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PHYSICAL PROPERTIES OF THE MULTIPHASE IONIC-PLASMA COATINGS

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The article includes the following topics: obtaining coatings in the conditions of deposition of multicomponent plasma flow and study the structure of the obtained coatings; the influence of ion and laser irradiation on the structure and properties of multiphase coatings. A direct impact on the structure and physical properties of coatings obtained by ion-plasma deposition, provide the following parameters, which are determined experimentally: the pressure of a reactive gas in the working chamber; potential basis; discharge current of the arc; the properties of the material of the cathode; the temperature of the substrate.

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INTRODUCTION

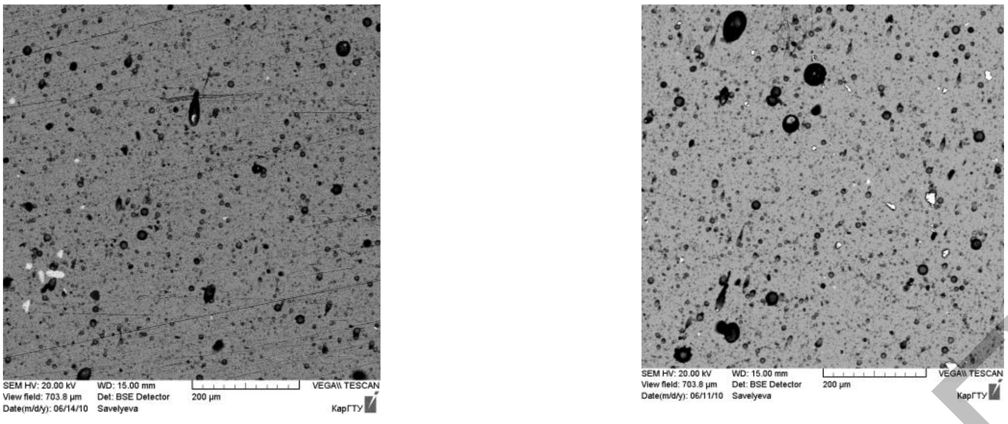
Among the methods of application of protective coatings, based on the impact on the surface of the part of the flows of particles and photons with high energy, great attention is attracted by vacuum ion-plasma methods [1-7]. A characteristic feature of their direct transformation of electric energy into the energy of the technological impact, based on structural-phase transformations in the besieged the condensate surface or in the surface layer of the items placed in the vacuum chamber. The main advantage of these methods is the possibility of building a very high level of physical and mechanical properties of materials in thin surface layers, application of a dense coatings of refractory compounds, as well as diamond-like, which are impossible to obtain by conventional methods.

This article presents the results on the properties of multiphase coatings obtained by ion-plasma method. Previously the experimental results are described in the works [8-18].

INFLUENCE OF TECHNOLOGICAL PARAMETERS ON THE STRUCTURE OF ION-PLASMA COATINGS

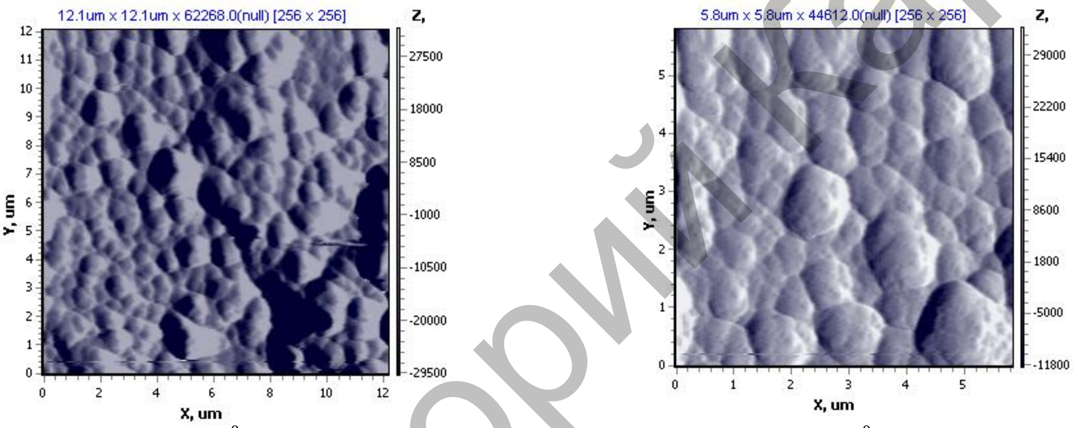
A direct impact on the structure and physical properties of coatings obtained by ion-plasma deposition, provide the following parameters [1-3, 10-12]: pressure reactive gases in the working chamber; potential basis; discharge current of the arc; the properties of the material of the cathode; the temperature of the substrate. In figure 1, as an example, showing electron microscopic images of composite coatings at temperatures substrate 350 and 450 ^{0}C. Figure 1 shows that at a temperature of 450 ^{0}C happens coagulation zinc phase in larger increments, and the rest (most), is becoming more uniform. This is clearly seen in atomic-force microscope (Fig. 2). The situation is similar for other coatings.

