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SOME PROPERTIES OF PLATINUM AND PALLADIUM MODIFIED ALUMINIDE COATINGS DEPOSITED BY CVD METHOD ON NICKEL-BASE SUPERALLOYS

WŁAŚCIWOŚCI WARSTW ALUMINIDKOWYCH MODYFIKOWANYCH PLATYNĄ I PALLADEM WYTWORZONYCH METODĄ CVD NA PODŁOŻU NADSTOPÓW NIKLU

In the paper some functional properties (hardness and oxidation resistance) of platinum and palladium modified aluminide coatings deposited by the CVD method on a nickel-based superalloy were determined. The platinum and palladium microlayers, 3 μm thick were deposited by electroplating process. The heat treatment of electroplating microlayers was performed for 2h at the temperature 1050°C in an argon atmosphere as to increase adhesion between the coating and the substrate. The low activity CVD aluminizing process of platinum heat treated coatings 3 μm thick at the 1050°C for 8h using IonBond equipment was performed. The effects of aluminizing process were verified by the use of an optical microscope (microstructure and coating thickness); a scanning electron microscope and an energy dispersive spectroscope (chemical composition of the surface and cross-section of the modified aluminide coating). The hardness measurements on the cross-section of nonmodified and platinum or palladium modified aluminide coatings were performed. Oxidation tests of modified aluminide coatings at the 1100°C for 1000 h in the air atmosphere were carried out. On the grounds of the obtained results it was found that the main phase of the platinum modified aluminide coating is β -(Ni,Pt)Al. Consequently, the palladium modification of aluminide coating causes the formation of β -(Ni,Pd)Al phase. The platinum modified aluminide coating has better oxidation resistance than nonmodified and palladium modified aluminide coating. The XRD analysis of the surface of oxidized platinum modified aluminide coating confirmed the presence of the thermodynamically stable oxide layer Al_2O_3 , that has good protective properties. The oxides of NiAl_2O_4 , $\text{Al}_{1.98}\text{Cr}_{0.02}\text{O}_3$ and TiO_2 were found on the surface of the palladium modified aluminide coating after 1000 h oxidation at the 1100°C the in the air atmosphere.

Keywords: platinum and palladium modified aluminide coating, low-activity CVD process, Ni-base superalloy, oxidation resistance

W pracy określono niektóre właściwości użytkowe (twardość oraz żaroodporność) warstwy aluminidkowej modyfikowanej platyną i palladem wytworzonej metodą CVD na podłożu nadstopów niklu, polikrystalicznym Inconel 713 LC i monokrystalicznym – CMSX 4. Powłokę platyny i palladu (grubość – 3 μm) wytworzono metodą galwaniczną. Poprawę przyczepności powłoki galwanicznej do podłoża uzyskano przez wygrzewanie w temperaturze 1050°C w czasie 2 h w atmosferze argonu. Warstwę aluminidkową wytworzono w procesie niskoaktywnym CVD (temperatura – 1050°C, czas – 8h). Efekty procesu aluminowania weryfikowano w badaniach mikroskopowych (mikrostruktura i głębokość warstwy) oraz w analizie składu chemicznego na powierzchni i przekroju warstwy modyfikowanej. Pomiary twardości prowadzono na przekroju niemodyfikowanej warstwy aluminidkowej oraz warstwie modyfikowanej platyną i palladem. Próbę zmęczenia cieplnego wykonano w temperaturze 1100°C i w czasie 1000 h w atmosferze powietrza. Analiza uzyskanych wyników badań pozwala stwierdzić, że głównym składnikiem fazowym mikrostruktury modyfikowanej platyną warstwy aluminidkowej są kryształy fazy β -(Ni,Pt)Al. Modyfikowanie palladem warstwy aluminidkowej prowadzi do tworzenia się kryształów fazy β -(Ni,Pd)Al jako głównego składnika fazowego mikrostruktury warstwy. Warstwę aluminidkową modyfikowaną platyną charakteryzuje większa żaroodporność w porównaniu do warstwy aluminidkowej modyfikowanej palladem lub niemodyfikowanej. Analiza składu fazowego na powierzchni warstwy aluminidkowej modyfikowanej platyną po próbie zmęczenia cieplnego wykazała obecność zgorzeliny składającej się z termodynamicznie stabilnego tlenku Al_2O_3 . Tlenek NiAl_2O_4 , $\text{Al}_{1.98}\text{Cr}_{0.02}\text{O}_3$ oraz rutil TiO_2 zaobserwowano na powierzchni warstwy aluminidkowej modyfikowanej palladem po 1000 h utleniania w temperaturze 1100°C w atmosferze powietrza.

