Investigation of the Influence of Crystallization Energy on the Size of Nanostructures During Copper Ion-Plasma Treatment

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Abstract. The paper presents the results of the calculation of the crystallization energy and investigates its effect on the size of the nanostructured grain during ion-plasma treatment of copper with oxygen and nitrogen ions. It is shown that the crystallization energy increases the energy of ions required to obtain nanostructures. At energies near 300 eV, it ranges from 0.1 to 7 eV, ie can be ignored, but at energies close to 15,000 eV, the crystallization energy is from 200 to 11,000 eV, and the energy for oxygen ions is greater**.** Calculations also showed that the ion charge significantly affects the crystallization energy for large ion charges in the direction of increase. All these results confirm that it is necessary to take into account the crystallization energy only at energies of $2{\cdot}10^3$–$2{\cdot}10^4$ eV, and this allows to clarify the technological parameters of ion-plasma treatment of copper to increase the probability of obtaining nanostructures.

Keywords: Crystallization energy · Surface hardening · Micro-coarseness · Wear resistance · Diffusion layer

1 Introduction

In modern research, many scientists are studying the issue of obtaining nanostructures in various structural materials. This gives not only new opportunities for their use, but also quite interesting new properties for known materials. The study of copper is especially interesting because it has a very wide range of possibilities for using both as mono material and in combination with others. For example, by deposition of silver nanostructures on copper substrates [1] or its oxidation followed by heat treatment [2], superhydrophobic anti-corrosion coatings are obtained. Developed in the [3] hydrothermal method, a superhydrophobic copper surface is obtained, which has not only resistance to chemical exposure and UV radiation, but also a self-cleaning effect. With the development of technology, researchers are particularly interested in nanostructures in copper and its combinations. Thus, in [4], copper nanostructures are used for chemical analysis using Raman spectroscopy. And [5] developed a resistive memory device based on copper oxide synthesized by ion implantation.

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It is quite natural that with the spread of interest in the use of nanostructured copper, the interest in the methods and technologies of its production also spreads. A lot of research is being done to expand them. For example, [6] investigated the effect of nitrogen ion implantation on the properties of thin films of copper oxide obtained by direct current magnetron sputtering. And in [7] the influence of radiation on the submicrostructures of copper and copper alloys is considered. The effect of implantation of nitrogen ions of different charges into copper was also studied in [8]. In [9], the structural characteristics of nanocrystalline copper after implantation of carbon ions were studied. Particular physical properties were also studied. Thus, [10] studied the control of residual stress gradients in copper films by implantation of inert ions.

But there are far fewer studies of ion-plasma methods for obtaining nanostructures in copper. Thus, the effect of ion-plasma treatment of the copper surface on its resistance to high-vacuum breakdowns was studied in [11]. In [12, 13] the evolution of the charge positions of ions in the plasma of the cathode vacuum arc was studied. And [14, 15] are practical works using vacuum-arc plasma to obtain nanostructured films. Practical work on measuring the dependence of the erosion rate on the parameters of the arc on nanostructured copper cathodes was also carried out in [16, 17].

As we can see, a lot of practical works [12–15] are focused on obtaining nanostructured materials, but much less work is devoted to theoretical research [18, 19]. Although it should be noted that in [20, 21] the study of energy required to create nanostructures in some structural materials was given and the evaluation of the action of ions of a certain energy, charge and grade was carried out [22, 23], which allows to assess the possibility of formation of nanostructures. However, the crystallization processes were not considered, which means that the energy expended on crystallization when obtaining nanostructures by the ion-plasma method was not estimated. This means that the accuracy of calculations of the energy required to obtain nanostructures by the above method decreased. All this indicates the need to assess the impact of crystallization energy on the energy of nanostructures, which will determine the technological parameters of ion-plasma treatment where its accounting is mandatory and were not. In general, this will make it possible to more accurately determine the technological modes of processing at which there is a high probability of obtaining nanostructures.

2 The Main Part

To solve this problem, we take in [22] a model where the solution of the joint problem of thermal conductivity and thermoelasticity in the area of action of an individual ion of the corresponding energy, charge and grade, which allows to estimate the possible number of particles in the nanostructure, then calculates the energy and chemical compounds. Taking into account these energies and the number of atoms and chemical compounds in the grain, we find the total energy of atomization of the grain E_{ac}.

