PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 13 (2020), 11-22

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Nickel Base Superalloy Rene®80 – The Effect of High Temperature Cyclic Oxidation on Platinum-Aluminide Coating Features

M. M. Barjesteh[1], S. M. Abbasi[1*], K. Zangeneh Madar[1], K. Shirvani[2]

[1.] Metallic Materials Research Center, Malek Ashtar University of Technology (MUT), P.O. Box: 15875-1774, Tehran, Iran.

[2.] Department of Advanced Materials and New Energies, Iranian Research organization for Science and Technology (IROST), P.O. Box: 33535-111, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 7 Dec 2018
Final Revised: 4 MAr 2019
Accepted: 5 Mar 2019
Available online: 10 Jul 2019

Keywords:
Rene®80
Aluminizing
Platinum-Aluminide
Microstructure
Cyclic Oxidation.

ABSTRACT

Nickel base superalloy alloys are used in the manufacture of gas turbine engine components, which in use are exposed to high temperatures and corrosive environments. The platinum aluminide coatings described here have been developed to protect nickel base superalloy alloys from oxidation. In this study, the effect of cyclic oxidation, platinum layer thickness and aluminizing process on behavior of Pt-Aluminide (Pt-Al) coating on nickel-based superalloy Rene®80 have been investigated. For this purpose, after applying different thicknesses of Pt-layer (2, 6 and 8µm), diffusion aluminide coating in two types, high temperature-low activity (HTLA) and low temperature-high activity (LTHA) methods was performed. The results of microstructural investigations by Scanning Electron Microscopy and the X-ray diffraction analysis indicated that coatings include three zones in all thicknesses of the platinum layer and in both methods of aluminizing. The results of cyclic oxidation (1100 °C and 120 cycles) test showed that Pt-Al in all conditions improved the oxidation resistance of Rene®80. The best oxidation resistance is related to the specimen coated with 6 µm Pt by LTHA method, whereas the lowest resistance was related to 2µm Pt in the case of HTLA method. The weight changes during cyclic oxidation of 6µm Pt (LTHA) and 2µm Pt (HTLA) coatings were 3.8 and 6 mg, respectively. Also, the parabolic oxidation rate constants of these coatings were calculated as 1.5×10^{-12} and 3.8×10^{-12}, respectively. Prog. Color Colorants Coat. 13 (2020), 11-22© Institute for Color Science and Technology.

1. Introduction

As nickel-based superalloy, Rene®80 provides appropriate mechanical properties at elevated temperatures, it has been widely used in the manufacturing of turbine engine blades [1]. In order to enhance the corrosion and oxidation resistance of this alloy, its surface is commonly subjected to aluminide diffusion coating treatment [2]. Nowadays this kind of coatings which are based on intermetallic β-NiAl compound, are modified with such precious metals as platinum to enhance their oxidation and corrosion resistance [3]. At first, an initial layer of platinum was applied on the surface and after that, aluminum is diffused into it by two ways: High Temperature-Low Activity (HTLA) or Low Temperature-High Activity (LTHA). The investigation results about the effects of temperature and Al-concentration on the formation mechanism of aluminide coating applied on a nickel

*Corresponding author: sma.abbasi@yahoo.com,
sma_abbasi@mut.ac.ir

base superalloy IN738LC via low activity gas phase aluminizing process, showed that coating formed by inward diffusion of Al at 850 °C, whereas it was initially formed by inward diffusion of Al, followed by outward diffusion of Ni at 1050 °C [4]. The microstructure and high-temperature corrosion behaviors of aluminide coatings by low-temperature pack aluminizing process applied on carbon steel have been investigated by Zhan et al. [5]. The results of this work indicated that the aluminide coating significantly enhanced the high-temperature oxidation and sulfidation resistance of the alloy. The oxidation behavior of platinum aluminide coated nickel-based superalloy CMSX-4 has also been investigated by Reed et al. [6]. Their results showed that the oxidation performance at 1100 °C improved with increasing Pt thickness. In addition, the degree of rumpling of the alumina scale was also decreased with increasing platinum. The superior oxidation resistance of platinum modified aluminide coating is a consequence of the β-NiAl formed during aluminization containing an enhanced Al/Ni ratio and decreased concentrations of the refractory elements [6]. Also, the presence of platinum in the aluminide coatings enhances the adherence of the alumina scale formed on the coated substrate during high-temperature exposure and thereby improves its resistance to oxidation [3]. The coating microstructure plays a big role in the diffusion behavior of Pt in platinum aluminide coatings during thermal cycles. Investigations showed [7] that after several thermal cycles in the single-phase β-(Ni,Pt)Al coating, Pt diffused from inside to outside by the processes of the Ni sublattice, and Kirkendall porosity, while in the two-phase coating [$PtAl_2$+ β-(Ni,Pt)Al] this kind of porosity was not detected.

Although in the past years, several investigations have been made on the influence of Pt-Al coatings on oxidation resistance of alloys, the effect of interaction, variation in the thickness of the initial platinum layer and the aluminizing process (in two methods of high and low activity) on the cyclic oxidation is still challenging. Therefore, in the present study, the influence of significant parameters on cyclic oxidation of platinum-aluminide coating of nickel base superalloy alloy Rene®80 was investigated.

2. Experiment

The cast nickel base super alloy Rene®80 (nominal composition: 0.16 C, 13.81 Cr, 9.69 Co, 4.23 Mo, 4.02 W, 3.02 Al, 4.87 Ti, 0.12 Fe, 0.05 Zr, 0.05 V, 0.03 Mn, 0.02 B, 0.02 Si, and balanced Ni, in %wt.) was used as the substrate material. Cylinder-shaped samples of 23 mm in length and 5.75 mm in diameter were cut from the same rods of the alloy.

Solution and first precipitation heat treatment were performed on samples at 1205 °C for 2 hours and at 1095 °C for 4 hours [8]. After cleaning the samples with acetone, the middle layer of nickel with 1-2 µm in thickness, coated on the surface for decreasing the negative effect of the chromium (available on the composition of the alloy) on the lack of adhesive property of platinum [9]. The platinum was plated using an electrolyte solution containing 14-18 mL of type P salt (di-nitro di-amino platinum), 70-90 g/L calcium carbonate (Na_2CO_3), 40-70 g/L sodium acetate ($NaCH_3COO$) and 1liter of distilled water at 90 °C under a flow density of 0.2-0.4 A/dm^2 and electrolyte pH of about 10.5 [10]. In order to achieve a platinum layer with a thickness of either 2 µm, 6 µm or 8µm, different times (150, 360 and 480 min) were considered in the plating process. It is worth noticing that the rate of 1 µm/min is obtained from producing the platinum layer with the selected condition for the platinum bath. Heat treatment at 1050 °C for 2 hours was applied on the platinum layer to enhance the adhesion and improve the platinum distribution in the substrate under the vacuum of the 10^{-5} torr, followed by cooling the specimens in the furnace at 400 °C followed by air-cooling [11]. The aluminizing process was performed under two conditions, namely low temperature-high activity (LTHA, at 750 °C for 4 hours and after that post aluminizing at 1050 ºC for 2h) and high temperature-low activity (HTLA, 1050 °C for 2 hours) via powder cementation. Compositions of the cementation powders used for LTHA and HTLA were selected as $2NH_4Cl$-12Al-86Al_2O_3 (wt.%) and $1NH_4Cl$-4Al-95Al_2O_3, respectively. After the formation of the platinum-aluminide coating on the surface, an aging treatment was carried out at 845 ºC for 16 h [8].

