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MICROSTRUCTURE AND OXIDATION RESISTANCE OF AN ALUMINIDE COATING ON THE NICKEL BASED SUPERALLOY MAR M247 DEPOSITED BY THE CVD ALUMINIZING PROCESS

MIKROSTRUKTURA I ŻAROODPORNOŚĆ WARSTWY ALUMINIDKOWEJ WYTWORZONEJ METODĄ CVD NA PODŁOŻU NADSTOPU NIKLU MAR M247

An investigation was conducted to synthesize βNiAl coating on the nickel based superalloy Mar M247 in a chemical vapor deposition process (CVD). The low activity process of aluminizing was carried out for 8 hours at the temperature 1050°C. Surface morphology and cross-section microstructure of the diffusion coating were studied and compared by using an optical microscope, a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy and an X-ray diffractometer. It was found that aluminide coating with the thickness of 37 μm consisted of two layers: an outer one and the inner interdiffusion one. The outer layer consists of single phase βNiAl. The inner one, consisted of βNiAl phase and carbides: MC and $M_{23}C_6$ types which were originally present in the substrate. Cyclic oxidation test was performed at 1000°C for 1000h in the air atmosphere. The aluminized samples exhibited a small mass increase and the α- Al_2O_3 oxide formed during oxidation test had a good adherence to the coating. The decrease of aluminum content in the coating with the prolongation of the oxidation time and the phase transformation of βNiAl to γ' Ni_3Al and to γNi solid solution were observed. The samples without the coating showed a strong mass decrease in comparison to the coated samples.

Keywords: Mar M247 Ni-base superalloy, CVD method, aluminide coating, oxidation resistance

Niskoaktywny proces aluminiowania prowadzono w temperaturze 1050°C i w czasie 8 h. Badania mikrostruktury na przekroju oraz powierzchni warstwy dyfuzyjnej prowadzono za pomocą mikroskopu optycznego oraz skaningowego mikroskopu elektronowego wyposażonego w detektor EDS. Skład fazowy określano metodą rentgenowskiej analizy fazowej. Uzyskano warstwę aluminidkową o grubości 37 μm składająca się z dwóch stref: zewnętrznej oraz wewnętrznej (dyfuzyjnej). Strefa zewnętrzna składa się z fazy βNiAl. Natomiast wewnętrzna – z fazy βNiAl oraz węglików typu MC oraz $M_{23}C_6$. Badania cyklicznego utleniania prowadzono w temperaturze 1000°C i w czasie 1000 h w atmosferze powietrza. Podczas utleniania warstwy aluminidkowej powstaje tlenek α-Al_2O_3 o dobrej przyczepności do warstwy dyfuzyjnej. Zwiększenie czasu utleniania od o do 1000 h powoduje zmniejszenie zawartości aluminium oraz przemianę fazową β-NiAl do γ'-Ni_3Al i do stałego roztworu γ-Ni. Materiał bez warstwy aluminidkowej charakteryzuje się większą szybkością utleniania w porównaniu do materiału z warstwą aluminidkową.

1. Introduction

Aluminide coatings are widely used for high temperature oxidation and hot corrosion protection of turbine blades used in an engine hot sections. Depending on the working environment of turbine blades different types of coatings are used, such as coatings based on Al-Ni, Al-Fe, or Al-Ti alloys [1-3]. In the aircraft turbine industry the aluminum based diffusion coatings are generally used. These coatings are produced by different methods: magnetron sputtering, thermal spray technology, Electron Beam Physical Vapor Deposition (EB-PVD), pack cementation or chemical vapor deposition [4-6]. In the paper [7] the possibility of producing Al-Ni intermetallic layers by a duplex method is presented. This method consists of oxidizing an Inconel-type substrate coated with aluminum as to transform (through diffusion) this coating and the adjacent substrate regions into an intermetallic layer and to produce a heat resistant aluminum oxide coating in the external zone of the layer. NiAl and Ni_2Al_3 phases form on nickel superalloys, whereas CoAl and $FeAl_2$ form on cobalt – and iron- based superalloys. The NiAl phase has an excellent oxidation and hot corrosion resistance at room and at the elevated temperature, high melting point and low density [8]. During oxidation at high temperature the superalloy constituents react with oxygen, which is the primary environmental condition that affects service life. Aluminum in the coating combines with oxygen at the substrate surface, forming a protective Al_2O_3 oxide. When the oxide cracks and spalls due to thermal cycling, additional aluminum from the coating diffuses to the surface to reform the oxide. When the aluminum content in the coatings drops