Further, taking the energy of grain formation as $E_c = 1.1E_{ac}$, we can find the energy required for grain formation. Given this value, we determine all the characteristics in the ion's range: temperature, rate of temperature rise, temperature stresses and strain rate, grain size, volume of nanostructure and depth of its occurrence and the actual number of particles in the nanostructure.

2.1 Research Methodology

Using the above, we obtain new values of the considered quantities, which will make it possible to determine their influence on the occurrence of nanostructures.

Having determined the number of particles in the nanostructure, we need to determine the atomization energy of particles in the structure, which can be determined taking into account two energies: the Coulomb repulsion energy E_k and the ionic bond energy E_{ib} by the expression:

$$\begin{aligned} \mathrm{E}_c &= \mathrm{E}_k + \mathrm{E}_{ib} = \varepsilon^2 U + \left(1-\varepsilon^2\right)^{\frac{1}{2}} D_0 N \\ &= -\frac{\varepsilon^2 k\,\mathrm{M}\,\mathrm{e}^2\,\mathrm{Z}^2\,\mathrm{N}}{R_0}\left(1-\frac{\rho}{R_0}\right) + \left(1-\varepsilon^2\right)^{\frac{1}{2}} D_0 N \end{aligned} \tag{1}$$

where ε is the degree of ionicity; U is the energy of interaction of ions; k is electrostatic constant,

$$k = \frac{1}{4\pi\varepsilon_0} \approx 8,987742438 \cdot 10^9\left[\frac{H * \mathrm{M}^2}{\kappa\pi^2}\right];$$

M is Madelung constant; *e* is electron charge;

z is the ion charge; N is the number of particles;

R_0 is the shorter interatomic distance; ρ is the degree of repulsion; D_0 is the dissociation energy of one particle of matter.

The degree of ionicity ε for substances AB is determined by the expression:

$$\varepsilon = \frac{X_A - X_B}{X_A + X_B}, \tag{2}$$

where X_A, X_B are oxidation states for elements A and B on the Pauling scale.

The Madelung constant M is defined as follows:

$$M = \sum\nolimits_j^n \frac{z_i z_j}{P_{ij}}; \tag{3}$$

where z_i, z_j are charges of interacting ions.

The energy of the electrostatic Coulomb interaction is defined as follows:

$$P_{ij} = \frac{e^2 z_i z_j}{R_{ij}}, \tag{4}$$

where R_{ij} is the distance between charges i, j, which can be expressed as $R_{ij} = P_{ij} * R_0$.

Then the energy of interaction of the *i*-th ion with all other ions (n) is represented as:

$$U = 1/2\left(n\sum_i^n \frac{e^2 z_i z_j}{R_0} * \frac{1}{P_i j} + n\sum_j^n \frac{e^2 z_i z_j}{R_0} * \frac{1}{P_i j}\right) = \frac{ne^2}{R_0}\sum_j^N \frac{z_i z_j}{P_i j}; \quad (5)$$

The use of the factor $\frac{1}{2}$ in (1) is due to the fact that we will use the interacting pair of ions only once.

The degree of repulsion ρ depends on the magnitude and characteristics of grain deformation. As the compression of the crystal increases, its resistance increases rapidly. The ions repel each other, and the closer the ions get closer to each other, the greater the repulsive forces. Since the electronic shells of ions that penetrate each other are repelled, the correct description of these forces is possible on the basis of quantum mechanics or by the Bourne method [20] by the expression:

$$\frac{1}{\rho} = \frac{2}{R_0} + \frac{9V}{\mathrm{M}\beta}; \quad (6)$$

where V is the mole volume of the crystal; M is the Madelung constant; β is compressibility of crystals.

There is a relationship between repulsion indices and orbital exponents that connect atomic orbitals [20]. For oxides and chalcogenides this relationship can be represented as follows:

$$\frac{1}{\rho} \approx (1+\varepsilon)(\xi_{\mathrm{M}} + \xi_{\mathrm{X}}); \quad (7)$$

Where ξ_M Ta ξ_X are the orbital exponents of the atomic orbitals of metal (m) and halogen (x).

