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Effect of ion irradiation on the surface energy of deposited coatings

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Abstract. We investigated multi-element coatings exposed to argon ion bombardment. The coatings were irradiated using a multi-ampere hollow-cathode ion source. The arc current was 1 A, and the potential of the substrate was maintained equal to 300 V. The surface tension (surface energy) of the coatings was measured before and after irradiation through the size-dependence of the microhardness and electrical resistivity of coatings on their thickness. Ion irradiation was found to affect the surface energy of the coatings in different ways. This is due to both the structure of the coating and its elemental composition.

1. Introduction

In recent years, the concept of high entropy multi-element alloys and coatings based on these alloys has been widely developed [1–5]. Various properties of these coatings are being investigated, including radiation resistance under irradiation by ions at different energies [6-8].

The properties of the coatings are primarily affected by ion bombardment at the stage of their origination due to relaxation of stresses in the area subjected to ion irradiation and crystal structure rearrangement. Point defects, active adsorption centers, are formed on the surface. The mobility of adatoms on the surface (surface diffusion) enhanced by low-energy inert gas ion bombardment of the growing film also plays an important role. The number of point defects can be increased by increasing either the ion flux energy or the ion current density. Defect formation is followed by the reverse process of defect recombination, "annealing", which reduces defect concentration. These two processes result in an equilibrium number of nucleation centers, which can be varied by changing the ion irradiation parameters.

This paper presents the results of the research in the ion bombardment induced effect on the surface energy of some multi-element coatings.

2. Materials and methods

In the experiments, we used Zn-Cu-Al, Mn-Fe-Cu-Al and Cr-Mn-Si-Cu-Fe-Al cathodes manufactured through induction melting. These cathodes were used to deposit coatings on a steel substrate using the ion-plasma unit HHB-6.6-11 at different process conditions.

The atomic force microscope NT-206 was used to perform a nanoscale study of the coating surface. Two methods developed and reported by the authors in [9, 10] were used to determine the surface tension (surface energy) of the deposited coatings. The first method involves measurement of the surface tension by determining the dependence of the microhardness on the deposited coating thickness. The dependence of the microhardness of the deposited coating on its thickness is described by the formula:

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

where μ is the microhardness of the deposited coatings; μ_0 is the microhardness of the "thick" sample; h is the thickness of the deposited coating. The parameter d is related to the surface tension σ by the formula:

$$d = \frac{2\sigma v}{RT} \quad (2)$$

Here, σ is the surface tension of the bulk sample; v is molar volume; R is gas constant; T is temperature. The coordinates $\mu \sim 1/h$ ($1/h$ is the inverse thickness of the coating) indicate a straight line, the slope determined by d , and the surface tension of the deposited coating (σ) is calculated by formula (2).

The second method is used to measure the dependence of electrical conductivity Ω of the deposited coating on its thickness h that is described by the formula (1):

Argon ion irradiation of the coatings was performed using a hollow cathode multiampere ion source. The arc current was 1 A, and the substrate potential was maintained equal to 300 V.

3. Results and discussion

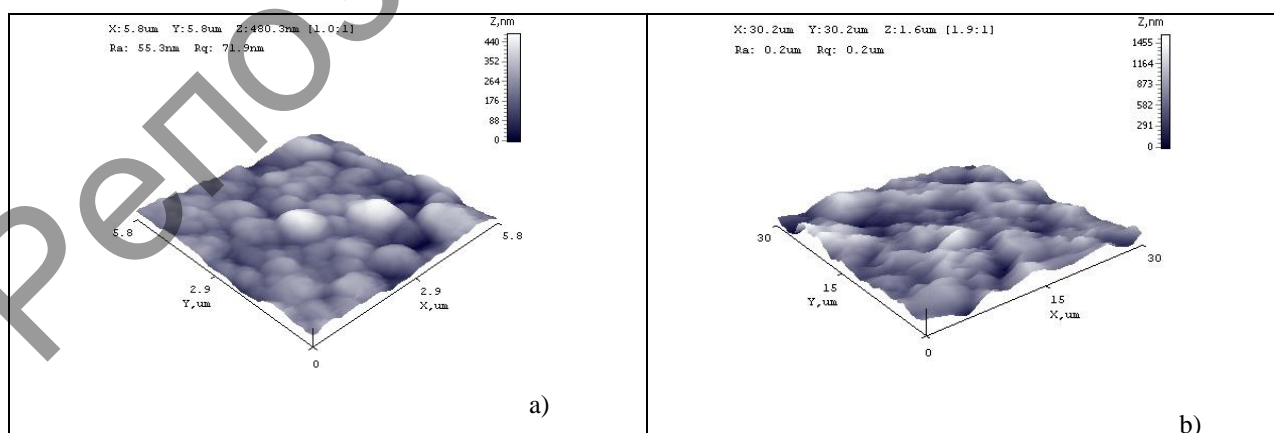
Figure 1 shows the AFM images, and Table 1 presents the surface energy values of the investigated coatings.

