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**ELECTRICAL SURFACE  
TREATMENT METHODS**

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## **Peculiarities of the Influence of an Inductance–Capacitance Device on the Initial Stage of the Crystallization of Electrolytic Coatings of Copper**

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**Abstract**—It was experimentally determined that, depending on the conditions of the molybdenum monocrystal processing and due to the application of the inductance–capacitance device, crystals of various configurations and sizes are deposited first and significantly influence the copper formation with the deposition time increasing.

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### INTRODUCTION

The nature and state of the cathode surface, together with the electrolysis conditions, determine the origin and surface distribution of the particles responsible for the subsequent character of the deposition formation [1, 2]. At the initial stage of the coating development, the substrate has an orienting influence on its structure. The coating deposition is characterized by the development of various clusters that turn into crystalline, nanocrystalline, or amorphous formations as they grow. The character of the cathode deposition proliferation depends on the ratio of the rates of the arising and growth of the crystallization centers; therefore, the cathode structure influences it greatly.

When the cathode surface is covered by dense oxide films with a fine-crystalline structure, in the copper deposition process, there arise a considerable quantity of crystallization centers. During the process of deposition on the copper substrate, the number of crystallization centers diminishes, and, on the surface, massive crystals are found to be formed, the feed of which is provided both due to the surface diffusion and the diffusion from the depth of the solution.

The substrate affects the crystallization of the deposits also by the ratio of the active and passive sites on it and its macro- and microrelief. The value of the active surface prevails on the polished surfaces versus the roughly processed ones, which significantly influences the origin of the germs and their disposition on the surface, because the diffusion-feed mode of the active sites abruptly changes depending on the electrode's surface relief. The character of the initially forming deposit, due to the surface relief's influence and the degree of the

surface activity, remains unchanged for 20–30 min during the electrolysis process [2].

A more uniform and ordered structure of the coatings was obtained during the copper deposition on monocrystalline electrodes [3, 4]. On the surface of a copper cathode, the disposition of the crystalline germs was correlated with the crystal-plane index. The orienting influence of the cube planes was found to be stronger than that of the octahedron plane.

In the case of the significant passivation of the cathode surface, the orienting influence of the plane's character on the crystalline germs' origination was minor. The germs were found to occur at the sites of structural irregularities of the oxide film, where its thickness appeared to be less.

Along with the substrate influence, the formation of deposits is affected by the electrolysis conditions [3, 4]. By means of the current density and substrate type varying, there were obtained crystals of various kinds that differed by their configuration and sizes. The formation of each kind of crystals is closely connected with the distinct type of the substrate and the electrochemical conditions.

In the prior publications, it was shown that the parameters (the inductance and capacitance) of the inductance–capacitance facility (ICF) connected to the current source significantly influence the kinetics of the process and the structure and physicomechanical properties of the coatings, including those of copper [5–7]. Therefore, in the present paper, the influence of the above facility (ICF) on the initial stage of crystallization of the electrolytic copper coatings was particularly studied.

## METHODS OF INVESTIGATION

The coatings of copper were deposited on the surface of a (110) molybdenum monocrystal obtained by zone melting using an electronbeam device [8]. The specimen's surface was processed according to the following techniques: 1—polishing using a rotating moist felt disk using a powder of chromium oxide with dimensions up to 2  $\mu\text{m}$  with subsequent degreasing using French chalk and activation in 30% chlorohydric acid for 2 sec; 2—electrochemical polishing by means of a sulphate electrolyte ( $\text{CuSO}_4$ —112 g/l,  $\text{H}_2\text{SO}_4$ —159 g/l) with its temperature being 20°C and the current density being 0.2  $\text{kA/m}^2$  (under these conditions of polishing, the surface passivation does not take place); 3—hand-polishing with the help of a diamond paste with the fractions' dimensions being up to 2  $\mu\text{m}$  and with subsequent degreasing using surgical spirit.

