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## FUNCTIONAL PROPERTIES OF ALUMINIDE LAYER DEPOSITED ON INCONEL 713 LC Ni-BASED SUPERALLOY IN THE CVD PROCESS

### WŁAŚCIWOŚCI UŻYTKOWE WARSTWY ALUMINIDKOWEJ WYTWORZONEJ W PROCESIE CVD NA STOPIE NIKLU INCONEL 713 LC

In the paper there was established the influence of temperature and process time on the functional properties of aluminide layer deposited on nickel based – Inconel 713 LC superalloy. The low-activity CVD processes were done at the temperature 760 and 1050°C during 4 and 8h. The effects of aluminizing were verified by the use of optical microscope (microstructure and depth layer); scanning electron microscope and energy dispersive spectroscopy (chemical composition on the surface and cross-section of aluminide layer). The high temperature oxidation resistance of superalloy was a main criterion of aluminizing process effectiveness. Therefore, the isothermal oxidation tests were performed at the temperature 1150°C during 100h in air atmosphere. Surface topography of the aluminide layer was carried out after isothermal oxidation test. Hardness measurements on the cross-section of aluminide layer were performed before and after oxidation tests.

On the grounds of obtained results it was found that aluminizing process temperature of 1050°C let to get a diffusion layer with a proper structure and properties. The temperature increase from 760°C to 1050°C and the time prolongation from 4 to 8 h improves the oxidation resistance of superalloy. The XRD analysis from the surface of aluminide layer has confirmed the presence of thermodynamically stable oxide layer  $\text{Al}(\text{Cr})_2\text{O}_3$  with good protective properties.

*Keywords:* aluminide layer, low-activity CVD process, Inconel 713LC superalloy, oxidation resistance

W pracy określono wpływ parametrów procesu CVD (temperatura, czas) na właściwości użytkowe warstwy aluminidkowej wytworzonej na podłożu z stopu niklu Inconel 713 LC. Proces niskoaktywny prowadzono w temperaturze 760 i 1050°C oraz w czasie 4 i 8h. Efekty procesu aluminiowania weryfikowano w badaniach mikroskopowych (mikrostruktura i głębokość warstwy) oraz w badaniach składu chemicznego na powierzchni i przekroju warstwy. Jako kryterium efektywności procesu chemicznego osadzania z fazy gazowej przyjęto odporność na utlenianie w wysokiej temperaturze. Wykonano próbę utleniania izotermicznego w temperaturze 1150°C i w czasie 100h w atmosferze powietrza. Prowadzono badania topografii powierzchni warstwy aluminidkowej po procesie utleniania izotermicznego. Określono rozkład twardości na przekroju warstwy przed i po procesie utleniania. Na podstawie uzyskanych wyników badań stwierdzono, że temperatura procesu 1050°C pozwala uzyskać warstwę dyfuzyjną o prawidłowej budowie i właściwościach. Podwyższenie temperatury do 1050°C oraz zwiększenie czasu procesu aluminiowania do 8h powoduje znaczny wzrost żaroodporności. Analiza składu fazowego na powierzchni warstwy wykazała obecność zgorzeliny składającej się z termodynamicznie stabilnego tlenku  $\text{Al}(\text{Cr})_2\text{O}_3$  o dobrych właściwościach ochronnych.

## 1. Introduction

The heat and creep resistant Ni- and Co- base superalloys are used for turbine elements of aircraft engines [1-3]. These elements are exposed to severe mechanical loads, high temperature, as well as corrosion and erosion media [4]. The use of surface engineering methods enable to obtain protective layers on Ni and Co base superalloys. The aluminizing by CVD method let to obtain a diffusion coatings which are mostly based on in-

termetallic compound NiAl. The aluminide layers NiAl characterize good hot corrosion resistance, low thermal conductivity and good microstructure stability. A diffusion structure of aluminide layers results in good adhesiveness to a substrate and makes possible to produce coatings on the elements with complicated shape for example turbine blades. The aluminide layer obtained on nickel based superalloy in a low-activity CVD process consists of intermetallic phase crystallites (NiAl) [5-6]. During annealing of elements at a high temperatures

