УДК 621.793.71

F. I. Panteleenko, a member- correspondent. NAN B, Ph. D., Professor, **V. A. Okovity**, Ph. D**., O. G. Devoino**, Ph. D., Professor, **T. I. Bendik**, Ph. D**., V. V. Okovity, A. A Litvinko,**
Belarusian National Technical University, Minsk, Belarus
Tel. / Fax+375 17 293-95-99, niil_svarka@bntu.by
V. M. Astashinsky, a member- correspondent. NAS B, D. Phys. - math. n., prof.
A. V. Lykov Institute of Heat and Mass Transfer of the National Academy of Sciences of Belarus, Minsk, Belarus
Tel. / Fax +375 17 284-24-91, ast@hmti.ac.by)

INFLUENCE OF THE QUALITY OF INITIAL M-ROLL POWDERS ON THE STRUCTURE AND PROPERTIES OF MULTILAYER PLASMA COATINGS

The article describes the influence of the quality of initial m-rabbit powders on the structure and properties of multilayer plasma coatings. The qualitative indicators of the heat resistance of the alloys and the resulting coatings are associated with the formation of a continuous oxide film on their surface during deposition, which prevents the interaction of an aggressive environment and material. Most 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.). For spraying, five types of powders were used. Metallographic studies have established that calcium-thermal powders are conglomerates with a highly developed specific surface. However, the degree of sphericity can vary within very wide limits, and this shortcoming can probably be eliminated to a large extent by mechanical methods. Atomized powders have a spherical shape, but the peculiarity is that on the surface of some particles there is an alloy film that peels off during the preparation of thin sections and has a structure different from the body of the particle. For powders melted under flux, such a film is thicker and occurs on particles more often than for powders melted in vacuum. However, in both cases, X-ray microanalysis established that in the film, in comparison with the body of the particle, the oxygen content is increased by an order of magnitude and the aluminum content is several times higher.

Keywords: *nickel-based metal alloys, oxide ceramics, calcium thermal powder, atomized powder, submerged flux melted powder, operational characteristics, morphology and structure.*

Ф. И. Пантелеенко, В. А. Оковитый, О. Г. Девойно, Т. И. Бендик, В. В. Оковитый, А. А. Литвинко, В. М. Асташинский

ВЛИЯНИЕ КАЧЕСТВА ИСХОДНЫХ ПОРОШКОВ М-КРОЛЕЙ НА СТРУКТУРУ И СВОЙСТВА МНОГОСЛОЙНЫХ ПЛАЗМЕННЫХ ПОКРЫТИЙ

В статье описаны влияние качества исходных порошков м-кролей на структуру и свойства многослойных плазменных покрытий. Качественные показатели жаростойкости сплавов и полученных покрытий связана с формированием на их поверхности при напылении сплошной оксидной пленки, которая препятствует взаимодействию агрессивной среды и материала. 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.). Для напыления было использовано пять типов порошков. Металлографическими исследованиями установлено, что кальцийтермические порошки представляют собой конгломераты с сильно развитой удельной поверхностью. Однако степень сферичности может изменяться в весьма широких пределах и, вероятно, этот недостаток в значительной степени может быть устранен механическими методами. Распыленные порошки имеют сферическую форму, но особенностью является то, что на поверхности некоторых частиц имеется пленка сплава, отслаивающаяся при приготовлении шлифов и имеющая отличную от тела частицы структуру. Для порошков, плавленных под флюсом, такая пленка более толстая и встречается на частицах чаще, чем для порошков, плавленных в вакууме. Однако в обоих случаях микроренгеноспектральным анализом установлено, что в пленке по сравнению с телом частицы на порядок увеличино содержание кислорода и в несколько раз - алюминия.

Ключевые слова: *металлические сплавы на основе никеля, оксидная керамика, кальцийтермический порошок, распыленный порошок, порошок, плавленный под флюсом, эксплуатационные характеристики, морфология и структура.*