Optimum temperature of the substrate for all of composite coatings was equal to 400 ^{0}C. Refinement of the structure of the coating material with the increase of the substrate temperature is accompanied by growth of hardness up to a critical medium grain size. Decrease of hardness on further reduction of the average grain size in the coating is due to slippage along the grain boundaries (rotary effect). In this case, to further increase hardness is required to slow down the process of sliding along the grain boundaries. Such braking can be achieved through the formation of a corresponding nanostructures with hardening of the grain boundaries when using multicomponent streams.



350 ^{0}C 450 ^{0}C

Fig.1. Electron - microscopic images of coating Zn - Al



350 ^{0}C 450 ^{0}C

Fig.2. Image of the coating Zn - Al atomic force microscope

The increase of the discharge current of the arc increases the thickness of the cover, however, with an increase in current over 130 A decreases the perfection of the structure and dramatically increases the number of drop phase, which is the reason of decrease in the strength of adhesion to the substrate with a coating. When low power discharge (arc current < 20-30 A) due to a decrease of the coefficient of ionization in the film introduced neutral particle reactive gas and cathode, which contributes to increasing concentration of media defects.

We have investigated the dependence of the properties of composite coatings on the nitrogen pressure in the working chamber; thus the current strength, voltage reference, the cathode material, the terms and conditions of allocation and heat sink, the processes of cleaning and spraying remained constant. Table 1 presents the results of the microhardness.

At a pressure of nitrogen P = 0.058-0,81 Pa formed small dense texture, close to the stoichiometric composition, which is characterized by optimal, from the point of view of the metal properties, the ratio of metallic and ionic components of the communication. The contents of drop phase is reduced and the number of pores and delaminations increases. When the pressure is increased, a large number of free ions leads to a sharp increase in the number of pores and delaminations.

Table 1 - Dependence of the microhardness of coating from the gas pressure in the chamber

Residual gas pressure in the chamber	Microhardness HV			
	Al - Fe	Zn – Cu - Al	Zn –Al	Al - Fe
10^{-8}	0,662			0509
10^{-7}	0,66			0,512
10^{-6}	0,60	0,573	0,569	0,514
10^{-5}	0,61	0,600	0,520	0,470

Having analyzed the research results, we can conclude that the samples obtained at a pressure of nitrogen P = 0,081-0,81 Pa have the most uniformly distributed small dense structure, the minimum contents of drop phase, then, overlaps, delaminations, and the highest values of microhardness.

INFLUENCE OF ION IRRADIATION ON PROPERTIES OF MULTIPHASE COATINGS

The main influence of the ion bombardment on the properties of the coatings is carried out at the stage of their origin due to stress relaxation in the field of ion impact and restructuring of the crystal structure. On the surfaces of point defects formed, which are active centers of adsorption. Also important, the mobility of the atoms on the surface (surface diffusion), which are intensified under the low energy bombardment of the growing film ions inert gas. Increase the number of point defects formed, you can either increase the energy flow of ions, any increase in the density of ion current. Simultaneously with formation of defects is the reverse process of recombination «annealing», which reduces the concentration of defects. As a result of these two processes is established equilibrium quantity nucleation centers, which may be affected by changing the parameters of ion irradiation.

Figures 3-5 shows images of the surface of composite coatings before and after irradiation received by atomic-force microscope.

