Journal of Physics: Conference Series

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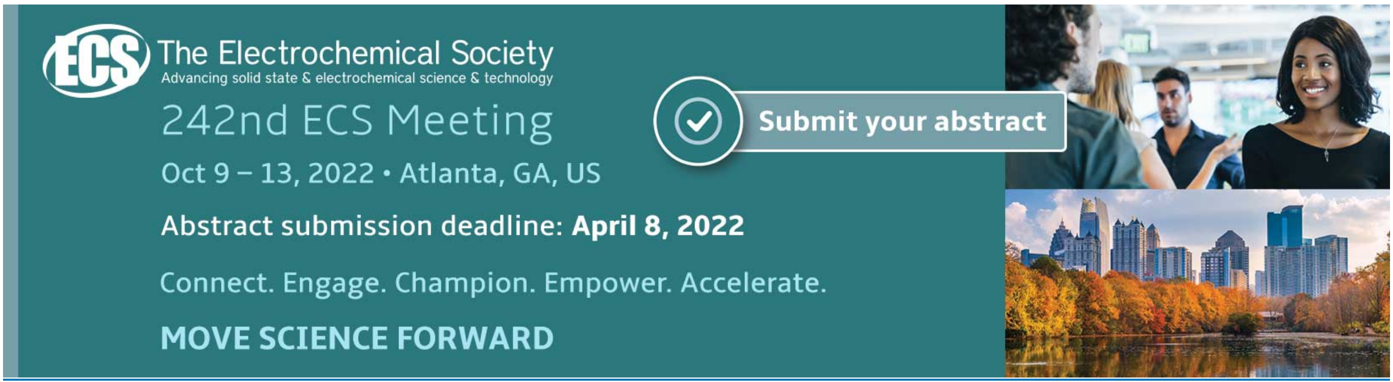
To cite this article: E N Eremin *et al* 2020 *J. Phys.: Conf. Ser.* **1441** 012006



AMSD-2019 IOP Publishing
Journal of Physics: Conference Series **1441** (2020) 012006 doi:10.1088/1742-6596/1441/1/012006

Influence of ION-plasma spraying regimes on the formation and properties of multi-element coatings

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Abstract. The technological parameters of deposition of high-entropy ion-plasma coatings based on 12Kh18N10T alloyed steel by zirconium, copper and aluminum were studied. It has been established that with increasing evaporator arc current, the surface energy of the coating decreases, which is explained by a rapid increase in its thickness, leading to an increase in the dislocation density in the coating being formed. The optimal value of the arc current is 90-110 A. Coatings obtained at a nitrogen pressure of $P=10^{-3}$ mm Hg. and the substrate temperature of 400 °C, have the most evenly distributed fine dense structure, the minimum content of the droplet phase, pores, influx, detachments, the highest values of surface energy and an increase in microhardness by 30%.

1. Introduction

Currently, there is progress in metalworking, methods of surface modification, the creation of new composite materials, which is due to advances in the study of the structure and properties of thin coatings (films).

The application of films on the surface of a material changes its mechanical (strength, hardness, elasticity), physical (light, melting temperature), technological, operational (reliability and durability of the products) and chemical (corrosion resistance, oxidation) properties.

One of the most modern methods of surface treatment is ion-plasma sputtering - a method in which the source of ions is a gas-discharge plasma, from which positive ions are drawn by a negatively charged target. Using vacuum methods of applying protective coatings, it is possible to form surface films of various metals and their compounds. These methods are very popular due to the ecological purity of production and the high quality of the obtained protective films.

The most widespread single-phase coatings based on titanium nitride and some other metals. At the same time, in recent years, the concept of the development of high-entropy (multi-element) coatings has been obtained [1-6]. The processes of structure and phase formation in such coatings, as well as the diffusion mobility of atoms, the mechanisms of formation of mechanical properties and thermal stability differ significantly from similar processes in traditional alloys and require additional research. The effect of the technological parameters of the application of multi-element ion-plasma coatings on their quality is also not studied.

The following basic parameters directly affect the structure and physical properties of coatings obtained by ion-plasma deposition: arc current, pressure of the reaction gas in the working chamber, substrate temperature.

Therefore, the purpose of this work is to identify changes in surface microhardness and the formation of coatings under the influence of the above regime parameters in the process of ion bombardment in vacuum.

2. Objects and research methods

For coating, an automated ion-plasma installation NNV-6.6 I1 was used, including a vacuum-arc generator of metallic plasma and a source of gas plasma with a combined incandescent and hollow cathode.

