

Oxidation behaviour of palladium modified aluminide coatings deposited by CVD method on nickel-based superalloys under air atmosphere

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ABSTRACT

Purpose: In this paper the oxidation resistance of palladium modified aluminide coatings deposited by CVD method on nickel-based superalloy was evaluated.

Design/methodology/approach: Palladium coatings 3 and 7 μm thick were deposited by the electroplating process. The heat treatment of electroplating coatings at the temperature 1050 $^{\circ}\text{C}$ for 2 h under argon atmosphere was performed. Low activity CVD aluminizing process of palladium heat treated coatings (3 and 7 μm thick) at the 1050 $^{\circ}\text{C}$ for 8 h using IonBond equipment was performed. Oxidation resistance was evaluated at 1100 $^{\circ}\text{C}$ for 1000 h in air atmosphere using furnace of Czylok company. The microstructure investigations of palladium modified aluminide coatings were conducted by the use of optical microscope (Nikon Epiphot 300) and a scanning electron microscope (Hitachi S-3400N) equipped with an Energy Dispersive Spectroscopy EDS (VOYAGER of NORAN INSTRUMENTS). The phase composition was identified by X-ray (ARL X'TRAX) diffractometer. The surface roughness parameter - Ra of modified aluminide coatings was evaluated by Perthometer S2 MAHR equipment.

Findings: The microstructure of palladium modified aluminide coatings (3 and 7 μm thick) consists of (Ni,Pd)Al phase and two zones: outer and internal one. Low activity CVD aluminizing at 1050 $^{\circ}\text{C}$ for 8 h causes the increase of surface roughness parameter of modified coatings. The increase of platinum thickness from 3 to 7 μm causes a greater surface roughness of aluminide coatings. On the ground of the obtained results, it was found that palladium modification of aluminide coatings to increases the oxidation resistance of CMSX 4 Ni-base superalloy.

Practical implications: The palladium modified aluminide coatings are used as an alternative for platinum modified aluminide coatings in turbine blades of aircraft engines.

Originality/value: It was proved that palladium modification of aluminide coatings has a positive effect on the oxidation resistance of CMSX 4 Ni-base substrate.

Keywords: Palladium modification; Aluminide coatings; CVD method; Oxidation resistance

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1. Introduction

Nickel base superalloys have good plasticity, high corrosion and thermal fatigue resistance [1]. These superalloys are used for a wide variety of applications. The majority of which involve corrosion resistance and heat resistance application. The nickel base superalloys are the most commonly used in the hot section of the turbine. The superalloys may be applied approximately to 1000°C. Further increase of temperature requires the modern protective coatings application [2]. In the aircraft turbine industry the aluminum based diffusion coatings are generally used. These coatings can be used as a stand-alone coatings or as an interlayer for thermal barrier coatings (TBC). But aluminide coatings based on the NiAl phase deposited by the CVD method do not fulfil the requirements such as a long term oxidation resistance at high temperature. Modification of aluminide coatings by platinum is the most effective way to increase oxidation resistance of turbine blades [3-8]. Pt-modified aluminide coatings affirm the protection of nickel-base blades from oxidative gases even at the gas temperature above 1400°C [9]. However platinum leads to formation of the PtAl₂ phase in the coating microstructure [10-11]. The low ductility of PtAl₂ and large difference of thermal expansion coefficients between the substrate and platinum causes the coating degradation under the cyclic thermal stress. Authors of the paper [12] have undertaken attempts to replace the platinum modification by the palladium one. Palladium is four times cheaper than platinum. Daxiong He et al [12] proved that Pd-Ni-Al coatings in cyclic oxidation tests at 1050°C showed a higher performance than platinum modified and conventional aluminide coatings. Alperine et al. [13] showed that the palladium modified aluminide coating has higher oxidation and hot corrosion resistance than conventional aluminide coatings. On the other hand Lehnert et al. [14] showed that a palladium modified aluminide coating is a low protector.

In this paper the oxidation behaviour of palladium modified aluminide coatings deposited by CVD method on nickel based superalloys was evaluated.

2. Experimental procedure

The superalloys used in this study were Inconel 713 LC and CMSX 4. Chemical composition of the used superalloys is given in Table 1.