The coatings were deposited in a sulphate electrolyte ( $\text{CuSO}_4$ —250 g/l,  $\text{H}_2\text{SO}_4$ —50 g/l) with its temperature being 20°C and the current density being 0.2  $\text{kA/m}^2$  in the following succession: first, the coating was deposited for 15 sec, and, after the examination of the morphology, the surface was coated again for 30 sec with further deposition for 30 min. All the experiments were carried out with the deposition of copper on one and the same specimen in order to eliminate the monocrystal structure's influence.

As the power source, there was used a single-phase transformer with a capacity of 40 W and a rectifying unit, which the inductance—capacitance facility (ICF) was connected to, with an inductance of  $L = 10$  H and a capacitance of  $C = 17600$   $\mu\text{F}$  [9]. The selected parameters  $L$  and  $C$  act maximally on the copper deposition process [5]. Taking into account the specimen's diameter, in order to provide for the specified current density, the current intensity was established equal to 60 mA. The specimen was installed in a special attachment that enabled one to perform the deposition of copper only at a preset surface of a monocrystal.

The morphology of the deposits was examined using a TESCAN scanning electron microscope.

## RESULTS AND DISCUSSION

The experiments showed that, depending on the conditions of the surface preparation and the electrolysis, crystals of copper that differed both by their dimensions and configuration were formed at the cathode.

At the copper deposition without the ICF for 15 sec on the surface processed according to the first technique, there were formed crystals of a dendritic type [3, 4]. Crystals 15–20  $\mu\text{m}$  in diameter and with a round form prevailed among them. In some places, there occurred their linking without the formation of distinct boundaries (Figs. 1a and b).

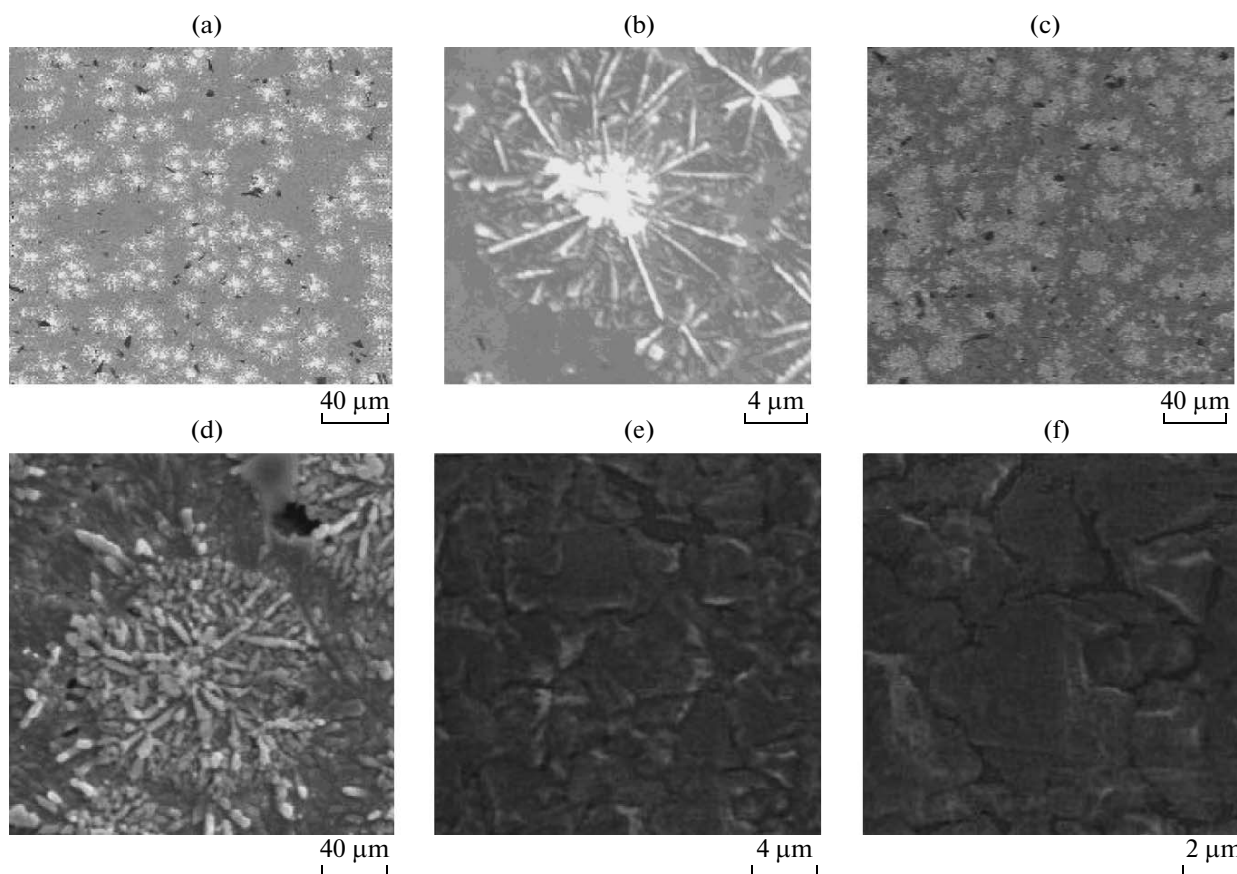
As is seen from the obtained pictures, a crystal grows from one center in which the germ was formed and then it enlarges in the radial direction in the shape of closely adjoined "petals." On this layer, there grow dendrites 0.15–0.5  $\mu\text{m}$  in cross section and with a length up to 10  $\mu\text{m}$ .