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1. Introduction

Aluminide coatings are widely used for high temperature oxidation and hot corrosion protection of turbine blades used in the engine hot section. There are different types of coatings depending on the working environment of turbine blades. In the aircraft turbine industry the aluminum based diffusion coatings are generally used [1-9]. High temperature coatings based on the β -NiAl intermetallic phase are extensively used to protect components against oxidation in gas turbine engines. Aluminum in the coating combines with oxygen at the substrate surface and forms a protective Al_2O_3 scale. Platinum improves stability of the coating microstructure by eliminating chromium-rich precipitation from the outer coating layer and prevents the diffusion of refractory elements, such as molybdenum, vanadium and tungsten, into the outer layer.

Moreover, platinum leads to formation of the PtAl_2 phase in the coating microstructure [10-12]. The low ductility of PtAl_2 and large difference of thermal expansion coefficients between the substrate and platinum causes the coating degradation under the cyclic thermal stress. Alperine et al. [13-14] showed that the palladium modified aluminide coating has higher oxidation and hot corrosion resistance than the conventional aluminide coating. Lehnert et al. [12] showed that palladium modified aluminide coating is a low protector due to the formation of pores by the Kirkendall effect. Monceau et al. [15] investigated the influence of oxygen partial pressure, heating rate and surface treatment on the high temperature oxidation kinetics of Pd-modified aluminide coating, used as a bond coat for partially stabilized zirconium (PSZ) thermal barrier coatings (TBC).

The aim of this paper is to determine some properties (hardness and oxidation resistance) of platinum and palladium modified aluminide coatings deposited on Inconel 713 LC and CMSX 4 Ni-base superalloys.

2. Experimental procedure

The Inconel 713 LC and CMSX 4 superalloys of chemical composition presented in Table 1 were used in this study.

The platinum and palladium microlayers with thickness of $3 \mu\text{m}$ were deposited by the electroplating process.

The material surface preparation for platinum electroplating process includes four basic operation: surface degreasing, surface etching, rinsing in cold water and surface activation. The platinum electroplating was performed for 1h by means of tetraamineplatinum (II) composite bath $-\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ 15 g/dm^3 , which enables the rapid growth of an adherent and relatively homogeneous coating. The current density during the platinum electroplating process was about 10 A/dm^2 . Titanium was used as an anode for electroplating. The appropriate electroplating was done for the current density of 0.1 A/dm^2 .

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 $-\text{NaOH}$ 60 g/dm^3 and sodium carbonate $-\text{Na}_2\text{CO}_3$ 30g/dm^3 . The degreasing was carried out at 60°C . The electrolytic etching was performed in the bath, which consists of: sulfuric acid H_2SO_4 -100 g/cm^3 and sodium chloride NaCl -20g/cm^3 at the room temperature. Surface activation was carried out in the bath that consists of: nickel chloride Ni_2Cl -20 g/cm^3 and hydrochloric acid HCl -120 g/cm^3 at the room temperature. The palladium electroplating process was conducted in the bath of palladium chloride PdCl_2 -10 g/cm^3 , sulfamates acid H_2NSO_3 -100 g/cm^3 , hydrochloric acid HCl -20 g/cm^3 and ammonium chloride NH_4Cl -50 g/cm^3 at 35°C .

Platinum and palladium electroplating microlayers were heat treated at the temperature 1050°C for 2 h under the argon atmosphere.

