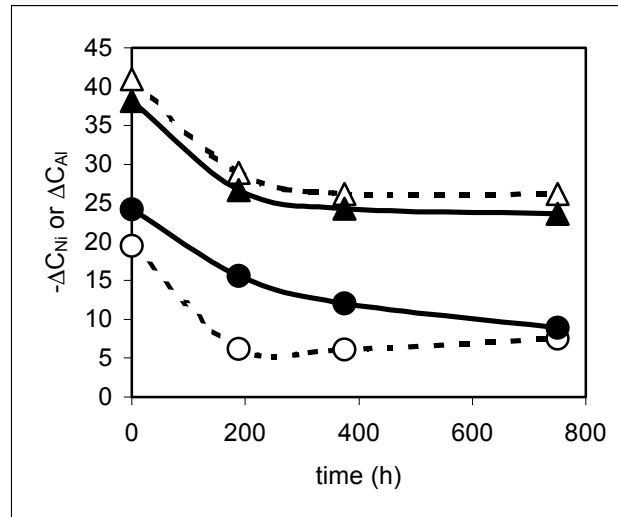


Figure 5 Concentration differences between alloy and coating Ni (○, ●) and Al (△,▲) contents, open symbols NiAl, filled symbols Pt modified NiAl (Ni expressed as negative of value for easy comparison)

In contrast, Ni equilibration occurs within 188 hours for the NiAl coating whilst for the Pt modified coating the equilibration is still in progress after 750 hours. Comparisons of the various curves clearly shows that for the NiAl coating, Ni equilibration is more rapid than that for Al as previously observed by Basuki et al. [1] whilst for the Pt modified coating, the converse is true for the

initial stages after which Ni equilibration continues. It can therefore be concluded that Ni transport into the coating is the rate controlling step for the morphological changes occurring in the NiAl coating adjacent to the substrate whereas, for the Pt modified coating the more changes are initially controlled by Al transport and then by Ni transport. The change in rate controlling process is clearly a result of the presence of Pt in the Pt modified coating. However, no definitive compositional data enabling the solution of why this should occur is available either from the literature or from the present study.

One possible effect of platinum may be to increase the stability of the  $\beta$ -NiAl, not by extending its range of stoichiometry but by lowering its free energy. If this were the case then higher adjacent activities of Ni or lower local activities of Al would be required for the  $\beta$  to  $\gamma'$  phase change than would be the case if the  $\beta$ -phase was not Pt stabilised. Some evidence for this is provided by the microstructures presented for the regions of the Pt modified coating which had undergone internal oxidation / pitting. The bright band in figure 4b is Pt enriched compared to the external and internal darker layers. Furthermore, if the relevant M: X ratios, where M=Ni + Co + Fe +Pt and X=Al + Cr + Ti are evaluated for the dark and bright regions in Figure 4b they correspond to M: X ratios for  $\gamma'$  +  $\beta$  (bright region) and  $\gamma' + \gamma$  (dark regions). The detail afforded with SEM - based analysis was not, of course, sufficient to evaluate if Ni or Al activities adjacent to the bright  $\beta$  containing region were consistent with a more stable  $\beta$ -phase. More detailed TEM - based quantitative analyses would be required to fully establish this or, alternatively, more exact free energy data for Pt modified  $\beta$ -NiAl.

## Conclusions

1. Platinum modification of a  $\beta$ -NiAl coating on Nimonic 80A alloy increases the rate of diffusion of aluminium into the subscale region and decreases the probability of  $\gamma'$  formation in the subscale region.
2. Platinum modification of a  $\beta$ -NiAl coating on Nimonic 80A alloy decreases rates of Ni transport into the coating and Al transport into the alloy with the result that the local Ni and Al activity changes required for  $\alpha$ -Cr precipitation are slowed and the growth of the diffusion zone is less for a Pt modified coating compared to that of a NiAl coating.
3. The majority of chemical equilibration of a NiAl coating with Nimonic 80A alloy is controlled by Nickel transport into the coating whilst for a Pt modified NiAl coating it is brought about initially by the transport of aluminium into the alloy and then by Ni into the coating. This chemical equilibration induces the development of an aluminium depleted layer which undercuts the coatings.

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## References

- !ref1 E. Basuki, A. Crosky and B Gleeson, *Materials Science and Engineering*, **A224**, pp27-32, 1997
- !ref2 P. Moretto, J. Bressers, D. J. Arrel, *Materials Science and Engineering*, **A272**, pp310-320, 1999
- !ref3 J. H. Chen, J. A. Little, *Surface Coatings Technology*, **92**, pp69-77, 1997



- !ref4 D. J. Young, B. Gleeson Alloy phase transformations driven by high temperature corrosion processes, *Corrosion Science*, **44**, pp345-357, 2002
- !ref5 C. J. Smithells, E. A. Brandes, G. B. Brook, Metals Reference Book, 7th edition, (Publ. Butterworth-Heinmann, Boston), 1998
- !ref6 E. J. Felten, use of platinum and rhodium to improve oxide adherence on Ni-8Cr-6Al alloys *Oxidation of Metals*, **10**, pp23-28, 1976
- !ref7 S. B. Newcomb, W. M. Stobbs, Degradation of aluminide and platinum aluminide diffusion coatings on CMSX-4, in N. B. Dahorte, J. B. Hampikian (eds.) *TMS Annual Meeting, Elevated Temperature Coatings: Science and Technology II*, p 265-274, 1996
- !ref8 K. Fujiwara, Z. Horita, Measurement of intrinsic diffusion coefficients of Al and Ni in Ni<sub>3</sub>Al using Ni/NiAl diffusion couples, *Acta Materiala*, **50**, pp1571-1579, 2002
- !ref9 Y. Minamino, Y. Koizumi, N. Tsuji, M. Morioka, K. Hirao, Y. Shirai, Pt diffusion in B"-type ordered NiAl intermetallic compound and its diffusion mechanisms, *Science and Technology of Advanced Materials*, **1**, pp237-249, 2000
- !ref10 H. M. Tawancy, N. Sridar, B. S. Tawabini, N. M. Abbas, T. N. Rhys-Jones, thermal-stability of a platinum aluminide coating on nickel-based superalloys, *Journal of Materials Science*, **27**, pp6463-6474, 1992