

A REVIEW ON THE CYCLIC OXIDATION BEHAVIOR AND MECHANICAL PROPERTIES OF THE Pt–Al-COATED CAST Ni-BASED SUPERALLOYS

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Abstract

The turbine section of turbojet engines operates above 900 °C. The cast Ni-based superalloy blades and vanes are used in this section. These components which are working in a very aggressive environment are usually applied with diffusion coatings. These coatings are used to increase oxidation resistance of parts and have evolved from plain aluminide coating to platinum-doped coating. Although the positive effect of platinum–aluminide coatings on the oxidation resistance of the superalloys is reported in several studies, the influence of this type of coatings on the mechanical properties of superalloys is somewhat challenging. This tutorial review of Pt–Al coatings covers: how

they supply protection against cyclic oxidation, how they are employed, their microstructure characterization, and their influence on the mechanical behavior of Ni-based superalloys. The present review tries to collect all the available information on the subject and seeks the optimum correlation between Pt–Al coating characterization and mechanical/cyclic oxidation behavior of the coated superalloys.

Keywords: nickel-based superalloy, Pt–Al coating, cyclic oxidation, tensile, creep rupture, low cycle fatigue

Introduction

When resistance to creep, fatigue and environmental degradation in the high temperature condition is required, cast nickel-based superalloys are the best choice for the designers of the turbojet engines. In superalloys, for purposes of enhancing the mechanical properties or other material characteristics at elevated temperatures, the alloying elements such as Mo, W, Co, Cr, Ti, Al, etc., are added to their chemical composition. In Ni-based superalloys, these elements form several phases in the microstructure: 1- γ' (Ni₃Al), which is an intermetallic compound and known as strengthening phase. 2- γ , which is a Ni (Al) solid solution and known as matrix. 3-Carbides (M₂₃C₆, MC, M₆C, ...) and borides (M₃B₂). 4-Topologically Close-Packed (TCP) phases such as σ , μ and laves.¹⁻⁷

Although superalloys have enough strength at high temperature, enhancement of their oxidation/corrosion resistance has also been a significant consideration.⁸⁻¹²

Aluminide diffusion coatings are widely used to protect the turbine blades (rotary parts) and nozzle guide vanes (stationary parts) which are produced from the superalloys. Alumina (α -Al₂O₃), which is formed during aluminizing process can offer good protection due to its slow growth rate, excellent adhesion to the substrate and high chemical barrier to oxygen transport and thermodynamic stability.

The aluminide coating is modified by the addition of platinum to increase its performance in the harsh environment of a turbine section. The main reasons for modification of the aluminide coating by platinum are as follows: 1—Pt improves the adherence of alumina scales, 2—Pt can promote selective oxidation of Aluminum, 3—Pt relieves the harmful effects of Sulfur, 4—Pt decreases void formation at the interface of metal/oxide, 5—The coating/substrate interdiffusion can be hindered by Pt, and 6—Pt improves the stability of β -NiAl phase and delays the transformation of γ -NiAl to the γ' -Ni₃Al phase.¹³⁻¹⁸

The effectiveness of platinum–aluminide (Pt–Al) coatings on the protection of superalloys against hot corrosion and cyclic oxidation has been approved by several studies.¹⁹⁻²⁵

Although the beneficial effect of Pt–Al coatings on the hot corrosion/cyclic oxidation resistance of the nickel-based superalloys has been cited in the literature, there are few performance data for the evolution of the mechanical properties (such as tensile, creep, fatigue and ...) of coating/ substrate (nickel-based superalloys) systems.

Recently, several systematic researches have been performed by Defence Metallurgical Research Laboratory^{26–37} in Hyderabad/India and Malek-Ashtar University of Technology^{38–46} in Tehran/Iran about the effect of Pt–Al coatings on the mechanical properties of nickel-based superalloys. Also, some investigations in these fields have been carried out sporadically, by other researchers.^{47–52}

Because of the mechanical properties of coated superalloy is very important point for the designers of turbojet engines, inquiry in these areas continues to obtain the new developments. The current article tries to review and collate the accessible data on the cyclic oxidation behavior and mechanical properties of Pt–Al-coated nickel-based superalloy at high temperatures condition. In this review, the different microstructure of Pt–Al coating affected by pre-aluminizing and aluminizing heat treatment, the influence of high temperature cyclic oxidation on Pt–Al coating features and the effect of Pt–Al coating on several types of nickel-based superalloy, have been considered.

According to the results which were reported in the literature, this review paper attempted to determine an optimum method for applying the Pt–Al coating on the nickel-based superalloy. This information can be helpful for designers when they select a Pt–Al coating, and they expect to improve the cyclic oxidation resistance without sacrificing the mechanical properties of the nickel-based superalloys.

Characterization of the Microstructural Variations of Pt–Al Coatings Used for the Nickel-based Superalloys

Turbine blades are critical components in both aeronautical and industrial gas turbines which are manufactured by nickel-based superalloys due to their high performance at elevated temperatures.

Depending on manufacturing methods, nickel-based superalloys are divided into three types: 1- Polycrystalline superalloys with equiaxed grains, for example, IN713LC, IN738, B1900 and Rene[®]80. In this kind of superalloys, the grain boundaries were strengthened by Carbides and Borides. 2—Directional solidification (DS), in this type the transversal grain boundaries have been eliminated and all grains oriented the same. (For example, Mar-M200Hf, PWA 1422, CM247LC and Rene 142) 3—Single crystal (SC) superalloys, the grain boundaries have been

completely removed from the structure of the SC superalloys (For example, RR2000, CMSX4, PWA 1484 and ReneN6). The creep strength of the SC superalloy is more than DS and polycrystalline superalloys.⁵³

Superalloys are strengthened by different stages of heat treatment. First is the solution heat treatment to homogenize the microstructure and decrease the effects of elemental segregation. The second is precipitation treatment to develop the γ' -Ni₃(Al, Ti) precipitates, and the last step is aging treatment to finalize the morphology (shape and distribution) of γ' phase and carbide reactions according to this equation: $MC + \gamma \rightarrow M_6C$ or $M_{23}C_6 + \gamma'$. $M_{23}C_6$ carbides are located as discrete particles along the grain boundaries, when MC carbides are precipitated as separate particle within the grains. In Ni-based superalloys, γ' phase and carbides provide the significant mechanism for strengthening.^{54–57} The morphologies of γ' and carbide phases in the nickel-based superalloy are shown in Figure 1.

Six steps are used to form the Pt–Al coating on the surface of the superalloys:^{16,46}

First Step (preparation of the substrate): grit blasting and degreasing (cleaning by acetone and ethanol) the specimens.

Second Step (Ni-plating): in order to active the surface of superalloy, the applying of a nickel layer (1–2 μm) on the surface, is required. Superalloys are promptly passivated by the formation of surface oxide films.⁵⁸ Chromium is added to composition of nickel-based superalloy in order to increase the hot corrosion resistance. A layer of passive Cr_2O_3 is formed on the surface of the superalloys by the reaction of this element with the oxygen. To remove the effect of passive oxide layer and improve the adhesion of Pt layer on the surface, a layer of nickel is plated on the surface, before Pt electroplating. Nickel can be plated on the surface of nickel-based superalloys by different methods. Watts nickel and nickel sulfamate bathes are two famous ways for deposition of nickel on the superalloys surfaces. In the Watts method, NiSO_4 is the main source of Ni^{2+} ions and in the nickel sulfamate method $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ is the origin of Ni^{2+} ions.^{59–61}

Third Step (Pt-plating): An initial deposition of the layer of pure Pt (typically 2 μm –10 μm thick) is produced on the surface of superalloy by electrodeposition, physical vapor deposition (PVD) or fused salt electrolysis.¹⁶ For example, it has been reported that by means of an electrolyte solution bath containing 14–18 ml type P-salt ($\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$), 70–90 $\text{g}\cdot\text{L}^{-1}$ Na_2CO_3 , 40–70 $\text{g}\cdot\text{L}^{-1}$ NaCH_3COO and 1 L distilled water, (at temperature of 90 °C, current density of 0.2–0.4 $\text{A}\cdot\text{dm}^{-2}$, pH = 10.5 and time=360 min), the dense platinum layer with the thickness of 6 μm has been formed on the surface of a nickel-based superalloy.^{41,62} Also, in

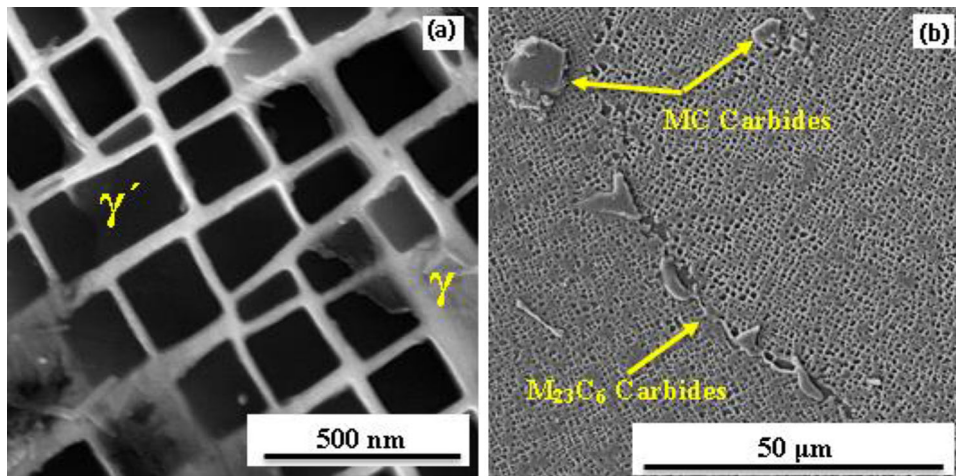


Figure 1. SEM (Secondary Electron Detector (SE)) images of (a) Cubic γ (CMSX-4) and (b) MC and $M_{23}C_6$ carbides (Rene 80)-fully heat treated.

other literature using of Q-salt ($(NH_3)_4Pt(HPO_4)$) for electro plating has been reported.^{63,64} For example, in Ref 63 the Pt layer with the thickness of 4–7 μm has been obtained by using of Q-bath with pH10.2–10.6, and at temperatures of 90–95 °C (the concentration of Pt in the bath was about 5 g L⁻¹). The current density during Pt-plating process was controlled to be within 2–5 mA/cm². Hanna⁶⁵ used fused salt electroplating method to apply the Pt-layer on the surface of nickel-based superalloy IN-738 LC. In this method has been used an eutectic salt mixture with the composition of 53 percent of sodium cyanide and 47 percent of potassium cyanide, which has a melting temperature of about 520 °C. A deposition rate of 20–25 μm per hour can be achieved using this method. A typical image of Pt layer which is formed on the surface of the Rene[®]80 (a polycrystalline nickel-based superalloy) is shown in Figure 2.

