

COPPER CRYSTALS WITH FRAGMENTED STRUCTURE AND DEVELOPED SURFACE IN TEMPERATURE FIELDS

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Abstract. The effect of electrodeposition regimes of copper polycrystalline foils and coatings on their structure, morphology and behavior during subsequent heat treatment is studied. Electrodeposition is carried out with simultaneous mechanical activation of the surface of foils and coatings, which leads both to the materials internal structural changes and to the appearance of features of the surface morphology: the specific faceting of growth terrains, the formation of polyatomic growth steps, and the appearance of crystals (grains) with pentagonal symmetry. The results of changes in the morphology, structure and phase composition of the polycrystalline copper obtained during the heat treatment in oxidizing or inert atmospheres are presented.

Keywords: electrodeposition; copper polycrystalline foils; structure; morphology.

1. Introduction

Materials based on metals with a developed surface are widely used as catalysts in the gas processing, petrochemical and chemical industries, as well as in solving various problems in the field of ecology [1-3]. The main goal of creating such materials is to obtain particles, microcrystals, granules, layers, foils and coatings with the maximum possible specific surface; it is believed that the catalytic activity of metallic materials is mainly determined by chemical reactions on their surfaces [1, 4-6]. There is another conception [7, 8], based on the fact that the catalytic activity of metallic materials is determined not only by their specific surface, but also strongly depends on the internal structure of the material and the features of the morphology of its surface.

The latter concept has not yet been realized, firstly, because of the difficulties in manufacturing catalysts with preferential development of certain morphological features of the surface, i.e. faces, edges and vertices with given crystallography and growth steps with specific geometry; secondly, because of the thermal instability of these morphological features of the surface in the course of catalytic processes. Still, the development of this direction for creating new catalysts is very promising. To do this, metal materials with a specific surface structure should be used to carry out catalytic reactions at relatively low temperatures, in which the processes of surface morphology reconstruction proceed very slowly, so that the non-equilibrium surface structures remain relatively stable.

In this paper, we investigate the effect of the regimes for producing polycrystalline copper foils on their structure, morphology, and behavior in temperature fields. The interrelation between defects of disclination type of growth origin in crystals with features of their morphology, such as the presence of pentagonal symmetry, specific faceting and the formation of terraces and polyatomic steps of growth, is shown. The results of studies of the evolution of

the morphology, structure and phase composition of copper foils subjected to the heat treatment in oxidizing and inert atmospheres are presented. The dependence of the stored elastic energy and the temperature of its relaxation on the presence of high-energy disclination defects is discussed.

2. Methods of materials preparation and characterization

The foils under investigation were fabricated by electrodeposition of copper exploring the author's method [9-10]. Electrodeposition was carried out on stainless steel plates using mechanical activation of the growing crystals with abrasive microparticles suspended in the electrolyte [9-10]. Activation was applied either at the initial stage of electrocrystallization or periodically, in particular, three minutes with stirring of the electrolyte and three minutes without stirring. The purpose of surface activation was to create high-energy defects in the crystalline structure, to form so-called fragmented structures, and, as a result, to produce copper polycrystalline foils with developed surface and specific morphological features, such as the pentagonal symmetry of individual grains, the specific crystallography of faceting, and with of polyatomic growth terraces.

For a comparative analysis of the samples, copper foils were grown by electrodeposition with and without mechanical activation of the cathode.

Changes in the surface morphology and crystal structure before and after heat treatment were observed using electron microscopes Carl Zeiss Sigma and JEOL JCM 6000.

Calorimetric experiments were performed on the differential scanning calorimeter HITACHI EXTARX-DSC 7000. The investigations were carried out in the temperature range from 25 to 700 °C with a heating rate of 10 deg / min and a gas flow rate of 50 ml / min.

To study the evolution of the morphology of the surface of crystals with defects in temperature fields, disks with a mass of 5.7-6.7 mg were cut out from electrodeposited copper foils. The temperature studies were carried out both in the oxidizing (oxygen) and in the inert (nitrogen) atmospheres.

