

Microstructure and oxidation performance of a γ - γ' Pt-aluminide bond coat on directionally solidified superalloy CM-247LC

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Abstract. The microstructure of a Pt-modified γ - γ' bond coat on CM-247LC Ni-base superalloy has been examined and its cyclic oxidation performance at 1100 °C in air is comparatively evaluated with that of a conventional β -(Ni, Pt)Al bond coat. The γ - γ' bond coat was effective in imparting oxidation resistance to the CM-247LC alloy for about 100 h, whereas the β coating imparted oxidation resistance for significantly longer duration of about 1000 h. The nature of surface damage that occurred to the γ - γ' coating during oxidation has been compared with that reported in the case of β coating.

Keywords. Platinum aluminide bond coat; coating; cyclic oxidation; superalloy; microstructure.

1. Introduction

Directionally solidified (DS) Ni-base superalloy aerofoil components are used in the hot sections of advanced gas turbine engines. Although these alloys possess good elevated temperature strength, they are moderate to poor in terms of their resistance against high-temperature oxidation, especially under cyclic heating and cooling conditions that typically prevail in gas turbine engines. Inadequate oxidation resistance of these alloys can cause large-scale material loss because of oxide formation and, therefore, lead to reduction in load-bearing cross section of the superalloy component (Bose 2007; Alam *et al* 2010a). Further, oxidation-related surface damage to the superalloy can also result in significant degradation in the mechanical properties of the alloy (Alam *et al* 2010a). In order to protect these superalloys against the deleterious effects of high-temperature oxidation, superalloy components are typically provided with an oxidation resistant bond coat (Pichoir 1978; Strang and Lang 1982; Bose 2007). At present, Pt-modified β -NiAl (or β -(Ni, Pt) Al) type bond coats are widely being used in thermal barrier coating systems (TBCs) applied on turbine components such as blades and nozzle guide vanes (Pichoir 1978; Strang and Lang 1982; Bose 2007). The protective nature of these Pt-aluminide bond coats is derived from their ability to form a continuous regenerative layer of α -Al₂O₃ on the surface (Farrell *et al* 1987; Sun *et al* 1994; Das *et al* 1999, 2000a,b). The presence of Pt in the coating enhances the adherence of the alumina scale and, thereby, significantly improves its ability to resist spallation under

the stresses caused by mismatch of coefficients of thermal expansion (CTE) between the coating and the oxide layer (Tatlock and Hurd 1984; Farrell *et al* 1987; de Wit and van Manen 1994; Purvis and Warnes 2008; Tawancy *et al* 2008; Svensson *et al* 2009).

Despite the widespread use of β -(Ni, Pt)Al type bond coats for oxidation protection of Ni-base superalloys, it has been recognized that these coatings are both chemically and mechanically incompatible with the superalloy substrate. Because of the appreciably high Al contents of these coatings, there is interdiffusion of Al, Ni and other elements between the coating and the substrate during coating process and the subsequent high-temperature service affecting the local phase equilibrium conditions (de Wit and van Manen 1994; Das *et al* 1999). Further difference in the coefficients of thermal expansion between the β -(Ni, Pt)Al coating and the superalloy substrate induces stresses during thermal cycling, which can contribute to the undesirable roughening or rumpling of the bond coat surface (Pennefather and Boone 1995; Deb *et al* 1987). In order to overcome these drawbacks, diffusion aluminide bond coats having a γ - γ' rather than β -NiAl structure are currently being explored (Gleeson *et al* 2004a,b, 2006, Zhang *et al* 2006; Hazel *et al* 2007). Pt modified γ - γ' -type coatings, which contain much lower Al than their β counterparts and possess the same phase constitution as the substrate superalloy, have been reported to have good chemical and mechanical compatibility with the substrate (Gleeson *et al* 2004a,b, 2006). Two methods have been adopted for forming γ - γ' bond coats on superalloy substrates. In the first method, a layer of Pt (approximate thickness 7–10 μ m) is electroplated on the substrate, following which the plated substrate is diffusion annealed at a temperature above 1000 °C for a few

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hours (Zhang *et al* 2006; Haynes *et al* 2008). During the diffusion treatment, interdiffusion between the Pt layer and the substrate takes place, leading to the formation of a γ - γ' coating. In the second method, a small amount of Al is added to the coating by pack aluminizing process after the diffusion treatment. The pack composition is so maintained such that the γ - γ' coating structure is retained after aluminization (Gleeson *et al* 2004a, b, 2006). Occasionally, small amounts of other elements such as Hf are also introduced into the coating during aluminization by co-deposition technique (Gleeson *et al* 2006). In the present study, a Pt-modified γ - γ' coating formed on directionally solidified (DS) Ni-base superalloy CM-247LC has been examined for its microstructure and oxidation performance in air under thermal cycling conditions. Its oxidation behaviour has been compared with that of a high-activity Pt-modified β bond coat in order to examine the possibility of utilizing the γ - γ' bond coats as an alternative to their β counterparts in thermal barrier coating systems.

2. Experimental

DS CM-247LC alloy was used as the substrate material in the present study. The nominal composition of this alloy (in wt%) is 9.2 Co–8.1 Cr–9.5 W–5.6 Al–3.2 Ta–1.5 Hf–0.7 Ti–0.015 Zr–0.5 Mo–0.15 B–0.07 C–balance Ni. This alloy was available in the form of 13-mm-diameter rods. The $\langle 001 \rangle$ solidification direction was along the length of the rods. The rods were given a two-stage solutionizing treatment in vacuum. The treatment was carried out at 1230 °C for 30 min, followed by 3 h at 1260 °C. Disc-shaped samples of 2 mm thickness were sliced from the solutionized rods and used as substrates for the formation of Pt-aluminide bond coats. For the formation of γ - γ' coating, the disc samples were deposited with a 5 μ m thick layer of Pt by electroplating method. The plated samples were given diffusion heat treatment at 1080 °C for 4 h in vacuum during which the interdiffusion between the Pt layer and the substrate led to the formation of γ - γ' bond coat on the surface of the samples (Haynes *et al* 2008). For the formation of β bond coat, the disc samples were first applied with a 5 μ m thick layer of Pt. Subsequently, the Pt-plated samples were subjected to vacuum diffusion heat treatment; after which, they were pack aluminized using a high-activity pack at 830 °C for 5 h. The pack used for aluminization consisted of (in wt%) 10% Ni–Al alloy powder, 2% NH_4Cl and balance calcined Al_2O_3 powder. The Al content in the above Ni–Al alloy powder was 50 wt%. The aluminizing treatment was carried out in a tube furnace in an argon atmosphere. The aluminized samples were then subjected to a post-coating treatment at 1080 °C for 4 h in vacuum. All the coated samples (both γ - γ' and β) were finally aged at 870 °C for 20 h in vacuum.

