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Study of the strength characteristics and radiation resistance of thin-film coatings based on CuX (X=Bi, Mg, Ni)

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The paper presents the results of changes in the strength characteristics of thin-film coatings based on compounds of copper-bismuth, copper-magnesium, copper-nickel. The dependences of the influence of the phase composition on the strength characteristics, such as the coefficient of friction, bending strength and impact coefficient, are established. The effect of irradiation with helium ions with a high radiation dose of 10¹⁵ -10¹⁷ ion/cm² on the strength characteristics is evaluated. It is shown that an increase in the radiation dose leads to a decrease in strength properties due to the appearance of a large concentration of defects in the structure.

Keywords: radiation resistant coatings, thin films, radiation defects, strength, resistance to external influences.

Introduction

One of the most promising applications of thin-film coatings is their use as local protection of the most important components of microelectronic devices from the destabilizing effect of ionizing radiation [1-5]. The main principle of applying

local protection is the use of thin films of complex phase composition and crystal structure to reduce the energy of incident particles due to the difference in energy losses in the crystal structure of coatings of different phase composition [6, 7]. In this case, the presence of two or more types of atoms in the structure of the crystal lattice of different types, properties, and sizes can have a significant effect on the change in the energy of the incident particles and the maximum mean free path, which directly affects the absorption coefficient of protective coatings [8, 9]. However, the phase composition, coating thickness and number of layers, as well as their structure, plays a double role in the efficiency of shielding of ionizing radiation. On the one hand, an increase in the number of layers and their thickness leads to a significant increase in the absorption efficiency and a decrease in the risk of destabilization of the operation of microelectronic devices. On the other hand, a large number of layers and their thickness can significantly increase the mass-dimensional parameters and weight the microcircuit design [10-15]. In this connection, research in the field of selection of optimal conditions for thickness, number of layers, and also the study of the effect of phase composition is one of the most promising studies in the field of creating local protection from exposure to ionizing radiation [16, 17]. Moreover, today in most microelectronic circuits, massive protection is used based on ceramic dielectric materials with high radiation resistance [18-23]. However, the use of dielectric matrices significantly increases the mass of microelectronic devices due to the creation of additional massive cases made of dielectric ceramics. In turn, the use of local protective coatings can significantly reduce the weight and size parameters, while not decreasing the radiation resistance [24, 25].

Earlier, our research team established the dependences of the influence of synthesis conditions on the phase composition and corrosion properties of synthesized thin film coatings based on CuX (X=Bi, Mg, Ni) obtained using the electrochemical deposition method [26, 27]. As the substrates for the preparation, polymer films were used that have good surface adhesion properties, which makes it possible to obtain thin-film coatings on them that are isotropic in thickness and composition. Interest in two-component thin-film coatings based on selected metals is due to their structural properties and the potential for use as protective coatings [27-30]. The choice of elements of bismuth, magnesium and nickel in combination with copper is due to the possibility of obtaining structures with different phases, which can have a significant effect on resistance to external influences.

Experimental part

Synthesis of thin film coatings

To obtain thin-film coatings of different phase composition, the following electrolyte solutions were selected: 1) the composition of the electrolyte solution to obtain copper-bismuth films: $CuSO_4 \cdot 5H_2O(238 \text{ g/l})$, $Bi_2(SO_4)_3$ (10 g/l), H_2SO_4 (21 g/l); 2) the composition of the electrolyte solution to obtain copper-magnesium films: $CuSO_4 \cdot 5H_2O(238 \text{ g/l})$, $Mg(NO_3)_2$ (15 g/l), H_2SO_4 (21

g/l); 3) the composition of the electrolyte solution to obtain copper-nickel films: CuSO₄ \cdot 5H₂O (238 g/l), Ni(CH₃COO)₂ (15 g/l), H₂SO₄ (21 g/l). The range of applied potentials was 1.5-2.0 V, with a step of 0.25 V [26]. The choice of the difference in applied potentials is due to the possibility of obtaining coatings of different phase composition. The thickness of the obtained films was 1 µm. To obtain films of a given thickness at different potential differences, which affects the film formation rate, the deposition time was varied. The thickness of the obtained films was controlled by the method of evaluating lateral cleavages using scanning electron microscopy. A detailed study of structural changes, phase and elemental composition is presented in [26].

Determination of strength characteristics

Wear resistance tests were carried out by rolling with 10% slip at a load of 100 N. Test duration are 20 000 cycles.