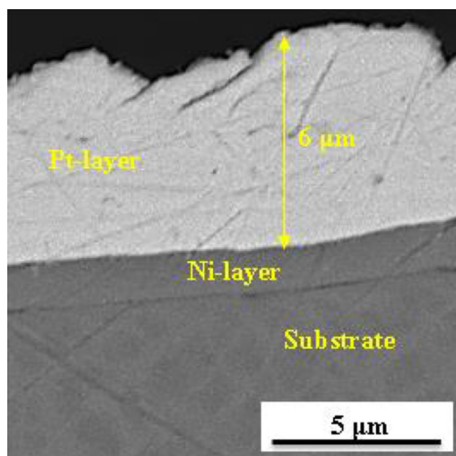


Figure 2. The SEM (back scatter electron detector (BSE)) image of the initial layer of platinum with the approximate thickness of 6 μm (achieved with P-salt).⁶⁶

Forth Step (Diffusion of Pt): In order to improve the adhesion between the substrate and Pt-layer, Pt-electroplated samples are given a diffusion heat treatment in vacuum. This step is named “prior diffusion”, “pre-aluminizing diffusion” or “annealing treatment”.^{16,18,67–70} In this case, the diffused layer is fabricated by simultaneous inward diffusion of Pt and outward diffusion of alloying elements from the substrate during this process.⁶²

Das and his colleagues⁶⁷ evaluated the effect of pre-aluminizing diffusion treatment on the microstructure of Pt–Al coating. They selected two different diffusion treatment conditions for Pt layer (8 to 10 μm) which was applied on the CM-247 (Low Carbon): 1–0.5 hours at 850 °C and 2–five hours at 1034 °C. The results of this investigation showed that the suitable diffusion has taken place in the second condition, i.e., five hours at 1034 °C. The thickness of the diffusion layer, for two above methods, was measured 15 μm and 25 μm , respectively. Also, the presence of intermetallic phase (NiPt) was found in the diffusion layer by XRD (X-Ray Diffraction).

Increase in the thickness of Pt-layer after diffusion treatment has been also reported by Barjesteh et al.³⁹ In this research, different thicknesses of Pt-layer (2, 4, 6 and 8 μm) were plated on the specimens and then, pre-aluminizing diffusion was performed at 1050 °C for 2 hours. The thickness of Pt-layer after annealing treatment was measured 12.9 μm , 16.54 μm , 18.2 μm and 22.79 μm , respectively. These results of this evaluation showed that the final thickness of the diffusion layer has been raised in the same condition of the time and temperature for diffusion treatment by increasing the thickness of the initial platinum layer. From the results which have been recorded in the Ref. 67 and Ref. 39 can be concluded that the application of pre-aluminizing treatment on the Pt layer (with the thickness of 8 μm) led to an increase in the thickness of Pt-diffused layer (64–68%).

Binary phase diagram of the platinum-nickel exhibited 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.⁷¹ This binary diagram functions as a reference for the phases formed during Pt-diffusing on pure Ni which will be given in detail. The presence of NiPt intermetallic phase has been detected in the research which has been performed by Barjesteh et al.^{39,66} (Figure 3).

Figure 4 shows typical microstructures of the platinum coating after the prior diffusion treatment. The Pt diffusivity appears to be a function of Pt concentration, i.e., increasing the thickness of initial Pt layer led to an increase in Pt diffusion range. Zhang et al.⁷² calculated the Pt diffusivity (m^2/s) for 2h at 1175 °C for nickel-based superalloys. In this research they selected SX ReneN5 and DS Rene142 as the substrates. Pt diffusivity for diluted Pt in γ and γ' phases was calculated 2.8×10^{-15} and 1.4×10^{-15} , respectively. Elements in the Ni-base superalloy substrates did not display any significant effect on the diffused layer microstructure.^{63,72}

As can be observed from Figure 4, the coating morphology consists of pores and/or particles. The black particles in the outer portion may result from the originally grit-blasted surface, as typically evaluated in other investigations.^{13,73}

On the other side, several Kirkendall porosities have also been observed in the diffusion layer in Figure 4. Differing diffusion rates of the platinum and substrate at 1050 °C for 2 hours can generate voids in the interfacial surface. The outward diffusion of Ni is faster than the inward diffusion of Pt;^{10,74–77} therefore, Ni with the faster diffusion rate diffuses into Pt and leaves behind voids which are not filled by the slower diffusion of Pt. Because of the level of diffusion in the interface depends on time and temperature,⁷⁸ the formation of Kirkendall voids is accelerated by increased temperature and dwelling time. In the literature has been recorded that Kirkendall pores are created due to

unequal diffusion fluxes between the platinum and the substrate (nickel-based superalloy) caused by inter-diffusion during coating formation.¹⁹ It is expected that Kirkendall voids will be eliminated by the completion of Pt–Al coating process. These voids will be occupied by Al, Ni, Pt and other elements during the aluminizing process and final heat treatment.⁷³

On the other hand, as can be seen from Figure 4, Pt-diffused layer consists of two phases (bright and dark). This morphology known as ‘cauliflower’ and shows truly interdiffusion between Pt layer and substrate occurred. The chemical composition of this layer has been cited in different references. For example, the line scan EDS report for Pt-diffused layer which has been applied on Rene[®]80 superalloy is as Figure 5.⁶⁶ It has been cited that the percentage of Pt, Ti and Al in the bright phase is higher than their contents in the dark phase, while the percentage of Cr and Co in the dark phase is more in comparison with their amounts in bright phase.⁶²

Figure 5 also shows the simultaneous inward diffusion of Pt and outward diffusion of alloying elements from the substrate during the annealing treatment. This phenomenon has been reported in other literature.^{13,62,80}

Several studies^{13,19,41,80–82} have demonstrated that the pre-aluminizing process has beneficial effect on the final microstructure of the Pt–Al coatings. It has been reported that by means of this process, the maximum adhesion of the Pt-plated coating to the substrate can be achieved. In addition, pre-aluminizing treatment improves the platinum distribution in the surface of the substrate, and provides a good source of Pt for the next step of coating process.

Fifth Step (Platinum-Aluminide coating): Aluminide coating can be applied to Pt-electroplated turbine blades and vanes, in order to produce the Pt–Al coating, by a variety of techniques including pack-cementation,^{41,83–85} slurry

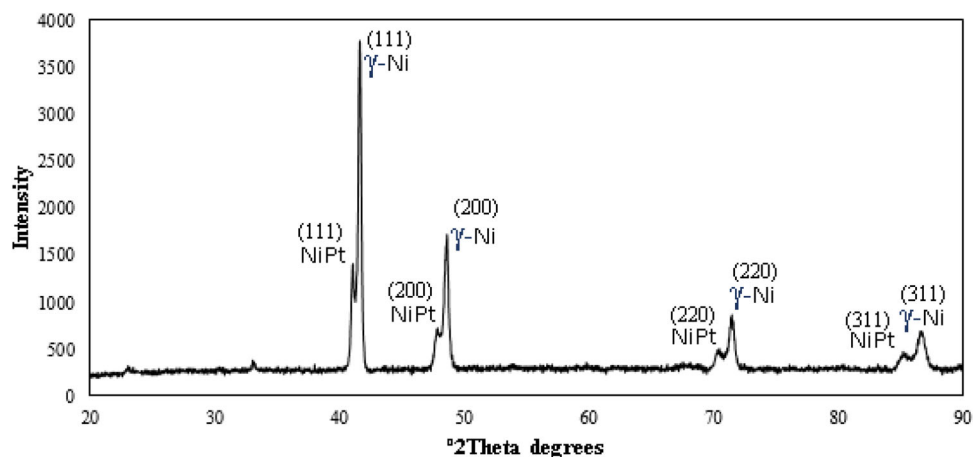


Figure 3. XRD peaks after pre-aluminizing treatment (at 1050 °C for 2 hours).⁶⁶

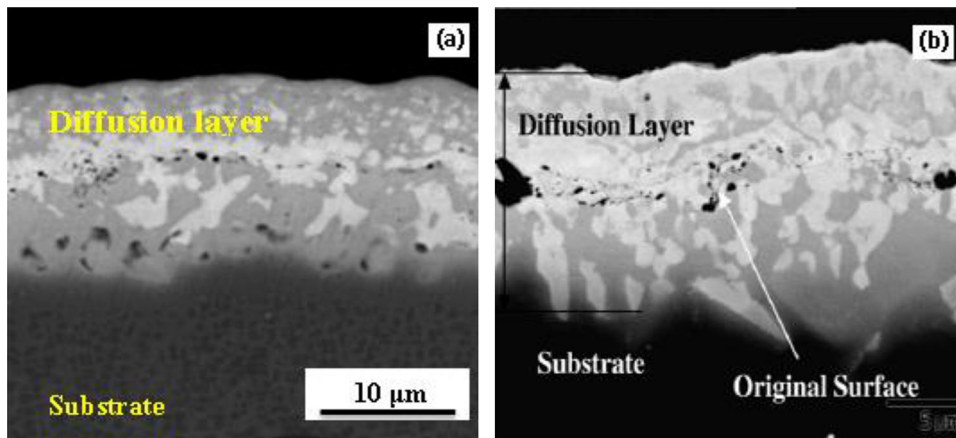


Figure 4. SEM/BSE image of microstructure of the Pt-electroplating (a) after prealuminizing treatment at 1050 °C for 2 h (substrate: Rene[®]80, initial Pt layer: 6 μm)^{39,66} and (b) after prealuminizing treatment at 1052 °C for 1h (substrate: MarM-247, initial Pt layer: 7 μm).⁶³

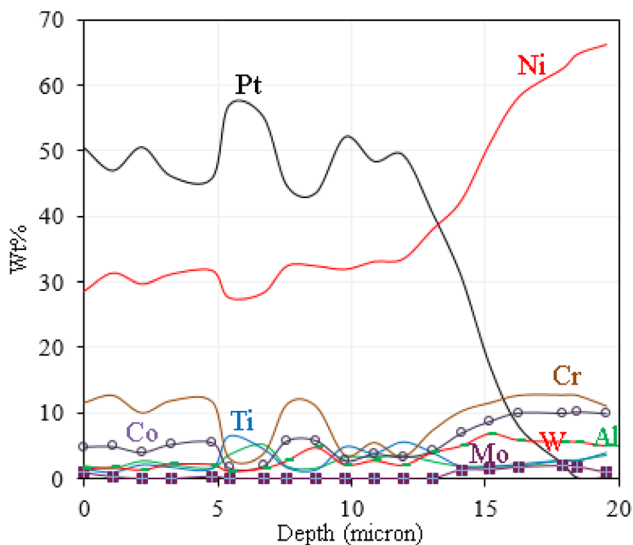


Figure 5. Concentration profile (line scan EDS) of major alloying elements in the Pt-diffused layer. (Substrate: Rene[®]80, thickness of Pt: 6 μm and prealuminizing treatment: at 1050 °C for 2 hours).⁶⁶

cementation,¹⁴ out-of-pack,⁸⁶ and chemical vapor deposition.^{80,87}

Depending on the concentration of Al and Pt on the surface of nickel-based superalloys, different types of intermetallic phases such as ξ -PtAl₂, β -(Ni, Pt) Al, δ - Ni₂Al₃, PtAl, Pt₃Al, Pt₂Al₃, Pt₅Al₃, Pt₂Al^{88,89} can be produced in the structure of coating system. In the literature it has been reported that when the amount of Pt is about 30–35 at. %, the maximum solution of Pt in the β -NiAl takes place at 1100 °C.¹⁸ Altering the thickness of the initial Pt layer leads to changing in the Pt percentage in the coating. In the high concentration of Pt on the surface, the probability of PtAl₂ phase creation is extremely high. Therefore, it can be concluded that increase in the thickness of Pt leads to an

increase in the probability of PtAl₂ formation. Also, the content of Pt in the coating can be controlled by the prealuminizing treatment.¹⁶