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

The aluminide coatings were obtained in the low-activity CVD process by means of the BPX-PRO3252 equipment of IonBond company in R&D Laboratory for Aerospace Materials. The gas atmosphere ($\text{AlCl}_3 + \text{H}_2$) 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 process parameters. The chemical vapor deposition process was carried out on cylindrical samples. The low-activity CVD process was performed at the temperature 1050°C for 8h. In order to obtain thermodynamically stable conditions the CVD process consisted of several heating stages. The hardness measurements on the cross-section of modified aluminide coating were performed by the Berkovich indenter under 0.02 N load. The oxidation tests of aluminide coating were performed at the temperature 1100°C for 1000h in the air atmosphere. Microstructure investigations of the modified aluminide coating were performed by the use of the light microscope Nikon 300 and the scanning electron microscope (SEM) HITACHI S-3400N equipped with the EDS spectrometer. Samples were etched by the use of reagent with chemical composition as follows: $100\text{ cm}^3\text{ HNO}_3$, $7\text{ cm}^3\text{ HF}$ and $11\text{ cm}^3\text{ H}_2\text{O}$. Evaluation of phase composition of the investigated coatings was made using ARL X'TRA X-ray diffractometer, equipped with filtered copper lamp of the voltage of 45 kV and heater current of 40 mA.

3. Results and discussion

Aluminizing of a heat treated platinum electroplating coating at the temperature 1050°C for 8 h results in

obtaining to obtain a $52.7\ \mu\text{m}$ thick diffusion coating on the Inconel 713 LC Ni-base superalloy. The microstructure of platinum modified aluminide coating ($3\ \mu\text{m}$ Pt layer before CVD) consisted of two zones: an outer and internal (diffusion) one (Fig. 1a). The XRD phase analysis showed that the main phase in the outer zone is (Ni,Pt)Al phase. The M_{23}C_6 chromium carbides besides (Ni,Pt)Al phase were found in the internal (diffusion) zone. The chemical composition on the cross-section showed the outward chromium, molybdenum and nickel diffusion from the substrate to the surface and the inward aluminum and platinum diffusion from the surface to the substrate (Fig. 1b). The thickness of the palladium modified aluminide coating on Inconel 713 LC Ni-base superalloy is about $49.4\ \mu\text{m}$ (Fig. 2a). The outward diffusion of the substrate elements and the inward diffusion of the palladium and aluminum was found (Fig. 2b). The XRD phase analysis showed, that (Ni,Pd)Al phase is the main phase in the coating. The M_{23}C_6 chromium carbides in the diffusion zone of platinum and palladium modified aluminide coatings were found. The thickness of platinum modified aluminide coating ($3\ \mu\text{m}$ Pt layer before CVD) on the CMSX 4 Ni-base superalloy is about $35.2\ \mu\text{m}$ (Fig. 3a). It is about $17.5\ \mu\text{m}$ thinner than the same coatings on Inconel 713 LC Ni-base superalloy. The thickness of palladium modified aluminide coating ($3\ \mu\text{m}$ Pd layer before CVD) is about $36.7\ \mu\text{m}$ and it is close to the thickness of platinum modified aluminide (Fig. 4a). The thickness of the modified aluminide coating depends on the chemical composition of the investigated superalloy and the type of the added element (platinum or palladium) [16]. CMSX 4 superalloy has higher total content of chromium, molybdenum, tungsten, titanium, tantalum and rhenium which segregate in

