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FORMATION OF THE STRUCTURE AND PROPERTIES OF MULTI-ELEMENT ION-PLASMA COATINGS

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Preliminary Note – Prethodno priopćenje

The article presents the results of the studies related to the development of hardening, antifriction, heat-resistant, corrosion-resistant coatings. There have been considered the models of concentration supercooling associated with the presence of a radial concentration gradient of metal nitride impurity; Benard cells, the occurrence of which is caused by the presence of a vertical temperature gradient; a cellular dislocation structure associated with the presence of plastic deformations in the coating; the emergence of auto-waves in the most diverse environments, including living beings. From the studies presented in the work, it follows that self-organization of forming coatings can occur only under conditions of a large value of the surface energy.

Keywords: multi-element coating, x-ray research, metal nitride, corrosion, hardness

INTRODUCTION

Present day industrial production that is faced with the limitation of material resources in the development of structural materials, resorts to new technological solutions. New technologies lie in the fact that instead of expensive materials made of iron and refractory elements obtained in metallurgy, there are used hardening, antifriction, heat-resistant, corrosion-resistant coatings [1]. Increasing the coating thickness is accompanied by increasing internal mechanical stresses, which results in decreasing the adhesion strength. Increasing the durability of surfaces with the help of special coatings is still one of the most effective methods of improving the functional and operational characteristics of products and parts for various purposes [2].

At present, instead of single-phase coatings, such as titanium nitrides or carbides, multi-element coatings have been used, which have a number of unique properties and cannot be obtained by traditional metallurgy. Such an alloy based on a multi-element composition, including such elements as Fe, Cr, Ni, Ti, Al, was studied in [3, 4]. Some investigators [5] have claimed that multilayer nanoscale structures are more effective compared to single-layer coatings, in particular, in increasing hardness and strength. A more complete presentation of multi-element coatings can be found in [6]. In this work, it is shown that ion-plasma coatings deposited on a modernized HNV-6.6I1 installation have the following technological parameters: the optimal substrate temperature for all the applied coatings is 400 ^{0}C; with increasing the arc current of the evaporator, the surface energy of the coating decreases, which is explained by a rapid increasing of its thickness that leads to increasing the dislocation density in the formed coating; coatings obtained at nitrogen pressure P = 10^{-6} Pa have the most uniformly distributed fine dense structure, the minimum content of the droplet phase, pores, sags, delaminations and the highest values of surface tension and microhardness. These parameters wil bel adhered to in this work. In recent years, atomic force microscopy (AFM) has been used very often in connection with a complete study of the morphology and surface properties of coatings, metal and other films, as well as in the synthesis of new materials, including biomaterials and living beings.

The purpose of the work is studying the properties of coatings that contain copper and applying them to steel surfaces of mining equipment parts in order to protect them against corrosion.

RESEARCH OBJECTS AND METHODS

Our studies of the surface morphology of coatings obtained by ion-plasma and magnetron sputtering in vacuum was carried out on a JEOL AFM JSPM – 5400. Our coating has a cellular (“pencil”) microstructure. This is especially evident in the section of the coating made by the Quanta 200 3D system that directs a focused ion beam that allows precise removing the materials by determining the coating thickness (Figure 1).

Figure 2 shows the cellular (columnar, “pencil”) microstructure of the coating (FeCuCrMnNiTi)N.

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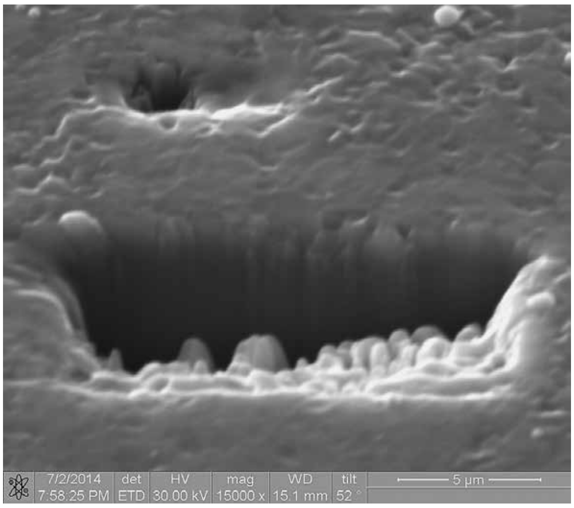

Figure 1 Cross section of the (FeCuCrMnNiTi)N coating

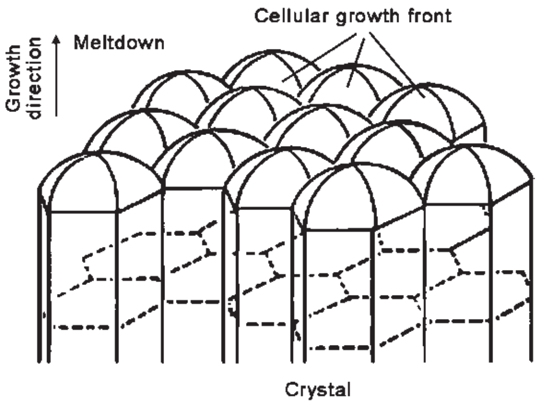

Figure 2 Cellular (columnar) structure of a crystal that is formed during its growth from a melt

