



Oxidation Behavior of Non-Modified and Rhodium- or Palladium-Modified Aluminide Coatings Deposited on CMSX-4 Superalloy

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Received: 28 June 2018; Accepted: 2 August 2018; Published: 6 August 2018



Abstract: Rhodium-modified as well as palladium-modified and non-modified aluminide coatings on CMSX-4 Ni-based superalloy were oxidized in air atmosphere at 1100 °C. Uncoated substrate of CMSX-4 superalloy was also oxidized. The microstructure of coatings before oxidation consists of two layers: an additive and an interdiffusion one. The NiAl intermetallic phase was found in the microstructure of non-modified coatings, while the (Ni,Rh)Al intermetallic phase was observed in the microstructure of rhodium-modified aluminide coatings before oxidation. The (Ni,Pd)Al phase of palladium-modified aluminide coatings in the additive layer was observed before oxidation. The microstructure of the oxidized non-modified coatings consists of the γ' -Ni₃Al phase. The oxide layer (10 µm thick) consists of the NiAl₂O₄ phase and porous Ni-rich oxide. The oxide layers (5 µm thick) formed on the surface of rhodium or palladium-modified coatings consist of the α -Al₂O₃ phase and the top layer of the NiAl₂O₄ phase. Al-depleted (30 at. %) β -NiAl grains besides the γ' -Ni₃Al phase were found in the rhodium-modified coating, while only the γ' -Ni₃Al phase region was revealed in the palladium-modified coating, Rhodium-modified coatings with small rhodium content (0.5 µm rhodium layer thick) can be an alternative for palladium-modified ones with bigger palladium content (3 µm thick palladium layer).

Keywords: oxidation; CMSX-4 superalloy; rhodium; palladium; aluminide coating

1. Introduction

Nickel-based superalloys are widely used on turbine blades and vanes in the hot section of aircraft engines [1]. Aluminum content in the nickel-based superalloys is kept at a level below 6% wt. [2]. Exposure of superalloys to an environment of high-pressure turbine engines leads to their degradation from oxidation, hot corrosion and thermal fatigue [3]. Usage of nickel-based superalloys covered by diffusion aluminide coatings ensures high-temperature oxidation resistance of turbine blades and vanes [4]. Platinum modification of aluminide coatings improves their performance, and resistance to oxidation and hot corrosion [5]. However, usage of platinum-modified aluminide coatings has two main limitations: poor ductility, due to the presence of the PtAl₂ brittle phase, and the high price of platinum. These reasons motivate the replacement of platinum with palladium [6].

According to Li et al. [7] palladium stabilizes the β -(Ni,Pd)Al phase, retards degradation of coatings and increases oxidation resistance. Hong et al. [8] showed that the addition of palladium accelerates the θ -Al₂O₃ to α -Al₂O₃ transition and simultaneous diffusion of titanium from the substrate to the coating's surface. He et al. [9] proved that palladium stabilizes protective alumina scale and restrains outward diffusion of substrate elements to the β -(Ni,Pd)Al phase. Consequently, it increases the lifetime of the β -NiAl phase and hot corrosion resistance of coatings. Hong et al. [8] alleged that a great number of pores present in the substrate during annealing and aluminizing of palladium-coated superalloy limits coatings usage and oxidation resistance.



Wu et al. [10] introduced iridium to the aluminide coatings as a cost alternative to platinum. Firstly, the iridium layer (6 μ m thick) was deposited on TMS-75 nickel-base single-crystal superalloy. Secondly, the coated superalloy was aluminized by the pack-cementation method and then cyclic oxidation tests were performed. A dense and uniform layer of the β -(Ir,Ni)Al phase was identified after aluminizing. The growth rate of oxide on Ir-Al coated superalloy was lower than on the aluminized one. Moreover, the transformation from β -NiAl phase to the γ' -phase was decelerated due to the presence of the (Ir,Ni)Al layer. The presence of iridium in the aluminide coating retarded the outward and inward diffusion of solute elements during oxidation (nickel and aluminum).