Table 1. - Surface energy of the deposited coatings.

Coating	Before irradiation	After irradiation
	$\sigma, \text{J/m}^2$	$\sigma, \text{J/m}^2$
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

As shown in Table 1, all three investigated coatings behave differently under ion irradiation: the Zn-Cu-Al coating exhibits radiation resistance, and the surface tension value remains practically unchanged; the surface tension of the Cr-Mn-Si-Cu-Fe-Al coating increases by a factor of two, and the tension of the Mn-Fe-Cu-Al coating decreases by a factor of three. These changes are associated with changes in the surface coating structure during ion bombardment (Fig. 1).

Radiation resistance of the Zn-Cu-Al coating is attributed to its distinct globular structure (Fig. 1). The presence of the system of "balls" leads to elastic scattering of argon ions, so that the local deformation is negligible.



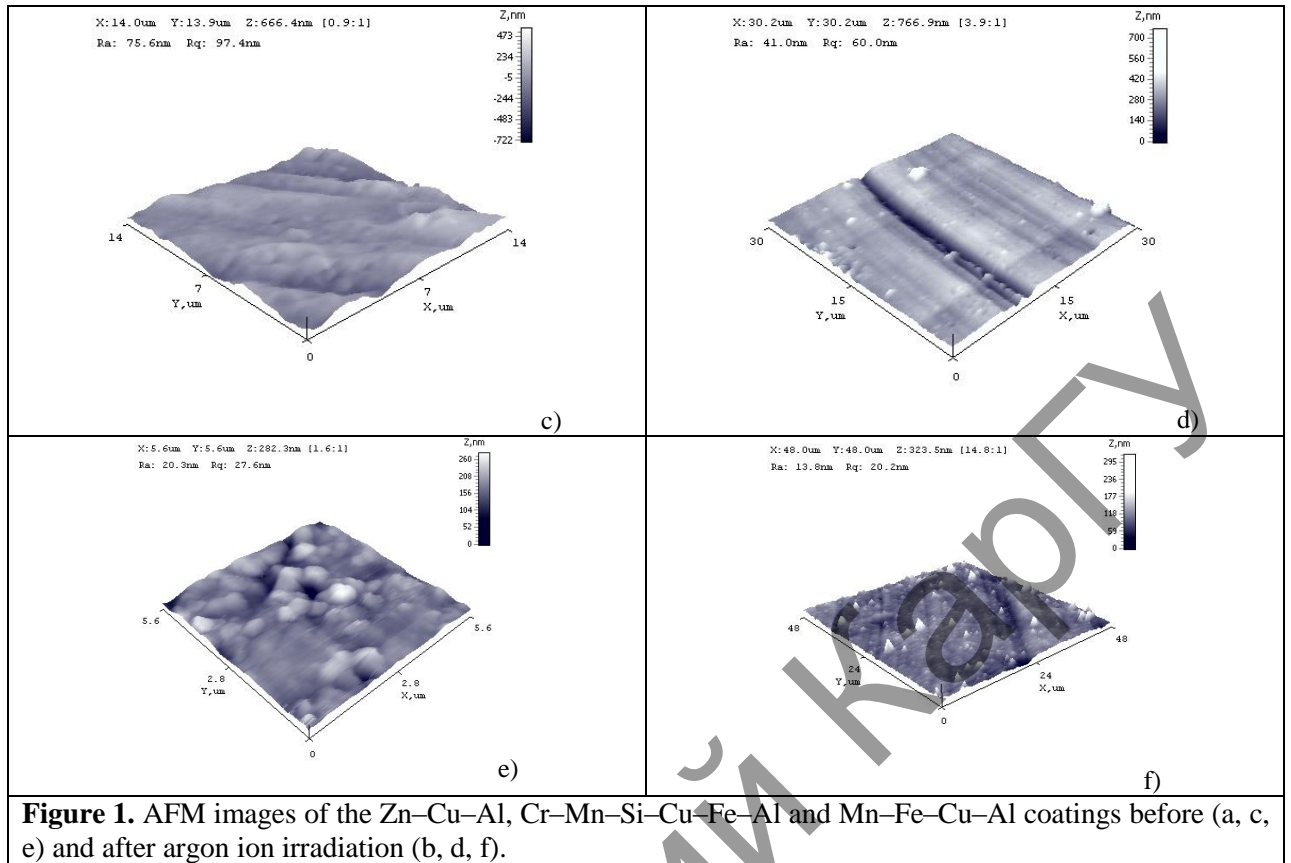


Figure 1. AFM images of the Zn–Cu–Al, Cr–Mn–Si–Cu–Fe–Al and Mn–Fe–Cu–Al coatings before (a, c, e) and after argon ion irradiation (b, d, f).

The wear resistance of the coating depends on the work of its destruction, which is equal to:

$$A = \sigma \cdot S, \quad (3)$$

where S is the sample surface area.

Table 2. Surface tension of pure metals (M) at 300 K [10].

M	σ_{300} , J/m ²	M	σ_{300} , J/m ²	M	σ_{300} , J/m ²	M	σ_{300} , J/m ²	M	σ_{300} , J/m ²	M	σ_{300} , J/m ²	M	σ_{300} , J/m ²
Li	0.152	Sr	0.730	Sn	0.205	Cd	0.294	Fe	1.508	Gd	1.285	Ac	1.023
Na	0.071	Ba	0.683	Pb	0.300	Hg	0.07	Co	1.463	Tb	1.331	Th	1.723
K	0.037	Al	0.633	Se	0.193	Cr	1.873	Ni	1.426	Dy	1.380	U	1.105