Estimation of the value of the orbital exponent can be obtained using the first ionization potential (I), determined in Ridbergs *(1Ry = 13.6 eV = 313 kcal)*:

$$\xi = \sqrt{I}; \quad (8)$$

The interatomic distanceR_0 for substances A and B is defined as the sum of covalent radii:

$$R_0 = R_{\kappa}(\mathrm{A}) + R_{\kappa}(\mathrm{B}); \quad (9)$$

The dissipation energy D_0 has been experimentally determined for many substances, but to avoid limitations in estimating the energies of covalent bonds for D_0 crystals, we use Pauling's general postulate:

$$D_0 = \sum_{i=1}^m \Delta H_{\mathrm{aT}}(i); \quad (10)$$

To test the developed model, consider the effect of nitrogen and oxygen ions in the plasma medium on copper. Theoretical calculations of the crystallization energy depending on the ion energy, which takes into account the number of particles in the cluster, obtained without taking into account the crystallization energy, are given in [22]. In the future, on the basis of a refined theoretical model, we will compare the size of the theoretically calculated nanograin, taking into account and without taking into account the crystallization energy. If we assume that the crystallization energy is equal to or close to the atomization energy, then as a result of calculations we obtain the atomization energy for chemical compounds at different charge numbers, degrees of repulsion and dissociation energies.

3 The Results of Calculations and Their Discussion

Using the calculated values of the atomization energy and knowing the number of particles in the nanocluster, which are taken from [22], we obtain the energy required to obtain grain. To ensure a greater probability of its creation, increase this value by 10% and use in further calculations.

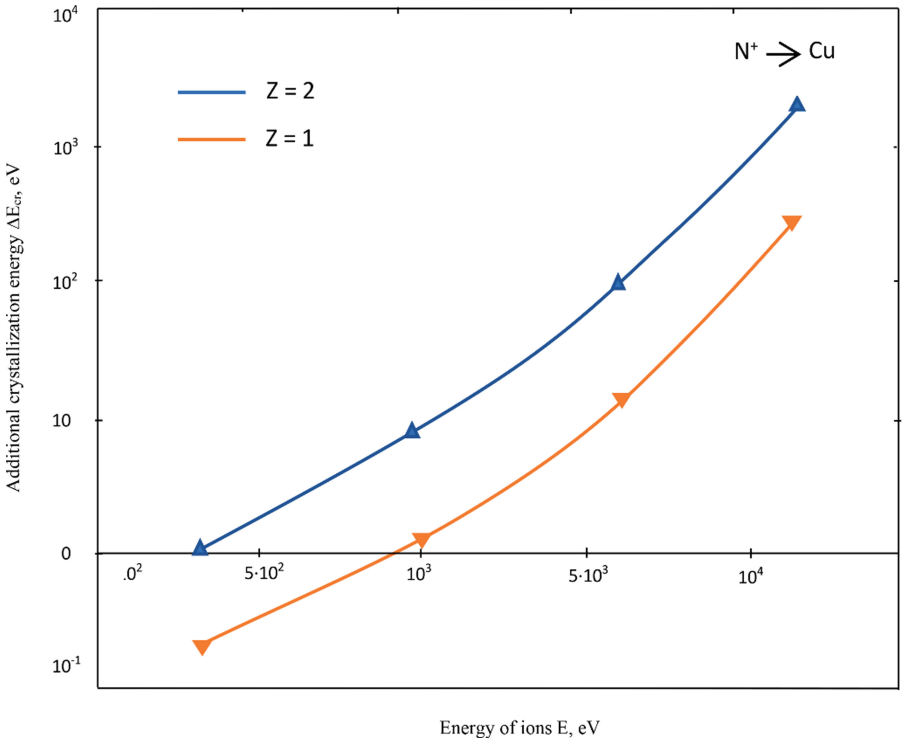

Fig. 1. Dependence of additional crystallization energy on the energy of ions at different ion charges N^+ when it acts on copper.

The results of the study of the dependence of the crystallization energy on the energy of ions acting on copper are presented in Fig. 1, 2 for the case of action of nitrogen ions (see Fig. 1) and oxygen (see Fig. 2).