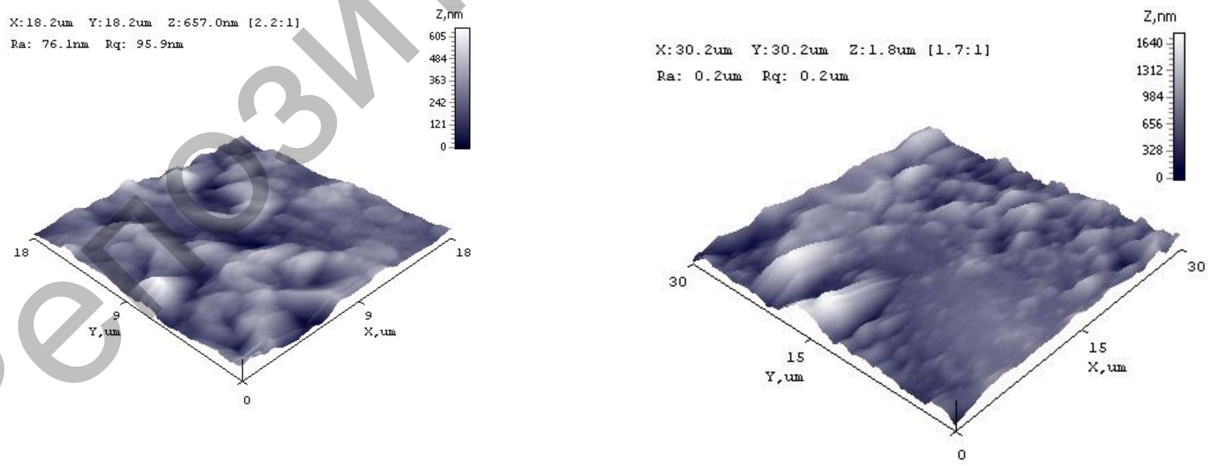


Fig.3.The Image of a surface coatings of Fe-Al before and after irradiation

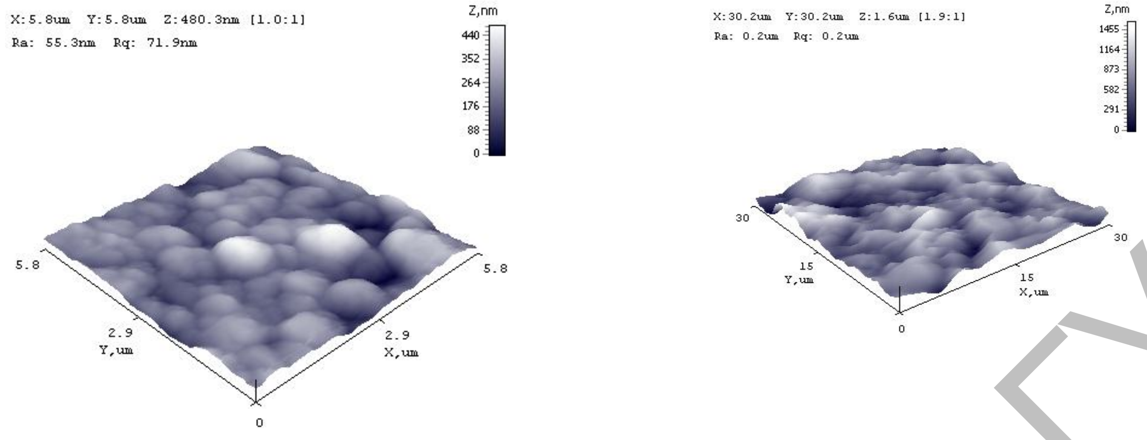


Fig.4. The image of a surface coatings of Zn-Al before and after irradiation

From the figures 3-5 should be that the ion irradiation influence on structure of coating. The exception is the coverage of Zn-Al, which appeared radiation-resistant. This behavior coverage Zn-Al binds us with his pronounced globular structure (Fig. 4). The presence of such a system of «balls» leads to the elastic scattering of ions of argon, so that the local deformation is insignificant.