Microstructural studies were conducted using a Tescan scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) both prior to cyclic oxidation test (to ensure the quality of the coatings) and after the test according to ASTM E3 [12] and ASTM E883 [13]. X-ray diffraction analysis was also performed using an XRD apparatus (Inel Equinox 6000 with X'Pert High Score Plus v2.0, Cu Kα1 with Graphite monochromatic, 2θ = 16° to 93°, 40Kv, 37 mA) to determine distributions of different phases

across the coating thickness before and after cyclic oxidation. The residual stresses also were measured by XRD in as-coated condition.

Cyclic oxidation tests were evaluated on two samples for each coated and uncoated condition at 1100 °C for 120 cycles using a cubic Exciton furnace (1500±5 °C) with a heating rate of 30°/min. It should be mentioned that all of the surfaces of the samples have been coated. Each cycle included heating the samples at 1100 °C for 1h followed by natural cooling outside the furnace at room temperature for 30 min, which was long enough to cool the specimens to 24 °C. It is mentioned that before testing each sample was cleaned with acetone prior to oxidation. The samples were removed per cycle from the furnace to determine weight change. Their weights were measured by an electronic balance named Sartorius with a sensitivity of 10^{-4} g.

3. Results and Discussion

3.1. Microstructure and composition of the coatings

Figure 1 and 2 show the SEM images of the microstructure of the coating for various thickness of platinum after two HTLA and LTHA aluminizing methods, respectively.

As it may be seen, the microstructure of the coating on the outer layer is two-phase and includes β-(Ni, Pt) Al and ξ- $PtAl_2$. The next layers also are β-(Ni, Pt) Al (middle layer) and inter-diffusion zone (IDZ). A three-layer structure in Pt-Al coating is named as an equilibrium structure by Das et al. [15]. The XRD phase analysis also was performed on the samples whose results are provided in Figure 3. Accordingly, the $PtAl_2$ and (Ni, Pt)Al phases were identified which is in good agreement with the results obtained by Krishna et al. [3].

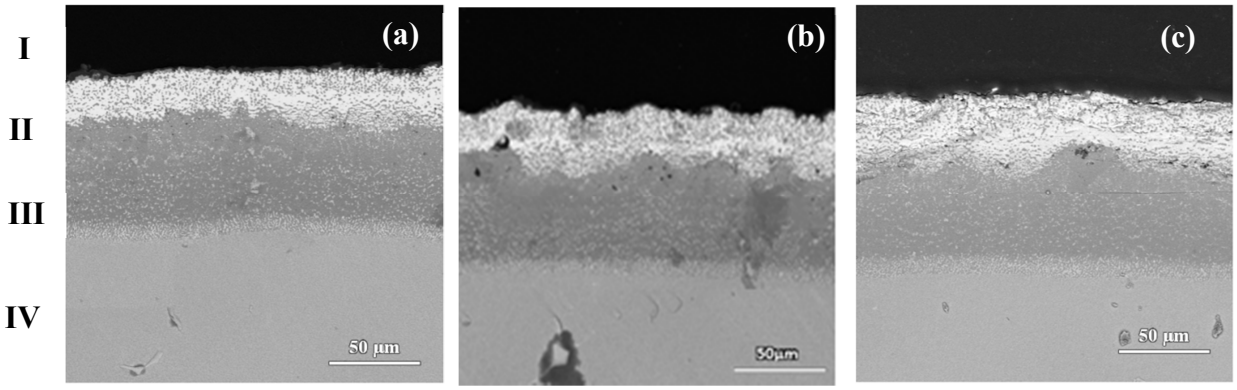

Figure 1: SEM images of the Pt-Al coating (the HTLA method) for the platinum layer with the thickness of a) 2µm, b) 6µm and c) 8µm. (I: ξ-$PtAl_2$ + β-(Ni,Pt)Al, II: β-(Ni,Pt)Al, III: interdiffusion zone, IV: substrate).

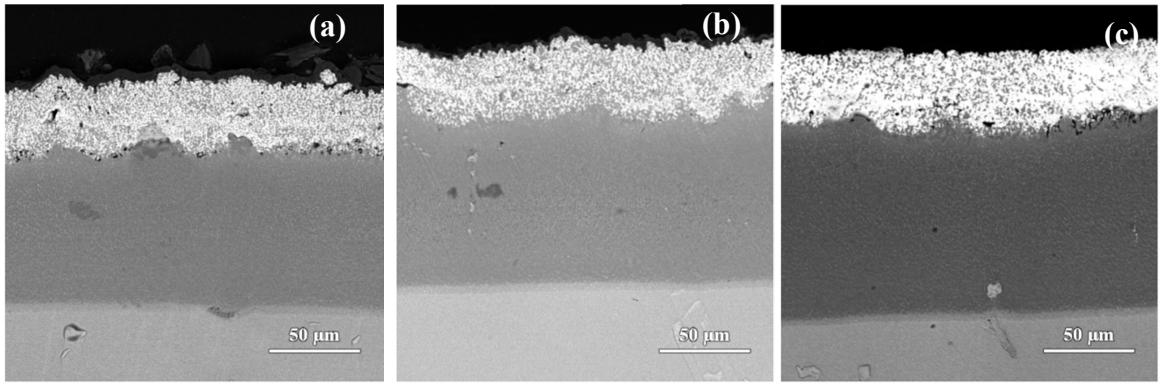

Figure 2: SEM images of the Pt-Al coating (the LTHA method) for the platinum layer with the thickness of a) 2µm, b) 6µm and c) 8µm.

