OVERALUMINISING OF NiCoCrAIY COATINGS BY Arc PVD ON Ni-BASE SUPERALLOYS

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Abstract. Investigations of depositing high temperature coatings on Ni base superalloys by the Arc-PVD method, using exothermic reaction processes between Ni and Al with NiAl intermetallic formation are presented in the article. By diffusion heating at 1323K, a NiAl high temperature diffusion coating containing 21 % at. Al and 50 µm thick was obtained. In the next stage coatings with more complex chemical composition- NiCoCrAlY were formed. The NiCoCrAlY coatings were made with two targets. Good consistence between the chemical composition of the targets and a uniform distribution of elements in the coatings was shown. Then the surface was also covered with aluminium by the Arc-PVD method. In the vacuum chamber of the equipment a synthesis reaction between NiCoCrAIY and Al with the formation of NiAl intermetallics of high Co, Cr, Y content was initiated. The final heat treatment of coatings was conducted in air and vacuum at 1323K. Strong segregation of yttrium into the oxide scale in the specimens heated in air was shown. It was possible to obtain NiAl intermetallics phase coatings modified by Co, Cr and Y by the Arc-PVD method. The coatings were formed on cast Ni base superalloy ZS6K and single crystal CMSX-4. An example of the application of this method for the aircraft engine turbine blades was presented.

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Introduction

Diffusion coatings with an aluminide base are widely used to protect stationary and aircraft gas turbines against high temperature corrosion [1-5]. One of the limitations characterising those coatings is that during their formation, great amounts of elements, included in the coated alloy composition are introduced into their chemical composition. Even small amounts of elements such as molybdenum, tungsten or titanium can decrease the corrosion resistance of the coatings significantly at high temperature. There is a need, therefore, to obtain coatings free of these detrimental elements by forming coatings of which both the chemical composition and the protective properties would be independent of the substrate chemical composition. That was the reason for development of a protective system by forming the MeCrAlY coatings by the EB-PVD method, plasma spraying and the modified methods of PtAl and CrAl coating formation [5]. The development of modern technology and SIP (sputter ion plating) and Arc-evaporation equipment and their modification increased the possibility of producing the MeCrAlY coatings more easily [6-9]. The SIP equipment has certain attractive features such as electron beam evaporation. Furthermore, the equipment is simple. The estimated cost of SIP is also attractive compared with that of plasma sprayed coatings. This is partly because the total cost of SIP is low and also because some processing steps such as post deposition polishing have been eliminated [10]. The best results, however, have been obtained by combining methods of coating based on the MeCrAlY coating deposition followed by the diffusion aluminising [3,11,23]. The investigations of protective coatings and the deposition process by Arc and SIP (sputter ion platting) PVD methods for nickel-base alloys and y-titanium aluminides were realised in the COST 501 program.[4,12]. The PVD method has been used to deposit PtAl₂ heat resistant coatings on TiAl alloys [13,14].

Intensive investigations on obtaining coatings with low sulphur content (clean coatings) are being conducted [15-18]. The purity of (Ni,Pt)Al is directly related to its oxidation resistance. Over aluminizing of MCrAIY coatings can be one of the ways to obtain coatings without detrimental impurities [18]. Arc-PVD methods allow obtaining clean overaluminising MeCrAIY coatings with very small or without active impurities such sulphur, which are present in standard aluminide coatings The Arc-PVD method gives a lot of possibilities for its industrial application [19-23].

Materials

Experimental

The nickel base superalloys with the following chemical composition (wt.%): ZS6K - 9% Cr, 5% Co, 4.5% Al, 5% W, 10,5% Mo, <0,1% C, balance Ni and CMSX-4 - 6.54Cr, 10.34Co, 1.03Ti, 4.69Al, 4.06Re, 5.92Ta, 5.9W, 0.5Mo, Ni-balance were used. Targets for Arc-PVD were produced by a melting method in a Leybold-Heraeus vacuum furnace IS III/5. Then they underwent homogenising in the protective atmosphere at 1373K and their chemical composition was determined. The assumed chemical composition of MCrAlY targets was following (wt.%): Co-32; Ni-38; Cr-21; Al-8; Y-1. The Al and Al-Si targets were also used. The coatings were made on samples and finally on rotor turbine blades of aircraft engine.

