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DEVELOPING THE MODIFICATION OF NICKEL CATHODES FOR APPLYING THE ION-PLASMA COATINGS ON THE PARTS OF AIRCRAFT ENGINES

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This paper reports studying the effect of such highly active, surface-active modifying elements as Y, Hf, and La on the structure and properties of the Ni–Cr–Al system's consumable cathodes, which are used to apply heat-resistant coatings onto the gas-turbine engines' blades. Y, Hf, and La are introduced to form the nanoscale separation of phases that stabilize the alloy structure.

In order to obtain cathodes of the required quality, a method of vacuum-arc autocrucible melting has been chosen. The selected technique makes it possible to use raw materials of different dispersity for the manufacture of ingots (in the form of powders or pig metal). The charge was prepared by shredding the materials mechanically, using various methods (cutting and crushing).

It has been shown that the introduction of elements such as Y and La into the cathodes has a similar effect on structural formation processes. It has been established that when Hf is introduced, the structure of the resulting consumable cathodes is characterized by a greater degree of homogeneity. There is also a positive effect of Hf on the uniformity of the distribution of doping elements (Al, Cr) in the volume of the material compared to alloy samples modified by Y and La.

It has been shown that the introduction of Hf has made it possible to achieve the higher quality indicators in comparison with Y and La. An analysis of coating structure has revealed that samples with Hf have a greater degree of homogeneity and fewer defects, which is especially important when applying coatings of greater thickness (over 40 μm). It has been established that the introduction of Hf makes it possible to apply coatings up to 90 μm thick by obtaining a less defective structure. It has been found that the Hf modification increases the adhesion between the substrate and coating, as well as makes it possible to achieve maximum even distribution of doping elements throughout the entire thickness of the coating applied

Keywords: gas-turbine engine, blade, composition, modification, cathode, coating, structure, adhesion, defect, properties

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1. Introduction

The operational reliability of the gas turbine engine (GTE) blades depends primarily on the resistance of the surface to the high-temperature effects of the oxidative environment [1, 2] as the destruction of a turbine's blades mostly originates from the surface. One of the main ways to improve the resistance of blades to various types of hot corrosion is to apply protective coatings by an ion-plasma method. Therefore, the strength and durability of coatings applied directly affect the lifecycle of articles [3].

The quality indicators of heat-resistant coatings include:
– the uniformity of the chemical composition;
– the homogeneity of the structure and phase composition;
– adhesive properties;
– the uniformity of application (a layer thickness);
– manufacturability (a layer thickness, a drip phase) [4].

These parameters, in turn, depend on the characteristics of cathodes used as a consumable material in the application of coatings by an ion-plasma method.

The issue of applying the heat-resistant coatings in modern aviation engine construction is a relevant field of technology and materials science.

2. Literature review and problem statement

A comprehensive analysis of the operating conditions of the gas-turbine engines' blades and the character of their damage has led to the conclusion that there were disruptions of the protective layer integrity. The cause of such damage and decrease in the quality of coatings applied can be related to a set of factors (defects):
– the uneven coating application in the area of intense wear;
– the heterogeneity of the coating structure;
– the presence of liquation phenomena in the structure of the coating.

The existence of the aforementioned coating defects depends on the homogeneity of the structure and the chemical composition of consumable cathodes, whose quality can be ensured through the use of appropriate technology of their fabrication [5].

At present, improving the performance of the blades of gas-turbine engines made from heat-resistant alloys employs protective coatings based on the Ni–Cr–Al system (in different ratios). Nickel heat-resistant alloys are the complex multicomponent and multiphase systems. Under the influence of high temperatures and stresses, they continuously undergo phase and structural transformations, that is, in terms of the physical-chemical provisions these alloys are the dynamic systems. The use of complex doping systems is predetermined by the need to stabilize the structure, and, consequently, the properties of the coatings applied. These alloys are made with the use of modification and microalloying. Rare earth metals (REM) are generally used for these purposes, specifically yttrium [6]. The authors carried out preliminary studies into obtaining cathodes and applying protective coatings made from them on the blades of GTE with heat-resistant alloys based on Co [7] and Ni [8]. In both cases, the alloys contained up to 1.6 % of Y to improve the heat resistance of the coating.

It is known that in the production of heat-resistant alloys on a nickel basis, they are introduced with the highly active, surface-active elements (Y, Hf and La) in order to form the nanoscale separation of phases that stabilize the structure of the alloy and improve its properties. These elements actively interact with impurities – interstitial elements (mostly with carbon and oxygen) – and can form stable carbides and oxides at the phase boundary (interphase borders, clusters of dislocations, etc.). It is also possible to form excess compounds with nickel and aluminum [9].

