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Influence of the content of aluminum on the structure of gradient detonation coatings based on NiCr-Al

This paper studies the effects of aluminium content in the composite powder on the structure of detonation gradient coatings based on NiCr-Al. Gradient coatings were obtained by detonation spraying with a gradual stepwise decrease in the barrel filling volume with an acetylene-oxygen gas mixture from 50% to 25%. The elemental and phase composition, microstructure and surface roughness of coatings based on NiCr-Al with different aluminium content of 15%, 20%, and 30% were investigated. By varying the aluminium content in the powder composition, coatings with a gradient structure were obtained. The study results showed that the phase composition of the gradient coating strongly depends on the mass fraction of Al. In the case of an aluminium content of 30% in the composition of the composite powder, the formation of aluminium oxide was detected. It is established that under the same detonation deposition modes, the formation of the gradient structure of coatings will strongly depend on the aluminium content in the NiCr-Al composition. The study results showed that the optimal composition of the powder is NiCr – 80% and Al – 20% to obtain NiCr-Al coatings with a gradient structure.

Keywords: NiCr-Al coatings, gradient coatings, MCrAlX coating, detonation spraying, thermal spraying, structure, SEM.

Introduction

Currently, the components of power plants are under the influence of high temperatures suffer from corrosion, oxidation, hot corrosion, etc. This is because the heat-resistant superalloys from which the components are made cannot provide simultaneous heat resistance and erosion-corrosion resistance. Therefore, protective coatings with heat resistance and wear resistance are obtained on the surface of superalloys. Among the heat-resistant protective coatings, the most common is obtaining coatings in the system MCrAlX (M = Ni, Co or NiCo; X = Y, Ce, Si, Ta) [1]. This is because the coating is heat-resistant when M and Cr provide wear and heat resistance, and Al resists oxidation of the coating, forming Al_2O_3 on the coating surface. Elements such as Y increase the adhesion of the coatings. However, the coatings of this system still require further improvement. Many Al and Cr elements in the coating composition lead to cracking of the coating. A small amount of Al causes the insufficient formation of an Al_2O_3 film on the coating surface, which prevents oxidation. Therefore, more research is being conducted to improve the exploitation properties and extend the service life of the MCrAlX coating.

In recent years, research on improving the corrosion resistance of MCrAlY coatings has mainly focused on modifying MCrAlX coatings using reactive elements by laser treatment and the production of multilayer and gradient coatings. Reactive elements or their oxides can increase the resistance of MCrAlX coatings to high-temperature corrosion and oxidation. However, there are conflicting opinions about the effect of the inclusion of reactive element oxide in the oxidising properties of MCrAlY coatings [2]. Therefore, more attention has recently been paid to multilayer and gradient coatings based on MCrAlY. The structure and chemical composition of multilayer/functional gradient materials are gradually changing to improve their properties (for example, mechanical, thermal, physical, etc.) [3–5]. Functionally graded coatings have recently been developed and successfully applied to work at high temperatures and difficult thermal conditions [4, 6, 7].

Typically, MCrAlX coatings are obtained using the following methods: electron beam physical vapour deposition (EB-PVD), thermal spraying methods [1,8]. After application, both EB-PVD and thermal spraying coatings have a relatively thin microstructure. However, a high level of Al is oxidised during thermal spraying, and, after spraying, Al_2O_3 at the coating boundaries is formed, which protects from the oxidation process. Recently, modern heat-resistant gradient coatings have been obtained by thermal spraying. According to studies by Kim et al. [9] and Choi et al. [10], functional gradient heat-resistant coatings were obtained using detonation and plasma spraying methods. They were sprayed in the form of multilayer gradient coatings in thickness. The structural characteristics of the obtained coatings based on the formation of microcracks during high-temperature operation are investigated and, accordingly, compared with homogeneous coatings. In another study, a gradient coating of MCrAlX was obtained based on three main layers: an outer layer, an Al-rich, Cr-rich middle layer, and a standard MCrAlX layer [11]. The functional gradient coating MCrAlY to hot corrosion has significantly increased compared to the homogeneous coating MCrAlY.

