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PROPERTIES OF MULTILAYER PLASMA COATINGS FROM MATERIALS BASED ON M-CROLL

The article describes the structures and properties of m-croll plasma powder coatings deposited under optimal conditions. Most of the modern nickel-based alloys used in technology used to form plasma coatings contain 6-12% aluminum, 20-30% chromium, and 0.15-1.0% reactive element (yttrium, tantalum, etc.). With an increase in the concentration of the reactive element, the production of new oxide grains during deposition inside the film itself is inhibited and, in the presence of more than 0.82% yttrium, it completely stops, and the rate increases with oxygen diffusion. This is caused by a significant refinement of the oxide film and alloy grains and the formation of yttrium-rich phases - Ni5Y, Ni9Y, Ni3Al2Y, (NiCo)4.25Al0.15Y, which have low resistance to high-temperature oxidation. All this should be taken into account during the formation of the coating when optimizing the content of rare earth (REM) metals in the alloy. Consequently, the introduction of reactive elements into the plasma coating contributes to the absence of stresses in the film caused by internal oxidation. However, an increase in the concentration of the reactive element is limited by an increase in the oxygen diffusion rate and the processes of alloy embrittlement. Therefore, most NiCrAlYTa alloys for sputtering are limited in oxygen content to 0.05%. The mechanical properties of alloys are significantly improved when they are alloyed with tantalum, niobium, and titanium, since in their presence a superlattice of the β-phase (Ni2AlTa, Ni2AlNb) is formed due to the ordering of elements in the aluminum sublattice. However, the formation of such a superlattice requires a concentration of elements that exceeds a certain limit. Niobium has a positive effect on the heat resistance of the NiCrAlI alloy, but reduces its corrosion resistance. Tantalum has the most favorable effect on both the mechanical and protective properties of MCrAlI alloys. In addition to participating in the formation of the β-phase superlattice, tantalum increases heat resistance and resistance to high-temperature salt corrosion of grain boundaries, segregating primarily in the alloy regions, and also binds free carbon into carbides. All refractory elements form inclusions, which in most cases reduce the diffusion mobility of atoms in the coating. High-quality wear-resistant coatings based on titanium dioxide - aluminum oxide and nickel-chromium-aluminum-yttrium-tantalum alloy must be formed from materials with strictly defined sizes and morphology of the particles of the initial powder, with a chemical and phase composition uniform over the cross section of the initial powders and a minimum grain size of phase inclusions.

***Keyword**s plasma spraying processes, powder compositions, plasma spraying in air, nickel-based metal alloys, oxide ceramics, performance characteristics, morphology and structure.*

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СВОЙСТВА МНОГОСЛОЙНЫХ ПЛАЗМЕННЫХ ПОКРЫТИЙ ИЗ МАТЕРИАЛЛОВ НА ОСНОВЕ М-КРОЛЕЙ

В статье описаны структуры и свойств напыленных при оптимальных режимах плазменных порошковых покрытий из м-кроллей. Большинство современных используемых в технике сплавов на основе никеля применяющихся для формирования плазменных покрытий, содержат 6-12 % алюминия, 20-30 % хрома, а также 0,15-1,0 % реактивного элемента (иттрия, тантала и др.). При увеличении концентраций у реактивного элемента получение новых зерен оксидов при напылении внутри самой пленки тормозится и при наличии иттрия более 0,82 % полностью останавливается, увеличивается скорость при диффузии кислорода. Это вызвано значительным измельчением оксидной пленки и зерна сплава и образованием богатых иттрием фаз - Ni_5Y, Ni_9Y, Ni_3Al_2Y, $(NiCo)_{4,25}Al_{0,15}Y$, обладающих низкой стойкостью к высокотемпературному окислению. Все это должно учитываться во время формирования покрытия при *оптимизации содержания редкоземельных (РЗМ) металлов в сплаве. Следовательно, введения реактивных элементов в плазменное покрытие способствует отсутствию напряжений в пленке, вызываемых внутренним окислением. Тем не менее, увеличение концентрации реактивного элемента ограничено ростом скорости диффузии кислорода и процессами охрупчивания сплава. Поэтому большинство NiCrAlYTa сплавов для напыления имеют ограничения по содержанию кислорода до 0,05 %. Механические свойства сплавов значительно улучшаются при легировании их танталом, ниобием, титаном, так как в их присутствии образуется сверхрешетка β-фазы (Ni_2AlTa, Ni_2AlNb) благодаря упорядочению элементов в алюминиевой подрешетке. Однако, для образования такой сверхрешетки необходима концентрация элементов, превышающая некоторую предельную. Ниобий оказывает положительное влияние на жаростойкость сплава NiCrAlI, но снижает его коррозионную стойкость. Наиболее благоприятное влияние как на механические, так и на защитные свойства сплавов MCrAlI оказывает тантал. В дополнение к участию в образовании сверхрешетки β-фазы, тантал увеличивает жаростойкость и стойкость к высокотемпературной солевой коррозии границ зерен, сегрегируя прежде всего в областях сплава, а также связывает свободный углерод в карбиды. Все тугоплавкие элементы образуют включения, которые в большинстве случаев снижают диффузионную подвижность атомов в покрытии. Качественные износостойкиепокрытия на основе диоксида титана - оксид аллюминия и никель-хром-алюминий-итрий-танталового сплава необходимо формировать из материаловпри строго определенных размерах и морфологии частиц у исходного порошка, с равномерным по сечению исходных порошков химическим и фазовым составом и минимальным размером зерна фазовых включений.*