In addition, yttrium and lanthanum are localized at the interphase boundaries and structural components, forming redundant compounds, both with nickel and aluminum and with the impurities' elements [10].

Yttrium in appropriate proportions stabilizes aluminum and chromium oxide films, improves the adhesion of applied coatings to the substrate material, increases the thermal stability of alloys, slows down the coagulation of hardening phases [9]. It was established that the yttrium, dissolved in the nickel matrix, favorably affects the heat-strength of nickel alloys, which is explained by the inhibition of diffusion processes. The introduction of yttrium in quantities exceeding its soluble limit (for nickel, it is 0.2–0.3 % by weight) leads to its separation inside and along the boundaries of the compound's grains, close to the Ni_3Y phase in its chemical composition. At the same time, there is a decrease in the short-term strength and viscosity [9].

Hf is also insoluble in solid solutions and is localized at the interphase boundaries, which leads to a similar effect.

There is almost no information about the effect of Hf and La on the characteristics of consumable cathodes (their homogeneity), and, as a result, on the properties of applied coatings. It is known that the La solubility in Ni is 0.3–0.4 %; Hf in Ni is at the level of about 2 %. La and Hf have a positive effect on the homogeneity of the chemical composition and the homogeneity of the structure of alloys on a nickel basis.

Since the quality of the cathodes used plays a fundamental role in the characteristics of the coatings applied, it is necessary to ensure that their chemical, structural, and phase homogeneity is obtained with a minimum number of defects [6, 7]. As the concentration of modifying elements is at a tenth of a percent level, their introduction and even distribution is difficult and very important. The use of vacuum-induction melt (VIM) entails a series of defects such as porosity, the existence of irregularities, neslitin, and liquation processes [7].

Given the above, the following decision was made:
– to apply the vacuum-arc autocrucible melting method to replace existing technologies in order to produce cathodes of the required quality;
– to use elements such as La and Hf as alternative micro-additives to replace yttrium in order to increase the homogeneity of the chemical composition, the homogeneity of the structure, and the manufacturability of the coating process.

3. The aim and objectives of the study

The aim of this study is to improve the quality of consumable cathodes used in the application of heat-resistant ion-plasma coatings, by selecting the optimal modification composition and devising the technology of their introduction.

To accomplish the aim, the following tasks have been set:
– to explore the impact of cathode modification on the microstructure and the distribution of doping elements in them;
– to study the impact of cathodes' composition on the quality of coatings obtained.

4. Research materials and methods

To produce ingots, an installation for the vacuum-arc autocrucible melting (Fig. 1) was used, which allows the use of fine-dispersed raw materials (in the form of powders or pig metal), which has a positive effect on the homogeneity of the ingots received [6].

The charge was prepared by shredding the materials mechanically and corresponded to the data given in Table 1.

Table 1

The chemical composition of the experimental alloys' charge

Chemical composition, % by weight						
Alloy No.	Ni	Cr	Al	Hf	La	Y
1	67.55	22.00	13.00	0.56	–	–
2	67.55	22.00	13.00	–	0.55	–
3	67.55	22.00	13.00	–	–	0.6
Transition coefficient	1.00	0.91	0.93	0.90	0.87	0.85

The following materials were used as charge materials for melting an alloy of the appropriate quality: primary aluminum (min 99.9 %) grade A99, GOST 11069-2001; metallic yttrium (99.5 %) ItM-1, TU 48-4-208-72; lanthanum brand LaM-1 GOST 23862.5-79; hafnium iodide GFI-1, GOST 22517-77; cathode nickel H1U, GOST 849-97; metallic chrome X99N1, GOST 5905-2004.

Melting was carried out in a graphite crucible with the preliminary autocrucible melting and the subsequent pouring of the melt into the graphite chill mold. The resulting ingots had the following geometric parameters: a diameter of 127 mm, a height of 45–50 mm.

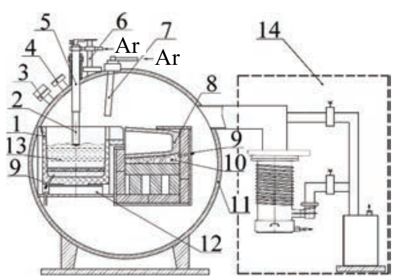


Fig. 1. VDGP installation diagram: 1 – crucible; 2 – non-consumable electrode; 3 – viewing window with video registration; 4 – viewing window; 5 – electric holder; 6 – move drive; 7 – argon feed; 8 – chill mold; 9 – thermocouple; 10 – heaters; 11 – melting chamber; 12 – anode; 13 – melt; 14 – vacuum system

Melting was carried out in the following range of the process technological modes: I=450...1,800 A, U=35...40 V, τ=25...30 min; the pre-creation of a vacuum 1×10^{-4} mbar, work environment – a mixture of Ag/He gases (70/30), pressure P=0.5 atm. The temperature of the chill mold heating, t_{cmh}=300...450 °C, the chill mold heating time before smelting was 30...35 min, the melt temperature before pouring into the chill mold, t_p=1,550...1,750 °C; cooling time is 60...90 min. The application of the above parameters allowed us to ensure high-quality melting and mixing of all components of the alloy.