3. Results of experiments and discussion

Microscopic studies of the surface of copper obtained with mechanical activation of the cathode (Fig. 1) showed the appearance of the following features: pentagonal pyramids (PPs) (Fig. 1a), cone-shaped crystals (CCs) with high (polyatomic) growth steps (Fig. 1b), as well as crystals containing defects of the disclination type – defective crystals (DCs) (Fig. 1c).

Pentagonal pyramids (PPs) and CCs (Figs. 1a,b) were found in samples subjected to mechanical activation at the initial stage of electrodeposition, and coatings with the DCs (Fig. 1c) were obtained by periodically stirring the electrolyte with the particles during electrocrystallization. In our opinion, the mechanical activation of crystals growing in the process of electrodeposition promotes the formation of disclination defects [11-12], which in turn determine the features of the morphology of foils (Fig. 1). To confirm this idea, structural studies of PPs (Fig. 1a) and CCs with a stepped structure (Fig. 1b), and DCs with a developed surface (Fig. 1c) were carried out.

Electron microscopic studies of PPs formed during electrodeposition under cathode activation conditions (Fig. 1a) showed that they grow in the direction of $\langle 110 \rangle$ -type and have a fragmented/twin structure, possess fifth-order symmetry axes (Figs. 1a and 2a). In addition, PPs' interior were separated by twin boundaries into five main parts (sectors) containing a high concentration of twin lamella of $\{111\} \langle 112 \rangle$ -type, parallel to the boundaries of the parts (Fig. 2a).

The conical crystals (CCs) (Fig. 1b) also grow in the direction of $\langle 110 \rangle$ -type. They are separated by the high-angle grain boundaries of growth origin into fragments, contain a high concentration of twin lamella (Fig. 2b), but do not have fifth-order symmetry axes and the common twinning center. The main structural elements of such crystals are twins whose height

and width correlate with the growth steps on the surface of the crystal. The presence of the twin boundaries separating the fragments in the PPs and CCs and the high concentration of twin lamella testifies the manifestation of the relaxation processes even during electrodeposition. The fragmented/twin initial structure of these crystals, the presence of twin lamella, and disclination-type defects (Figs. 2a,c) are the reason for the formation of the developed surface in the form of polyatomic growth steps (Figs. 1a,b) with certain crystallographic planes, mainly of $\{111\}$ - and $\{110\}$ -type. The shape of the crystals is related to the features of the electrodeposition process.

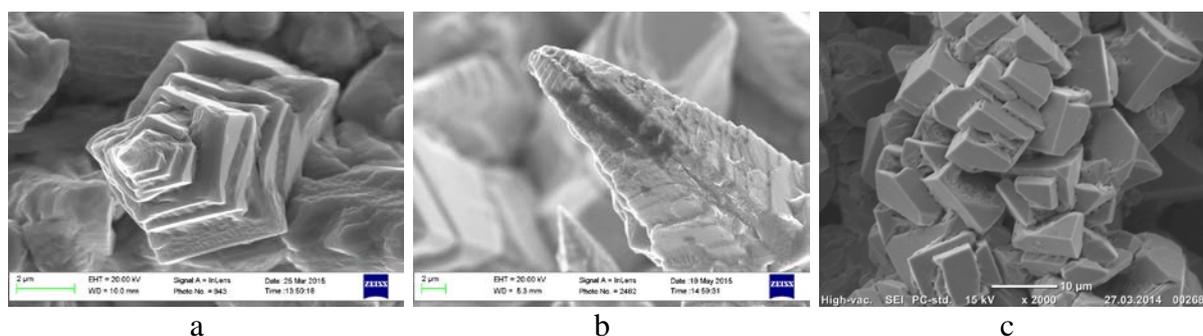


Fig. 1. Morphology of crystals and coatings obtained by electrodeposition using mechanical activation: a) pentagonal pyramids (PPs); b) cone-shaped crystals (CCs), which have polyatomic growth stages; c) coatings with a developed surface of defective crystals (DCs).