Structural steel was chosen as a coating substrate, which is widely used for the manufacture of various parts, mechanisms, and structures in engineering and construction. Multi-element coatings 12KhX18N10T+Zr, 12KhX18N10T+Cu, 12KhX18N10T+Al were chosen as objects of study.

The NT-206 multifunctional scanning probe microscope was used to study the surface of the coatings at the nanoscale. To study the microstructure of the sample coatings, the «Epicuant» metallographic microscope was used. The quantitative analysis of the elemental composition of composite cathodes and coatings and the determination of the stoichiometric composition of the obtained samples was carried out on a JEOLJSM-5910 scanning electron microscope. To measure the microhardness was used microhardness tester HVS-1000A.

3. Experimental results and discussion

It is established that the magnitude of the arc current has the greatest influence on the properties of multi-element coatings. The balance of power released on the electrodes of vacuum-arc evaporators, is essential meaning, both for their constructive calculation, and for the technological processes realized with their help.

The surface properties of coatings are determined by their surface energy. There are many methods for determining the surface energy of solids [7–9]. The method of determining the surface energy of a solid based on the change in the luminescent dependence of the X-ray luminescence intensity determined by the photoelectric method was used [10, 11]. The results of the obtained values of the surface energy of the investigated coatings, depending on the arc current, are given in Table 1.

Table 1. The dependence of the surface tension of the coating on the arc current

Coating	Surface tension of the coating, j/m^2			
	30 A	70 A	110 A	140 A
12Kh18N10T+Zr	0.798	0.785	0.742	0.710
12Kh18N10T+Al	0.978	0.934	0.867	0.801
12Kh18N10T+Cu	1.134	1.128	1.087	1.032

As can be seen, with increasing evaporator arc current, the surface energy of the coating decreases. This is due to the fact that with an increase in the arc current of the evaporator, the coating thickness increases quite rapidly, and this leads, in turn, to an increase in the dislocation density in the coating layer being formed.

The results of the studies of the microhardness of multi-element coatings for various values of the arc current are given in Table 2.

Table 2. The dependence of the surface tension of the coating on the arc current

Coating	Microhardness, MPa		
	30 A	110 A	140 A
12Kh18N10T+Zr	285.6	477.2	324.2
12Kh18N10T+Al	238.7	401.9	309.2
12Kh18N10T+Cu	287.4	543.1	342.3

At a low discharge power (arc current 30 A), due to a decrease in the plasma ionization coefficient, neutral particles of the reaction gas and cathode are “bricked” into the film, which contributes to an increase in the concentration of coating defects and causes a decrease in its microhardness. As the current increases above 110 A, the thickness of the multi-element coating increases, the structure perfection decreases, and the droplet phase increases abruptly, which causes the adhesion strength of the coated substrate to decrease. The optimal value of the arc current is 110 A. At the same time, the content of the droplet phase, the number of pores and delaminations decreases. For an example, in Fig. 1 shows an image obtained by scanning electron microscopy (SEM), a 12Kh18N10T+Zr coating deposited in a nitrogen atmosphere on an arc current of 110 A.

The quantitative elemental composition of such a coating, obtained by X-ray photoelectron spectroscopy (XPS), is shown in Fig. 2.

According to experimental XPS data, the elemental composition of such a coating was determined (Table 3).

It has been established that zirconium prevails in the coating, its content is 2 times higher than the iron content, 3.9 times the nitrogen content and 5.5 times the chromium content.