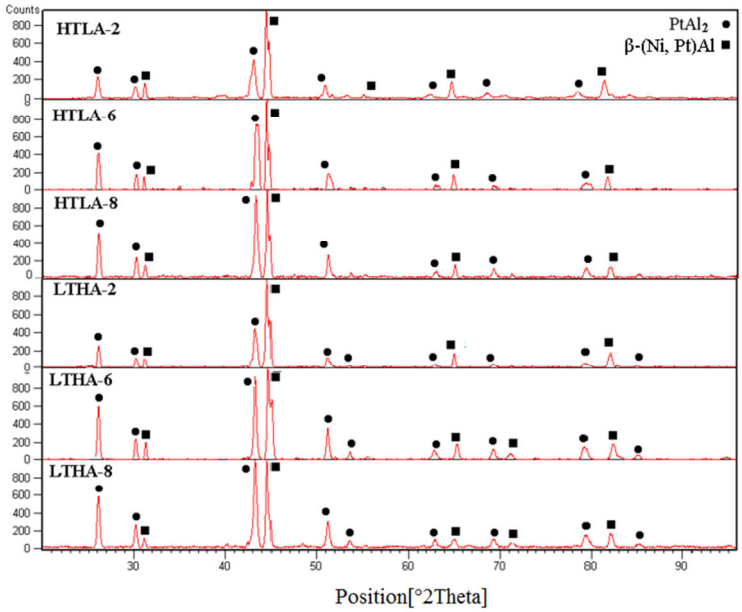

Figure 3: The results of XRD analysis of different thicknesses of initial platinum layer for two HTLA and LTHA methods of aluminizing process.

XRD results indicated the lowest formation of $PtAl_2$ phase occurred after HTLA with an initial platinum layer thickness of 2µm. The highest amount of the $PtAl_2$ phase was formed by the LTHA method with a platinum thickness of 8µm.

Results of thickness measurement in the case of HTLA and LTHA methods revealed a direct impact of the platinum layer and aluminizing method on the final thickness of the coatings. Increase of the initial platinum layer thickness from 2 to 6 and 8µm in HTLA led to final thicknesses of 92, 97 and 102 µm, respectively; with the same order, the thicknesses were 128, 140, and 149 µm for LTHA. The variation in the thickness of the platinum-aluminide coating for different initial platinum thicknesses for the HTLA and LTHA methods is listed in Table 1 (three sections are measured and reported with accuracy ±4µm for the outer layer, ±7 µm for the middle layer and ±1µm for IDZ).

It can be observed that increase of the initial platinum layer thickness resulted in the enhancement of the β (NiAl) +ξ ($PtAl_2$) outer layer for both HTLA and LTHA methods. The reason could be attributed to the direct relationship of increased initial platinum layer thickness with higher amount of the ξ- $PtAl_2$ phase. Also, results demonstrated the increased thickness of the middle layer of β- (Ni, Pt) Al after the LTHA method compared to HTLA. The thickness of coating has been increased in the middle layer, however in the case of the LTHA method this growth is related to the presence of higher amount of aluminum in the pack source. This means that the percentage of aluminum in the aluminizing method affects the thickness of the final coating. Thus, the increased aluminum concentration is associated to the increased thickness of the middle layer of β- (Ni, Pt) Al in addition to the increased outer layer of ξ +β.

Table 1: The thickness of the different layers of Pt-Al coating for the various thicknesses of the initial platinum layer for two HTLA and LTHA methods.

Thickness of the initial platinum layer (µm)		2			6			8		
	Layer	β+ξ	β	IDZ	β+ξ	β	IDZ	β+ξ	β	IDZ
Thickness of the Coating (µm)	HTLA	32	51	9	44	39	13	47	42	13.5
	LTHA	39	84.5	4.5	44	92	4	45	97	4

The thickness of the IDZ layer by the HTLA has grown from 9 µm to 13.5 µm with the increased thickness of the platinum layer, however, the thickness of this layer became constant by the LTHA method. On the other hand, the lesser thickness of IDZ layer, which is the place of gathering the refractory elements such as tungsten, titanium, chromium, molybdenum, and cobalt, is one of the features of the LTHA compared with the HTLA method. The reason is the presence of higher amount of aluminum by the LTHA method than in the case of other method, which leads to an increase in the thickness of the middle layer, where higher amount of the carbide-forming elements have been dissolved. This process caused a decrease in the thickness of the IDZ layer.

The EDS line-scan was performed in evaluating the variety of concentration of nickel, platinum and aluminum perpendicular to the coating in the different thickness of the platinum layer and as dependence on aluminizing method. The results of this analysis, which are illustrated in Figure 4 and 5, show the inward diffusion of the platinum and aluminum and outward diffusion of nickel. Also, the depth of the diffusion and the concentration gradient of the platinum were affected by the initial thickness of the platinum layer, so that after the both methods, i.e. HTLA and LTHA, the higher percent of platinum has diffused into the surface by increasing the initial platinum thickness.

According to EDS results, the depth of platinum diffusion is higher during HTLA and it has been identified throughout the coating with a higher thickness of the initial layer. The reason for this behavior may be ascribed to the higher amount of aluminum by the LTHA method which prevents further diffusion of platinum. According to the diffusion mechanisms and also based on the Fick's laws for diffusion phenomena, in addition to the time and temperature, the concentration of the available elements affects the diffusion.

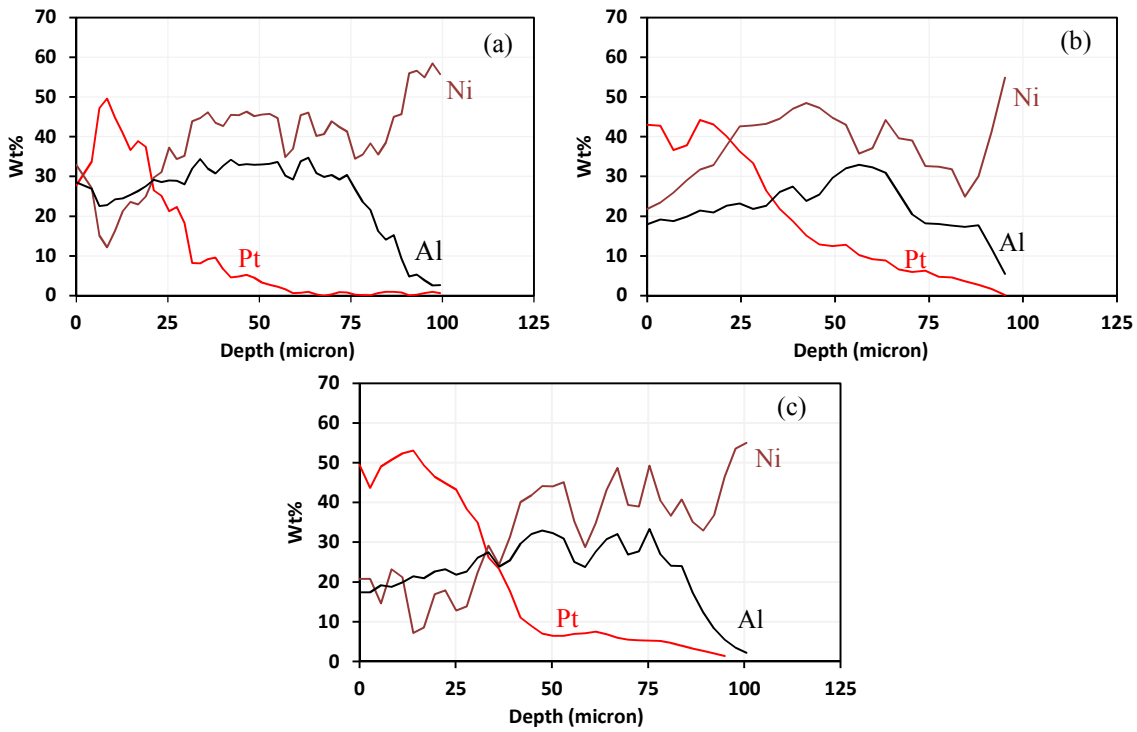

Figure 4: The variation of the concentration and the depth of the diffusion of nickel, platinum and aluminum (the HTLA method) for the initial platinum layer with the thickness of a) 2µm, b) 6µm and c) 8 µm.