On the other side, Al amount in the coating can be changed by the selection of aluminizing method. Three major methods of aluminizing process are identified: (1) the pack or slurry, (2) above the pack, and (3) chemical vapor deposition (CVD) (closed or open retort).^{78,90} In the pack procedure, the part is surrounded by pack mix in a heated retort and the pack produce the halide vapors. On the other hand, in the above-the-pack method, the part which is selected to coat is located in a retort with the option of flowing inert gas, therefore the parts are not in contact with the pack powder. The halide vapors are efficaciously plumbed on to the both internal and external surfaces of the part. In the CVD method, the halide vapors are produced by separate generators which are located external of the reactor. The vapors are plumbed on to the part which is held inside a reactor in a heated retort.⁹⁰

Based on the activity of Al in the gas phase and the selected temperature for aluminizing process, two different methods are described for aluminizing. The high temperature low activity (HTLA) procedure is a “one-step” method, in which Ni diffuses outwardly and β -(Ni, Pt)Al is formed directly. For instance, the mechanism of coatings which are produce by MDC150L or Howmet 150 L process is outward growth.⁹⁰ On the other side, in the low temperature high activity (LTHA) process, Al diffuses from the surface to the substrate inwardly. This type of pack cycle is known as the RT22 coating.^{90,91} According to the formation mechanism of this method, at first δ - Ni₂Al₃ is formed as the coating. The subsequent heat treatment is necessary to convert δ -phase to β -phase. In the literature, δ - Ni₂Al₃ is known as the brittle phase which has lower mechanical property than β phase.⁴²

HTLA is usually carried out at 1050–1150° C for 2–4 hours, while LTHA is performed at 750–800 °C for 4-5 hours, and after that post-aluminizing at 1050–1150 °C for 2-4h.^{35,42,65,78} In case of Pt–Al coatings, it has been documented in the literature that the diffusivities of Al or Ni in β or ξ phases have not been affected by the presence of Pt.¹⁶ Also, in the references demonstrated that the thickness of inter-diffusion zone (IDZ) which is created by HTLA procedure is thicker than LTHA method. It should be noted that IDZ layer is a place for concentration of heavy transition elements such as tungsten, titanium, chromium, molybdenum, and cobalt.^{42,73}

Three main microstructures for Pt–Al coatings have been reported in the literature depends on thickness of initial Pt, prealuminizing process and the type of aluminizing procedure as follows: 1-single phased (β –(Ni, Pt) Al) structure 2-bi-phased (ξ –Pt–Al₂+ β –(Ni, Pt) Al) structure (inter-metallic PtAl₂ phase dispersed in a matrix β –(Ni,Pt)Al) and 3- bi-phased structure with a continuous PtAl₂ layer.

The typical microstructures of Pt–Al coatings (three main microstructures) which are applied on the different nickel-based superalloys have been shown in Figure 6.

The structure of single phased coating (Figure 6a) consists of two layers (β +IDZ), while bi phased coating (Figure 6b) has been made from three layers (ξ + β +IDZ). Third structure which has been shown in Figure 6c consists of four layers (ξ + β +IDZ+ continuous PtAl₂).

The correlation between initial Pt thickness and the microstructure of final Pt–Al coating, produced using a single-step high-activity aluminizing process, has been reported by Krishna et al.¹⁷ The results of this research revealed that in the case of 1 μ m thickness of Pt, this element remains in the solid solution of NiAl (single phase), while a Pt with thickness of 15 μ m creates a continuous layer of PtAl₂ on the top of the bi phase layer. Also, they did not find any differences between microstructure of Pt–Al coatings when the thickness of Pt lies in the range of

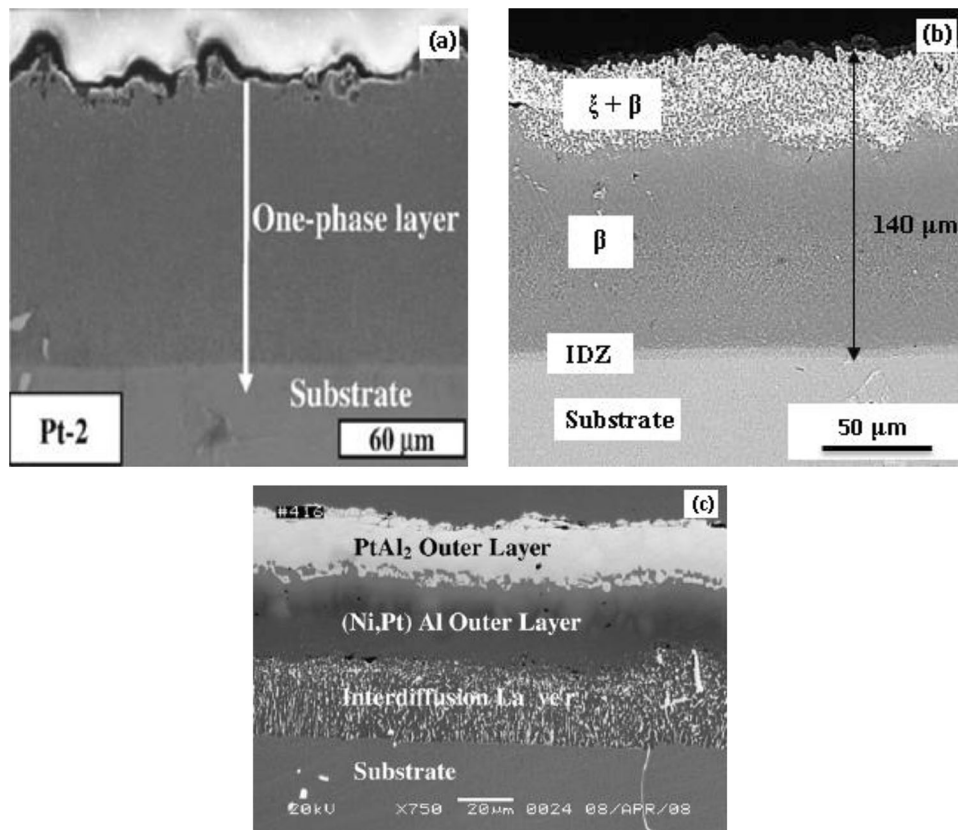


Figure 6. SEM images of typical microstructures of Pt–Al coatings (a) single phased structure (substrate: CM-247LC, initial Pt layer: 2 μ m)⁶⁹ (b) bi-phased structure (substrate: Rene[®]80, initial Pt layer: 6 μ m, aluminizing method: LTHA (6 μ mPt/LTHA))^{43–46} and (c) bi-phased structure with a continuous PtAl₂ layer (substrate: MarM-247, initial Pt layer: 7 μ m).⁶³

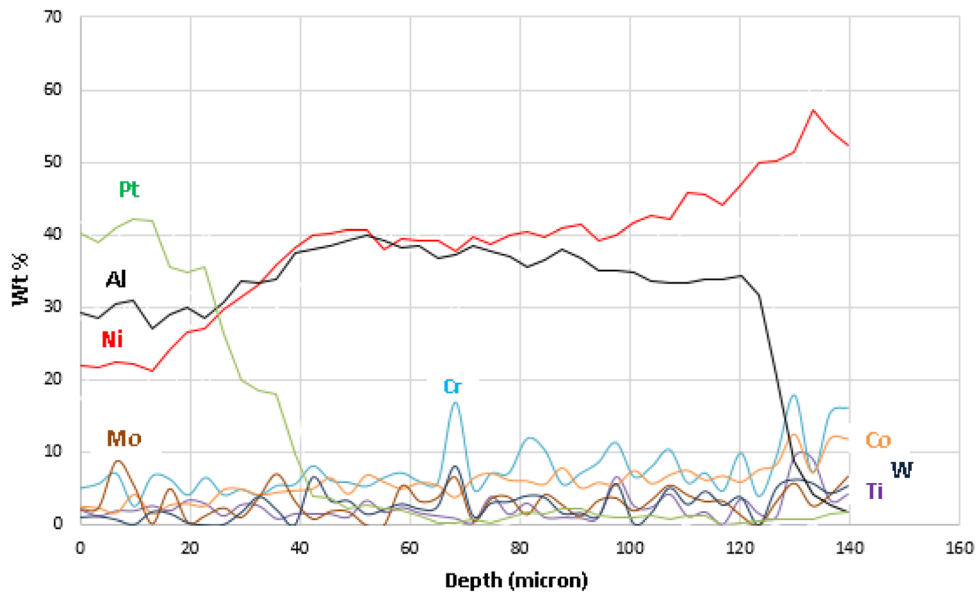


Figure 7. Composition profile (line scan EDS) of Pt, Al, Ni and refractory elements in the typically Pt–Al coating (substrate: Rene[®]80, (6 μ mPt/ LTHA)).⁶⁶

2.5 μ m and 10 μ m. In all of cases (2.5-10 μ m) bi phased coatings are produced.

Figure 7 depicts the variations of the concentration of nickel, platinum, aluminum and refractory elements, such as W, Mo, Co, and Cr in the perpendicular direction of the typically Pt–Al coating (substrate: Rene[®]80, initial Pt layer: 6 μ m, pre-aluminizing: for 2h at 1050 °C and LTHA aluminizing process).⁶⁶

The presence of (Ni, Pt) Al and PtAl₂ in the microstructure of single phase and bi phased of Pt–Al coatings has also been confirmed by XRD technique and reported in the literature.^{12,13,39–46}

It is well known that coatings are not in thermodynamic equilibrium with the substrate alloys as a whole. At elevated temperatures, the difference between the chemical compositions of the coatings and the substrates furnishes the driving force for inter-diffusion of different elements.⁹⁰ It has been also stated that the alloying elements play a significant role in obtaining a single or a bi-phase structure.¹³ Migration of Al and Pt inward toward the substrate and outward diffusion of Ni and refractory elements especially Cr from the alloy to the Pt–Al coating, at 1050 °C, as evident from Figure 7.

Several advantages as better compatibility, improved metallurgical stability and higher creep strength are reported for bi-phase microstructure of Pt–Al coating.⁷² It has been reported by Das¹⁶ that the bi phase (β + ξ) microstructure of the Pt–Al coating (Figure 6b) can tolerate much more strain in comparison with other microstructures and also, has a good cyclic heating/cooling endurance and provide a suitable oxidation protection. Pedraza et al.¹³

reported higher Pt surface concentrations, lower temperatures and shorter aluminizing treatments all play a key role in the forming of bi-phase microstructure of Pt–Al coating.