<u>Coatings</u>

Coatings were obtained by use of two targets in the form of discs. with 100 mm diameter in PVT-550 equipment (Plasma und Vacuum Technik GmbH). The samples were made in the form of rod slices with 10 mm diameter. Before the process the samples were ground on the abrasive papers and then rinsed carefully with detergents at 343K. After that they were degreased in trichloroethylene with use of ultrasonic and dried carefully. During coating the samples rotated on the special plate, and in addition to it around their own axis. The shortest distance from the target was 150 mm. On the basis of earlier tests the basic coating parameters: current of 80A, ion cleaning at a bias from 600V to 50V for 5 minutes, were determined during the whole process. The aluminium deposition process was conducted in the following way: 5 min - 600V, 80 min. - 50V. The sample temperature was 473K during coating. Then the formed coatings were subjected to the diffusion heat treatment process, at 1323K, 4 hours. The obtained coatings underwent examinations of morphology, EDX, structure on a SEM microscope. The distribution of chemical elements was analysed by microprobe analysis.

<u>Results</u>

Coatings on ZS6K alloy

Depositing the heat resistant coatings on the nickel base superalloys by the Arc-PVD method was divided into two steps: NiCoCrAIY deposition and the aluminium deposition on the NiCoCrAIY coating. After the aluminium deposition process the temperature was increased until the moment of the exothermic reaction initiation between Al and Ni contained either in NiCoCrAIY or in the Ni-base superalloys. Those investigations were preceded by an analysis of phenomena during the aluminium deposition on the pure nickel in order to form intermetallic phases by the Arc-PVD method. The final structure formation of the coating takes place in the heat treatment process at 1323K.

<u>Aluminide coatings.</u> Aluminide coatings, which can be classified into HTLA (High Temperature Low Activity), were obtained. The structure and the EDX analysis results of the coating are presented in fig. 1 (a-c).

The outer zone matrix is a β -NiAl phase with the substochiometric Al content. In the precipitates (point of the analysis) greatly increased molybdenum and tungsten concentration and low aluminium and chromium content was found. Between the β -NiAl outer coating and the substrate there is a transient zone with the elongated precipitates with the increased content of the high-melting elements. This zone was formed during the heat treatment as a result of dominant diffusion of nickel in β -NiAl

<u>Overaluminising NiCoCrAlY</u>. The developed technological principles of obtaining and characteristic of the aluminide and NiCoCrAlY coatings were the basis of developing the principles of the technology of obtaining the complex MeCrAlY+Al coatings in the Arc-PVD process. The NiCoCrAlY coatings were formed by the Arc-PVD method and then this surface was also covered with aluminium by the same method. That system of coatings was subjected to diffusion heating at 1323K for 4h in vacuum. The structure and EDX results of the obtained coating is presented in fig.2.







Figure 1: The structure of the Al coating obtained by the Arc-PVD method on ZS6K alloy, heat treated at 1323K/4h (a) and the EDX analysis in point 1(b) and point 2(c).

C.



Figure 2: The structure of the NiCrAlY+Al coating obtained by the Arc-PVD method on the ZS6K superalloy: the structure of the coating (a), the EDX analysis in point 1 (b).

The coating formed was about 35 µm thick. The analysis of the chemical composition of elements in the microareas showed that in spite of heat treatment of the specimens in the vacuum, on the surface there was a very thin oxidised zone in which oxygen, aluminium and yttrium are concentrated. In the 2-4 μm zone below the oxidised zone the amount of aluminium and yttrium decreased and the content of nickel, cobalt and chromium increased.