Ключевые слова: *процессы плазменного напыления, порошковые композиции, плазменное напыление на воздухе, металлические сплавы на основе никеля, оксидная керамика, эксплуатационные характеристики, морфология и структура.*

1. Introduction

Almost all oxide powder materials used for deposition of wear-resistant plasma coatings have a fairly high melting point. The main properties of these materials include their low electrical and thermal conductivity characteristics. The vast majority of oxides are characterized by high hardness and the ability to resist wear. They can also be used as electrical insulating, heat-shielding, decorative, corrosion-resistant. Due to the low-cost factor of the used powders of industrial oxide materials and their versatility, they contribute to the widespread introduction of sprayed wear-resistant coatings based on them [1–7]. Probably the most common disadvantage as a result of the process of plasma spraying of oxide materials is the partial delamination of the formed coatings, as a rule, if the values of the thermal expansion coefficients of the product sprayed by the plasma and the oxide powder coating do not match [8]. To significantly improve the quality characteristics of oxide plasma powder coatings (porosity, cohesive and adhesive strength, plasticity), plastic components based on metallide-type alloys are added to them, for example, NiAl, NiCr and NiCrAlY powder compositions. To significantly increase the antifriction properties of ceramic powder plasma coatings under operating conditions at high temperatures, it is necessary to introduce a nickel-chromium-aluminum-yttrium-tantalum composition into the composition of the powders [9–11]. During the last decades, M-rabbit coatings (MeCrAlY, where Me is Ni, Co, Fe) have been studied as oxidation/corrosion resistant coatings, and the MeCrAlY alloy has been used not only as a separate coating, but also as a bond coating for plasma thermal barrier coatings (TBC). Due to their excellent strength properties, high hardness, low density, oxides are widely used as a matrix for plasma-sprayed composite coatings. In the present study, NiCrAlYTa/oxide ceramic composite plasma coatings will be obtained by air sputtering. Formed plasma coatings based on the titanium dioxide-aluminum oxide-nickel-chromium-aluminum-yttrium-tantalum powder composition have increased temperature and impact resistance, ductility, structure homogeneity, and minimal total porosity in comparison with the titanium dioxide-oxide powder system. aluminum [12]. The main feature of nickel-chromium-aluminum-yttrium-tantalum powder material is the ability to plastically relax stresses during deposition. The reason for their occurrence is an inconsistent change in the volumes during heating and cooling of the ceramic coating and the materials of the sprayed base of the part. As a result of high-temperature oxidation during operation, the plasticity of the metal base of the product deteriorates significantly, while the layer of ceramic formed during deposition is permeable to gases, so it is necessary to add a material with impact strength and high heat-resistance characteristics to ceramics.

2. Study of the structure and properties of plasma-sprayed ceramic powder coatings under optimal conditions

Figure 1 shows the appearance of the Al2O3-TiO2-NiCrAlYTa coating applied by plasma spraying. It can be seen from the figure that the coating has a good density and no surface defects such as cracks are visible. Al2O3-TiO2 ceramic aggregates are bound to each other, and some of the large-sized ceramic particles are embedded in the molten NiCrAlYTa coatings. Such microstructural characteristics are associated with the mobility of molten liquid-phase NiCrAlYTa components, which can fill the gaps and cracks that occur during the plasma deposition of an oxide coating and improve the coating density. Figure 2 shows the microstructures of composite coatings NiCrAlYTa / Al2O3-TiO2-NiCrAlYTa wt.% Analysis of the microstructures shows that the Al2O3-TiO2 ceramic phase looks dark gray, while the NiCrAlYTa phase looks light gray. It can be seen from the microstructure that the composite coatings are dense and uniform, pores can be observed, while the quality of the intercontact contacts is good for all coatings. It can also be seen that NiCrAlYTa is present in the coatings in the form of thin plates. As shown in Figure 2, particle structures are the result of remelted or non-melted feedstock particles. Lamellar microstructures indicate that the sprayed droplets have not yet solidified before impact, impacting the substrate or previously deposited layers at high speed. The degree of particle melting largely determines the porosity, microhardness, and subsequent properties of the coating. It is noticeable that a mutually displaced structural grid is present at the substrate-coating boundary.