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(above 1000°C) in the air, a thermodynamically stable and highly protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer forms on the surface of aluminide layer. The aluminum oxide layer protects substrate before further oxidation. The investigations with the early stage of oxidation, which were performed on nickel based superalloys, have proved that the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> protective oxide layer depends on the temperature and annealing time [7]. At the beginning of the substrate oxidation and at temperatures lower than 1000°C, the transient oxide phases forms before the formation of stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. To such phases belong:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. The increase of temperature and annealing time prolongation causes the transformation of metastable phases into a stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [8].

### 2. Experimental procedure

The alloy used in this study is Inconel 713 LC. Chemical composition of the used melt is given in Table 1. The aluminide layers were obtained in the low-activity CVD process by means of the BPXPRO3252 equipment of IonBond company in R&D Laboratory for Aerospace Materials (Fig. 1). The gas atmosphere (AlCl<sub>3</sub> + H<sub>2</sub>) was prepared in an external generator and transported into the retort with elements. The CVD device is equipped with the control and dosing gas system, which allows to control the process parameters.

TABLE 1

Chemical composition of investigated

Elements content, % mass					
Al	Nb	Cr	Mo	Ti	Ni
6,0	2,0	12,0	4,5	0,6	osnowa

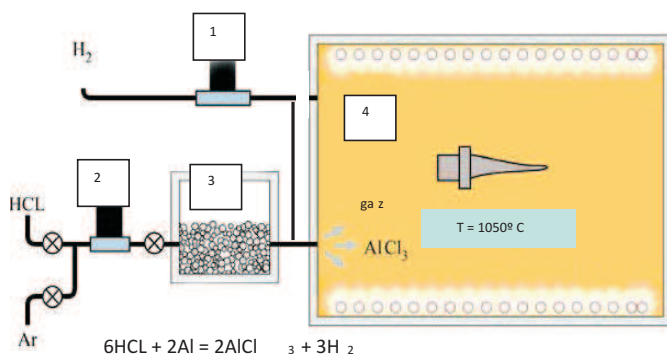


Fig. 1. A scheme of the low-activity CVD process: 1; 2 – mass flow controllers ; 3 – external generator with Al – 99, 999 % ; 4 – retort

The chemical vapor deposition process was carried out on cylindrical samples. The samples of cylindrical shape with 14 mm diameter and 4 mm height were used. The samples were polished by means of SiC paper (up to

600), sandblasted and ultrasonically cleaned in an iso-propyl alcohol. The low-activity CVD processes were done at the temperature 760 and 1050°C during 4 and 8h. In order to obtain a thermodynamically stable conditions the CVD process consisted of several heating stages. The changes of temperature and heating time inside retort during the CVD process is presented on Figure 2.

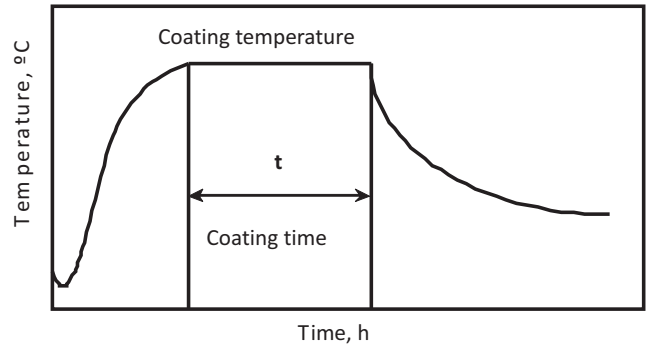


Fig. 2. A scheme of the CVD process

The isothermal oxidation tests of aluminide layer were performed at the temperature 1050°C during 100h in the air atmosphere. The effectiveness of the CVD aluminizing process was evaluated in microstructure and chemical composition investigations and by hardness measurements. Microstructure investigations of aluminide layer were performed by the use of light microscope Nikon 300 and scanning electron microscope (SEM) HITACHI S-3400N equipped with EDS spectrometer [9]. The samples were etched in Marble’s a reagent. The chemical composition of etchant was as follow: 10g CuSO<sub>4</sub> + 50 cm<sup>3</sup> HCl + 50 cm<sup>3</sup> H<sub>2</sub>O. The hardness measurements of the aluminide layer were performed by the Vickers method under 0,5 N load. The topological surface investigations were made by the use of 3D scanner of Hommelwerke company equipped with measurement T8000 system. The basic parameters of the surface layer roughness were determined.