The chemical composition was examined using the multipurpose raster electron microscope REM 106I, equipped with a microanalysis system.

Samples for the thin sections of structures were made by successive grinding, polishing, and etching. A metallographic study of the resulting structures was carried out using the optical and electron microscopes.

The microstructure was examined on micro thin sections using the Axio Observer. Dlm microscope, the scanning electron microscope JEOL JSM 6360LA, and the Neophot-32 inverter microscope.

The energy-dispersion analysis was carried out using the multipurpose raster microscope JSM–6360LA with an integrated microanalysis system, which makes it possible to investigate the chemical composition of local areas of the microstructure of alloys.

After the castings were received, following the chemical and metallographic studies, they were used to make (by a machining method) consumable cathodes of the required geometric sizes, which were used for coating application.

We compared the coatings applied in line with a standard technology using the cathodes obtained by VIM method and the coatings obtained on the basis of an experimental technology using cathodes after vacuum-arc melting. For comparative studies, we selected the cathodes modified with yttrium, as the only composition used in the industrial production, and an experimental one. The chemical composition of the coating was determined by X-ray spectral microanalysis (RSMA).

5. Results of the work carried out on the modification of the chemical composition of nickel cathodes

5. 1. Studying the structure and chemical composition of experimental cathodes

The results of studying the chemical composition of the ingots obtained are given in Table 2.

Table 2

Chemical composition of experimental alloys containing various REM

Alloy	Chemical composition Basic elements, % by weight						
	Ni	Cr	Al	Hf	La	Y	impurities
1	Main	18–22	11–13	0.3–0.6	–	–	≤1.5
2	Main	18–22	11–13	–	0.3–0.6	–	≤1.5
3	Main	18–22	11–13	–	–	0.3–0.6	≤1.5

The results of the analysis of the microstructure and the distribution of the elements are shown in Fig. 2–4.

The comparison of the results of metallographic studies of the microstructure of experimental samples (Fig. 2–4, *a*) suggests that the introduction of elements such as Y and La has a similar effect on the structure-forming processes. The modification of Y and La makes it possible to obtain a homogeneous enough structure of samples. At the same time, when Hf was introduced (Fig. 4, *a*), the resulting structure was more homogeneous than that modified with Y (Fig. 2, *a*) and La (Fig. 3, *a*). There is also a noticeable positive effect of Hf (Fig. 4, *b–e*) on the uniform distribution of doping elements (Al, Cr) in the volume of the material compared to samples with Y (Fig. 2, *a–e*) and La (Fig. 3, *a–e*). It should also be noted that in comparison with Y (Fig. 2, *e*) and La (Fig. 3, *e*), Hf (Fig. 4, *e*) has the highest level of distribution by the area of the thin section. This ensures a more homogeneous structure with the minimal phenomena of liquation processes.

An analysis of the results obtained allows us to conclude that all experimental alloys obtained by arc smelting have a homogeneous structure with a uniform distribution of doping elements, which is confirmed by the distribution maps of the latter over the area of the thin section. Regardless of the use of the modifying element, the structure of the alloys examined lacks characteristic defects in the form of irregularities or pores. These data make allow us to conclude that it is possible to obtain a coating with high quality characteristics and a higher level of homogeneity of the structure and uniformity of coating application on the material of the substrate.