The deposition on the same surface for another 30 sec resulted in the formation of a continuous layer due to the origination of new germs and their growth at the sites free from the coating (Figs. 1c and d). Simultaneously, there occurs leveling of the coating surface provided by the filling in of the cavities. On this copper substrate, there were found to be formed microcrystal aggregations predominantly with a round form and with a pronounced center, the majority of which were 0.3–0.5  $\mu\text{m}$  in size. In some places, their linking and the formation of larger-sized particles were observed to occur. In addition, there was also detected the growth of dendrites with a length of up to 6  $\mu\text{m}$ . Such coating formation seemed to occur as a result of either the coherency or structural bonding with the previous layer [3, 4].

The copper deposition on this surface for another 30 minutes resulted in the formation of crystalline aggregates different in their sizes of insignificant deposit thickness because of the presence of uncoated spots and unlinked boundaries between the aggregates (Figs. 1e and f).

The ICF application significantly influenced the formation of the deposits. After the copper deposition for 15 s, 25–30% of the cathode surface was a continuous coating. At the remaining part of the surface, the copper was deposited in the form of round spots with a pronounced center and diameters of 30–40  $\mu\text{m}$  that significantly differed from the previous ones both by their thickness and configuration (Figs. 2a and b). Although the dendrite growth persisted, the surface layer consisted of a multitude of "threads" (0.2–0.3  $\mu\text{m}$  diameter), which produced new branching—new dendrites. This surface in certain places was subjected to "filming," which made it smooth. Microcrystals started growing on it, which formed the dendrites or even larger particles due to linking. Such a character of the coating growth under the initial conditions of the deposition might lead to a situation when, at certain sites, they could have both crystalline and noncrystalline structures [3, 4]. The continuous coating formed both from the above linked dendrite crystals and from the closely adjoining separate particles of  $\sim 0.5$   $\mu\text{m}$  with various configurations (Fig. 2c). At careful examination, one can observe the oriented disposition of several particles, which suggests the formation of crystals due to the self-assembly of clusters [3].

The deposition time increase by 30 s (similar to the experiments without the ICF), which ensured the completion of the formation of the smooth surface layer of copper, where the fine particle deposition occurred mainly at the sites with a round form



**Fig. 1.** Morphology of the deposited copper onto the monocrystal surface after polishing by chromium oxide: (a, b) after 15 s; (c, d) after 45 s; and (e, f) after 30 min.

