

The effect of the platinum layer and the aluminizing method on the structure, and microhardness of the Pt-Al Coating

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ABSTRACT

In this study, the effect of the platinum layer and the aluminizing method on the structure and hardness of Pt-Al coating which was applied on the superalloy Rene-80 have been investigated. The layer of platinum with various thicknesses was applied on the surface. The heat treatment of this layer was performed, and then the aluminum coating was applied in two different conditions of high activity and low activity. Subsequently aging treatment was performed. The results of the structural investigations indicated there is three-layer structure in all thicknesses of platinum layer as well as in the two methods of aluminizing. The thickness of the final coating has changed by the increased thickness of the platinum layer. The hardness of the coating has been enhanced by the increased thickness of the platinum layer especially in high activity method. More density of the PtAl₂ phase on the surface can be the main reason for increasing the thickness and hardness of coating.

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Introduction

For the first time, the nickel based superalloy Rene-80 was introduced and used by General Electric Company[1]. This alloy has good strength properties and corrosion-resistance in the high temperature region. In addition, the surface of this alloy is coated for improving these properties against chemical degradation. The common high-temperature-resistant coatings for superalloys are overlay coatings, aluminide and Pt-modified aluminide diffusion coatings, and thermal barrier coatings[2]. Aluminide coatings are produced based on intermetallic phase of β -NiAl. The structure and composition of these coatings strongly depends on substrate compositions. These coatings are modified by adding are elements such as Platinum. The enhanced stability of the coating in the presence of Platinum is attributed to different mechanisms[3]such as the formation of PtAl₂ layer, increasing the Aluminum activity near the surface in result of Chromium remaining in solution and impediment to transition of the refractory elements from reaching the outer layer.

The Pt-modified aluminide coatings are usually produced by electroplating, a layer of Platinum on the superalloy which is then given a diffusion heat treatment. Subsequently, the diffusion treated alloys are aluminized by using the pack cementation Method[4]. It should be noted, the diffusion treatment can be done in two methods of low temperature-high activity and high temperature-low activity, based on Aluminum content in aluminize source.

The effect of the aluminum content on structure and corrosion properties of Pt-modified aluminide coatings was investigated by Das et al. [5]. The results of their study confirmed a three-layer structure for coating which include two-phase (Ni, Pt) Al-PtAl₂ layer. According to this study, if the amount of aluminum in the aluminize source is low, the two-phase layer in the high temperature will immediately convert to the one-phase layer of (Ni, Pt)-Al.

Krishna et al.[4]investigated the effect of the thickness of platinum layer on the structure of the Pt-modified

aluminide coating applied on the alloy CM-247LC. They reported the three-layer structure for various thicknesses of the platinum layer. While in the 1 μ m thickness of platinum, this entire element remains in the solid solution of NiAl; however, a platinum with thickness of 15 μ m produces a continuous layer of PtAl₂ on the top of the two phase layer.

Considering the importance of Pt-modified aluminide coating for alloy Rene-80, in the present study, the interaction variation in the thickness of the initial layer of platinum and the aluminizing process(in two methods of high and low activity) on the structure, the elements distribution and hardness of the coating, have been studied.

Experimental

The chemical composition of nickel based superalloy Rene-80 which is selected in the present study as a substrate is given in Table 1. This alloy was treated under two-stage solution treatment at the temperature 1205°C for 2 hours and the primary aging at the 1095°C for 4 hours according to standard of GE-C50TF28 (Class A)[6]. Then, the thin layer of the nickel was produced on the surface with the aim of improving the adhesion of the platinum layer. The processes of platinum electroplating were performed by using electrolyte solution including 14-18 ml Pt(NH₃)₂(NO₂)₂(type P), 70-90 gr/L Na₂CO₃, 40-70 g/L NaCH₃COO and one liter of the distilled water. Different times from 2 to 6 hours at the temperature of 90°C, the current density of 0.2-0.4 A/dm² and PH 10.5 were selected for electrolyte to achieve various thicknesses of platinum layer (2, 4, 6, and 8 μ m). Also, heat treatment of the platinum layer has been performed at the temperature 1050°C for 2 hours with the aim of improving the adhesion and better distribution of platinum in the substrate[7].

Table 1: The chemical composition of the nickel based superalloy Rene-80 (%wt)

C	Cr	Co	Mo	W	Al	Ti	Fe	Zr	V	B	Si	Mn	Ni
0.16	13.8	9.69	4.23	4.02	3.02	4.87	0.12	0.05	0.05	0.02	0.02	0.03	bal.

Table 2: The components of powder mixture used in the pack cementation processes (%wt)

Powder Components		NH ₄ Cl	Aluminum powder (Mesh: 0-45µm)	Aluminum oxide (Mesh: 180µm)
Aluminizing - Process	LTHA	2	12	86
	HTLA	1	4	95
Role of Component		Activator	Main Agent	Filler

The process of aluminizing was performed under two different conditions named LTHA (the low temperature 750°C for 4 hours for higher activity of aluminum), post aluminizing 1050°C for 2 hours, and HTLA (the high temperature 1050°C for 2 hours for lower activity of aluminum) by powder-pack cementation method. The components of the powder mixture in pack-cementation processes are shown in Table 2. In the final step, after forming Pt-modified aluminide coating on the surface of the alloy, the aging heat treatment was performed on the coated sample at the temperature of 845°C for 16 hours.