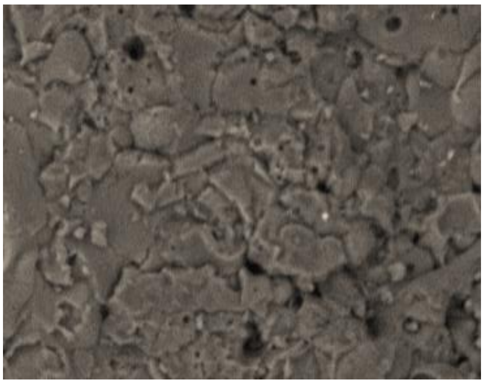


Figure 1. Images of the surface areas of the formed wear-resistant coating from Al2O3-TiO2-NiCrAlYTa powder material (×1000)

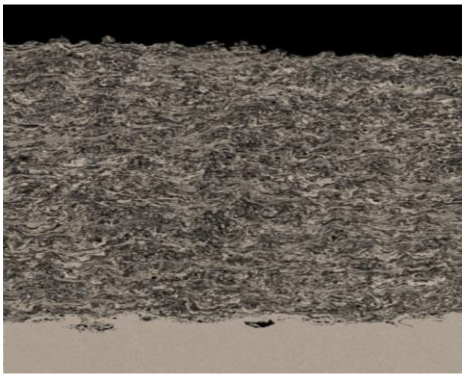
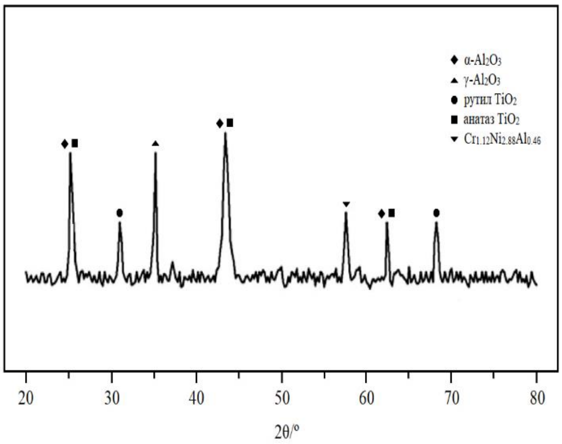


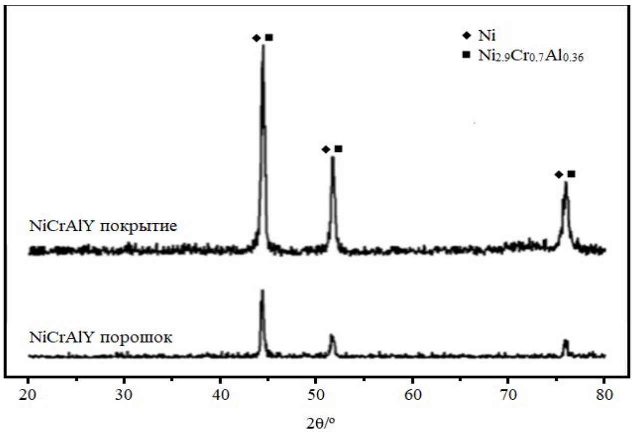
Figure 2. Microstructure of the cross-section of the deposited composite coatings NiCrAlYTa / Al2O3-TiO2 (×500)

Figure 2 shows the microstructures of composite coatings NiCrAlYTa / Al2O3-TiO2-NiCrAlYTa wt.% Analysis of the microstructures shows that the Al2O3-TiO2 ceramic phase looks dark gray, while the NiCrAlYTa phase looks light gray. It can be seen from the microstructure that the composite coatings are dense and uniform, pores can be observed, while the quality of the intercontact contacts is good for all coatings. It can also be seen that NiCrAlYTa is present in the coatings in the form of thin plates. As shown in Figure 2, particle structures are the result of remelted or non-melted feedstock particles. Lamellar microstructures indicate that the sprayed droplets have not yet solidified before impact, impacting the substrate or previously

deposited layers at high speed. The degree of particle melting largely determines the porosity, microhardness, and subsequent properties of the coating. It is noticeable that a mutually displaced structural network is present at the substrate-coating boundary.