The samples were cut in the shape of cylinders. The surface of the samples was grounded by means water resistant 500 grade paper. Afterwards the samples surfaces were washed and degreased.

The palladium 3 and 7 μm thick was deposited by electroplating process [15]. Process of palladium electroplating was performed in the Warsaw Institute of Precision Mechanics. The material surface preparation for palladium electroplating includes: degreasing by means of ultrasound, electrolytic etching and surface activation. The degreasing was performed by means of sodium hydroxide - NaOH 60 g/dm³ and sodium carbonate - Na₂CO₃ 30g/dm³. The degreasing was carried out at 60°C. The electrolytic etching was performed in the bath, which consists of: sulfuric acid H₂SO₄ - 100 g/cm³ and sodium chloride NaCl - 20 g/cm³ at the room temperature. Surface activation was carried out in the bath that consists of: nickel chloride Ni₂Cl - 20 g/cm³ and hydrochloric acid HCl - 120 g/cm³ at the room temperature. The palladium electroplating process was conducted in the bath of palladium chloride PdCl₂ - 10 g/cm³, sulfamates acid H₂NSO₃ - 100 g/cm³, hydrochloric acid HCl - 20 g/cm³ and ammonium chloride NH₄Cl - 50 g/cm³ at 35°C.

The samples after electroplating were heat treated at the temperature of 1050°C for 2 h under argon atmosphere.

The aluminide coating was obtained in low-activity CVD process by means of the BPXPRO3242 equipment of IonBond company in the R&D Laboratory for Aerospace Materials, Rzeszów University of Technology, Poland. The gas atmosphere (AlCl₃+H₂) was prepared in an external generator and transported into the retort with samples. The CVD device was equipped with the control and dosing gas system, which allowed to control the process parameters. The chemical vapor deposition was carried out on cylindrical samples. The low activity CVD process was performed at the temperature 1050°C for 8h. In order to obtain a thermodynamically stable conditions the CVD process consisted of several heating stages.

The surface roughness parameter - Ra was evaluated by Perthometer S2 MAHR. The average value of surface roughness parameter and a standard deviation was calculated. Oxidation resistance was investigated at temperature 1100°C for 1000 h in air atmosphere. The samples were annealed isothermally for 20 h and then were cooled down to the room temperature. The 51-cycles of heating and cooling were carried out. The mass change after each cycles was measured. The palladium electroplating samples after diffusion treatment and aluminizing process were cut to study the cross-section. Polished sections were etched by the use of reagent with chemical composition as follows: 100 cm³ HNO₃, 7 cm³ HF, 11 cm³ H₂O. Microstructure investigations of samples were performed by the use of light microscope Nikon 300 and scanning electron microscope (SEM) HITACHI S-3400N equipped with EDS spectrometer. Evaluation of phase composition of the investigated coatings was made using ARL X'TRAX-ray diffractometer, equipped with filtered copper lamp with the voltage of 45 kV.

Table 1.
Chemical composition of the Inconel 713LC and CMSX 4 Ni-base superalloys

Superalloy	Elements content, % mas.														
	Ni	Cr	C	Mo	Nb	Ta	Al	Ti	Co	W	Hf	Fe	S	Si	Re
Inconel 713 LC	74.71	12.0	0.05	4.6	1.96	-	5.7	0.7	0.08	-	-	0.19	0.007	0.003	-
CMSX 4	61.7	6.5	-	0.6	-	6.5	5.6	1	9	6	0.1	-	-	-	3

3. Results and discussion

Heat treatment of palladium electroplating coatings (3 and 7 μm thick) leads to formation of a diffusion zone in coating. The diffusion zone forms as a result of outward diffusion of nickel, chromium and aluminium elements and inward diffusion of palladium [15]. The diffusion aluminide coating (49 μm deep) after aluminizing process on the surface of a heat treated palladium coating (3 μm thick) of Inconel 713 LC Ni-base superalloys was formed. The increase of palladium electroplating thickness from 3 to 7 μm leads to the growth of aluminide coatings thickness from 49 to 52 μm . The aluminide coating consisted of two zones: an outer and an internal (diffusion) one (Fig. 1a). The outer zone was enriched in aluminium (37-42% at.), nickel (51-53% at.) and palladium (about 6% at). The internal zone was enriched in chromium (17.72% at.), titanium (1.31% at.) and molybdenum (5.91% at.) see Table 2. Chromium forms M_{23}C_6 carbides on the boundary of outer-internal zone. The columnar precipitations of brittle phases in the internal zone were enriched in nickel, titanium, chromium and molybdenum [16].