1. Introduction

The main feature of the m-roll powder material (nickel-cobalt-chromium-aluminum-yttrium) is the ability to plastically relax stresses during the deposition process. 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. The qualitative indicators of the heat resistance of alloys and the obtained coatings are associated with the formation of a continuous oxide film on their surface during deposition, which prevents the interaction of an aggressive medium and material [1–8]. For heat-resistant alloys, such a protective film is a film of Al2O3 aluminum oxide powder modified with oxides of other components of the obtained alloy. The film of chromium oxide Cr2O3, which has a higher fracture toughness than Al2O3, has a number of its drawbacks - the tendency to rapid evaporation of chromium oxide in an oxidizing environment when operating at temperatures above 1370 K; due to insufficient diffusion mobility, chromium has a lower rate of formation compared to aluminum. The most important is that it is chromium that contributes to the formation of Al2O3 oxide in the plasma nickel-aluminum coating, significantly increasing the activity of aluminum. And finally, it is chromium that can undergo internal oxidation and promote the formation of Al2O3 oxides. To optimize the content of chromium and aluminum in the plasma coating, it is important that there is a certain limiting concentration of aluminum in the alloy, which is necessary to obtain a continuous protective layer of Al2O3 oxide. The value of this limiting aluminum concentration decreases with increasing chromium concentration and increases with increasing test temperature. Most of the modern nickel-based alloys used in aviation and rocket technology used to form plasma coatings contain 6-12% aluminum, 20-30% chromium, and 0.15-1.0% reactive element (yttrium, tantalum, etc.) [3-6]. With an increase in the concentration of the reactive element, the production of new grains of oxides 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 grain of the alloy and the formation of yttrium-rich phases - Ni_5Y, Ni_9Y, Ni3Al2Y, $(NiCo)_{4.25}Al_{0.15}Y$, 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. Therefore, 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 rate of oxygen diffusion and the processes of alloy embrittlement [16]. Therefore, most NiCrAlYTa alloys for sputtering are limited to an oxygen content of up to 0.05%.

2. Structure and properties of M-rabbits

To study the properties of coatings, two methods were tested:

- plasma spraying in air (APS);
- low pressure plasma spraying (VPS).

In both cases, argon-hydrogen mixtures were used as plasma-forming gases. The plasma spraying method has a significant impact on the structure and properties of the coating. When using the APS - method, the oxygen content in coatings of powders melted in vacuum increases to 0.9-1.3 wt.%. These coatings have a characteristic layered structure due to the formation of thin oxide films, which is the most significant difference from VPS coatings.

The test results of ZrO2-7%Y2O3 HRC with plasma sublayers from AMDRY-995 powder are presented in Table 1.

Table 1. Test results of the HRC system ZrO_2-7%Y_2O_3 - AMDRY-995

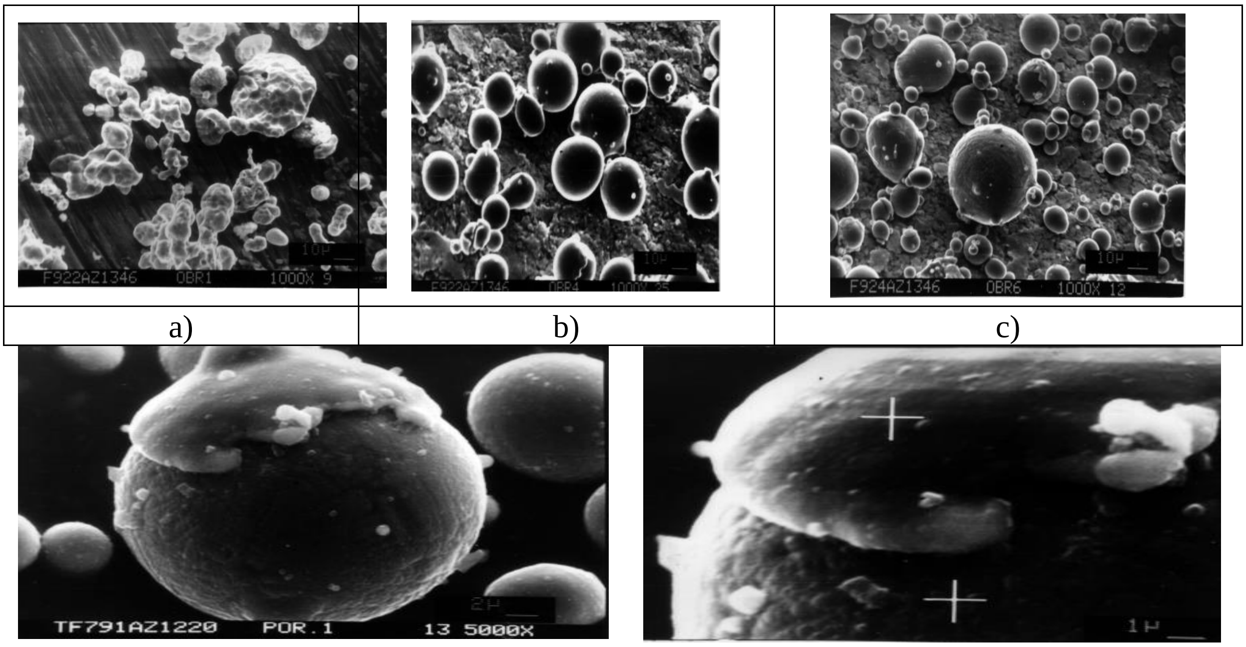
№ п/п	Method application	Heat treatment of coatings	K_{1C}, $MPa{\cdot}m^{1/2}$	Number of thermal cycles up to coating failure	
				1100-20°	850-20°
1	APS	no	2,7±0,8	21...24	144
2	APS	1100°C, 2 hours	2,1±0,8	28...31	211
3	VPS	no	1,5±0,4	35...38	206
4	VPS	1100°C, 2 hours	1,1±0,2	30...36	-