The bond-coated samples along with some uncoated samples were subjected to cyclic oxidation at 1100 °C in air. Each oxidation cycle consisted of 30 min exposure at 1100 °C, followed by cooling at ambient temperature for 30 min outside the furnace. The microstructural aspects of the coated samples were studied using a Quanta 400 scanning electron microscope (SEM) operating at 20 kV. A Cameca SX-100 electron probe micro-analyser (EPMA) operating at 20 kV was used for chemical analysis of the coating microstructures. The phase constitution of the coatings and the oxide scales formed during thermal cycling was determined by X-ray diffraction method using $\text{CuK}\alpha$ radiation.

3. Results

3.1 As-coated microstructure

The cross-sectional view of the γ - γ' coating formed on the present superalloy is shown in figure 1(a). The thickness of this coating was approximately 40 μ m. The γ - γ' structure of the coating was confirmed by XRD (figure 2). As seen in figure 1(a), the brighter phase in the coating corresponds to the γ' phase, while the greyish matrix

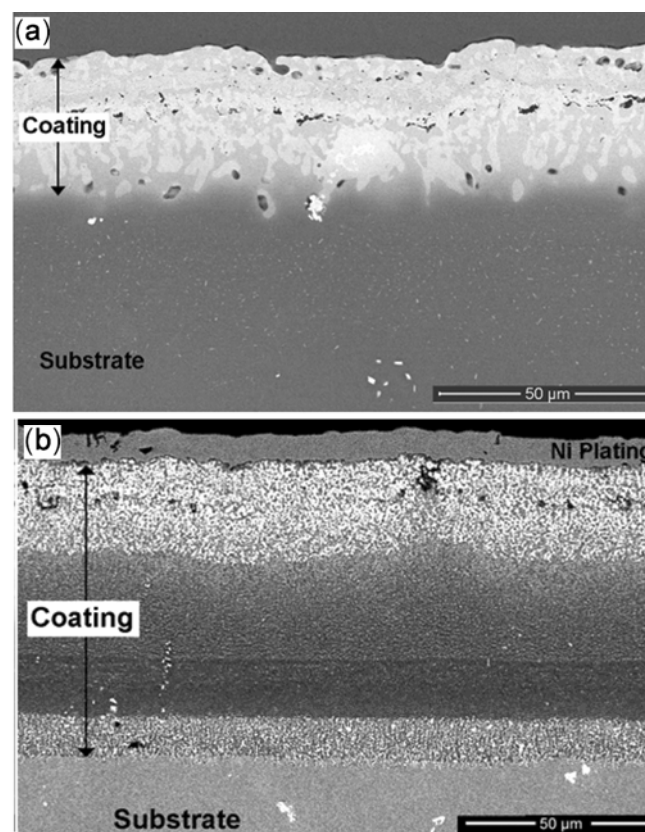


Figure 1. SEM images showing cross-sectional microstructure of coatings in as-coated condition: (a) γ - γ' coating and (b) β -coating.

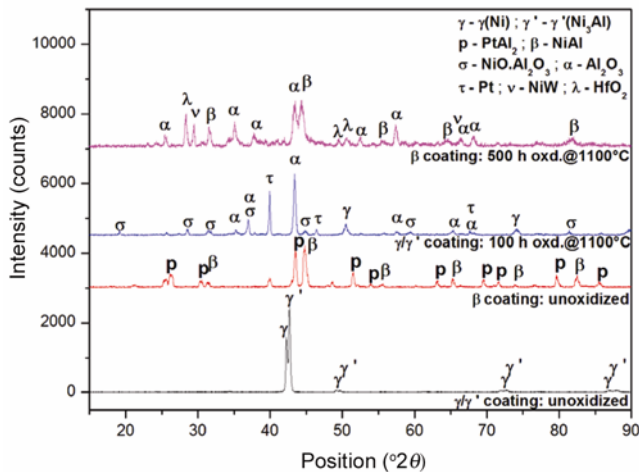


Figure 2. XRD patterns obtained from the sample surfaces in as-coated and oxidized conditions. CuK α radiation was used for obtaining the patterns.

phase is γ . The coating microstructure obtained on the present alloy is similar to the structures reported in previous studies (Zhang *et al* 2006; Das *et al* 2009). In addition to γ and γ' phases, several Kirkendall porosities were present in the coating. Such porosities are generated due to unequal mass transfer between the Pt layer and the substrate caused by interdiffusion during coating formation (Zhang *et al* 2006; Das *et al* 2009). The porosities could also be seen in the surface view of the coated sample, as presented in figure 3(a). The γ and γ' phases of the coating were also evident on the surface, as shown in the inset of figure 3. The grain structure of the coating could also be identified in the surface view (figure 3b). The β coating, as shown in figure 1(b), revealed the typical three-layer structure found in high-activity coatings (Das *et al* 1999; Alam *et al* 2010b). While the outer layer consisted of B2–NiAl and PtAl₂ phases, the intermediate layer had a single-phase B2–NiAl structure. The B2–NiAl and PtAl₂ phases of the outer coating layer were confirmed by XRD, as shown in figure 2. The inner layer, referred to as the interdiffusion zone (IDZ), consisted of a B2–NiAl matrix dispersed with numerous refractory element-rich precipitates. Some amount of Pt remained in solid solution in the B2–NiAl phase throughout the coating. In addition to the above-mentioned phases, the outer layer, and, to a lesser degree, the intermediate layer, of the coating contained fine W-rich precipitates, as evident from figure 1(a). The thickness of the coating was approximately 100 μm . The microstructural details and the mechanism of formation of the above high-activity β -type Pt-aluminide coatings have been reported in our previous publications as well as in those by other researchers (Das *et al* 2000a,b; Angenete and Stiller 2002).