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to about 4 to 5% wt., the Al_2O_3 oxide can no longer form and rapid oxidation occurs. The rate of aluminum diffusion is influenced by the substrate composition [9-11].

The aim of the present work was to determine the microstructure of aluminide layer obtained on the nickel based superalloy Mar-M247 by the CVD method and the estimation of oxidation resistance during the air exposition at the high temperature.

2. Materials and methodology

The commercial, polycrystalline superalloy Mar M247 of the following chemical composition: C – 0.15%, Co – 10%, Cr – 8.25%, Mo – 0.7%, Al – 5.5%, Ti – 1.0%,W – 10%, Ta – 3%, Fe- 0.5% B – 0.015%, Zr – 0.005%, Hf – 1.5% (weight percentage) Ni – matrix, was used in this study [12].

The cylindrical samples of 15mm diameter and 4mm high were cut and grounded up to SiC No 600, degreased in ethanol, ultrasonically cleaned and finally aluminized.

The aluminide coatings were made using the CVD equipment BPXPR0325S manufactured by IonBond company (Fig. 1) [12-17]. Depending on the content of aluminum in the pack and the processing temperature there are possible two kinds of the process, a low-activity and the high-activity one. The low – activity process takes place when the aluminum activity is low and the temperature is higher than 1000°C. Nickel is a predominant component, which diffuses out of the alloy, producing an 'outward diffusion' coating. The low-activity coating appears to have two zones, the external one and the inner one, both of which are NiAl phase. The total coating thickness includes both zones. The NiAl phase that is formed in the inner zone has very low solubility for many of the alloying constituents of the alloy. These constituents precipitate as carbides and intermetallic phases.

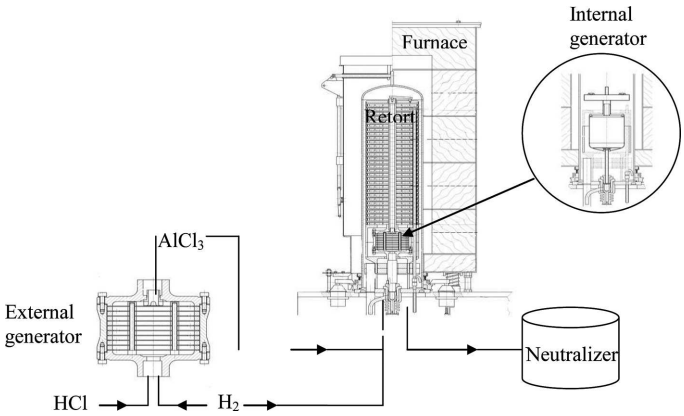


Fig. 1. A scheme of equipment for deposition of aluminide coatings by the CVD method [17]

In the experiments presented in this paper the low activity process of aluminizing was conducted for 8h at the temperature 1050°C. In this process aluminum chloride vapor ($AlCl_3$) was produced in an external generator at the temperature 330°C according to the reaction: $2Al+6HCl \rightarrow 2AlCl_3+3H_2$. Then the $AlCl_3$ was transported in a stream of hydrogen into the CVD reactor, where nickel based samples were placed. The $AlCl_3$ vapor reacted with nickel, the main constituent of the samples at 1050°C and grains of intermetallic phase (NiAl) were formed according to the reaction:

$$2AlCl_3 + 2Ni + 3H_2 \rightarrow 2AlNi + 6HCl.$$

Oxidation tests of uncoated and coated samples were conducted at 1100°C in the air atmosphere for 1000h. Samples were heated up to 1100°C, kept at that temperature for 20 hours and then cooled down in air to the room temperature and then weighed with accuracy of 0,0001g.

