

## Compositional factors affecting the establishment and maintenance of Al<sub>2</sub>O<sub>3</sub> scales on Ni–Al–Pt systems

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**Abstract** The beneficial role played by platinum addition in promoting the formation of a protective Al<sub>2</sub>O<sub>3</sub> scale on representative  $\gamma'$ -Ni<sub>3</sub>Al+ $\gamma$ -Ni coating compositions during high-temperature oxidation is discussed. This beneficial effect can be primarily ascribed to the fact that Pt is non-reactive, and its addition decreases the chemical activity of aluminum in  $\gamma'$ . Related to the latter, Pt partitions almost solely to the Ni sites in the ordered L1<sub>2</sub> crystal structure of  $\gamma'$ , which has the effect of amplifying the increase in the Al: Ni atom fraction on a given crystallographic plane containing both Al and Ni. Such an effective Al enrichment at the  $\gamma'$  surface kinetically favors the formation of Al<sub>2</sub>O<sub>3</sub> relative to NiO. A further contributing factor is that the Pt-containing  $\gamma'$ -based alloys show subsurface Pt enrichment during the very early stages of oxidation. This enrichment reduces Ni availability and can increase the Al supply to the evolving scale, thus kinetically favoring Al<sub>2</sub>O<sub>3</sub> formation. This observed benefit of Pt addition promoting exclusive Al<sub>2</sub>O<sub>3</sub>-scale growth is inferred to be a special form of the third-element effect.

### Introduction

The development of heat-treatable nickel-based superalloys has, almost entirely, been motivated by the requirement to

improve the efficiency, reliability, and operating life of gas turbines. The most advanced single-crystal superalloy turbine blades are now operating at a temperature greater than 85% of their absolute melting temperature ( $T_m$ ) [1]. Ni-based superalloys achieve high strengths at elevated temperatures through strengthening by a relatively high volume fraction of  $\gamma'$ -Ni<sub>3</sub>Al-based precipitates (up to about 70% by volume) in the  $\gamma$ -Ni matrix. These alloys are also strengthened by constituents in solid solution (i.e., W, Ta, Mo, and Re) and perhaps even carbide dispersoids. However, the melting point of nickel (1455 °C) provides a natural ceiling for the temperature capability of nickel-based superalloys [2, 3]. Thus, further increases in the operating temperatures have required advances in external and internal cooling technologies, coupled with the use of thermal barrier coating (TBC) systems [4–6]. Use of a TBC system on an internally cooled component offers the potential to decrease the metallic surface temperature of that component by up to about 150 °C [7].

Commercial advanced TBC systems are typically two-layered, consisting of a ceramic topcoat and an underlying metallic bond coat. The topcoat, which is usually applied either by air plasma spraying (APS) or electron beam-physical vapor deposition (EB-PVD), is most often partially stabilized zirconia (PSZ), with the stabilizing constituent typically being Y<sub>2</sub>O<sub>3</sub>. The properties of PSZ are such that it has a low thermal conductivity, high oxygen permeability, and a relatively high coefficient of thermal expansion. The PSZ topcoat is also made “strain tolerant” by depositing a structure that contains numerous pores and/or pathways. The consequently high oxygen permeability of the PSZ topcoat imposes the constraint that the metallic bond coat must be resistant to oxidation attack. Thus, the bond coat is typically rich in aluminum to form a protective, thermally grown oxide (TGO) scale of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In

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addition to imparting oxidation resistance, the TGO serves to bond the ceramic topcoat to the substrate/bond coat system. Even so, it is often found that spallation and/or cracking of the thickening TGO scale is the ultimate failure mechanism of commercial TBCs, particularly EB-PVD TBCs [7–9]. Thus, improving the adhesion and integrity of the interfacial TGO scale is critical to the development of more reliable TBCs.

Given that the potential of a TBC can only be exploited if it remains adhered to the substrate, improving the stability and oxidation behavior of the bond coats continues to be a high-priority for research and development [5]. Strategies to enhancing the bond coat temperature capability have included:

- (1) reducing the TGO growth rate and the concomitant buildup in strain energy [4];
- (2) increasing the yield/creep strength of the bond coat to suppress cyclic plasticity effects, such as surface rumpling during repeated thermal cycles [10]; and
- (3) minimizing interdiffusion with the substrate that leads to Al depletion and migration to the coating surface of elements that are deleterious to oxidation resistance (e.g., Ti, S, Re, etc.) [11].