According to the standards ASTM E3 [8] and ASTM E883 [9], the microstructure studies were performed at the all steps of coating from electroplating, heat treatment of the platinum layer and diffusion of aluminum by using LEICA MEF4A Optical Microscopy and VEGA3 TESCAN Scanning Electron Microscopy equipped with an EDS, operated at

20KV. X-ray diffraction analysis (Inel Equinox 6000 in the voltage 40 KV, current 27 mA, the range of angle 10 to 100 and at the room temperature) was also performed to determine the phase types and their distribution based on the various thicknesses of the Pt-modified aluminide coating. The hardness test was performed at two macro and micro scales on the substrate and coating, According to the standards of ASTM E384 [10] and ASTM E18 [11].

Results and Discussion

The cast structure of the alloy Rene-80

Figure 1 shows the γ' and γ - γ' eutectic phases in the alloy Rene-80 before and after solution and primary aging treatments. The amount of the undesirable γ - γ' eutectic which has the lower melting temperature than other regions [12] is minimized in the structure after heat treatments (according to Figure 1-d).

According to Safari and Nategh [12] studies who investigated the effect of the heat treatment on microstructure of the alloy Rene-80, the size of the γ' phase in the inter-dendrites regions is larger than the dendrite's core. More uniform distribution of the γ' phase is produced in the structure by performing the solution and primary aging treatments. These treatments also eliminated the γ - γ' eutectic phase.

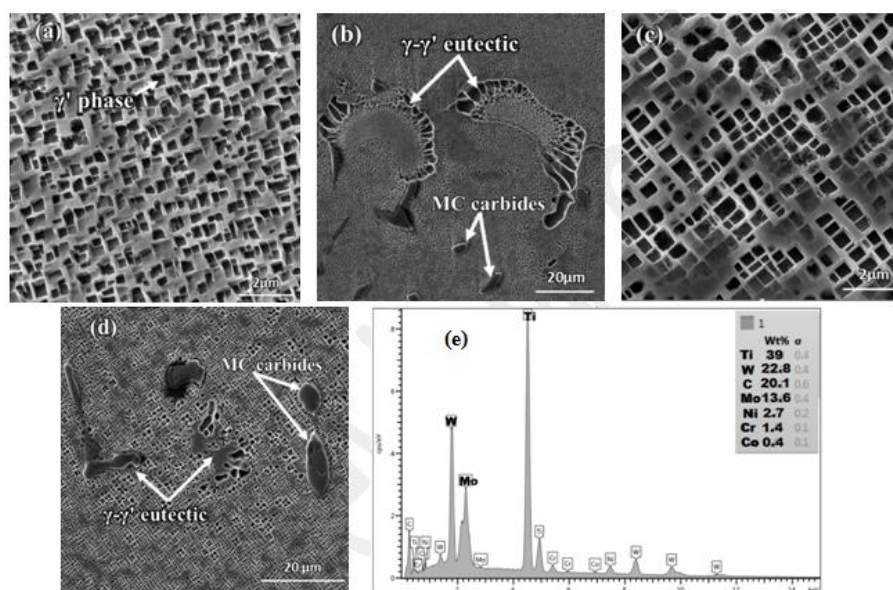


Figure 1: The SEM images of the γ' , γ - γ' eutectic and MC carbide phases in the alloy Rene-80; a and b) before, c and d) after the solution and primary aging treatments, e) the results of EDS analysis of the MC carbide

According to Figure 1, the amount of the γ' phase is increased after the solution treatment and primary aging from 33 to 37 percent. Also, the distribution of the γ' phase is improved and the morphology of this phase approximately is formed a cubic shape. The hardness of the alloy Rene-80 is also affected and the amount of that has been decreased from 35 HRC (as cast) to 26 HRC after the above heat treatments. One of the most important reasons for reduced hardness is the elimination of the γ - γ' eutectic during the solution at 1205°C. It should be noted that according to the results of the SEM-EDS analysis (Figure e-1), up to this stage the MC carbide phase only has been produced in the structure which is rich of titanium,

tungsten, and molybdenum. This results is in agreement with the results of Yang et al. [13] studies. They reported the carbide phases in the inter-dendrites area were the MC type.

The platinum electroplating and diffusion coating

Before the electroplating of platinum, a thin layer of nickel (1-2 µm) was applied on the surface in order to decrease the negative effect of the chromium (available in the composition of alloy) on the adhesion property of platinum [14]. In the next step, the platinum layer with various thicknesses of 2, 4, 6, and 8 µm in different times of 150, 240, 360, and 480 minutes was electroplated on the

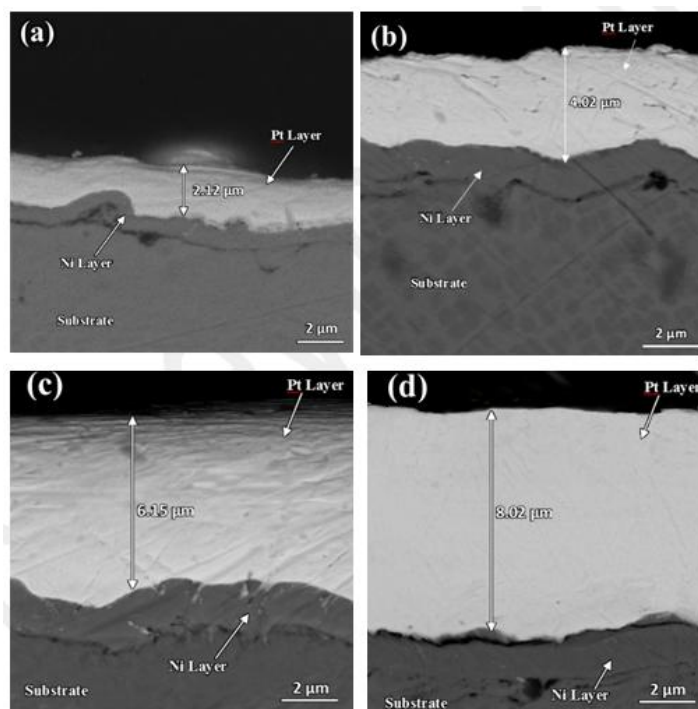


Figure 2: The SEM images of the initial layer of platinum with the approximately thickness of a) 2 μm , b) 4 μm , c) 6 μm and d) 8 μm