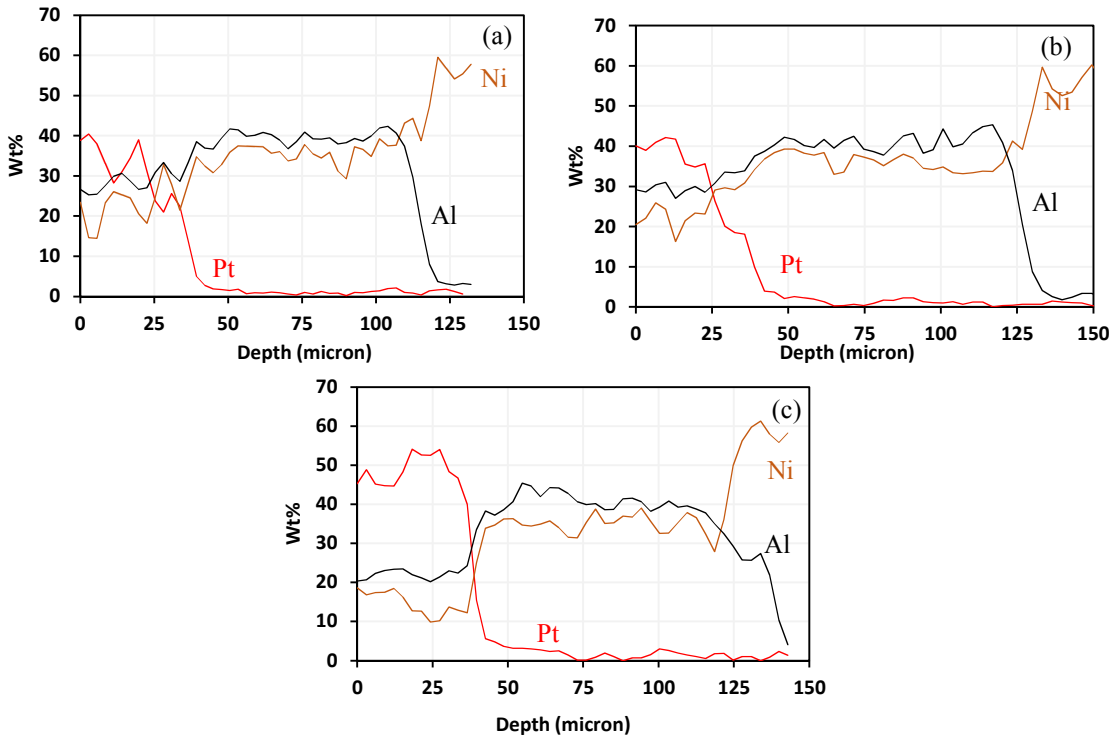

Figure 5: The variation of the concentration and the depth of the diffusion of nickel, platinum and aluminum (the LTHA method) for the initial platinum layer with the thickness of a) 2 μm, b) 6μm and c) 8μm.

According to the first Fick's law ($J= -D\ dC_i/\ dx$) where J is atomic diffusion flux, D is the diffusion constant with the unit of (m^2/s), dC_i/dx is a concentration gradient with the unit of (kg/m^3), $C_i= N_i /V_m$ in which N_i is the composition of the element i according to molar fraction or atomic fraction, and V_m is the molar volume with the unit of (m^3/mol). The negative sign indicates that the direction of the diffusion is against the increased concentration. This means that the difference between concentrations of atoms in the two places adjacent to each other is the driving force for atomic diffusion. According to this rule, Kiruthika et al. [14] explained the diffusion interference of platinum and aluminum in the β-(Ni,Pt)Al phase. The results showed that a higher amount of aluminum led to increasing the activity of this element. As a result, aluminum decreases the activity of platinum and nickel reducing their diffusion coefficients, which is an agreement with the results of the present study.

Aluminum exists throughout the Pt-Al coating in the two methods, which has been proved by the EDS analysis. These results indicate the diffusion coefficient of aluminum is higher than platinum in the Pt-Al diffusion coatings. On the other side, the presence of aluminum in all three layers of the coating is higher by the LTHA method than that of HTLA. Therefore, this result shows the direct effect of the amount of aluminum in the aluminizing method for the distribution of its concentration in the coating.

According to EDS analysis, nickel has been identified in all coating layers. Increased diffusion of nickel in the outer layer of the coating (β+ξ) is obvious for fewer thicknesses of the initial platinum layer. Also, the outward diffusion of nickel by the HTLA method is higher than by LTHA. This is due to the lesser presence of aluminum in the coating resulting in more space for nickel diffusion.

3.2. Cyclic oxidation testing

The weight of the uncoated sample was measured before the cyclic oxidation test as 4.8701 g. The weight of the coated samples before cyclic oxidation test and after completion of the test at 1100 °C for one hour, followed by cooling outside the furnace to the ambient temperature for 120 cycles are listed in Table 2. The results of weight variations of the samples (uncoated and coated) during the cyclic oxidation test are shown in Figure 6.

Table 2: Coated sample weight before and after cyclic oxidation test (120 cycles at 1100 °C).

Aluminizing Method		HTLA			LTHA		
Thickness of the initial platinum layer (μm)		2	6	8	2	6	8
Weight(g) Before cyclic oxidation test	Sample 1	5.028	5.033	5.0455	5.0905	5.1111	5.1268
	Sample 2	5.0282	5.0371	5.0451	5.0901	5.1117	5.1266
Weight(g) after cyclic oxidation test	Sample 1	5.034	5.0397	5.05	5.0959	5.1153	5.1318
	Sample 2	5.0343	5.0399	5.053	5.0957	5.1151	5.132