Considerable past research has focused on understanding and developing metallic bond coats based on the ordered intermetallic compound  $\beta$ -NiAl [12]. In addition to exhibiting a high melting temperature and good thermal conductivity [13, 14],  $\beta$ -NiAl is capable of forming a protective  $\text{Al}_2\text{O}_3$  scale. Moreover, the adherence of the  $\text{Al}_2\text{O}_3$  scale can be significantly improved by the addition of platinum to the  $\beta$  coating to produce the so-called Pt-modified aluminide coatings. The addition of Pt to an  $\text{Al}_2\text{O}_3$ -scale forming alloy has been known to improve scale adhesion since the 1970s [15, 16]. However, despite numerous studies of Pt-modified aluminides [17–19], the exact mechanism by which Pt improves the coating performance is still not well understood. It has been proposed that Pt may interact with indigenous sulfur [19, 20], reduce the growth rate of interfacial voids [21, 22], or limit the outward diffusion of minor alloying elements (e.g., Ti, Ta, Re, etc.) from the superalloy substrate [23], all of which would serve to improve scale adhesion.

There are, however, limitations associated with  $\beta$ -NiAl-based coatings owing to surface instabilities (e.g., surface rumpling) and interdiffusion with the Ni-based superalloy substrate. The latter can lead to unwanted topologically close-packed (TCP) phase formation [24, 25]. Indeed, next-generation superalloys containing higher levels of refractory metals are even more susceptible to the formation of TCP phases underneath  $\beta$ -NiAl-based coatings [26]. Thus, there is an increasing need for alternative bond coating compositions. Gleeson et al. [27] recently reported that the

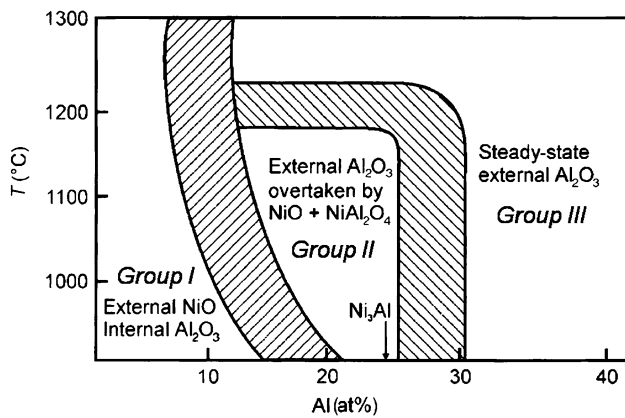
addition of platinum to  $\gamma$ -Ni+ $\gamma'$ -Ni<sub>3</sub>Al alloys is highly beneficial to promoting exclusive  $\alpha$ - $\text{Al}_2\text{O}_3$  scale growth. It was shown by Gleeson et al. that the  $\gamma$ + $\gamma'$  phase constitution could be retained for up to  $\sim 35$  at.% Pt and an Al range of  $\sim 12$ – $22$  at.%. Moreover, oxidation resistance could be substantially improved by Hf addition [28].

The purpose of this article is to briefly review the factors affecting  $\text{Al}_2\text{O}_3$ -scale development followed by a more detailed discussion on the high-temperature oxidation behavior of the Ni–Al system and the influence of platinum in promoting  $\text{Al}_2\text{O}_3$ -scale formation. It will be shown that platinum provides a beneficial third-element effect that is similar in terms of outcome to the more well-known chromium effect, but mechanistically different.

### $\text{Al}_2\text{O}_3$ -scale formation on Ni–Al-based alloys

There has been much research into the development of protective  $\alpha$ - $\text{Al}_2\text{O}_3$  scales [29–33] on Al-containing alloys. The systems investigated ranged from simple binary alloys to complex commercial alloys, with or without additions of reactive elements such as Y and Hf. Clearly, a critical factor is the aluminum content in the alloy or coating, which must be sufficiently high to develop and maintain an alumina layer and prevent subsequent breakaway oxidation. A further critical factor in the oxidation of  $\text{Al}_2\text{O}_3$ -scale formers is the reaction temperature, which must be high enough to promote the formation of  $\alpha$ - $\text{Al}_2\text{O}_3$  in preference to the faster growing transition aluminas. Specifically, there are several cubic or transitional  $\text{Al}_2\text{O}_3$  structures, such as  $\gamma$ ,  $\delta$  and  $\theta$  that form during a certain transient stage of oxidation at temperatures below about 1100 °C (e.g., during heating). The metastable, transitional  $\text{Al}_2\text{O}_3$  structures often grow as blades or whiskers [34], and their growth can influence considerably the overall amount of oxidation and the subsequent growth of the stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase. For example, eventual transformation from metastable  $\theta$ - $\text{Al}_2\text{O}_3$  to  $\alpha$ - $\text{Al}_2\text{O}_3$  produces an 8–13% volume reduction, which results in apparent tensile stresses in the scale [35, 36] and scale cracking [37].