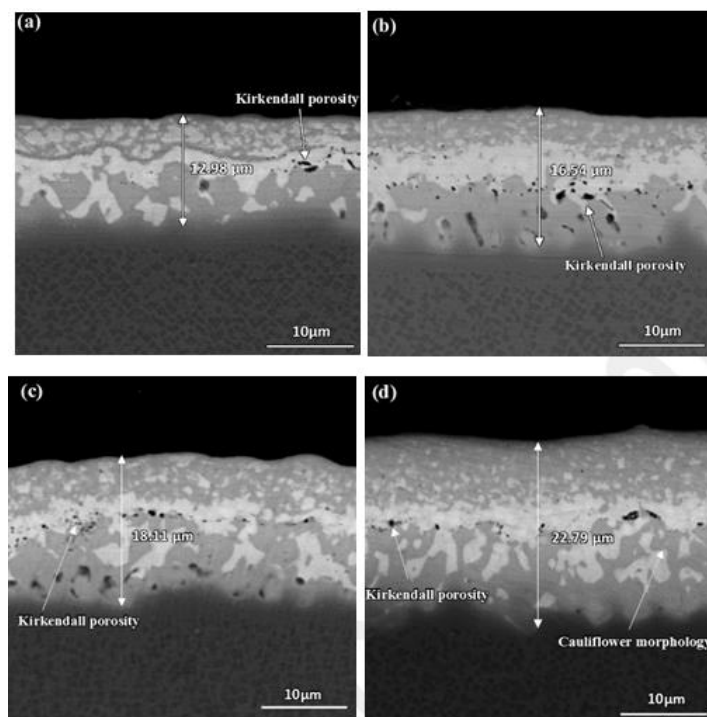


Figure 3: The SEM images of coating after diffusion treatment on the initial layer of platinum with thickness of a) 2 μm , b) 4 μm , c) 6 μm and d) 8 μm

surface of the alloy uniformly, according to Figure 2. It is worth noting that the rate of 1 $\mu\text{m}/\text{min}$. is obtained for producing the platinum layer with the selective condition for platinum bath.

In the following, the diffusion treatment of the platinum layer has been performed for improving the adhesion and also the diffusion of Pt into the substrate at the temperature of 1050°C for 2 hours under the vacuum of

10⁻⁵ torr. Then the samples were cooled up to 400°C in the furnace and then were cooled to room temperature in the air. Figure 3 shows the structure of the platinum coating after the diffusion treatment. As it is observed, the variations of the thicknesses of the diffusion layer have been recorded from 13 to 23 μm by increasing the initial platinum layer from 2 to 8 μm .

The variations of the diffusion layer thicknesses vs. initial platinum layer is shown in Figure 4. According to this Figure, the final thickness of the diffusion layer has been increased in the same condition of the time and temperature for diffusion treatment with increasing the thickness of the initial platinum layer.

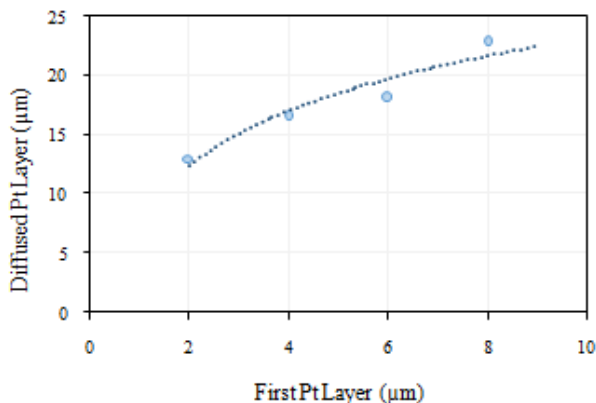


Figure 4: The thickness variations of the initial layer of platinum with the thickness of the diffusion layer after diffusion process (1050° C for 2 hours)

According to Figure 3, the bright areas which have the structure similar to cauliflowers are rich of platinum (based on the EDS analysis). The morphology of these areas depends on the voltage and the current density during electroplating of platinum[15]. The kirkendall porosities which are shown in this Figure have been produced due to the outward diffusion of nickel and loss of it in the substrate. It is expected that the completion of heat treatment and coating reaches in the lowest amount of these porosities.

Figure 5 shows the distribution of platinum and nickel from surface to depth, for all four thicknesses based on the EDS line scan that was performed perpendicular to the coating.

