

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

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### Manufacturing and processing

#### ABSTRACT

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

**Design/methodology/approach:** Platinum coatings 3 and 7  $\mu\text{m}$  thick by the electroplating process were deposited. The heat treatment of electroplating coatings at the temperature 1050°C for 2 h under argon atmosphere was performed. Low activity CVD aluminizing process of platinum heat treated coatings (3 and 7  $\mu\text{m}$  thick) at the 1050°C for 8 h using IonBond equipment was performed. Oxidation resistance at 1100°C for 1000 h in air atmosphere using furnace of Czylok company was evaluated. The microstructure investigations of platinum and 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 platinum modified aluminide coatings (3 and 7  $\mu\text{m}$  thick) consists of (Ni,Pt)Al phase and two zones: outer and internal one. Low activity CVD aluminizing at 1050°C for 8 h causes the increase of surface roughness parameter of modified coatings. The increase of platinum thickness from 3 to 7  $\mu\text{m}$  lets to get a greater surface roughness parameter of aluminide coatings. On the ground of the obtained results, it was found that platinum modification of aluminide coatings provides to increase of oxidation resistance Ni-based substrates.

**Practical implications:** The platinum modified aluminide coatings are widely used as coatings for turbine blades of aircraft engines.

**Originality/value:** It was proved that platinum modification of aluminide coatings has a positive effect on the oxidation resistance of substrate.

**Keywords:** Platinum modification; Aluminide coatings; CVD method; Oxidation resistance

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## 1. Introduction

The improvement of engine turbines efficiency is achieved by the effective cooling system of turbine blades and by diffusion protective coatings on nickel based superalloys [1-3]. High temperature coatings based on the  $\beta$ -NiAl intermetallic phase are extensively used to protect components against oxidation in gas turbine engines. However aluminide coatings based on the NiAl phase deposited by CVD method do not fulfil the requirements such as 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 [2-10]. Pt-modified aluminide coatings affirm the protection of nickel-base blades from oxidative gases even at gas temperature above 1400°C [11].

Several studies showed that platinum additions improve the properties of both superalloy and aluminide coating [2-5]. Platinum accelerates formation of thermal stable oxide  $Al_2O_3$  and improves the oxide scale adherence [12]. Pedraza et al [13] showed that platinum reduces void formation at the interface of metal/oxide. The platinum modification of aluminide coatings improves the stability of  $\beta$ -NiAl phase and delays the transformation of  $\beta$ -NiAl to the  $\gamma'$ -Ni<sub>3</sub>Al phase. Niu et al [14] showed that platinum accelerates aluminium diffusion, then reduces the vacancies flux from the metal to the surface and inhibits vacancy coalescence and internal void formation. Platinum decreases the diffusion of alloying elements to the coating, promotes a selective alumina scale formation and accelerates healing after spallation [14]. The important factor of platinum coatings after electroplating is the diffusion treatment. The application of diffusion treatment of platinum coatings provides their good adherence. The aluminizing process of platinum heat treated coatings provides excellent oxidation resistance of Ni-based substrate.

In this paper the oxidation behaviour of platinum modification 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 platinum 3 and 7  $\mu$ m thick was deposited by electroplating process. The material surface preparation for platinum electroplating process includes four basic operation: surface degreasing, surface etching, rinsing in cold water, surface activation.

The electrochemical degreasing was carried out in gluconate electrolyte at the temperature of 50°C. The electrolyte contained 180-240 g/dm<sup>3</sup> sodium gluconate -  $C_6H_{11}NaO_7$  and 18-240 g/dm<sup>3</sup> sodium hydroxide - NaOH. The rinsing in a heat water was carried out in order to clean samples surface from  $C_6H_{11}NaO_7$  and NaOH. The samples surface activation was carried out by etching in the mixture of: 90 g/dm<sup>3</sup> HF + 530 g/dm<sup>3</sup> HNO<sub>3</sub>.

