

M. ZIELIŃSKA\*, J. SIENIAWSKI\*, M. YAVORSKA\*, M. MOTYKA\*

## INFLUENCE OF CHEMICAL COMPOSITION OF NICKEL BASED SUPERALLOY ON THE FORMATION OF ALUMINIDE COATINGS

### WPLYW SKŁADU CHEMICZNEGO NADSTOPU NIKLU NA BUDOWĘ WARSTWY ALUMINIDKOWEJ

The aim of the present work was to determine the influence of chemical composition of the nickel based superalloy on the thickness and microstructure of aluminide layer obtained in the CVD low activity process. For this purpose cylindrical samples were cut from the rods and castings made of commercially produced nickel superalloys: Inconel 713LC, Inconel 625, Inconel 738LC, Inconel 100, Inconel 718. The surface of the samples was ground up, degreased and cleaned. Then samples were placed in the retort and aluminized. The low activity process of aluminizing at the presence of  $\text{AlCl}_3$  and  $\text{H}_2$  was conducted. The cross –sections of aluminide coatings were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

There was established that a chemical composition of superalloy influences the microstructure and thickness of aluminide layer. Higher total concentration of superalloy elements such as Cr, Mo, W, Ti which segregate in the diffusion zone decrease the thickness of aluminide layer.

*Keywords:* nickel based superalloys, CVD process, aluminide coatings

Celem niniejszej pracy było określenie wpływu składu chemicznego nadstopów niklu na głębokość i mikrostrukturę warstwy aluminidkowej wytworzonej w niskoaktywnym procesie CVD. Do badań przyjęto pięć gatunków nadstopów niklu, najczęściej stosowanych do wytwarzania łopatek turbin silników lotniczych: Inconel 713LC, Inconel 625, Inconel 738LC, Inconel 100, Inconel 718. Z prętów i odlewów wycięto próbki walcowe, które następnie szlifowano, piaskowano i odtłuszczono. Następnie próbki umieszczono w retorcie i poddano procesowi aluminizacji. Niskoaktywny proces aluminizacji prowadzono w temperaturze  $1050^\circ\text{C}$  w obecności  $\text{AlCl}_3$  i  $\text{H}_2$ . Badania mikrostruktury prowadzono na przekrojach poprzecznych uzyskanych warstw przy użyciu skaningowego mikroskopu elektronowego wyposażonego w detektor EDS.

Stwierdzono, że skład chemiczny nadstopu wpływa na mikrostrukturę i głębokość wytworzonej warstwy. Większa sumaryczna zawartość składników stopowych tj. Cr, Mo, W, Ti, które segregują się w strefie dyfuzyjnej powoduje zmniejszenie głębokości warstwy aluminidkowej.

### 1. Introduction

Aluminide diffusion coatings are widely used for high temperature oxidation and hot corrosion protection of turbine blades used in engine hot sections [1-9]. These blades are made of nickel based superalloys [9, 11]. Aluminide coatings have an ability to form a protective and slowly growing oxide ( $\text{Al}_2\text{O}_3$ ) film at higher temperature (above  $900^\circ\text{C}$ ).

Diffusion aluminide coatings on superalloys are classified by microstructure as being of the “inward diffusion”(high activity process) or “outward diffusion”(low activity process) type [2-4]. An inward coating is formed when the aluminum activity is higher than the nickel

activity. Aluminium diffuses inward faster than nickel diffuses outward through the nickel – aluminide intermetallics that is formed on the surface. A brittle  $\delta\text{Ni}_2\text{Al}_3$  outer layer with adjacent  $\beta\text{NiAl}$  intermetallic phase is formed due to high aluminium activity. As such a coating is brittle and has a low melting point, the additional heat treatment is required to convert the brittle  $\delta\text{Ni}_2\text{Al}_3$  phase into less brittle  $\beta\text{NiAl}$  – Al rich >50%at [2-4].

Outward diffusion coatings are formed when aluminium activity is lower than the nickel activity and processing is carried out at a higher temperature (between  $980$  and  $1090^\circ\text{C}$ ). Under these conditions, coatings are formed by the selective diffusion of nickel outward through the monoaluminide layer. Compared to in-

\* RZESZÓW UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING AND AERONAUTICS, 35-959 RZESZÓW, 2 W.POLA STR., POLAND