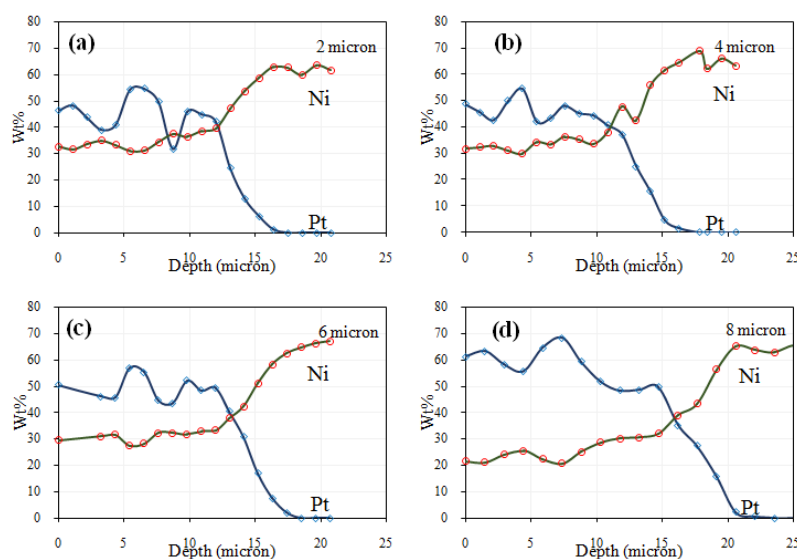


Figure 5: The variations of the concentration and depth of the Ni and Pt diffusion after diffusing treatment of the platinum layer with the thickness of a) 2μm, b) 4μm, c) 6μm and d) 8 μm

According to this Figure, the thickness of the initial platinum layer significantly has affected the amount of platinum presence in the coating after diffusion treatment. So that, the amount of platinum in the surface and depth of the diffusion layer has been elevated by increased thickness of the initial platinum layer. The concentration of platinum in the surface of coating for thicknesses of 2, 4, 6, and 8 μm of the initial platinum layer were measured as 46.3, 48.6, 50.5, and 61 weight percent, respectively. Also, the depth of diffusion for this element was determined 17.5, 17.9, 18.5 and 23.6 μm for thicknesses of 2, 4, 6, and 8 μm, respectively. The results indicate the direct correlation between the increased thickness of initial platinum layer with more presence of this element in the coating and also the increased depth of its penetration. Kiruthika et al. [16] reported that platinum is replaced in the atomic structure of nickel, and the diffusion rate of it increases by higher percent of platinum due to the decreased energy for the defects formation and loss of energy for migration of atoms at the inter metallic phase. According to the results of the EDS (line scan-Mag. 750), in addition to the presence of nickel, aluminum, chromium, cobalt and tungsten were also identified in the coating which shows the outward diffusion of those.

Binary diagram of the platinum-nickel elements demonstrated the complete dissolution of these two elements in one another in the solid state and as a result of their dissolution the intermetallic phase of NiPt is formed. According to the results of the XRD analysis (Figure 6), the NiPt phase has been identified in all samples. In Figure 6, widening the peaks in the samples with the higher thickness of coating can be result of the gradual changes of the concentration of the dissolved elements (platinum in the nickel and vice versa) and forming a deeper layer. In this situation, the platinum penetrates in to the wider range of the substrate and it affects the lattice constant of nickel in this layer. Since the diffraction angle in XRD analysis has a direct correlation with the crystalline plates distance and the lattice constant, nickel reaches the peak in a wider range than diffraction angle and in practice its peak become wider.

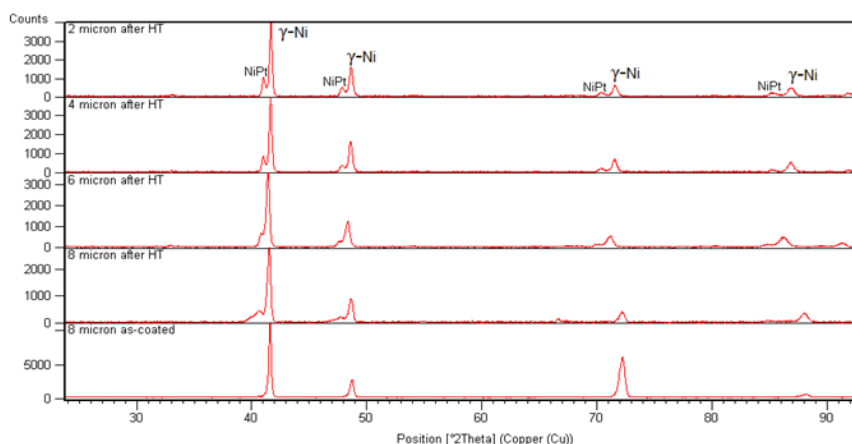


Figure 6: The results of XRD analysis after platinum electroplating and diffusion treatment

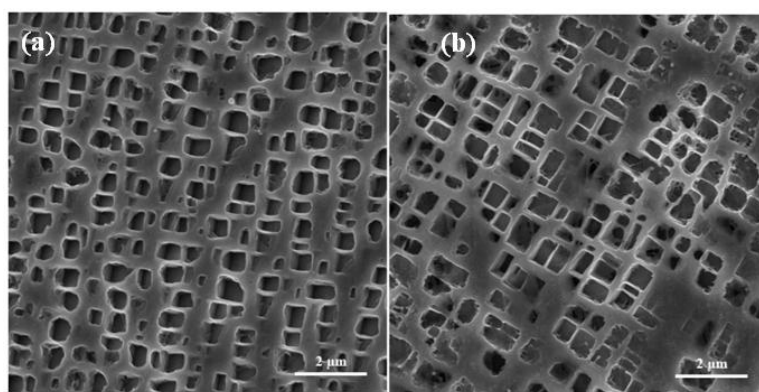


Figure 7: The SEM images of the γ' phase changes after aluminizing by the methods of a) LTHA, and b) HTLA

The aluminizing processes and final aging

Being sure of the suitable condition of the diffusion coating of platinum, the aluminizing processes have been performed in the next step in two different conditions of HTLA and LTHA by the powder-pack cementation method on the samples. Finally, heat treatment on aluminized coated samples was performed (Aging in 845°C for 16 hours).