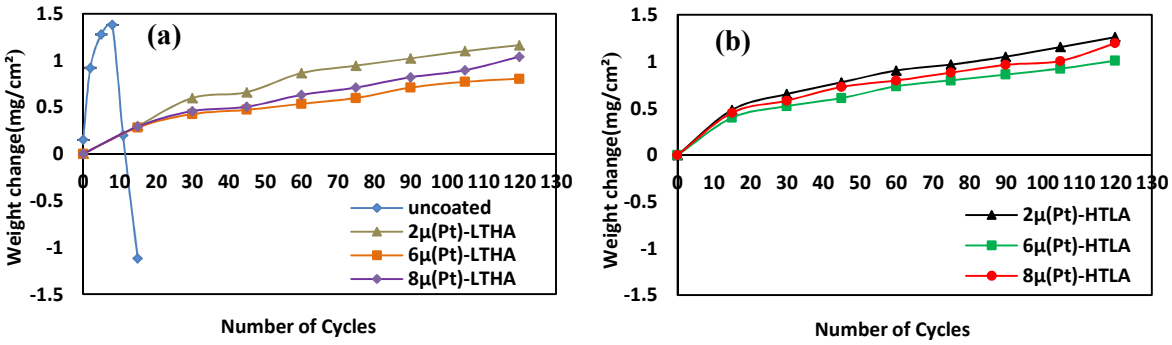

Figure 6: Sample weight change versus number of cycles for cyclic oxidation of the superalloy Rene-80 at 1100 ºC a) uncoated and coated samples (the LTHA method) for different initial platinum layer and b) coated samples (the HTLA method) for different initial platinum layer.

As can be seen, the uncoated sample after only 8 cycles at 1100 ºC showed a severe weight loss indicating fast oxidation, and then (after 8 cycles) rumpling of oxidation layer from the surface occurred. This reveals the low resistance of this alloy against cyclic oxidation at 1100 °C. The SEM image (Figure 7a), EDS (Figure 7b) and also XRD (Figure 8) results show that in the uncoated sample, after 120 cycles of oxidation, TiO_2, Al_2O_3, and spinel $Ni(Cr_2O_4)$ have been formed.

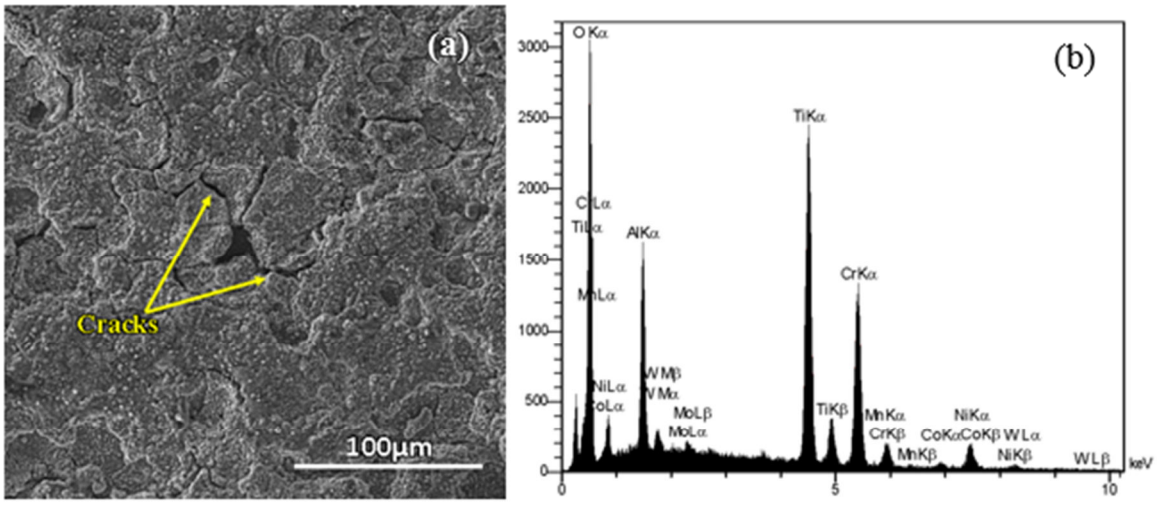

Figure 7: a) The SEM image of oxide scale on uncoated sample surface and b) The EDS result of oxide scale.

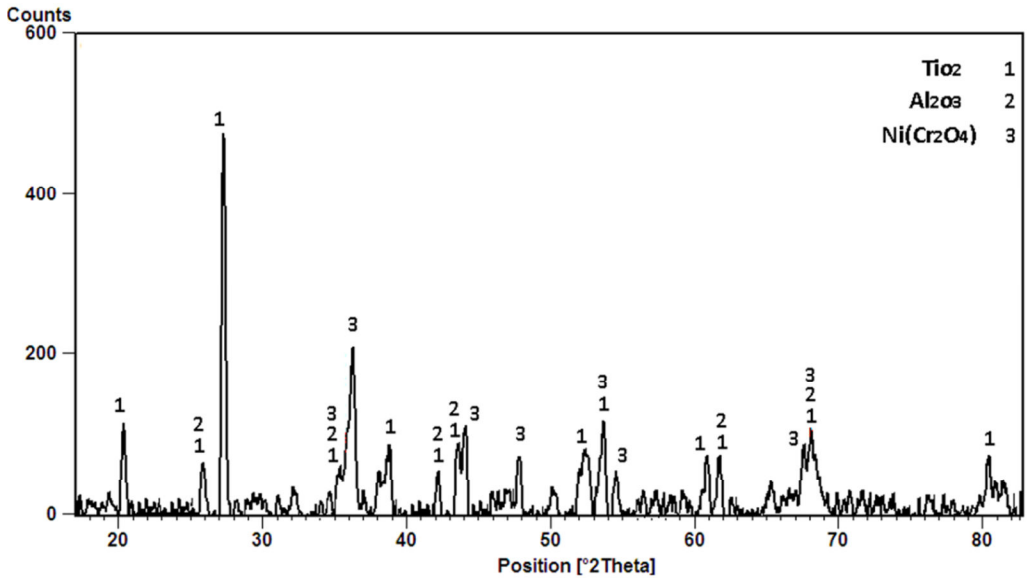

Figure 8: The results of XRD analysis for oxide scale of uncoated sample.

This spinel is produced by the reaction between NiO and Cr_2O_3 ($NiO+Cr_2O_3 \rightarrow Ni(Cr_2O_4)$). The formation of harmful spinel ($Ni(Cr_2O_4)$) shows the low resistance of this alloy against cyclic oxidation at 1100 °C. Due to the high chromium content of the Rene®80 (about 14%), in addition to aluminum oxide (Al_2O_3), chromium oxide (Cr_2O_3) and then spinel $Ni(Cr_2O_4)$ were also produced on the surface. Since these oxides are volatility oxides at temperatures above 1000 °C, rapid removal their scale from the surface will result in oxygen penetration and alloy destruction.

On the other hand, all of the coated samples exhibited better resistance to cyclic oxidation and their weight difference before and after the test were much lower than that of the uncoated sample, reflecting an improvement in the oxidation resistance of this alloy through applying a platinum-aluminide coating. One of the reasons for this behavior could be the role of platinum in reducing the rate of oxygen diffusion from the aluminide oxide scale on the surface into the alloy [16], and also preventing diffusion of refractory elements, such as chromium, from the alloy to the coating at high temperatures.