The addition of 5 % wt. rhodium to the Ni-8Cr-6Al alloy increases oxide-scale adherence to the alloy and improves its oxidation resistance [11]. Rhodium addition to the aluminide coatings also increases oxidation resistance of coated alloys [12]. Therefore, rhodium-modified aluminide coatings can be an alternative for palladium-modified aluminide ones. However, there is a lack of data about comparison of the oxidation resistance of rhodium or palladium-modified aluminide coatings. That is why this paper presents comparison of the oxidation resistance of the oxidation resistance of rhodium or rhodium-modified aluminide coatings and uncoated substrate.

2. Experimental Procedure

CMSX-4 superalloy (single-crystal) was used as a substrate material. The chemical composition of the superalloy was as follows: 61.7% wt. Ni, 6.5% wt. Cr, 9% wt. Co, 0.6% wt. Mo, 5.6% wt. Al, 1% wt. Ti, 6% wt. W, 0.1% wt. Hf, 3% wt. Re, 6.5% wt. Ta.

Substrate samples were coated by the rhodium layer (0.5 μ m thick) or by the palladium layer (3 μ m thick). The rhodium electroplating process was conducted in a bath of rhodium sulphate Rh₂(SO₄)₃—10 g/dm³, sulfuric acid H₂SO₄—15 g/dm³, and selenium acid H₂SeO₄—1 g/dm³ at 50 °C. The current density during the electroplating process was about 2 A/dm².

Palladium electroplating process was conducted in a bath of palladium chloride $PdCl_2$ —10 g/cm³, sulfamates acid H_2NSO_3 —100 g/cm³, hydrochloric acid HCl—20 g/cm³ and ammonium chloride NH_4Cl —50 g/cm³ at 35 °C. The current density during the electroplating process was about 1 A/dm² [13].

The formation of aluminide coatings is obtained by aluminizing process. Samples were aluminized with pre-deposited rhodium or palladium layers at 1040 °C for 12 h by the CVD method using the CVD BPXPR0325S equipment manufactured by the IonBond company. Several samples were aluminized without pre-deposited rhodium or palladium layers [14].

The rhodium-modified as well as palladium-modified and non-modified aluminide coatings on the CMSX-4 Ni-based superalloy were oxidized in the air atmosphere at 1100 °C. The samples were coated on all sides for oxidation.

Uncoated substrate of CMSX 4 superalloy was also oxidized. Samples were placed in the furnace heated to 1100 °C, removed from the furnace after 20 h and cooled in the air atmosphere to the room temperature. 21 cycles of oxidation were performed. The duration of one cycle was 22 h. Specimens were weighed after each cycle of oxidation.

The surface and microstructure of the cross-sections of the coatings after oxidation were investigated by the scanning electron microscope (SEM) Hitachi S-3400N and energy dispersive spectroscopy (EDS). SEM, EDS analysis was performed at working distance 10–12 mm and accelerating voltage 15 kV. Phase composition of the oxidized coatings was investigated using the ARL X'TRA X-ray diffractometer, equipped with a filtered copper lamp (wavelength, λ = 0.15406 nm) with a voltage of 40 kV and heater current of 30 mA.

3. Results

3.1. Aluminide Coatings Before Oxidation

The microstructure of non-modified and rhodium- or palladium-modified aluminide coatings consisted of two layers: an additive and an interdiffusion one (Figure 1a,c,e). The NiAl intermetallic phase was observed in the microstructure of non-modified coatings (Figure 1a). The (Ni,Rh)Al intermetallic phase was observed in the microstructure of rhodium-modified aluminide coatings (Figure 1c). The non-modified and rhodium-modified aluminide coatings are about 30 μ m thick (Figure 1a–d). The palladium modification increased the coating's thickness to 37 μ m (Figure 1e,f). The distribution of Ni and Al in the cross-section confirms the presence of the NiAl phase (Figure 1b). Rhodium content between the additive layer, only Kirkendall-like porosity and few particles of Topologically Closed-Pack phases (Figure 1c). Distribution of palladium in the additive layer is quite regular (Figure 1d). This phenomenon indicates the presence of the (Ni, Pd)Al phase in the additive layer. The interdiffusion layer and the substrate/interdiffusion interface are rich in inclusions containing alloying elements. The analysis of the chemical composition of these phases suggests the presence of Topologically Closed-Pack μ and σ phases. Phase composition and aluminide coatings thickness before oxidation are shown in Table 1.