Before evaluating the Pt-Al diffusion coating, for investigating the possible variations of the γ' phase, the microstructure of the substrate is examined. Figure 7 shows the distribution of the γ' phase for both two methods of the LTHA and HTLA. This phase was not changed and its volume fraction for two methods was determined 37.00% (LTHA) and 36.25% (HTLA), respectively. These results are in good agreement with the Safari and Nategh [12] studies which calculated the volume fraction of this phase after aging for $40 \pm 5\%$.

In the next step, the final Pt-Al coating on the surface of the alloy was investigated. Figures 8 and 9 respectively show the SEM images from microstructure of the coating for various thicknesses of platinum after two aluminizing methods of the LTHA and HTLA. As it is observed, the microstructure of the coating at the external layer is two-phase and includes β -(Ni,Pt)Al and ξ -PtAl₂. The next layers also are β -(Ni,Pt)Al (middle layer) and inter-diffusion zone (IDZ).

The X-ray diffraction analysis has been performed on all samples for identifying the available phases in the coating

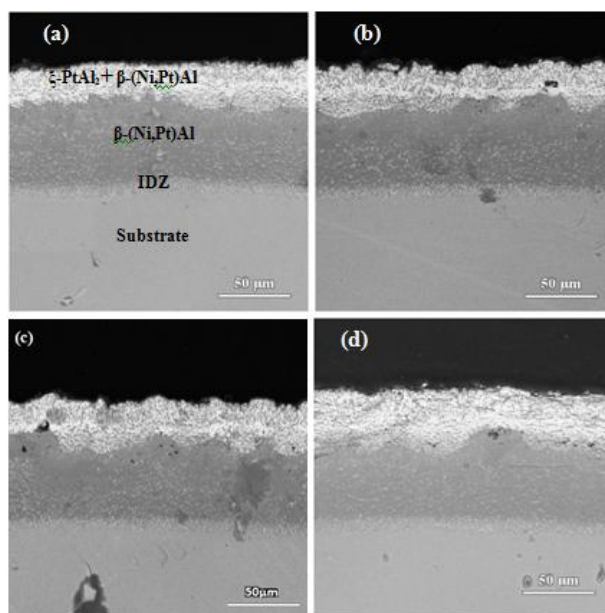


Figure 8: The SEM images of the Pt-Al coating in the HTLA condition for the platinum layer with the thickness of a) 2 μ m, b) 4 μ m, c) 6 μ m and d) 8 μ m

(especially ξ -PtAl₂ phase) and also to ensure the conversion of hard phase (Ni₂Al₃) to the softer phase (β -NiAl) (in the LTHA method). The results of this analysis have been shown in Figure 10.

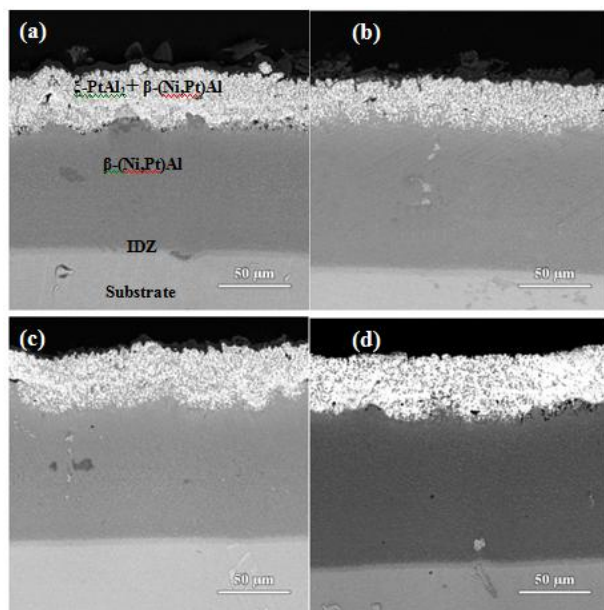


Figure 9: The SEM images of the Pt-Al coating in the LTHA condition for the platinum layer with the thickness of a) 2 μm, b) 4 μm, c) 6 μm and d) 8 μm

According to this figure, the phases of $PtAl_2$ and $NiAl$ were identified in all of the coatings and were in good agreement with the results of the Shirvani et al. [17] and Krishna et al. [4] studies that characterized the present phases in the Pt-Al coating. The results demonstrated that the minimum amount of $PtAl_2$ phase was in the method of HTLA with the initial thickness of 2 μm for Platinum layer and the maximum amount of this phase was formed in the LTHA method with the initial thickness of 8 μm for platinum layer. It is important to consider the effect of the thickness of the initial platinum layer and the method of aluminizing on the final thickness of the Pt-Al coating.

As it is demonstrated in the Figure 11, the final thickness of coating has been increased from 91.55 μm to 102.18 μm by elevating the thickness of the initial platinum layer from 2 to 8 μm in the HTLA method. In the method of LTHA, the final thickness of coating also has been increased by elevating the thickness of platinum layer from 128.13 to 148.67 μm.