Chemical composition of investigated superalloys

Superalloy	Elements content, %mas.														
	Ni	Cr	Co	Mo	W	Ta	Al	Ti	C	B	Zr	Fe	Nb	Si	Mn
Inconel 713LC	74	12.5	–	4.2	–	–	6.1	0.8	0.05	0.012	0.1	–	2.0	–	–
Inconel 625	61.0	21.5	–	9.0	–	–	0.2	0.2	0.05	–	–	2.5	3.6	0.2	–
Inconel 738	61.0	16	8.51	1.7	2.6	1.7	3.4	3.4	0.11	0.01	0.05	–	0.9	–	–
Inconel 100	60	10	15.0	3.0	–	–	5.5	4.7	0.18	0.014	0.06	–	–	–	–
Inconel 718	52.5	19.0	–	3.0	–	–	0.5	0.9	0.03	–	–	18.5	5.1	0.2	0.2

ward diffusion coatings, these coatings are modified to a lesser degree by the slower diffusing refractory elements in the substrate, and the overall aluminium content is hypostoichiometric, providing somewhat better ductility in the coating. A typical as-coated microstructure consist of the external NiAl zone and the internal zone – so-called interdiffusion zone which consist of refractory metal (tungsten molybdenum, tantalum etc) carbides, and/or complex intermetallic phases in NiAl and/or Ni<sub>3</sub>Al formed by the removal of nickel from underlying alloy [2-4].

The structure and the composition of an aluminide coating varies for different superalloys for a given set of coating parameters. The microstructure and composition of a coating depend on the rate at which alloying elements such as chromium, molybdenum, and tungsten of the superalloy segregate in the coating. It was found that for nickel alloys, the absence of aluminium precludes the formation of the interdiffusion zone that usually appears in nickel superalloys [2].

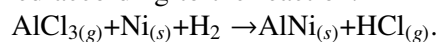
The aim of the this work is to determine the influence of chemical composition of the nickel based superalloy on the thickness and microstructure of aluminide layer obtained in the CVD low activity process.

## 2. Materials and methodology

The superalloys used in this study were: Inconel 713LC, Inconel 625, Inconel 738LC, Inconel 100, Inconel 718 of the chemical composition given in Table 1. The cylindrical samples of the diameter 15mm and 4mm high were cut and grounded up to SiC No 600, degreased in ethanol and next grit blasted, ultrasonically cleaned and finally aluminized.

The aluminide coatings were made using the CVD equipment BPXPR03252 manufactured by IonBond company [11, 12]. The low activity process of aluminizing was conducted at the temperature 1050°C and time 8h. In this process aluminium chloride vapour (AlCl<sub>3</sub>) was produced in an external genera-

tor at the temperature 330°C according to the reaction: Al(s)+HCl(g)→AlCl<sub>3</sub>+H<sub>2</sub>. Then the saturation atmosphere was transported in a stream of hydrogen gas into the CVD reactor, where nickel based samples were placed. The AlCl<sub>3</sub> vapour reacted with the nickel, the main constituent of the samples at the temperature 1050°C and grains of intermetallic phase (NiAl) were formed according to the reaction:



The microstructure of cross-sections of the synthesized coatings were investigated by an optical microscope Nikon Epiphot 300, a scanning electron microscope (SEM) Hitachi S-3400N and energy dispersive spectroscope (EDS) [9-13]. Polished samples were etched with reagent: 10gCuSO<sub>4</sub> +50cm<sup>3</sup>HCl +50cm<sup>3</sup>H<sub>2</sub>O. The coatings thicknesses were determined by means of NIS-Elements software. There was made 8 measurements for each sample.

## 3. Results and discussion

The aluminized coatings consists of the two layers: an outer one and the inner (interdiffusion) one (see Fig. 1-5). Different coatings microstructures were observed depending on the different substrate. The outer layer of all investigated superalloys is composed of single phase β-NiAl and contains, dissolved, alloying elements that were derived from the substrate: chromium, cobalt, molybdenum etc. The aluminium content in the β-NiAl ranges from 23 to 24.7% mass (Fig.1-5), so is more or less the same in all investigated superalloys.

The thickness of the outer zones varies from 16.5 to 23.8 μm and depends on the chemical composition of the superalloy (see Table 2). The thickest layer (β-NiAl) was observed on Inconel 713C samples which has the highest nickel content of all investigated superalloys (74%). Superalloy of Inconel 718 with nickel content of 52.5% has thinnest β-NiAl layer. Alloys: Inconel 625, Inconel 738 and Inconel 100 have very close nickel contents (60-61%) but different thickness of the aluminide layer

(Table 2). This is due to the chromium, molybdenum and tungsten presence. These elements segregate to the coating (see Fig 1-5) and form precipitates such as carbides MC and  $M_{23}C_6$ , or sigma phases which make the nickel diffusion difficult [14, 15]. The alloy of Inconel 100 has the lowest refractory elements content

(Cr+Mo+W=13%) but high cobalt and nickel content (Ni+Co=75%) so the thickness of the layer is very close to the thickness of the coating obtained on Inconel 713C. It was found that cobalt can substitute for nickel and form  $\beta$ -(Co, Ni)Al phase [16].