Figure 1. Cont.



Figure 1. Microstructure on the cross-section of the non-modified (**a**), rhodium-modified (**c**), palladium-modified (**e**) aluminide coating and elements' distribution on the cross-section of the non-modified (**b**), rhodium-modified (**d**) and palladium-modified (**f**) aluminide coating.

Table 1. Aluminide coatings thickness and phase composition before oxidation on CMSX-4 superalloy.

Rh or Pd Coating Thickness, µm	Aluminide Coatings Thickness, μm	Phase Composition of Additive Layer		
0	30 ± 3	NiAl		
0.5	30 ± 2	(Ni,Rh) Al		
3	37 ± 2	(Ni,Pd) Al		

3.2. Oxidation Resistance of Aluminide Coatings and Bare Superalloy

Oxidation kinetics curves (Figure 2) were prepared to show resistance to oxidation under cyclic conditions of coatings and bare superalloy. Each one of the coatings exhibits a rapid weight growth during first cycles of oxidation which was caused by quick oxide layer formation. The obtained results indicate that the best oxidation resistance exhibits rhodium-modified aluminide coatings, which failed after 13 cycles (Figure 2a). Weight change that reaches up to 0.2 mg/cm^2 is during the 3 cycles of oxidation. Afterwards, the weight change of coating is subtle until the 9th cycle when the weight of the sample starts to decrease slowly, which indicates the onset of oxide-scale spallation. Eventually, the coatings weight fell below its initial value in the 14th cycle. The palladium-modified aluminide coating reaches a maximum weight gain of 0.2 mg/cm^2 after 1 cycle of oxidation (Figure 2b). Afterwards, until approximately the 4th cycle, the weight change is subtle, probably due to repeated oxide-scale spallation and formation. After the 4th cycle the weight change of the coating decreases. Non-modified aluminide coating reaches the maximum weight change of 0.7 mg/cm^2 in the 3rd cycle (Figure 2c). Such weight change is due to very fast oxide layer formation. Afterwards, the weight change is almost subtle and is about $0.6-0.5 \text{ mg/cm}^2$, which is probably due to repeated oxide-scale formation and spallation. After the 7th cycle of oxidation, weight change quickly decreases, which is probably due to an inability of the oxide layer to heal after spallation. The weight change of bare CMSX-4 superalloy decreases after just 1 cycle of oxidation (Figure 2d). This is due to by-bed protective properties of the oxide layer that formed on its surface.



Number of oxidation cycles

Figure 2. Oxidation resistance of the rhodium (**a**), palladium (**b**), non-modified (**c**), aluminide coatings and bare CMSX-4 superalloy (**d**).

3.2.1. Non-Modified Aluminide Coating after the Oxidation Test

The surface of non-modified aluminide coating after oxidation is presented in Figure 3. The results of chemical composition analysis in microareas are presented in Table 2. The surface consists of the oxide layer formed during oxidation and visible as gray-scale areas and bright areas of the substrate after oxide layer spallation.

Chemical composition in microareas indicates that three types of oxides may coexist. Chemical composition of microareas 1 and 3 corresponds to $(Ni,Cr)Al_2O_4$ oxides. Above these microareas is slightly darker oxide layer, marked 2. The predominant elements present in this area are Al, O and Ni. There are also small amounts of Cr, Co and W. However, the concentration of the main elements indicates the presence of NiAl₂O₄ spinel, which was also detected using XRD (Figure 4). There are also some porous oxides (marked 4). Chemical composition of these regions indicates Ni-rich oxide occurrence. Chemical composition of the brightest and distinct areas marked 5 is very similar to that of the substrate alloy, which indicates that it was exposed by oxide layer spallation. A Ni₃Al phase was identified by XRD analysis.