The concentration profiles of Al and Pt across the thickness of both β and γ - γ' bond coats are shown in figure 4. The Al concentration of the γ - γ' coating was

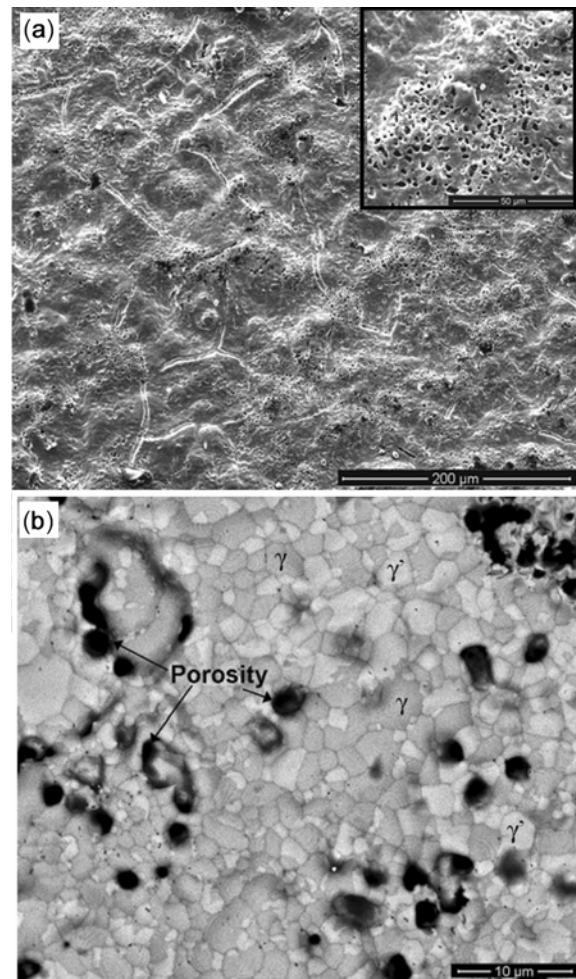


Figure 3. Surface view of the γ - γ' coating in as-coated condition: (a) a low magnification general view and (b) a magnified view (BSE) showing γ and γ' phases. The inset in figure 3(a) shows a magnified view of the surface revealing the Kirkendall porosity.

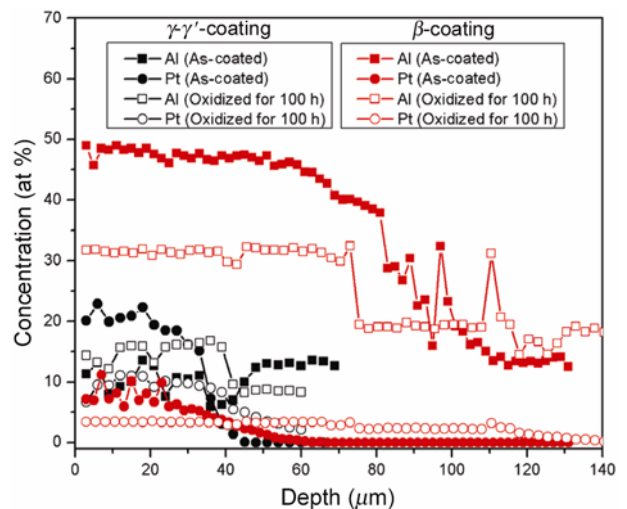


Figure 4. EPMA concentration profiles of Al and Pt across the coating depth for γ - γ' and β coatings in as-coated condition and after cyclic oxidation for 100 h at 1100 $^{\circ}\text{C}$ in air.

approximately 10 at%, which was slightly lower than the substrate Al concentration of 13 at%. The lower Al concentration of the coating was because of the nature of coating formation which involved alloying of the substrate with Pt. The concentration of Pt in the above coating was close to 20 at%. As compared to the γ - γ' coating, the β coating contained a lot more Al, which was close to 46 at%. Correspondingly, its Pt concentration was much lower at about 8 at% as compared to that of the γ - γ' coating.

3.2 Cyclic oxidation performance

The weight change plots corresponding to cyclic oxidation of both β and γ - γ' coated samples at 1100 °C in air are presented in figure 5. The uncoated superalloy had extremely poor oxidation resistance and underwent severe weight loss due to oxide spallation under the influence of CTE mismatch stresses from the very beginning of the test. The γ - γ' coating, on the contrary, provided a reasonable degree of oxidation resistance to the alloy, as indicated from the weight gain observed over first 100 h (200 cycles) of exposure. Beyond this duration, progressive weight loss was registered, with the sample weight becoming lower than the initial weight after about 220 h. The β coating, in comparison, provided protection for a much longer duration, as evident from figure 5. The β coated sample showed weight gain for nearly 1000 h (2000 cycles), beyond which progressive weight loss was registered. The parabolic rate constant, k_p , for both the coatings was determined from the slope of the straight line that was fitted to square of weight gain vs time plot. For this calculation, only the rising portion of the weight change plot (indicating progressively increasing weight gains) was used (figure 5). It may be mentioned that,

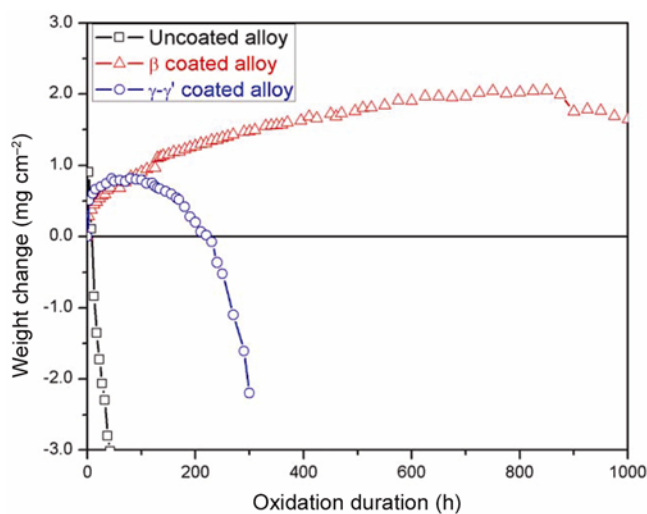


Figure 5. Weight change recorded for γ - γ' and β coatings during their cyclic oxidation at 1100 °C in air.

during the period over which the coated samples showed weight gain, i.e. the rising portion of plots in figure 5, no spallation of oxide was observed during thermal cycling. Therefore, it can be assumed that the weight gain during this period was caused exclusively by the formation of oxide on the sample surface. Using the above method, the k_p value for the γ - γ' and β coatings were determined to be 1.7×10^{-12} and $1.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, respectively. Despite these similar k_p values, the γ - γ' coating showed much poorer oxidation resistance than its β counterpart and began losing weight after about 100 h (200 cycles) of exposure.