Pettit [38] assessed the oxidation behavior of Ni–Al alloys over the temperature range 900–1300 °C and identified three groups of scaling behavior, as shown in Fig. 1. Group I corresponds to internal oxidation of the aluminum, with external formation of NiO doped with aluminum. Group II consists of alloys that contain enough aluminum to form an external  $\alpha$ - $\text{Al}_2\text{O}_3$  layer, but this depletes the surface to the point at which, if the scale breaks down in some manner, NiO and  $\text{NiAl}_2\text{O}_4$  may be formed. A protective  $\text{Al}_2\text{O}_3$  layer may reform in time, but a layered scale develops as these processes repeat. With a higher aluminum content, an exclusive  $\text{Al}_2\text{O}_3$ -scale layer is established



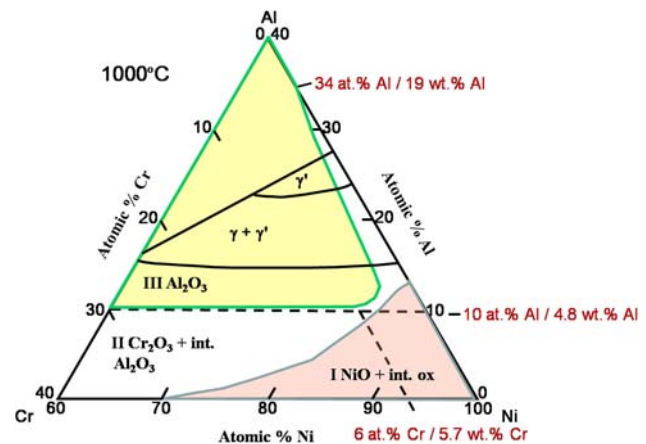
**Fig. 1** Dependence of the mechanism of oxidation for Ni–Al alloys on temperature and alloy composition according to Pettit [38]. Oxidation tests were carried out in 0.1 atm pure  $O_2$

and maintained, and corresponds to Group III behavior. Figure 1 shows that an increase in the oxidation temperature helps to promote external  $Al_2O_3$  formation (i.e., Al content for the transition from Group I to Group II decreases with increasing temperature). This is a consequence of the activation energy for (substitutional) aluminum diffusion in the alloy being larger than that for (interstitial) oxygen permeation in the alloy.

The transition from internal to external  $Al_2O_3$  formation requires that a critical concentration of Al in the alloy or coating,  $N_{Al}^*$ , be exceeded [1, 39]. As indicated above, the value of  $N_{Al}^*$  is dependent on kinetic rather than thermodynamic factors; although, clearly, a sufficient Al concentration must exist at the  $Al_2O_3$ /alloy or coating interface during steady-state growth in order to maintain  $Al_2O_3$  stability. This latter, “thermodynamically required” concentration is usually quite small for a highly stable oxide such as  $Al_2O_3$  [40, 41], and it is significantly below the critical concentration required by kinetics.

In relation to the above discussion regarding Fig. 1, ternary and higher order alloying additions that cause the solubility for oxygen in the alloy to decrease should in turn cause  $N_{Al}^*$  to decrease and therefore favor exclusive  $Al_2O_3$ -scale formation (i.e., Group III behavior). This effect is difficult to isolate due to the potential influence of microstructural and other contributing factors, but it has been invoked as a possible explanation for the beneficial effect of 2% Si (weight percent, wt%) and 1 wt% Ti additions in promoting  $Al_2O_3$  scale formation on NiCrAlY-base alloys [42].

In accordance with the generally so-called third-element effect, the value of  $N_{Al}^*$  in Ni–Al-based alloys may also be decreased by additions of elements that form an oxide of intermediate thermodynamic stability to NiO and  $Al_2O_3$ . For instance, it is well known that a lower Al content is needed to establish and maintain an  $Al_2O_3$  scale on



**Fig. 2** Oxide-scale map for the Ni–Cr–Al system oxidized at 1000 °C in air for 20 h and showing the regimes for  $Al_2O_3$ ,  $Cr_2O_3$ ,  $NiAl_2O_4$ ,  $NiCr_2O_4$ , and NiO formation (after Wallwork and Hed [44])

M–Cr–Al alloys (where  $M = Ni, Co, \text{ or } Fe$ ) than on M–Al alloys [43]. This is shown in the 1000 °C oxide map in Fig. 2 for the Ni–Cr–Al system (based on [44]), where it is seen that exclusive  $Al_2O_3$  scale growth on a Ni–Al alloy requires an Al concentration of at least ~34 at.%; whereas, only 10 at.% Al is required if the Ni–Al alloy also contains 6 at.% Cr.