a)



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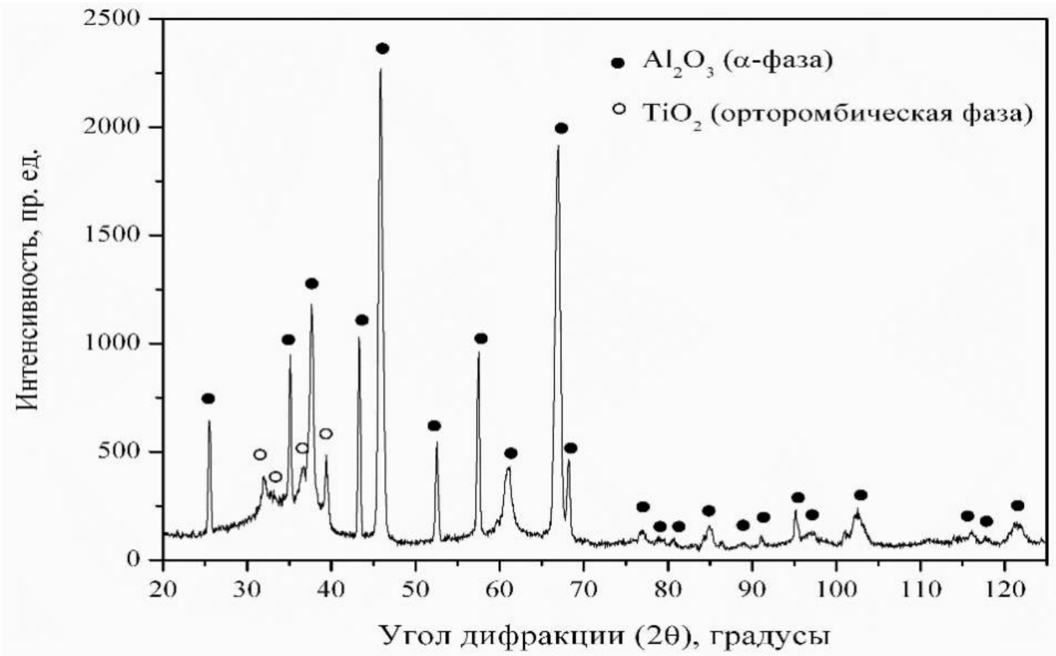

c)

Figure 3. X-ray pattern of the coating: a- NiCrAlYTa-Al_2O_3-TiO_2; b NiCrAlY; c- Al_2O_3-TiO_2

It can be seen from the obtained Al2O3-TiO2-NiCrAlYTa structure that the thickness of the formed coating layer is approximately 50 μm. Its elemental analysis confirmed the presence of aluminum, oxygen, yttrium, tantalum, nickel in it with a uniform distribution along the entire thickness of the layer of these. For comparison, Figure 3b shows the X-ray diffraction patterns of the NiCrAlY powders and the plasma-sprayed NiCrAlY coating. It can be seen from the figure that NiCrAlY contains mainly homogeneous Ni crystals and the composite phase Ni2.9Cr0.7Al0.36; after plasma deposition, a new crystalline phase is not formed, and the intensity of the diffraction peak of all crystalline phases increases significantly, which indicates that that, as the sputtering process continues, the crystallinity of the NiCrAlY powders increases somewhat due to the high-temperature melting effects. Table 2 shows the calculated contents of homogeneous Ni and Ni2.9Cr0.7Al0.36 crystals in the NiCrAlY phase. This shows that the Ni2.9Cr0.7Al0.36 composite phase occupies most of the system. After plasma spraying, the content of the homogeneous Ni crystalline phase decreases, while the content of Ni2.9Cr0.7Al0.36 increases, indicating that the spraying process is favorable for the crystallinity of the internal elements in the system. The conclusion is consistent with the intensity trend of the diffraction peak. The elemental composition of the resulting two-layer composite plasma coatings based on Al2O3 and TiO2 oxides was studied using the energy-dispersive X-ray spectral microanalysis. The obtained elemental composition of the formed protective coatings is given in Table 3. Using the obtained spectra of characteristic X-rays, when recorded on layers with a thickness of about 1–2 μm, a detailed analysis of the obtained elemental composition was carried out from the surface. The upper layer of the formed wear-resistant coating contains approximately 67.2% oxygen atomic fractions and 32.0% aluminum atomic fractions, which exceeds the stoichiometry of aluminum oxide. The resulting coating in the form of TiO2 - titanium oxide contains an excess fraction of atoms and about 0.6% atomic fractions of titanium, due to the presence of impurities in the source material of the powder in the surface layer, there are 0.2% atomic fractions of silicon. Figure 4 shows the resulting structure of the surface layer of the plasma coating on a transverse section. It can be seen from the given data that in the initial state, the near-surface layer of the formed coating is characterized by a large number of defects - pores, splits, microcracks, propagating in different directions deep into and along the surface.