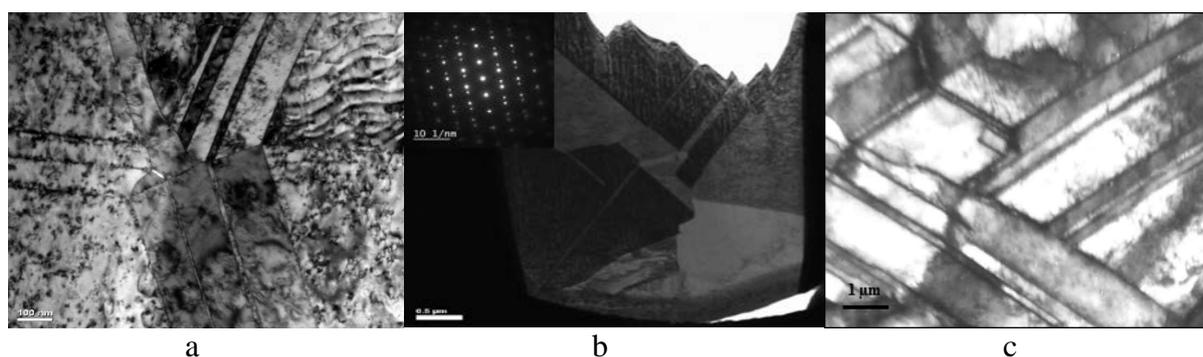


Fig. 2. Electron microscopic images of copper crystals grown by electrodeposition using mechanical activation: a) pentagonal pyramids (PPs); b) conical crystals (CCs) with twinned structure; c) defective crystals (DCs) with a fragmented structure.

In case mechanical activation of the deposited foils with abrasive microparticles was carried out periodically, the materials with a developed surface in the form of terraces and polyatomic growth steps (Fig. 1c), consisting of relatively large but defective crystals (DCs) (Fig. 2c) can form. Electron microscopic studies of DCs showed that they have nonequilibrium dislocation-disclination structure, contain twins, dislocation and high-angle grain boundaries, including broken ones. They demonstrate characteristic mesoscale (0.1-1.0 μm) of structural elements, i.e. misorientation bands, twin lamella and fragments (Fig. 2c). Usually, such fragmented structures can be formed at the large plastic deformations [13]. In our case, they appear in electrodeposited metal subjected to *in situ* mechanical activation (Fig. 2c). All defects of the dislocation-disclination type are, as it can be seen from the extinction contours (Fig. 2c), powerful sources of long-range internal stress fields.

Electron microscope studies of foils and coatings grown without the mechanical activation showed that such samples have a relatively smooth surfaces, consist of crystals with a block sub-structure (Fig. 3), and do not have the above-mentioned morphological features

(Fig. 3a,b). The most commonly observed defects are multilayered dislocation boundaries (Fig. 3b) and deformation twins of $\{111\}\langle 112 \rangle$ -type. The dislocation boundaries separating grains into blocks (Fig. 3b) are non-equilibrium and create long-range stress fields [14]. This is because their formation during electrodeposition occurred at room temperatures, i.e. in conditions, when dislocation climb is limited.

The results of the experiments allows one to say, that the mechanical activation of crystals growing in the process of electrodeposition causes the formation of fragmented structures with high-energy disclination defects. The exit of twin lamella, fragments and misorientation bands on the crystal surface led to the formation to a specific microrelief. The height of microrelief correlates with the size of the structural elements. Using mechanical activation of growing crystals we have created favorable conditions for the formation of disclination-type defects, controlled the appearance of high-energy fragmented structures and, as a result, provided developed surface (Fig. 1).