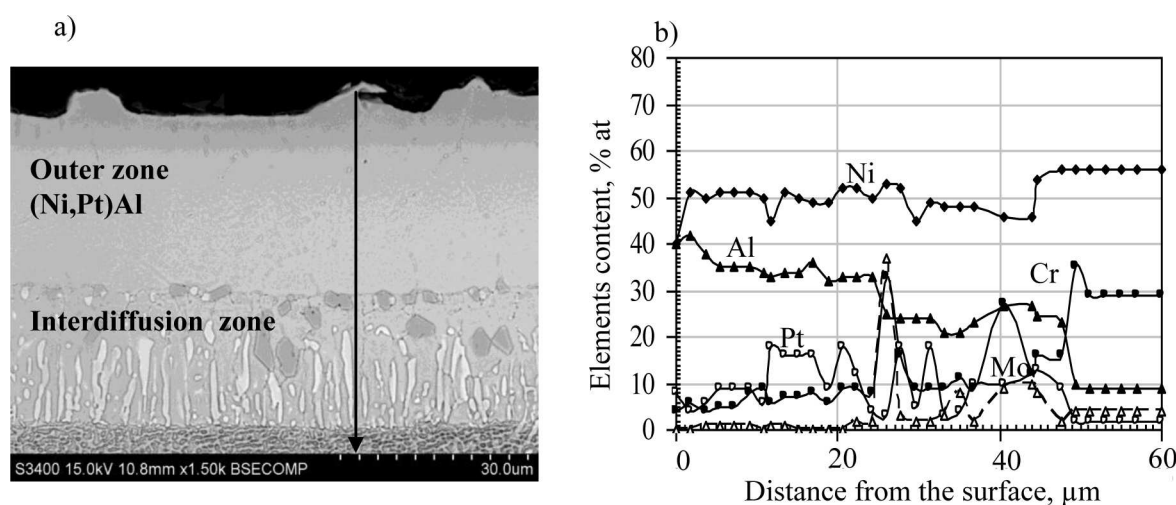


Fig. 1. Microstructure (a) and chemical composition on the cross-section (b) of platinum modified aluminide coating ($3\ \mu\text{m}$ Pt layer before CVD) on Inconel 713 LC Ni-base superalloy after the low-activity CVD aluminizing process

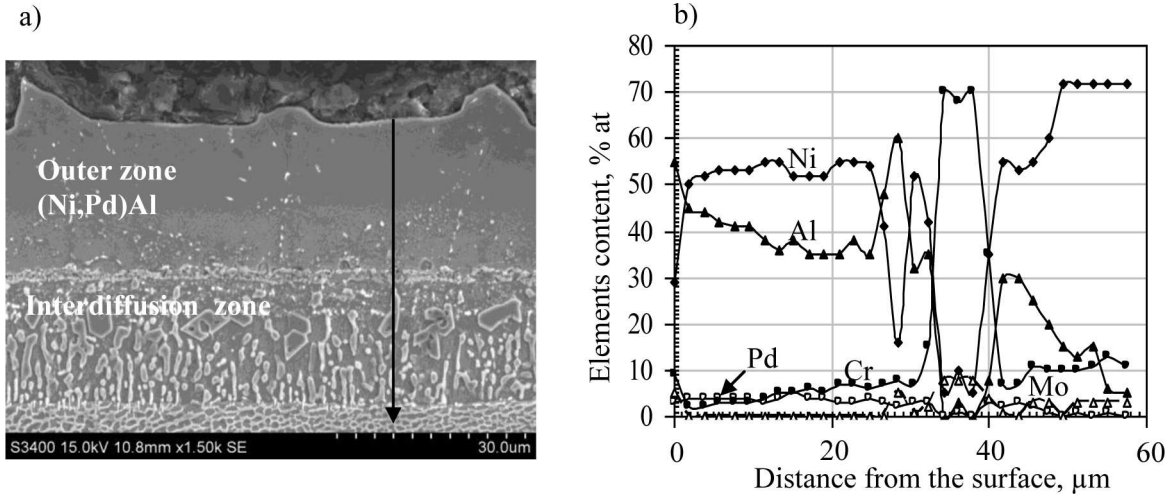


Fig. 2. Microstructure (a) and chemical composition on the cross-section (b) of palladium modified aluminide coating (3 μm Pd layer before CVD) on Inconel 713 LC Ni-base superalloy after the low-activity CVD aluminizing process