3.3 Microstructural aspects after oxidation exposure

X-ray diffractograms corresponding to a β -coated sample after it was exposed to cyclic oxidation for 500 h are presented in figure 2. As expected (Das *et al* 1999), α - Al_2O_3 scale formed on the sample surface was detected in XRD along with other coating phases. The α - Al_2O_3 phase in the scale was detected even up to 1000 h of exposure for the β -coated sample. In comparison, both spinel ($\text{NiO} \cdot \text{Al}_2\text{O}_3$) and Al_2O_3 oxide phases were detected in case of γ - γ' coated sample (figure 2). In addition, pure Pt was also detected in the oxide layer after oxidation exposure of the above coating. The concentrations of Al and Pt across the coating thickness for both γ - γ' and β coatings after 100 h of oxidation are presented in figure 4. It is evident that the Al concentration of γ - γ' coating in an oxidized condition was significantly higher at about 15 at% than the value of 10 at% in as-coated condition. This was unlike the case with the β coating, where the Al concentration decreased to about 31 at% from its initial (as-coated) value of 46 at%. Unlike the Al concentration, the Pt concentration in γ - γ' coating decreased from the as-coated value of 20 at% to about 6 at% after oxidation exposure. Similarly, the Pt content of the β -coating decreased from its initial value of 8 to about 3.5 at% after 100 h of oxidation.

A low-magnification cross-sectional micrograph of a γ - γ' -coated sample after 10 h of cyclic exposure at 1100 °C is shown in figure 6(a). The oxide layer on the sample surface was mostly uniform, although large oxide masses had formed at some locations indicating localized oxidation. Because of the loss of Al from the coating towards scale formation, a surface γ layer was formed, as shown in the inset of figure 6(a). With increase in oxidation duration, the number of localized regions of oxidation and the extent of damage at these regions increased. By about 50 h of exposure, the coating got completely punctured at several locations and the underlying substrate was oxidized because of such localized attack, as typically seen in figure 6(b). The typical cross-sectional view of the coating after 50 h of exposure, along with the corresponding X-ray images for various elements, is

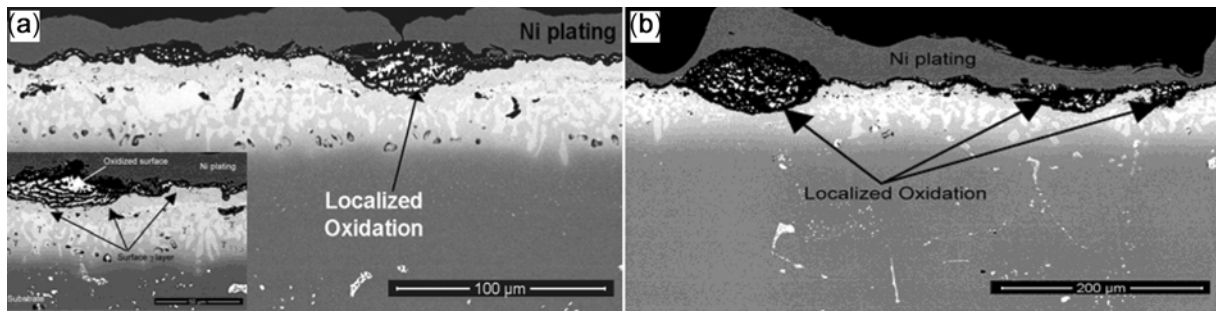


Figure 6. Cross-sectional microstructure of the γ - γ' coating after cyclic oxidation exposure for (a) 10 h and (b) 50 h. The inset in figure 6(a) shows the surface γ layer.

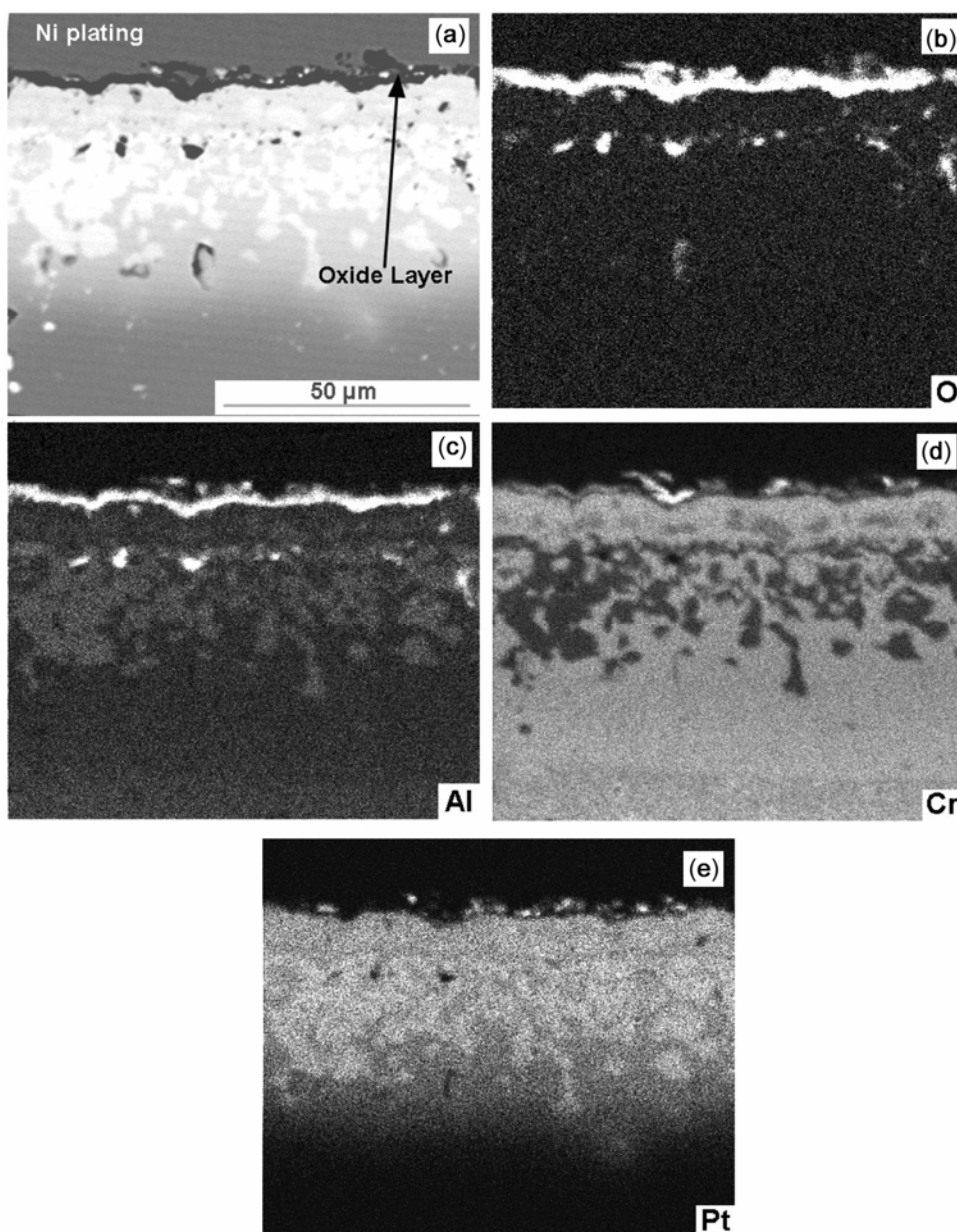


Figure 7. Typical oxide layer formed on the γ - γ' coating after cyclic oxidation exposure for 50 h along with the corresponding EPMA X-ray maps: (a) back scattered electron (BSE) image showing the uniform oxide layer, (b) O map, (c) Al map, (d) Cr map and (e) Pt map.