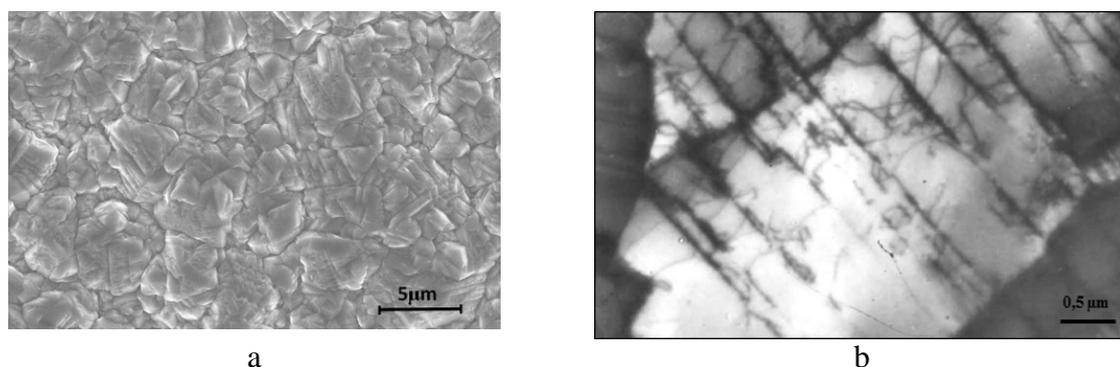


Fig. 3. Surface morphology (a) and electron microscopic image (b) of copper electrodeposited without mechanoactivation.

In our opinion, foils consisting mainly of defective crystals with fragmented structures and showing polyatomic growth steps (Fig. 1 and 2) have large stored elastic energy that should relax in temperature fields. A crystal growing in the process of electrodeposition is an open thermodynamic system, as it exchanges energy and matter with the surrounding medium. In the final state, its volume does not change, external stresses are absent, and internal stresses due to structural defects are the driving force for the system to return to an equilibrium. In the temperature field (T_{ann}), the relaxation processes are realized, in such way that the energy leaving the open system (crystal) $\Delta Q = T\Delta S_{str}$ should be maximum, where ΔS_{str} is the structural entropy. Structural entropy is a measure of the disequilibrium of open systems, including the presence of internal stresses due to defects of crystalline structure [15]. The structural entropy can be related to the energy released when annealing the defective crystals.

To confirm this idea, we applied the heat treatment in a differential scanning calorimeter (DSC) to copper foils of two types: (i) electrodeposited without mechanical activation (Fig. 3a) and (ii) electrodeposited applying mechanical activation (Figs. 1, 2). Earlier, we used a similar method to study structural changes in electrodeposited nickel coatings subjected to the heat treatment [16].

Calorimetric studies in oxygen showed that on thermograms of foils grown without mechanical activation (Fig. 3a), two discretely located exothermic peaks can be observed (Fig. 4a). The first clear peak appeared at temperatures 350-413 °C, the second weak peak – at 500-580 °C. For the foils grown with mechanical activation (Fig. 1), a diffuse exothermic peak was also observed at 220 °C. It decreases at approximately 360 °C (Fig. 4b). More significant peak was found at approximately the same temperatures (500-580 °C) as for the foils without mechanical activation. We associate the exothermic peaks on thermograms not only with the

phase transformations that occur during the oxidation of copper in oxygen (Fig. 5), but also with the simultaneous occurrence of other processes in the investigated temperature range.