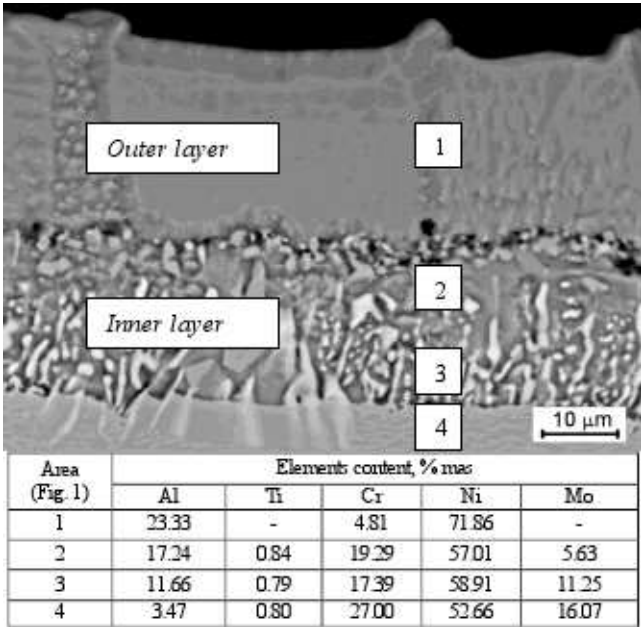


Fig. 1. Microstructure of aluminide coating on IN713LC obtained in a low activity CVD process at the temperature 1050°C for 8h and corresponding chemical compositions in the areas marked in the figure

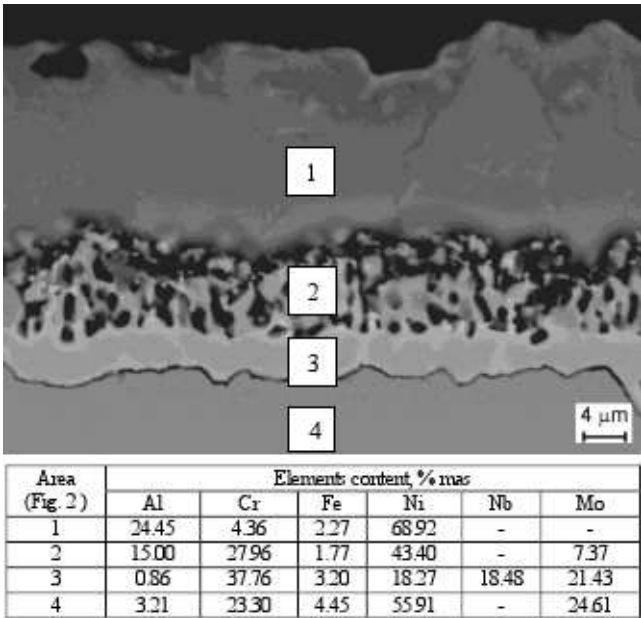


Fig. 2. Microstructure of aluminide coating on IN625 obtained in a low activity CVD process at the temperature 1050°C for 8h and corresponding chemical compositions in the areas marked in the figure

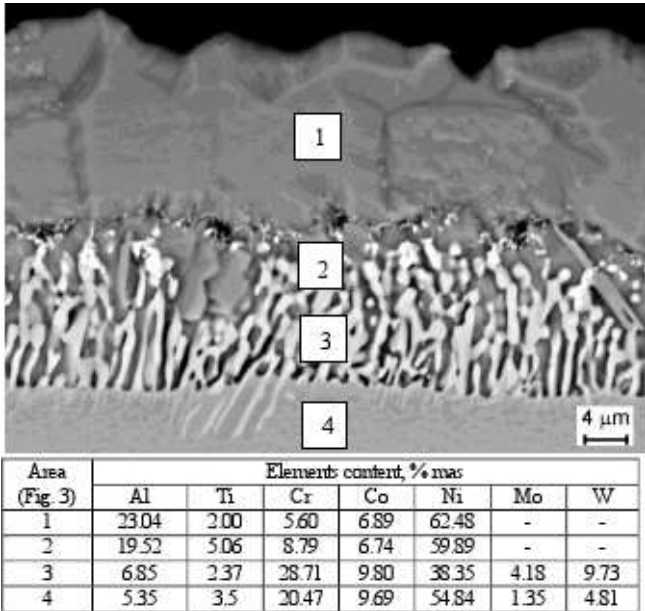


Fig. 3. Microstructure of aluminide coating on IN 738 obtained in a low activity CVD process at the temperature 1050°C for 8h and corresponding chemical compositions in the areas marked in the figure