Our previous work [12] proposed a method for obtaining a gradient coating based on NiCr-Al by detonation spraying. The peculiarity of this method is to obtain the necessary gradient structure by changing the barrel filling volume with gas during the coating process, by managing the distribution of NiCr-Al composite powder from the substrate to the coating surface. That is, forming heat-resistant and wear-resistant in most particles Ni and Cr on the surface of substrate, and Al gradually increasing on the coating surface from the substrate to the surface, forming a large number of Al on the surface. This makes it possible to form a sufficient amount of Al_2O_3 on the coating surface. In addition, our work [13] compared the structure and properties with homogeneous and gradient coatings based on NiCr-Al obtained by detonation spraying.

The main purpose of this work is to study the effect of the mass proportion of alumina composite powder on the structure and properties of gradient coatings based on NiCr-Al.

Experimental

Heat-resistant steel 12Kh1MF was chosen as the substrate. The chemical composition of steel: 0,15% C; 0,37% Si; 0,7% Mn, 0,3% P, 1,2% Cr; 0,35% Mo, 0,3% V, 0,2% Cu. To obtain coatings, steel was cut with a diameter of 50 mm and a thickness of 3 mm and ground with P100 to P1000 SiC grinding paper. Before obtaining coating, the sample's surface was sandblasted. NiCr and Al powders (99.99%) were mixed in various ratios (Table 1) in a PULVERISETTE 23 planetary ball with a frequency of 30 Hz for 2 hours, and composite powders were prepared.

The coating was obtained on the CCDS 2000 detonation unit [14-15]. Oxygen-acetylene mixtures of O_2/C_2H_2 = 1.856 were used as explosive gas and nitrogen as a carrier gas. Gradient coatings were obtained by reducing barrel filling volume with gas from 50% to 25%. Our previous work explained the method of obtaining a gradient coating in detail [12]. Table 1 demonstrates the technological parameters for obtaining coatings.

Table 1

Technological parameters for obtaining NiCr–Al gradient coatings

№	Composition, Powder, wt %	O_2/C_2H_2	Barrel Filling Volume,%	Spray Distance, mm	Number of Shots
1	NiCr70Al30	1,856	50-25	250	40
2	NiCr80Al20	1,856	50-25	250	40
3	NiCr85Al15	1,856	50-25	250	40

We determined the phase composition of the sprayed coatings via the X-ray diffraction technique (XRD) using an X'PertPRO diffractometer with Cu-Kα radiation (λ = 2.2897 Å) at a voltage of 40 kV and a current of 30 mA. The diffractogams were decoded using the HighScore program with measurements performed in the range of 2Θ equal to 200–900 with 0.02 step size and 0.5 s/step counting time. The surface roughness of the coatings was estimated according to GOST 2789-73 using the Ra parameter by profilometer model 130. We photographed the surface of the coatings at 5× optical magnification using a metallographic microscope (Altami MET 5S model). We employed scanning electron microscopy (SEM) using backscattered electrons (BSE) at accelerated voltages of a JSM-6390LV (Jeol, Tokyo, Japan) scanning electron microscope to study the morphology of sample cross-section [16].

Results and Discussion

Gradient coatings of NiCr-Al of the various mass proportion of aluminium have been successfully obtained using the CCDS2000 single-dossier detonation unit. The cross-sectional view of the obtained coatings and coating surface roughness is shown in Figure 1. The cross-sectional surface was pickled to see the microstructure of the coating and substrate. According to the microstructure, it can be seen the ferrite-pearlite structure of the substrate and the wave-like obtained coating on the substrate. The thickness of the obtained coatings is in the range of 70–116μm. The thickest coating (116μm) was obtained in the mass proportion of Al 15%. And the coating with the smallest thickness (70 μm) Al was obtained with a mass proportion of 30%. Probably, during detonation spraying, an important content of a soft element in the composition of the powder, in our case, Al, is melted and fixed on the surface of the processed material. Particles of relatively solid elements are driven into the plastic matrix [17, 18]. The surface roughness of the obtained coating was represented in the average surface roughness according to the parameter Ra. The values of the average roughness of the coating surfaces are similar. The highest value was obtained in the Al mass proportion of 30% (Ra=6.06 μm).

