

The Influence of Pd on the Structure and Oxidation Performance of β -NiAl Diffusion Coatings

E. Pauletti^a , A.S.C.M d' Oliveira^{b*} 

^aUniversidade Federal do Paraná (UFPR), Programa de pós-graduação em Engenharia e Ciência dos Materiais, Curitiba, PR, Brasil.

^bUniversidade Federal do Paraná (UFPR), Departamento de Engenharia Mecânica, Curitiba, PR, Brasil.

Received: August 08, 2022; Revised: November 15, 2022; Accepted: December 12, 2022

Aluminized coatings on Ni based alloys greatly contribute to achieve process efficiency at higher operating temperatures. The present study characterized Pd-modified and unmodified aluminized coatings and compared with those of Pt-modified coatings regarding the mechanisms of formation and oxidation performance. The results show that Pd reduces the driving force for diffusion of Al during coating formation, increases outward diffusion of Ni and reduces diffusion of alloying elements (Cr and Ti) into the intermetallic layer. In contrast, Pt increases the driving force for diffusion of Al and the mobility of Al in the intermetallic layer of the aluminized coating. These characteristics have a direct impact on oxidation at 1000 °C that showed that Pd reduced the rate of θ -Al₂O₃ → α -Al₂O₃ transformation, accounting for higher density of voids at the interface β -(NiAl)/ θ -Al₂O₃, diffusion of oxygen into the coating, spalling and faster degradation of coatings.

Keywords: Ni-based superalloy, Diffusion coatings, Aluminides, Palladium, Oxidation, Al₂O₃.

1. Introduction

Pt is known to improve the oxidation performance of aluminized coatings formed on Ni-based superalloys. This behavior can be explained by different mechanisms discussed in the literature, most notably in studies by Haynes et al.¹ and Svensson et al.², who found that the presence of Pt inhibits the formation of voids at the β -(NiAl)/ α -Al₂O₃ interface, increasing adhesion between the oxide scale and the intermetallic layer. A possible explanation for this behavior lies in the increased mobility of Al in the β -(NiAl) lattice in Pt modified coatings, leading to reduced Kirkendall porosity at the coating/oxide scale interface during oxidation and, therefore, reduced displacement of the α -Al₂O₃ scale.

To reduce the dependence on Pt as a performance enhancement of aluminized coatings, there is a need to identify alternative elements in the platinum group metals (PGM) that allow aluminized coatings with similar properties to those modified with Pt to be produced at a competitive cost. Notable among these elements is Pd, which has properties similar to those of Pt³.

Data for Pd in the literature shows that Pd reduces the diffusion of alloying elements from the substrate towards the intermetallic layer stabilizes β -(NiAl)⁴. However, contrary to the results for Pt, the impact of Pd on the oxidation behavior of β -(NiAl) intermetallic is still the subject of debate. Studies have shown that Pd improves the oxidation performance of β -(NiAl) intermetallic above 1100°C^{5,6}, associated with greater stability of the Al₂O₃ scale. However, at temperatures close to 1000°C there is no agreement as to the impact of Pd on the oxidation performance. Under

isothermal conditions He et al.⁷, reported that the mechanisms for high temperature oxidation prevail but others⁸⁻¹⁰ have found that in aluminized coatings exposed to oxidation at 1100 °C and lower temperatures, Pd either has no impact on, or might even increase, degradation of the intermetallic layer. The latter results are strengthened by investigations on aluminized coatings modified with Pd and another element (Pd + Pt or Pd+Hf)¹¹⁻¹⁴. In aluminized coatings modified with Pt + Pd, the presence of Pd in the intermetallic layer prevents the formation of PtAl₂^{11,12}, a very brittle intermetallic phase that can compromise the mechanical properties of the coating¹⁵. Hong et al.¹¹ and Swadzba et al.¹² results showed an enhanced oxidation performance above 1100 °C for aluminized coatings modified with a combination of Pd/Pt. Yet, some authors refute this result and claim that Pd does not impact the oxidation behaviour of β -(NiPt)Al^{10,14}.

Existing studies on the effect of Pd in aluminized coatings fail to elucidate the impact of Pd on the phenomena that determine oxidation behavior, particularly the properties of the intermetallic that acts a reservoir of Al in coatings and the characteristics of the Al₂O₃ scale formed during oxidation at the lower range of temperatures 900-1000 °C. The present study seeks to clarify the influence of Pd on the oxidation performance at 1000 °C of aluminized coatings on Ni superalloys of particular relevance for equipment that have a heavy on/off cycle exposing material to a wider range of temperatures. The study investigates the influence of Pd on coating structure and the diffusion of alloying elements from the substrate to the coating, as well as on the characteristics of the oxide scale formed on the surface of the coating after exposure to 1000 °C. A comparison with Pt-modified aluminized coatings is also made.

*e-mail: sofmat@ufpr.br

Table 1. Chemical composition of the NI-183 alloy measured by EDX (wt. %).

Ni superalloy	Ni	Al	Cr	Co	Ti	W	Ta	Mo
NI-183	Bal.	3.2	14.5	9.2	2.7	2.9	2.1	1.9

2. Experimental procedures

A precipitation-hardened Ni superalloy commercially available as NI-183 with the chemical composition shown in Table 1 was used as the substrate. The microstructure of the NI-183 alloy substrate consists of a γ -Ni matrix containing γ' -Ni₃Al precipitates (60%), MC carbides (M= Ti, W and/or Ta) and M₂₃C₆ (M = Cr and/or Mo).