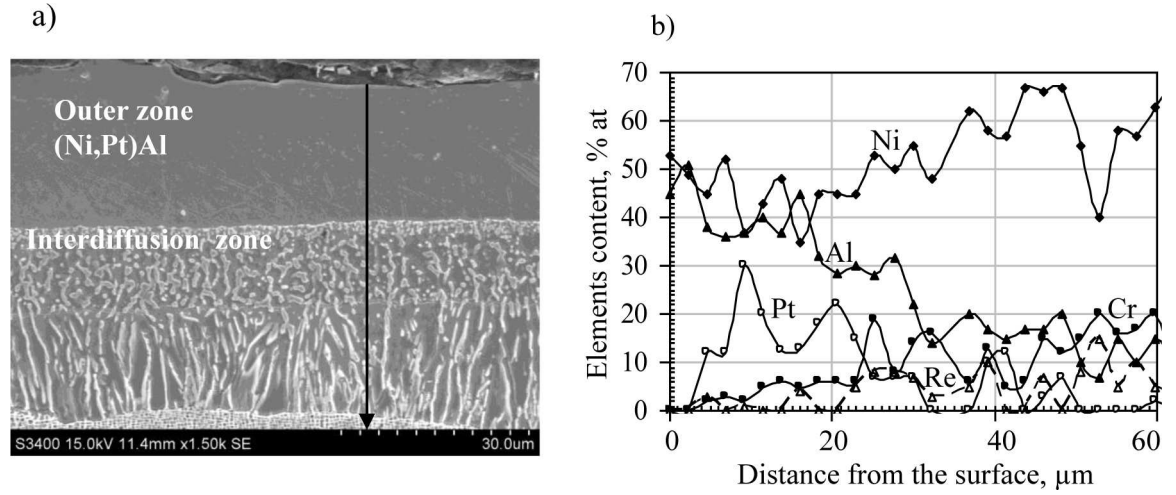


Fig. 3. Microstructure (a) and chemical composition on the cross-section (b) of platinum modified aluminide coating (3 μm Pt layer before CVD) on CMSX 4 Ni-base superalloy after the low-activity CVD aluminizing process

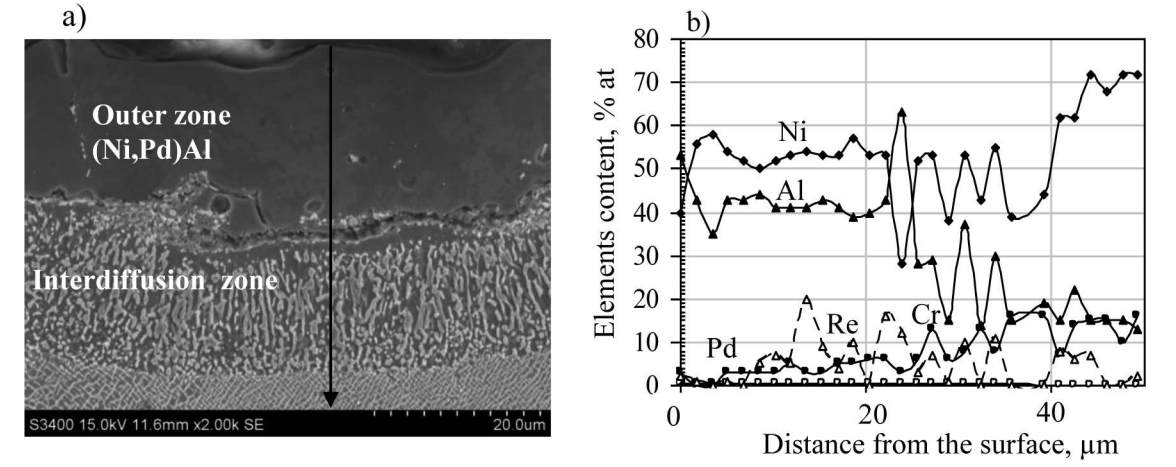


Fig. 4. Microstructure (a) and chemical composition on the cross-section (b) of palladium modified aluminide coating (3 μm Pd layer before CVD) on CMSX 4 Ni-base superalloy after the low-activity CVD aluminizing process