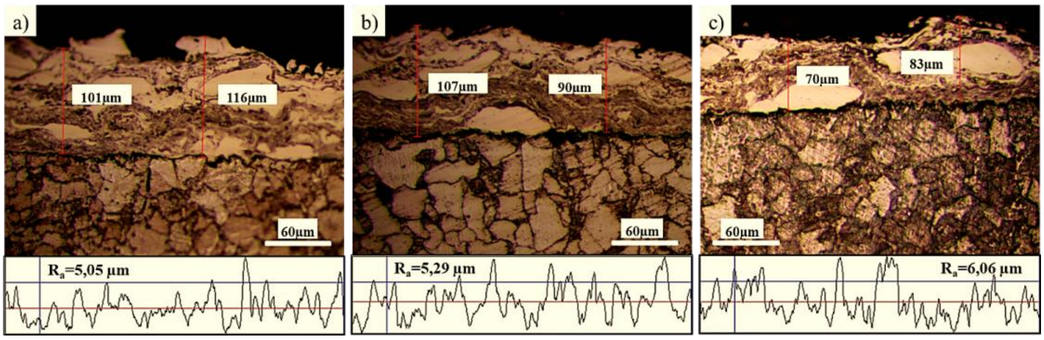


Figure 1. The microstructure results of the cross-section of the gradient coating NiCr-Al and the average surface roughness obtained with a different content of Al: a) NiCr85Al15, b) NiCr80Al20, c) NiCr70Al30

The X-ray diffraction phase analysis of the obtained gradient coatings NiCr-Al at a different mass proportion of aluminium (15%, 20%, 30%) is shown in Figure 2. Figure 2 shows that changing the mass proportion of Al leads to phase changes in the gradient NiCr-Al coatings. When the mass proportion of Al in the coating was 15% and 20%, the coating consisted of $CrNi_3$ and Al phases, and with a mass fraction of Al of 30%, it could be seen that a new phase of γ-Al_2O_3 appeared.

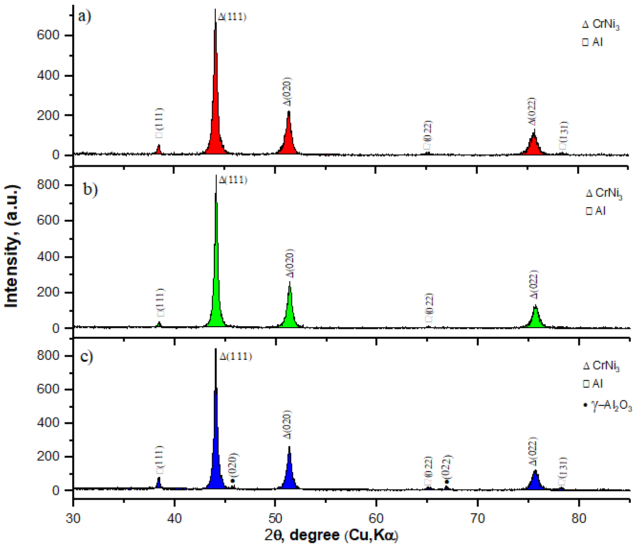
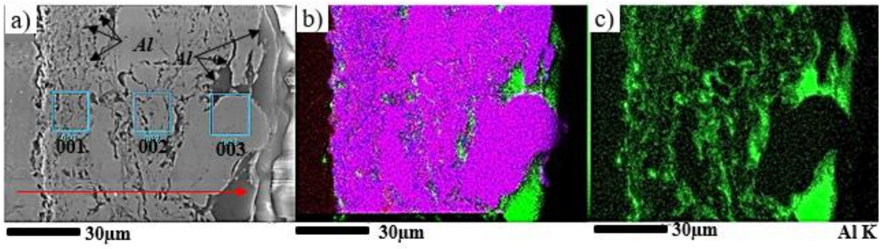