According to the results obtained, the K1C parameter has higher values for coatings with an APS sublayer compared to a VPS sublayer, which is primarily due to the higher surface roughness of the former. Nevertheless, the thermal fatigue of coatings with a sublayer is much higher. It should be noted that due to the increased effect of oxidation on the properties of HRC under operating conditions, the differences in the quality of HRC with APS and VPS - sublayer will be even more significant.

The quality of VPS - coatings is significantly affected by the spraying conditions, in particular, to increase the dispersion of the β - phase, complete penetration of the particles is necessary, which sets the lower limit of the plasma jet enthalpy and pressure in the chamber. On the other hand, in a dynamic vacuum, the evaporation of elements from the surface of powder particles is intensified. Thus, the evaporation of low-melting alloying elements limits the possibility of increasing the enthalpy of the plasma jet during the deposition of metal-chromium-aluminum-yttrium coatings.

Heat treatment makes it possible to change the structure of VPS - AMDRY powder coatings in the direction of improving the uniformity of phase distribution and increasing their thermal stability. In this case, however, the dimensions of the β-phase increase somewhat and diffusion of the base elements in the coating occurs. In APS coatings, oxide films are largely dissolved in the metal matrix, but the layering of the structure is not completely eliminated.

It has been established that for both types of HRC sublayers, the quality of metal-ceramic bonding somewhat deteriorates as a result of heat treatment (K_{1C} value decreases). In this case, the thermal fatigue of the HRC increases only in the case of the APS - sublayer, however, significantly, by 1.5 times (Table 2). This is explained by the fact that for APS - coatings during heat treatment, the most significant changes in the structure occur. The data obtained suggest that the mechanical properties of the ceramic layer deteriorate as a result of the heat treatment of the coating in vacuum.



a) b) c)

d) e)

Figure 1. Morphology of powders of M-rabbits: a-calcium-thermal powders ПКХ27Ю7И; atomized powders b-Metco1037D; c-AMDRY 995) (x1000); obtained by submerged arc melting followed by sputtering with argon d- ПМ-1; e- ПМ-2) (×5000).

Three types of powders were selected for comparative studies (Fig. 1):
1) obtained by the calcium thermal method (ПКХ27Ю7И);2) obtained by submerged arc melting followed by sputtering with argon (ПМ-1; ПМ-2);

3) obtained by melting in vacuum followed by sputtering with argon (Metco10370, AMDRY962).

Metallographic studies have established that calcium-thermal powders are conglomerates with a highly developed specific surface. However, the degree of sphericity can vary within very wide limits, and this shortcoming can probably be eliminated to a large extent by mechanical methods. Atomized powders have a spherical shape, but the peculiarity is that on the surface of some particles there is an alloy film that peels off during the preparation of thin sections and has a structure different from the body of the particle. For powders melted under flux, such a film is thicker and occurs on particles more often than for powders melted in vacuum. However, in both cases, X-ray microanalysis established that in the film, in comparison with the body of the particle, the oxygen content is increased by an order of magnitude and the aluminum content is several times higher. This allows us to conclude that the film is a metal layer oxidized during sputtering.

Comparison of the structures of powders of NiCoCrAlY - alloys indicates a uniform distribution of the β - phase in the γ - matrix for molten powders, while the formation of large (5-10 microns and more) homogeneous inclusions is characteristic of calcium-thermal materials, β - phase, as a rule, has a pronounced form.