### 3. Results and discussion

The microstructure of aluminide layer obtained at the temperature 760°C during 4 h was not a proper one. The use of a higher temperature of aluminizing (1050°C) and prolongation of process time from 4 to 8 h enabled to obtain an aluminide layer with 50 μm thickness and proper structure (Fig. 3). The structure of aluminide layer consisted of the two zones: an external and internal (diffusion) one. An external zone was enriched with the Ni and Al elements: 55, 06% at and 44,94% respectively (Table 1). An internal (diffusion) zone consisted of the Cr, Mo enriched precipitations with high melting temper-

ature. The thickness of an external zone is approximately 28  $\mu\text{m}$  and internal one is 22  $\mu\text{m}$ .

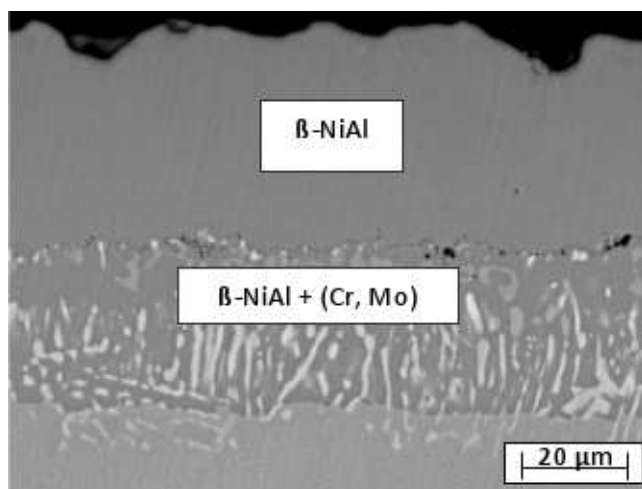


Fig. 3. The microstructure of aluminide layer deposited in the low-activity CVD process at the temperature 1050°C during 4h on Inconel 713 LC Ni-base superalloy

The chemical composition analysis of the cross section of aluminide layer has confirmed the nickel outward diffusion from the material substrate (Fig. 4). The decrease of nickel and aluminum content from the surface to the material substrate is typical for the low-activity aluminizing process.

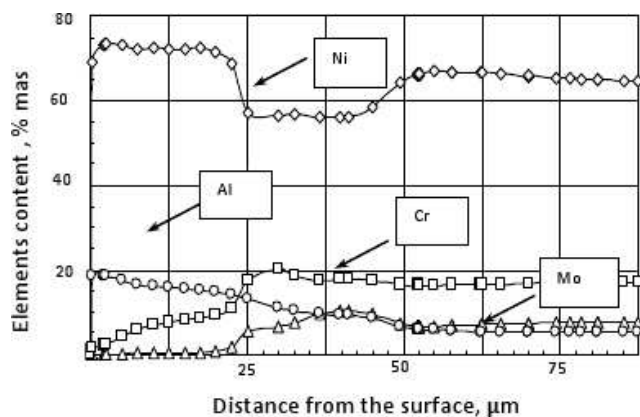


Fig. 4. Distribution of elements content on the cross-sections of aluminide layer

TABLE 2  
The chemical composition on the surface aluminide layer deposited on the Inconel 713 LC Ni-base superalloy

Elements content, % at			
Al	Cr	Mo	Ni
46,12	1,02	6,61	46,25

The analysis of the surface composition of aluminide layer deposited at the temperature 1050°C have confirmed the presence of NiAl intermetallic phase (Table 2)

[10]. The proportion of aluminum and nickel atoms is approximately 1:1. The surface layer of the aluminide coatings consists of NiAl grains with average diameter of 25  $\mu\text{m}$  (Fig. 5).