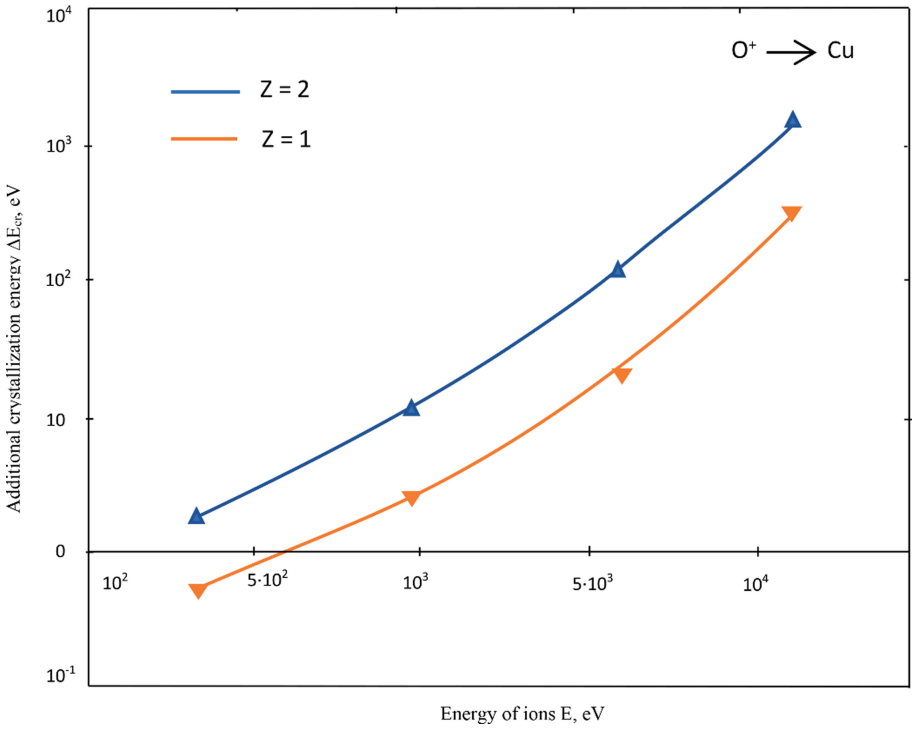

Fig. 2. Dependence of additional crystallization energy on the energy of ions at different ion charges O^+ when it acts on copper.

We can see that at the energy of ions ($E = 3{\cdot}10^3$ eV), the crystallization energy is (0.1–3) eV for N^+ and (0.25–9) eV for O^+, with large values corresponding to a larger charge of ions ($z = 2$). At the energy of ions $E = 1, 5{\cdot}10^4$ eV, the crystallization energy is already ($2.7{\cdot}10^3 - 9{\cdot}10^4$) eV for N^+ ions and ($10^3 - 1.1{\cdot}10^3$) eV for O^+ ions, with large values corresponding to larger ion charges. This change in the crystallization energy is associated with a decrease in the volume of the nanocluster, with an increase in the ion energy and, accordingly, with the crystallization energy.

Obviously, the crystallization energy will affect the technological parameters necessary for the formation of nanostructures. For this purpose, the dependences of the grain size on the ion energy, taking into account and without taking into account the crystallization energy, were calculated according to the model [22]. Such dependences are presented in Fig. 3 and Fig. 4 for the case of action of nitrogen and oxygen ions.

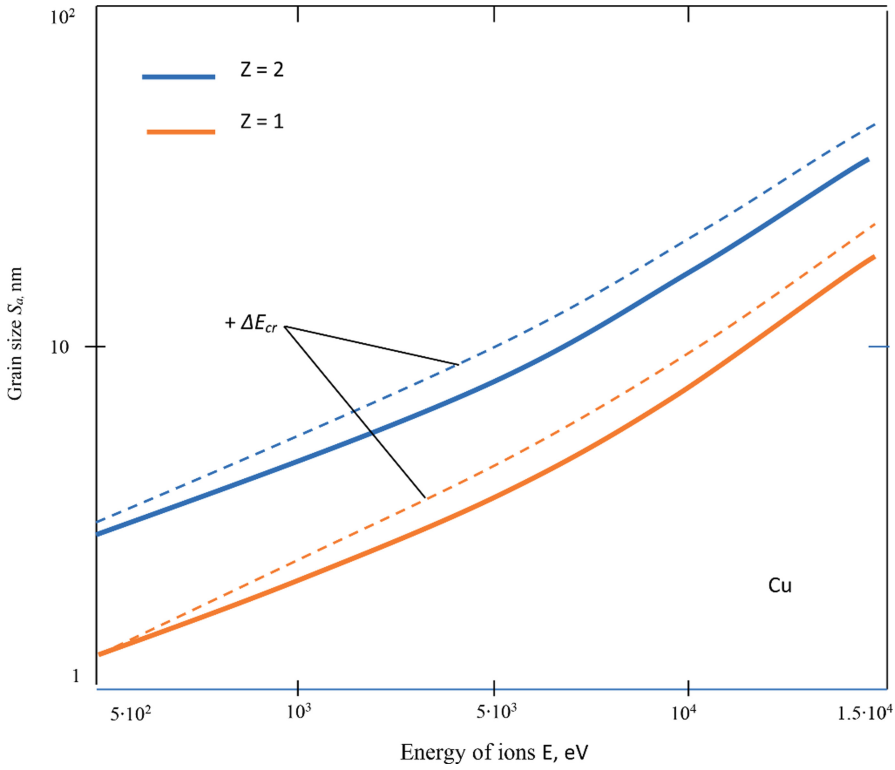

Fig. 3. Dependence of grain size on the energy of ions N^+ (with charge: z = 1; z = 2) when they act on copper, taking into account (ΔE_{cr}) and without taking into account (–) the energy expended on crystallization.