Study of radiation resistance

Thin-film coatings based on Cu, Cu-Bi, Cu-Mg, Cu-Ni obtained at a potential difference of 1.5-2.0 V, in increments of 0.25 V were selected as objects of study. Changing the potential difference during the synthesis leads to the formation of structures of different phase composition with the formation of both complex oxide phases and phases of the substitutional solid solution. As incident particles, low-energy He²⁺ ions with an energy of 40 keV and a fluence of 10¹⁵-10¹⁷ ion/cm² were chosen. The choice of ions and energies is due to the ability to simulate radiation exposure comparable to that of cosmic radiation, as well as the products of nuclear reactions in nuclear energy.

Results and discussion

Determination of strength characteristics of nanostructured thin-film coatings

The wear resistance of the synthesized coatings was studied by determining the tribological characteristics, such as dry friction coefficient, bending strength, and impact coefficient. As is known, one of the important parameters affecting the strength characteristics is the presence of various phases in the structure of the coatings and the concentration of dislocation defects. Table 1 presents data on the dependence of changes in the parameters of the flexural strength and toughness depending on the synthesis conditions.

According to the data obtained, in the case of coatings based on Cu-Bi, the appearance of the CuBi₂O₄ phase in the crystal structure leads to an increase in strength characteristics, which indicates an increase in the wear resistance and strength of the coatings to external influences. Moreover, the increase in strength is due to a decrease in dislocation defects and disordered regions in the structure, and hence an increase in the degree of crystallinity of the coatings. In the case of coatings based on Cu-Mg, the presence of the substitutional solid solution phase Cu $_{0.9687}$ Mg $_{0.0313}$ with a low magnesium content in the lattice for samples obtained at a difference in applied potentials of 1.75-2.0 V leads to a decrease in strength characteristics, which is due to the presence of distortions and deformations in the structure crystalline structure, leading to the formation

of microcracks and disordered areas under external influences. For coatings based on Cu-Ni, the formation of the cubic phase of the CuNi substitutional solid solution does not significantly affect the change in strength parameters. Figure 1 presents data on changes in the value of the coefficient of dry friction depending on the number of test cycles. Wear resistance tests were carried out by rolling with 10% slip at a load of 100N, the number of test cycles was 20.000.

Parameter	Potential difference, V	Type of coating		
		Cu-Bi	Cu-Mg	Cu-Ni
Bending Strength	1.5	$144{\pm}5$	137±6	142±3
(MPa)				
	1.75	178 ± 6	132 ± 5	140 ± 5
	2.0	$214{\pm}4$	$114{\pm}5$	137±4
Coefficient of	1.5	1.11 ± 0.15	1.21 ± 0.13	1.19 ± 0.14
impact strength				
(kJ/mm2)				
	1.75	$1.45 {\pm} 0.11$	1.17 ± 0.11	1.15 ± 0.11
	2.0	$1.94{\pm}0.22$	1.09 ± 0.10	1.13 ± 0.12

Parameters of strength characteristics.

Table 1.

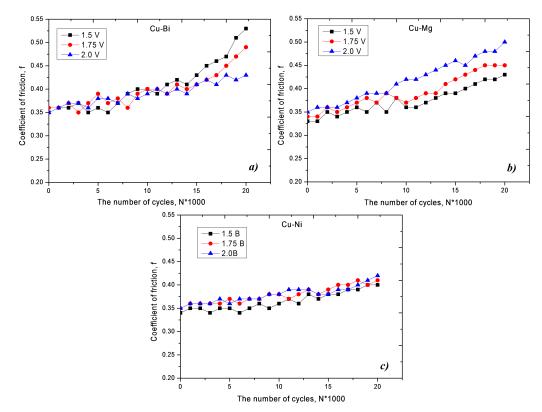


Figure 1. Graphs of the dependence of the change in the coefficient of friction on the number of test cycles.

As can be seen from the data presented, for coatings based on Cu-Bi obtained with a potential difference of 1.5-1.75 V, a slight increase in the coefficient of dry friction with an increase in the number of cycles of more than 10.000 is observed.

This is due to the partial destruction of the surface layer and subsequent peeling and cracking of the surface in places of accumulation defects. In this case, the formation of the oxide phase of CuBi_2O_4 leads to an increase in strength properties and a smaller change in the value of the dry friction coefficient. Unlike coatings based on Cu-Bi, an increase in the difference in the applied potentials when producing coatings based on Cu-Mg, which leads to the formation of a non-stoichiometric phase of the Cu_{0.9687} Mg_{0.0313} solid solution, leads to an increase in the coefficient of dry friction due to the formation of microcracks in the structure of coatings and degradation surfaces with an increase in the number of test cycles. In turn, for systems based on Cu-Ni, the change in the friction coefficient depending on the number of test cycles is minimal, which indicates the resistance of the coatings to external influences.