The microstructure of the surface and cross-sections of the synthesized coatings were investigated by an optical microscope Nikon Epiphot 300, scanning electron microscope (SEM) Hitachi S-3400N and energy dispersive spectroscope (EDS) [14, 17, 19-20]. Polished samples were etched with reagent: $10gCuSO_4+50cm^3HCl+50cm^3H_2O$. The coatings thicknesses were determined by means of NIS-Elements software. There was made 8 measurements for each sample.

Phase composition of the investigated coatings was made using ARL X'TRA X- ray diffractometer, equipped with a filtered copper lamp with the voltage of 45kV and heater current of 40mA.

3. Results and discussion

The surface area of the deposited coating was tight and uniform in aspect of chemical composition (Fig 2 a). The main elements content in different areas of the coating were determined. It was estabilished that an aluminum content is 43%at., nickel – 49%at. and cobalt – 6%at (mean of 3 measurements). The aluminum and nickel contents indicate the NiAl phase formation.

The cross-section image (Fig. 2b) indicates that aluminide coating consists of two layers: an outer one 18.4 μm thick of a homogenous structure and the inner (interdiffusion) one 19.6 μm thick of the different structure. This type of coating is characteristic for the low activity process [18]. Chemical analysis were performed in different areas of the coating (Table 1, Fig. 2). It was established that the outer layer contains 40%at. Al and 49%at. Ni. The inner layer has a higher Cr – 29%at., W – 22%at. and Co – 21.5% content. X-ray diffractions confirmed that the external zone of the coating consits of the βNiAl phase (Fig. 3).

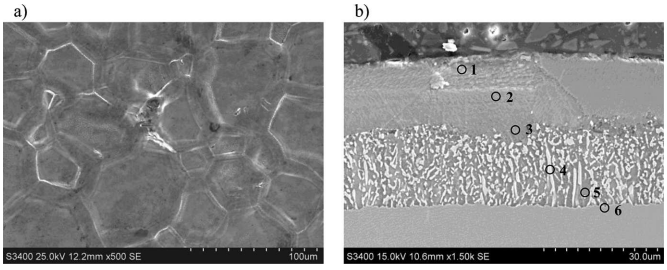


Fig. 2. a) Surface morphology and b) cross-section microstructure of an aluminide coating obtained by the CVD method at 1050°C/8h. 1-6 chemical analysis areas

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TABLE 1
The results of EDS analysis from area presented in Fig. 2b

Area (Fig. 2b)	Elements content, %at.					
	Al	Ti	Cr	Co	Ni	W
1	41.1	-	2.1	7.4	49.4	-
2	40	-	3.7	6.2	50.1	-
3	34.3	1.4	5.8	9.9	48.6	-
4	4.6	-	29.2	21.5	22.6	22.1
5	32.7	1.7	6.8	8.1	50.7	-
6	17.1	1.0	9.2	11.2	61.5	-