Figure 2. The result of the analysis of the X-ray phase structure of the NiCr-Al gradient coatings at various Al mass proportions: a) NiCr85Al15, b) NiCr80Al20, c) NiCr70Al30

Figure 3 represents an SEM image of the cross-section of the NiCr-Al gradient coating with a mass proportion of Al 15%, maps of the distribution of elements, EDS analysis and the results of the distribution of elements. The SEM figure of the coating cross-section (a) shows that aluminium spreads from the substrate to the coating surface, and it can be seen an increase in the amount of aluminium on the coating surface. Also, it can be sighted in the mapping of aluminium by element distribution maps (b, c) and the results of element distribution (e). However, the aluminium mapping (c) shows the uneven distribution of aluminium. Also noticed is an insufficient distribution of aluminium on the coating surface. Based on these results, the mass proportion of aluminium in 15% may not be enough to form the required amount of aluminium on the coating surface.



d)

Element	Al, Mass%	Cr, Mass%	Ni, Mass%	O, Mass%	Total, Mass%
Spectrum 001	6,92	20,99	72.09	0	100,00
Spectrum 002	7,1	20,79	68,47	3,64	100,00
Spectrum 003	7,11	20,41	70,70	1,78	100,00

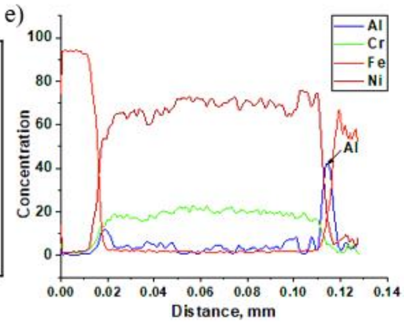
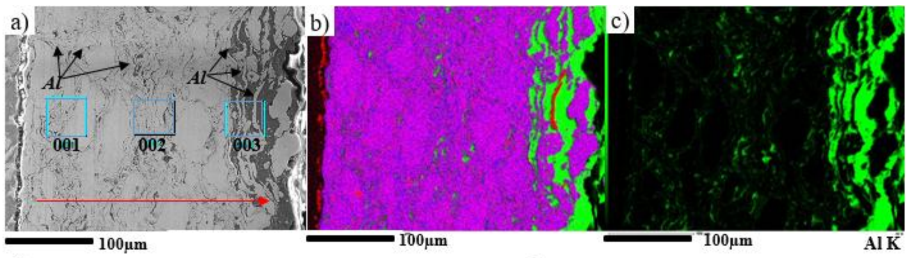


Figure 3. Gradient coating NiCr-Al with a mass fraction of NiCr85Al15: cross-sectional picture of the SEM (a), maps of the distribution of elements (b,c), the results of the analysis of EDS (d) and the distribution of elements (e)

Figure 4 illustrates the SEM image, element distribution maps, EDS analysis and element distribution results of a cross-section of the NiCr-Al gradient coating obtained at a mass proportion of Al 20%. The SEM image of the cross-section of the coating (a) shows that aluminium is gradually distributed from the substrate to the coating surface, and a large amount of aluminium is uniformly formed on the coating surface. The element distribution map (b) and the aluminium distribution map (c) also see aluminium, which increases from the substrate to the coating. The analysis of EDS (d) and the distribution of elements (e) results also confirm this. Based on these results, it can be seen that in the NiCr-Al gradient coating obtained with a 20% mass proportion of aluminium, the elements were successfully distributed over the structure. The Ni and Cr elements formed on the substrate surface ensure the wear resistance of the coating, aluminium formed in large quantities on the coating surface can form a sufficient amount of Al_2O_3 film, which resists oxidation.