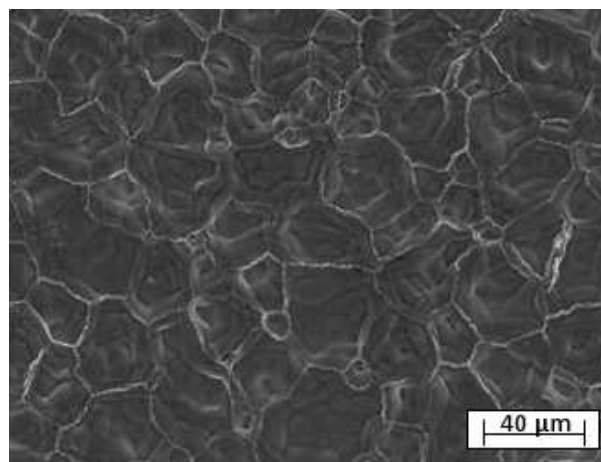


Fig. 5. The microstructure of the surface aluminide layer deposited in the CVD process at the temperature 1050°C during 8h on the Inconel 713 LC Ni-base superalloy

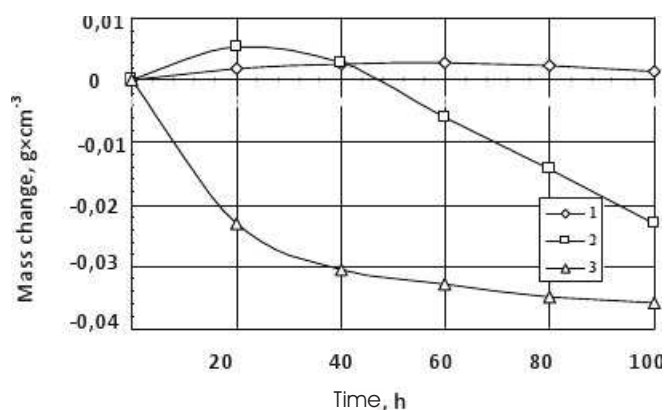


Fig. 6. The kinetics of isothermal oxidation of aluminide surface layer deposited on the Inconel 713 LC substrate at the temperature 1150°C during 100h : 1 – low-activity CVD process carried out at the temperature 1050°C during 8h; 2 – low-activity CVD process carried out at the temperature 760°C during 4h; 3 – without of aluminide layer

The isothermal oxidation tests were performed on the samples with and without aluminide layer at the temperature 1150°C during 100 h. Five cycles of heating and cooling were carried out. The samples mass measurements with and without aluminide layer were done. The loss of weight was observed for the samples without aluminide layer, for example after oxidation time 100 h the mass loss of the samples was  $0.035 \text{ g} \times \text{cm}^{-3}$  (Fig. 6). This is due to the spalling of oxide layer from the substrate. The aluminide layer deposited at the temperature 760°C / 4 h has a protective properties but only during 40h annealing. After that time the oxidations kinetic of aluminide layer is similar to the substrate one. The increase of the aluminizing temperature from the 760°C to

the 1150°C and process time prolongation from 4 to 8 h improves oxidation resistance of Inconel 713C (Fig. 6).

Analysis of chemical composition on the cross-sections of aluminide layer after isothermal oxidation test at the temperature 1150°C during 100 h showed, that thickness of external zone decreased. The aluminum content in the external zone is 21,51% at (Table 3). The thickness decrease of external zone is a result of aluminum outward diffusion from the oxide layer and substrate. In the internal (diffusion) zone there were observed M<sub>6</sub>C type carbides (area 2, Fig. 7). Intermetallics phases, enriched with chromium, nickel and molybdenum were observed in the diffusion zone (area 3, Fig. 7). The chemical composition analysis of aluminide layer after isothermal oxidation test showed, that aluminum content increased (Fig. 8, Table 4). Corrosion products such as: Al(Cr)<sub>2</sub>O<sub>3</sub>; Al<sub>2</sub>O<sub>4</sub>; TiO were found after isothermal oxidation test on the surface of aluminide layer [11].