Table 1. The content of phases in the NiCrAlY- Al_2O_3-TiO_2 coating after plasma spraying

Phase components	α-Al_2O_3	γ-Al_2O_3	rutile TiO_2	anatase (TiO_2)	$Cr_{1,12}Ni_{2,88}Al_{0,46}$
Components, %	30,4	6,6	15,4	32,2	15,4

Table 2. Content of phases in NiCrAlY powder and coating

Components	Ni, % conten	$Ni_{2,9}Cr_{0,7}Al_{0,36}$, % conten
NiCrAlY powder	14,37	83,21
NiCrAlY coating	11,42	87,53

Table 3. Formed elemental composition in the initial state (obtained coating)

Elements Present	Percent Concentration	
	in weight fractions	in atomic fractions
aluminum	43,7	32,0
titanium	1,4	0,6
silicon	0,4	0,2
oxygen	54,5	67,2

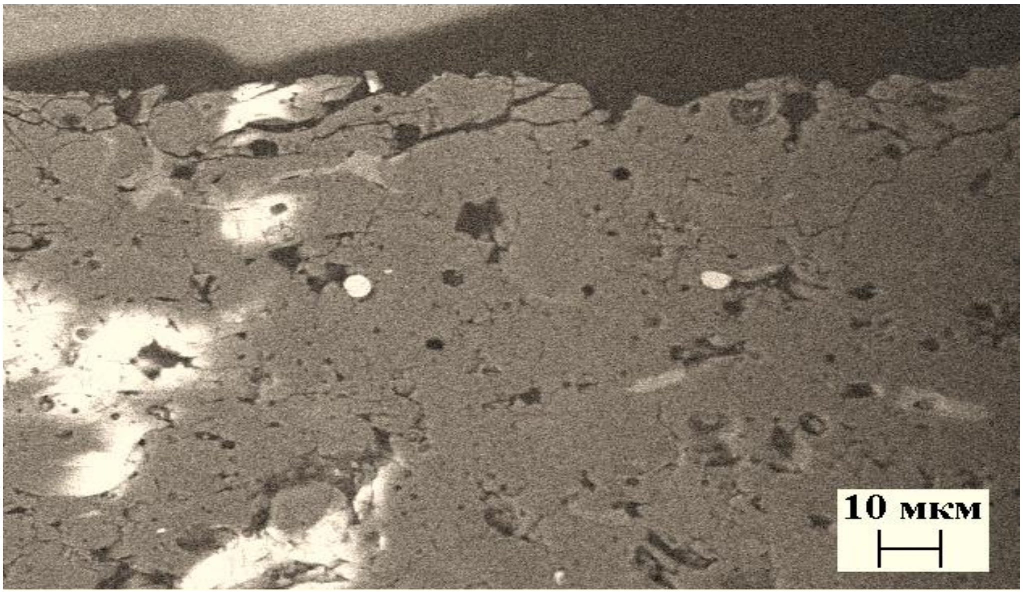

Figure 4. The resulting structure of the surface layer of the plasma coating (transverse section)

