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Effect of ion irradiation on the properties multi-element plasma coatings

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Abstract. The paper presents the results of the study of ion irradiation on the properties of multi-element plasma coatings. The coatings were bombarded by argon ions using heavy current ion source with a hollow cathode. After ion irradiation, the structure and physical properties of the coatings change, however, the nature of the changes is different for different coatings. To predict the behavior of the coating exposed to irradiation is virtually impossible. Therefore, structural studies and investigation of physical properties of the coatings to determine their functional characteristics are to be conducted.

1. Introduction

The main effects of ion irradiation on the properties of the coatings occur at the stage of their emergence due to stress relaxation in the region of ion impact and restructuring of the crystal structure [1-3]. Point defects and active adsorption centers are formed on the surface. The mobility of adatoms on the surface (surface diffusion), which is enhanced by low-energy bombardment of the growing film with ions of inert gas, is also considered to be essential. The number of point defects can be increased either through an increase in the ion flux energy, or an increase in the density of the ion flux. Simultaneously with the defect formation, the reverse process of their recombination, "annealing", occurs, which reduces the concentration of defects. As a result of these two processes, the amount of nucleation centers becomes equilibrium, and it may be changed through varying parameters of ion irradiation. The effect of ion irradiation on films and coatings has been investigated in a number of studies [3–11]. Ion irradiation includes low-energy and high-energy ion bombardment. In [4] it is shown that the level of radiation impact on materials can be divided into three groups: a) "most resistant", substantial changes occur only at the substructure level (for example, Ti-Zr-V-Hf-Nb-Ta-N multiple system), b) the "madium resistance", significant changes occur in a macro stress-strain state (for example, TiN system), c) "structural variable", substantial changes occur at the macro-level and in phase composition (for example, MoN system).

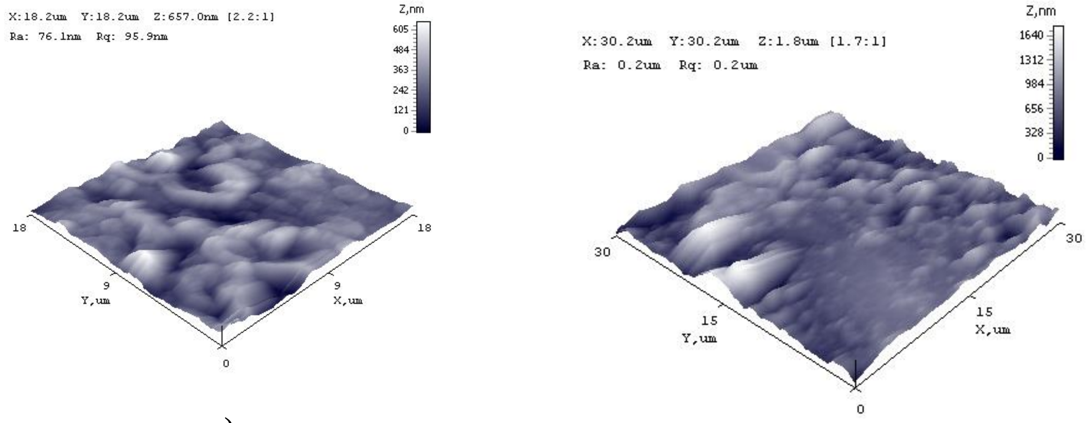
This paper discusses the experimental and theoretical aspects of the effects of ion irradiation on the structure and properties of multi-element coatings.

2. Objects and experiment techniques

In the experiments, we used composite cathodes Cr-Mn-Si-Cu-Fe-Al, Zn-Al, Zn-Cu-Al, Mn-Fe-Cu-Al and Al-Fe produced through induction melting. These cathodes were used to deposit coatings on a steel substrate under different process conditions with ion-plasma installation HHB-6.6I1. The cathode made of steel 12X18H10T and Ti, Zr, Cu, Zn-Al, Zn-Cu-Al and Al-Fe cathodes were used for simultaneous sputtering. The coatings were exposed to argon ion bombardment using the high current ion source with a hollow cathode by N.N. Koval (IHCE SB RAS, Tomsk). The arc current was 1 A, and the potential on the substrate was maintained equal to 200 V. The quantitative analysis of the elemental composition of the coating was carried out with the electron microscope JEOL JSM-5910. The microhardness of the coatings study was measured using the microhardness tester ISOSCAN OD. The atomic force microscope NT-206 was used to perform a nanoscale study of the surface coatings.

3. Results and discussion

As an example in the Figure 1 shows the AFM image images of the surface of the Fe-Al surface coating a) (before irradiation) and b) (after irradiation). Table 1 presents roughness of the multi-element coatings and Table 2 provides their microhardness before and after irradiation.



a) b)

Figure 1. AFM image of the Fe-Al surface coating a) (before irradiation) and b) (after irradiation)

Table 1. Roughness of the coating

Coating	after irradiation R_a (nm)	before irradiation R_a (nm)
Cr-Mn-Si-Cu-Fe-Al	22.26	13.34
Zn-Al	76.39	78.0
Mn-Fe-Cu-Al	23.08	29.89
Fe-Al	147.06	56.14

As can be seen in Figures 1, ion irradiation affects the coating structure. An exception is the Zn-Al coating, which turned out to be radiation-resistant. The roughness value measured before and after irradiation correlates with the obtained result (Table 2). We attribute this behavior of the Zn-Al coating to its pronounced globular structure. The presence of the "ball" system leads to elastic scattering of argon ions; as a result, the local deformation is negligible.