NI-183 alloy samples (area - 1 cm², thickness - 5 mm) were prepared with 600-grit carbide paper to obtain a similar surface on all the samples and then cleaned in an ultrasonic bath for 15 min and degreased by immersion in a NaOH (60 g/L) + Na₂CO₃ (30 g/L) solution at 60 °C for 5 min¹⁶. Before electrodeposition, surface activation was carried out by anodic attack with H₂SO₄ and Ni electroplating was performed in a Watts bath with processing parameters adapted from the ASTM B558 standard¹⁷. These are typical procedures to enhance the adherence of both Pt and Pd electrodeposited layers.

Pd electroplating was performed with PdCl₂ salt (60% Pd basis) (Sigma Aldrich). The reagents used in the electroplating bath are shown in Table 2¹⁸.

The parameters used for electrodeposition of Pd on the surfaces of the NI-183 Ni superalloy are listed in Table 3. These were chosen to obtain continuous, thick and adherent Pd layers that allow to obtain rich Pd aluminized coatings. Considering the low uniformity of the Pd deposited layers two similar thicknesses of 8.0 μ m and 9.6 μ m [samples referred to as Pd (8.0 μ m) and Pd (9.6 μ m)] were deposited and then heat treated at 830 °C for 2 h in an argon atmosphere. Heat treatment is necessary because of the large amount of hydrogen adsorbed during Pd electroplating³, generating high internal stress that could lead to spallation of the electrodeposited Pd layer. In addition, the heat treatment causes interdiffusion between the Pd, Ni and alloying elements.

The surfaces with and without Pd were processed by pack aluminization with the samples immersed in the pack mixture, which was composed of 30% Al, 3% NH₄Cl and 67% Al₂O₃ (%wt.). Pure Al (99.95%) was used as the source of Al. Pack aluminizing was carried out at 1030 °C for 3 h in a controlled overpressure argon atmosphere¹⁹.

Isothermal oxidation was performed in an air furnace at 1000 °C for 200 h, to assess the impact of Pd on the polymorphic transformation of alumina. The $\theta \rightarrow \alpha$ -Al₂O₃ transformation is reported to occur at 950 °C^{20,21}, also equipment exposed to repeated on/off cycles are more frequently exposed to lower temperature than those found during continuous operation. For the first 80 h of testing, the mass gain was measured at 8 h intervals and then 24 h intervals. For comparative purposes, the oxidation performance was also evaluated for aluminized NI-183 Ni alloy without Pd.

Cross sections of the aluminized coatings before and after isothermal oxidation were prepared following standard metallographic grinding and polishing procedures. A Ni layer was electroplated on the surface of the oxidized samples

Table 2. Analytical reagents used for electroplating in the Pd bath.

Analytical reagent	Chemical formula	Concentration in the bath
Palladium chloride	PdCl ₂	10 g/L
Ammonium chloride	NH ₄ Cl	50 g/L
Ammonium hydroxide	NH ₃ .H ₂ O (28%)	15 mL/L
Ammonium phosphate dibasic	(NH ₄) ₂ HPO ₄	50 g/L

Note: reagents were diluted in distilled water.

prior to metallographic preparation to avoid spallation of the oxide scale.

The coatings were characterized (after aluminization and isothermal oxidation) by X-ray diffraction (XRD) using Cu K- α and a scanning speed of 1 °/min with 2 θ ranging from 10 to 110 °; by scanning electron microscopy (SEM) and semiquantitative EDS analysis; and by confocal Raman microscopy with a 532 nm laser (green) and a spectral band between 14,000 and 15,000 cm⁻¹ (absolute units). The Raman mapping was performed with an integration time of 0.108 s, a diffraction grating with 600 lines/mm and a blaze wavelength of 500 nm. The study by Tolpygo and Clarke²² was used as a reference to determine the spectral ranges for θ -Al₂O₃ and α -Al₂O₃.

3. Results and Discussion

3.1. Effect of Pd on the aluminized coatings

The microstructure of the coating cross sections (Figure 1), the elemental composition (Table 4) and XRD at the surface (Figure 2) show that the coatings are constituted of rich Al intermetallic phases: δ -Ni₂Al₃ and Al-rich β -(NiAl) matrix, in agreement with reports in the literature^{5-7,11,23,24}. The former forms at the upper surface of coatings and in the early stages of oxidation losses in Al induce the transformation to rich Al β -(NiAl)^{19,25}. Hence, for the duration of the oxidation cycle only β -(NiAl) is present. As the concentration of Pd increases, Ni atoms ($r_a = 125$ pm) are replaced by Pd atoms ($r_a = 139$ pm) in the crystal structure of β -(NiAl), confirmed by the shift in the XRD peak of β -(NiAl) toward smaller angles (increasing lattice parameter). When present, Pd has a gradient that decreases from the surface to the Ni-based substrate, the maximum Pd content is given by its solubility of more than 30 at. % in this intermetallic²⁶. Pd gradient in coatings varies depending on the of the electrodeposited layer. The Pd chemical profile at the cross section of coatings exhibits a similar trend across coatings but at the top layer (40 μ m) Pd average content is higher over a larger width in coatings processed on the 9.6 μ m thicker Pd layer, Table 4. Across the diffusion zone where precipitates formed with alloying elements from the substrate Pd content reduces to a residual content over a region of 30 μ m and 50 μ m on coatings processed on the 8.0 μ m and 9.6 μ m Pd layer, respectively.