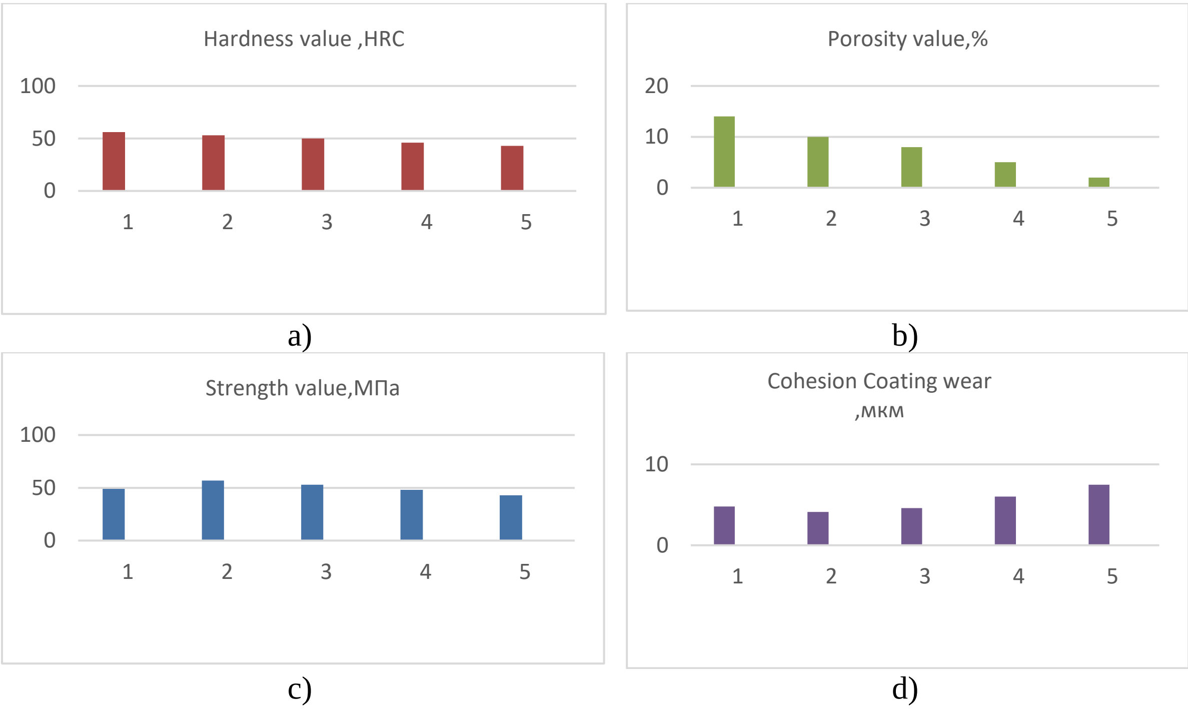

Figure 5. Characteristics of sprayed wear-resistant coatings: a - hardness; b - porousness; c - adhesion strength; g - wear resistance (1-70 % Al_2O_3-TiO_2 – 30 % Ni-Cr-Al-Y-Ta; 2 – 60 % Al_2O_3-TiO_2 – 40 % Ni-Cr-Al-Y-Ta; 3-50 % Al_2O_3-TiO_2 - 50% Ni-Cr-Al-Y-Ta; 4-40 % Al_2O_3-TiO_2 – 60 % Ni-Cr-Al-Y-Ta; 5-30 % Al_2O_3-TiO_2 – 70 % Ni-Cr-Al-Y-Ta)