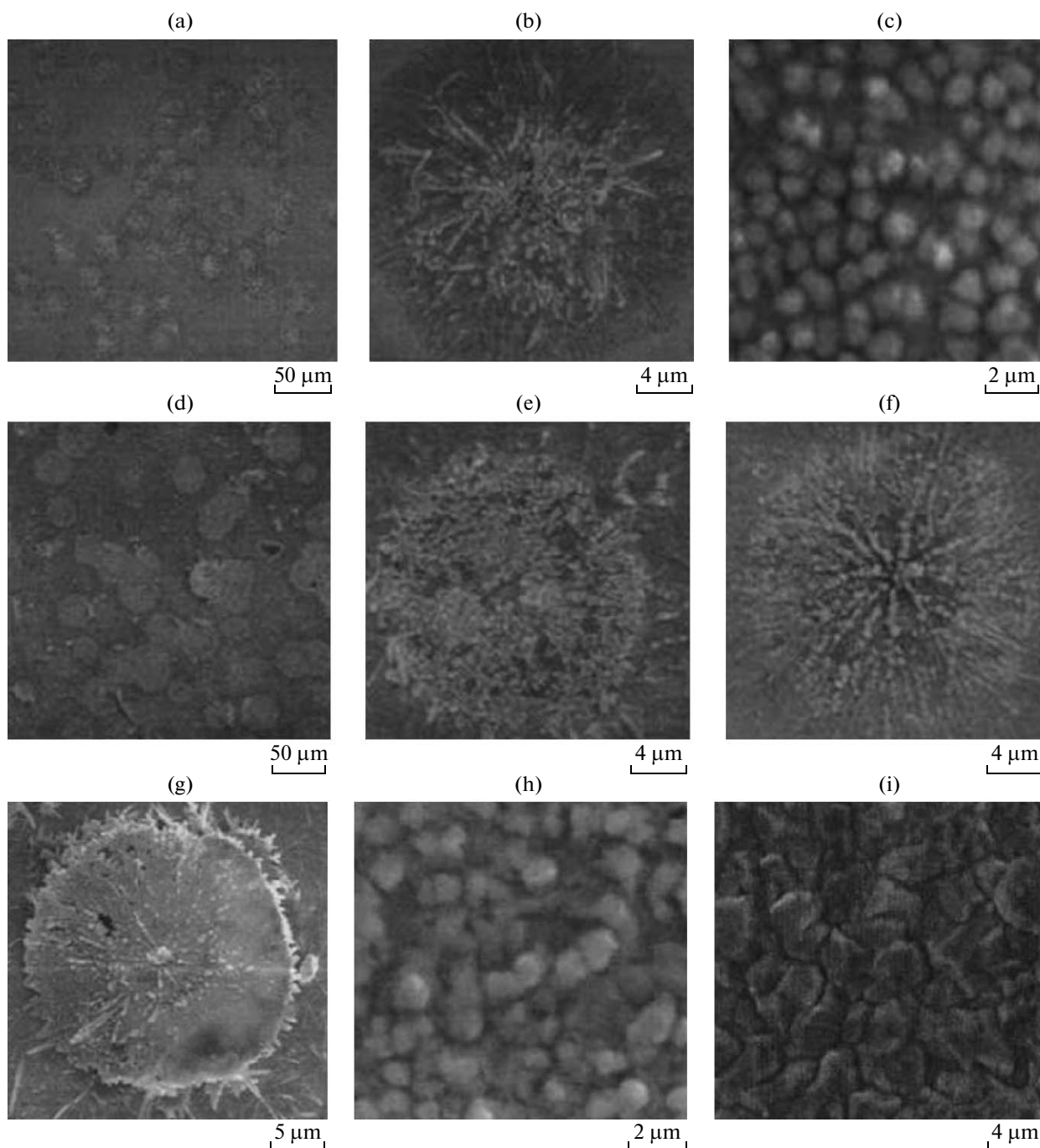
(Fig. 2d). Some of them exhibited the formation of fine particles ( $0.2\text{--}0.4\ \mu\text{m}$ ) not oriented around a strongly pronounced center (Fig. 2e), while the others displayed a well defined center and the radial disposition of microparticles, which diminished their sizes from the center towards the periphery (Fig. 2f). Moreover, there was also determined the coating growth in the form of discs, with the diameter of the majority of them equaling  $45\ \mu\text{m}$ , having a pronounced center and the radial disposition of the microparticles. Certain sites of their surface were observed to have porosity, but others were of high integrity.