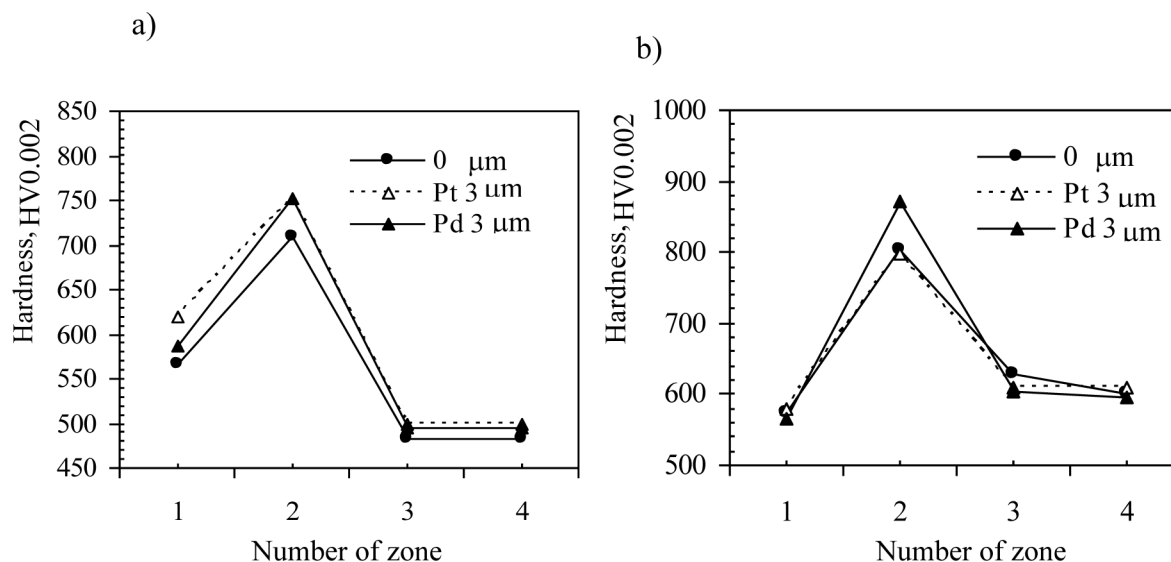


Fig. 5. Hardness measurements of the cross-section of aluminide coating without and after platinum and palladium modification (3 μm layer before CVD) on the Inconel 713 LC (a) and CMSX 4 (b) Ni-base superalloys. 1 – outer zone, 2 – diffusion zone, 3,4 – substrate

the diffusion zone than Inconel 713 LC superalloy. These elements diffuse to the diffusion zone of the aluminide coating. It results in a smaller thickness of the aluminide coating formed on CMSX 4 than formed on Inconel 713 LC. The examination of the chemical composition on the cross-section of platinum and palladium revealed that coating are formed by means of the outward diffusion of substrate elements (Fig. 3-4b).

Hardness measurements were carried out on the cross-section of aluminide coating. The hardness on the cross-section of outer layer is about 567HV0.002. The platinum modification of aluminide coating increases of the outer layer hardness to about 587-619 HV0.002. The hardness of the diffusion zone of platinum and palladium aluminide coating deposited on Inconel 713 LC is about 750 HV0.002 (Fig. 5a). The similar dependences of hardness of diffusion zone of aluminide coating was found on the CMSX 4 Ni-base superalloy (Fig. 5b). The increase of diffusion zone hardness is due to the presence of chromium carbides $M_{23}C_6$ (superalloy – Inconel 713 LC) and intermetallic phases σ and μ (superalloy – CMSX 4).

The oxidation test was performed on the samples with and without platinum and palladium modification at the temperature 1100°C for 1000 h. Fifty cycles of heating and cooling were carried out. The samples mass measurements with and without platinum and palladium modification were done. The platinum modification (3 μm Pt layer before CVD) improves oxidation resistance of aluminide coating deposited on both Inconel 713 LC and CMSX 4 Ni-base substrate (Fig. 6 a-b). Improvement of the oxidation resistance of aluminide coating after palladium modification was found on the

CMSX 4 Ni-base superalloy. Palladium modified (3 μm Pd layer before CVD) aluminide coating deposited on Inconel 713 LC substrate has the same oxidation resistance as nonmodified aluminide coating (Fig. 6 a). There are several hypothesis of palladium influence on oxidation resistance of aluminide coating [17-18]. The palladium easy absorbs hydrogen during electroplating process and than heat treatment and aluminizing process leads to the dissolution of hydrogen and blisters formation in the coating. The blisters decrease oxidation resistance of aluminide coating. Some authors [14] showed, that mass loss of palladium modified aluminide coating is also due to the Kirkendall Effect. Mrowec [19] showed, that palladium at the temperature above 800°C does not form oxides and mass change is due to the oxygen absorption through the intermetallic phase.