Thus, in the case of the activity of nitrogen ions with an energy of $3{\cdot}10^2$ eV, the grain size can be 1.7–6 nm, whereas at an ion energy of 1, $5{\cdot}10^4$ eV, they can grow up to 15–30 nm. For oxygen ions with an energy of $3{\cdot}10^2$ eV, they are in the range of 1.5–5.5 nm, while the grain size increases to 10–50 nm under the action of oxygen ions with an energy of 1, $5{\cdot}10^4$eV.

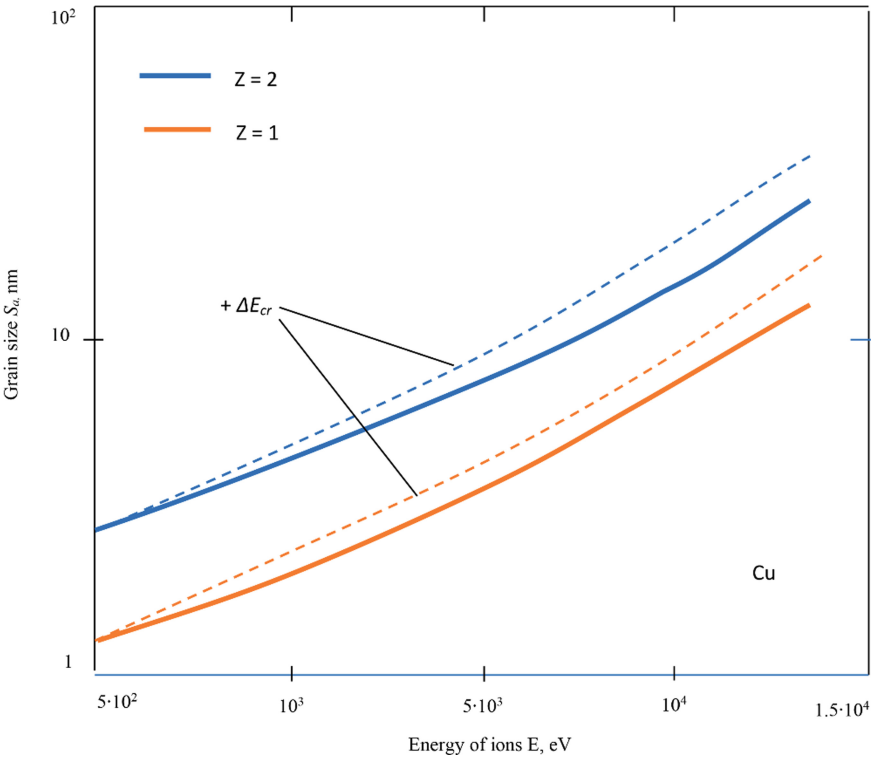

Fig. 4. Dependence of grain size on the energy of ions O^+, (with charge: z = 1; z = 2) when they act on copper, taking into account (ΔE_{cr}) and without taking into account (–) the energy expended on crystallization.

4 Conclusions

Theoretical studies have shown that the crystallization energy increases the energy of ions required to obtain nanostructures. The crystallization energy, at values ranging from 0.1 to 7 eV, which corresponds to ion energy of about 300 eV, can be neglected. But at ion energies close to $1.2 \cdot 10^4$ eV, the crystallization energy is from $2 \cdot 10^2$ to $1.1 \cdot 10^3$ eV. Also, calculations have shown that the ion charge significantly affects the crystallization energy for large ion charges in the direction of increase.

All this suggests that it is necessary to take into account the crystallization energy only at ion energies $2 \cdot 10^3$–$2 \cdot 10^4$ eV. Its consideration will allow to clarify the technological parameters in the ion-plasma treatment of copper to increase the probability of obtaining nanostructures. It may be interesting for professionals engaged in developing devices for nanostructures.

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