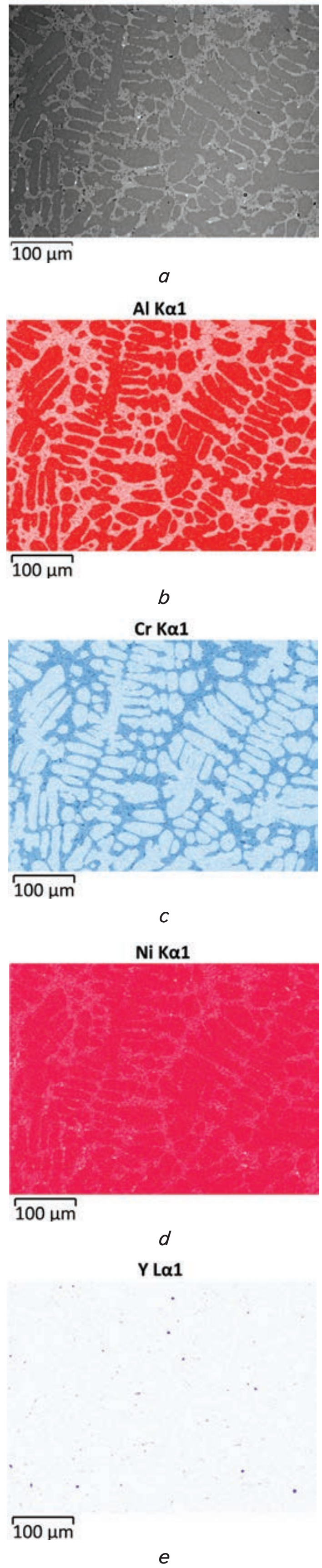


Fig. 2. The microstructure and distribution of elements in the structural components of the Ni–Cr–Al–Y alloy system: *a* – microstructure of the sample; *b* – Al distribution; *c* – Cr distribution; *d* – Ni distribution; *e* – Y distribution

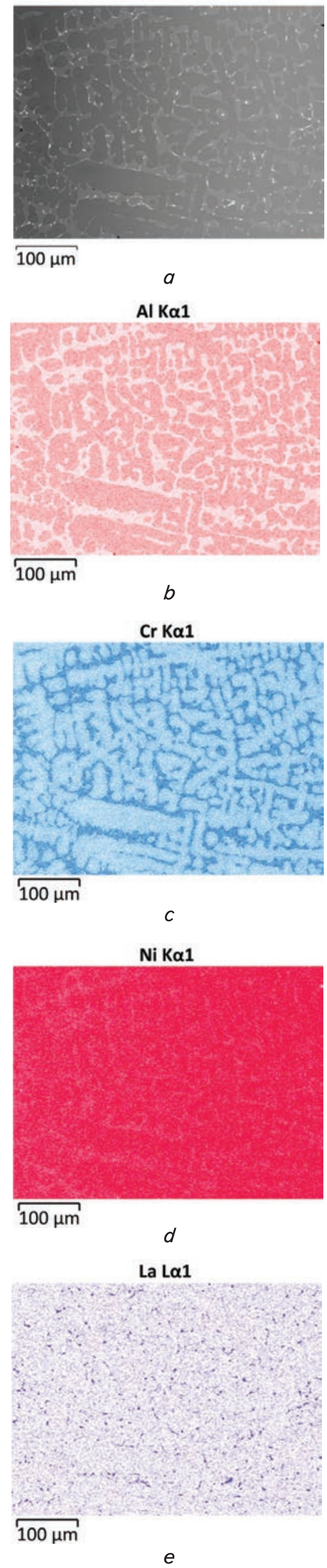


Fig. 3. The microstructure and distribution of elements in the structural components of the Ni–Cr–Al–La alloy system: *a* – a microstructure of the sample; *b* – Al distribution; *c* – Cr distribution; *d* – Ni distribution; *e* – La distribution