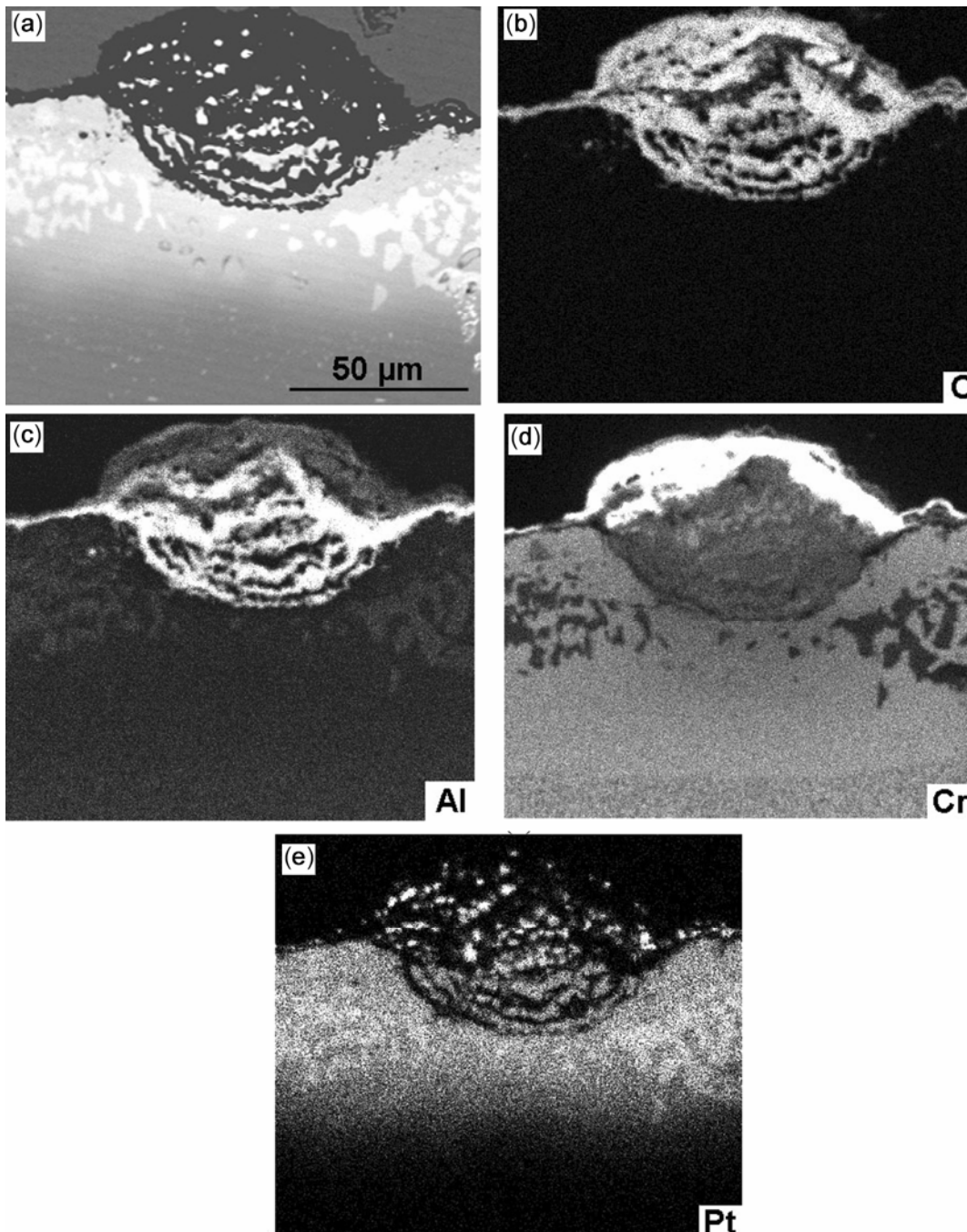


Figure 8. Oxide mass formed at a region of localized oxidation on a γ - γ' sample exposed to 50 h of cyclic oxidation and the corresponding EPMA X-ray maps: (a) back scattered electron (BSE) image showing the oxide mass, (b) O map, (c) Al map, (d) Cr map and (e) Pt map.

presented in figure 7(a–e). As is evident from figure 7(a), the oxide layer was largely uniform and consisted of Al_2O_3 . Some amounts of Cr- and Ni-rich oxides (possibly spinels) were also present in the oxide layer. The oxide layer formed at a location of the same sample, where localized oxidation damage to the coating had occurred, is shown in figure 8(a). From this figure and the corresponding elemental X-ray maps (figure 8(b–d)), it is clear

that the oxide mass formed at the localized damage region consisted of mixed oxides, i.e. alumina and spinels. Further, several Pt-rich particles were found embedded in the above oxide mass (figure 8(a and e)). These particles are actually portions of the coating which have got embedded into the oxide layer and subsequently got oxidized. Some of these particles were found to be virtually pure Pt, as indicated by the EDS elemental analysis

carried out in SEM. The presence of these Pt particles was consistent with the Pt peaks detected through XRD, as mentioned earlier (figure 2). The process of embedment of portions of the coating in the oxide layer began early during oxidation, as evident from figure 6(a), and continued throughout the exposure duration (up to 250 h or 500 cycles).