Coatings on CMSX-4

Investigations of NiCoCrAIY and Al coating deposition on the ZS6K cast superalloy experiments and formation of coatings on the CMSX-4 single crystal alloy were made. The coatings were made in the following series: a) NiCoCrAIY deposition on CMSX-4, heat treatment at 1323K, 4h, b) NiCoCrAlY deposition on CMSX-4, Al-Si deposition on NiCoCrAlY, exothermic reaction, heat treatment at 1323K, 4h. The coatings obtained in the particular batches differed in structure and chemical composition.

a.

NiCoCrAlY coatings. The structure of the NiCoCrAlY coating obtained on the CMSX-4 alloy is presented in Fig.3. The concentration of elements in the characteristic microareas of the coating is presented in table 1. The coating thickness is 36 µm. The deep etching revealed characteristic features of the coating structure. It has been shown that the coating consists of elongated discontinuous zones, which are parallel to the surface. Such a structure of the surface results from the deposition process. Specimens were rotated around their own axis and around the axis of the table on which they were placed. Therefore, rotation rate and deposition intensity have significant influence on the coating structure. Single zones have thickness of about 0.5 to 3 µm. Particular zones have a good bond between each other and they were free of any defects, Between the NiCoCrAIY layer and the substrate there is a thin continuous diffusion zone ensuring good adhesion of the coating to the substrate. This zone is formed in the first stage of the process during ion cleaning, when the deposition parameters have the maximal values and temperature of the specimen surface increases.

The EDX quantitative analysis presented in Table I shows that it is possible to deposit, by the Arc-PVD method, all elements which were present in the target. On the basis of the evaluation of the mean concentration of elements in the coating measured on the whole thickness of the coating and width 3mm, presented in table I. The following observations were made. The aluminium concentration in the coating is lower than the concentration of this element in the target, the yttrium concentration is also lower, the amount of cobalt increased, whereas amount of nickel is slightly lower. Good compatibility was obtained with chromium content. The average concentration of this element in the target was 21 wt.% whereas measured in the coating it was 21.82 wt.%, table I. Those results constitute important information for selection of the chemical composition of the target.



Figure 3: Structure of NiCoCrAIY coating obtained by Arc-PVD method on CMSX-4 alloy.

<u>Aluminide coatings.</u> Aluminide coatings on the CMSX-4 alloy were formed by the Arc-PVD method by deposition of Al-Si from the target with the eutectic composition (11 wt. % Si). After forming the Al-Si coating by changes in the deposition parameters the temperature was increased on the specimen surface above the melting temperature of the Al-Si coating to initiate the exothermic reaction between nickel and aluminium. A coating, being a mixture of phases of strong segregation of elements, with 30 μ m thickness was obtained. The X-ray diffraction analysis showed that the NiAl₃ phase was the matrix. The characteristic feature of this coating is presented in fig.4.



Figure 4: Structure of Al-Si coating on CMSX-4 alloy after the deposition process and exothermic reaction.

The structure of the Al-Si coating obtained by the Arc-PVD method on the CMSX-4 alloy after heat treatment is presented in Fig. 5(a) and (b). The EDX analysis results are shown in Fig. 5(c) and (d). Quantitative analysis results of elements in the microareas are presented in table II.

The structure, presented in fig.5a, has three clear zones formed as a result of diffusion processes in the outer zone and on the boundary with the base alloy. The outer zone is characteristic for high activity coatings of which the matrix of coating is NiAl>50at.% or Ni₂Al₃ phase with high concentration of fine precipitates. The morphology of precipitates in the outer zone with the marked points of the quantitative analysis is presented in fig.5b.

The diffusion zone is formed as a result of dominant outward nickel diffusion. Morphology and size of precipitates differs considerably from one observed in the outer zone. They are bigger and have more irregular shapes. The similar structure was observed in the coatings on cast alloy. However, below the diffusion zone there is a zone which was absent in the aluminium coatings both on traditional cast superalloys and coatings on the CSMX-4 alloy before the heat treatment, fig. land fig.4.

Table I The concentration of elements in the NiCoCrAlY coating on the the CMSX-4 in the point marked in fig. 3.