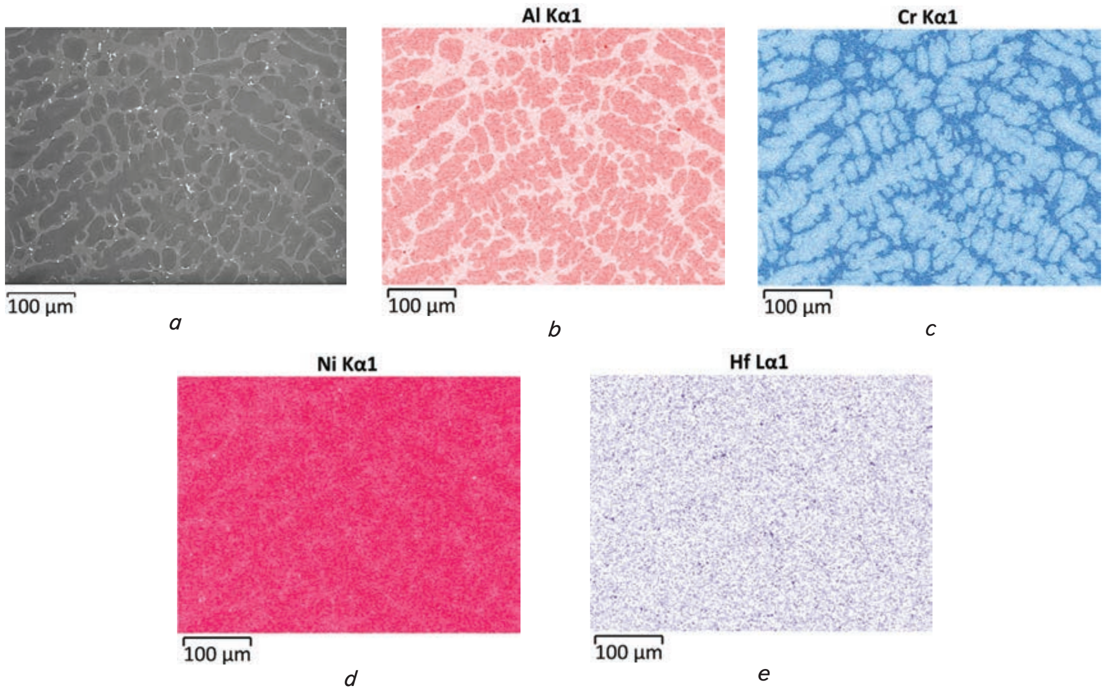


Fig. 4. The microstructure and distribution of elements in the structural components of the Ni–Cr–Al–Hf alloy system: *a* – a microstructure of the sample; *b* – Al distribution; *c* – Cr distribution; *d* – Ni distribution; *e* – Hf distribution

5. 2. Studying the coatings applied by experimental cathodes

The results of the analysis of the resulting coatings are shown in Fig. 5–7.

The metallographic studies of the microstructure of the resulting coatings (Fig. 5–7, *a, b*) show that the introduction of Hf as a doping element has achieved the best quality indicators of applied coatings in comparison with Y and La. An analysis of the coating structure revealed that samples with Hf have a greater degree of homogeneity and fewer defects. This is especially important when applying coatings of greater thickness (above 40 μm) because an increase in the thickness of the coating inevitably leads to an increase in the total number of defects. The introduction of Hf makes it possible to apply coatings up to 90 μm thick through obtaining a less defective structure. It was established that Hf modification makes it possible to increase the adhesion of the coating material with a substrate, compared to Y and La.

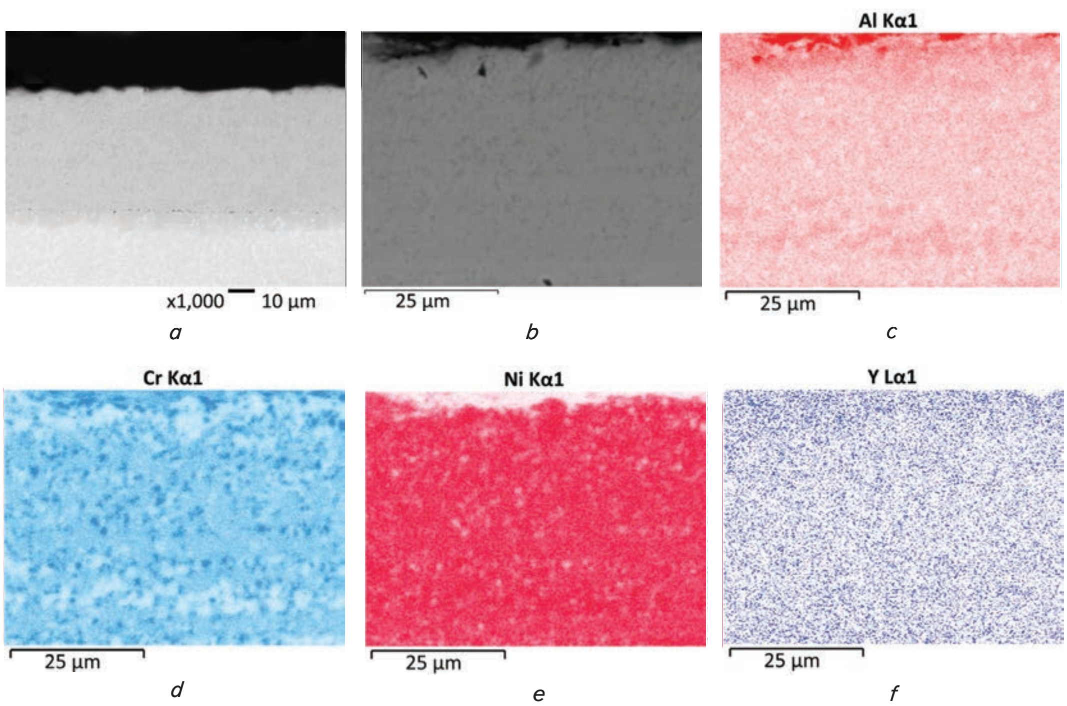


Fig. 5. The microstructure and distribution of elements in a coating (Ni–Cr–Al–Y system): *a, b* – the microstructure of the coating; *c* – Al distribution; *d* – Cr distribution; *e* – Ni distribution; *f* – Y distribution

And most importantly, in our view, that the Hf modification makes it possible to achieve the maximally even distribution of the doping elements (Fig. 7, *c*–*e*) throughout the entire thickness of the applied coating, that is, to reduce the negative impact of the liquation processes to a minimum. It is shown that in samples modified with Hf, the even distribution of Cr is not inferior to samples with Y. All the above positively affects the technological parameters and the uniformity of application, as well as the operational properties, in particular the heat resistance of coatings modified with Hf.