The degradation of the β -coating during oxidation exposure occurred in a similar manner, as extensively reported in the literature (Chen and Little 1997; Das *et al* 1999; Angenete *et al* 2002). Apart from the formation of a protective scale of α -alumina on the surface of the sample, the coating microstructure underwent significant changes during cyclic oxidation at 1100 °C. The two-phase outer layer of the coating transformed to a single-phase β -(Ni, Pt)Al structure after about 10 h (20 cycles) of exposure (figure 9a). As a result, the starting three-layer coating structure (figure 1b) changed to a two-layer one with the entire outer layer consisting of β -phase (figure 9a) (Das *et al* 1999; Alam *et al* 2010b). After exposure of about 100 h, the β phase of the outer coating layer further degraded to a $\beta + \gamma'$ structure in which the γ' phase started forming at the boundaries of β grains, as shown in figure 9(b) (Das *et al* 1999, Angenete 2002; Alam 2010b). The volume fraction of γ' phase increased and that of β decreased throughout the coating as the duration of cyclic exposure increased. Further, the β phase exhibited transformation to a martensitic lath structure, as typically observed in β -NiAl upon oxidation (Smialek and Hehemann 1973; Chen *et al* 2003). The above-mentioned degradation of the present β coating was primarily driven by the loss of Al from the coating towards the formation of the alumina scale on the coating surface as well as its loss into the substrate under the concentration gradient that existed between the coating and the

substrate. Interdiffusion of the other elements, including Ni, between the coatings and the substrate also contributed to the above-mentioned changes in the coating during the oxidation exposure.

Figure 10(a) presents the typical surface view of the γ - γ' coated samples after oxidation for 10 h. A uniform coverage of the surface with the oxide layer, which was consistent with observation in the cross-sectional view (figure 7a), was observed along with the grain structure of the original coating (figure 10a). The localized oxidation to the coating could be identified on the surface beyond about 25 h of oxidation, as shown in figure 10(b). Once started, the size of these oxidized regions continued to grow throughout the oxidation exposure. By 250 h (500 cycles), several oxidized regions of size larger than 0.5 mm could be seen on the surface (figure 10c). In contrast, the oxidation of β coating resulted in the formation of a uniform layer of Al₂O₃ on the sample surface throughout the 1000 h exposure, as typically shown in figure 9. Such oxide formation in β platinum-aluminide coatings has been reported in other studies (Chen *et al* 1997; Das *et al* 1999; Angenete *et al* 2002).

4. Discussion

The present substrate superalloy (CM-247LC) had the typical γ - γ' structure in as-heat-treated condition wherein the cuboidal γ' -Ni₃Al precipitates were distributed in a γ -Ni solid solution matrix (Alam *et al* 2010a, b). The approximate volume fraction of the γ' phase in the alloy was 0.65. The oxidation behaviour of this alloy in air in the temperature range of 1000–1200 °C has been reported by Das *et al* (2003). Oxidation exposure of the alloy causes depletion of Al and consequent dissolution of γ'

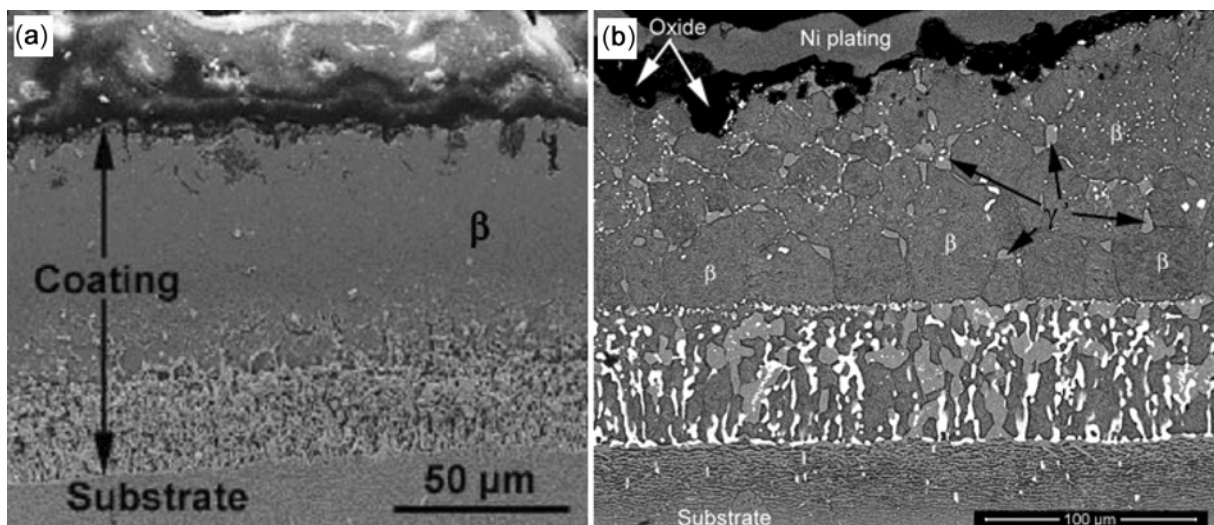


Figure 9. The microstructure of the β bond coat after oxidation exposures of (a) 10 h and (b) 100 h, showing gradual degradation of coating microstructure showing cyclic oxidation.