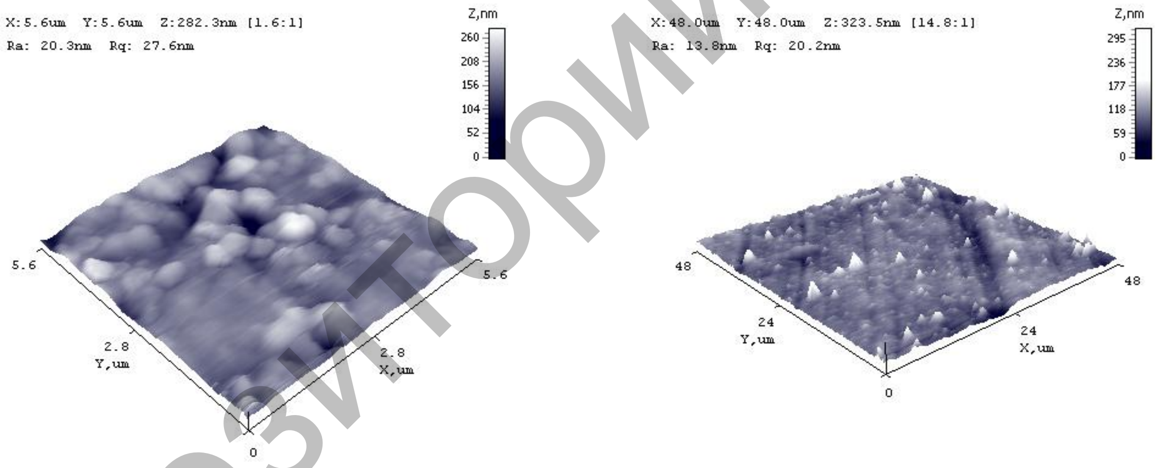


Fig.5. The image of a surface coatings Mn-Fe-Cu-Al before and after irradiation

THE INFLUENCE OF LASER IRRADIATION ON PROPERTIES OF MULTIPHASE COATINGS

As a source of laser radiation in the work of the used laser алюмоиттриевом grenade neodymium doped ($\lambda = 1064 \text{ nm}$). Flash duration lamps laser pump, working in the mode of free generation, was 2 10^{-3} s. The laser-pulse Energy was 1 j and before the experiment was measured by the IMO-2H and repetition rate of the laser pulses is adjustable from 0.1 to 35 Hz. Laser radiation by quartz spherical lens with a focal length of 50 mm is focused on the sample surface stain diameter, depending on the conditions of the experiment could be 60 microns and more. The pulse repetition frequency is chosen so that when the fixed and irregular speed of moving of a sample minimum distance between the centers of laser spots of light on the surface of the object does not exceed their diameter, and was 5 Hz.

On Fig. 6 shows the microstructure coatings before and after laser treatment. Table 2 shows the values of microhardness HV (HV) samples Cr-Mr - Si - Cu - Fe - Al +Ti in argon without laser processing and after the laser treatment.

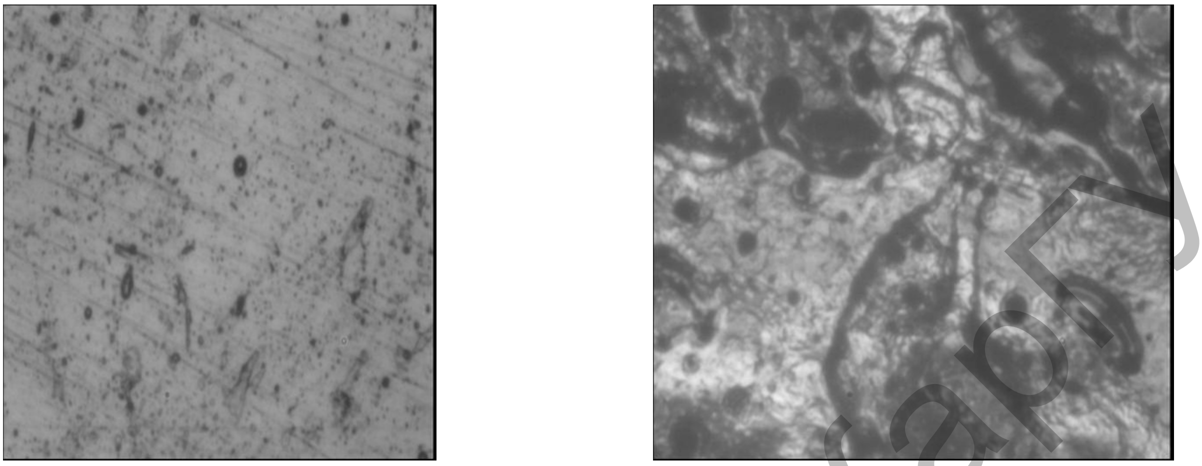


Fig.6. the Microstructure of the coating Cr-Mr - Si - Cu - Fe - Al +Ti in the gas medium of argon before and after laser irradiation

Table 2 - Results of studies of microhardness coverage Cr-Mr - Si - Cu - Fe - Al +Ti, resulting in argon