In work [7] there are considered the models of concentration supercooling associated with the presence of a radial gradient of the metal nitride impurity concentration; of Benard cells, the occurrence of which is caused by the presence of a vertical temperature gradient; a cellular dislocation structure associated with the presence of plastic deformations in the coating. All these models correspond to the processes of self-organization, including the formation of coatings. Self-organization processes include the emergence of auto-waves in various media, including living beings [8, 9]. In this work, the following experiment was carried out: it was assumed that the cellular structure “in static” or “in frozen form” corresponds to a wave process. In this case, the coating microhardness was measured on a microhardness tester HVS - 1000 A with the use of the Vickers method along, across and diagonally of the samples.

The cathodes made of pure copper Cu metals and steel X10CrNiTi18 – 10 (European Union) were made using cylinders with the diameter of 100 – 120 mm on a lathe, Figure 3.

The deposition was carried out simultaneously from two cathodes on a modernized ion-plasma chamber vacuum installation HNV-6.6I1 in the nitrogen atmosphere. If the electrodes are turned on in alternation, then multiphase flows and multilayer coatings will occur.

Figure 3 Cu and X10CrNiTi18 – 10 cathodes

X-ray fluorescent quantitative analysis (XPS) of the coating composition carried out on a JEOL JSM – 5 910 electron microscope, is shown in Figure 4. The quantitative analysis of the elemental composition of coatings has the following distribution: Fe – 47,4 %; Cu – 22,5 %; Cr – 15,0 %; N – 13,1 %; Mn – 4,0 %; Ni- 3,5 %; Ti – 0,9 %.

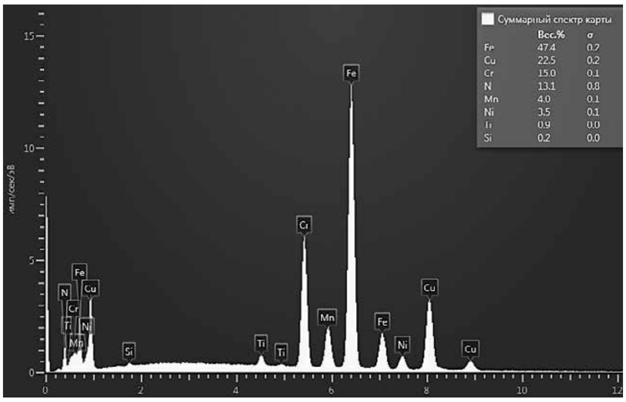

Figure 4 XPS of the (FeCuCrMnNiTi)N coating

RESEARCH RESULTS

Studying the phase composition and structural parameters of the samples was carried out on an XRD – 6 000 diffractometer using CuKα radiation. As a result, two phases were found: BCC and FCC. These phases are formed due to nitrides and copper. Figure 5 shows the microstructure of coatings measured with a Tescan Vega LSU scanning electron microscope (SEM). The study shows that the alloy of the (FeCuCrMnNiTi)N system consists of large elongated grains with the aver-

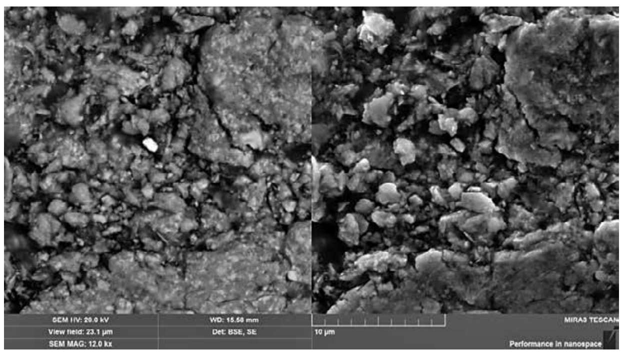

Figure 5 SEM of microstructure of the (FeCuCrMnNiTi)N coating

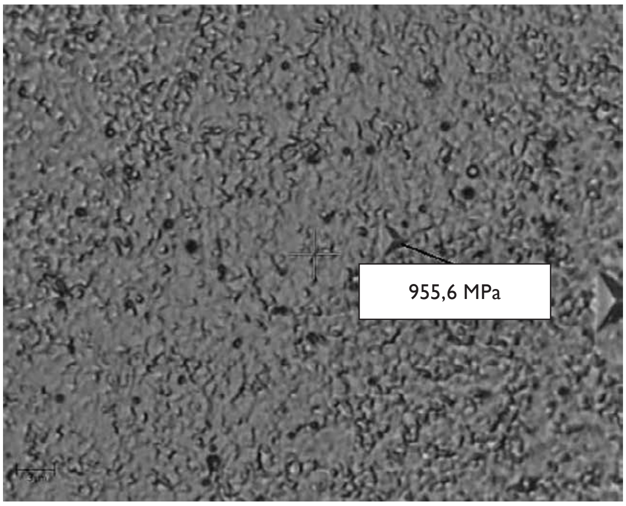

Figure 6 Measuring nanohardness of a sample with the (FeCuCrMnNiTi)N coating

age width of (100 – 150) µm and an average length of (200 – 300) µm.