In the X-ray microspectral analysis of impurities in the compared analyzes, the most significant differences were found in the oxygen content. The method of reductive melting in a carrier gas flow also revealed the dependence of the oxygen content on the fraction of calcium-thermal powders.From the powders of the NiCrAlY and CoCrAlY alloys, coatings were deposited on samples of the ЖС6К alloy by the low-pressure plasma spraying (VPS) method. Some of the coatings (nickel-based alloys) were used as sublayers under the ZrO2-Y2O3 heat-shielding ceramics. These samples were subjected to thermal cycling tests (heating to 1220°C, holding for 15 min., cooling into water). Another part of the coatings (cobalt-based alloys) was heat-treated and then oxidized at 1100°C for 5 hours. Before and after each test, the structure of the coatings was studied by optical and scanning electron microscopy.The following main patterns of structure formation of coatings and their behavior during testing were revealed.Nickel-based alloy coatings in the initial state are dense homogeneous layers in the case of sprayed powders, while for calcium-thermal powders, it is practically impossible to avoid some residual porosity of the coatings. This effect is probably associated with insufficiently effective degassing of calcium-thermal powders with a developed surface during their preparation and spraying.The structure of the coatings after sputtering almost completely repeats the structure of the original powders. At the same time, the dispersity of the structure in the coatings deteriorates in a number of powders used: melted in vacuum - melted under a flux - calcium-thermal.Thermal cycling tests at 1220°C for 1 hour lead to oxidation of the outer layer of metal sublayers, expressed for coatings from molten powders in the form of formed thin films with a depleted (non-etching) zone under them with a width of 25-30 μm. For coatings from thermal calcium powders, oxidation is expressed in the formation of oxide inclusions and even oxide interlayers at a depth of up to 25 μm, which indicates a significantly higher oxidation rate of such coatings caused by intense diffusion of oxygen through structural defects and extended phase boundaries.The destruction of coatings also occurs as a result of their diffusion interaction with the base. In this case, both the structure of the base and the coating are destroyed, and in both cases, these destructions increase in a series of coatings obtained from vacuum-melted, flux-fused, and calcium-thermal powders (Table 4).

As a result of high-temperature tests, the structure of the coatings is enlarged. At the same time, the structural heredity is preserved: the size of the phases in the coatings after the tests is the greater than it was before the tests. The structure of coatings from CoCrAlY powders after standard heat treatment also largely inherits the structure of the original powders, however, in this case, the differences in the shape and dispersion of phases in coatings from sprayed and calcium-thermal powders are even more pronounced.

Table 2. Properties of plasma coatings NiCoCrAlY/ZrO_2-7%Y_2O_3 (1 mm)

№ п/п	Base	Spray medium	Heat treatment in vacuum	$\sigma_{сц}$, MPa	850-20°C
1	40Х10С2М (ЭИ107)	air	no	24	144
2		air	1050°C, 2 h	90	211
3		dynamic vacuum	no	108	206
4		dynamic vacuum	1050°C, 2 h	236	220
1	20Х25Н20С2 (ЭИ283)	air	no	28	139
2		air	1050°C, 2 h	142	237
3		dynamic vacuum	no	93	275
4		dynamic vacuum	1050°C, 2 h	278	301

Table 3. Results of X-ray microanalysis of the content of elements on the surface of ПМ-1 powder particles

Analysis	Content of elements Содержание элементов, %						
	aluminum	chromium	nickel	tantalum	oxygen	iron	iron
On a surface films	0,22	30,95	56,67	8,92	0,22	2,70	0,31
On a surface particles	0,06	29,63	57,22	10,61	0	1,88	0,61

Table 4. The width of the zone of destruction of the structure of the base ЖС6К and NiCrAlY - coatings as a result of their diffusion interaction during thermal cycling tests

Grade of powder for coating	Width of the destruction zone of the structure, microns	
	coating	bases
1. ПХ16Н77Ю6И	30-38	75-83
2. ПМ-1	20-23	65-73
3. AMDRY962	15-18	58-60

Table 5. Change in the size of β - phases in NiCrAlY - coatings after thermal cycling tests

Grade of coating powder	Size range β- phases, µm	
	initial coating	coating after tests
1. ПХ16Н77Ю6И	1,0-5,3	2,0-6,6
2. ПМ-1	0,7-2,2	1,3-5,3
3. AMDRY962	0,7-1,6	1,3-3,3

The structure of the coatings also changes accordingly after oxidation at 1100°C: the depletion zone under the oxide film increases in a series of coatings obtained from vacuum-fused, flux-fused, and calcium-thermal powders. In this case, however, the zone of destruction of the structure of the base as a result of diffusion interaction with the coating for all coatings is approximately the same, while the zone of destruction of the structure of the coating increases in the order similar to that described above (Table 6).