Sample	Load tests, kg	Microhardness, HV
Cr –Mr – Si – Cu – Fe – Al +Ti without laser processing	0,01	190,5
Cr –Mr – Si – Cu – Fe – Al +Ti after the laser treatment	0,01	328,0

As follows from table 2 to coating Cr-Mr - Si - Cu - Fe - Al +Ti in argon microhardness increases. This effect is due to the formation of dislocation structure coating sharp heating-cooling. When the coating Cr-Mr - Si - Cu - Fe - Al +Ti nitrogen in the environment in the latter formed the field containing the nitrides of titanium and chromium, and according to the data of x-ray analysis the contents of both components is approximately the same. The size of particles of titanium nitride and chromium according to electron microscopy is 100-150 nm. Microcrystals of nitrides of titanium and chromium have priority orientation (presumably in the direction of the (200)) that differs from the spherical symmetry of micro-crystals of pure titanium. All this, along with the cellular structure of coating, leads to its high microhardness (table 2).

THE SURFACE TENSION OF THE ION-PLASMA COATINGS

Because the technical characteristics of coatings is determined by its surface properties, for process control of their reception it is necessary to learn how to measure the surface properties of coatings and, first of all, the surface tension.

Methods of experimental determination of the surface tension of solids started in the 20s of the last century. Overview of these methods is given in [19-22]. It is noted that currently there is no method that could be used for determination of surface tension in the solid phase in a wide temperature range. Each of the methods is practically limited or temperature, or values, that experimentally determined with low accuracy.

Recently we have offered new methods of experimental determination of the surface tension of solids [23]. These methods are based on the measurement of the dimensional effect associated with modifying some physical properties of small particles or thin film while reducing their size. The dimensional effects are based and methods of definition of a superficial tension of deposited coatings, used in this work [24].

Objects of research were selected nitrides of titanium, zirconium, hafnium, niobium and tantalum, one of the most studied and widely applied as strengthening coatings. Study microhardness nitride coatings was conducted on the device ISOSCAN OD. The dependence of the microhardness of the deposited coating on its thickness is described by the formula [24]:

$$\mu = \mu_0 \cdot \left(1 - \frac{d}{h}\right), \qquad (1)$$

where μ - microhardness of the deposited coating; μ_0 - massive sample; h - the thickness of the deposited coatings. The parameter d is associated with surface tension σ formula:

$$d = \frac{2\sigma\upsilon}{RT}. \qquad (2)$$

here σ is the surface tension of a massive sample; v - volume one mol; R is the gas constant, T is the temperature. In the coordinates $\mu \sim 1/h$ ($1/h$ reverse thickness of the deposited coating) get the direct, the tangent of the angle that defines d, and formula (2) is calculated surface tension of the deposited coating (σ). As described above measured surface tension nitride coatings (table 3).

Table 3. Surface tension and properties of nitride coatings

Nitride	Temperature melting coating ^{0}C	Micro hardness coating GPa	Electrical conductivity coating μОм$^{-1}\cdot$m^{-1}	On top of. tension coating j/m^2	On top of. tension metal j/m^2
TiN	2945	20,0	40	0,474	1,933
ZrN	2955	16,0	18	0,518	2,125
HfN	3330	22,0	32	0,610	2,503
NbN	2320	14,0	78	0,670	2,741
TaN	3360	17,5	180	0,735	3,014

For pure metals magnitude of the surface tension defined in [25]. From table 3 we can see that in the range of TiN→TaN surface tension increases almost in 2 times. Compared with pure metals is reduced approximately 4 times for all coatings, i.e. nitrogen, reacting with metal and forming a chemical bond, operates almost throughout all metals in the same way. A distinct correlation between the surface tension and microhardness is not observed, but correlates conductivity coating. Given that the surface energy Gibbs, $G = \sigma \bullet S$, (S is the area of coating) in most cases is the additive, you can change the surface tension, and the changing composition of the coating.

CONCLUSION

A variety of factors gave rise to a great number of technological methods of formation of coatings [1-17]. In recent years, the most popular are the method of deposition of multi-phase materials with high entropy [26].

However, the use of multiple-element or multiphase materials for functional coatings creates a task with many options - altering their composition by trying requires large material and time costs. In this case, many researchers have high hopes for the computer modeling of the properties of composite materials and coatings [27, 28].

However, in this case the number of parameters is still quite large, which makes the computer models far removed from the actual situation. In our opinion enough two-three control parameter to optimize the coating process. One of such parameters, as shown in this paper, may be the surface tension of the deposited coatings.

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