Platinum electroplating process included the activation and appropriate electroplating. The activation electroplating was performed during 1 h by means of tetraamineplatinum (II) composite bath -  $Pt(NH_3)_2(NO_2)_2$  15 g/dm<sup>3</sup>, which enables the rapid growth of an adherent and relatively homogeneous coating. The current density during the activation electroplating process was about of 10 A/dm<sup>2</sup>. Titanium was used as an anode to electroplating. The appropriate electroplating was done with the current density of 0.1 A/dm<sup>2</sup>. 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 R&D Laboratory for Aerospace Materials, Rzeszów University of Technology, Poland. The gas atmosphere ( $AlCl_3+H_2$ ) was prepared in an external generator and transported into the retort with samples. The CVD device is equipped with the control and dosing gas system, which allows to control the process parameters. The chemical vapor deposition was carried out on cylindrical samples. The low activity CVD process was done at the temperature 1050°C for 8 h. In order to obtain a thermo-dynamically stable conditions the CVD process consisted of several heating stages.

The surface roughness parameter - Ra of was evaluated by Perthometer S2 MAHR. The average value of surface roughness parameter and standard deviation were 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 input down to the room temperature. The 51-cycles of heating and cooling were carried out. The mass change after each cycles was observed. The platinum 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 cm<sup>3</sup> HNO<sub>3</sub>, 7 cm<sup>3</sup> HF, 11 cm<sup>3</sup> H<sub>2</sub>O. 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 and heater current of 40 mA. Measurements were made in the range of 15 to 140°.

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 platinum electroplating coatings (3 and 7  $\mu\text{m}$  thick) leads to formation of diffusion zone in the microstructure of coating. The diffusion zone forms as a result of outward nickel and inward platinum diffusion. The platinum and substrate elements such as nickel, aluminium, chromium, on the surface of heat treated platinum coatings were found [11]. The diffusion aluminide coating (53  $\mu\text{m}$  depth) after aluminizing process on the surface of heat treated platinum coatings (3  $\mu\text{m}$  thick) of Inconel 713 LC Ni-base superalloys was formed (Figs. 1a-b). The aluminide coating consisted of the two zones: an outer and internal (diffusion) one. An outer zone was enriched in aluminium (30-40% at.), nickel (50-53% at.) and platinum (4-11% at.)

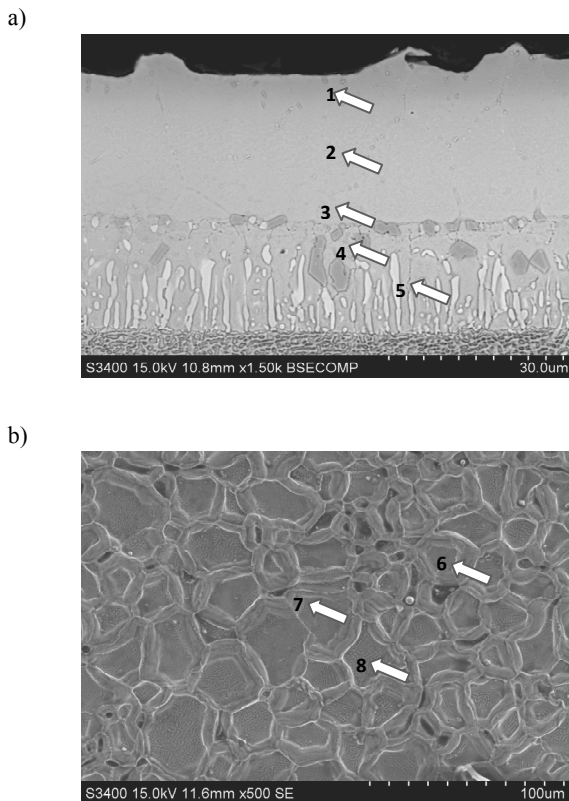


Fig. 1. Microstructure on the cross-section (a) and surface (b) of platinum heat treated coating (3  $\mu\text{m}$  thick) after low-activity CVD aluminizing process on Inconel 713 LC Ni-base superalloy

The internal zone was enriched in chromium (17.38% at.), titanium (1.10% at) and molybdenum (2.36% at.) (Table 2). The chromium creates of  $\text{M}_{23}\text{C}_6$  carbides on the boundary of outer-internal zone. The columnar precipitation of brittle phases in the internal zone were enriched in nickel, titanium, chromium and

molybdenum. The surface of platinum modified aluminide coating (3  $\mu\text{m}$  thick) consisted of grains with average diameter about 25  $\mu\text{m}$ . The NiAl intermetallic phase was observed in the microstructure of nonmodified aluminide coating. The modification of aluminide coatings leads to the platinum segregation on the grains boundary of NiAl phase.