Table 2. Microhardness of the coating before and after irradiation

Coating	Microhardness (MPa)	
	before irradiation	after irradiation
12X18H10T+Zr	477.2	514.8
12X18H10T+(Zn-Cu-Al)	406.3	485.2
12X18H10T+(Zn-Al)	474.4	476.1
12X18H10T+(Fe-Al)	401.9	475.6
12X18H10T+Cu	543.1	585.7

The structure of the Fe-Al coating is significantly different from the structure of the Zn-Al coating. In this case, non-closed nanostructures can be observed (Fig. 1). The roughness of this coating after irradiation increases nearly three-fold. The same roughness pattern can be observed for the Mn-Fe-Cu-Al coating.

3.1. Surface tension of the deposited coatings

The structure and properties of solid surfaces and coatings are mainly determined by their surface energy or surface tension. We measured the surface tension through determining the dependence of the microhardness on the thickness of the deposited coating. The dependence is given by the formula [11]:

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

where μ is the microhardness of the deposited coating; μ_0 is for "thick" model; h is the deposited coating thickness.

The parameter d is related to the surface tension σ through the formula [11]:

$$d = \frac{2\sigma\upsilon}{RT}, \tag{2}$$

where σ is the surface tension of the bulk sample; υ is one mole volume; R is gas constant; T is temperature.

In the $\mu \sim 1/h$ coordinates ($1/h$ is the reverse thickness of the deposited coating) we obtain a straight line, the slope determined by d, and formula (2) is used to calculate the surface tension of the deposited coating (σ).

Table 3. Surface tension of the multi-element coatings produced in argon

Coating	σ (J/m^2)	Coating	σ (J/m^2)
12X18H10T+Zr	0.970	12X18H10T+Zn-Al	1.098
12X18H10T+Zn-Cu-Al	1.093	12X18H10T+Al	1.144
12X18H10T+Fe-Al	1.292	12X18H10T+Cu	1445

Table 4. Surface tension of the multi-element coatings produced in nitrogen

Coating	σ (J/m^2)	Coating	σ (J/m^2)
12X18H10T+Zr	0.185	12X18H10T+Zn-Al	0.784
12X18H10T+Zn-Cu-Al	0.744	12X18H10T+Al	0.801
12X18H10T+Fe-Al	1.034	12X18H10T+Cu	1.032
Zn–Cu–Al	0.243	Cr–Mn–Si–Cu–Fe–Al	0.711
Mn–Fe–Cu–Al	0.367		

The data in Tables 3 and 4 shows that the surface tension of the coatings produced in nitrogen atmosphere is less than that of the coatings produced in argon. Hence, formation of the nitride phase causes decrease in the surface energy of the coatings.

Table 5 shows the results of the effect of ion bombardment on some of the surfaces.

As can be seen in Table 5, all the three tested coatings behave differently under ion bombardment: Zn-Cu-Al coating is radiation-resistant, and the value of the surface tension remains practically unchanged; the surface tension of the Cr-Mn-Si-Cu-Fe-Al coating increases twofold, and the Mn-Fe-Cu-Al coating decreases threefold.

Table 5. Surface tension of the coatings after ion irradiation

Coating	Before irradiation	after irradiation
	σ (J/m^2)	σ (J/m^2)
Zn – Cu – Al	0.243	0.241
Cr – Mn – Si – Cu – Fe – Al	0.711	1.422
Mn – Fe – Cu – Al	0.367	0.122

3.2. Evaluation of the melting point of the deposited coatings

The temperatures of steel melting and solidification depend on its composition. Typically, when calculating Ts, allowance is made for the additive effect of dopants on these values.

It should be emphasized that the T_s value is of no practical interest, since the elements between the liquid and the solid phases in crystallization are considerably redistributed and as a result, the liquid is doped with segregates, primarily carbon, sulfur and phosphorus (which determine the ability of the elements to segregation).

The above results of the experimental evaluation of the surface tension of multi-element coatings, the results of its calculation by the elemental analysis and the data on the surface tension of pure metals reported in [13] can be used to show that the averaged value of the surface tension is an additive value. In this case, the melting point of the coating can be estimated by the formula:

$$T_m = 1.4 \cdot 10^3 \cdot \sigma \ (K). \tag{3}$$

The data from Table 3 were used to provide the evaluation in Table 6.

Table 6. Melting point of the multi-element coatings produced in argon

Coating	T (K)	Coating	T (K)
12X18H10T+Zr	1358	12X18H10T+Zn-Al	1537
12X18H10T+Zn-Cu-Al	1530	12X18H10T+Al	1602
12X18H10T+Fe-Al	1809	12X18H10T+Cu	2023

The melting point of steels depends on their chemical composition, but it keeps in the range of (1450–1520) K. As can be seen in Table 6, the melting point of 12X18H10T + Al, 12X18H10T + Fe-Al and Cu + 12X18H10T coatings produced in argon is significantly higher than that of steels. The melting temperature of Zn-Cu-Al, Cr-Mn-Si-Cu-Fe-Al and Mn-Fe-Cu-Al coatings is low. Table 7 shows the melting point of the investigated coatings after ion bombardment.

Table 7. Melting point of the coatings produced in nitrogen atmosphere, before and after irradiation in the medium

Coating	Melting point (K)	
	Before irradiation	After irradiation
12X18H10T+(Zn-Cu-Al)	1042	1250
12X18H10T+(Fe-Al)	1448	1454
12X18H10T+(Zn-Al)	1098	1296
12X18H10T+Cu	1445	1561

As can be seen in Table 7, the melting point slightly increases. For 12X18H10T+(Fe-Al) coating, this change is negligible.

4. Conclusion

The results of the studies provided in this paper show that ion irradiation largely affect all the properties of the coatings. However, the properties of radiation-resistant coatings change insignificantly. It should be noted that the behavior of the coating under irradiation can hardly be predicted so far. Therefore, structural studies and research into physical properties of the coatings to determine their functional characteristics are to be conducted.

Acknowledgements

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