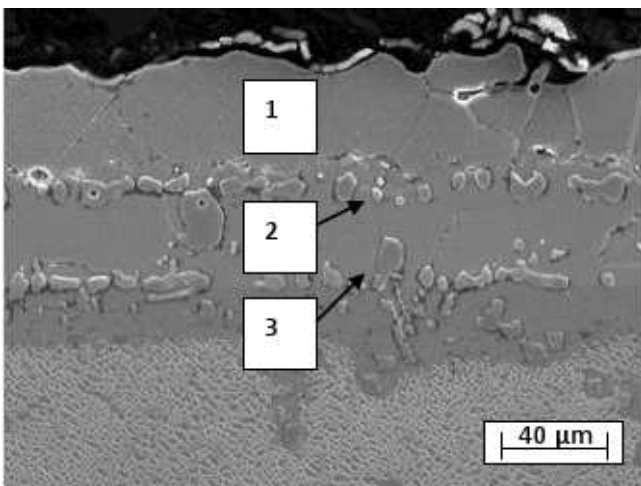


Fig. 7. The microstructure of the aluminide layer after isothermal oxidations tests carried out at the temperature 1150°C during 100h 1: – the phase crystallites of NiAl; 2 – carbides of M<sub>6</sub>C; 3 – the intermetallics phases enriched in chromium, nickel and molybdenum

TABLE 3  
Chemical composition on the cross-section of aluminide layer (Fig. 7)

Area	Elements content, % at				
	Al	Ti	Cr	Ni	Mo
1	21,51	0,8	5,33	72,25	–
2	–	–	78,70	8,26	13,04
3	7,48	0,71	20,55	37,18	34,08

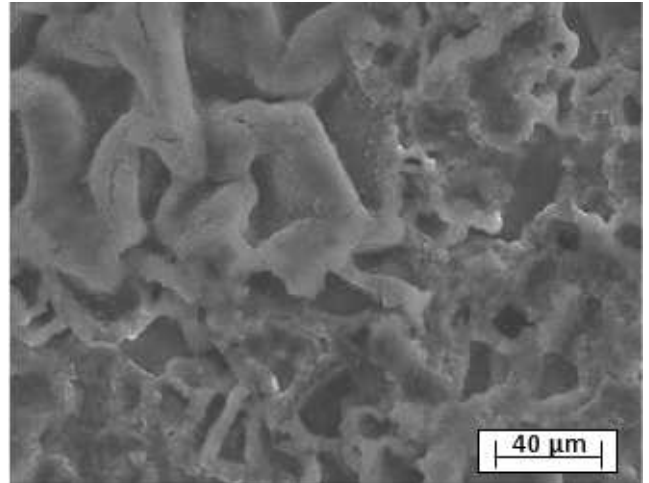


Fig. 8. The microstructure of surface aluminide layer deposited in the low-activity CVD process (1050°C/8h) on Inconel 713 LC superalloy after isothermal oxidation test, which was carried out at the temperature 1150°C during 100 h

TABLE 4  
Chemical composition of the surface of aluminide layer after isothermal oxidation test which was carried out at the temperature 1150°C during 100 h