Table 2.

Chemical composition on the cross-section and surface of coating (Figs. 1a-b)

Area	Elements content, % at					
	Al	Ti	Cr	Mo	Ni	Pt
1	40.16	-	2.50	0.41	52.51	4.42
2	32.32	-	6.62	0.71	50.22	10.13
3	30.41	0.49	8.96	0.65	50.52	8.97
4	25.55	0.48	17.38	2.36	44.40	9.83
5	29.03	1.10	9.27	1.02	52.36	7.22
6	40.47	-	1.30	0.32	55.88	2.03
7	41.04	-	1.40	0.13	54.48	2.95
8	38.75	-	2.58	0.23	56.26	2.18

It was found, that platinum is uniformly distributed on the cross-section of aluminide coating (Fig. 2).

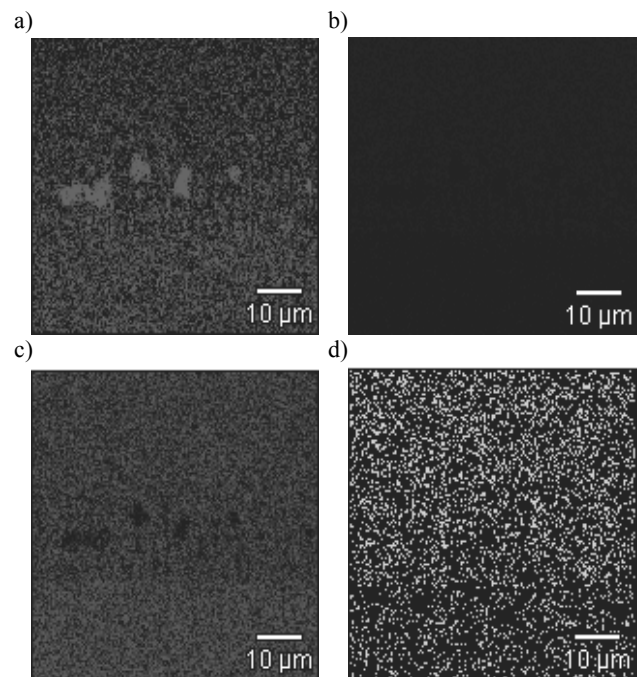


Fig. 2. Distribution of elements on the cross-section of platinum heat treated coating (7  $\mu\text{m}$  thick) after low-activity CVD aluminizing process: a) aluminium, b) chromium, c) nickel, d) platinum

The thickness of platinum modified aluminide coatings on CMSX 4 Ni-base superalloy is about 35  $\mu\text{m}$ . The microstructure consists of two zones (Fig. 3). The analysis of chemical composition on the cross-section showed the most platinum content is in the diffusion zone. The refractory elements such as Ta, Ti, W, Hf and Re form the  $\mu$  and  $\sigma$  phases in the diffusion zone. The surface of platinum modified aluminide coating (3  $\mu\text{m}$  platinum thick) consists of grains with average grain size about 35  $\mu\text{m}$ . Grains boundaries have higher content of platinum, aluminum and lower nickel in comparison to substrate (Table 3). This is due to the nickel atoms substitute for platinum.