Measurement	A	Al.		Y	(Cr	(Co	Ni		
Points	at. %	wt. %									
1	10.44	5.19	0.47	0.77	16.97	16.26	33.11	35.97	38.29	41.43	
2	17.06	8.86	0.48	0.82	15.39	15.41	34.84	39.54	30.41	34.38	
3	2.61	1.26	-	-	29.72	27.61	37.02	38.98	30.65	32.15	
Average	8.61	4.26	0.30	0.48	22.92	21.82	35.60	38.42	32.57	35.02	



Figure 5: Structure and chemical composition of aluminide coatings obtained by Arc-PVD method and heat treatment at 1323K, 4h: the structure of the coating (a), a fragment of the structure with the marked points of the EDX and quantitative analysis (b), the EDX analysis results in point 1(c) and point 2(d).

Results of qualitative and quantitative analysis of elements in the coating are presented in fig. 5 (c, d). The analysis of elements in precipitates (point 1 fig. 5(b)) showed very high contents of Si, W, Mo and Re. The Re concentration is particularly high and equals to 15.81%. In the coating matrix besides precipitates the chemical composition is completely different. It is the NiAl phase composition without such elements as W, Mo, Re with the small amount of Cr and Si.

<u>Overaluminising of NiCoCrAIY</u>. The structure of coating obtained in the process of the NiCoCrAIY deposition in the first stage and the aluminium deposition in the second stage, initiation of the exothermic reaction and performing the heat treatment, is presented in fig. 6(a)-(d). As can be seen in the figure 6(a) the coating structure consists of three zones: outer zone bordering with the specimen surface, the diffusion zone bordering with the substrate and the zone belonging to the base alloy with the structure of which characteristic features will be presented in the discussion of results. In the outer zone shown in fig. 6(b) there are precipitates of irregular shapes and size at the surface. The structure of the boundary between the outer zone and diffusion zone is presented in fig. 6(c).

The results of analysis of elements in the microareas of overaluminising of the NiCoCrAIY coating are presented in fig.7 and table III. Precipitates in the outer zone show very high chromium content, being 86 wt.% in point 1 in fig. 6(a) and table III, and in other precipitates in this zone above 59 wt.%. In the coating matrix in point 2, fig. 6(b) and table III, the aluminium concentration is 15 wt.%, whereas there was a significant increase in the nickel content and decrease in chromium and cobalt content in comparison with their content in the initial NiCoCrAlY coating. In this zone chromium was found in the amount of 1.31 wt.%. Besides large precipitates having elevated Cr concentration there are also fine spherical precipitates which contain not only basic elements but silicon and yttrium as well, fig. 6(b) point 3, fig. 7(c) and table III point 3. Near the diffusion zone there are also present very fine (white) precipitates marked in fig. 6(c) as point 5. Their approximated chemical composition due to accuracy of the microanalysis at such small precipitates, is presented in fig. 7(d) and table III. The analysis of chemical composition on the boundary with the diffusion layer, point 9, and between precipitates, point 7 fig. 6 (c) and 7 (e, f) and table III revealed significant diversification neither in the qualitative nor in quantitative composition. The white precipitates in the diffusion zone had elevated concentration of tantalum titanium and silicon.



d.

Figure 6: Structure of overaluminising of NiCoCrAIY coatings after heat treatment at 1327K, 4h (a), fragment A (b) fragment B (c) fragment C (d).

Table II Concentration of elements in the aluminide coating shown in fig. 5(b).

	Table if Concentration of elements in the aratimitide county shown in h.g. s(o).																	
point	Al		Al Si		W T		ĩ	Cr		Co		Ni		Re		Mo		
	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %
1	13.94	6.40	22.41	10.71	4.19	13.10	1.19	0.97	9.40	8.31	9.61	9.64	32.97	32.93	4.99	15.81	1.31	2.13
2	36.88	21.53	1.95	1.18	-	-	-	-	3.11	3.50	6.21	7.92	51.85	65.87	-	-	-	-

Table III Concentration of elements in the NiCoCrAlY+Al coating in the points marked in fig. 6(b) and (c).