The surface of palladium modified aluminide coating (7 μm thick) consisted of grains with 42 μm average diameter (Fig. 1 b). The NiAl intermetallic phase was observed in the microstructure of nonmodified aluminide coating. The palladium 5% at is distributed at the surface and at the grain boundary of aluminide coating.

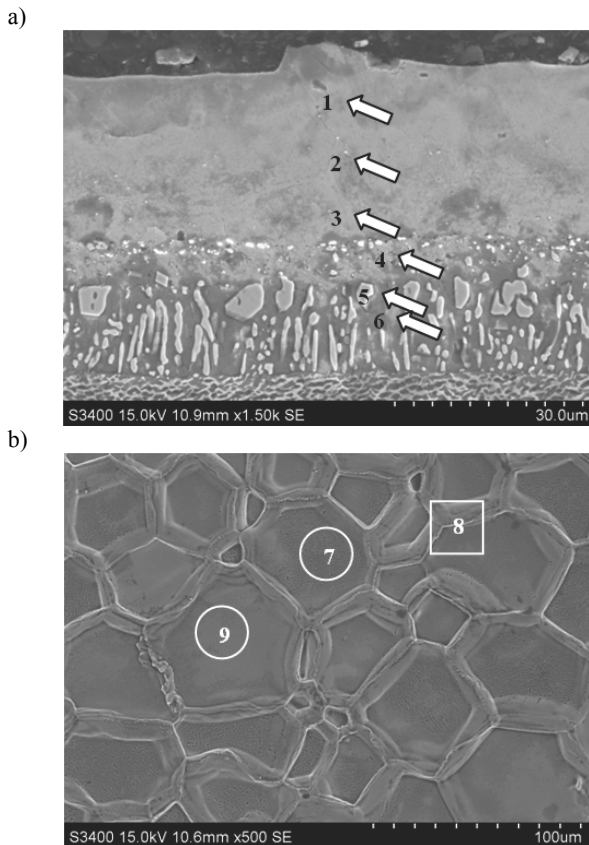


Fig. 1. Microstructure on the cross-section (a) and surface (b) of palladium heat treated coating (7 μm thick) after low-activity CVD aluminizing process on Inconel 713 LC Ni-base superalloy

Table 2.

Chemical composition on the cross-section (Point 1-6) and on the surface of coating (Point 7-9) (Fig. 1a-b)

Area	Elements content, % at					
	Al	Ti	Cr	Mo	Ni	Pd
1	41.55	-	1.54	-	50.75	6.16
2	38.65	-	3.24	-	52.04	6.07
3	37.00	-	4.32	-	53.03	5.65
4	35.15	1.31	5.58	-	53.65	4.31
5	26.26	0.49	17.72	5.91	46.97	2.65
6	29.33	0.49	11.00	3.33	52.85	3.00
7	42.46	-	1.31	0.09	51.21	4.93
8	42.44	-	0.97	0.11	51.35	5.13
9	41.05	-	1.30	0.13	52.48	5.04

The analysis of chemical composition on the cross-section shows outward diffusion of nickel, chromium and molybdenum and internal diffusion of aluminium and palladium (Fig. 2 a,b). Palladium content decreases from the surface of aluminide coating to the substrate. This is similar to the distribution of aluminium on the cross-section of an aluminide coating.