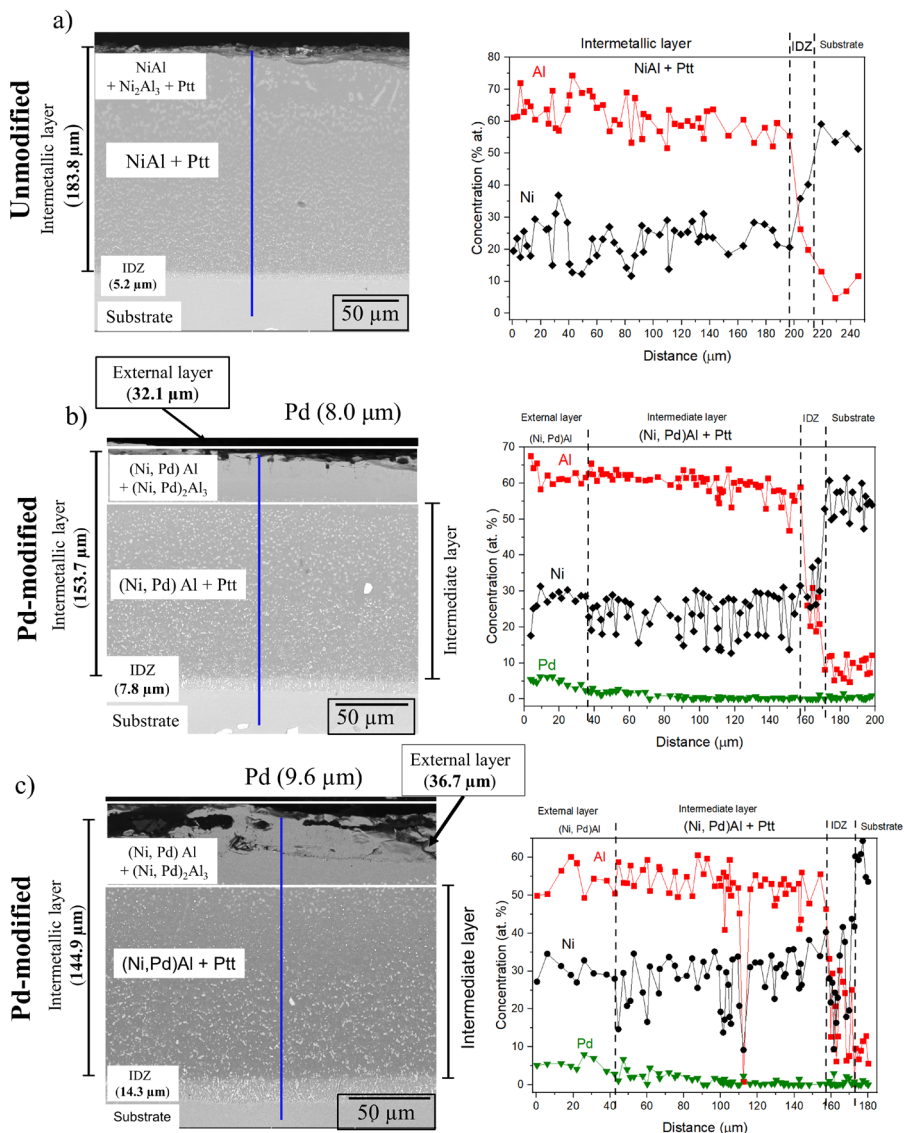
Table 3. Parameters used to Pd electroplate the surface of the Ni superalloy.

Palladium salt	Pd concentration in bath (g/L)	Temperature ($^{\circ}$ C)	pH	Current density (mA/cm^2)	Voltage (V)	Electroplating rate ($\mu\text{m}/\text{min}$)
PdCl_2	10	between 40 and 45	7.3	7.0	1.8 to 1.9	0.3

Table 4. Average chemical composition (at. %) of layers for the unmodified and Pd-modified aluminized coatings after processing at 1030 $^{\circ}$ C.

Thickness of electroplated Pd layer	Layer	Ni	Al	Cr	Ti	Pd
0 μm	External	23.9	62.5	5.9	2.4	0
	IDZ	50.3	12.7	17.8	6.3	0
8.0 μm	External	27.9	62	3.1	0.2	5.3
	Intermediate	23.9	62.1	5.3	2.2	1.7
9.6 μm	IDZ	29.3	33.8	17.7	8.3	0
	External	29.9	56.7	5.0	1.1	4.4
	Intermediate	29.9	54.9	5.2	2.7	2.0
	IDZ	30.5	30.7	17.7	9.8	0

Note: The total concentration (100%) is obtained by adding the concentrations of the remaining elements (W, Mo, Ta).

**Figure 1.** Cross section and chemical profile for Ni, Al and Pd of aluminized coatings (SEM, BSE mode) processed at 1030 $^{\circ}$ C: a) unmodified; b) and c) modified with Pd layers measuring 8.0 and 9.6 μm , respectively (Ptt: precipitates; IDZ: interdiffusion zone).