Table 6. Width of zones of destruction of the structure of CoCrAlY - coatings as a result of oxidation at 1100°C and diffusion interaction with the base of ЖС6К alloy

Powder brand for coatings	Width of the destruction zone of the structure, microns		
	coatings under oxide film	coating basics	basics
1. ПКХ27Ю7И	27-40	24-27	7-10
2. ПМ-2	14-21	10-17	7-11
3. Metco1037D	10-14	7-9	9-14

3. Conclusion

Thus, there is a direct relationship between the heat resistance of coatings of the MeCrAlY system and the morphology and structure of the initial powders. The developed surface of powders is highly undesirable for deposition of coatings of this type at reduced pressure, since this leads to the formation of residual porosity in the coatings, which accelerates their oxidation. Due to the heredity of the structure of powders by coatings, it is necessary that the initial powders have a uniform distribution of elements and a maximally dispersed structure with the shape of phase inclusions having a small specific boundary surface. In particular, β- phases, with the approach of its shape to the spherical and more uniform distribution in the γ- matrix. Comparative studies of powders and coatings indicate that with a decrease in the oxygen content in them, the heat resistance of coatings increases.

LITERATURE

1. Panteleenko, F. I. Formation and study of multilayer composite plasma coatings based on M-rabbits and oxide ceramics with subsequent high-energy effects / Panteleenko F. I., Okovity V. A., Sidorov V. A., Okovity V. V., Devoino O. G., Volodko A. S., Astashinsky V. M., Uglov V. M. // International collection of scientific papers of the Donetsk National Technical University "Progressive technologies and systems of mechanical engineering", DonNTU - Donetsk.-2021.№2.-p.68-83.

2.Panteleenko, F.I. Modern application of ceramic-metal coatings based on metal-chromium-aluminum-yttrium (M-rabbit) systems / Panteleenko F. I., Okovity V. A., Devoino O.G., Sidorov V. A., Okovity V. V., Volodko A. V., Astashinsky V. M. // International collection of scientific papers of the Donetsk National Technical University "Progressive technologies and systems of mechanical engineering", DonNTU - Donetsk.-2021. No. 3.-S.72-81.

3.Panteleenko, F. I. Formation and study of multilayer composite plasma coatings / Panteleenko F. I., Okovity V. A., Devoino O. G., Okovity V. V., Astashinsky V. M., V. V. Uglov, V. I. // Bulletin of the Gomel State Technical University. .#2. 2021.S.15-27.

4. Panteleenko, F. I. Overview of the modern application of ceramic-metal coatings / Panteleenko F. I., Okovity V. A., Sidorov V. A., Okovity V. V., Astashinsky V. M. // Bulletin of the Kuzbass State Technical University. No. 3.2021. pp. 5-17.

5. Okovity, V. A. Optimization of the process of applying coatings from cermet powders by plasma spraying in air / Okovity V. A., Panteleenko F. I., Okovity V. V., Astashinsky V. M. // "Science and technology", BNTU - Minsk. -2021. Issue 5.- S.369-374.

6. Panteleenko F. I., Okovity V. A., Devoino O. G., Astashinsky V. M., Switala F. (2022) Multi-Layers Composite Plasma Coatings Based on Oxide Ceramics and M-Croll. Science and Technology. 21(2), 93–98.

7. Panteleenko, F. I. Selection of optimal parameters for deposition of multilayer plasma coatings from materials based on nickel M-rabbits / Panteleenko F. I., Okovity V. A., Sidorov V.A., Okovity V. V., Astashinsky V. M., Svitala F., Blumenshtein V. M. // Bulletin of the Kuzbaz State Technical University. 2022. №1. pp.12-22.

8. Panteleenko, F. I. Options for deposition of multilayer coatings from ceramic powders and M-rabbits / Panteleenko F. I., Okovity V. A., Devoino O. G., Sidorov V. A., Astashinsky V. M. // International collection of scientific papers of the Donetsk National Technical University "Progressive technologies and systems of mechanical engineering", DonNTU - Donetsk. -2022.№1(76).C.66-72.

Поступила в редколлегию 12.02.2024