At the free surface of a crystal, at the redeposition, there appear new centers of crystallization and the recurrence of the above forms of crystallization of the copper deposition, and, in some cases, there is observed the growth of large narrow “petals” (Fig. 2b). Probably, these forms of the coating growth are significantly influenced by the structure of the layer deposited directly on the monocrystal surface. In the places where, after 15 s deposition, the crystals were being formed from separate clusters, new layers of minute particles were growing and their size increase was insignificant both in the process of their growth and as a result of linking (Fig. 2h).

At 30 min copper deposition, the entire surface of the specimen was coated. A more fine-crystalline structure was found to appear at the specimen in the places of the observed dendrite growth of the coating (Fig. 2h). On the remaining surface sites, the crystals were of large sizes and there was revealed their pyramidal development. The aggregates of greater dimensions resulted from the linkage of smaller crystals (Fig. 2i).

The change of the conditions of the surface processing (the preparation according to the second technique) influenced in a certain way the initial stage of the copper deposition. Just as in the previous case, without the ICF action, at the monocrystal surface, there was deposited a limited quantity of the metal during 15 s (Fig. 3a). Besides, the nonuniform distribution of the crystals, which varied by their sizes and configuration, was observed. The clusters of certain crystals were located symmetrically with regard to the center, and the quantity of “petals” might vary from 6 to 14. In the central part, the growth of new clusters took place, the quantity of which also differed.

The crystals that were composed of clusters different in quantity and linked in space had much greater sizes [3, 4]. The formation of crystals different in size and configuration on the substrate surface is obviously

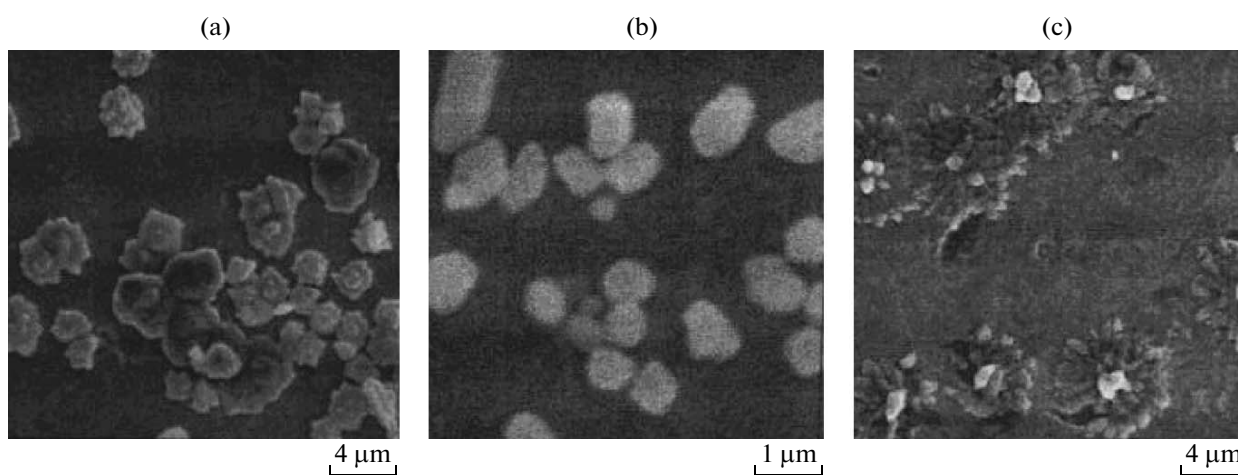


**Fig. 2.** Morphology of the deposited copper with the ICF application onto the monocrystal surface after polishing by chromium oxide: (a, b, c) after 15 s of deposition; (d, e, f, g, h) after 45 s; and (i) after 30 min.