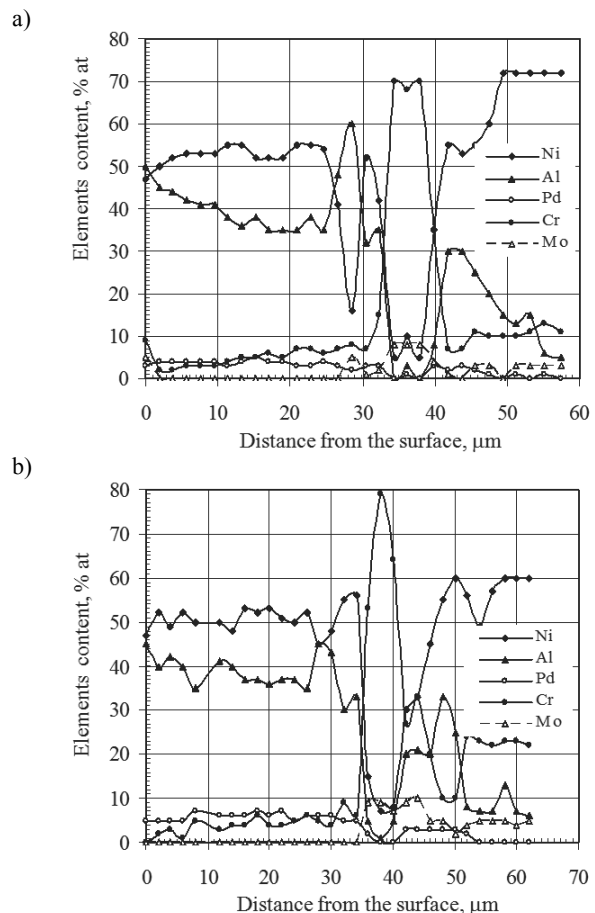


Fig. 2. Chemical composition on the cross-section of a palladium modified aluminide coating: a) 3 μm Pd layer before CVD, b) 7 μm Pd layer before CVD on Inconel 713 LC Ni-base superalloy after the low-activity CVD aluminizing process

The thickness of palladium modified aluminide coatings (3 μm palladium thick before) on CMSX 4 Ni-base superalloy is about 37 μm . The increase of palladium electroplating thickness from 3 to 7 μm leads to the growth of aluminide coatings thickness from 37 to 39 μm . The microstructure consists of two zones (Fig. 3 a). The refractory elements such as W and Re form the μ and σ phases in the diffusion zone. The surface of palladium modified aluminide coating (7 μm palladium thick) consists of grains with average grain size about 20 μm (Fig. 3 b). Grains boundaries have higher content of palladium, aluminum and lower nickel content in comparison to the substrate (Table 3). This is due to the nickel atoms substitution for palladium.

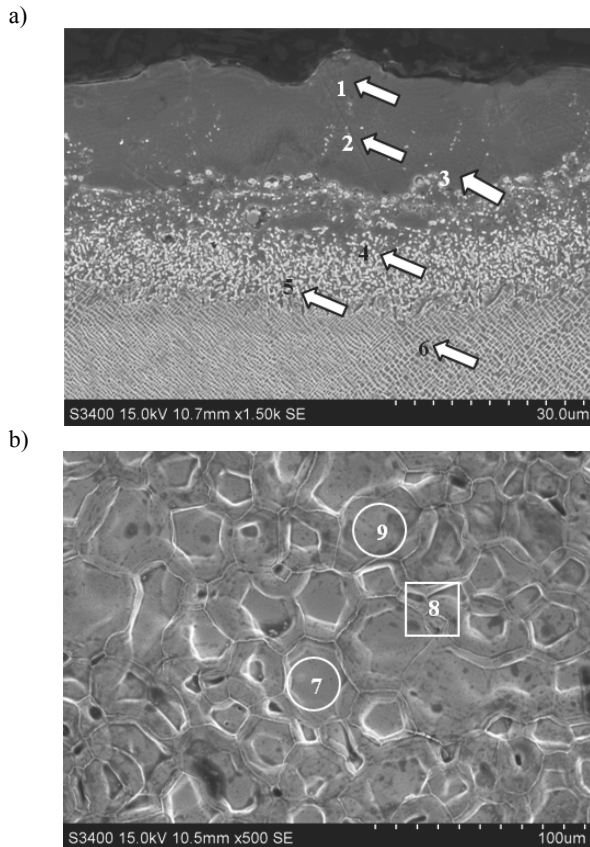


Fig. 3. Microstructure on the cross-section (a) and surface (b) of palladium heat treated coating (7 μm thick) after low-activity CVD aluminizing process on CMSX 4 Ni-base superalloy

The analysis of chemical composition on the cross-section shows outward diffusion of nickel, chromium and rhenium and internal diffusion of aluminium and palladium (Fig. 4 a,b). Palladium content decreases from the surface of aluminide coating to the substrate.