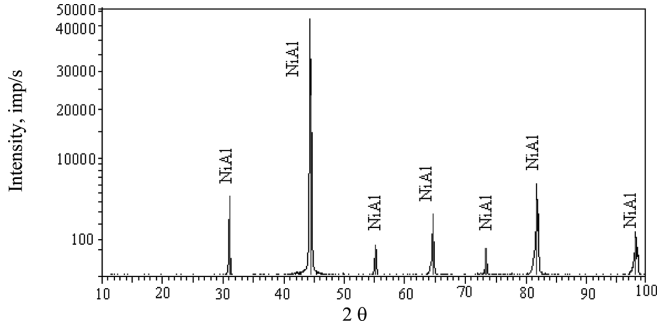


Fig. 3. XRD results of aluminide coating deposited by CVD method

Gradual removal of the outer zone was done by grinding. The microstructure of aluminide coating between the outer and inner layer is presented in Fig. 4a. There are visible the homogenious areas (grey ones) which contain: Al (35%at.), Ni (52%at.), Co (6.8%) and small amount of Hf (0.6%). Moreover nonhomogenious areas containig Al (23%at.) Ni (46%at.), and Hf (16%at.) were observed. Chemical analysis of the inner layer areas by the EDS method (see Fig 4b, Table 2) revealed the presence of several phases. Some phases with longitudinal shape were rich in Ta (31%at.) Ti (27%at.), W (16%at.) and Hf (6%at.). Such elements form MC type carbides which are the microstructure constituents of Mar M 247 superalloy [19]. The fine precipitates enriched with Cr (62%at.) what correspond to the chemical composition of Cr–rich $M_{23}C_6$ type carbide were present in the interdiffusion zone. The phase composition of the interdiffusion zone is presented in Fig. 5.

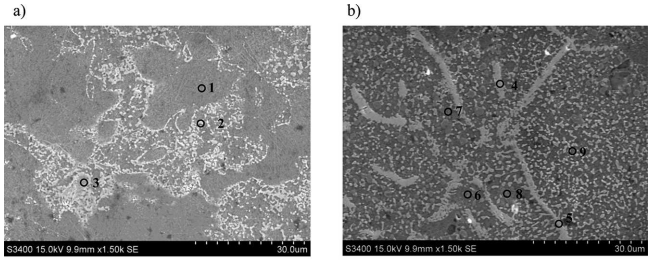


Fig. 4. Microstructure of the inner layer of aluminide coating: a) on the boundary of the outer and inner layer, b) the interdiffusion zone. 1-9 – chemical analysis areas

The oxidation test results of coated and uncoated samples are shown in Fig. 6. The uncoated samples showed mass loses after 40h of oxidation due to the scale spallation. The coated samples exhibit small mass gain. The oxidation follows the parabolic rate law indicating that oxide scales forming on the surface can act as a diffusion barrier. This results confirmed the efficiency of the aluminizing process.

TABLE 2
The results of EDS analysis from the area presented in Fig. 4

Area (Fig.4)	Elements content, %at.								
	Al	Ti	Cr	Co	Ni	Mo	Hf	Ta	W
1	33.2	1.7	5.5	6.5	51.3	-	0.4	0.7	0.7
2	24.6	1.7	6.3	6.2	45.5	0.3	12.3	1.5	1.6
3	22	2.0	6.5	5.3	40.4	0.2	20.2	1.8	1.6
4	-	27	4.3	2.9	11.1	1.5	6.2	31.2	15.8
5	-	25.9	5.1	4.0	11.8	-	6.0	30.6	16.6
6	23.2	-	25.1	7.3	40.2	-	-	0.8	3.4
7	6.1	-	62	5.8	12.8	1.4	-	0.6	11.3
8	24.8	-	11	10.2	43.2	0.8	-	0.7	9.3
9	32.1	1.1	6.1	7.4	50.4	0.3	-	0.4	2.2

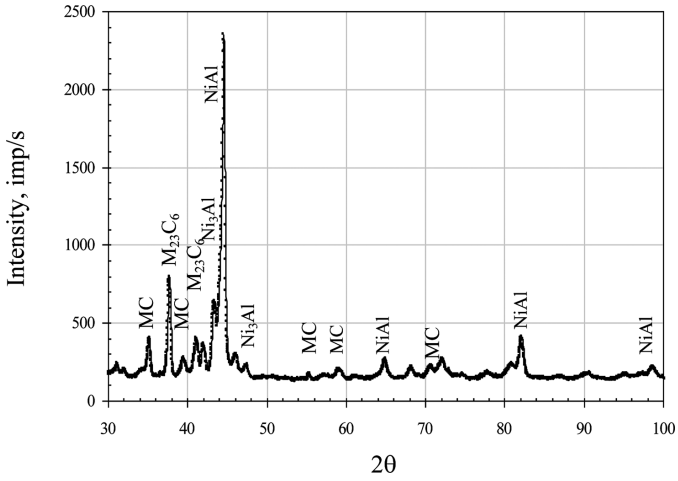


Fig. 5. XRD results of the interdiffusion zone of aluminide coating deposited by CVD method