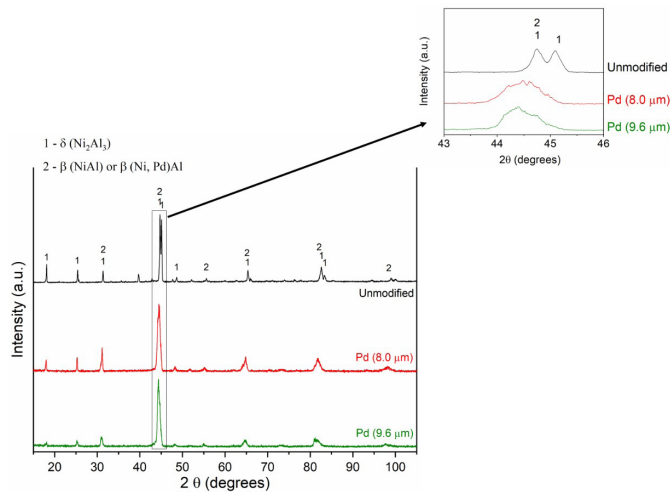


Figure 2. XRD of the surface of (unmodified and Pd-modified) aluminized coatings after processing at 1030 °C. Insert is a zoom-in view of the main peak region.

A thin interdiffusion zone (IDZ) and the presence of carbides in the intermetallic layer (Figure 1) can be observed in all the coatings, reflecting the preferential inward diffusion of Al^{19,25}.

Inward diffusion of Al occurred in all the coatings, but differences can be identified between the coatings without Pd (Figure 1a) and those with this element (Figure 1b and c). The presence of Pd in the intermetallic layer led to a thicker IDZ, a thinner intermetallic layer and the formation of a precipitate-free external layer. This result contrasts with reports claiming that Pd induces the formation of an intermetallic layer with precipitates in aluminized coatings^{5-7,11,23}.

An important contribution to the understanding of the role of Pd was made by Lamesle et al.²⁷, who showed that for stoichiometric β -(NiAl), Pd caused an increase in the mobility of Ni in β -(NiAl). Extrapolation of this analysis to the Al-rich β -(NiAl) intermetallic identified in the present study would suggest that as the concentration of Pd increases so does the mobility of Ni in the intermetallic layer. This is corroborated by the increase in the thickness of the IDZ (Figure 1) with the thickness of the electrodeposited Pd layer (concentration of Pd), a consequence of the increasing diffusion of Ni in the coatings. Similar behavior has been observed by other authors^{5,28}. Further evidence of the increase in the mobility of Ni with increasing concentration of Pd is the formation of Ni-rich intermetallic phases, is shown by the reduction in the intensity of the peak corresponding to the δ -(Ni₂Al₃) intermetallic (presented enlarged in Figure 2), a compound in which the mobility of Ni is lower than that of Al²⁹.

The literature shows that the impact of Pd on the diffusion characteristics of alloying elements is not yet well understood over the range of processing conditions that coatings might be processed^{5,9,23,24}. Under the processing conditions used in the present work, a reduction in the driving force for diffusion of Al was identified, and this was confirmed by the reduction in the thickness of the intermetallic layer.

For coatings processed on the same substrate, contrasting behaviors are observed when the influence of Pd and of Pt on the mobility of Al and Ni in the intermetallic layer

Table 5. Microstructural alterations due to modification of aluminized coatings with Pd and the proposed mechanisms.

Microstructural alteration due to modification of coating with Pd	Proposed mechanism
Reduction in thickness of intermetallic layer	Reduction of driving force for diffusion of Al
Increase in size of IDZ	Increase in outward diffusion of Ni from substrate to intermetallic layer
Absence of Cr and Ti precipitates in external layer	Reduction in diffusion of Cr and Ti to outer layer

are compared: unlike Pd, Pt causes an increase in coating thickness³⁰ associated with enhanced mobility of Al in the microstructure of β -(NiAl)^{31,32}. To understand the impact of Ti and Cr on oxidation performance in Pd- and Pt-modified coatings, it is important to identify how their distribution is altered in these coatings. In Pd-modified coatings an external layer free of Ti and Cr precipitates is observed due to their lower diffusion into the intermetallic layer when Pd is present (Table 4), a finding corroborated by He et al.⁷. In contrast, Pt has little impact on diffusion of Ti in the intermetallic layer, allowing Ti-rich phases to precipitate at the surface^{30,33}, but reduces diffusion of Cr³⁰.

Figure 3 summarizes the differences observed between aluminized coatings with and without Pd: modification of the aluminized coatings with Pd led to a thinner intermetallic layer, thickening of the interdiffusion zone (IDZ) and formation of an external precipitate-free layer. The mechanisms associated with each observed change are summarized in Table 5.

3.2. Coatings after isothermal oxidation at 1000 °C

High temperature equipment exposed to heavy duty on/off cycles are required to have an enhanced oxidation behaviour over a wider range of temperatures, that depend on the features of the oxide scale that forms during exposure to temperature. Assessing the impact of Pd on the formation of the

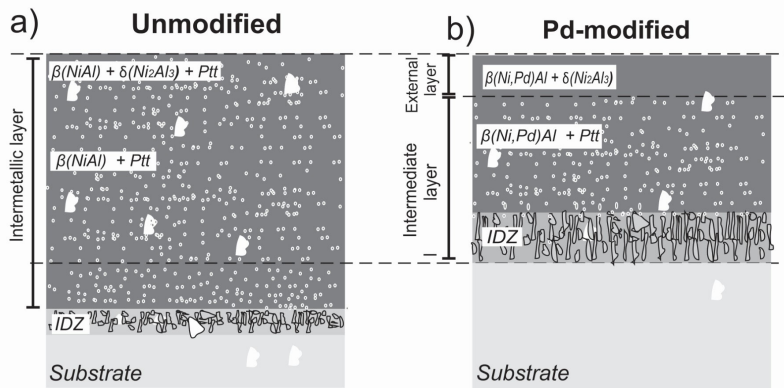


Figure 3. Schematic representation highlighting the different microstructures for aluminized coatings: a) unmodified; b) Pd-modified.