Swadźba et al. [15] identified also Al_2O_3 oxides after oxidation of aluminide coatings, but in the presented research, Al_2O_3 oxides were not found.



Figure 3. Surface of non-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**) with marked microareas analyzed using EDS (**b**) after oxidation.

Microarea	0	Al	Ti	Cr	Со	Ni	W
1	52.2	17.7	2.2	11.5	4.8	11.5	0.1
2	49.7	33.3	-	2.5	2.6	11.8	0.1
3	54.7	18.3	1.8	10.6	4.1	10.4	0.1
4	44.4	7.3	-	8.5	3.8	35.9	0.1
5	-	7.9	-	11.1	13.3	65.5	2.2

Table 2. Chemical composition in microareas 1–5, Figure 3b, at. %.



Figure 4. XRD results from the surface of non-modified aluminide coating after oxidation at 1100 °C for 21 cycles.

After oxidation, non-modified aluminide coating consists of the aluminum depleted γ' -Ni₃Al phase (Figure 5a–c). Swadźba et al. [15] allege that presence of γ' -Ni₃Al phase is a result of $\beta \rightarrow \gamma'$ transformation which occurred due to the aluminum depletion from the β phase. The γ' phase contains about 11 at. % Al, 66 at. % Ni, 9 at. % Cr, 11 at. % Co and 5 at. % W (Table 3). Aluminum concentration in the γ' -Ni₃Al phase is too low to form an oxide layer consisting of the Al₂O₃, so oxides containing nickel, chromium and aluminum are being formed [16].



Figure 5. Cross-sectional microstructure of non-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**), EDS spectrum of microarea 1 (**b**), EDS spectrum of microarea 2 (**c**).

Microarea	Al	Cr	Со	Ni	W
1	10.4	9.0	10.7	65.6	4.3
2	10.7	9.1	11.1	64.3	4.8

Table 3. Chemical composition in microareas 1,2, Figure 5, at. %.

3.2.2. Rhodium-Modified Aluminide Coating after the Oxidation Test

The surface of the rhodium-modified aluminide coatings after oxidation is presented in Figure 6. The results of chemical composition in microareas are presented in Table 3. The surface consists mainly of gray areas of oxides and bright areas of substrate formed by oxide layer spallation. The predominant kind of oxides are the darkest oxide layer (Point 1) containing 45.6 at. % Al and 54.4 at. % O (Table 4). Such chemical composition indicates the presence of Al₂O₃. The presence of Al₂O₃ was confirmed by the XRD analysis (Figure 7). Another type of oxide (light gray color) contains 10.1 at. % Ni as well as Al and O and small content of W, Co and Cr. XRD results reveal the presence of NiAl₂O₄ spinel (Figure 7). There are no porous oxides as in the non-modified aluminide coatings. Chemical composition of the brightest areas marked 3 is very similar to that of the substrate alloy, which indicates that it was exposed by oxide layer spallation. It was identified as Ni₃Al phase by the XRD analysis, similar to the non-modified coating.



Figure 6. Surface of rhodium-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**) with marked microareas analyzed using EDS (**b**) after oxidation.

Microarea	0	Al	Cr	Со	Ni	W	Rh
1	54.4	45.6	-	-	-	-	-
2	59.6	25.4	2.4	2.3	10.1	0.2	-
3	-	19.4	5.4	8.4	64.3	2.3	0.2

Table 4. Chemical composition in microareas 1–3, Figure 6b, at. %.

The cross-section of coating consists of light-gray and dark-gray grains (Figure 8a–c). The light-gray γ' -Ni₃Al grains, marked 2 in Figure 8, contain 18.7 at. % Al, 65.4 at. % Ni and among others 0.1 at. % Rh (Table 5) formed due to Al depletion from the β -NiAl phase. The Al-depleted β -NiAl phase grains contain 30.2 at. % Al, 56.9 at. % Ni and higher amount of rhodium 0.5 at. %. The aluminum content indicates that this phase has not yet transformed into the γ' phase. Considering the presence of the β -NiAl phase grains, it is evident that this type of coating is more stable during oxidation in comparison to the non-modified one.