point	Al		Si		Y		Т	Ti		Cr		Co		Ni		a
	at. %	wt. %														
1	3.13	1.61	5.86	3.14	-	-	-	-	51.18	50.65	21.72	24.37	18.11	20.24	-	-
2	27.04	14.92	2.28	1.31	-	-	-		8.45	8.98	13.74	16.56	48.49	58.23	-	-
3	27.35	15.02	2.37	1.35	1.20	2.16	-		8.46	8.95	13.31	15.96	47.32	56.55	-	-
4	10.61	3.48	15.28	5.21	-	-	11.94	6.94	4.57	2.89	7.30	5.22	23.09	16.46	27.22	59.80
5	26.27	14.57	3.81	2.20) -	-	1.03	1.02	6.86	7.33	10.68	12.93	51.36	61.96	-	-
6	27.72	15.35	2.32	1.34	-	-	0.73	0.71	6.17	6.58	10.90	13.18	52.16	62.84	-	-

c.



Figure 7: Results of EDX analysis in the marked point shown in fig. 6(a), 6(b) and 6(c): point 1(a), 2(b), 3(c), 4(d), 5(e), 6(f).

Discussion

The process of overaluminising of MeCrAlY consists of the following mechanisms assuming as a criterion of classification, the physical phenomena influencing shaping of the structure: 1. the stage of sputtering and deposition of nickel cobalt, chromium, aluminium and yttrium from the target having these elements; 2. the stage of aluminium and silicon deposition from target with eutectic composition; 3. the stage of the exothermic reaction between aluminium and nickel contained in the alloy; 4. the stage of the diffusion growth during diffusion heating in the vacuum furnace.

The earlier investigations showed that it was possible to select such deposition parameters at which the content of Ni, Cr and Co in the coating diverges slightly from the chemical composition of targets. In the selection of deposition parameters J.A. Thornton's model [24], which formulates relationship of the coating structure with the ratio of the substrate temperature to the melting temperature of the deposited element (T_s/T_m) and argon pressure, can be used. Those parameters have an influence on the structure of the obtained coatings. Using those conclusions resulting from that model is needed and possible only in the initial period of deposition when the structure with fine thickened crystallite influencing adhesion is required.

In the next stage when high efficiency of the process is required to obtain appropriate coating thickness (to $25 \ \mu$ m) the deposition process parameters diverge greatly from the requirements resulting from Thornton's model. Shaping the MeCrAIY coating structure is conditioned by a system of the specimen rotation. Both the rate of the table rotation around main axis and the rotation of specimens around their own axis decides about configuration of the structure. Another factor influencing the MeCrAIY coating structure is a number of sources from which evaporation takes place. Two sources ensure high effectiveness and uniformity of coating.

The Al and AlSi deposition by the Arc-PVD method constituted a certain problem, though greater stability of the process was observed during the AlSi alloy deposition.

The Al or Al-Si coating immediately after the deposition was remelted on the surface of the alloy or MeCrAIY coating by an increase in the temperature. Magnitude of thermal effect after initiating the exothermic reaction depended on size of specimens and amount of the deposited aluminium (coating thickness). It has been shown that the NiAl coating structure can be shaped by changes in time of maintaining high temperature of the surface in which aluminium can react totally with the surface or the reaction can be interrupted by which the phase composition of coatings can be shaped. However after finishing the exothermic reaction in which heat came only from this reaction supplied from the external source, thin layer of the pure aluminium was always found on the surface.