d)

Element	Al, Mass%	Cr, Mass%	Ni, Mass%	O, Mass%	Total, Mass%
Spectrum 001	10.88	21,82	62,42	4.88	100,00
Spectrum 002	16.28	19,23	58,52	5.97	100,00
Spectrum 003	74.09	7,54	9,88	8.49	100,00

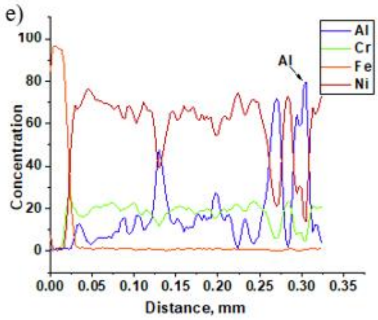
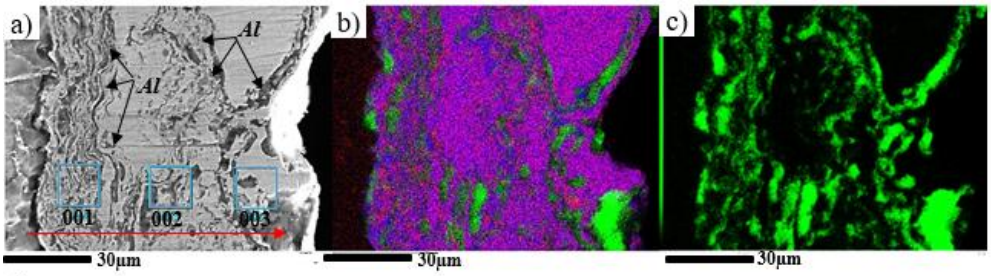


Figure 4. Gradient coating NiCr-Al with a mass fraction of NiCr80Al20: cross-sectional picture of the SEM (a), maps of the distribution of elements (b,c), the results of the analysis of EDS (d) and the distribution of elements (e)

Figure 5 shows an SEM image of a cross-section of the NiCr-Al gradient coating with a mass proportion of Al30%, maps of the distribution of elements, EDS analysis and the results of the distribution of elements. The SEM figure of the cross-section of the coating (a) shows that aluminium in large quantities and uneven spreads from the substrate to the coating surface. It can be seen in the mapping of aluminium by element distribution maps (c) and in the results of element distribution (e).



d)

Element	Al, Mass%	Cr, Mass%	Ni, Mass%	O, Mass%	Total, Mass%
Spectrum 001	22.2	10,88	27,22	39,70	100,00
Spectrum 002	34,74	8,68	25,27	31,31	100,00
Spectrum 003	27,21	15,15	37,99	19,65	100,00

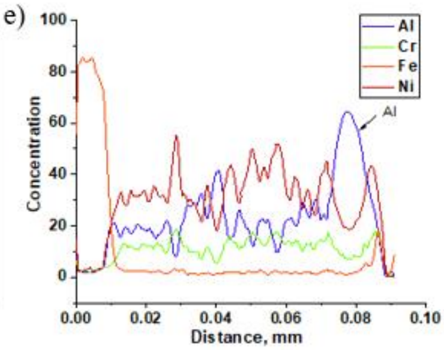


Figure 5. Gradient coating NiCr-Al with a mass fraction of NiCr70Al30: cross-sectional picture of the SEM (a), maps of the distribution of elements (b,c), the results of the analysis of EDS (d) and the distribution of elements (e)

Conclusions

Analyzing the experimental results obtained in the work, we can make the following conclusions:

– NiCr-Al coatings with a different aluminium content of 15%, 20%, and 30% were obtained by detonation spraying. The process of forming the coating structure depending on the composition of the powder was investigated. The technological mode of detonation spraying was chosen to obtain a gradient structure by gradually varying the barrel filling volume with an acetylene-oxygen gas mixture from 50% to 25% during the NiCr-Al coating process. The obtained results showed that the composite composition of NiCr – 80% and Al- 20% powder is optimal for the formation of a gradient structure of coatings with a high Al content in the surface layers of coatings;

– It was found that at 30% Al content in the coatings, aluminium oxides γ-Al_2O_3 are formed. The study results of the elemental composition of coatings by EDS analysis showed a high oxygen content in the composition of coatings obtained with the composite composition NiCr70Al30 and are consistent with the results of X-ray phase analysis.