This is similar to distributing of aluminium on the cross-section of palladium modified aluminide coating. The increase of palladium thickness from 3 to 7 μm leads to the increase of aluminide coating thickness and palladium content on the surface of aluminide coating (Table 4). The palladium modified aluminide coatings thickness (3 and 7 μm Pd) deposited on Inconel 713 LC is higher in comparison to CMSX 4 superalloy (Fig. 5). The different

thicknesses is due to the difference in chemical composition of the superalloy such as: lower nickel and higher Ta, Ti, W and Re contents in CMSX 4 in comparison to Inconel 713 LC. The large content of refractory elements inhibits outward nickel diffusion and limits the coating formation [16,17].

Table 3. Chemical composition on the cross-section (Point 1-6) and on the surface of coating (Point 7-9) (Fig. 3 a-b)

Area	Elements content, % at						
	Al	Cr	Co	Ni	W	Re	Pd
1	43.68	1.31	3.51	43.80	0.17	0.53	7.0
2	38.42	2.90	5.38	46.97	-	0.14	6.19
3	44.9	2.71	5.74	41.27	0.72	-	4.66
4	18.21	12.87	11.31	40.19	10.13	4.93	2.36
5	12.84	11.78	12.52	56.41	3.73	2.72	-
6	11.12	9.72	11.83	62.13	2.94	2.26	-
7	44.49	0.79	3.67	45.38	-	-	5.67
8	45.60	0.50	3.15	43.82	-	-	6.93
9	42.76	0.57	3.83	47.95	-	-	4.89

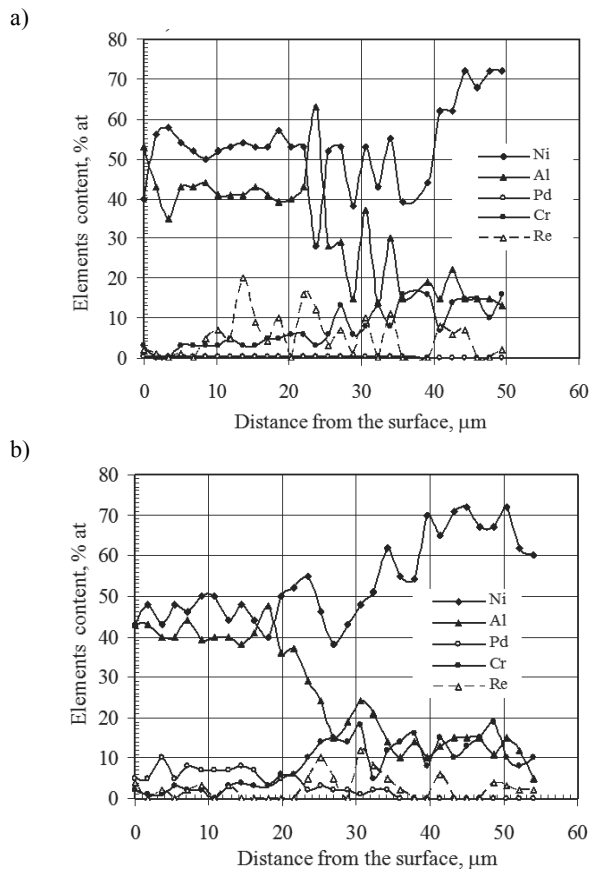


Fig. 4. Chemical composition on the cross-section of a palladium modified aluminide coating: a) 3 μm Pd layer before CVD, b) 7 μm Pd layer before CVD on CMSX 4 Ni-base superalloy after the low-activity CVD aluminizing process

Table 4.
The influence of palladium electroplating thickness on the aluminide coating thickness

Super alloy	Palladium thickness, μm	Aluminide thickness, μm	Palladium content, % at	Aluminum content, % at
Inconel 713 LC	0	45	-	44.7
	3	49	3.2	43.9
	7	52	5.05	41.9
CMSX 4	0	29	-	50.8
	3	37	2.38	48.11
	7	39	5.7	44.3