Figure 7. XRD results from the surface of rhodium-modified aluminide coating after oxidation at 1100 $^{\circ}$ C for 21 cycles.



Figure 8. Cross-sectional microstructure of rhodium-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**), EDS spectrum of microarea 1 (**b**), EDS spectrum of microarea 2 (**c**).

Microarea	Al	Cr	Со	Ni	W	Rh
1	30.2	5.1	6.6	56.9	0.7	0.5
2	18.7	5.2	8.1	65.4	2.5	0.1

Table 5. Chemical composition in microareas 1,2, Figure 8, at. %.

3.2.3. Palladium-modified Aluminide Coating after the Oxidation Test

The surface of the palladium-modified aluminide coating after oxidation is presented in Figure 9. The results of chemical composition in microareas are presented in Table 6. The surface consists of gray areas of oxides and bright areas of substrate formed by oxide layer spallation. The gray oxide layer contains 48.3 at. % Al and 51.7 at. % O (Table 6). Such chemical composition indicates the presence of Al_2O_3 , confirmed by the XRD (Figure 10). Chemical composition of the brightest areas, marked 1, is very similar to that of the substrate alloy, which indicates that it was exposed by oxide layer spallation. It was identified by the XRD analysis as the Ni₃Al phase, similar to the non-modified and rhodium-modified aluminide coatings. NiAl₂O₄ spinel above Al_2O_3 was also identified (Table 6, Figure 10).

The cross-sectional microstructure of the investigated coating consists of the γ' -Ni₃Al phase in the outer zone (Figure 11a,b, Point 1, Table 7). Chemical composition of oxidized coating below outer zone (Point 2) is similar to Point 1 (Figure 11a,c). Therefore, phase composition in these two points is the same. Significant porous areas below the outer zone of coating was also observed.



Figure 9. Surface of the palladium-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**) with marked microareas analyzed using EDS (**b**) after oxidation.



Table 6. Chemical composition in microareas 1, 2, Figure 9b, at. %.

Figure 10. XRD results from the surface of the palladium-modified aluminide coating after oxidation at 1100 °C for 21 cycles.



Figure 11. Cross-sectional microstructure of palladium-modified aluminide coating after oxidation at 1100 °C for 21 cycles (**a**), EDS spectrum of microarea 1 (**b**), EDS spectrum of microarea 2 (**c**).

Table 7. Chemical composition in microareas 1,2, Figure 11, at. %.

Microarea	Al	Cr	Со	Ni	W	Pd
1	18.7	5.3	8.1	67.8	-	0.1
2	18.4	4.6	9.4	67.4	-	0.2

4. Discussion

The non-modified aluminide coating's formation is a result of two processes [14]: diffusion of nickel, cobalt, chromium, titanium and other superalloys' elements from the substrate to the surface, leading to formation of the interdiffusion layer, reaction of nickel with aluminum supplied by the gas phase in the CVD process and formation of the additive layer.

The total coating thickness includes two layers. Both consist of the β -NiAl phase. As solubility of alloying elements in the β -NiAl phase is very low, these elements precipitate in Topologically Closed-Pack phases (μ and σ).

Rhodium content between additive and interdiffusion layers is 4 at. %. According to the Al-Ni-Rh phase diagram, it is too low to form rhodium-rich precipitations. Therefore, rhodium dissolves in the β -NiAl phase.

The formation of the rhodium-modified aluminide coating seems to take place in several steps: rhodium probably dissolves in $\gamma + \gamma'$ phases near the surface of CMSX-4 alloy during heating of the alloy with 0.5 µm of rhodium; aluminum during aluminizing in the CVD process arrives at the surface where Rh is diluted by Ni and since aluminum has more affinity to nickel than rhodium, it forms the (Ni,Rh)Al phase layer.

The formation of the palladium-modified aluminide coating seems to take place in the next steps [13]: Palladium dissolution in $\gamma + \gamma'$ phases near the surface of CMSX-4 alloy during heating of alloy with 3 µm of palladium; reaction of dissolved in the substrate palladium with aluminum; and (Ni,Pd)Al phase formation.