An analysis of the results obtained led to the conclusion that there is a correlation between the homogeneity of the structure and the chemical composition of consumable cathodes and the coatings applied using them. All coating variants are characterized by a high enough structure homogeneity and minimal liquation with a slight advantage of the coating obtained using the cathode doped with Hf. All this is the basis for further experiments, as well as research into the joint influence of Hf, La, and Y on the quality of cathodes and the resulting coatings.

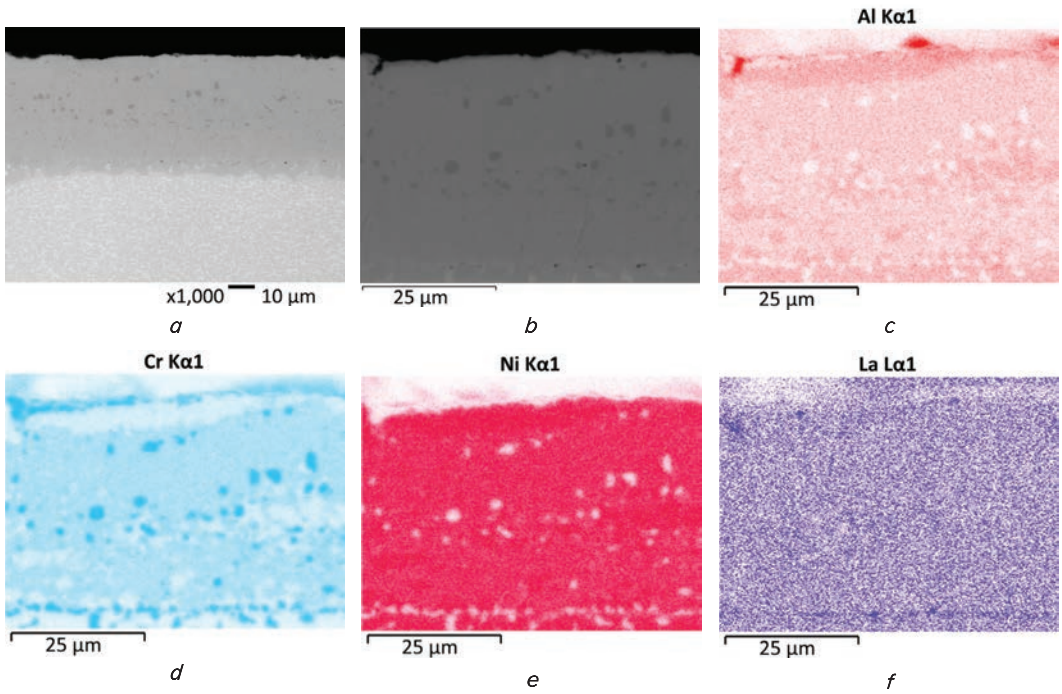


Fig. 6. The microstructure and distribution of elements in a coating (Ni–Cr–Al–La system): *a, b* – the microstructure of the coating; *c* – Al distribution; *d* – Cr distribution; *e* – Ni distribution; *f* – La distribution