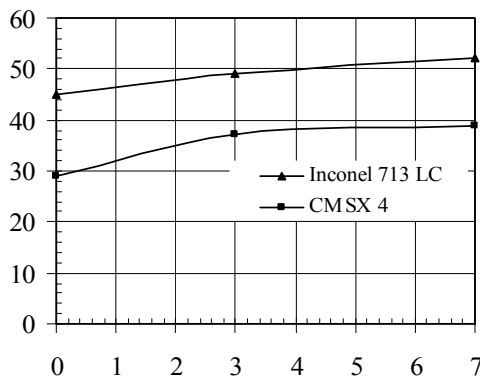


Fig. 5. Influence of palladium electroplating thickness on the aluminide coating thickness deposited by the CVD method on Inconel 713 LC and CMSX 4 Ni-base superalloys

The increase of surface roughness parameter value R_a of palladium modified aluminide coating with the increase of palladium electroplating thickness was found (Table 5). The modification of aluminide coating causes the dissolution of palladium in the NiAl phase. The (Ni,Pd)Al phase has different lattice parameter than NiAl phase. This phenomena can influence the increase of surface roughness parameter value. It is similar to platinum modified aluminide coatings.

Table 5.
Values of surface roughness parameter R_a of palladium modified aluminide coatings

Superalloy	Surface roughness parameter R_a		
	Without palladium 0 μm	Palladium electroplating	
		3 μm	7 μm
Inconel 713 LC	2.552	3.0694	3.6048
Standard deviation	0.109	0.170	0.477
CMSX 4	2.7712	2.7382	4.9086
Standard deviation	0.048	0.093	0.502

It is found, that palladium modified aluminide coatings (3 and 7 μm thick) deposited on the Inconel 713 LC show the same oxidation resistance as nonmodified aluminide coating (Fig. 6). Weight change of palladium modified aluminide coatings (3 and 7 μm thick) after 1000 h oxidation in the air atmosphere is -12 mg/cm^2 . There are many theories of the wrong influence of

palladium on the oxidation resistance of aluminide coating [18]. Palladium easily absorbs hydrogen during electroplating process. Annealing and aluminizing process after palladium electroplating leads to the dissolution of hydrogen in the aluminide coating. Increase of oxidation rate may be result of bubbles which are formed in hydrogen dissolved palladium modified aluminide coatings. Lehnert and Meihardt [14] found that a palladium modified aluminide coating was poorly protective because of numerous voids in the coating which were interpreted as Kirkendall porosity. Authors [19] claim that palladium does not form oxides at the temperature above 800°C . Decrease of oxidation resistance is a results of oxygen adsorption by the (Ni,Pd)Al intermetallic phase.

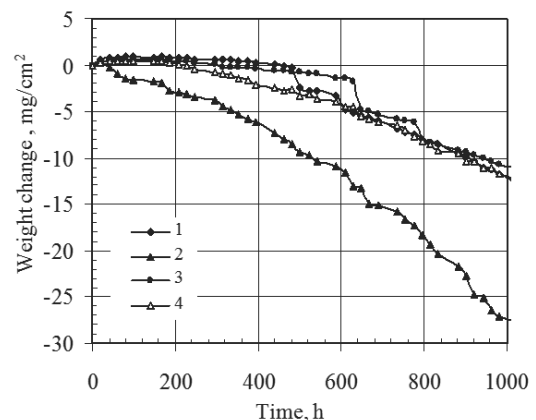


Fig. 6. The kinetics of the oxidation test of aluminide coating deposited on Inconel 713 LC Ni-base superalloy at the 1100°C for 1000 h in the air atmosphere: 1 - thickness of platinum electroplating 3 μm ; 2 - substrate; 3 - thickness of platinum electroplating 7 μm ; 4 - nonmodified aluminide coating

The Pd modified aluminid coating (3 and 7 μm thick) deposited on CMSX 4 Ni-base superalloy protects the substrate during 1000 h oxidation (Fig. 7). During annealing of palladium electroplating coating $\text{Ni}_{0.52}\text{Pd}_{0.475}$, AlPd_2 and Ni_3Al phases are formed. (Ni,Pd)Al phase forms during aluminizing process as a result of larger aluminium affinity to nickel. Palladium atoms replace nickel atoms in the NiAl phase. This phenomena does not depend on the palladium electroplating thickness. Authors [20] proved that microstructure formation of palladium modified aluminide coating consists of 2 stages:

- reaction of $\text{Ni}_{0.52}\text{Pd}_{0.475}$ phase with aluminium and (Pd,Ni)Al phase formation;
- aluminium and nickel diffusion through β -(Pd,Ni)Al phase and NiAl phase formation near the substrate. (Pd,Ni)Al phase forms in the internal and external zone of coating.