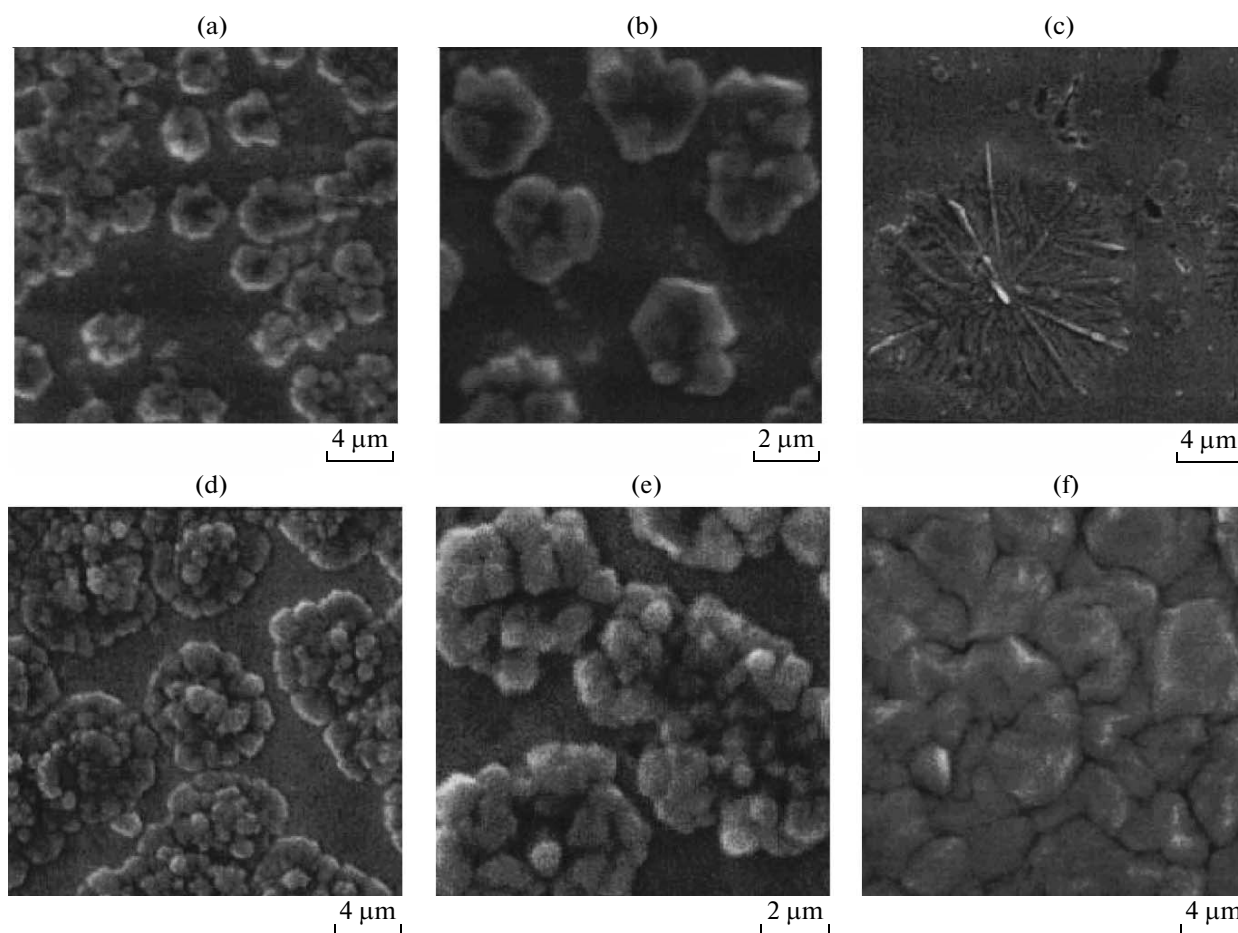
correlated with the fact that the germs appear at various periods of the deposition and, already from the start, they differ among themselves (Fig. 3b). At the cathode periphery, there were determined crystals that were of different configurations as compared to the previous ones (Fig. 3c).