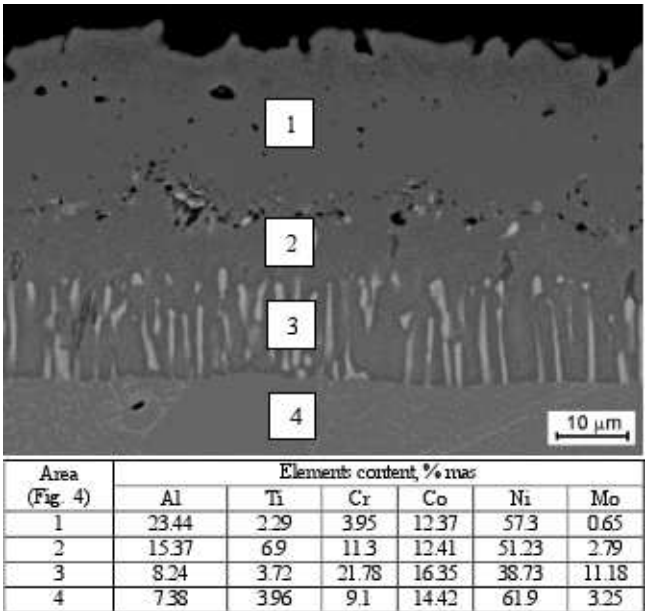
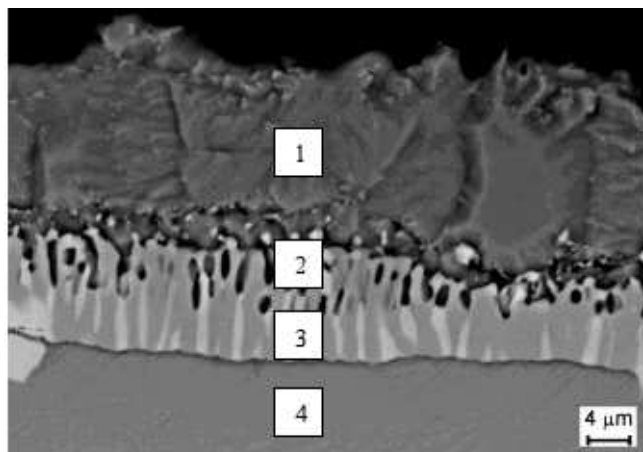


Fig. 4. Microstructure of aluminide coating on IN100 obtained in a low activity CVD process at the temperature 1050°C for 8h and corresponding chemical compositions in the areas marked in the figure



Area (Fig. 5)	Element content, % mas						
	Al	Ti	Cr	Fe	Ni	Nb	Mo
1	24.71	-	5.31	8.69	61.3	-	-
2	18.87	1.51	6.82	9.50	59.69	3.61	-
3	1.43	0.37	37.83	22.84	17.64	19.9	-
4	4.11	1.13	20.35	18.94	49.08	3.67	2.7

Fig. 5. Microstructure of aluminide coating on IN718 obtained in a low activity CVD process at the temperature 1050°C for 8h and corresponding chemical compositions in the areas marked in the figure

TABLE 2

The thickness of aluminide coatings obtained on superalloys: Inconel 713C, Inconel 625, Inconel 738LC, Inconel 100, Inconel 718 in a low activity CVD process

Superalloy	Thickness, μm		
	Inner layer	Outer layer	Total layers
Inconel 713LC	21.4	23.8	45.2
Inconel 625	11.7	20.6	32.3
Inconel 738LC	17.5	18.4	35.9
Inconel 100	23.1	21.2	44.5
Inconel 718	11.1	16.5	28.4

The interdiffusion layer of the coatings have different thickness. Superalloys with higher Al content (3.4-6.1%): Inconel 713C, Inconel 738 and Inconel 100 have thicker interdiffusion layer: 17.5- 23.4 μm. The inner layer of alloys Inconel 625 and Inconel 718 with low concentration of aluminium (0.2-0.3%) has thickness of 11.1-11.7μm (Table 1, 2). These results suggest that higher aluminium content in the superalloy produces a higher coating thickness.

The microstructure of aluminide coatings is not a homogeneous one. Chemical composition on the cross section of aluminide coatings is not stable (Fig. 1-5).