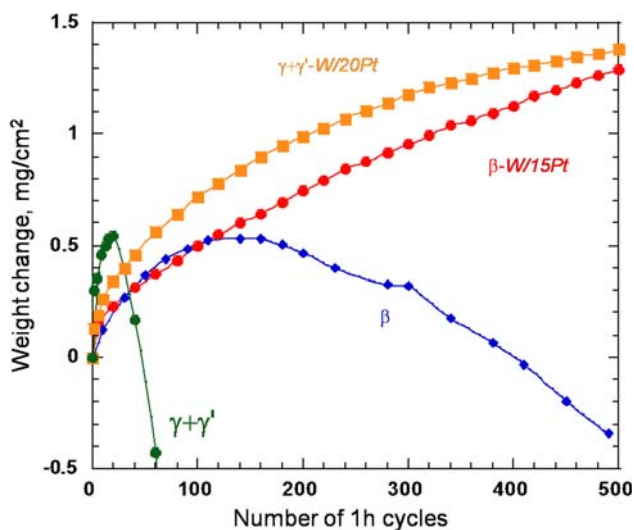
The classical interpretation for the third-element effect is based on “secondary gettering”, a phenomenon first proposed by Wagner [45] to explain the promotion of  $Al_2O_3$ -scale formation by Zn additions to Cu–Al alloys and Cr additions to Fe–Al alloys. According to the generally purported mechanism for secondary gettering, the oxide of the ternary addition develops extensively in the transient scale and thereby reduces the oxygen potential at the alloy/scale interface to a value which is significantly lower than if there were no ternary addition. In the case of M–Cr–Al alloys, the lowered oxygen potential reduces the inward flux of oxygen into the alloy and consequently enables Al to diffuse to the surface from the bulk without precipitating as an internal oxide, thus resulting in the development of a continuous  $Al_2O_3$  scale layer at lower Al concentration than in the corresponding binary alloy.

Although secondary gettering is an often-cited mechanism for explaining the third-element effect, not all ternary additions that form oxides of intermediate stability have the desired effect [46]. For instance, the addition of Mn to Fe–Al alloys does not facilitate the establishment of an  $Al_2O_3$  scale when present in high concentrations even though the stability of MnO is intermediate to FeO and  $Al_2O_3$  [46–48]. In this case, the Mn stabilizes the austenite ( $\gamma$ ) phase which is hypothesized to sufficiently lower Al diffusivity relative to that in the ferritic  $\alpha$ -Fe(Al) phase to the extent that the third-element effect is nullified (work of Jackson and Wallwork reported in Stott et al.’s review article [46]).

Alternative mechanisms to explain the third-element effect, based, for example, on modification of subsurface diffusion behavior [49, 50] have also been proposed, reflecting the fact that there is not a complete understanding of how a third element may influence the formation of a protective scale on a single-phase alloy [46].

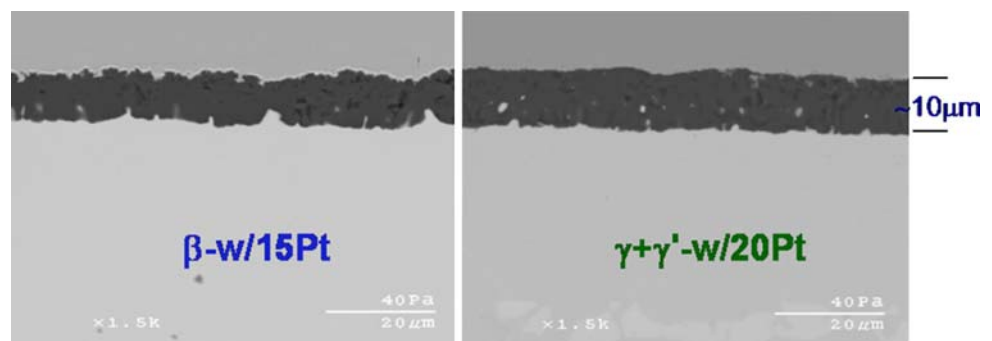
### Pt Effects on $\text{Al}_2\text{O}_3$ -scale formation