The Effect of Pt–Al Coatings on the Oxidation Resistance of Nickel-based Superalloys

Effect of Initial Platinum Thickness on Oxidation Behavior

In general, during the service, the surface of bare nickel-based superalloys reacts with oxygen, which is the basic environmental parameter affecting designed life of parts. Also, in the superalloys, the increase in temperature leads to an increase in oxidation rate progressively.

There are many references in the published literature, in which the enhancement of oxidation resistance of superalloys by Pt–Al coatings in comparison with bare and plain aluminide-coated superalloys have been reported.^{15,17,18,25,40,65,86,92,93}

In the research which has been performed by Barjesteh et al.⁴⁰ has been reported that after 120 cycles of oxidation at 1100 °C, TiO₂, Al₂O₃, and spinel Ni (Cr₂O₄) have been formed on the surface of bare Rene[®]80 (Figure 8a). Ni (Cr₂O₄) is produced by the reaction between NiO and Cr₂O₃. The formation of this spinel shows that uncoated Rene[®]80 has no perfect resistance against cyclic oxidation at 1100 °C. It is well known that the presence of refractory elements such as Cr and Ti in the coating composition decreases the oxidation resistance. Also, the out-ward diffusion of Al, Ti and Cr from substrate toward coating, leads to the decrease in the strength of the superalloy.^{41,94}

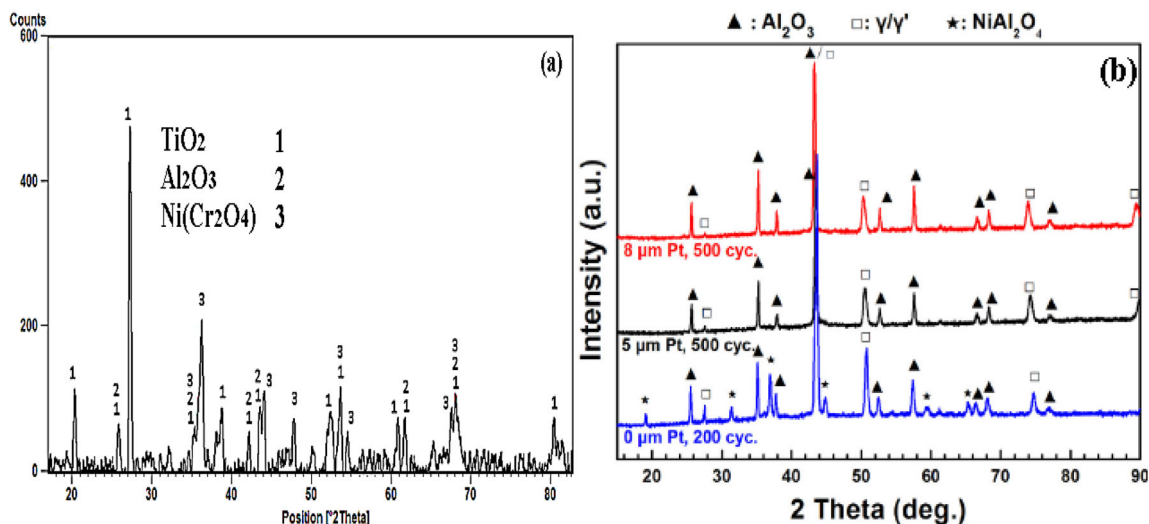


Figure 8. XRD patterns of (a) oxide scale of uncoated Rene® 80 after 120 cycles⁴⁰ and (b) Pt-Al-coated nickel-based superalloy after different cycles. Both tests were performed at 1100 °C.¹⁸

Yang et al.¹⁸ also showed that after 200 cycles of oxidation at 1100 °C of a plain aluminide coated nickel-based superalloy, Al₂O₃ and NiAl₂O₄ spinel were formed on the surface. While, at this condition and after 500 cycles, only Al₂O₃ was formed on the surface of this superalloy which was coated by Pt-Al. (Figure 8b). The formation of only Al₂O₃ on the surface of Pt-Al-coated nickel-based superalloys after several hundreds of cycles of oxidation depending on the temperature of exposure has been reported by others.^{12,16,40,85} Tawancy et al.⁹³ demonstrated that the presence of Pt in the composition of β-NiAl promotes formation of pure Al₂O₃ scale and decreases scale growth rate. This element also increases the Al₂O₃ scale adherence.⁹⁰ It is also documented in the literature that the presence of Pt confidently affects on the re-formation of Al₂O₃ scale after spalling of the oxide layer.⁹⁴ However, no formation of the other oxides and spinel shows that the oxidation resistance of Pt-Al coatings is higher than plain aluminide coatings.

However, Krishna et al. demonstrated that the oxidation resistance of nickel-based superalloys can be improved by applying the Pt-Al coatings on their surfaces, when the minimum content of Pt (a 6μm thick initial Pt layer) in the coating has been provided.¹⁷

As mentioned before, PtAl₂ phase plays a significant role for creation of suitable reservoir source of Al at high temperature,⁴⁰ the initial thickness layer of Pt below of 6μm mainly does not enable to provide enough reservoir source of Al in the outer portion of the coating. In this condition, the percentage of Pt in Pt-Al coating is not enough to resist local spallation caused by micro-voids. Therefore, the excited aluminum in the coating will be rapidly used during oxidation and the next oxide scales will be produced by the outward diffusion of Al content from

the substrate. This phenomenon will be repeated and cause weight loss of the base alloy.

On the other hand, the increase in Pt initial layer thickness from 6μm to 15μm leads to a decline in oxidation resistance of nickel-based superalloys. The similar results have also been reported by other researchers.^{18,40}

Two main reasons are behind of this finding. One of them is an increase in the thickness of the final coating by increasing the initial platinum thickness, and another one is decreasing in the elastic modulus of the coating by increasing the initial platinum thickness. As a result, an increase in the thickness of the final coating (Pt-Al) leads to a decline in elastic modulus of the coating.

During hot cyclic oxidation condition, because of the difference between the thermal expansion coefficients of the substrate, Pt-Al coating and Al₂O₃ oxide layer, the coated sample will sustain tensile stress during the heating process, while it will tolerate compressive stress when it is cooled down. Therefore, due to the low elastic modulus, thick coated sample will show less resistance to deformation and will damage and rumple from the surface more quickly.⁴⁰ Yang et al.¹⁸ also demonstrated that increasing the thickness of initial Pt plating in the Pt-Al coating, lead to a decline in the values of hardness and Young's modulus. Hence, the thick coating has the softer feature and can be deformed easily and so its degree of rumpling is severer. According to the results which are published in the literature, it seems that the initial platinum thickness between 5 and 6μm shows the best cyclic oxidation resistance.^{17,18,40}

These explanations exhibit that the initial platinum thickness plays a great influence on the rumpling behavior of Pt-Al coating during cyclic oxidation.

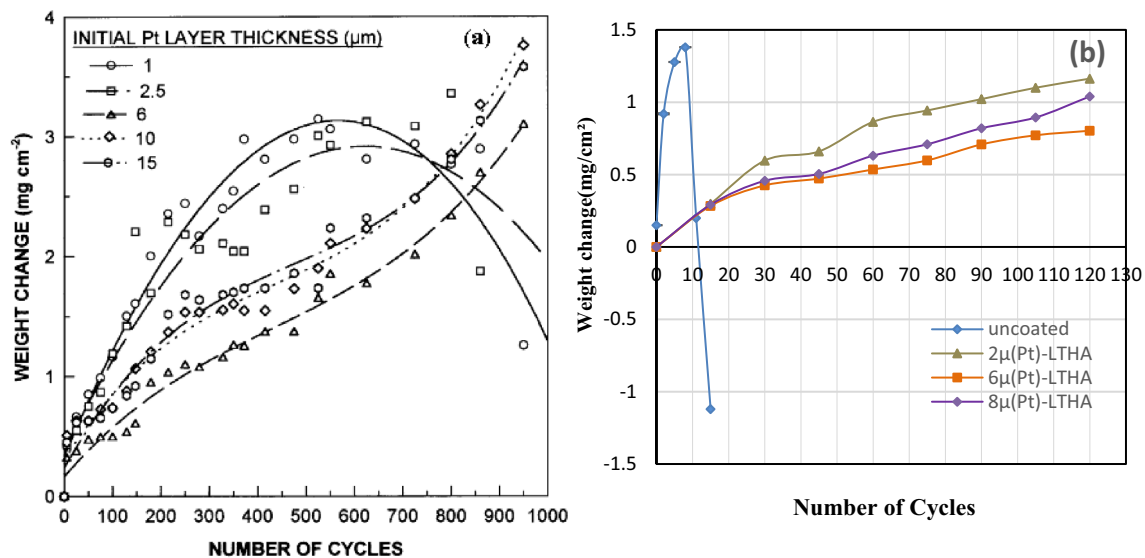


Figure 9. Sample weight change versus number of cycles for cyclic oxidation (at 1100 °C) of the nickel-based superalloys with different Pt initial thickness layer (a) CM-247(LC), Aluminizing method: LTHA¹⁷ and (b) Rene® 80, Aluminizing method: LTHA.⁴⁰

The relationship between Pt initial layer thickness and oxidation resistance is shown in Figure 9. As evident from this figure, the coating corresponding to 6 μm Pt (initial thickness) shows the optimum resistance to oxidation.

Effect of Pt–Al Coating Microstructure on Oxidation Behavior

The effect of Pt–Al coating microstructure on the oxidation behavior of the nickel-based superalloys has been evaluated in the literature.^{40,93}

In the research which has been performed by Tawancy,⁹³ two types of Pt–Al coating named RT22LT (inward diffusion of Al- aluminized by the pack cementation method) and Howmet 150 L (outward diffusion of Ni- aluminized by the CVD method) have been applied on the MAR M002DS (nickel-based superalloy). Note that in this case, the initial thickness of 7 μm of platinum is considered. By applying of Howmet 150 L and RT22LT procedures on the surface of MAR M002DS, single-phased and bi-phase microstructure of Pt–Al coating have been obtained, respectively. The results of this evaluation showed that the thermal stability characteristics of the single-phased microstructure were better than bi-phased microstructure, and therefore as a result the cyclic oxidation resistance of single-phased microstructure was higher than bi-phased microstructure at 1150 °C.

Tawancy⁹³ concluded that the thicker IDZ of Howmet 150 L coating plays an important role in the reduction of diffusion rate of substrate elements into the coating, therefore, as a result, this coating shows higher thermal stability than

coating which applied on the surface by RT22LT procedure.

In this research, author also demonstrated that the thermal stability of the two coatings depends on Pt concentration across the coatings during the cyclic oxidation test. Figure 10a shows the fast inward diffusion of Pt from coating into the substrate in the RT22LT coating after 48 and 120h at 1150 °C while the coating which has been applied on the surface by Howmet 150 L process shows uniform distribution of Pt with little rate of inward diffusion at 1150 °C even after 120h (Figure 10b).

As a result, the oxide on RT22LT coating grows at a faster rate in comparison with that on Howmet 150 L. Littner et al.²⁵ demonstrated that the cyclic oxidation behavior of coated nickel-based superalloys has been affected significantly by Pt concentration in the coating more than coating's microstructure. Cyclic oxidation behavior of PWA 1484 which was coated by bi and single phased Pt–Al coatings, at 1150 °C, has been evaluated in this research.