– The study of the characteristics of coatings showed the dependence of the thickness of coatings on the composition of the composite powder. With NiCr70Al30, coatings are formed with a relatively minor thickness than NiCr85Al15 and NiCr80Al20. Probably, during detonation spraying, an important content of a soft element in the composition of the powder, in our case, Al, is melted and fixed on the surface of the processed material. Particles of relatively solid elements are driven into the plastic matrix. The study results of the microstructure of the cross-section of NiCr70Al30 coatings confirm this assumption.

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Алюминий құрамының NiCr-Al негізіндегі градиентті детонациялық жабындардың құрылымына әсері

Мақалада композиттік ұнтақ құрамындағы алюминийдің массалық үлесінің NiCr-Al негізіндегі детоанациялық градиент жабындарының құрылымына әсері зерттелді. Градиенттік жабындар оқпанды ацетилен-оттегі газ қоспасымен толтыру көлемін 50%-дан 25%-ға дейін біртіндеп азайта отырып, детонациялық бүрку арқылы алынды. NiCr-Al негізіндегі жабындардың элементтік және фазалық құрамы, микроқұрылымы және бетінің кедір-бұдырлығы 15 %, 20 % және 30 % алюминийдің әртүрлі құрамымен зерттелді. Ұнтақтың композиттік құрамындағы алюминий құрамын өзгерту әдісімен градиент құрылымы бар жабындар алынды. Зерттеу нәтижелері градиент жабынының фазалық құрамы Al массалық үлесіне қатты тәуелді екенін көрсетті. Композиттік құрамдағы алюминийдің 30% жағдайында алюминий оксидінің түзілуі анықталды. Детонациялық тозаңдандырудың бірдей режимдерінде жабындардың градиенттік құрылымын қалыптастыру NiCr-Al құрамындағы алюминий құрамынан қатты әсер ететіні анықталған. Зерттеу нәтижелері градиент құрылымы бар NiCr-Al жабындарын алу үшін NiCr 80% және Al 20% ұнтағының композиттік құрамы оңтайлы екенін көрсетті.

Кілт сөздер: NiCr-Al жабыны, градиентті жабындар, детонациялық бүрку, құрылымы, ұнтақтың композиттік құрамы.

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Влияние содержания алюминия на структуру градиентных детонационных покрытий на основе NiC–Al

В статье было изучено влияние массовой доли алюминия в составе композиционного порошка на структуру детоанционных градиентных покрытий на основе NiCr–Al. Градиентные покрытия были получены детонационным напылением с постепенным ступенчатым уменьшениием объема заполнения ствола газовой смесью ацетилен–кислород от 50 % до 25 %. Были исследованы элементный и фазовый составы, микроструктура и шероховатость поверхности покрытий на основе NiCr–Al с разным содержанием алюминия 15 %, 20 и 30 %. Методом варьирования содержания алюминия в композиционном составе порошка были получены покрытия с градиентной структурой. Результаты исследования показали, что фазовый состав градиентного покрытия сильно зависит от массовой доли Al. В случае содержания алюминия в составе композиционного пророшка 30 % обнаружено образование оксида алюминия. Установлено, что при одинаковых режимах детонационного напыления формирование градиентной структуры покрытий сильно зависит от содержания алюминия в составе NiCr–Al. Результаты иследования показали, что для получения NiCr–Al покрытий с градиентной структурой оптимальным является композиционный состав порошка NiCr 80 % и Al 20 %.

Ключевые слова: покрытия NiCr–Al, градиентные покрытия, детонационное напыление, структура, композитный состав порошка.