Figure 3 shows plots of the 1150 °C cyclic oxidation kinetics in air of  $\beta$  and  $\gamma+\gamma'$  cast alloys with and without Pt addition. The  $\beta$  alloys contain 50 at.% Al, while the  $\gamma+\gamma'$  alloys contain 22 at.% Al (i.e., Pt is always added at the expense of Ni). Each thermal cycle consisted of 1 h at 1150 °C followed by 20 min at about 80 °C. Mass change was measured periodically using an analytical balance. Any weight loss in these plots corresponds to scale spallation. Two important inferences can be drawn from the results presented in Fig. 3. First, the addition of Pt to either



**Fig. 3** Cyclic oxidation kinetics of  $\beta$ -Ni<sub>50</sub>Al<sub>50</sub>,  $\beta$ -Ni<sub>35</sub>Al<sub>50</sub>Pt<sub>15</sub>,  $\gamma+\gamma'$ -78Ni-22Al, and  $\gamma+\gamma'$ -58Ni-22Al-20Pt alloys in air. Each thermal cycle consisted of one-hour at 1150 °C followed by 20 min at about 80 °C

**Fig. 4** Cross-sectional secondary electron microscope (SEM) images of  $\beta$ -Ni<sub>35</sub>Al<sub>50</sub>Pt<sub>15</sub> and  $\gamma+\gamma'$ -58Ni-22Al-20Pt alloys after 500 one-hour thermal cycles to 1150 °C in air (corresponding to Fig. 3). Each alloy formed an adherent and continuous  $\text{Al}_2\text{O}_3$ -scale layer of similar thickness



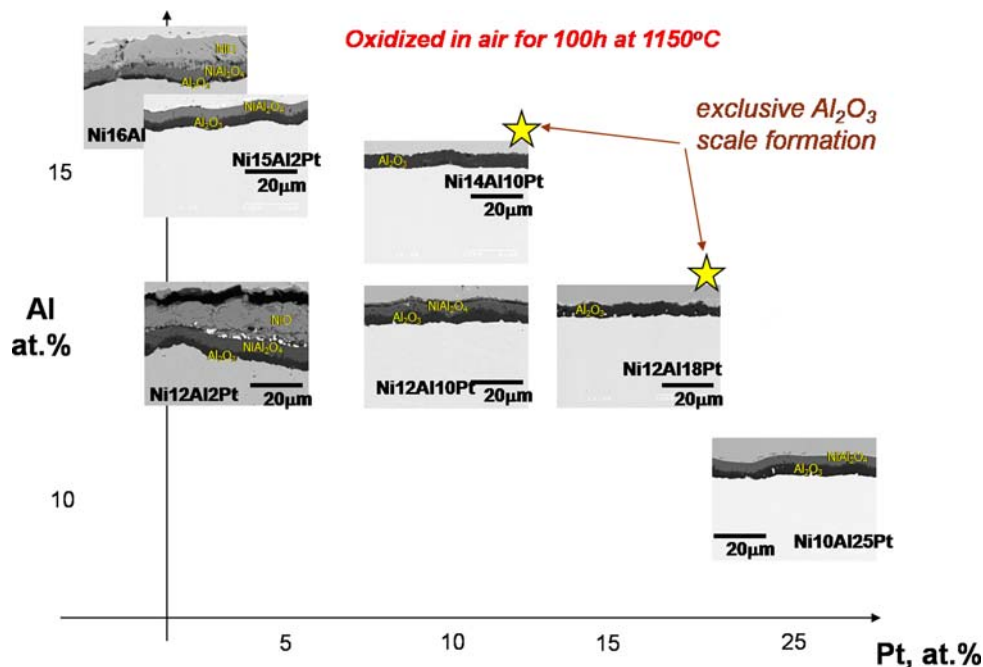
the  $\beta$  or the  $\gamma+\gamma'$  alloy results in improved scale adhesion, as indicated by the absence of weight loss from the Pt-containing alloys. Second, Pt addition caused the  $\gamma+\gamma'$  alloy to oxidize in a manner similar to that of the Pt-modified  $\beta$  alloy. This is further confirmed in Fig. 4, which shows cross-sectional images of the Pt-modified  $\gamma+\gamma'$  and  $\beta$  alloys after 500 cycles of 1-hour duration at 1150 °C. The scale formed on both alloys was  $\alpha$ - $\text{Al}_2\text{O}_3$  and of similar thickness. Although not shown, the Pt-free  $\gamma+\gamma'$  alloy does not form an exclusive scale layer of  $\text{Al}_2\text{O}_3$  and instead forms a non-protective scale consisting of NiO and NiAl<sub>2</sub>O<sub>4</sub> outer layers and a discontinuous inner  $\text{Al}_2\text{O}_3$  layer. Thus, and as will be discussed in more detail in the following, Pt had the added beneficial effect for the  $\gamma+\gamma'$  alloy of promoting exclusive  $\text{Al}_2\text{O}_3$  formation.