The results of mentioned evaluation showed that the Pt-concentration is higher in the vicinity of bi-phased coating surface, than the percentage of Pt close to the single-phase coating surface. On the contrary, the high amount of Pt was detected in the middle thickness of single-phased coating in comparison with the percentage of this precious element in the same area of bi-phased coating. In the single-phased coating, the Pt-content showed a tenuous reduction within the IDZ before abruptly dropping down to zero at the coating substrate interface. According to the result of this research, both of the coatings (single and bi-phased) can be improved the hot cyclic oxidation resistance of superalloys,

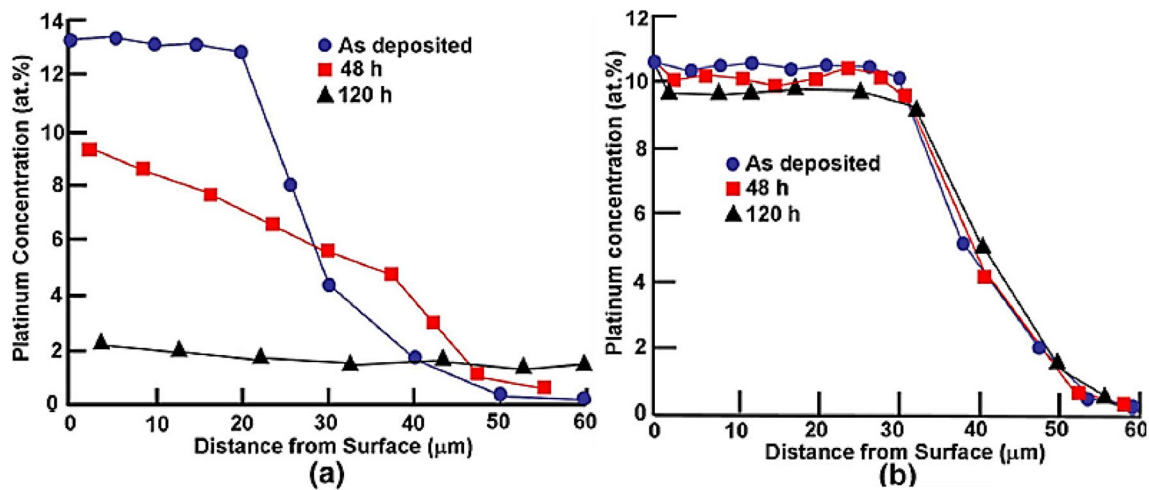


Figure 10. Concentration profiles of Pt along cross sections of RT22L (a) and Howmet 150 L (b) coatings at 1150 °C and different exposure times.⁹³

similar to each other, if the average percentage of Pt within the coating surpasses a minimum value of around 3 at.%. Shirvani et al.¹⁵ also demonstrated that the presence of low percentage of Pt element (2.5 at.%) in the composition of NiAl structure is enough to retain the cyclic oxidation resistance of the system (coating + substrate).

Microstructure characterization of bi-phased Pt–Al coating (ξ -PtAl₂ + β -(Ni, Pt)Al) showed that after only a few cycles of oxidation (50 cycles), two-phase layer was converted into β -(Ni, Pt) Al single-phase layer (ξ + β → β). This phenomenon has been observed and reported by others.^{12,40,79,85,86}

The conversion of bi-phased structure to single-phase has been ascribed to the inter-diffusion between Ni (outward diffusion from the substrate) and Pt (inward diffusion toward the substrate). According to the thermodynamic rules, bi-phased layer which is rich of Ni, favors the retention of only β -(Ni,Pt)Al with the Pt in solid solution.⁷⁹ With the increasing of cyclic oxidation number, β itself subsequently transforms to γ' -Ni₃Al phase. This type of phase transformation has been reported in both outward (HTLA) and inward (LTHA) methods of alienization.^{16,90} On the other hand, it has been documented in the literature that the presence of refractory elements such as Cr, Co, W, Ti, and Mo in the structure of β phase play a significant role in the stability of this phase. Although, Ti, Mo and W plays a destabilizing role in the structure of β phase, Cr and Co has a stabilize effect.¹⁶

Figure 11 shows the XRD results of bi-phased Pt–Al-coated Rene[®]80 after 120 cycles of oxidation at 1100 °C. This result confirms that the bi-phased Pt–Al coating has been replaced by single phase platinum modified β -(Ni, Pt) Al. As can be also seen from SEM image (inset in Figure 11), after thermal cycles the bi-phased structure has been disappeared.

Mechanical Properties of Pt–Al-Coated Nickel-based Superalloys

There are a few systematic investigations on the influence of Pt–Al coatings on the mechanical properties of nickel-based superalloys. On the other side, published literature in terms of mechanical properties of coated superalloys has reported various results.

In this section, author tried to collect all of the researches which have been performed on this subject and compare their results.

Tensile Properties (Monotonic Stress-Strain Behavior)

Several factors such as ductile-to-brittle transition temperature (DBTT), the thickness of initial Pt layer, the method of “aluminizing”, chemical composition of coating/substrate, stoichiometric state of coatings (hyper or hypo) and residual stresses can have a significant impact on the mechanical properties of the coated nickel-based superalloys.^{35–37,41}

In the research which has been done by Parlikar et al.,³⁵ the influence of a bi-phased PtAl coating feature (thickness and stoichiometry) on the tensile properties (yield strength (YS), ultimate tensile strength (UTS) and ductility (% plastic strain to fracture)) of DS CM-247LC nickel-based superalloy was evaluated in the temperature range between room temperature to 1000 °C. The results of this study showed that the tensile properties (YS, UTS and ductility) of coated superalloy are most significantly affected by DBTT. The DBTT is the temperature at which the slope of the strain-temperature graph alters significantly.⁹⁰ Pt–Al diffusion coatings indicate low ductility below DBTT, whereas above that temperature ductility rapidly increases.

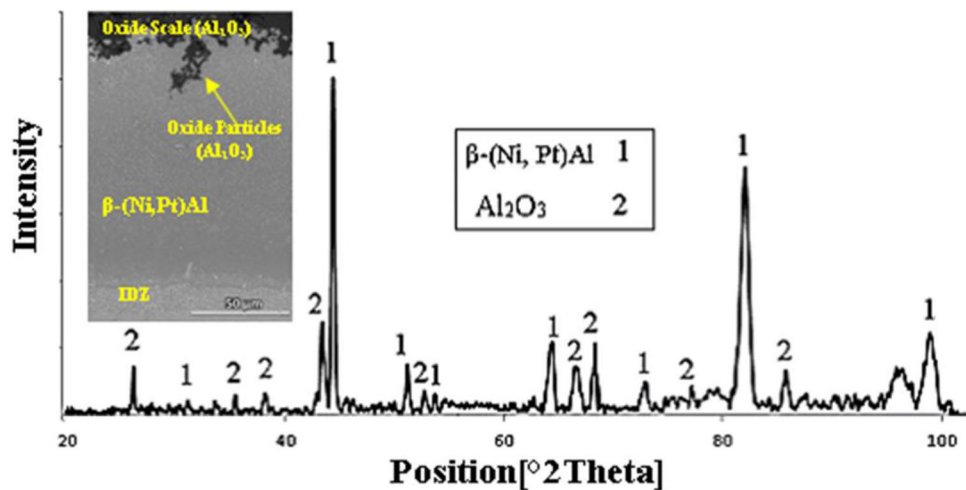


Figure 11. The results of XRD analysis for bi-phased Pt–Al-coated Rene® 80 (6µmPt/LTHA), after 120 cycles of oxidation at 1100° C.⁴¹

The DBTT is affected by the coating process (thickness of initial Pt layer, post-Pt diffusion and aluminizing process), phase distribution, coating/substrate composition, heat treatment history, and microstructure of the coatings.⁹⁰

Alam et al.^{28,32} stated that there is a relationship between thickness of initial Pt-layer and DBTT as follows:

$$T_{DBTT} = 698 + 10 t_{Pt} \quad \text{Eqn. 1}$$

Where T_{DBTT} stands for DBTT (°C) of the coating and t_{Pt} replaced for thickness of initial plating layer. They concluded that phases which are formed in the Pt–Al coatings such as (Ni, Pt) Al and PtAl₂, create an obstacle against dislocation movement, also solute atoms play a significant role in the pinning of dislocations. Therefore, impediments to dislocation motion can be potential reason causing increase in the BDTT of Pt–Al coating with alloying addition.²⁸ An increase in the Pt content led to an increase in the PtAl₂ phase concentration in the microstructure of Pt–Al coating and therefore the DBTT

will be increased. As is evident from Figure 12a, diffusion coatings (Al and Pt–Al) which are applied on the surface of nickel-based superalloys lead to an increase in the DBTT. On the other hand, Figure 12b also shows that the DBTT increased significantly with the increase in Pt content of the coating.

For more data generation in the effect of DBTT on the tensile properties of coated nickel-based superalloys fields, the tensile properties of Rene® 80 in the coated and uncoated condition and at different temperatures have been evaluated by Barjesteh et al.^{41–45} in the systematic studies. The results of these studies are summarized in Table 1.

As is shown in this table, by increasing the testing temperature from 800 °C to 982 °C, in both uncoated and coated specimens, UTS and YS have been sharply decreased while ductility (elongation (EI%) and reduction of area (RA%)) of uncoated and coated specimen increased. Increasing the temperature from 800 °C to 982 °C led to the reduction in the UTS and YS of the bare

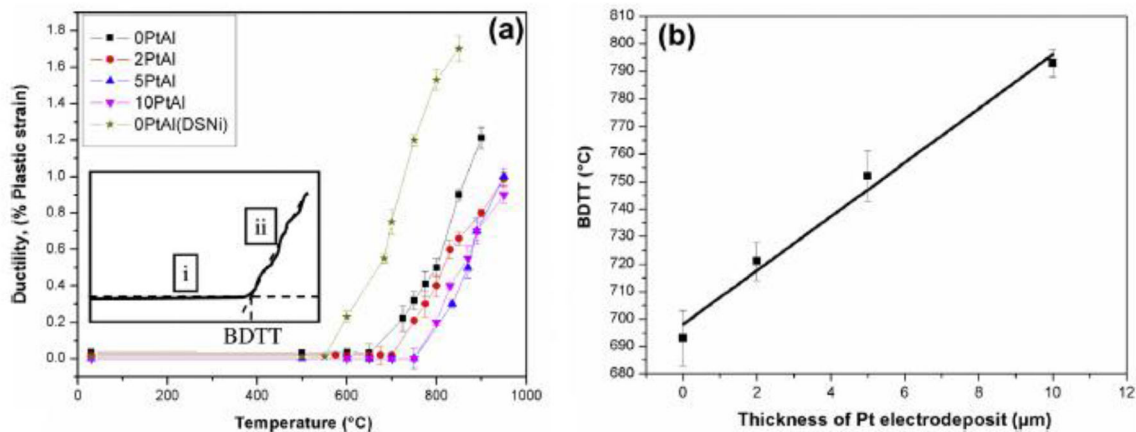


Figure 12. Al and Pt–Al coatings: (a) variation of ductility with temperature (different thickness of initial Pt layer) (b) variation of DBTT with initial thickness of Pt layer.³²

Table 1. Results of Tensile Test on Coated (6 μ mPt/LTHA) and Uncoated Rene[®]80 at Different Temperatures^{41,43–45,95}

Tensile Properties		UTS (MPa)	YS (MPa)	El%	RA%
AMS 5403 (min) (T = 871 °C) ⁹⁵		620	415	–	15
800 °C ⁴⁴	Uncoated	828	742.5	6.5	11.5
	Coated	787.5	701	5.5	10.5
871 °C ⁴¹	Uncoated	706	595	9	16.5
	Coated	655	550	7	16
930 °C ⁴⁵	Uncoated	517.5	345	10.2	17.5
	Coated	490	320	11.5	19
982 °C ⁴³	Uncoated	355	265	12	20
	Coated	345	245	12.5	26

and coated Rene[®]80 about 56–57% and 64–65%, respectively. According to the results which are inserted in the Table 1, the tensile properties gap between uncoated and coated specimens gets smaller with increasing the temperature. For example, the difference between UTS of bare and coated Rene[®]80 at 800 °C is 40.5 MPa, while this difference is only 10MPa at 982 °C.