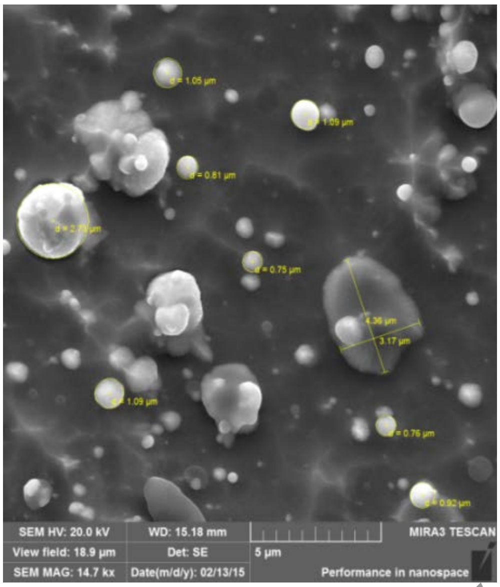

Figure 1. REM image of 12Kh18N10T+Zr coatings obtained in a nitrogen atmosphere

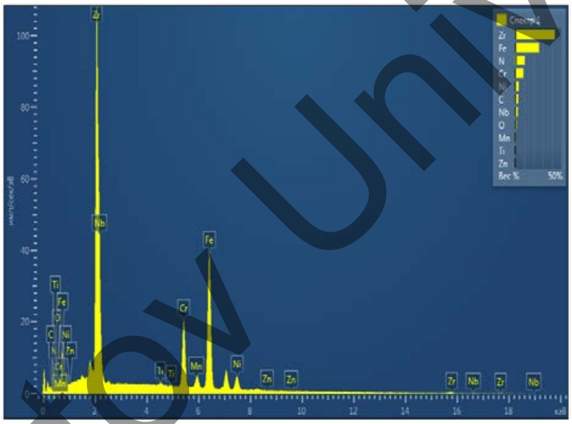

Figure 2. XPS coating 12Kh18N10T+Zr, obtained in a nitrogen atmosphere l

Table 3. The elemental composition of the coating 12Kh18N10T+Zr

Element	Line type	Conditional concentration	Ratio k	Mass %
N	K series	35.23	0.06272	12.53
Ti	K series	0.76	0.00759	0.26
Cr	K series	28.24	0.28243	9.00
Mn	K series	2.65	0.02652	0.87
Fe	K series	75.61	0.75606	24.37
Ni	K series	10.36	0.10359	4.34
Zr	L series	131.76	1.31757	49.63
Amount:	-	-	-	100.00

Further, the dependence of the properties of coatings on the pressure of nitrogen in the working chamber was investigated; at the same time, the current, the reference voltage, the cathode material, the conditions for fixing and heat dissipation, the time of the cleaning and spraying processes remained constant. In Table 4 shows the microhardness values of the coatings depending on the pressure of nitrogen in the chamber.

Table 4. The dependence of the microhardness of the coating on the pressure of nitrogen in the chamber

Coating	Microhardness, MPa		
	10^{-4} mm Hg	10^{-3} mm Hg	10^{-2} mm Hg
12Kh18N10T+Zr	385.6	477.2	344.2
12Kh18N10T+Al	338.4	401.9	359.2
12Kh18N10T+Cu	487.6	543.1	442.1

It is established that the highest microhardness values are achieved at a pressure of $P=10^{-3}$ mm Hg.

At this pressure of nitrogen, a fine dense texture is formed, which is close to the stoichiometric composition, which is characterized by the optimum, in terms of metallic properties, the ratio of metallic and ionic components of the bond. The content of the droplet phase decreases. With a further increase in pressure, a large number of free ions leads to a sharp increase in the number of pores and delaminations.

After analyzing the results of the study, it follows that the samples obtained at a nitrogen pressure of $P=10^{-3}$ mm Hg have the most evenly distributed fine dense structure, the minimum content of the droplet phase, pores, influxes, delaminations and the highest microhardness values.

Next, the effect of the substrate temperature on the microhardness of the coatings was studied, the results of which are presented in Table 5.

Table 5. Microhardness of coatings at different substrate temperatures

Coating	Microhardness, MPa		
	350 °C	400 °C	450 °C
12Kh18N10T+Zr	401.6	477.2	398.8
12Kh18N10T+Al	376.2	401.9	358.1
12Kh18N10T+Cu	502.7	543.1	511.4

These values of microhardness correlate with the values of the surface energy for these temperatures, presented in Table 6.

Table 6. Dependence of the surface tension of the coating on the substrate temperature

Coating	Surface tension of the coating, j/m^2		
	350 °C	400 °C	450 °C
12Kh18N10T+Zr	0.772	0.785	0.764
12Kh18N10T+Al	0.786	0.801	0.745
12Kh18N10T+Cu	0.832	1.032	0.878

It is established that the optimum substrate temperature for all applied coatings is 400 °C. This is explained by the fact that the refinement of the grain structure of the coating material with increasing substrate temperature is accompanied by an increase in hardness to a certain critical average size of nanograin. This is the effect of the size factor on the mechanical properties of nanostructures [12-14].

4. Conclusion

The technological parameters of deposition of high-entropy ion-plasma coatings with simultaneous spraying of multi-element cathodes were established:

– with an increase in the arc current of the evaporator, the surface tension of the coating decreases, which is explained by the rapid increase in its thickness, leading to an increase in the dislocation density in the coating being formed. The optimal value of the arc current is 110 A;

– coatings obtained at a nitrogen pressure of $P = 10^{-3}$ mm Hg. and the substrate temperature of 400 °C, have the most evenly distributed fine dense structure, the minimum content of the droplet phase, pores, flows, delaminations and the highest values of surface energy;

– the established parameters of deposition of ion-plasma coatings provide the highest values of surface energy and an increase in microhardness by 30%.

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