Thus, we can conclude that the change in the strength properties directly depends on the influence of synthesis conditions and the concentration in the structure of amorphous and impurity inclusions that occur at high potential differences. In this case, the transition of the crystalline structure from cubic to hexagonal leads to a significant increase in strength characteristics.

Investigation of the effect of phase composition on the radiation resistance of thin-film coatings

Thin protective coatings with a thickness of 1 μ m were chosen to study the effect of the phase composition on the efficiency of absorption and changes in structural characteristics under the influence of low-energy ions with a high radiation dose characteristic of defects accumulation in the structure. Figure 2 shows the dependence of the change in the dislocation density in the coating structure on the irradiation fluence.

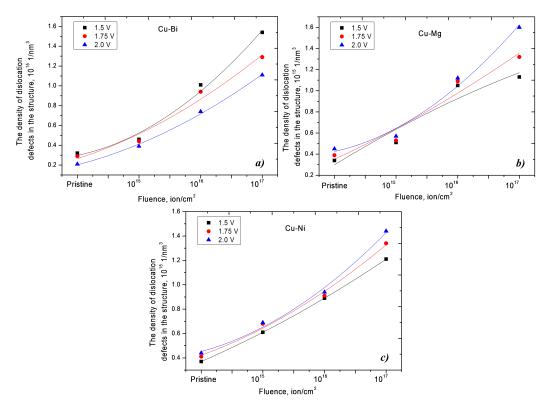


Figure 2. Graph of changes in the dislocation density in the structure of coatings from irradiation fluence.

As can be seen from the data presented, the appearance of an oxide phase in the structure of coatings in the Cu-Bi system leads to a decrease in the dislocation density compared to coatings based on Cu-Mg and Cu-Ni, which indicates less radiation damage in the Cu-Bi coatings as a result exposure to ionizing radiation. The presence of an oxide phase in the crystal structure leads to the formation of additional scattering centers, which leads to greater energy absorption and a significant decrease in the dislocation density. For coatings based on Cu-Mg, the appearance of the nonstoichiometric phase of a substitutional solid solution leads to an increase in the dislocation density with an increase in the irradiation fluence. Moreover, the dislocation density for coatings based on Cu-Mg is comparable to the dislocation density of coatings based on Cu-Bi, while for coatings based on Cu-Ni, the dislocation density is lower. The decrease in the dislocation density for the Cu-Ni system, with an increase in the irradiation fluence compared with other systems, is due to the stability of the Cu-Ni system to external influences and high strength characteristics to wear. An increase in the dislocation density in the structure of coatings can lead to the appearance of additional disordered regions containing a high concentration of defects, which can lead to partial amorphization and the formation of microcracks in the structure, which will significantly affect the strength characteristics and wear resistance of protective coatings. In turn, an increase in the dislocation density can also be due to the partial accumulation and agglomeration of poorly soluble helium ions that can lead to the formation of helium inclusions with subsequent degradation of the surface layers. Also, the high mobility of helium ions can lead to its migration deep into the coating to a depth significantly exceeding the maximum mean free path of ions in the material. The penetration of helium ions deep into the surface can lead to the formation of additional defects that can have a significant effect on the structural parameters of coatings and their radiation resistance.

Conclusion

During the research it was found that the change in the strength properties and hardness of the coatings directly depends on the influence of the synthesis conditions and the concentration in the structure of amorphous and impurity inclusions that occur at high potential differences. In this case, the transition of the crystalline structure from cubic to hexagonal leads to a significant increase in strength characteristics, and a small porosity (less than 1%) leads to a significant increase in the hardness of the coatings. During the radiation resistance tests of thin-film coatings, it was found that the appearance of an oxide phase in the structure of coatings in the Cu-Bi system leads to a decrease in the dislocation density compared to coatings based on Cu-Mg and Cu-Ni, which indicates less radiation damage to the coatings Cu-Bi as a result of exposure to ionizing radiation. The presence of an oxide phase in the crystal structure leads to the formation of additional scattering centers, which leads to greater energy absorption and a significant decrease in the dislocation density. For coatings based on Cu-Mg, the appearance of the nonstoichiometric phase of a substitutional solid solution leads to an increase in the dislocation density with an increase in the irradiation fluence. Moreover, the dislocation density for coatings based on Cu-Mg is comparable to the dislocation density for coatings based on Cu-Bi, while for coatings based on Cu-Ni, the dislocation density is lower.

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