By substituting the obtained values of the changes in samples weight before and after the test (Table 2), as well as applying the test conditions in equation 1 [17, 18], the parabolic oxidation rate constant can be calculated for any of the aluminizing methods and different Pt thicknesses (Eq.1). The calculated results after 120 cycles (120 h) are presented in Table 3.

$$(\Delta m/A)^2 = K_P t \quad (1)$$

where Δm is weight changes (g), A is oxidation area (cm^2), K_p is parabolic oxidation rate constant ($g^2cm^{-4}s^{-1}$) and t is oxidation time (s).

Table 3: Parabolic oxidation rate constant for Pt-Al coatings after HTLA/LTHA methods and different platinum layer thicknesses (120 cycles at 1100 °C).

Aluminizing Method	HTLA			LTHA		
Platinum Thickness(μm)	2	6	8	2	6	**8**
Oxidation Area(cm^2)	4.7549	4.7585	4.764	4.7875	4.7984	4.8056
Wight change (g)	0.006	0.0048	0.0057	0.0055	0.0038	0.0052
parabolic oxidation rate constant ($g^2.cm^{-4}.s^{-1}$)	3.8×10^{-12}	2.4×10^{-12}	3.4×10^{-12}	3.2×10^{-12}	1.5×10^{-12}	2.8×10^{-12}

Results of Figure 6 and Table 3 show that in both LTHA and LTLA coatings, the 6μm thickness of platinum exhibited a more robust resistance to cyclic oxidation under the defined conditions. The best resistance to this type of oxidation under the test conditions defined in this study was related to the 6μm platinum sample by LTHA method (6μm Pt/LTHA), which showed a weight variation of about 0.8029 mg/cm^2 after 120 cycles of oxidation. Its parabolic oxidation rate constant was calculated as 1.5×10^{-12}, while the 2 μm platinum sample by HTLA method (2μm/HTLA) experienced weight change of about 1.2618 mg/cm^2 and possessed the lowest cyclic oxidation resistance among the coated specimens with parabolic oxidation rate constant of 3.8×10^{-12}. Low weight loss of 6μm platinum sample by LTHA method indicates that the residual of this coating can still protect the alloy surface at 1100 °C. The parabolic oxidation rate constant of this study is in good agreement with the results of other researches [19] regarding the determination of this parameter for a single-phase platinum-aluminide coating.

All samples exhibited a weight increase under the test conditions; as the weight variation trend was ascending depending on oxidation cycle (up to 120 cycles) as shown in Figure 6. This behavior was similar for various platinum thicknesses by the HTLA method until the fifth cycle and for the LTHA method up to the 15th cycle. This phenomenon can be attributed to the presence of sufficient aluminum as well as the high partial pressure of oxygen on the surface of the coating, which will result in a high tendency of primary oxide scale growth. As depicted in Figure 6, the rate of weight changes is very slow relative to the cycle in the platinum-aluminide coating. Result of the research carried out by Smola et al. [20] and a comparison of the weight variation of single-phase coating of platinum-aluminide with a simple aluminide showed that the presence of platinum in the composition of NiAl coatings can reduce the growth rate of the oxide scale, as well as its removal tendency during the oxidation process.

To investigate the formed phases, XRD analysis was carried out on a 6μm platinum sample by the LTHA method (with the best oxidation resistance) and 2μm platinum sample by the HTLA method (with the weakest oxidation resistance) as shown in Figure 9.

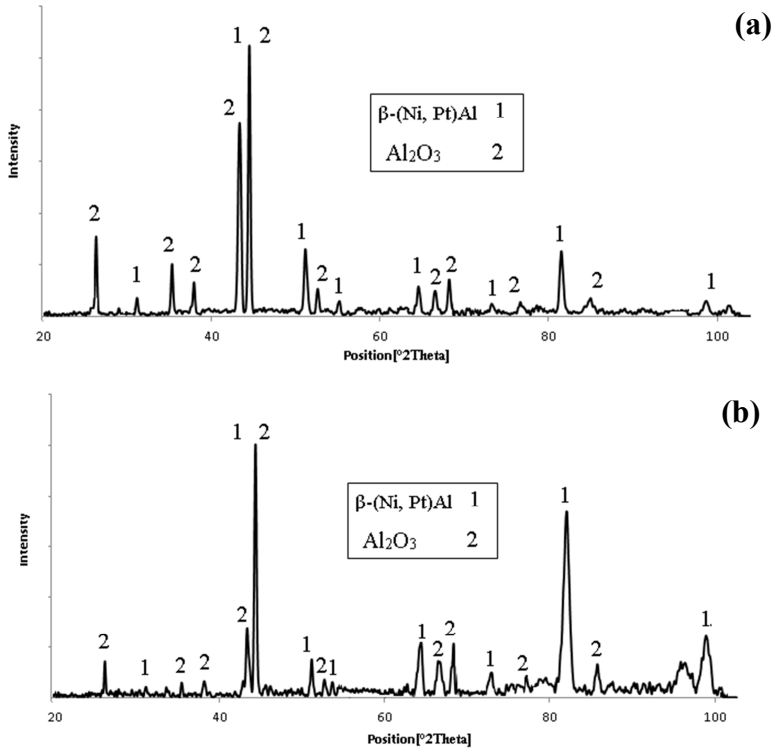

Figure 9: The results of XRD analysis for a) 2μ Pt and HTLA method and b) 6μ Pt and LTHA method after cyclic oxidation test (1100 ºC, 120 cycles).

As can be seen XRD results show that after 120 cycles, ξ-$PtAl_2$ + β-(Ni, Pt)Al two-phase layer was converted into β-(Ni, Pt) Al single-phase layer in both samples, also the oxide phase of Al_2O_3 was formed in both samples. The detection peaks of this phase are however different in the samples. Since the dimensions and sizes of the tested samples were quite similar, the higher peak intensity can be attributed to the greater volume of the corresponding phase. In Figure 9a, it is evident that the peak of Al_2O_3 is greater than that of Figure 9b indicating the higher oxidation of the base alloy in this case. These results are consistent with a greater weight variation in this sample (Table 3).

It should be mentioned that no other oxide has been detected in this layer, which can be considered as one of the positive effects of the presence of platinum in the coating composition. According to research by Pint et al. [21], platinum forms a protective layer on the alloy surface which limits the diffusion of other elements in the alloy to the coating. Therefore, oxides such as Cr_2O_3 and TiO_2 which have lower resistance against oxidation at temperatures above 1000 °C, will not be formed in the coating; hence the coating adherence to the substrate will be protected resulting in higher oxidation resistance. On the other hand, detection of Al_2O_3, as well as the absence of other phases on the alloy surface after 120 cycles of oxidation of platinum-aluminide coatings, reveals that this coating managed to protect the alloy surface at 1100 °C.