Elements content, % at		
Al	Cr	Ni
84,03	1,57	14,40

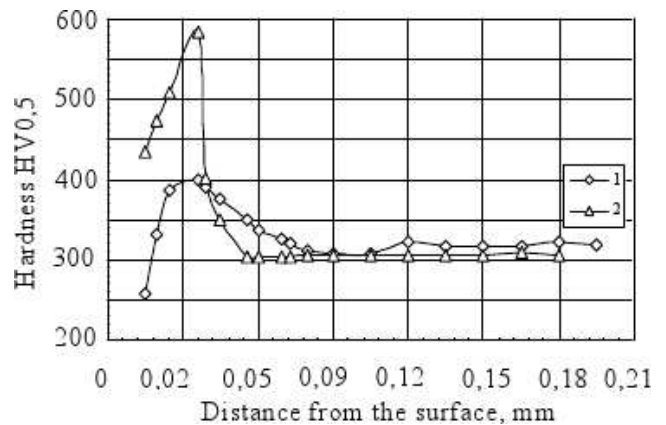


Fig. 9. Hardness distribution on the cross-section of aluminide layer deposited on the Inconel 713 LC Ni-base superalloy: 1 – after isothermal oxidation test, which was carried out at the temperature 1150°C during 100h; 2 – after low-activity CVD process, which was carried out at the temperature 1050°C during 8h

The largest hardness value 600 HV of aluminide layer was obtained at the distance about 30 µm from the surface. The hardness increase is due to the presence in this area of chromium and molybdenum hard inclusions. The hardness decrease of samples with aluminide layer was observed after isothermal oxidation test at the temperature 1150°C during 100 h. This is due to the

dissolutions of chromium and molybdenum carbides in the diffusion zone. After oxidation test there was observed the increase of substrate hardness (Fig. 9). The hardness increase is due to the growth and spheroidizing of  $\gamma'$  phase, dissolution of primary carbides and precipitated of secondary carbides in grain boundaries of  $\gamma$  phase [12].

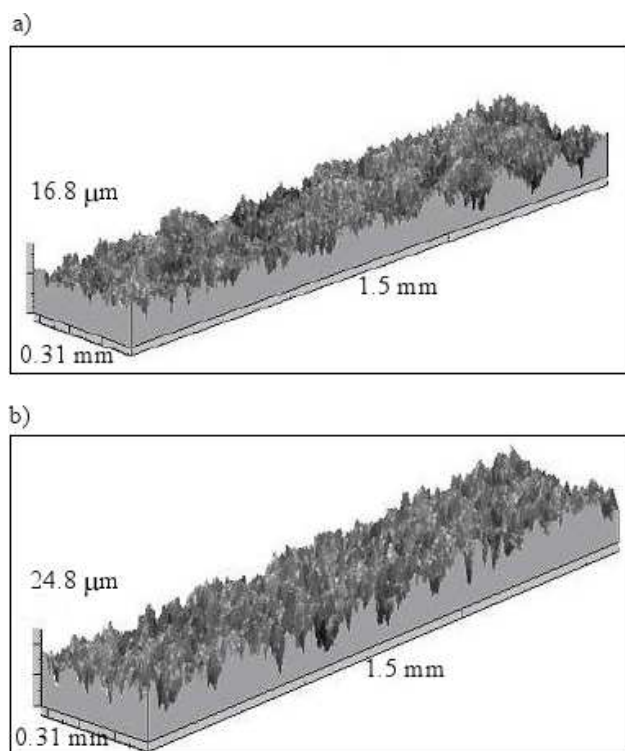


Fig. 10. The surface topography of Inconel 713 LC superalloy after isothermal oxidation test: 1 – after low-activity CVD process, which was carried out at the temperature 1050°C during 8h; 2 – without of aluminide layer

Main parameters of roughness were determined in the topography surface investigations (Fig. 10 a,b). The average arithmetic deviation of surface roughness is 1,52  $\mu\text{m}$  and 2,53  $\mu\text{m}$  for the samples with and without aluminide layer, respectively. The greater roughness value of samples without the coating is due to the lower corrosion resistance [13]. The surface cavities are the source of corrosion nucleation. The cavities presence increases the corrosion rate of samples in air atmosphere.