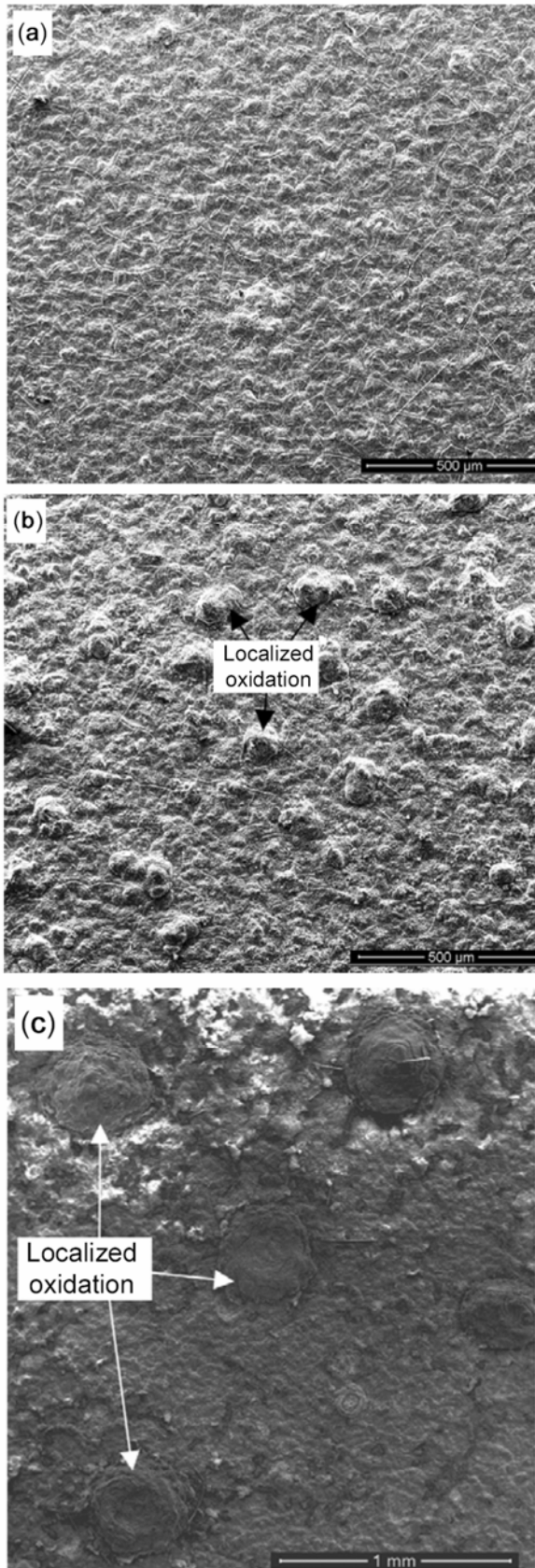


Figure 10. Surface morphology of the γ - γ' coated sample after various durations of oxidation exposure: (a) 10 h, (b) 25 h and (c) 250 h.

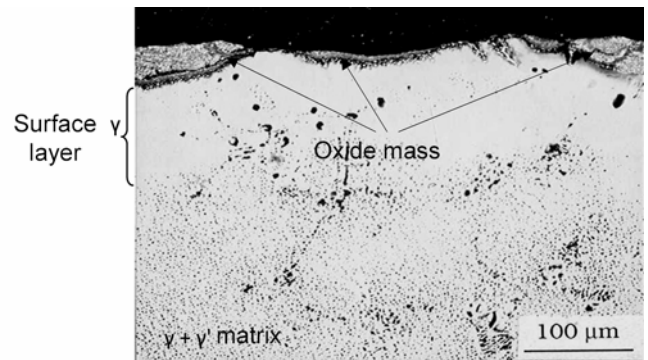


Figure 11. Cross-sectional microstructure of an uncoated CM-247LC sample cyclically oxidized for 15 h at 1200 $^{\circ}\text{C}$, as reported by Das *et al* (2003). The oxide masses formed due to localized oxidation have been shown.

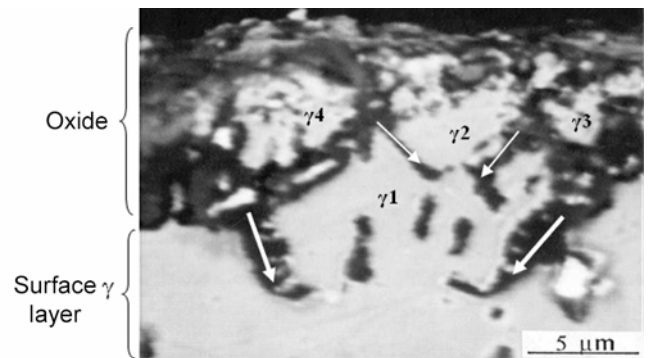


Figure 12. The process of detachment of pieces of the substrate by oxide undercutting and their embedment in the oxide layer, as reported by Das *et al* (2003), in case of uncoated CM-247LC after cyclic oxidation for 350 h at 1000 $^{\circ}\text{C}$. The paths of oxide undercutting are marked by arrows. While γ_1 and γ_2 are the substrate pieces which are in the process of being detached, γ_3 and γ_4 are the portions which have already been embedded in the oxide layer.

precipitates near the surface. As a result, a surface layer of (γ' -free) γ phase is created, whose thickness is a direct function of the exposure temperature and time. The oxide layer that develops on the alloy is fairly uniform during the initial period (up to about 10 h). However, as the oxidation duration increases, the oxide layer becomes non-uniform in thickness and is found to consist of localized oxide masses, as typically shown in figure 11. The oxide layer has a composite structure with its outer portion consisting of a mixture of spinel ($\text{NiO}\cdot\text{Al}_2\text{O}_3$) and NiO. The inner portion of the scale consists of alumina. The study by Das *et al* (2003) has also shown that the formation of localized oxide masses occurs because of the diffusion of oxygen into the alloy along the grain boundaries of the surface γ layer, which has an equiaxed structure. This method of oxide formation causes undercutting of the substrate by the oxide, which leads to the detachment of pieces of substrate and their embedment in the oxide

scale, as shown in figure 12 (Das *et al* 2003). While the pieces γ_1 and γ_2 in the above figure are in the process of getting detached from the substrate, γ_3 and γ_4 are lying embedded in the oxide scale after getting detached. Although the detached pieces were found embedded in the oxide scale at lower oxidation temperatures such as 1000 °C, they were not located in the scale at higher temperatures (such as 1200 °C), because these pieces get converted to oxide phases due to higher rate of oxidation (Das *et al* 2003).

It is clear from the reported study that the Al content in CM-247LC is insufficient to form a protective alumina scale. However, as the present study shows, the presence of a Pt-modified γ - γ' coating enhances the oxidation resistance of the alloy appreciably. The superior oxidation resistance of the coating, despite its low Al content (figure 5), is consistent with the recently reported results on the oxidation of ternary Ni–Pt–Al alloys (Gleeson *et al* 2004a,b; Pint 2004). It has been suggested that the presence of sufficient Pt (e.g. > 15 at%) in γ - γ' coating compositions such as Ni–22Al–30Pt (in at%) decreases the chemical activity of aluminum in the coating to the extent that there is uphill diffusion of Al from the underlying substrate into the coating. For example, in case of a γ - γ' (Ni–22Al–30Pt)/ γ - γ' (Ni–19Al) diffusion couple after 50 h interdiffusion at 1150 °C, an enrichment of Al on the Al-rich γ - γ' (Ni–22Al–30Pt) side of the couple was observed from the composition profiles (Gleeson *et al* 2004a,b). Such uphill Al diffusion was also observed when the Pt-modified γ - γ' alloy was coupled to the Ni-based superalloy CMSX-4 (Gleeson *et al* 2004a,b). Thus, effective increase in Al concentration of the Pt-modified γ - γ' coating during high-temperature exposure leads to an improvement in its oxidation resistance. Further, it has been suggested that the presence of Pt lowers oxygen permeability into the coating which promotes selective oxidation of Al and formation of a protective alumina scale even at relatively low Al concentrations (Gleeson *et al* 2004a,b; Das *et al* 2009). As a result, the oxidation resistance of the γ - γ' coating gets enhanced.