As stated in the literature^{42,96} the application of Al-coatings on the nickel-based superalloys has no effect on the substrate microstructure. Therefore, the variations in the tensile properties of the coated superalloys are because of the effect of applied coatings. As mentioned previously, DBTT plays an effective role in the coating behavior fracture. In the literature, the DBTT of plane Al-coating applied on the Rene[®]80 superalloy has been reported about 900 °C.⁹⁶ On the other hand, Alam et al.³¹, reported that the DBTT of the Pt–Al coating is nearly 100 °C higher than that of its simple aluminide counterpart. According these investigations, it can be concluded that Pt–Al coatings show more ductile behavior at high temperature (near to 1000 °C-Table 1).

As evident in Table 1, increasing the testing temperature from 800 °C to 982 °C led to an increase in the elongation and reduction of area of coated Rene[®]80 around 7% and 15.5%, respectively.

Large cleavage area (brittle fracture morphology) which is seen in Figure 13a and c⁴⁴ and large dimples (ductile fracture morphology) which is observed in the Figure 13b and d⁴³ exhibit the reason of variation in ductility (%El+%R.A) of Pt–Al-coated Rene[®]80 at different temperatures. Parlikar et al.³⁵ also reported a combination of cleavage facets and dimples in the fracture surface of Pt–Al-coated DS CM-247LC superalloy. In the results of this study has been reported that with enhancement in test temperature, abundant dimple formation taken place.

The results which are inserted in Table 1 also show that the strength and ductility of the substrate superalloy decreased with the application of the Pt–Al coatings at various temperatures. Different fracture stress between the Pt–Al coatings and substrate strengths causes the creation of some micro-cracks on the coating during the applying of tensile load. However, it is known that the inward propagation of these micro-cracks reduces the load bearing cross-section area of the substrate and cause a decrease in the strength of the substrate alloy especially at lower temperature.⁴²

As alluded to earlier, in addition to DBTT, such factors as the thickness of initial Pt layer and the method of aluminizing have a key role on the mechanical properties of the coated superalloys. Increase in thickness of the Pt–Al coating leads to a decrease in tensile properties of the substrate alloy.³⁵ The increase in the thickness of initial Pt layer leads to an increase in the thickness of Pt–Al coating and subsequently results a reduction in tensile properties of coated alloys. Comparison of cracks which are formed in the thick coatings with cracks which are created in the thin coatings showed that the length of cracks in the thick coatings is more than the cracks length in the thin coatings. Therefore, longer cracks tolerate greater stress field at their tip and perforate to larger depths than that of the shorter cracks in thin coating.^{35,41}

On the other side, the increasing of Al content in the composition of Pt–Al coatings by changing the aluminizing process from HTLA to LTHA causes the variation in stoichiometry of the (Ni, Pt) Al phase.^{35,90}

In the literature have been reported that in HTLA method, (Ni, Pt) Al phase is hypo-stoichiometric (Ni-rich), while this phase in LTHA process is hyper-stoichiometric (Al-rich). The hardness (Figure 14) and strength properties of Pt–Al coatings which are manufactured by LTHA method is more than the coatings which are applied on the surface by HTLA method.⁴¹ This is related to the nature of defects (vacancy or substitutional defects) which exist in the structure of hyper/hypo stoichiometric Pt–Al coatings. Therefore, it can be expected that nickel-based superalloy which is coated by LTHA method shows higher tensile strength than HTLA ones. In the study which have been performed by Barjesteh et al.⁴¹, the magnitude of UTS and YS of Pt–Al (6 μ mPt/ LTHA)-coated Rene[®]80 at 871 °C is reported 655 MPa and 550 MPa, respectively, while these quantities for 6 μ mPt/ HTLA-Coated Rene[®]80 at the same temperature are reported 558 MPa and 525 MPa.

The results of mentioned research⁴¹ showed that although the ductility property of the coated Rene[®]80 did not change significantly from 2 μ m to 6 μ m thickness of initial Pt-layer, this property decreased when the initial Pt layer with the thickness of 8 μ m was applied on the surface of this superalloy. As mentioned previously, Krishna et al.¹⁷ have

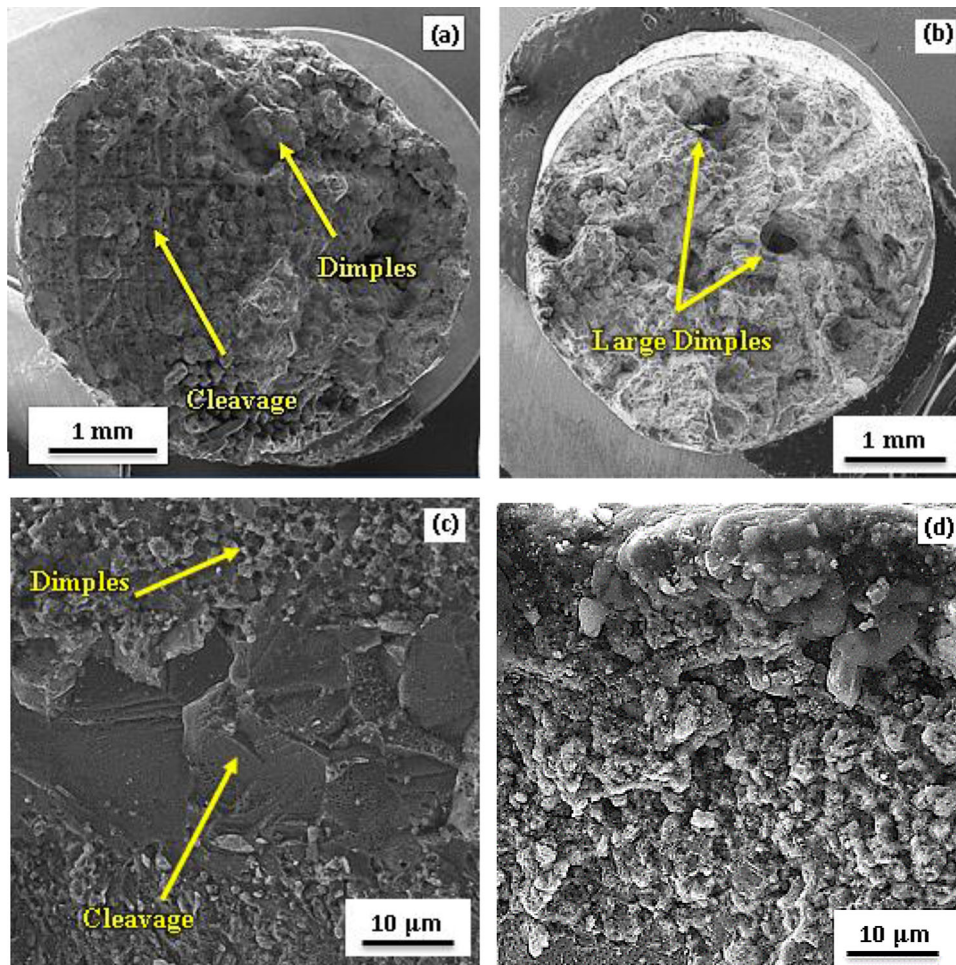


Figure 13. SEM/SE images of tensile fracture surface features of Pt-Al-coated Rene[®]80 (6µmPt/LTHA) (a) mixed mode fracture surface of the coated specimens at 800 °C⁴⁴ (small dimples and large area of cleavage) (b) mixed mode fracture surface of the coated specimens at 982 °C (large dimples and small area of cleavage)⁴³ (c) large area of cleavage at 800 °C⁴⁴ (d) large dimples area at 982 °C.⁴³

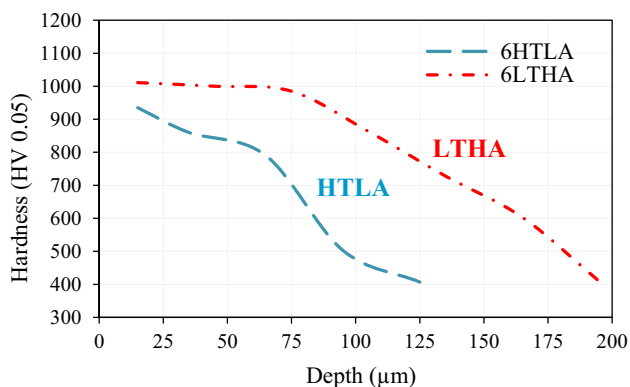


Figure 14. Hardness profile across the thickness of coatings for two aluminizing methods of HTLA and LTHA (initial Pt layer: 6µm).⁴¹

reported that the resistance of superalloys against cyclic oxidation will be improved by Pt-coatings, when the initial platinum layer thickness was at least 6µm. On the other

hand, Barjesteh et al.⁴¹ have reported that the tensile properties of a coated nickel-based superalloy (6µmPt/LTHA) did not significantly reduce below the standard tensile characteristics of the uncoated alloy. According to the results of these studies,^{17,41} it could be concluded that 6µm thickness of initial Pt-layer and LTHA method of aluminizing will supply the best resistance for oxidation while keeping the tensile properties of superalloys (especially ductility).

The effect of prior cyclic oxidation on the tensile properties of nickel-based superalloy, also has been investigated by researchers.^{37,45} The results of these studies showed that the Pt-Al coatings have a beneficial effect on the prevention of surface degradation of the superalloy during high temperature oxidation. Therefore, exposed Pt-Al-coated superalloys exhibited better tensile properties (especially ductility) in comparison with exposed bare superalloys. In bare superalloys during oxidation at elevated temperatures, Al

which exists in the composition of γ' -Ni₃(Al, Ti) diffuses from the substrate toward the surface to form the Al₂O₃ scale. As a result, near the surface will be depleted from the γ' (weakening the surface) and therefore a suitable site for crack initiation and propagation will be created. On the contrary, in the coated superalloys, Pt–Al coatings play a role as Al source and therefore the Al which exits in the composition of superalloys won't be consumed, during oxidation at elevated temperatures.