#### 4. Conclusions

The low-activity CVD process, which was carried out at the temperature 1050°C during 8h enabled to obtain diffusion aluminide layer. The thickness of aluminide layer deposited in the low-activity CVD process at the 1050°C during 8h on Inconel 713 LC superalloy is about 50  $\mu\text{m}$ . The oxidation resistance depends on the the aluminum content in the surface layer of ele-

ments. The NiAl intermetallic phase was observed in the microstructure of aluminide layer after low-activity CVD process, which carried out at the 1050°C during 8h. The aluminum and nickel content in the NiAl phase is 46,12% at and 46,25% at, respectively. The thermodynamically stable  $\text{Al}(\text{Cr})_2\text{O}_3$  oxide layer was formed on the surface of aluminide layer during isothermal oxidation test in air atmosphere. The presence of aluminum oxide layer in the microstructure of aluminide layer decreases the oxygen diffusion and protects the substrate from further oxidation. The microstructure changes after isothermal oxidation test decreases hardness value of aluminide layer.

The value of mean arithmetic deviation roughness for samples with aluminide layer is 1,52  $\mu\text{m}$ , however for samples without aluminide layer is 2,53  $\mu\text{m}$ . The lower value of roughness for the samples with aluminide layer increases oxidation resistance of Inconel 713 LC Ni-base superalloy.

#### REFERENCES

- [1] J. Sieniawski, Kryteria i sposoby oceny materiałów na elementy lotniczych silników turbinowych. Oficyna Wydawnicza Politechniki Rzeszowskiej. Rzeszów 1995.
- [2] J. Sieniawski, Nickel and titanium alloys in aircraft turbine engines. *Advances in Manufacturing Science and Technology* **273**, 23-34 (2003).
- [3] A. Onyszko, K. Kubiak, Method for production of single crystal superalloys turbine blades. *Archives of Metallurgy and Materials* **54**, 765-771 (2009).
- [4] J.L. Gonzalez-Carrasco, P. Pérez, P. Adeva, J. Chao, Oxidation behaviour of an ODS NiAl-based intermetallic alloy. *Intermetallics* **7**, 69-78 (2000).
- [5] C.J. Wang, S.M. Chen, Microstructure and cyclic oxidation behavior of hot dip aluminized coating on Ni-base superalloy Inconel 718. *Surface & Coatings Technology* **201**, 3862-3866 (2006).
- [6] J.A. Haynes, Y. Zhang, K.M. Cooley, L. Walker, K.S. Reeves, B.A. Pint High-temperature diffusion barriers for protective coatings. *Surface & Coatings Technology* **188-189**, 153-157 (2004).
- [7] L. Guangming, L. Meishun, Ming Zhu, Z. Yanchun, Transient of alumina oxide scale on  $\beta$ -NiAl coated on M38G alloy at 950°C. *Intermetallics* **15**, 1285-1290 (2007).
- [8] S.L. Yang, F.H. Wang, Y. Niu, W.T. Wu, Isothermal oxidation of  $\beta$ -NiAl alloy and sputtered coating at 1000°C in air. *Material science forum* **369-372**, 361-368 (2001).
- [9] M. Zielińska, J. Sieniawski, M. Wierzbińska, Effect of modification of mi-

crostructure and mechanical properties of cobalt casting superalloy. *Archives of Metallurgy and Materials* **53**, 887-893 (2008).

- [10] M. Yavorska, M. Poręba, J. Sieniawski, Kształtowanie mikrostruktury warstwy aluminidkowej na nadstopach niklu w niskoaktywnym procesie CVD *Inżynieria materiałowa* **6**, 749-752 (2008).
- [11] M. Yavorska, M. Zielińska, J. Sieniawski, Mikrostruktura oraz odporność na utlenianie izotermiczne warstwy aluminidkowej wytworzonej w niskoaktywnym procesie CVD na podłożu z nadstopu Inconel 713 LC. *Archiwum Technologii Maszyn i Automatyzacji* (przyjęty do druku).
- [12] P. Skocovsky, T. Podrabsky, J. Belan, Degradacja w wyniku eksploatacji warstwy aluminio-krzemowej łopatek turbinowych wykonanych na bazie Ni. *Archiwum Technologii Maszyn i Automatyzacji* **24** 45-52 (2004).
- [13] T. Burakowski, T. Wierzchoń, *Inżynieria powierzchni* Wydawnictwo Naukowo-Techniczne, Warszawa 1995.

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