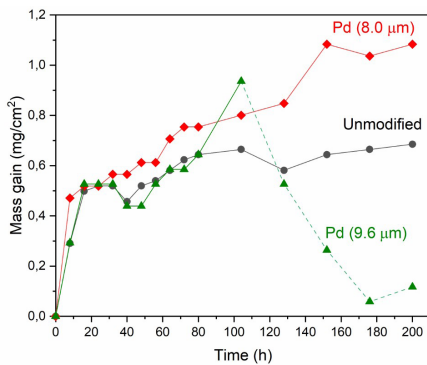


Figure 4. Mass gain of Pd-modified and unmodified aluminized coatings during isothermal oxidation at 1000 °C for 200 h.

alumina oxide scale at the outset of the stable α - Al_2O_3 brings important information to optimize performance of protective coatings and efficiency of equipment. Isothermal oxidation at 1000 °C, Figure 4, on aluminized coatings starts with a high mass gain associated with the formation of transient oxides and is followed by a stage with reduced oxidation rate due to the formation of stable α - Al_2O_3 . The higher mobility of Al in coatings without Pd accounts for a fast formation of a continuous Al_2O_3 scale, and a slower oxidation process. At the testing temperature used the rich Pd aluminized coatings influence the characteristics of the oxide scale formed on the surface of aluminized coatings. Although the stable oxide scale forms at the beginning of oxidation, that should have reduced diffusion of oxygen into the coating³⁴, under the testing conditions used Pd accelerates the oxidation kinetics, Figure 4, a finding corroborated by He et al.⁷ It is observed that aluminized coatings on both thick Pd layers accelerated the kinetics of oxidation compared to those of the unmodified aluminized coating. Also, is worth noting that the thicker 9.6 μm electroplated Pd layer showed that mass gain increased at a faster rate leading to spallation after 100 h. This behavior might be associated with a less uniform thickness and micro defects in this thick Pd layer were magnified during exposure to temperature leading to premature failure of coatings.

Further understanding of the differences induced by Pd on the oxidation of aluminized coatings is given by analysis

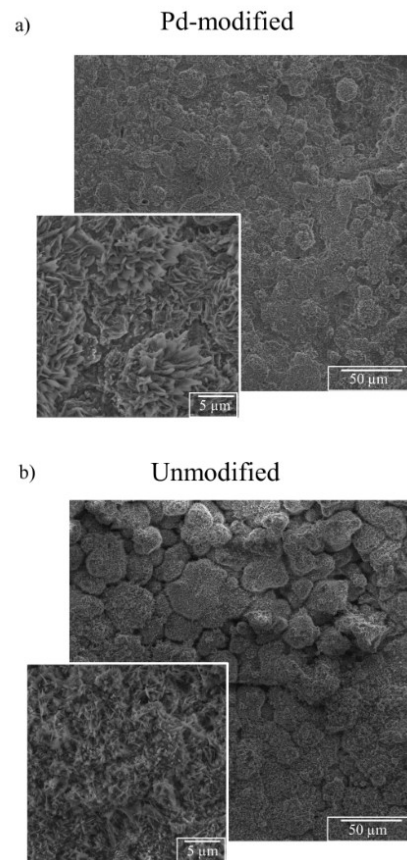


Figure 5. Morphology of Al_2O_3 scale at the surface of aluminized coatings after isothermal oxidation at 1000 °C for 200 h; a) Pd-modified coating (9.6 μm); b) unmodified coating.

of the Al_2O_3 scale on the surface of the coatings shows the impact of Pd on its morphology, Figure 5. For Pd-modified coatings (Figure 5a), evidence that metastable θ - Al_2O_3 is predominant at the surface of the coatings is provided by the needle-like (or whisker-like) morphology of the scale^{20,22}. Raman spectroscopy (Figure 6) confirms that metastable θ - Al_2O_3 formed over a large surface area (Figure 6b, c, and e) but that α - Al_2O_3 is also present (Figure 6a, c and d).