Creep Properties of Pt–Al-Coated Nickel-based Superalloys

At high-temperature applications ($T > T_m$, where T_m is the melting temperature of the superalloy), a time-dependent, inelastic deformation known as creep is very important for designers and should be regarded.^{1,48,97}

Despite several research works on creep property of diffusion plane aluminide-coated superalloys, the effect of Pt–Al coatings on creep behavior of substrate superalloys has not been evaluated in a systematic form.

The effect of Pt–Al coating (5 μ m Pt/LTHA) on the creep behavior of a first-generation nickel base single crystal superalloy has been studied by Parlikar et al.³⁶. The results of this research in the form of creep curves for uncoated and Pt–Al-coated samples are exhibited in Figure 15a. As shown in this figure, the presence of Pt–Al coat on the surface of teste alloy led to a definite level of deterioration in the creep property of the alloy. Also, the reduction in the resistance to creep rupture of Rene[®]80 (a polycrystalline nickel-based superalloy), after applying the Pt–Al coating (6 μ m Pt/LTHA and HTLA), has been reported by Barjesteh et al. (Figure 15b).⁴⁶ The reasons of this degradation can be explained as follows: 1- Pt–Al coatings are weaker than the superalloys 2- the degradation of the coating and coating/substrate interface during creep test (diffusion of

elements, TCP formation and ...) 3- Pt–Al coating encouraged surface cracks (these surface cracks decreased the load bearing cross-section) 4- Pt–Al coating increases DBTT and 5- the quantity of residual stresses in the coating.^{33,36,46}

In addition, coating stoichiometric constitution (Al-rich or Ni-rich) play an effective role in the creep property impairment of the nickel-based superalloys. As is evident from Figure 15b, specimen which was coated by 6 μ m Pt/HTLA showed the lowest resistance to creep rupture.

The coating parameters such as the chemical composition of coating, residual stresses and regime of elemental diffusion in the coating/substrate region can be affected by aluminizing methods (HTLA or LTHA). Therefore, the creep behavior of the HTLA-coated nickel-based superalloys will be different from the LTHA coated. It is mentioned in the literature^{41,42} that the magnitude of the tensile residual stress in the Pt–Al coatings which are manufactured by LTHA aluminizing method is lower than Pt–Al coatings which are formed by HTLA aluminizing packs. During the creep tests at elevated temperatures because of big amount of tensile stress in the HTLA coating, the cracks revel in this coating sooner than Pt–Al coating which is produced by LTHA aluminizing method. As a result, these coating cracks reduce the load bearing cross-section of substrate and therefore the specimen will be yielded in shorter time.

Service temperature of the coated nickel-based superalloy has an important impact on the mechanical properties. As stated in the previous section (4.1), Pt–Al coating show a brittle behavior below the DBTT. Although, several cracks have been detected across the Pt–Al coating at 760 °C during the creep test, no cracks have been created in the Pt–Al coating at 982 °C (Figure 16).⁴⁶ No detection of any cracks in the Pt–Al coating area exhibits that the coating was ductile enough at 982 °C to resist cracking up to

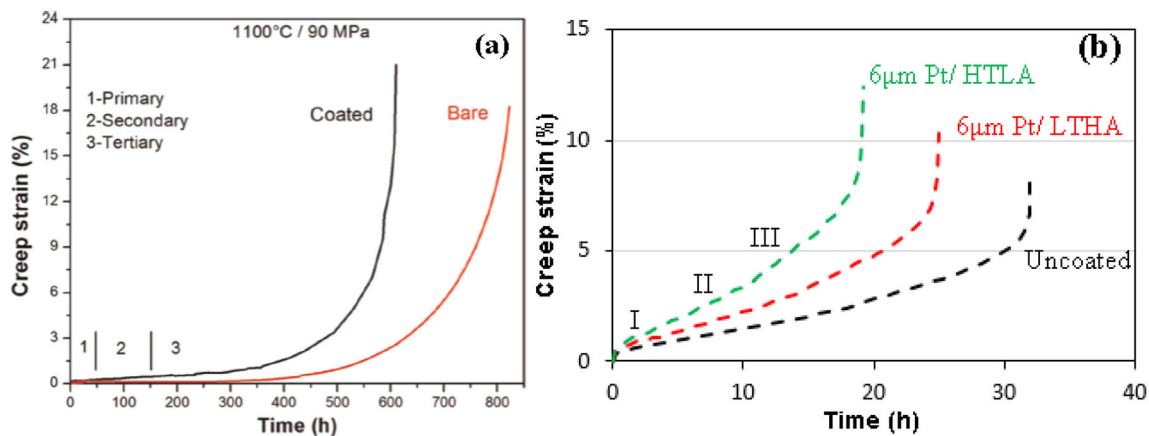


Figure 15. Creep curves for bare and coated alloy (a) a single crystal nickel-based superalloy at 1100 °C/90 MPa³⁶ and (b) a polycrystalline nickel-based superalloy (Rene 80) at 982 °C/190 MPa.⁴⁶

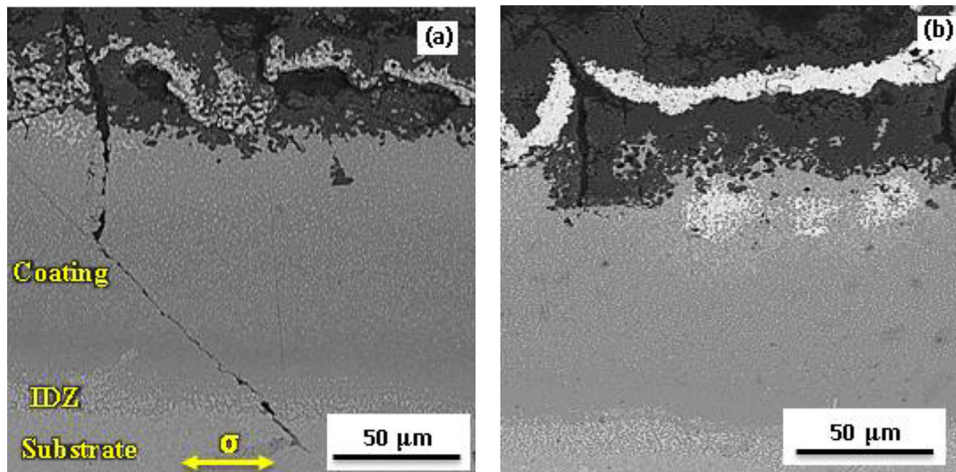


Figure 16. Backscattered SEM images of Pt–Al-coated Rene[®]80 (6µm Pt/LTHA) after creep rupture test at (a) 760 °C/657 MPa (b) 982 °C/190 MPa.⁴⁶

fracture. It shows that this temperature is well above the DBTT.

Low Cycle Fatigue Properties of Pt–Al-Coated Nickel-based Superalloys

Since low cycle fatigue (LCF) cracks initiate and propagate mainly at the surface of the rotary parts, the surface treatment such as coating plays a significant role in the fatigue life. The LCF life of coated superalloy relates to the surface condition (scratches, notches), flaws in the coating micro-structure, presence of TCP phases in the IDZ region and coating thickness.⁸ On the other side, DBTT has also a significant effect on the LCF behavior of the coated nickel-based superalloy. In the systematic studies which have been done by Barjesteh et al. has been reported that the application of bi-phased Pt–Al coating (6µmPt/ LTHA), on the Rene[®]80 alloy, showed a decrease in the LCF life at 800 °C and 871 °C.^{42,44} On the contrary, Pt–Al coating (6µmPt/ LTHA) showed a positive effect on the LCF strength of this superalloy at 930 °C and 982 °C.^{43,45}

Figure 17a and b shows the stress–strain hysteresis loops of Rene[®]80 Pt–Al coated and uncoated specimens, at the first cycle, for $\Delta\epsilon_t=0.8\%$ at different temperatures,^{42–45} respectively.

As seen from Figure 17, the coated specimen at 800 °C (at the first cycle) has tolerated the maximum stress range ($\Delta\sigma = \sigma_{\max} - \sigma_{\min}$). This amount is almost equal to 1447 MPa. Also, the minimum stress range belongs to the coated specimen which has been tested at 982 °C. The value of this stress has been reported 729 MPa. The number of LCF cycles which were tolerated by the coated (6µm Pt/LTHA) and uncoated Rene[®]80 samples under $\Delta\epsilon_t= 0.8\%$ and at different temperatures is shown in Figure 18. It should be mentioned that these data are collected from several studies

which are performed by Barjesteh et al.^{42–45} and for better comparison are summarized, in column chart, in this review article.

As is evident from Figure 18, the fatigue life of bare/coated Rene[®]80 decreases as temperature increases. At high temperature condition, oxidation phenomenon plays a significant role in the reduction of LCF life of bare specimens. During the high temperature LCF test, aluminum diffuses from base to surface of superalloy for creation of Al_2O_3 . This layer is brittle and a suitable site for crack nucleation. This brittle oxide layer is broken during the LCF test and therefore, new substrate is exposed to environment and more oxidation. This phenomenon leads to a faster crack growth rate and lowered fatigue life. On the other hand, when aluminum diffuses from base to surface, the base alloy will be depleted of $\gamma'(\text{Ni}_3(\text{Al,Ti}))$ (strengthening phase) vicinity the surface. Thus, this depleted zone will form a good location for crack initiation. By the nucleation of cracks, cross section of load bearing will be smaller and therefore the strength of the specimen will be decreased.⁴⁴

It is reported in the literature^{14,17,40} that the presence of Pt–Al on the surface of superalloys plays an important role to prevent an oxidation damage of the substrate alloy at high temperatures.

In Pt–Al-coated specimens, the presence of coating at 800 °C and 871 °C reduces the fatigue life of superalloy, but in the temperature of 930 °C and 982 °C fatigue lifetime of the coated specimens is more than that of uncoated specimens at the total strain of 0.8%. In the other words, by increasing the testing temperature from 800 °C to 982 °C, LCF life of coated sample has been improved as compared to the uncoated one. It seems that, by increasing the testing temperature, the more consistency between Pt–Al coating and the substrate (superalloy) is created. Higher ductility of

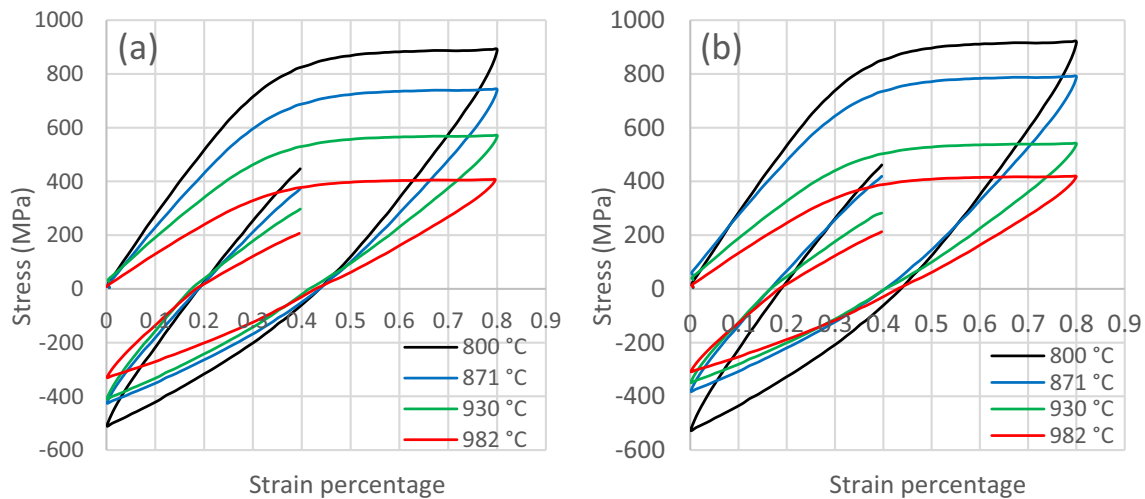


Figure 17. Stress-strain hysteresis loops at $\Delta\epsilon_t=0.8\%$ and $R=0$ for (a) uncoated and (b) coated ($6\mu\text{m}$ Pt/LTHA) Rene[®]80 alloy at different temperatures.