The oxidation of the non-modified aluminide coating probably takes places as follows: initial development of continuous Al_2O_3 oxides; diffusion of aluminum from coating to Al_2O_3 oxides; and to substrate. As a result of diffusion of aluminum a Ni₃Al phase is being formed and propagates inwards. Prolongation of oxidation leads to scale spallation with subsequent formation of poorly-protective oxides such as NiAl₂O₄ and (Ni,Cr)O. A schema of evolution of non-modified aluminide coating before oxidation and after oxidation is presented in Figure 12.



Figure 12. A scheme of evolution of non-modified aluminide coating: (a) before oxidation; (b) after oxidation.

Rhodium modification of aluminide coatings effectively improves oxidation resistance of superalloy. Moreover, deposition of thin rhodium layer (0.5 μ m thick) on the superalloy followed by aluminizing ensures better oxidation resistance than deposition of thicker palladium layer (3 μ m thick) on the superalloy followed by aluminizing.

The oxide layer formed on the surface of the rhodium or palladium-modified coatings consists of the Al₂O₃ phase matrix with top layer of the NiAl₂O₄ phase. On the surface of non-modified coating NiAl₂O₄ oxides and some porous oxides with chemical composition of (Ni,Cr)O phase were found. According to Swadźba et al. [15] NiAl₂O₄ forms mainly above the γ' -Ni₃Al regions where not enough Al is available for Al₂O₃ exclusive formation. It was also found that modification of rhodium (0.5 µm rhodium layer thick) and of palladium (3 µm palladium layer thick) decreases the oxide layer growth rate. The oxides layer thickness of the non-modified coating was about 10 µm, while the oxides layer thickness of the rhodium or palladium-modified coatings was about 5 µm (Figure 13).



Figure 13. Oxide layer thickness as a function of kind of aluminide coating: (**a**) non-modified; (**b**) rhodium-modified (0.5μ m rhodium layer) and (**c**) palladium-modified (3μ m palladium layer).

Cross-sectional microstructure of the rhodium-modified coatings after oxidation consists of three regions: Al-depleted (30 at. %) β -NiAl phase grains, the γ' -Ni₃Al phase region and the refractory-rich precipitates region. In comparison to the non-modified and the palladium-modified, the rhodium-modified coating exhibits β -NiAl phase stability, and stable α -Al₂O₃ layer. It seems that rhodium produces at the same time an increase of the diffusivity of aluminum and a decrease

of that of other superalloy elements, so that the rhodium containing coating acts as a filter enabling aluminum to diffuse more easily than the other elements, resulting in the formation of aluminum oxide layer. This also helps to form aluminum oxide layers more rapidly and under lower aluminum concentrations as well as to maintain the β -NiAl phase at the coating surface for longer periods. Chromium, cobalt and tungsten, as well as nickel, rhodium and aluminum, are found in the β -NiAl phase of rhodium-modified coatings after oxidation. However, contents of chromium, cobalt and tungsten in the β -NiAl phase are smaller than in the γ' -Ni₃Al phase. All these indicate that rhodium tends to be solid solutioned in the β instead of the γ' phase. The rhodium-modified aluminide coatings perform better than the non-modified and palladium-modified ones. In particular, protective oxide layer keeps for longer periods of time on the rhodium-modified coatings compared to the non-modified and palladium-modified ones. β phase remains in the rhodium-modified coatings while γ' phase is both non-modified and palladium-modified after oxidation. It is possible that the major function of rhodium is to produce a large initial reservoir of aluminum and to reduce the amount of aluminum lost by diffusion processes. Rhodium probably has similar effects on the aluminide coating, since rhodium belongs to the platinum group of metals. Rhodium, similar to platinum, may accumulate near the thermally grown oxide due to the selective oxidation of other elements. Then, the aluminum activity gradient is increased, and the flux of aluminum to the thermally grown oxide/intermetallic coating interface is increased as well. This phenomenon may promote alumina scale formation. Some inclusions enriched in substrates elements have been observed in the additive layer of non-modified aluminide coatings (Figure 1a), whereas far fewer incursions have been observed in the additive layer of rhodium-modified ones. Therefore, it may be assumed that increasing of the lifetime of the β -phase is possible by impeding the outward diffusion of substrate elements to the additive layers of coating. The amount of the γ' -Ni₃Al phase formed under oxide layer in the rhodium-modified coatings is much smaller than in the palladium-modified and non-modified ones. It indicates that transformation from the β -NiAl phase to the γ' -Ni₃Al phase is decelerated due to the presence of the (Ni,Rh)Al phase in the as-deposited coating [13]. Because the γ' -Ni₃Al phase has a poor oxidation resistance, the deceleration of the γ' -Ni₃Al phase formation leads to improvement of the oxidation resistance. The aluminum depletion in the palladium-modified aluminide coating was lower than in the non-modified one, nevertheless aluminum content was too low to maintain stable β -NiAl phase. McMinn et al. [17] allege that palladium-modified aluminide coating is a poor protector due to formation of pores by the Kirkendall effect. Hydrogen that dissolves in the coating during the aluminizing process results in blistering of the coating and subsequent rapid pitting at high temperature [18].