Only Al_2O_3 oxides and Ni_3Al intermetallic phases were found after the oxidation test of platinum modified aluminide coating (Fig. 7). Corrosion products such as: $NiAl_2O_4$, $Al_{1.98}Cr_{0.02}O_3$, Ni_3Al , TiO_2 were found after the oxidation test on the surface of palladium modified aluminide coating (Fig. 8). The higher oxidation resistance of platinum modified aluminide coating is due to the accelerated formation of the thermal stable Al_2O_3 oxide on the surface. Moreover platinum also inhibits outward diffusion of substrate elements to the oxide scale. Palladium does not inhibits outward diffusion of substrate elements (titanium or nickel) in substrate to the oxide scale and provides worse oxidation resistance in comparison to the platinum modified aluminide coating.

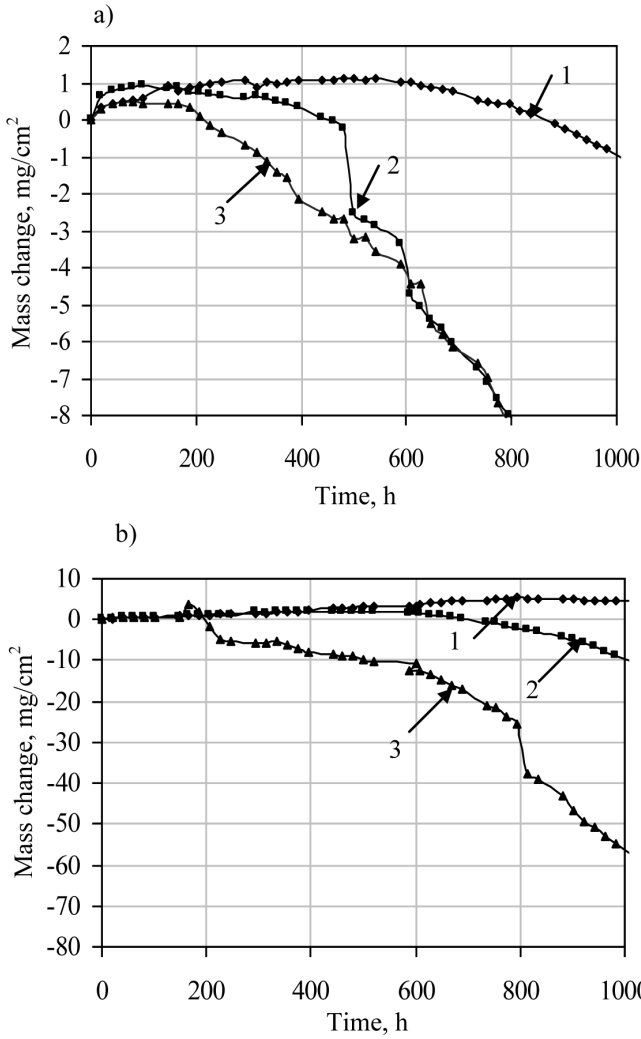


Fig. 6. Results of oxidation test of aluminide coating deposited on Inconel 713 LC (a) and CMSX 4 (b) Ni-base superalloys at the temperature of 1100°C for 1000h in the air atmosphere. 1 – thickness of platinum electroplating 3 μm, 2 – thickness of palladium electroplating 3 μm, 3 – nonmodified aluminide coating