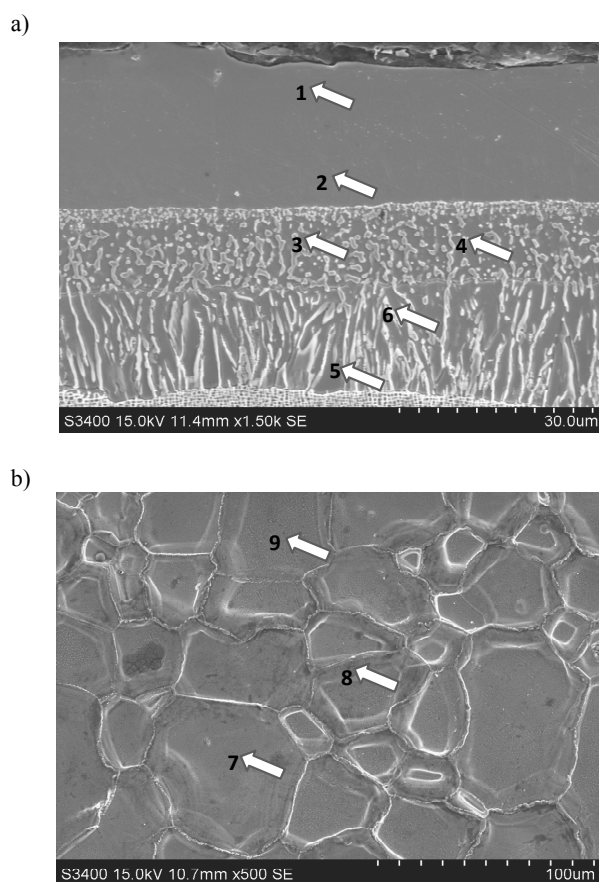


Fig. 3. Microstructure on cross-section (a) and surface (b) image of platinum heat treated coating (3  $\mu\text{m}$  thick) after low-activity CVD aluminizing process on CMSX 4 Ni-base superalloy

The main phase of platinum modified aluminide coating is (Ni,Pt)Al (Fig. 4). The  $\text{PtAl}_2$  phase did not form because aluminium activity was low and solubility of platinum in NiAl phase increased during aluminizing process. Aluminum content less than 50% at. in aluminide coating was obtained.

Table 3. Chemical composition on the cross-section and surface of coating (Figs. 3a-b)

Area	Elements content, % at						
	Al	Ni	Cr	Mo	W	Re	Pt
1	38.1	47.8	2.7	0.33	-	-	11.0
2	33.5	47.7	4.9	0.81	-	-	13.1
3	20.7	42.5	14.5	1.40	8.0	5.0	7.9
4	19.7	44.5	12.1	1.02	5.3	2.8	14.6
5	19.8	74.1	4.9	-	1.2	-	-
6	3.1	29.7	31.0	2.66	18	15.6	-
7	44.3	49.9	1.4	0.02	-	-	4.3
8	48.1	44.7	1.4	0.38	-	-	5.5
9	46.8	49.7	1.0	0.05	-	-	2.5

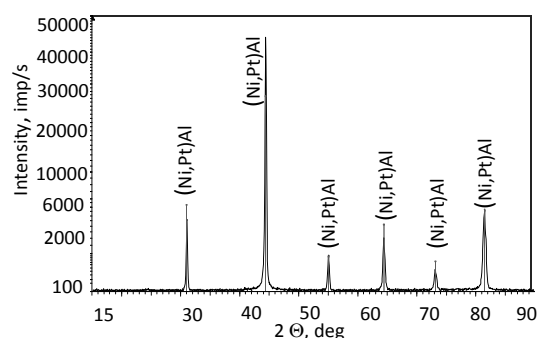


Fig. 4. X-ray diffraction results of platinum modified aluminide coating deposited by CVD method on Inconel 713 LC Ni-base superalloy

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

Super alloy	Platinum thickness, $\mu\text{m}$	Aluminide thickness, $\mu\text{m}$	Platinum content, % at	Aluminum content, % at
Inconel 713 LC	0	45.5	-	44.7
	3	52.7	2.4	40.09
	7	55.0	4	43.01
CMSX 4	0	28.8	-	50.8
	3	35.2	4.08	46.41
	7	39.2	6.83	42.3

The increase of platinum thickness from 3 to 7  $\mu\text{m}$  leads to the increase of aluminide coating thickness and platinum content on the surface of aluminide coating (Table 4). The platinum modified aluminide coatings thickness (3 and 7  $\mu\text{m}$  Pt thick) deposited on Inconel 713 LC is higher in comparison to CMSX 4

superalloy. The different thicknesses is due to the difference in chemical composition of superalloy such as: lower nickel and high Ta, Ti, W and Re contents in the chemical composition of Inconel 713 LC base in comparison to CMSX 4. The large content of refractory elements inhibits outward nickel diffusion and limits the coating formation [15].