The oxide scale formed on the surface of the rhodium-modified aluminide coatings is more adherent than on the non-modified one. According to Zhang et al. [19] oxide adherence at coating grain boundaries may be influenced by several mechanisms: chemical effects (short-circuit diffusion pathways for alloying elements and sulfur impurities), geometric effects and preferential void nucleation and coalescence sites. Refractory-rich particles were observed at the grain boundaries of the β -NiAl phase in the as-deposited non-modified aluminide coating, but were not observed at the grain boundaries of the β -(Ni,Rh)Al phase in the as-deposited rhodium-modified aluminide coating [13]. According to Zhang et al. [20] the presence of refractory elements on the coating grain boundaries may accelerate oxide spallation by degrading the oxide-metal bond strength, stabilizing the γ' -Ni₃Al phase formation or increasing the growth rate of the oxide layer once oxide layer spallation and reformation begin.

The analysis of chemical composition in microareas proves that rhodium is easy to solidify into solution in the β -NiAl phase. The higher content of rhodium in the β -NiAl phase sustains aluminum concentration. Addition of rhodium helps to stabilize the β -NiAl phase of high aluminum content and to delay the degradation of the aluminide coating.

5. Conclusions

The microstructure of non-modified and rhodium or palladium-modified aluminide coatings consist of two layers: an additive and an interdiffusion one before oxidation. The NiAl intermetallic phase was found in the microstructure of a non-modified coatings, while the (Ni,Rh)Al intermetallic phase was observed in the microstructure of rhodium-modified aluminide coatings. The (Ni,Pd)Al phase of palladium-modified aluminide coatings in the additive layer was observed before oxidation.

The oxide layer (10 µm thick) formed on the surface of the non-modified coating consists of the NiAl₂O₄ phase, moreover porous oxide with chemical composition of Ni-rich oxide was found. After oxidation, the microstructure of the non-modified coating consists of the γ' -Ni₃Al phase. The oxide layer (5 µm thick) formed on the surface of rhodium or palladium-modified coatings consists of the α -Al₂O₃ phase and the top layer of the NiAl₂O₄ phase. Al-depleted (30 at. %) β -NiAl phase grains as well as the γ' -Ni₃Al phase region were found in the rhodium-modified coating, while only γ' -Ni₃Al phase region was revealed in the palladium-modified coating. The rhodium-modified coating shows lower weight change than the non-modified and palladium-modified ones. Therefore, rhodium-modified aluminide coatings with small rhodium content (0.5 µm rhodium layer thick) can be an alternative for palladium-modified aluminide ones with bigger palladium content (3 µm palladium thick layer).

Funding: This research was funded by the National Science Centre, Poland (NCN), project number 2016/21/D/ST8/01684 and The APC was funded by the National Science Centre, Poland (NCN), project number 2016/21/D/ST8/01684.

Acknowledgments: The National Science Centre, Poland (NCN), project number 2016/21/D/ST8/01684.

Conflicts of Interest: The author declares no conflicts of interest.

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