To determine the resulting coatings nanohardness, there was used the Ntegra probe laboratory with a Berkovich indenter. The result is shown in Figure 6.

Coatings were tested for hardness using an HVC-1000A electronic microhardness tester. The hardness of the (FeCuCrMnNiTi)N coating and some steels: (FeCuCrMnNiTi)N coating microhardness 884,6 MPa; (FeCuCrMnNiTi)N coating nanohardness 995,6 MPa; Stainless steel 316 microhardness 189 MPa.

In the scientific work, there were used computer modeling methods, numerical studies were carried out using the ANSYS program. This program had already been used before, and examples of computer models and simulation results were presented in [10]. Simulating made it possible to exclude cumbersome and expensive full-scale tests of experimental samples.

INDUSTRIAL TESTING OF COATINGS

Parts of mining equipment are exposed to corrosion primarily due to the impact of mine water. Mine water is called groundwater that penetrates into the underground space worked out during the extraction of minerals and passes through the drainage system of the mine. The most acidic and highly mineralized mine waters are formed on the upper levels and mine workings on the territory of the first hydrochemical zone from the surface. The most acidic mine waters are formed in anthracite mines to depths of (250 – 300 m), at low angles of incidence of rocks when the content of total sulfur in the coal is more than 2,5 %, with a long length of workings and a large area of mined-out space.

At deeper levels (300 – 400 m), sulfate-chloride sodium or sodium-calcium waters are generated. At the depth of more than 400 m, chloride-sulfate waters are formed. Thus, in mine waters, the content of SO_4^{2-}, Ca^{2+}, Mg^{2+} decreases with depth and the content of K^+, Na^+, Cl^-, HCO_3- increases. But at the same depths, mine waters contain more calcium and magnesium sulfates than groundwater. Pumping out mine water from mine workings leads to corrosion of metal parts of pumps, pipelines, fittings, etc. Mine supports are also subjected to significant corrosion, despite significant efforts to improve their corrosion resistance. To increase corrosion resistance of a number of mining equipment parts, the (FeCuCrMnNiTi)N coating was applied that showed the best results in preliminary studies. Table 1 shows the results of testing parts with such anti-corrosion coatings.

Table 1 **Anti-corrosion coatings properties on the mining equipment parts**

Part	Coating	Corrosion rate / g/m^2·h
Steel 35	Without coating	3,21
Steel 35	(FeCuCrMnNiTi)N	0,15
Coupling, St. 35	(FeCuCrMnNiTi)N	0,15
Clutch 12 s, St. 35	(FeCuCrMnNiTi)N	0,15
Stopper HLG 30.002, St. 35	(FeCuCrMnNiTi)N	0,15
Housing of gas distributor	(FeCuCrMnNiTi)N	0,15
H13.07.130-01, St. 35	(FeCuCrMnNiTi)N	0,12
Plunger KSN01.311, St. SIH15	(FeCuCrMnNiTi)N	0,13
Sleeve M130.07.149, St. 40	(FeCuCrMnNiTi)N	0,13

Let's compare the obtained results with the corrosion rate of some corrosion-resistant stainless steels (Table 2).

Table 2 **Corrosion rate of the most corrosion resistant steels**

Steel grade	Corrosion rate / g/m^2·h
H23N28M3D3T	0,21
H23N27M3T	0,26
H18H12M3T	0,80

From this comparison it follows that our coating is not inferior to stainless steels in terms of corrosion but is much cheaper in cost. The following conclusion follows from the above results: the greater the surface energy σ of the coating, the greater its corrosion resistance. Thus, the tests carried out showed the economic feasibility of using multi-element ion-plasma coatings.

CONCLUSION

Mining machines for underground mining of coal and other minerals include winning machines, powered supports, drilling machines, loading and drilling-loading machines and auxiliary equipment of various types. The working tools of the mining machines are cutting and cone tools. Power subsystems of mining cutting machines contain auger, drum, chain, rotary and milling actuators. Shearers, road headers and plows also contain a large range of metal parts made of steels and alloys of various grades.

The proposed (FeCuCrMnNiTi)N coating has proven itself as an anti-corrosion coating on most metal parts of mine production introduced in the mines of the Karaganda coal basin. This coating hardness is 2 – 3 times greater than hardness of stainless steels, which, alongside with low friction, leads to a significant increasing of the service life of mining machine parts. Such operational parameters have been achieved on coatings, the formation of which is conditioned to their self-organization at the high surface energy. The very process of self-organization of ion-plasma coatings requires further studies.

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Note: Translated from Russian into English by N. Drak, translator of Karaganda Technical University