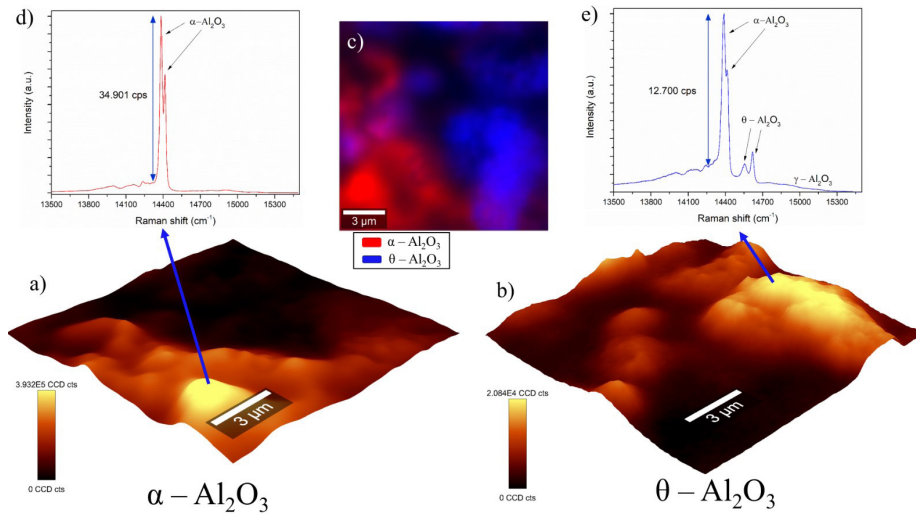


Figure 6. Confocal Raman mapping at the surface of the Pd-modified coating (9.6 μm) after isothermal oxidation at 1000 $^{\circ}\text{C}$ for 200 h: a) mapping in a spectral range from 14,308 to 14,472 cm^{-1} ($\alpha\text{-Al}_2\text{O}_3$); b) mapping in a spectral range from 14,506 to 14,663 cm^{-1} ($\theta\text{-Al}_2\text{O}_3$); c) mapping showing the distribution of polymorphic forms of Al_2O_3 ; d) and e) spectra in a specific region of the surface.

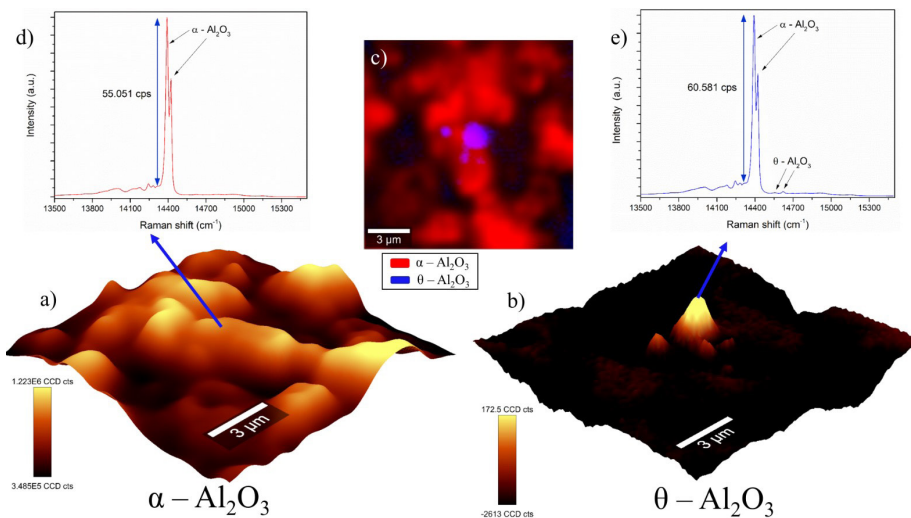


Figure 7. Confocal Raman mapping at the surface of the unmodified aluminized coating after isothermal oxidation at 1000 $^{\circ}\text{C}$ for 200 h: a) mapping in a spectral range from 14,308 to 14,472 cm^{-1} ($\alpha\text{-Al}_2\text{O}_3$); b) mapping in a spectral range from 14,506 to 14,663 cm^{-1} ($\theta\text{-Al}_2\text{O}_3$); c) mapping showing the distribution of polymorphic forms of Al_2O_3 ; d) and e) spectra in a specific region of the surface.

At the surface of the aluminized coating without Pd, Figure 5b, the platelet-like morphology is characteristic of stable $\alpha\text{-Al}_2\text{O}_3$ ^{20,22}. Raman spectroscopy analysis corroborates this finding as $\alpha\text{-Al}_2\text{O}_3$ predominates on this surface (Figure 7a, c and d), and only a small area with high-intensity $\theta\text{-Al}_2\text{O}_3$ bands can be identified (Figure 7b, c and e). These results agree with those of Rybicki and Smialek²⁰ and Tolpygo and Clarke²², who used similar oxidation conditions.

Refinement of the analysis of both aluminized coatings after oxidation at 1000 $^{\circ}\text{C}$ for 200 h shows that Pd reduces the rate of the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation and causes spallation of the oxide scale (Figure 4). The higher relative intensity of the $\theta\text{-Al}_2\text{O}_3$ bands for the Pd-modified aluminized coating (Figure 8) further confirms this behavior. These results

contrast with those of Li et al.²³, who argue that Pd accelerates the $\theta\text{Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation. However, processing conditions might have had a role on the data reported as these authors claim that the metastable $\theta\text{-Al}_2\text{O}_3$ predominates after 1000 h of oxidation at 1000 $^{\circ}\text{C}$ in coatings without Pd, a finding that goes against predictions based on literature and the experimental observations in our study.

A better understanding of the effect of Pd on the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation can be gained from an examination of the impacts of this element on the diffusion of the alloying elements at 1000 $^{\circ}\text{C}$. Pd mapping at the cross section shows a concentration near the top surface and elemental composition analysis in the external layer of the aluminized coatings after oxidation (Figure 9) shows that Pd

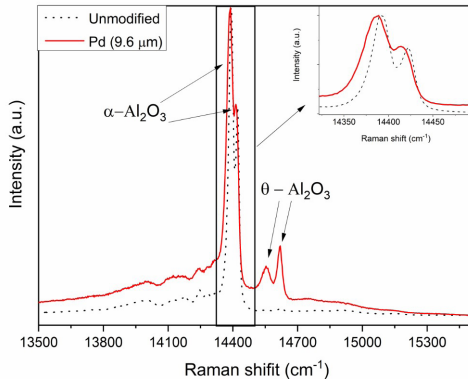


Figure 8. Confocal Raman analysis of Al_2O_3 oxide scale formed at the surface of a Pd-modified coating ($9.6\ \mu\text{m}$) (Figure 6e) and an unmodified aluminized coating (Figure 7e) after isothermal oxidation at $1000\ ^\circ\text{C}$ for 200 h.