The ICF application profoundly influenced the process of the copper deposition. A part of the cathode

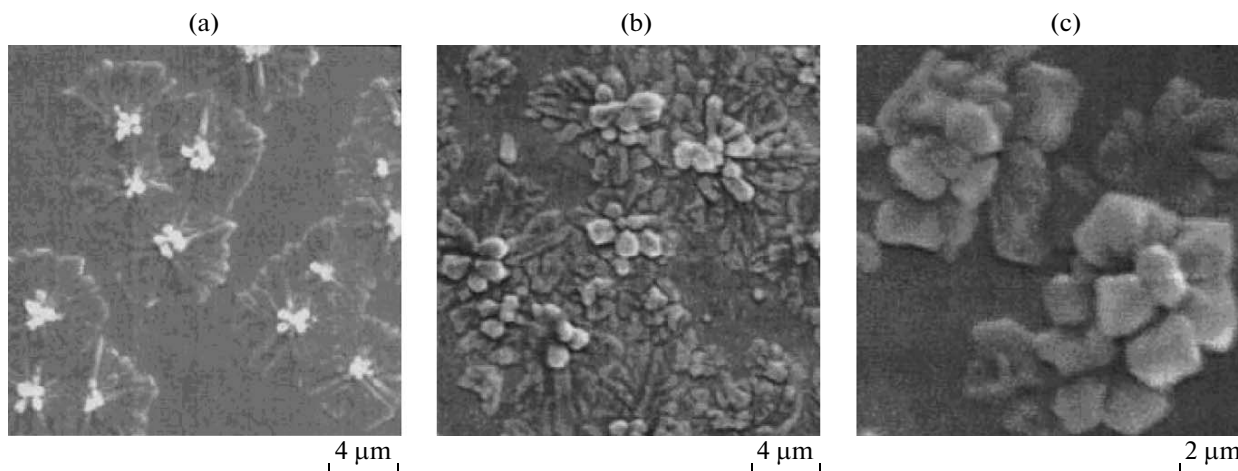
was coated by a continuous layer that consisted mainly of the crystals whose clusters were concentrated around the center, and, linking together, they were observed to form a continuous coating (Fig. 4a). Moreover, such kind of clusters can aggregate not only on a plane but in space as well. However, in both cases, they insignificantly differed by their sizes, which ensured the formation of a homogeneous structure. Just as in the previous case, at a separate site of the



**Fig. 3.** Morphology of the deposited copper onto the monocrystal surface after the electrochemical polishing: (a, b, c) after 15 s of the deposition.



**Fig. 4.** Morphology of the deposited copper with the ICF application onto the monocrystal surface after the electrochemical polishing: (a, b, c) after 15 s deposition; (d, e) after 45 s; (f) after 30 min.



**Fig. 5.** Morphology of the deposited copper onto the monocrystal surface after polishing by the diamond paste: (a) after 15 s deposition; (b, c) after 15 s of the ICF deposition.

monocrystal, there was detected the growth of dendrite crystals with their diameter being smaller versus the previous ones (Fig. 4c). In addition, the film growth was registered at the cathode surface with the films obviously lacking a crystalline structure. The deposition time increase involved the linkage of new clusters and the growth of a multitude of fine particles on their surface (Fig. 4d). Despite the expansion of the previous crystals, the cathode surface was not entirely coated. On a certain site, there was observed the crystal growth in the form of “hedgehogs” [3, 4] with a great number of “petals” (Fig. 4e). Such kind of coating formation at the cathode caused the subsequent (after 30 min deposition) nonuniform growth of the deposit (Fig. 4f).

The polishing of a monocrystal with the diamond paste (according to the third technique) also led to the copper crystallization modification in the initial period of the deposition (Fig. 5). In the ICF’s absence, there was found the dendrite growth of crystals with a form close to a circle and a diameter up to 10  $\mu\text{m}$  with the “petals” being adjacent to each other and the growth of fine particles in the center. At the substrate’s surface, the crystals were distributed uniformly, in certain cases being at a considerable distance from each other.

The ICF application had no impact on such a character of their growth. A certain distinction was observed in the central part of the specimen where the new “petals” grow like “hedgehogs.” In that case, the quantity of the deposited copper increased profoundly, and, at certain parts of the substrate, there was registered the formation of a continuous coating. In addition, at some sites of the substrate, there was detected the “hedgehog”-type crystal growth with symmetrically located clusters being adjacent to each other and differently directed (Fig. 5c).

The performed investigations showed that the copper crystallization process is influenced both by the deposition conditions and the technology of the substrate surface preparation prior to the coating deposition.