The increase of surface roughness parameter value Ra with the increase of platinum electroplating thickness (Table 5) was found. The modification of aluminide coating causes the dissolution of platinum in NiAl phase. The (Ni,Pt)Al phase has different lattice parameter in comparison to NiAl phase. This phenomena influences on the increase of surface roughness parameter value.

Table 5.

Values of surface roughness parameter Ra of platinum modified aluminide coating

Superalloy	Surface roughness parameter Ra		
	Without platinum 0 $\mu\text{m}$	Platinum electroplating 3 $\mu\text{m}$	Platinum electroplating 7 $\mu\text{m}$
CMSX 4	2.7712	2.5512	2.9694
Standard deviation	0.048	0.179	0.154
Inconel 713 LC	2.552	3.3516	3.1906
Standard deviation	0.109	0.137	0.128

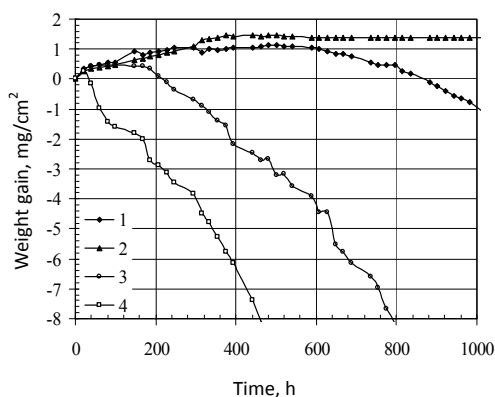


Fig. 5. The kinetics of oxidation test of aluminide coating deposited on Inconel 713 LC Ni-base superalloy at the 1100°C temperature for 1000h in air atmosphere: 1 - thickness of platinum electroplating 3  $\mu\text{m}$ ; 2 - thickness of platinum electroplating 7  $\mu\text{m}$ ; 3 - nonmodified aluminide coating; 4 - substrate

The platinum modification of aluminide coating (3 and 7  $\mu\text{m}$  platinum thick) provides to better oxidation resistance in comparison to nonmodified aluminide coating even to 1000 h in air atmosphere. Weight gain of platinum modified aluminide

coating (3  $\mu\text{m}$  platinum thick) from 600 h oxidation was found. The increase of oxidation time from 600 to 1000 h causes the decrease of coating weight (Fig. 5). The platinum modified aluminide coating (7  $\mu\text{m}$  platinum thick) characterizes a good oxidation resistance during 1000 h oxidation in air atmosphere.

The Pt modified aluminide coating (3 and 7  $\mu\text{m}$  thick) deposited on CMSX 4 Ni-base superalloy protects of substrate during 1000 h. The drop of nonmodified samples weight was observed after 200 h oxidation (Fig. 6).

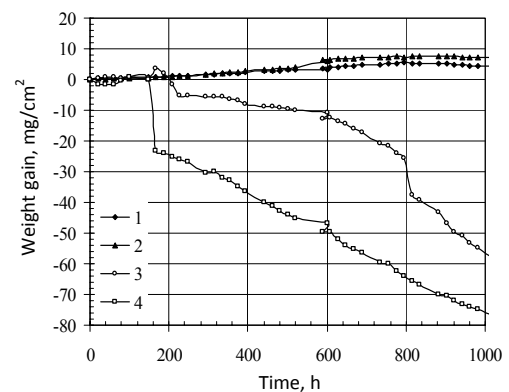


Fig. 6. The kinetics of oxidation test of aluminide coating deposited on CMSX 4 Ni-base superalloy at the 1100°C temperature for 1000h in air atmosphere: 1 - thickness of platinum electroplating 3  $\mu\text{m}$ ; 2 - thickness of platinum electroplating 7  $\mu\text{m}$ ; 3 - nonmodified aluminide coating; 4 - substrate