reduced the diffusion of Cr, Ti and Co towards the surface. As Cr favors nucleation of $\alpha\text{-Al}_2\text{O}_3$ ²¹ and Co contributes to the formation of a more stable $\alpha\text{-Al}_2\text{O}_3$ ³⁵, it is reasonable to raise the hypothesis that Pd reduces diffusion of Cr and Co towards the surface of the coatings, contributing to the reduction in the rate of the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation.

Comparison of the impact of Pd on the polymorphic transformation of Al_2O_3 discussed above with that of Pt carried out by Cadoret et al.³⁶, reveals contrasting behaviors. Different oxidation results are to be expected following observations from Cadoret et al. that the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation is accelerated in Pt-modified coatings, whereas in Pd-modified coatings the rate of the polymorphic transformation is reduced.

Further impacts of Pd in aluminized coatings can be observed at the oxide scale/NiAl coating interface, Figure 10. The behavior at this interface is better understood if considering that the metastable $\theta\text{-Al}_2\text{O}_3$ does not reduce

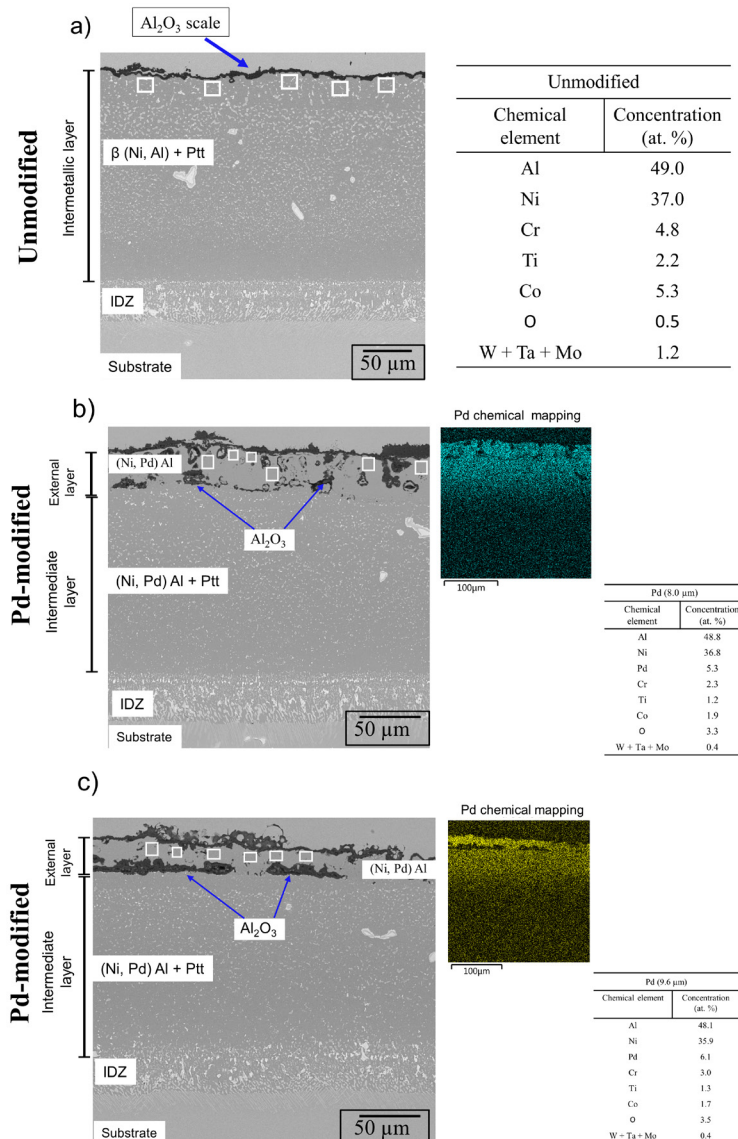


Figure 9. Average chemical composition (at. %) of aluminized coatings after isothermal oxidation at $1000\ ^\circ\text{C}$ for 200 h: a) unmodified; b) Pd-modified ($8.0\ \mu\text{m}$); Pd-modified ($9.6\ \mu\text{m}$). The regions chosen for analysis are indicated by white squares.

diffusion of O into the coating as effectively as $\alpha\text{-Al}_2\text{O}_3$ ²¹. As the kinetics of the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation is slower in Pd-modified coatings, diffusion of O into these coatings is expected to be more significant, leading to degradation (internal oxidation). This behavior is further aggravated by the defects in the coatings.

The characteristics of the $\beta\text{-(NiAl)}/\text{Al}_2\text{O}_3$ interface help to elucidate the oxidation behaviour of the Pd-modified coatings, in which the presence of Pd induced spallation of the oxide (Figure 4). This behavior is consistent with the presence of a discontinuous oxide scale and a large number of defects and voids concentrated at the interface (Figure 10b and c), findings also reported by Oquab and Monceau after oxidation for 6 h at 900 °C³⁷.