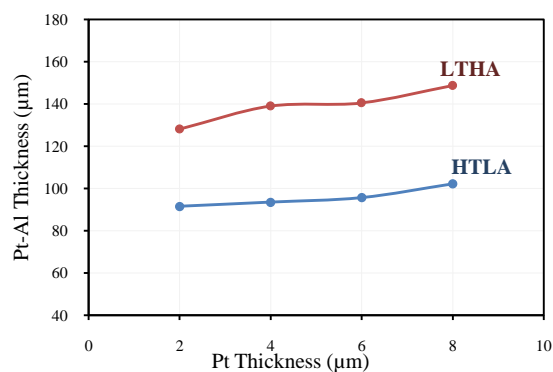
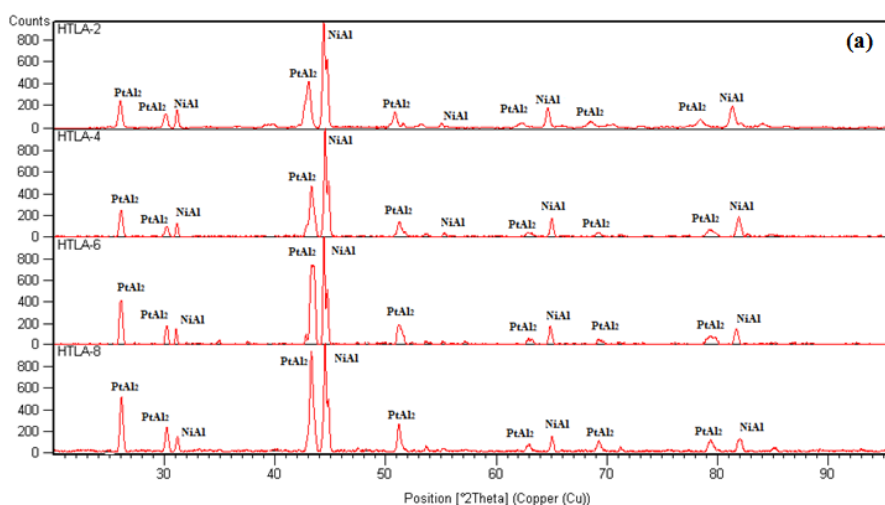


Figure 11: The thickness variation of the Pt-Al coating which was affected by the initial platinum layer and the aluminizing method

It is worth noting that the composition and thickness of the different layer of the coating for characterizing the three-layer structure of the Pt-Al coating is in good compliance with the results of Das et al. [18] studies. In Das's study, it is mentioned that the two-phase structure for coating in the lower percent of aluminum is only produced if the aluminizing process takes at least 10 hours. As in the present study, aging treatment for 16 hours was applied on all of the coated samples, so a two-phase structure on the surface of coating was obtained.

Table 3 shows the variation in the thickness of the different layers of Pt-Al coating for the various thicknesses of the initial layer of platinum in the two methods of HTLA and LTHA. It is observed that the increased thickness of the platinum layer elevates the thickness of the outer layer of $\xi + \beta$ for both two methods of HTLA and LTHA. Comparing with the HTLA, in the LTHA method the thickness of outer layer of $\xi + \beta$ has had significant growth in the initial layer of platinum with thickness 2 and 4 μm. Das et al. [18] found that the reason of this phenomenon is the presence of the higher amount of aluminum in the LTHA method. However, these changes were less in the thicknesses of 6 and 8 μm of initial layer of platinum. Therefore, it is concluded that the thickness of the initial layer of platinum affected the forming of $\xi - PtAl_2$ phase more than the amount of aluminum in the initial source. Also, results demonstrated



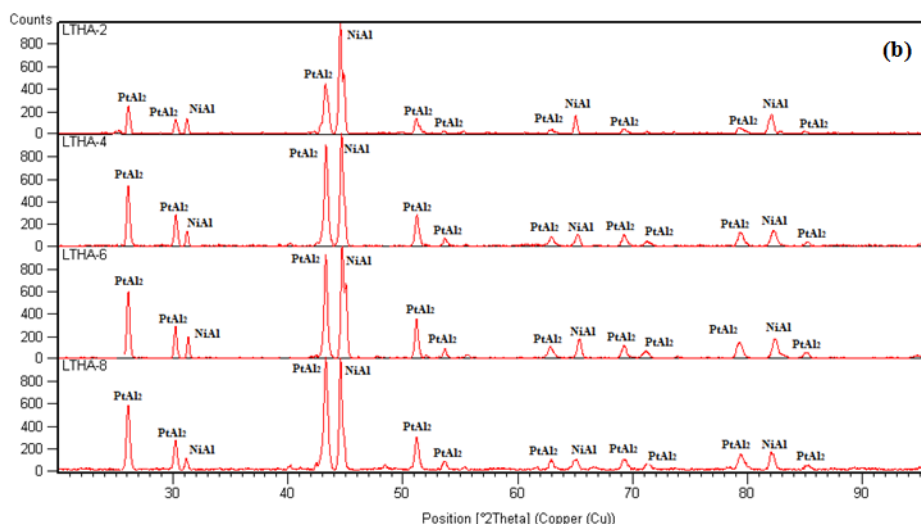


Figure 10: The results of XRD analysis for two methods of a) HTLA and b) LTHA aluminizing process for different thicknesses of initial platinum layer

Table 3: The thickness of the different layers of Pt-Al coating for the various thicknesses of the initial platinum layer for two methods of HTLA and LTHA