The crystals various in form and size obtained at the initial stage of the deposition confirm the possibility of their formation from the two- and three-dimensional germs and monocrystals of decahedral and icosahedral form [3, 4]. The majority of the crystals were formed from one center of crystallization with one symmetry axis. Some of them are characterized by the lateral uniform expansion of “petals” from the center preserving a round form, and others shape the crystal by linking to the central part of the new clusters or in the “hedgehog” form. For that kind of crystals, the presence of twinning subboundaries of the interface and a congenital cause is typical, which provides for their self-organization in the process of growth [3, 4]. The certain distinction noted at the initial stage of the crystal formation due to the various preparation of the substrate surface is probably caused by its substructure modification correlated with its polishing by the abrasive material and the electrochemical method. It is of special interest to consider the arising of dendrite crystals at the copper deposition on the surface processed according to the first technique and with the ICF application, since in that case, within 45 seconds of deposition, there forms a fairly thin and uniform surface layer (0.3–0.5  $\mu\text{m}$ ) on which there begins the growth of the edged fine particles. By means of varying the deposition conditions and its time, perhaps, one may obtain thin copper coatings with an ill-defined crystalline structure of high electroconductivity and thermal stability, which are of urgent interest for the electron, microelectronic, and other branches of industry [4].

Thus, the carried out research showed that the parameters of the inductance–capacitance facility

connected to the power source profoundly influence the initial stage of the copper crystallization, when a more uniform and fine-crystalline structure is formed (which predetermines the further growth of the deposit) and the quantity of the centers of the crystallization and the deposited metal increases as well.

#### REFERENCES

1. Gamburg, Yu.D., *Kristallizatsiya metallov i splavov* (Crystallization of Metals and Splavov), Moscow: Yanus-K, 1977.
2. Nichiporenko, O.S., Pomosov, A.V., and Naboichenko, S.S., *Poroshki medi i ee splavov* (Powders of Copper and its Alloys), Moscow: Metallurgiya, 1988.
3. Vikarchuk, A.A. and Volenko, A.P., Pentagonal Crystals of Copper: Variety of Forms of Growth and Peculiarities of Internal Structure, *Fizika Tverdogo Tela*, 2005, vol. 47, no. 2, pp. 339–344.
4. Vikarchuk, A.A., Volenko, A.P., Gamburg, Yu.D., and Bondarenko, S.A., On the Disclination Nature of Pentagonal Crystals Formed at Copper Crystallization, *Electrokhimiya*, 2004, vol. 40, no. 2, pp. 207–214.
5. Gologan, V.F., Bobanova, Zh.I., Ivashku, S.Kh., Popov, V.A., and Mazur, V.A., Peculiarities of the Deposition Process of Galvanic Coatings in Case of Application of a Single-Phase Power Source with Integrated Inductance-Capacitance Device, *Elektron. Obrab. Mater.*, 2007, no. 2, pp. 12–16.
6. Gologan, V.F., Bobanova, Zh.I., Ivashku, S.Kh., Volodlina, G.F., Mazur, V.A., and Pushkash, B.M., Morphology of Electrolytic Coatings of Copper in Case of Application of Power Source with Integrated Inductance-Capacitance Device, *Elektron. Obrab. Mater.*, 2008, no. 1, pp. 21–28.
7. Gologan, V.F., Bobanova, Zh.I., and Ivashku, S.Kh., The Influence of the Inductance-Capacitance Device on the Structure and Wear-Resistance of Electrolytic Coatings of Chromium, *Elektron. Obrab. Mater.*, 2008, no. 5, pp. 15–21.
8. Ol'shanskii, N.A., Shubin, F.V., Kakabadze, A.K., et al., *Elektronno-luchevaya svarka monokristallov tugoplavkikh i redkikh metallov* (Electron-Beam Welding of Monocrystals of High-Melting and Rare Metals), Moscow: Nauka, 1973.
9. Gologan, V., Bobanova, J., Ivashku, S., and Popov, V., Sursa monofazata pentru procese electrochimice, MD Inventor's Certificate no. 3258, *BOPI*, 2008, no. 2.