In the present γ - γ' coating, the Pt concentration in as-coated condition was nearly 20 at%. There was a small downhill gradient in Al concentration from the substrate (13 at%) to the coating (10 at%). After oxidation exposure, an enrichment of Al in the coating was observed, as evident from its concentration value of 15 at% after 100 h of exposure at 1100 °C (figure 4). The corresponding value for the substrate decreased to about 8 at%. The observed improvement in the oxidation resistance can be partially attributed to the above enrichment of Al in the coating in presence of Pt. Selective oxidation of Al to form an alumina scale, as mentioned above, was the other factor that led to the improvement in the oxidation resistance of the γ - γ' coated alloy. As the duration of oxidation exposure increased, the concentration of Pt in the coating decreased continuously, as evident from figure 7,

because of the diffusion of this element into the substrate. The coating also continuously lost Al towards the formation of the oxide scale, as evident from the formation of the surface γ layer in the oxidized samples (figure 7a). As a result, its oxidation resistance deteriorated after about 100 h, as indicated by the continuous weight loss observed (figure 5). From the present study, it appears that the nature of oxide formation on the γ - γ' coating, i.e. initial uniformity in the oxide layer (figure 8(a)) followed by localized oxidation (figure 10), was similar to that observed in case of the uncoated alloy (Sun *et al* 1994). Further similarity was also observed in terms of portions of the coating getting embedded in the oxide layer during oxidation (figure 8). Therefore, it can be assumed that the mechanism of oxidation in case of γ - γ' coated CM-247LC alloy was similar to that reported for the uncoated alloy (Das *et al* 2003). In other words, despite the beneficial role of Pt in enhancing the oxidation resistance of the alloy, its presence on the surface (in the form of γ - γ' coating) did not alter the mechanism of oxidation of the alloy. It is observed that once embedded in the oxide scale, the substrate pieces gradually get converted to oxides, leaving behind pure Pt because of its inertness. This is the reason for which pure Pt was detected after oxidation both by XRD (figure 2) and by EDS.

Unlike the γ - γ' coating, the β coating in as-coated condition had a much larger Al content (figure 4), which enabled the formation and maintenance of an alumina scale during the entire 1000 h period of cyclic oxidation. The presence of Pt in the coating assisted this process by enhancing the adherence of the oxide scale to the coated substrate (Felten and Petit 1976; Allam *et al* 1980). As a result, the β coating provided much superior oxidation resistance as compared to the γ - γ' coating. Such superior oxidation resistance of β -type Pt–Al bond coats has also been reported in several previous studies (Farrell *et al* 1987; Das *et al* 1999). It may be pointed out here that the penetration of the γ - γ' coating and damage to the underlying substrate by localized oxidation after about 50 h (figure 7b), as mentioned previously, could happen because the coating thickness was fairly less (40 μ m). In case of β coating, however, not only the coating thickness was much higher at 90 μ m, but also the oxidation damage to the coating did not occur in a localized manner as observed in γ - γ' coating.

From the previously reported studies (Zhang *et al* 2006; Stacy *et al* 2007; Haynes *et al* 2008; Das *et al* 2009), it can be concluded that the application of γ - γ' bond coats leads to reasonable enhancement of the oxidation resistance of substrate superalloys. However, it is unclear from these studies whether the oxidation resistance of these coatings provided is adequate from the standpoint of their use as bond coats in TBCs, especially under thermal cycling conditions. For example, Haynes *et al* (2008) have reported that the γ - γ' coating on alloy Rene 142 (composition in at%: Ni–14Al–12Co–8Cr–2Ta–2W–1Re–1Mo)

showed good cyclic oxidation resistance at both 1050 and 1100 °C, as indicated by positive weight change over 700 1-h cycles. Das *et al* (2009), on the contrary, have found such a coating on Ru-containing single crystal superalloys to exhibit positive weight change over a much shorter period of only 150–160 h. The corresponding value for the present coating on CM-247LC alloy (as examined in the present study) was even smaller at 110 h. It is well known that the elements such as W, Ta and Ru present in superalloys are deleterious from the standpoint of oxidation resistance of these alloys (Wu *et al* 2008). When present in substantial quantities, as in CM-247LC and in the alloys used by Das *et al* (2009), these elements from the substrate get incorporated into the diffusion coatings such as γ - γ' and cause degradation in their oxidation resistance. Thus, the poorer oxidation resistance of γ - γ' coating on CM-247LC as compared to that on Rene 142 (Haynes *et al* 2008) can be ascribed to the substantially higher contents of W and Ta in the former alloy.

As mentioned earlier, the primary reason for which Pt modified γ - γ' bond coats are being developed for TBCs is the potential they offer to prevent/reduce rumpling at the bond coat surface. However, in order to be an alternative to β bond coats in TBCs, it is also important that γ - γ' coatings have high temperature oxidation resistance compared to that of β coatings. The present study suggests that the cyclic oxidation performance of γ - γ' bond coats on superalloy CM-247LC is much inferior to that of β bond coats. A similar trend has also been reported in case of other superalloy substrates (Haynes *et al* 2009). Therefore, despite the potential of Pt-modified γ - γ' bond coats to reduce rumpling, it appears that their oxidation performance needs to be enhanced considerably before they can be considered as an alternative to their β counterparts. The oxidation performance of γ - γ' coatings can possibly be enhanced by adopting the second method of coating formation, as mentioned earlier, is adopted wherein a small amount of Al is added to the coating by pack aluminizing process after the diffusion treatment. Minor additions of reactive elements such as Hf to the coating during the aluminizing process may also enhance its oxidation resistance (Gleeson *et al* 2004b, 2006).

5. Conclusions

The present study has examined the microstructure of a Pt-modified γ - γ' bond coat on CM-247LC Ni-base superalloy and evaluated its cyclic oxidation performance at 1100 °C in air. The above coating has been compared with a conventional β -(Ni, Pt)Al bond coat on the same superalloy. The following conclusions can be drawn from the present study:

(I) The oxidation resistance of CM-247LC alloy was enhanced in the presence of the γ - γ' bond coat. However, the oxidation resistance provided by this coating was far inferior to that provided by the β coating.

(II) Oxidation exposure at 1100 °C caused significant localized surface damage to γ - γ' -coated superalloy samples. The coating got completely penetrated at the locations of such damage and the underlying substrate was oxidized. Such a mechanism of coating damage was not observed in case of the β bond coat even after prolonged oxidation exposure of nearly 1000 h.

(III) From this study, it appears that, despite the potential of γ - γ' bond coats to reduce rumpling, their oxidation resistance needs to improve significantly for them to be considered as an alternative to conventional β -(Ni, Pt)Al bond coats for use in TBCs.

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