Indeed, earlier reports by Coupland et al. [51, 52] and Tatlock and Hurd [53–55] showed that Pt improves oxidation and hot corrosion resistance of alloys with  $\gamma+\gamma'$  compositions. In addition, Felten [56] studied the effect of Pt with Cr addition in low Al (12 at.%)  $\gamma+\gamma'$ -based alloys and showed that these alloys were indeed alumina formers. Research efforts prior to 1987 that were concerned with platinum additions to Ni-based alloys for improved oxidation and hot-corrosion resistance were succinctly reviewed by Tatlock et al. [57]. These authors deduced that platinum can play a dual role of promoting  $\text{Al}_2\text{O}_3$ -scale formation and improving scale adhesion; however, the precise mechanisms leading to these roles were not identified.

Figure 5 shows cross-sectional SEM images of a series of Ni–Al and Ni–Al–Pt alloys after oxidation in still air for 100 h at 1150 °C. The images are arranged as a function of Al and Pt contents, which are all in at.%. The benefits of Pt addition in promoting more protective oxidation are clearly seen when comparing the various scale microstructures to that formed on the Pt-free Ni–16Al alloy. As indicated, the scale formed on this Pt-free alloy was multilayered, with a thick outer NiO layer, an intermediate mixed-scale layer of NiO+NiAl<sub>2</sub>O<sub>4</sub>, and innermost duplex NiAl<sub>2</sub>O<sub>4</sub> and discontinuous  $\text{Al}_2\text{O}_3$  layer. By contrast, an exclusive  $\text{Al}_2\text{O}_3$  scale developed on the Ni–14Al–10Pt and Ni–12Al–18Pt

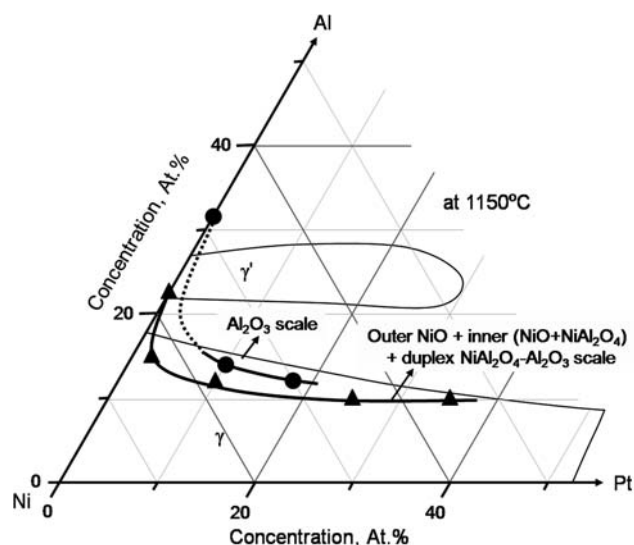


**Fig. 5** Cross-sectional SEM images summarizing the oxidation behavior of Ni–Al and Ni–Al–Pt alloys exposed to air for 100 h at 1150 °C



alloys. The thickness of the  $\text{Al}_2\text{O}_3$  scale that developed on Ni–12Al–18Pt was thinner than that on Ni–14Al–10Pt. The oxide scales that formed on the Ni–15Al–2Pt, Ni–12Al–10Pt and Ni–10Al–25Pt alloys consisted of a duplex structure comprised of an outer  $\text{NiAl}_2\text{O}_4$  layer and an inner continuous layer of  $\text{Al}_2\text{O}_3$ . The results in Fig. 5 suggest that the Al and Pt contents must be balanced in order to facilitate protective oxidation (i.e., more Pt is needed to compensate for a lower Al content).