Rb	0.012	Ga	0.003	Te	0.425	Mo	2.573	Ce	0.777	Ho	1.434	Np	0.613
Cs	0.002	In	0.129	Cu	1.056	W	3.373	Pr	0.908	Er	1.470	Pu	0.610
Be	1.258	Tl	0.276	Ag	0.934	Mn	1.217	Nd	0.998	Tm	1.518	Am	0.973
Mg	0.623	Si	1.386	Au	1.036	Tc	2.173	Sm	1.025	Yb	0.797	Bk	0.998
Ca	0.818	Ge	0.931	Zn	0.399	Re	3.123	Eu	0.875	Lu	1.625	-	-

Formula (3) demonstrates that increased surface energy will lead to the increase in wear and radiation resistance. The multi-element Cr-Mn-Si-Cu-Fe-Al coating presented in Table 1 meets this condition. Similar results were obtained in [6, 7].

Since the surface energy value for solid solutions is additive, the coating should be selected based on the surface energy of each component of the alloy in order to increase the radiation resistance of solid solutions (single-phase alloys). Table 2 shows the surface tension (surface energy) values for the majority of the metal elements of the periodic table.

Within the framework of the molecular theory, the friction force is equal to:

$$F_{tr} = \int \sigma dL \approx \sigma \cdot L, \quad (4)$$

where L is the path length.

Formula (4) indicates that growth in the surface energy causes decrease in friction. This case is valid for the Mn-Fe-Cu-Al coating.

4. Conclusion

The presented results show that ion irradiation (or any other irradiation) can be used to change the basic properties of coatings in either direction through the change in the surface energy. In practice, it is crucial for both aircrafts in the ionosphere and components of nuclear reactors.

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