Analysis of elements content on the cross section of aluminide layer revealed that in the outer layer and diffusion zone 1 (under the outer layer) has high nickel

content. It proves that nickel diffuses outward. The increase of chromium, molybdenum, tungsten, niobium and titanium content was observed in the diffusion zone (areas 2 or 3, Fig. 1-5) in comparison to their nominal contents in superalloys. The first zone of Inconel 713C, Inconel 738 and Inconel 100 (under the outer layer) probably consist of the mixture of  $\beta$ NiAl phase and other phases such as carbides or sigma phases. The aluminide phase is formed by transformation of  $\gamma + \gamma'$  to  $\beta$ NiAl because of nickel withdrawal to the outer coating zones, not by aluminium diffusion into the substrate [2-4, 14, 15].

## 4. Conclusions

The concentration of main nickel based superalloy constituents influences the properties of aluminide layer obtained in a low activity CVD process. The thickness of aluminide coating depends on the chemical composition of a superalloy. However, on the grounds of obtained results it is difficult to find how the particular elements influence on the thickness of aluminide coating. An investigated alloys contain more than five constituents which effect in a different way on the microstructure of alloy during the aluminizing process. It was found that superalloys with higher total concentration of nickel and cobalt which form  $\beta$ NiAl phase and lower concentration of elements Cr, Mo, W, Ti which segregate in the diffusion zone have higher thickness of aluminide layer.

This work was financially supported by the Ministry of Science and Higher Education PBZ-MNiSW-01/1/2007

## REFERENCES

- [1] J. S i e n i a w s k i, Nickel and titanium alloys in aircraft turbine engines, *Advances in Manufacturing Science and Technology* **27**, 3, 23-34 (2003).
- [2] J.R. D a v i s, Heat – Resistant Materials. ASM Speciality Handbook.
- [3] Y. T a m a r i n, Protective coatings for turbine blades. ASM International, 2002.
- [4] B. S u d h a n g s h u, High temperature coatings. Butterworth-Heinemann, Oxford 2007.
- [5] M. H e t m a n c z y k, L. S w a d z b a, B. M e n d a l a, Advanced materials and protective coatings in aero-engines application, *JAMME* **24**, 1, 372-381 (2007).
- [6] C. C h o u x, A.J. K u l i n s k a, S. C h e v a l i e r, High temperature reactivity of nickel aluminide coatings, *Intermetallics* **16**, 1-9 (2008).
- [7] C.-H. B a i, Y.-J. L u o, C.-H. K o o, Improvement of high temperature oxidation and corrosion resistance of superalloy IN-738LC by pack cementation, *Surface and coating Technology* **183**, 74-78 (2004).



- [8] F.S. Pettit, G.W. Goward, High temperature corrosion and use of coatings for protection, The Metallurgical Society of AIME, 603-619 (1981).
- [9] A. Onyszko, K. Kubiak, Method for production of single crystal superalloys turbine blades, Archives of Metallurgy and Materials **54**, 3, 765-771 (2009).
- [10] M. Zielińska, K. Kubiak, J. Sieniawski, Surface modification, microstructure and mechanical properties of investment cast superalloy, JAMME **35**, 1, 55-62 (2009).
- [11] M. Yavorska, M. Poręba, J. Sieniawski, Development of microstructure of aluminide layer on Ni-base superalloys in the low-activity CVD process, Materials Engineering **6**, 749-752 (2008).
- [12] M. Poręba, W. Ziaja, K. Kubiak, Microstructure and heat resistance of aluminide coating developed on Rene 77 superalloy in low activity CVD process, Materials Engineering **6**, 745-748 (2008).
- [13] M. Zielińska, J. Sieniawski, M. Wierzbńska, Effect of modification on microstructure and mechanical properties of cobalt casting superalloy, Archives of Metallurgy and Materials **53**, 3, 887-893 (2008).
- [14] N. Voudouris, Ch. Christoglou, G.N. Angelopoulos, Formation of aluminide coatings on nickel by a fluidized bed CVD process, Surface and Coatings Technology **141**, 275-282 (2001).
- [15] G.W. Goward, D.H. Boone, Mechanisms of Formation of diffusion Aluminide Coatings on Nickel-Base Superalloys, Oxidation of Metals, **3**, 1, 475-495 (1971).
- [16] Y.Q. Wang, G. Sayre, Synthesis of simple and platinum-modified aluminide coatings on cobalt (Co) – base superalloys via a vapor phase aluminizing process, Surface and Coatings Technology 2003, 256-263 (2008).

*Received: 20 August 2010.*