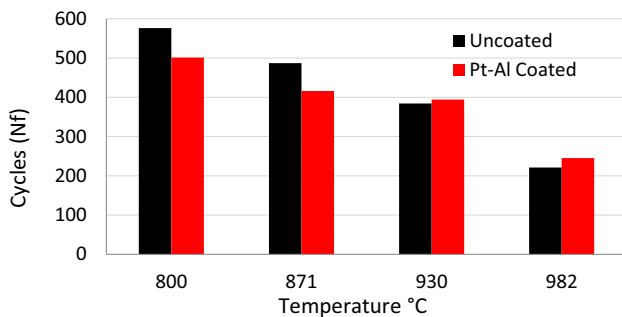


Figure 18. The number of LCF cycles under $\Delta\epsilon_t=0.8\%$ and $R=0$ at different temperatures (bare and coated ($6\mu\text{m}$ Pt/LTHA) Rene[®]80).

Pt–Al-coated specimens as compared to uncoated one, at 930 °C and 982 °C, has been reported in the references,^{43,45} while ductility of Pt–Al-coated specimen was reported lower than bare specimen at 800 °C and 871 °C.^{42,44} Ductility has a large influence on the fatigue strength of superalloys.

Parlikar et al.³⁵ studied the tensile properties of Pt–Al ($5\mu\text{m}$ Pt/LTHA)-coated CM-247 LC. In the results of this investigation has been reported that Pt–Al (with the thickness of $90\mu\text{m}$)-coated CM-247 LC showed better ductility as compared to the uncoated one at 1000 °C. In the other words the application of Pt–Al coated with the optimum specification (microstructure, thickness and ...) on the surface of nickel-based superalloy can improve the ductility property of the specimens at elevated temperatures.

At the temperature below DBTT, Pt–Al coating shows a brittle fracture behavior and cannot tolerate the deformation at high stress/strain. In this condition, cracks that form in the coating during service act as stress raisers on the substrate superalloy, hence reducing the fatigue life.⁷⁸

Figure 19 shows the surface of coated Rene[®]80 after LCF fracture at different temperatures of 800 °C, 871 °C, 930 °C and 982 °C.

As evident from Figure 19, at 800 °C and 871 °C (Figure 19a and b), the cracks nucleated from the coatings and grew in the perpendicular path to the direction of applied stress within the coatings. Although, the crack entered the substrate once passed through IDZ region at 800 °C, no penetration of cracks to the substrate has been detected at 871 °C. On the other side, at 930 °C and 982 °C (Figure 19c and d), no cracking in the coatings of specimens, was determined. The absence of any coating cracks reveal that the Pt–Al coating ($6\mu\text{m}$ Pt/LTHA) was ductile enough at the LCF test temperatures of 930 °C and 982 °C to withstand cracking up to fracture. In this case, the internal defects of substrates play an important role in the crack nucleation and propagation during the LCF testing.^{42–45}

It is mentioned in the literature that in the Pt–Al coatings, β (Ni, Pt) Al phase is so brittle at lower temperature and become progressively ductile when subjected above the DBTT.⁹⁰ On the other hand, in the working regime of a turbine engine, in the turbine (hot) section, oxidation play an effective role in the initiation and propagation of fatigue cracks on the surface of rotary parts. However, Pt–Al coatings which are applied on the surface of blades provide a rich source of Al and therefore, the surface of alloy is protected from the outward diffusion of Al to formation of Al_2O_3 , at elevated temperatures. For this reason, depleted zones from γ' phase as a result of oxidation by high temperature LCF testing, did not appear near the surface. As γ' phase is main strengthening precipitates of nickel-base superalloys, its diminution leads to surface failing and by cyclic stress, crack nucleated and propagated.⁴⁵ However, it seems that at elevated temperature besides DBTT effect, the positive influence of Pt–Al coating on the oxidation

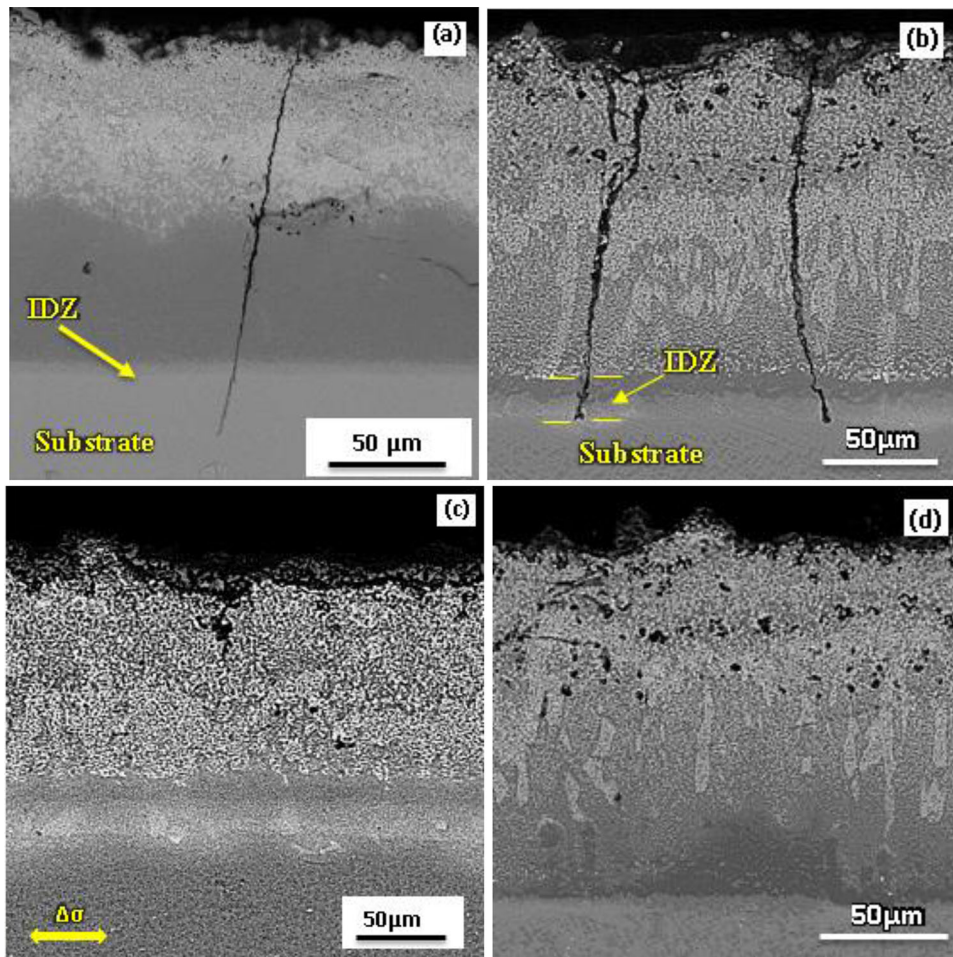


Figure 19. SEM longitudinal sectional view of the Pt–Al specimens (6 μ m Pt/LTH-Rene[®]80) after LCF test at different temperatures ($\Delta\epsilon_t = 0.8\%$, $R=0$) (a) 800 °C (b) 871 °C (c) 932 °C and (d) 982 °C.^{42–45}

Table 2. Main Results of Review on the Pt–Al Coatings Studies

Field of investigation	Result	References
Microstructure of Pt–Al coatings	Single phased, bi phased, bi-phased structure with a continuous PtAl ₂ layer	13–15, 17, 50, 62–64, 67–70, 76, 77, 79–81
The effect of Pt–Al coating on the cyclic oxidation	Improve the cyclic oxidation resistance	10, 16, 18–25, 40, 65, 73, 79, 85–87, 90, 92–94
The effect of Pt–Al coating on the Mechanical properties	Depends on DBTT (Improvement or reduction)	26–52, 78, 96, 97

resistance of nickel-based superalloys has an important role in the improvement of LCF life.

The outcomes of this review article show that a minimum percentage of Pt (approximately 6mm thickness of the initial Pt layer) in the Pt–Aluminide coating is necessary in order to reveal its beneficial effect on the enhancement of oxidation resistance of the nickel-based superalloys.¹⁷ On the other hand, selected aluminizing methods (HTLA or

LTHA) play an effective role in the oxidation resistance of the coated nickel-based superalloys. In a recent review has been reported that the Pt–Al coating which was produced by LTHA method (outward type) shows better oxidation resistance than the coating which was manufactured by HTLA method (inward type).⁴⁰ Also, the results of reviewed investigations showed that Pt–Al coating could have a beneficial effect on the LCF of nickel-based superalloy when the experimental temperature is much

higher than the DBTT (above 930 °C).^{42–45} Whereas LCF is the main failure mode in the rotating turbine blades, therefore, it may not be wrong to say that at high temperature (above DBTT) Pt–Al coatings have a beneficial effect on the life service of coated turbine blades.

Conclusions

The effect of Pt–Al coatings on the cyclic oxidation and mechanical properties of nickel-based superalloys has been reviewed. The main results of these studies are shown in Table 2.

Finally, the following main conclusions from this tutorial review may be drawn:

Based on the studies reported so far, the high temperature cyclic oxidation resistance of nickel-based superalloys was improved by the application of Pt–Al coatings. The oxidation resistance of Pt–Al coating reported to be higher in LTHA method as compared to HTLA.

Although the application of the platinum–aluminide coatings under either of the aluminizing conditions (LTHA/HTLA) and different thicknesses of platinum lead to a decrease in creep rupture life of Pt–Al-coated superalloys at different temperatures, by increasing the temperature, above the DBTT, LCF life of coated superalloys will be improved as compared to the uncoated one.

According to the obtained information from this review paper, it can be concluded that, when the working regime of turbine blades or vanes is much higher than the DBTT, Pt–Al coating with an initial platinum layer thickness of 6µm which is aluminized by LTHA method has a beneficial effect on the nickel-based superalloys, in order to support the mechanical properties, especially LCF life, and resistance to oxidation, simultaneously. However, the total thickness of Pt–Al coating play an important role and it is recommended between 50µm and 60µm.

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