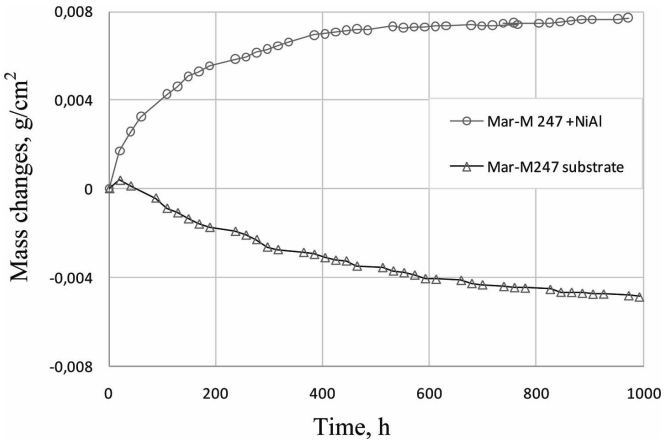


Fig. 6. Curves of sample mass changes of Mar M247 superalloy with and without aluminide coating

After 110h oxidation testing at 1100°C the NiAl coating consisted of dark-grey phases (point 2, Fig. 7a) and light-grey

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phases (point 3, Fig. 7a). In the light grey phase, the composition of Ni and Al (Ni – 60%at. and Al – 18%at.) is close to the stoichiometric composition of Ni_3Al indicating the presence of γ‘ phase. Dark grey areas have higher Al content indicating the presence of NiAl phase (see Table 3, point 2, Fig 7). During the high temperature exposure the outward aluminium diffusion occurs. Aluminum forms Al_2O_3 phase 3-4 μm thick according to the following reaction: $NiAl + \frac{3x}{4}O_2 \rightarrow NiAl_{1-x} + \frac{x}{2}Al_2O_3$.

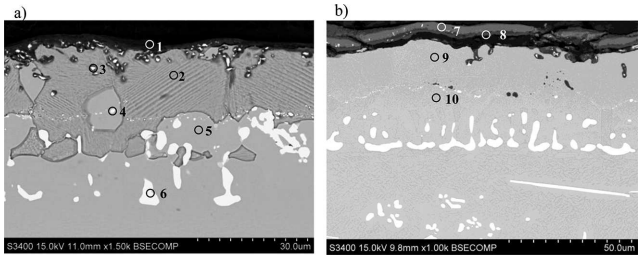


Fig. 7. Microstructure of the cross-section of aluminide coating deposited by CVD method after oxidation test at the temperature 1100°C for: a) 110h and b) 1000h

TABLE 3
The results of EDS analysis from area presented in Fig. 7

Area (Fig.7)	Elements content, %at.							
	O	Al	Ti	Cr	Co	Ni	Hf	W
1	66.5	33.5	-	-	-	-	-	-
2		29.3	-	6.6	7.2	55.4	-	1.5
3	71.1		-	-	-	5.3	23.6	-
4		18.1	1.2	5.1	8.9	60.1	3.6	3.0
5	-	18.7	1.5	5.3	7.1	64.4	-	3.0
6	-	-	-	25	16.1	26.4	-	32.5
7	62.6	22.6	-	3.2	-	11.6	-	-
8	62.2	37.4	-	-	-	0.4	-	
9	-	17.0	2.1	4.8	8.0	65.6	-	2.5
10	-	9.6	0.8	15.7	13.3	60.6	-	-

Moreover, there is an inward diffusion of aluminum from the coating towards the substrate [21]. Grain boundaries of NiAl phase make an easy path for aluminum diffusion therefore the areas near boundaries are depleated of Al. Ni_3Al phase forms on the grain boundaries of NiAl, NiAl-Al_2O_3 phases and NiAl-matrix (Fig. 7a).