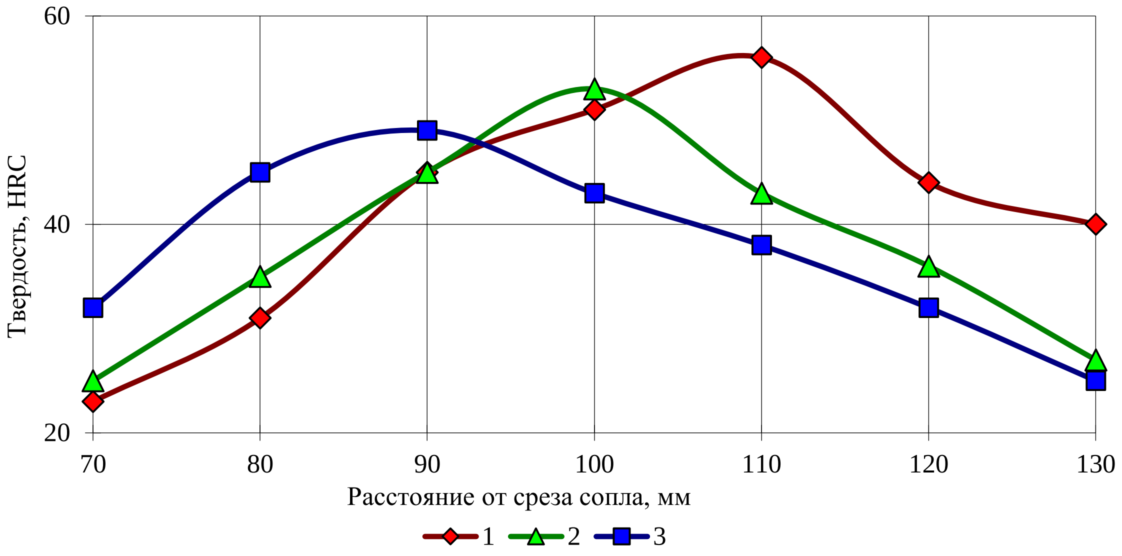

Figure 6. Dependence of hardness (HRC) on the distance from the surface to the cut of the plasma torch nozzle during spraying, mm for powders NiCrAlITa-Al_2O_3-TiO_2 (1 – 70 % Al_2O_3-TiO_2 - 30 % Ni-Cr-Al-Y-Ta; 2 – 60 % Al_2O_3-TiO_2 – 40 % Ni-Cr-Al-Y-Ta; 3 – 50 % Al_2O_3-TiO_2 – 50 % Ni-Cr-Al-Y-Ta; fraction 40...63 µm, I=500 A, R_N=45 l/min, Rpor=4.5 kg/h)

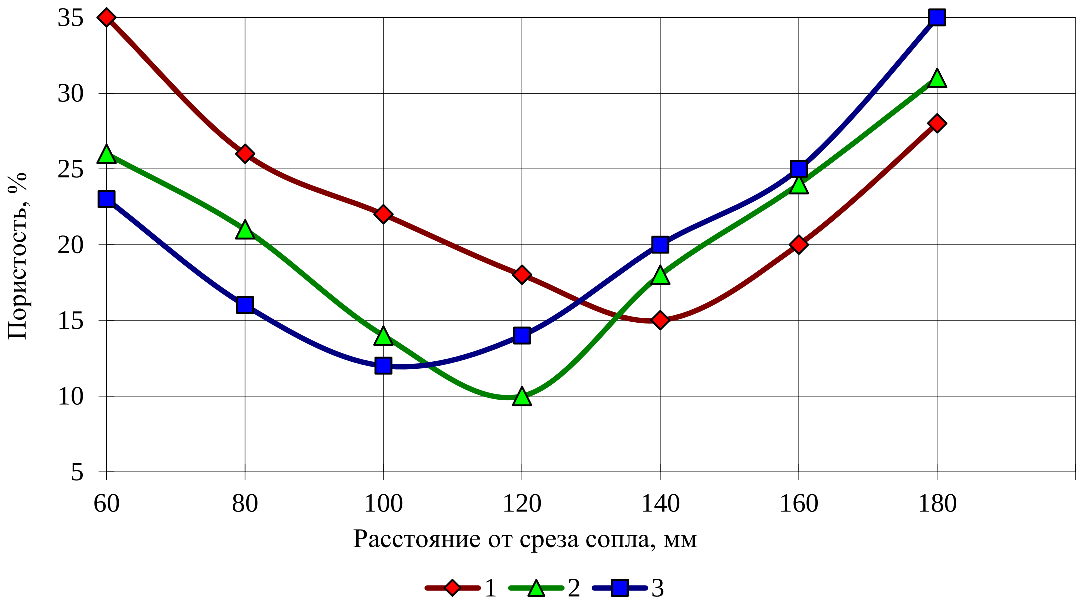

Figure 7. Dependence of porosity (%) on the distance from the surface to the cut of the plasma torch nozzle during spraying, mm for powders NiCrAlITa-Al_2O_3-TiO_2 (1 – 70 % Al_2O_3-TiO_2 – 30 % Ni-Cr-Al-Y-Ta; 2 – 60 % Al_2O_3-TiO_2 – 40 % Ni-Cr-Al-Y-Ta; 3 – 50 % Al_2O_3-TiO_2 – 50 % Ni-Cr-Al-Y-Ta; fraction 40...63 µm, I=500 A, R_N=45 l/min, Rpor=4.5 kg/h)