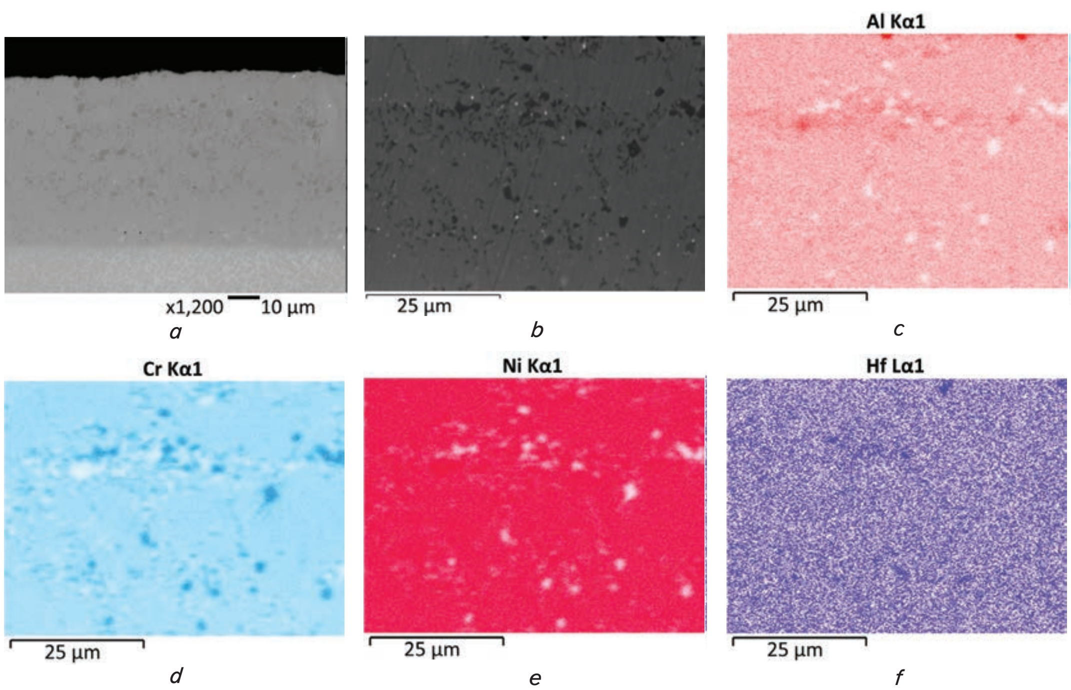
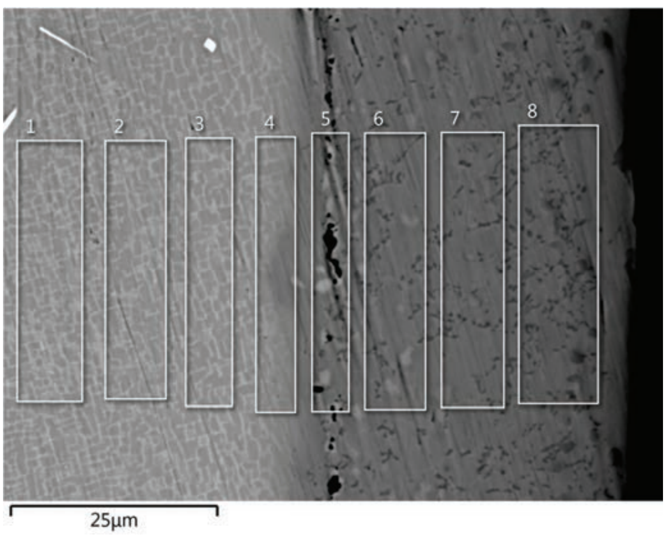


Fig. 7. The microstructure and distribution of elements in a coating (Ni–Cr–Al–Hf system): *a, b* – the microstructure of the coating; *c* – Al distribution; *d* – Cr distribution; *e* – Ni distribution; *f* – Hf distribution

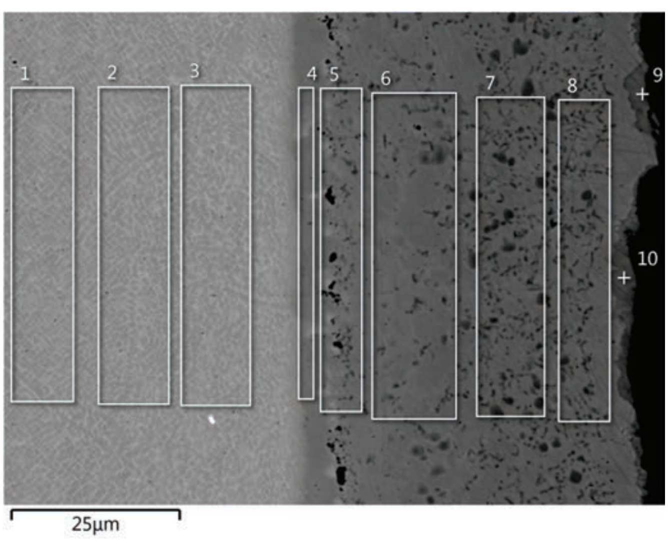
Examining coatings applied by the standard and experimental technologies.

The coating thickness for both technologies is the same and is 45...50 μm. A visual examination under the binocular showed that the coatings obtained by the standard technology (Fig. 8, *a*) and the experimental cathode (Fig. 8, *b*) were evenly applied. No chips or mechanical damage were found. The surface of the blades revealed a drip phase, whose size is within 0.01...0.08 mm (Table 3).