The small regions of internal oxidation on the depth of 8m were observed. The internal oxides have a two phase structure and are formed mainly on grain boundaries of NiAl and Ni_3Al. Chemical analysis of this areas revealed the presence of HfO_2 surrounded by Al_2O_3 in the regions called„pegs“ in the literature [9]. Oxide pegs have been found to be HfO_2 sheaths encapsulated with alumina [22]. Some of the authors consider that pegs act as a diffusion barrier for substrate elements diffusion. It was found that the presence of active elements like Hf can change the growth mechanism from outward movement of aluminum ions to inward movement of oxygen ions [9, 20]. Hafnium reduces the aluminum content necessary to form a continuous protective alumina scale. The oxides of HfO_2 are formed on the grain boundaries of NiAl/Al_2O_3 phases. Because HfO_2 oxide is more stable than Al_2O_3 oxide, Hf atoms can replace aluminum atoms in Al_2O_3 oxides. This phenomena let to stabilize NiAl phase.

A fine particle chain on the boundary of the outer and inner layer and the change in morphology of Cr and W carbides were observed (points 4 and 6, Fig. 7a). The presence of the NiAl, Ni_3Al, Al_2O_3 and HfO_2 phases was confirmed by the XRD analysis (Fig. 8).

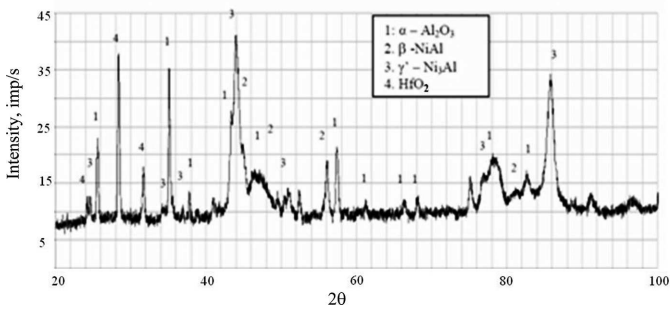


Fig. 8. XRD results of aluminide coating deposited by CVD method after oxidation test at the temperature 1100°C for 110h

After 1000h of oxidation the two phase oxide layer is formed (Fig 7b). One phase is Al_2O_3 and the second one is probably NiO +$NiAl_2O_3$+ Al_2O_3 oxides mixture [10]. It was observed the spalling of the oxides. The aluminum content decressed with the prolongation of the oxidation time and after 1000h droped to 17%at. in the outer zone and 9.6% in the interdiffusion zone. There are still visible the carbides enriched with Cr and W and a chain of fine particles in the coating.

4. Summary

Aluminizing by the low activity CVD method at 1050°C for 8h let to obtain the aluminide coatings 37 μm thick on the MAR M 247 superalloy. The coating consisted of two layers: the outer and the inner one. The first one consisted of NiAl phase. The inner one, besides of NiAl phase consisted of carbides: MC and $M_{23}C_6$ types which were originally presented in the substrate. Moreover, participates enrich with Cr , W and Co and the chain of very fine precipitates enriched with Hf were observed.

The cyclic oxidation test was performed at 1000°C for 1000h in the air atmosphere. The aluminized samples exhibited a small mass increase and the α- Al_2O_3 scale that was formed during oxidation test had a good adherence to the coating. Oxides inclusions called pegs were observed. The pegs consisted of HfO_2 core and outer Al_2O_3 layer. The grain boundaries of NiAl and Al_2O_3 are the places of precipitation of HfO_2. Since the HfO_2 is more thermodynamically stable then Al_2O_3 probably a large portion of Hf can simply replace aluminum and provide stabilization of NiAl phase. It was observed the decrease of aluminum content in the coating with the prolongation of the oxidation time and the phase transformation of β-NiAl to γ'-Ni_3Al and to γ-Ni solid solution. The samples without coating showed a strong mass decrease in comparison to coated samples.

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