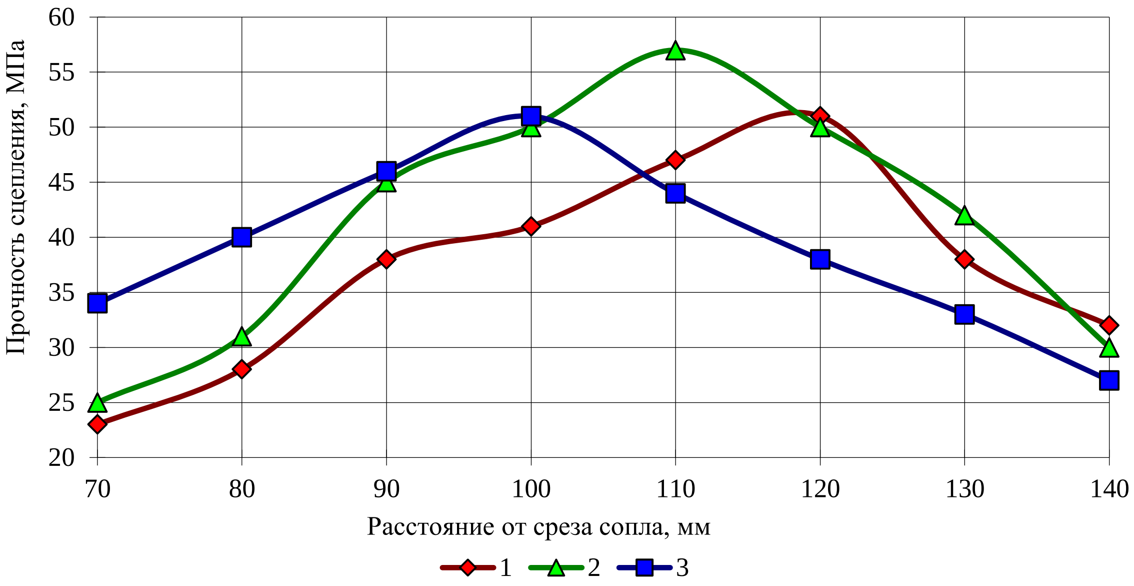

Figure 8. Dependence of the adhesion strength (%) on the distance from the surface to the cut of the plasma torch nozzle during spraying, mm for powders NiCrAlITa-Al_2O_3-TiO_2 (1 – 70 % Al_2O_3-TiO_2 - 30% Ni-Cr-Al-Y-Ta; 2 – 60 % Al_2O_3-TiO_2 – 40 % Ni-Cr-Al-Y-Ta; 3 – 50 % Al_2O_3-TiO_2 – 50 % Ni-Cr-Al-Y-Ta; fraction 40...63 µm, I=500 A, R_N=45 l/min, Rpor=4.5 kg/h)

The phase composition of plasma coatings based on powders of aluminum and titanium oxides was studied using X-ray diffraction analysis on a diffractometer. The depth of the layer under consideration, depending on the applied diffraction angle, was on the order of 10–50 µm. The main phases in the coating after plasma spraying are alumina α-Al2O3 and the orthorhombic phase of titanium oxide TiO2, as shown in the X-ray diffraction pattern shown in Figure 3c. The influence of the spraying distance on the performance characteristics of plasma wear-resistant coatings obtained at optimal spraying conditions are shown in Figures 5, and the values of performance characteristics are shown in Figure 6-8.

3. Conclusion

The structures and properties of Al2O3-TiO2-NiCrAlYTa plasma-sprayed powder coatings deposited under optimal conditions are studied. The coating has a good density, a minimum number of surface defects such as pores and cracks. Al2O3-TiO2 ceramic aggregates are bound to each other, and some of the large-sized ceramic particles are embedded in the molten NiCrAlYTa coatings. Such microstructural characteristics are associated with the mobility of molten liquid-phase NiCrAlYTa components, which can fill the gaps and cracks that occur during the plasma deposition of an oxide coating and improve the coating density. The interface is not well defined, indicating that during the high temperature deposition process, the ceramic constituents of the coating are melted into an organic whole with the metallic constituent at the interface, and that the elements of the two constituents diffuse and penetrate each other, there are no obvious boundaries between layered structures. In addition to chemical and mechanical bonds, there are some metallurgical bonds. At the specified values of technological parameters, a microheterogeneous structure of the sprayed coating is formed, containing elements that ensure its wear resistance (Cr1.12Ni2.88, α-Al2O3, γ-Al2O3, orthorhombic phase of titanium oxide TiO2). In this case, the spreading of molten particles on the substrate is achieved, there is no spattering and no loss during collision with the substrate. The main crystalline phases in the coating system are γ-Al_2O_3, anatase (TiO_2), $Cr_{1.12}Ni_{2.88}$ phase, in addition to α-Al_2O_3 and rutile TiO_2. Rutile TiO_2 diffraction peaks are found around 2θ=32° and 2θ=70°, its content increases after sputtering, which indicates that the transition from the anatase phase to the rutile TiO_2 phase occurs at high temperature. According to the results of quantitative analysis, the content of α-Al_2O_3 and rutile TiO_2 is 30.4% and 32.2%, respectively; they constitute the main phase structures of high-temperature ceramic coatings. The influence of the plasma spraying distance on the adhesion strength, hardness and porosity of the obtained coatings has been studied. At optimal conditions, the performance characteristics are as follows: hardness - 52-56 HRC; porosity - 7-9%; coating wear (friction with lubrication) - 4.1-4.6 microns; adhesion strength - 52-57 MPa.

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