A better understanding of the oxidation behavior exhibited by Pd-modified coatings is gained from the polymorphic transformation of alumina. The growth of $\theta\text{-Al}_2\text{O}_3$ is associated with vacancy formation that during oxidation agglomerate creating voids at the interface $\beta\text{-(NiAl)}/\theta\text{-Al}_2\text{O}_3$ ³⁸. Extrapolating this result to the processed coatings allows to state that as Pd favors $\theta\text{-Al}_2\text{O}_3$, hence the oxide scale is

expected to show a larger concentration of defects such as voids, compromising adherence. Lower adherence leads to spalling increasing degradation.

The characteristics of the oxide scale on the aluminized coatings are highlighted in the schematic representation in Figure 11 summarizing the main findings. In the Pd-modified coatings (Figure 11a), together with a high concentration of voids and defects, a whisker-like morphology associated with $\theta\text{-Al}_2\text{O}_3$ predominates because of the reduced rate of the $\theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation. In contrast, a continuous, defect-free $\alpha\text{-Al}_2\text{O}_3$ scale forms on the surface of the unmodified aluminized coating (Figure 11b), confirming that for the oxidation conditions used, $\theta\text{-Al}_2\text{O}_3$ was transformed into $\alpha\text{-Al}_2\text{O}_3$.

Findings in this study show that applications of aluminized coatings modified with Pd for equipment exposed to frequent on/off cycles have to be carefully selected. These systems are also exposed to temperatures lower than the typical operating isothermal temperature of 1100 °C or above, for long periods favoring the formation of $\theta\text{-Al}_2\text{O}_3$ scale that might compromise performance.

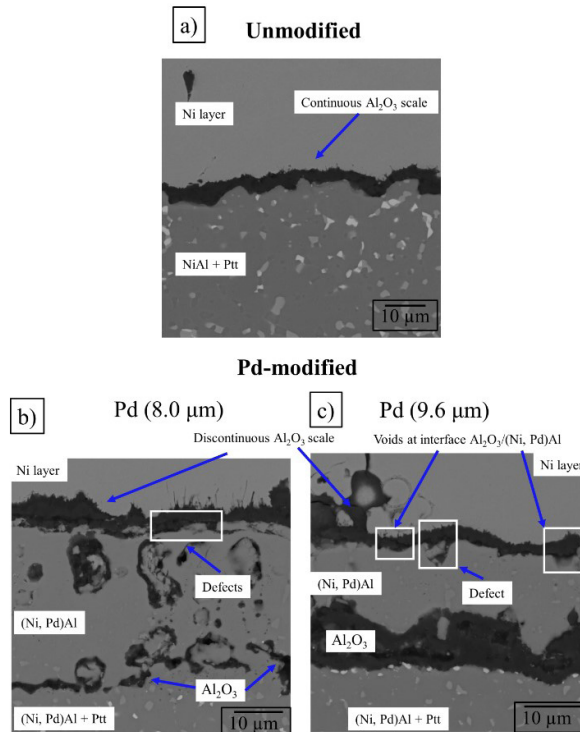


Figure 10. $\beta\text{-(NiAl)}/\text{Al}_2\text{O}_3$ and $\beta\text{-(Ni,Pd)Al}/\text{Al}_2\text{O}_3$ interfaces in aluminized coatings after isothermal oxidation at 1000 °C for 200 h: a) unmodified; b) Pd-modified (8.0 μm); c) Pd-modified (9.6 μm) (Ptt: precipitates).

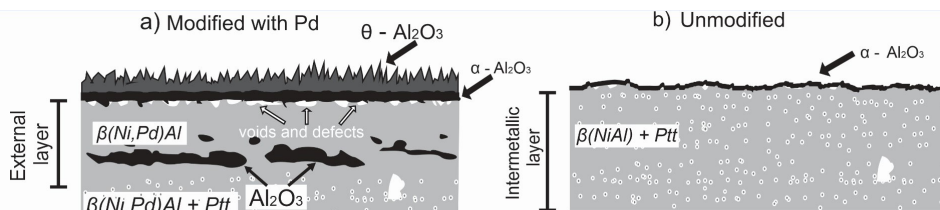


Figure 11. External layer of aluminized coatings after isothermal oxidation at 1000 °C for 200 h: a) Pd-modified; b) unmodified.

4. Conclusion

For the processing conditions used to assess the influence of Pd on the formation and oxidation performance at 1000 °C of aluminized coatings processed on NI-183 superalloy, it is possible to conclude that:

- in pack aluminized coatings modified with Pd, an Al-rich β -(Ni,Pd)Al intermetallic bilayer forms. This consists of a precipitate-free zone near the external surface on top of a precipitate-rich region and a thin IDZ near the Ni substrate;
- Pd and Pt have different impacts on the mobility of Al and Ni in the intermetallic layer. Pd increases the mobility of Ni, whereas Pt enhances the mobility of Al, and Pd produces a thicker IDZ, while Pt causes thickening of the intermetallic layer;
- At 1000 °C Pd reduces the rate of the θ -Al₂O₃ \rightarrow α -Al₂O₃ transformation, accounting for: a change in oxidation kinetics due to the predominance to the metastable scale which exhibits a large density of defects at the interface β -(NiAl)/ θ -Al₂O₃, that leads to the spalling of the oxide scale

5. Acknowledgments

Thanks are due to CAPES, CNPq, CNPq/INCT-INES and the ANEEL R&D program for supporting this project. Acknowledgments are also due to Petrobrás and Lactec Institutes for their helpful contributions.

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