Thickness of the initial platinum layer (μm)		2			4			6			8		
Thickness of the Coating (μm)	Layer	$\beta+\xi$	β	IDZ	$\beta+\xi$	β	IDZ	$\beta+\xi$	β	IDZ	$\beta+\xi$	β	IDZ
	HTLA	31.7	50.9	8.9	35.9	48.5	9.1	41.3	43.6	10.8	43.6	45	13.5
	LTHA	39.1	84.5	4.5	40.7	93.3	4.9	43.7	92.4	4.3	45.4	97.2	4.4

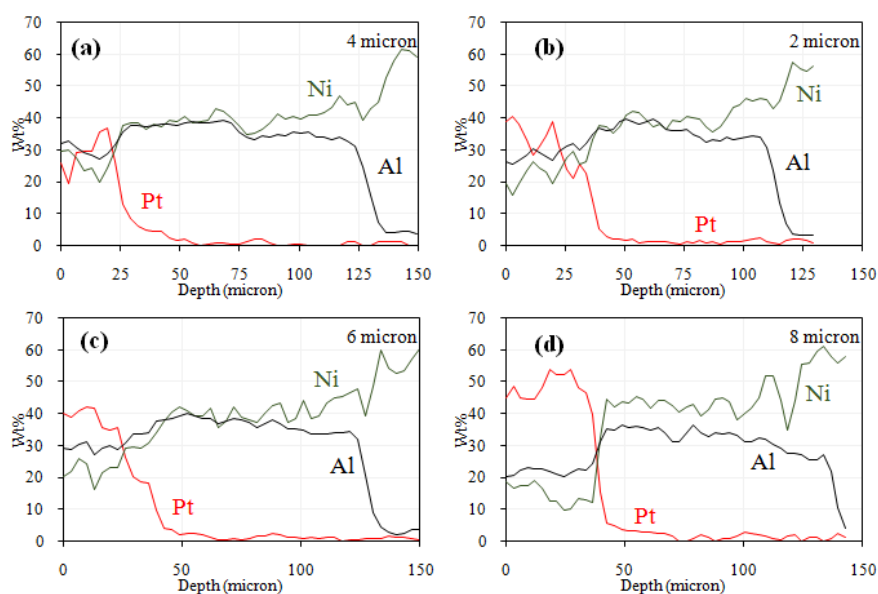


Figure 13: The variation of the concentration and the depth of the diffusion of the Nickel, Platinum and Aluminum in the LTHA for the initial platinum layer with the thickness of a) 2 μm , b) 4 μm , c) 6 μm and d) 8 μm

the increased thickness of the middle layer of β - (Ni, Pt) Al in the LTHA method compared to HTLA one. Increasing the thickness of coating in the LTHA method is due to the presence of more aluminum in the initial source of aluminum. This means that the percent of aluminum in the aluminizing method affects the thickness of the final coating. The increase of the %Al not only does affect the thickness of $\xi + \beta$ (outer layer) but also has influence on the thickness of β - (Ni,Pt)Al(middle layer).

The thickness of the IDZ layer in the HTLA has been elevated with the increased thickness of the platinum layer; however the thickness of this layer became constant in the

LTHA. The decrement of the 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 LTHA compared with the HTLA method. The reason of that is the presence of aluminum in the LTHA more than the other method which leads to an increase in the thickness of the middle layer and the great amount of the carbide-forming elements dissolve in this layer. This Issue caused a decrease in the thickness of IDZ layer.

The EDS Line-Scan (Mag.750) was performed for evaluating the variation of concentration of nickel,

platinum and aluminum perpendicular to the coating in the different thicknesses of the platinum layer and aluminizing method. The results of this analysis which is shown in the Figures 12 and 13, shows 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 initial thickness of the platinum layer, so that in the both two methods of HTLA and LTHA, the higher percent of platinum has diffused into the surface by increasing the initial thickness. This element diffuses more depth in the HTLA and it has been identified throughout the coating with higher thickness of the initial platinum layer.

One reason of this diffusion is the higher amount of aluminum in the LTHA method which does not let further diffusion of platinum. According to the diffusion mechanisms and also based on the Fick rules for diffusion phenomena, the concentration of the available elements affects the diffusion in addition to the time and temperature. According to the first rule of Fick:

$$J = -D \frac{dC_i}{dx} \quad (1)$$

Where, J is atomic diffusion flux, D is diffusion constant with the unit of (m^2/s), dC_i/dx is 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 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 are driving force for atomic diffusion. According to this rule, Kiruthika et al.[16] explained the diffusion interference of platinum and aluminum in the β -(Ni,Pt)Al phase. The results of this study indicated that the activity of the aluminum has been increased by higher amount of it. As a result, it decreases the activity of the platinum and nickel and finally it reduces their diffusion coefficient; which is in agreement with the results of the present study.

Table 4: The depth of the platinum diffusion in the different thickness of the initial platinum layer

Thickness of the initial platinum layer (μm)	2	4	6	8
Depth of the HTLA	60	65	95	100
Depth of the LTHA	50	52	67	77

Table 4 shows the depth of the platinum diffusion for two methods of HTLA and LTHA in the different thicknesses of the initial platinum layer. The results demonstrate the negligible changes of the platinum diffusion into the surface with 2 and 4 μm thicknesses. Also, its visible changes are in 6 and 8 μm thicknesses for two methods of HTLA and LTHA. The richer source of the initial platinum is the main reason for this event. It is worth noting that aluminum exists throughout the Pt-Al coating in the both methods, and it has also been identified by the EDS analysis (Figures 12 and 13). This shows the high diffusion coefficient for aluminum into the coating comparing with platinum. On the other hand, the presence of aluminum in all three layers of coating has been increased in the LTHA method more than HTLA one. Therefore, it shows the direct effect of the amount of aluminum in aluminizing method on the distribution of its concentration in the coating.