Degradation of $PtAl_2$ phase and its transformation to (Ni, Pt) Al phase after 120 cycles of oxidation at 1100 °C can be observed in SEM images (Figure 10).

According to EDS results after 120 cycles of oxidation, for 6µm Pt/LTHA condition, the initial amount of Al in the upper regions of the Pt-Al coating decreased from 28.4 wt.% to 18.8 wt.%, and the initial Pt content in the coating decreased from 41.7 wt.% to 12.5 wt. % . Also, the amount of Al and Pt in the 2µm Pt/HTLA condition was decreased from 26.16 wt.% and 32.28 wt.% to 12.83 wt.% and 6.74 wt.%, respectively. Results show that the amount of Al and Pt in 2µm Pt/HTLA condition is lower than in 6µm Pt/LTHA condition in the coating composition after 120 cycles of oxidation. Although these amounts of Al and Pt in 2µm Pt/HTLA condition can protect the surface of the alloy against oxidation compared to non-coated surface, the formed oxide is not as strong as that in 6µm Pt/LTHA condition.

By degradation of $PtAl_2$ phase, the thickness of (Ni,Pt)Al single-phase region increased by 40% compared with condition before the test. This increase was observed in both Pt thicknesses (6 and 2 µm) in the case of both LTHA and HTLA methods. As can be seen in Figure 10a, the oxide particles were penetrated into substrate, but in coated samples, these particles have remained in coatings.

On the other hand, as Table 3 suggests, the cyclic oxidation behavior of the coated alloy is different depending on the thickness of the platinum layer and the aluminizing process. The SEM images in Figure 1 and 2, as well as XRD results (Figure 3), indicate that increase in the thickness of platinum and percentage of aluminum in the aluminum source can enhance the concentration of $PtAl_2$ in the coating surface. The lowest amount of this phase was observed

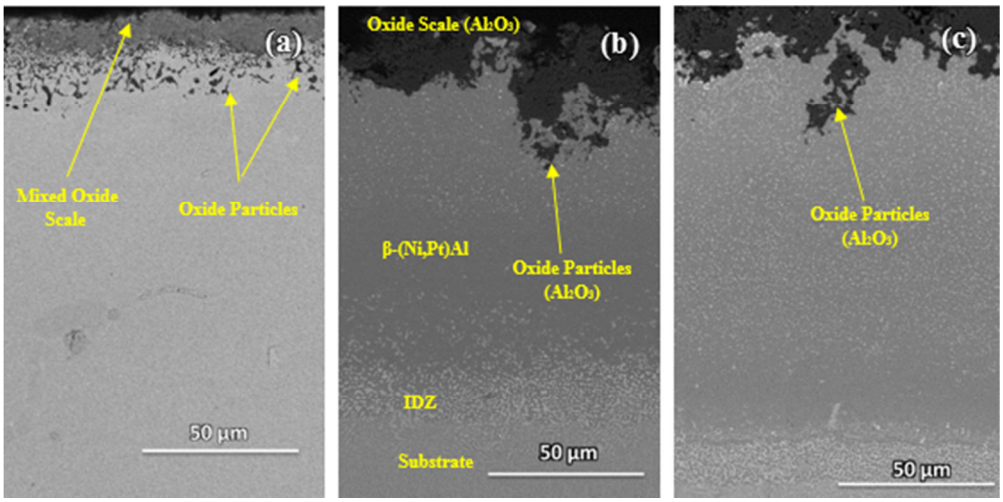

Figure 10: The SEM images of sample cross section after cyclic oxidation at 1100ºc for 120 cycles. a)uncoated b) 2µm Pt (HTLA method) and c) 6µm Pt (LTHA method).

In the sample with a 2µm platinum thickness (HTLA method), while the highest content was detected for the sample possessing platinum thickness of 8µm (LTHA method). As this alumina-rich phase plays an important role in providing the source of aluminum for Al_2O_3 phase formation, it is expected that a reduction in the amount of this phase in the two-phase coating layer will decrease the coating resistance to oxidation. According to the results that are shown in Table 3, the weight changes of HTLA were higher in all thicknesses compared to LTHA indicating that the cyclic oxidation resistance of this aluminizing method was also lower.

Besides, Alam et al. [22], in their research on the tensile properties of platinum aluminide coatings, found that the elastic modulus of this coating for the platinum thickness of 5µm at a strain rate of 10^{-4} and a temperature of 1000 ° C is 93 and 99 GPa for HTLA and LTHA, respectively. In our research also the residual stress of two types coated (2µm Pt/HTLA and 6µm Pt/LTHA), before the cyclic oxidation test, were measured as 170.3 MPa and 148.2 MPa by XRD, respectively. Watanabe et al. [23] calculated the residual stress as 140MPa for a single-phase platinum-aluminide coating. According to previously mentioned facts, it can be inferred that as a result of each oxidation cycle, due to the heating and cooling of the sample, the difference between the thermal expansion coefficients of the base alloy, platinum-aluminide coating and Al_2O_3 oxide scale, the coated sample will experience tensile stress during the heating process, while it will sustain compressive stress when it is cooled down. Due to the low elastic modulus of the HTLA coating and higher residual stress, it exhibited less resistance to deformation and was damaged and rumpled from the surface more quickly. The aluminum oxide rate will increase further to create the new oxide scale. However, owing to the lower concentration of $PtAl_2$ phase in this type of coating, a stable Al source will be less available, hence the lifetime of this coating against cyclic oxidation will be reduced compared to LTHA method.

On the other hand, by increasing the platinum thickness from 2 to 8µm, for both aluminizing conditions, the thickness of the final coating was increased, which will have a direct effect on the loss of elastic modulus in the coating [24]. As mentioned before, reduction of the elastic modulus of the coating also results in a decline in the cyclic oxidation resistance. According to Table 3, it is clear that in both aluminizing methods, samples with a platinum thickness of 6, 8 and 2µm showed the lowest weight loss, respectively. This phenomenon can be explained by the fact that the sample with a platinum thickness of 2µm is basically unable to provide a sufficient amount of $PtAl_2$ phase as a stable and Al-rich phase, therefore, the aluminum content of the coating will be rapidly consumed during oxidation and the next oxide scales will be created by the outward diffusion of Al content from the substrate. Repetition of this process will cause weight changes. Besides, over-increase in platinum thickness to 8µm, although will provide sufficient $PtAl_2$ but will decline the mechanical properties of the coating including its elastic modulus. The elastic modulus has a significant effect on the resistance to thermal stress caused by cyclic oxidation and its reduction will decline the adhesion of the coating to the surface, so the coating will be rumpled more quickly from the surface (Figure 11).

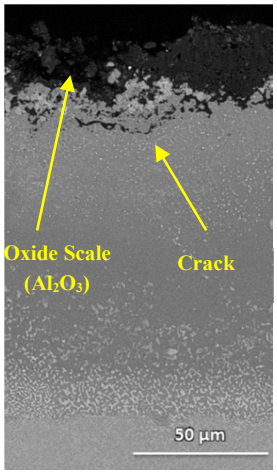

Figure 11: The SEM image showing cross section of 8 µm Pt in HTLA condition after cyclic oxidation at 1100 ºC for 120 cycles.