The coating, applied by the standard technology, revealed local areas of increased porosity, both the coating itself and the areas of its joint with the material of the substrate, which negatively affects the strength and operational properties of the coating and the product in general. The presence of a large number of different types and shapes of irregularities in the transition zone (substrate–coating) indicates the unsatisfactory adhesive properties of the material applied. The results of RSMA (Fig. 8, *a*) revealed the presence of significant structural heterogeneity of the applied coating, the presence of liquation processes, and a low depth of the diffusion layer.



a



b

Fig. 8. Areas on the coating, selected to determine the chemical composition: *a* – standard technology; *b* – cathode with experimental composition

Table 3

The number and size of the drip phase at the coating surface

Cathode	Drop fraction size, number per unit		
	0.01...0.02	0.02...0.04	0.04...0.08
Standard	142	84	5
Experimental	64	58	3

In comparison with the coating applied by standard technology (using cathodes obtained by regular methods), it can be noted that the amount of a drip phase is much smaller, which favorably affects the roughness of the coating in general. In addition, there is a significant reduction in the porosity of the coating and the area of the joint. There is also an increase in the adhesion properties of the material applied with the substrate material (a blade), an improvement in the structural homogeneity of the coating, an increase in the transitional diffusion zone, and almost complete absence of liquation phenomena (Fig. 8, *b*).

An analysis of Fig. 8 showing the results of studying the chemical compositions of the applied coatings makes it possible to draw conclusions that the homogeneity, dispersity, and homogeneity of the microstructure are observed when using cathodes obtained by the method of a vacuum-arc melting. It can be assumed that the comprehensive impact of elements such as Y, Hf, and La could have a more beneficial effect on the homogeneity of the structure and composition of the alloy and the elimination of liquation processes, which is an important issue for further research.

6. Discussion of results of studying the effect of modification on the characteristics of cathodes and the resulting coatings

The use of the arc melt method makes it possible to achieve a higher degree of the structure homogenization and even distribution of the doping and modifying elements in comparison with an induction melt technology.

Based on the results of studying the use of the modifiers La, Y, Hf, a series of new data on the impact on the structure were found.

The introduction of Hf, in comparison with Y and La, has a more significant impact on the change in structure. This is manifested in a greater degree of homogeneity of the structure (as seen in Fig. 2–4, *a*), as well as a more even distribution of the doping elements (Al, Cr) in the volume of the material (Fig. 2–4, *b, c*).

Our study of the microstructure (Fig. 5–7, *a*, *b*) and chemical composition of the coating (Fig. 5–7, *c–f*) has established patterns in the formation of a microstructure of the resulting coatings, which indicate that the introduction of Hf makes it possible to achieve the best quality indicators of the applied coatings. This is expressed in the minimal liquation of the doping elements, greater homogeneity and fewer defects, better adhesion of the coating material with a substrate (Fig. 8, *b*).

All this shows the possibility of regulating the processes of forming a quality coating structure. The application of a comprehensive modifier, which contains Hf and La, makes it possible to increase the thickness and heat resistance of the coating, and, as a result, the resource of its operation.

The application of the proposed vacuum-arc autocrucible melting technology, instead of the induction melt technology used, makes it possible to achieve the higher qualitative indicators of consumable cathodes. This is achieved by forming a more homogeneous cathode structure with an even distribution of the doping elements.

The implementation of experimental (with the introduction of modifiers) compositions, obtained as a result of this work, makes it possible to increase the manufacturability of applied coatings, reduce the total number of defects in the form of irregularities or pores both in the thickness of the coating and in the transition zone (substrate-coating), thereby increasing the adhesion of the coating material to the substrate.

The introduction of Hf into the nickel-based cathodes makes it possible to achieve a high homogeneity of the structure and chemical composition of the coatings applied, thereby minimizing the negative impact of the liquation phenomena. The manufacturability of the coating application process also improves by reducing the time and increasing the maximum thickness of the coating applied. This makes it possible to apply gradient coatings with an increase in the thickness of the layer in places of intense wear.

7. Conclusions

1. We have established the effect of modifiers on the processes of structure formation and the distribution of doping elements. Th introduction of Hf to the consumable cathodes on a nickel basis in the form of a modifying element makes it possible to achieve greater dispersity and, as a result, the homogeneity of the structure of the cathode and coating. The sizes of phases containing aluminum and chromium are between 10 and 80 μm, which is much smaller than the size of similar phases in the cathodes modified by Y and La. the morphology of these phases is different. The structural components containing aluminum have a more proper elongated shape without sharp angles. This is also the case for the cathodes modified by Y and La, but the samples with Hf are distinguished by the larger dispersity (80 μm vs. 200 μm), the homogeneity of the morphology and distribution throughout the volume of the material. Chromium phases, in contrast, are characterized by extensive morphology, but, compared to the samples containing Y and La, the samples modified by Hf have much greater dispersity and homogeneity.

2. Experimental processes of spraying protective coatings on a nickel basis have been carried out. It has been established that the use of cathodes, obtained by the experimental technology, reduces the amount of a drip phase by 65 %. It has been found that the introduction of modifying elements improves the adhesion of the coating with the material of the substrate by 40 % thereby reducing the number of defects (in the form of irregularities and pores). The use of the experimental cathodes makes it possible to increase the thickness of the applied coating over 40 μm (current technology) to 90 μm.

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