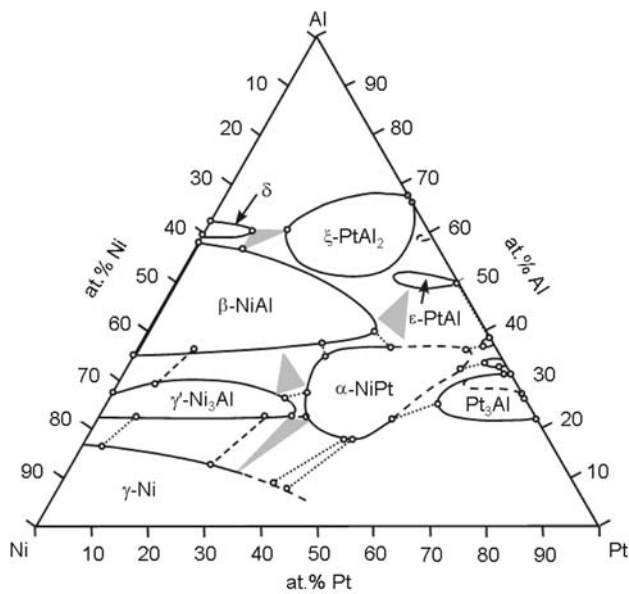
Figure 6 shows the experimentally determined oxide map for Pt-modified  $\gamma$ -Ni–Al alloys exposed to air at 1150 °C. It is seen that Pt significantly decreases the



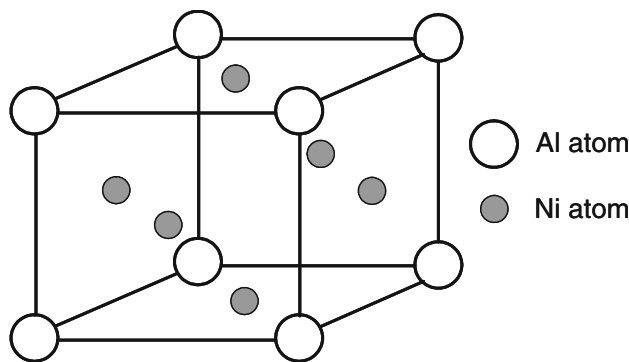
**Fig. 6** Oxide map for the Ni–Al–Pt system exposed to air at 1150 °C for 100 h

critical Al content for exclusive  $\text{Al}_2\text{O}_3$  formation. It is further seen that an increase in Pt content above  $\sim 10$  at.% did not provide any further beneficial effect in promoting  $\text{Al}_2\text{O}_3$  formation. The critical Al content for the formation of external  $\text{Al}_2\text{O}_3$  was found to be about 10 at.% for alloys containing more than  $\sim 10$  at.% Pt. Below this critical Al content,  $\text{Al}_2\text{O}_3$  was present either as internal precipitates or as an inner layer of a duplex scale structure.

It can be inferred from Fig. 6 that Pt can promote  $\text{Al}_2\text{O}_3$ -scale formation on  $\gamma$ ,  $\gamma+\gamma'$  and  $\gamma'$  alloys. Because the intermetallic  $\gamma'$ - $\text{Ni}_3\text{Al}$  and solid solution  $\gamma$ -Ni have the same face center cubic (FCC) crystal structure, the mechanism by which Pt affects oxidation behavior should be similarly applicable to both phases; although, the ordered  $\text{L}_{12}$  arrangement of the  $\gamma'$  structure would bring differences. The 1150 °C Ni–Al–Pt phase diagram in Fig. 7 shows that both  $\gamma'$  and  $\gamma$  have large phase regions, extending from the Ni-rich side to the Pt-rich side. The nature of these phase regions implies that Pt can be added into each phase solely at the expense of Ni while keeping a fixed Al content. This is particularly important for the  $\gamma'$ - $\text{Ni}_3\text{Al}$  phase, as it has a narrow Al composition range varying from 22 to 27 at.%. This phenomenological interpretation of Pt substituting almost solely for Ni in the  $\gamma'$  lattice was verified by a first-principles study by Chao et al. [58]. Their calculations showed that Pt has a predominant preference for the Ni sublattice (face centers) in the ordered  $\text{L}_{12}$  structure (Fig. 8) over a large temperature range and at compositions varying from Ni-rich, stoichiometric to Al-rich  $\text{Ni}_3\text{Al}$ . Consequently, Pt additions essentially enhance the effective Al content (relative to Ni) available for oxidation in a given crystallographic plane that contains



**Fig. 7** Isothermal phase equilibria on Ni–Pt–Al alloys at 1150 °C [27]



**Fig. 8** A schematic showing the L1<sub>2</sub> crystal structure of γ'-Ni<sub>3</sub>Al

both Al and Pt. In other words, because of its virtually non-oxidizing nature, the presence of Pt in place of Ni would affect the early-stage competitive oxidation of Al and Ni to the extent that Al<sub>2</sub>O<sub>3</sub> formation is kinetically favored.