An analysis of the structure of the coating obtained after the exothermic reaction showed from the surface presence of: phases-NiAl₃, Ni₂Al₃ and very thin NiAl and Ni₃Al phase zones on the boundary with the substrate. The further analysis of the Ni-base alloy aluminide coating deals with heat treatment in the vacuum at 1323K. Firstly, melting of aluminium takes place, after exceeding temperature of 933K, NiAl₃ melting after exceeding of 1127K and diffusion transformation leading to an increase in Ni₂Al₃ phase thickness. Further process of the increase in the diffusion layer in the system of Ni₂Al₃ should be considered. In a short time as a result of the Al diffusion to the substrate, the Ni₂Al₃ phase changes into NiAl>50 %at. Al phase in which there is also dominant Al diffusion and the layer growths as a result of Al diffusion to the substrate. When the NiAl<50 %at. Al phase occurs direction and kinetics of the growth change. In the NiAl <50 %at. Al phase nickel diffusion is dominant but the rate of this process is lower than in high aluminium phases [25,26]. From this moment formation process of the so called diffusion zones starts. The nickel diffusion to the substrate changes aluminium and nickel concentration in the outer zone and leads to changes in the phase composition. The temperature and time decided about final structure of the coating. An important problem to be explained is high diversification in the structure of the diffusion zone in the aluminide coatings obtained on the ZS6K and CMSX-4 alloys and the structure of the zone below the diffusion zone observed in the CMSX-4 alloy which was not seen in the coating on the ZS6K alloy.

Microphotograph of aluminide coating presented in fig. 1 shows high thickness of the diffusion zone in comparison with outer one and precipitates perpendicular to the surface and enriched in Cr, Mo, W and Ti. Such structure resulted from thermal treatment at 1323K for 3 h. The total thickness of the coatings is 41 μ m. The ratio of outer zone thickness to the transient zone can be measure of growth by Al diffusion inward and Ni diffusion outward. The ratio of the outer zone thickness to the transient zone in the aluminide coating on the ZS6K alloy was 1.6.

The structure of the coating on the CMSX-4 alloy presented in fig.3 is different from one on the ZS6K alloy for several reasons, among others: it is a Al-Si coating, the thickness of the preliminary deposited Al-Si coating was higher than Al on the ZS6K alloy, time of heat treatment of the coating on the ZS6K alloy was 3h whereas on the CMSX-4 alloy time of heat treatment was 4 h. The factors above had an influence on difference in the ratio of the outer zone thickness to diffusion one. The ratio of thickness in the coatings on the CMSX-4 alloy was 2.75 what shows significant dominance of the aluminium diffusion to the substrate over the outward diffusion of nickel.

Diversification of the structure of the zone directly beneath the diffusion zone from the substrate side requires explanation. As it is seen in fig. 1, in the coating on the ZS6K alloy directly under the diffusion zone there is a reinforcing γ phase whereas in the coating on the CMSX-4 alloy the structure of this zone is different what fig. 5 shows. This is a structure similar to one on the aluminide coatings on the single crystal alloys of the third generation. This type of microstructural instability has been found in superalloys containing high rhenium content. This instability has been termed second reaction zone (SRZ) [27] because it typically occurs beneath the diffusion zone of coatings that are typically applied to superalloys. As it is seen in fig. 5 the SRZ zone beneath the aluminide coating is about 10 μ m.

However, it was not the subject of the detailed analysis in this article, it seems that the SRZ structure is also present beneath overaluminising of NiCoCrAIY coating on the CMAX-4 alloy, fig. 6 (a,c).

Conclusion

The experimental investigations of which results are presented in this work show possibility of forming the diffusion coatings on the nickel base superalloys by the Arc-PVD method.

The concentration of elements in the MeCrAlY coatings differed insignificantly from their concentration in targets. There was a segregation of yttrium into the outer zone in the air thermally treated coatings.

The aluminide coatings, obtained in the Arc-PVD process and heated in vacuum at 1323K had the structure similar to the coatings obtained by the pack cementation process. NiAl with precipitates of phases with high concentration of Mo, W, Cr constituted the coating matrix.

In the overaluminising of NiCoCrAIY obtained by Arc-PVD and heated in vacuum the (Ni,Co,Cr,Y)Al phase contained very low amounts of detrimental elements such as Mo and W.

Forming the MeCrAIY coatings by the Arc-PVD method followed by diffusion aluminising or Al-Si process allowed to obtain coatings with the chemical composition without influence of the chemical composition of the base superalloys.

In the coatings obtained by the Arc-PVD method on the CMSX-4 alloy, presence of the SRZ zone (secondary reaction zone) was found and this zone was absent beneath the diffusion zone of coatings on a typical casting ZS6K superalloy.

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