According to Figures 12 and 13, nickel has been identified in all coating layers. Increased diffusion of nickel in the outer layer of the coating ($\beta + \xi$) is obvious for less thicknesses of the initial platinum layer. Also, nickel diffused outward in the HTLA method more than LTHA one. This is due to the less presence of aluminum in the coating and as a result, there is more space for nickel diffusion.

According to EDS (Line-scan Mag.750) results, the carbide-forming elements were identified in all three layers of the Pt-Al coating, however, it was more obvious in the IDZ layer. Due to the lower thickness of the β -NiAl in the HTLA method, the percent of these elements in the IDZ layer was more in this method. On the other hand, chromium was more than the other elements in all coating layers in the both two methods of HTLA and LTHA. This result is coincident to the result of the Pedraza et al.[19] study.

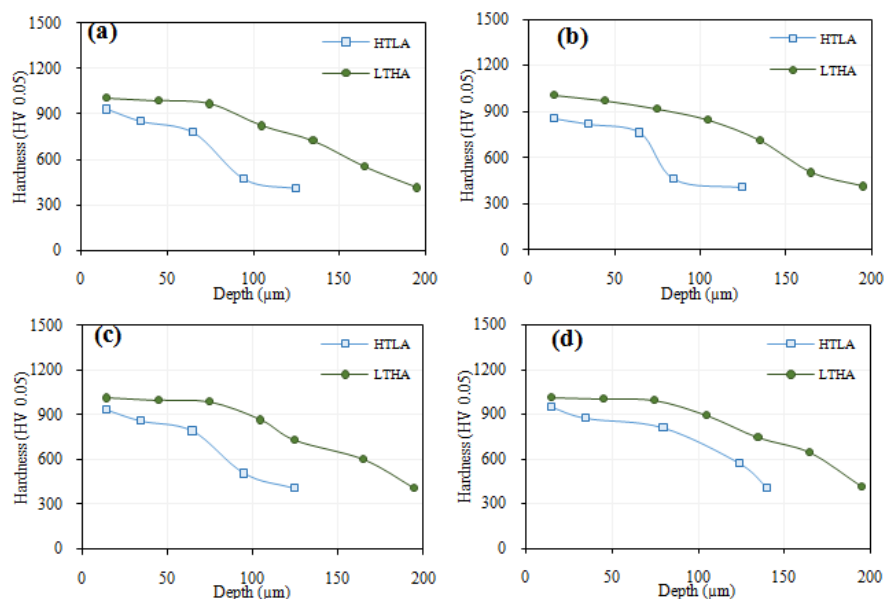


Figure 14: The hardness variation from surface to depth of the Pt-Al coating for HTLA and LTHA methods with the platinum layer with the thickness of a) 2 μm , b) 4 μm , c) 6 μm and d) 8 μm

They explained that the β -NiAl phase can dissolve only limited amount of chromium and the remainder diffuses in to other areas of the coating by increased time of the heat treatment.

The hardness of the Pt-Al coating

The hardness of the substrate and its variation from surface to depth of the coating were measured for the various thicknesses of the initial platinum layer in both two methods of HTLA and LTHA. The hardness of the substrate for HTLA and LTHA methods was obtained 406 and 420 Vickers, respectively. So, it shows lack of change in the substrate hardness in two methods of aluminizing process. The variation of the coating hardness from surface to depth and perpendicular to the coating was measured and it is shown in the Fig. 14.

The results of the micro-hardness test indicated the direct correlation between the increased hardness of the surface in the HTLA method and the increased thickness of the initial platinum. So, the hardness in the distance of 15 μm from the surface was measured 855 Vickers in the coating with an approximately thickness of 2 μm for initial platinum; however, it was 950 Vickers in the same distance from the surface of the coating with an approximately thickness of 8 μm for initial platinum layer. In the same condition, this scale was measured from 1008 to 1015 Vickers for the LTHA method. So, it shows the low changes of the hardness number in this distance from surface in the LTHA method. On the other hand, the results demonstrate the increased hardness of coating in the LTHA method is more than HTLA one. With regard to the results of the XRD analysis and SEM/EDS images, these changes are justifiable, and also its reason is forming the hard phase of PtAl_2 with more concentration on the surface of the coating.

Conclusions

1. In all Pt thicknesses, in the both two HTLA and LTHA methods, and after 16 hours aging, the structure of the final Pt-Al coating consists of three main layers, including ξ - PtAl_2 + β -(Ni,Pt)Al (external layer), β -(Ni,Pt)Al (middle layer) and IDZ. The results of the XRD analysis indicated the NiAl and PtAl_2 phases on the surface of the all coatings with different quantities.
2. The microstructure investigations indicated the thickness of ξ + β (outer layer) was increased by the higher thickness of the platinum layer for two methods of the HTLA and LTHA. The increased thickness of the middle layer of β -(Ni,Pt)Al is due to the presence of more aluminum in the LTHA than HTLA. Also, the thickness of the IDZ layer is more in the HTLA compared to LTHA.
3. According to XRD results, the concentration of PtAl_2 in the LTHA method (8 μm -Pt initial layer) has the largest quantity.
4. The results of the micro-hardness test demonstrated the increased of the hardness on the surface of the coating with the increased thickness of platinum layer in the HTLA. By increasing the thickness of the platinum layer the hardness variation is lower in LTHA; however the hardness in the LTHA is more than HTLA in all Pt-initial layers. (because of the more density of PtAl_2)

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