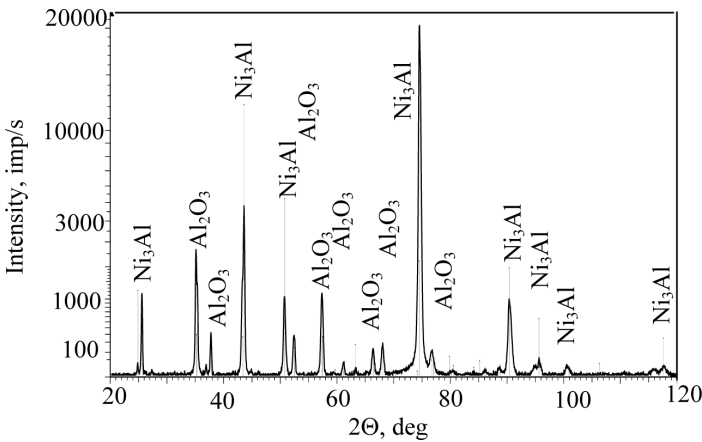


Fig. 7. X-ray diffraction results of platinum modified aluminide coating deposited by the CVD method on Inconel 713 LC Ni-base superalloy after oxidation test at the 1100°C temperature for 1000 h in the air atmosphere

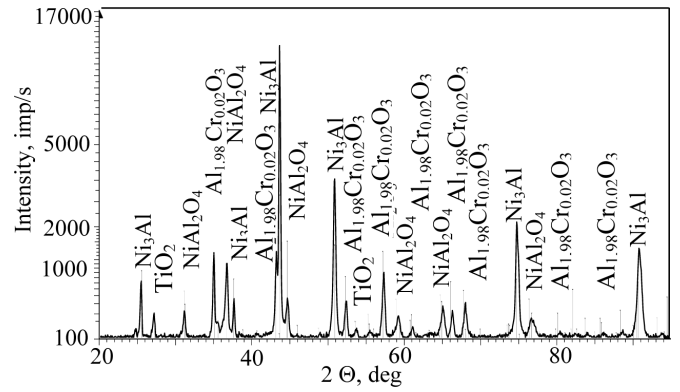


Fig. 8. X-ray diffraction results of palladium modified aluminide coating deposited by the CVD method on Inconel 713 LC Ni-base superalloy after oxidation test at the 1100°C temperature for 1000 h in the air atmosphere

4. Conclusions

1. The low-activity CVD process, which was carried out at the temperature 1050°C for 8h enabled to obtain two zones of aluminide coating. The main phase of platinum modified aluminide coating was (Ni,Pt)Al phase and (Ni,Pd)Al phase in palladium modified aluminide coating on both substrates: Inconel 713 LC and CMSX 4.

2. Platinum and palladium modified aluminide coating thickness depends on the chemical composition of the superalloy. Higher total content of elements such as: chromium, molybdenum, tungsten, titanium, tantalum and rhenium in CMSX 4 superalloy in comparison to their content in Inconel 713 LC results in the decrease of aluminide coating thickness. The chemical composition analysis of the cross section of aluminide coating confirmed the nickel, chromium and molybdenum outward diffusion from the substrate and the platinum, palladium and aluminum inward diffusion.

3. Modification of the aluminide coating by platinum and palladium increases the outer zone hardness. The same results was found by Oliver Franke et al. [20]. The large hardness of the diffusion zone of the modified aluminide coating is due to the presence of M₂₃C₆ carbides (Inconel 713 LC) and intermetallic phases σ and μ (CMSX 4).

4. Platinum modified aluminide coatings have better oxidation resistance than palladium modified ones. This phenomena is confirmed by Krishna et al. and Wang et al. [10,11]. The higher oxidation resistance of platinum modified aluminide coating is due to the accelerated formation of the thermal stable Al₂O₃ oxide on its surface. The oxidation resistance of palladium modified aluminide coating deposited on Inconel 713 LC substrate is the same as nonmodified aluminide one. The palla-

dium modified aluminide coating deposited on CMSX 4 has better oxidation resistance than nonmodified, but worse than platinum modified.

5. 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 palladium modified aluminide coating after the oxidation test. Palladium accelerates outward diffusion of substrate elements to the oxide scale and leads to the decrease of oxidation resistance of aluminide coating.

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