Another important factor is that Pt has a negative chemical interaction with Al such that the Al activity ( $a_{Al}$ ) decreases with increasing Pt content. Hayashi et al. [27, 59] reported this effect from a series of diffusion couples in which uphill diffusion of aluminum from the low-Al side to the high-Al side was measured. Copland [60] directly measured Al activity in a series of γ'-(Ni,Pt)<sub>3</sub>Al alloys with varying Al (24 and 27 at.%) and Pt (2 to 25 at.%) contents, and his results validated Hayashi et al.'s conclusions. Therefore, any Pt surface enrichment owing to the selective oxidation of Ni and/or Al during the initial stages of oxidation would locally decrease  $a_{Al}$  at the oxide/alloy interface in comparison to a Pt-free alloy. This local decrease in  $a_{Al}$  would result in an increased  $a_{Al}$  gradient

from the alloy to the scale/alloy interface, which, in turn, would lead to an increase in the outward diffusive flux of Al at the scale/alloy interface according to the relation [61]:

$$J_{Al}^i = -C_{Al}^i D_{Al} \frac{\partial \ln a_{Al}}{\partial x} \quad (1)$$

where  $C_{Al}^i$  is the interfacial Al content at the scale/alloy interface, and  $D_{Al}$  is the diffusion coefficient of Al. This increased Al flux would serve to assist in the fast and continuous development of an Al<sub>2</sub>O<sub>3</sub>-rich scale during the early stages of oxidation, as shown by Hayashi et al. [62].

It was also reported by Gleeson et al. [27] that Pt decreases the oxygen permeability in both γ-Ni and γ'-Ni<sub>3</sub>Al alloys. This inference was arrived at by comparing the thickness of the internal oxidation zones formed in a Pt-free and Pt-modified γ-Ni alloys. Such a decrease in oxygen permeability would decrease the critical Al content within the alloy necessary for Al<sub>2</sub>O<sub>3</sub> scale formation.

Thus, the following three effects of Pt in promoting Al<sub>2</sub>O<sub>3</sub>-scale formation have been identified as: (1) Pt has a predominant site preference for the Ni sublattice in the ordered L1<sub>2</sub> structure so that the effective Al/Ni ratio is enhanced in certain crystallographic planes; (2) Pt has a negative chemical interaction with Al, which results in an increased Al diffusive flux at the scale/alloy interface when there is the subsurface enrichment of Pt; and (3) Pt decreases the oxygen permeability into the alloy which in turn, decreases the critical Al concentration for Al<sub>2</sub>O<sub>3</sub> formation. Effect (1) is specific to the γ' phase, while the other two effects are relevant to both γ' and γ. All the three effects are believed to contrive to favor Al<sub>2</sub>O<sub>3</sub>-scale formation on γ, γ+γ', and γ' alloys.

### Summary

The beneficial effects of Pt in promoting exclusive Al<sub>2</sub>O<sub>3</sub> formation on Ni<sub>3</sub>Al alloys have been more recently elucidated by Gleeson and colleagues [19, 62, 63]. According to these authors, the so-called Pt-effect can be ascribed to a number of contributing factors. First and foremost, Pt has a strong preference for occupying Ni sites in the ordered L1<sub>2</sub> crystal structure of γ'-Ni<sub>3</sub>Al [58]. As a consequence, a given crystallographic plane of γ' containing both Al and Ni shows an increase in the Al: Ni atom fraction with increasing Pt addition. Such an effective Al enrichment at the γ' surface kinetically favors the formation of Al<sub>2</sub>O<sub>3</sub> relative to NiO. An important aspect of this inference is the non-reacting nature of Pt to oxidation. Another contributing factor is that the Pt-containing γ'-based alloys show subsurface Pt enrichment during the very early stages of oxidation [62, 63]. This enrichment reduces Ni availability

for oxidation and can increase the Al supply to the evolving scale owing to the negative chemical interaction between Al and Pt. With regard to the latter, Pt decreases the chemical activity of Al [60], so that a subsurface Pt enrichment would confer an increased subsurface gradient in the Al activity and, hence, an increased Al flux from the alloy to the evolving scale. This effect would also contribute to kinetically enhancing  $\text{Al}_2\text{O}_3$ -scale formation. In a study of single-crystal  $\gamma'$  alloys it was found that the Pt effect is most pronounced when the Pt content is increased from 0 to 10 at.%, with only a minor benefit when increased from 10 to 20% Pt [64]. Based on this interpretation, it is clear that the Pt-effect is much different from the Cr-effect in promoting  $\text{Al}_2\text{O}_3$ -scale formation on  $\gamma$ ,  $\gamma+\gamma'$ , and  $\gamma'$  alloys.

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