The rate of oxide scale formation depends on the chemical composition of substrate. Oxide scale thickness decreases with the increase of palladium electroplating thickness (Table 6, Fig. 8). Oxide layer of the palladium modified aluminide coating deposited on the CMSX 4 Ni-base superalloy was thinner in comparison to the oxides deposited on the Inconel 713 LC. Oxidation resistance of palladium modified aluminide coating deposited on the CMSX 4 superalloy was larger than on the Inconel 713 LC.

The NiAl_2O_4 , TiO_2 , $\text{Al}_{1.98}\text{Cr}_{0.02}\text{O}_3$ oxides and Ni_3Al intermetallic phase were found on the surface of the palladium modified aluminide coating after the oxidation test.

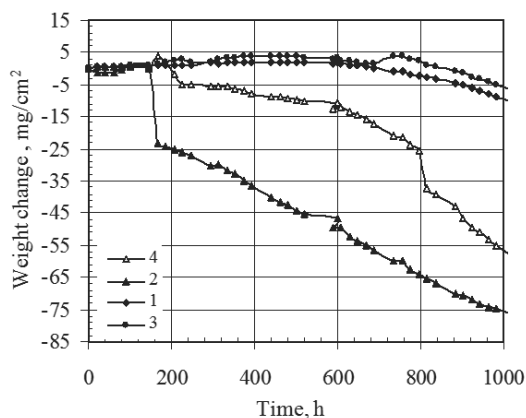


Fig. 7. The kinetics of the oxidation test of aluminide coating deposited on Inconel 713 LC Ni-base superalloy at the 1100°C for 1000 h in the air atmosphere: 1 - thickness of platinum electroplating 3 μm ; 2 - substrate; 3 - thickness of platinum electroplating 7 μm ; 4 - nonmodified aluminide coating

Table 6.

Oxide scale thickness after 354 h oxidation at the 1100°C temperature in the air atmosphere

Superalloy	Palladium electroplating thickness, μm	Oxide scale thickness, μm
Inconel 713 LC	0	18
	Pd 3	16
	Pd 7	8
CMSX 4	0	10
	Pd 3	5
	Pd 7	3

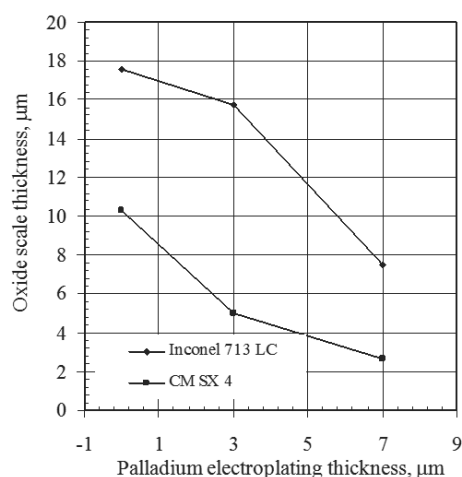


Fig. 8. The influence of palladium electroplating thickness on the oxide scale thickness after 354 h of oxidation at the 1100°C in the air atmosphere

4. Conclusions

The microstructure of platinum modified aluminide coating deposited on both Inconel 713 LC and CMSX 4 Ni-base superalloy consists of two zones. An outer zone consisted of $(\text{Ni,Pd})\text{Al}$ phase. An internal (diffusion) zone of aluminide coating deposited on Inconel 713 LC Ni-base superalloy consists of M_{23}C_6 carbides and $\text{Cr}_x\text{Ni}_y\text{Mo}_z$ intermetallic phase. The brittle phases of μ and σ was found in the diffusion zone of aluminide coating deposited on CMSX 4 Ni-base superalloy. It was found that palladium aluminide coating thickness depends on the chemical composition of superalloy.

Palladium modified aluminide coating deposited on the Inconel 713 LC substrate has worse oxidation resistance than palladium modified aluminide coating deposited on the CMSX 4 substrate. The increase of palladium electroplating thickness from 3 to 7 μm leads to the decrease of oxide scale thickness. Palladium accelerates outward diffusion of substrate elements to the oxide scale and leads to obtain the aluminide coating with worse oxidation resistance than the platinum modified aluminide coating.

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