The NiAl phase in the microstructure of aluminide coating improves oxidation resistance of the substrate. Thermodynamically stable oxide  $\text{Al}_2\text{O}_3$  formed on the surface of aluminide coating during oxidation test. The NiAl phase transformed into  $\text{Ni}_3\text{Al}$  phase with low oxidation resistance. This is due to aluminum diffusion from coating to  $\text{Al}_2\text{O}_3$  oxide layer and material substrate. The  $\text{Ni}_3\text{Al}$  phase forms on the grains boundary of NiAl phase, Ni- $\text{Al}_2\text{O}_3$  boundary and NiAl-substrate. The oxidation process is along  $\text{Ni}_3\text{Al}$  phase. This causes the detachment of NiAl phase and internal substrate oxidation.

The higher oxidation resistance of platinum modified aluminide coating is due to accelerated formation of thermal stable  $\text{Al}_2\text{O}_3$  oxide on its surface. The rate of oxide scale formation depends from chemical composition of substrate. It was observed the decrease of oxide scale thickness with increase of platinum electroplating thickness (Table 6, Fig. 7).

The platinum also decreases the diffusion of alloying elements such as: Ti, Cr, Co, Mo from CMSX 4 substrate to the coating. The platinum stabilizes of NiAl phase in the microstructure coating and delays NiAl $\rightarrow$ Ni $_3$ Al phase transformation.

Table 6.  
Oxide scale thickness after 354 h oxidation at the 1100°C temperature in air atmosphere

Superalloy	Platinum electroplating thickness, $\mu\text{m}$	Oxide scale thickness, $\mu\text{m}$
Inconel 713 LC	0	17.6
	Pt 3	5.07
	Pt 7	3.35
CMSX 4	0	10.3
	Pt 3	3.24
	Pt 7	2.47

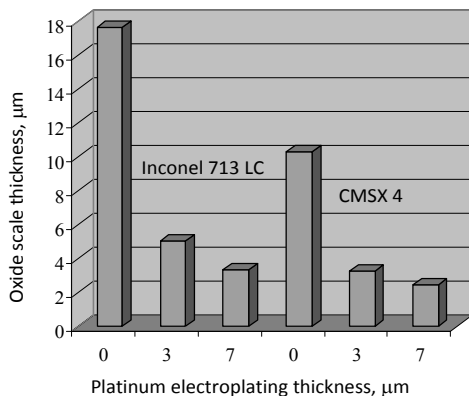


Fig. 7. The influence of platinum electroplating thickness on the oxide scale thickness forms after 354 h oxidation at the 1100°C temperature in air atmosphere

## 4. Conclusions

The microstructure of platinum modified aluminide coating deposited both on Inconel 713 LC and CMSX 4 Ni-base superalloy consists of two zones. An outer zone consisted of (Ni,Pt)Al phase. An internal (diffusion) zone of aluminide coating deposited on Inconel 713 LC Ni-base superalloy consists of  $\text{M}_{23}\text{C}_6$  carbides and  $\text{Cr}_x\text{Ni}_y\text{Mo}_z$  intermetallic phase. The brittle phases of  $\mu$  and  $\sigma$  was found in the diffusion zone of aluminide coating deposited on CMSX 4 Ni-base superalloy. It was found that platinum aluminide coating thickness depends on the chemical composition of superalloy. The increase of surface roughness parameter value of platinum aluminide coating is due to different lattice parameter of NiAl and (Ni,Pt)Al phases.

The thermodynamically stable  $\text{Al}_2\text{O}_3$  oxide layer was formed on the surface of aluminide coating during oxidation test in air atmosphere. The presence of aluminium oxide in the microstructure of aluminide coating decreases the oxygen diffusion and protects the substrate from further oxidation. The increase of platinum electroplating thickness from 3 to 7  $\mu\text{m}$  leads to the decrease of oxide scale thickness. The platinum inhibits

diffusion of substrate elements such as: Ti, Cr, Co, Mo and W from the CMSX 4 superalloy to the coating, increases of oxide scale adherence and delays NiAl $\rightarrow$ Ni<sub>3</sub>Al transformation.

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