4. Conclusions

In both methods of aluminizing and various platinum thicknesses, the coating is a three-layer composite consisting of an outer layer (two-phase ξ-$PtAl_2$ +β (Ni, Pt) Al), an intermediate layer (single-phase β (Ni, Pt) Al) and the end layer (IDZ metal-coating interface). According to XRD results, the highest $PtAl_2$ phase was produced in 8µm platinum by LTHA methods, while the lowest was recorded in the 2µm platinum sample prepared by HTLA. The results of cyclic oxidation tests indicated that the cyclic oxidation resistance was improved in all coated samples compared with uncoated sample, and it was because of the limitation of alloying elements (such as Ti and Cr) diffusion to the coating. On the other hand, in the coated specimens, the best resistance was found for the sample possessing platinum

thickness of 6μm prepared by LTHA method, while the one having a platinum thickness of 2μm by HTLA method showed the least resistance to cyclic oxidation. The reason can be found in the sufficient content of $PtAl_2$ phase in the coating with a platinum thickness of 6μm by LTHA method. In addition, this coating showed higher resistance to thermal stresses, due to higher elastic modulus, the parameter playing an important role in resistance to cyclic oxidation.

5. References

1. M. Lavella, Contact properties and wear behaviour of nickel based superalloy René 80, *Metals,* 159(2016), 1-15.
2. R. Strife, Protection of materials by advanced high temperature coatings, *J. Phys. IV*., 3(1993), 17-42.
3. G. R. Krishna, D. K. Das, V. Singh, Role of Pt content in the microstructural development and oxidation performance of Pt aluminide coatings produced using a high-activity aluminizing process, *Mater. Sci. Eng. A*., 251(1998), 40–47.
4. H. Rafiee, H. Arabi, S. Rastegari, Effects of temperature and Al-concentration on formation mechanism of an aluminide coating applied on superalloy IN738LC through a single step low activity gas diffusion process, *J. Alloys Compd*., 505(2010), 206–212.
5. Z. Zhan, Z .Liu, J. Liu, L. Li., Z. Li, L. Pibo, Microstructure and high-temperature corrosion behaviors of aluminide coatings by low-temperature pack aluminizing process, *Appl. Surf. Sci*., 256(2010), 3874–3879.
6. R. C. Reed, T. WuR, M. S Hook, C. M. F. Rae, R. G Wing, On oxidation behaviour of platinum aluminide coated nickel based superalloy CMSX-4, *Mater. Sci. Technol.* 25(2009), 276-286.
7. L. Ye, H. Chena, G. Yang, Y. Cui, H. Luo, B. Liu , L. Qian , Y. Gao, Diffusion behavior of Pt in platinum aluminide coatings during thermal cycles, *Int. J. Mater. Res.,* 19(2018), 3-9.
8. Specification for alloy casting, investment, corrosion and heat resistant. Aerospace material specification AMS standard, 5403A, 1995.
9. B. M. Warnes, N. S. Dushane, J. E. Cockerill, Cyclic oxidation of diffusion aluminide coatings on cobalt base superalloys, *Surf. Coat. Technol.,* 48(2001), 163-170
10. A. Rashidghamat, K. Shirvani, A. Firouzi, European Federation of Corrosion Workshop on solutions for high temperature corrosion protection in energy conversion system; 2009 Sep.-Oct. 30-2; Frankfurt, Germany.
11. M. Yavorska, J. Sieniawski, Effect of diffusion on platinum coatings deposited on the surface of nickel based superalloy by the electroplating process, *Arch. Mater. Sci. Eng.,* 45(2010), 56-60.
12. Standard Guide for Preparation of Metallographic Samples. Annual Book of ASTM Standard, ASTM Standard, E3-11, 2011.
13. Standard Guide for Reflected–Light Photomicrography. Annual Book of ASTM Standard, ASTM Standard, E883-11, 2011.
14. P. Kiruthika, A. Paul, A pseudo-binary interdiffusion study in the β-(Ni,Pt)Al phase, *Philos. Mag. Lett.,* 95(2015), 138-144
15. D. K. Das, V. Singh, S. V. Joshi, Effect of Prealuminizing diffusion treatment on microstructural evolution of high-activity pt-aluminide coatings, *Metall. Mater. Trans. A.,* 31(2000) 2037-2047.
16. K. Shirvani, S. Firouzi, A. Rashidghamat, Microstructures and cyclic oxidation behaviour of Pt-free and low-Pt NiAl coatings on the Ni-base superalloy Rene80, *Corros. Sci.,* 55(2012) 378-384.
17. C. Horst, S. Tetsuya, E. S. Leslie, Springer Handbook of Metrology and Testing, 2011, 721-725.
18. P. Kejzlar, A. Hotar, High temperature oxidation properties of iron-aluminides with Zr addition, Metals 2014, Brno, Czech Republic, EU. 2014.
19. S. Ford, R. Kartono, D. J. Young, Oxidation resistance of Pt-modified γ/γ′ Ni-Al at 1150 °C, *Surf. Coat. Technol.* 204(2010), 2051-2054.
20. G. Smola , W. Wang, J. Jedlinski, B. Gleeson, K. Kowalski, A. Bernasik, M. Nocun, Mechanistic aspects of Pt-modified-NiAl alloy oxidation, *Mater. High Tempe.* 26(2009), 273-280.
21. B. A. Pint, I. G. Wright, W. Y. Lee, Y. Zhang, K. Prussner, K. B. Alexander, Substrate and bond coat compositions: factors affecting alumina scale adhesion, *Mater. Sci. Eng. A.,* 245(1998), 201-211.
22. M. Z. Alam, S. V. Kamat, V. Jayaram, D. K. Das, Tensile behavior of a free-standing Pt-aluminide (PtAl) bond coat, *Acta Mater.* 61(2013), 1093-1105.
23. 23. M. Watanabe, D. R. Mumm, S. Chiras, A. G. Evans, Measurement of the residual stress in a Pt–aluminide bond coat, *Scripta Mater.* 46(2002), 67-70.
24. C. Parlikar, M. Z. Alam, D. Chatterjee, D. K. Das, Thickness apropos stoichiometry in Pt-aluminide (PtAl) coating: Implications on the tensile properties of a directionally solidified Ni-base superalloy, *Mater. Sci. Eng. A.*, 682(2017), 518-526.

How to cite this article:

M. M. Barjesteh, S. M. Abbasi, K. Zangeneh Madar, K. Shirvani, Nickel Base Superalloy Rene®80-The Effect of High Temperature Cyclic Oxidation on Platinum-Aluminide Coating Features. Prog. Color Colorants Coat., 13 (2020), 11-22.