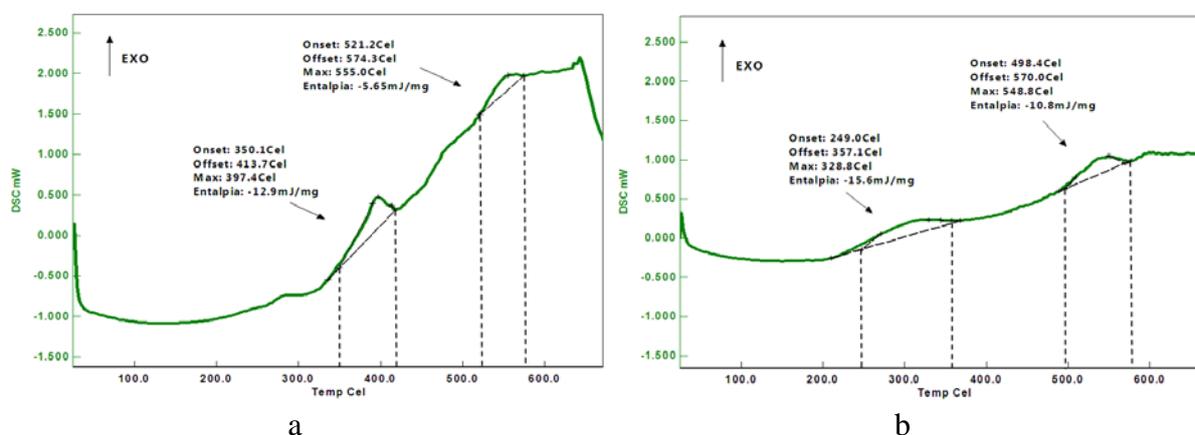


Fig. 4. Thermograms after heating of copper films in oxygen: a) foil electrodeposited without mechanical activation; b) foil grown with mechanical activation.

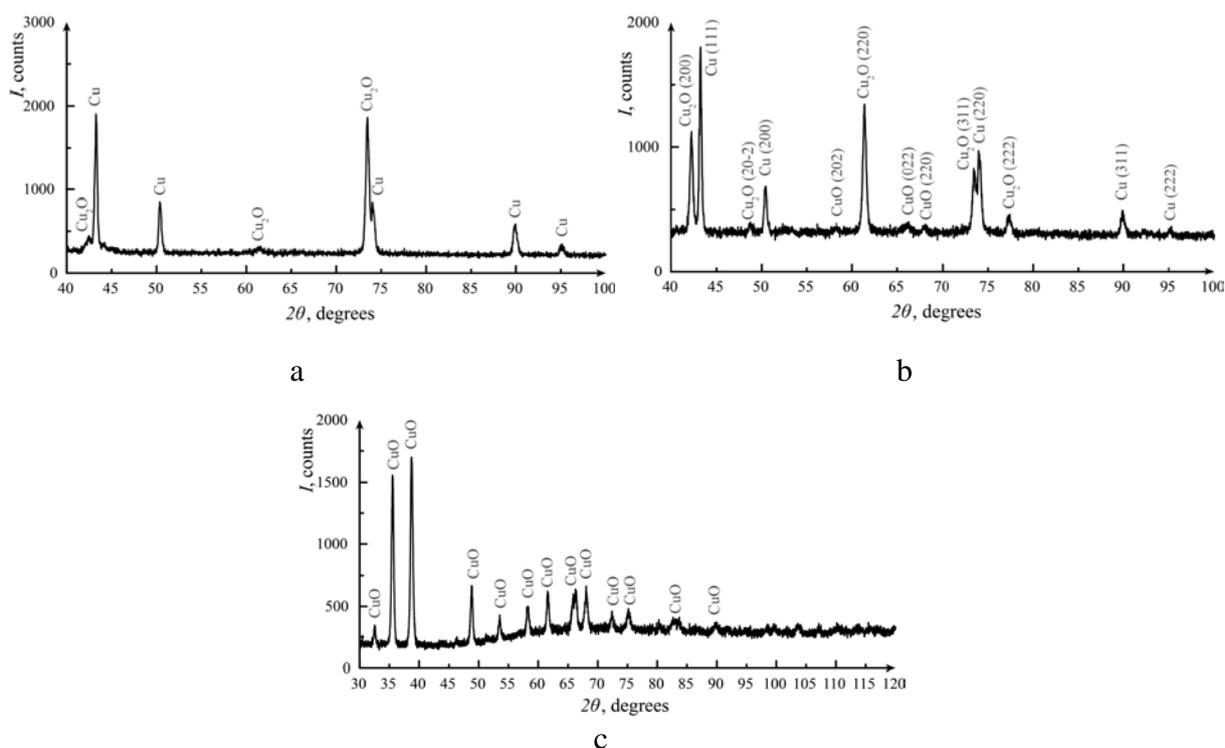


Fig. 5. X-ray patterns for copper foils heated in DSC in oxygen to a temperature of 300 °C (a), to a temperature of 400 °C (b), and to a temperature of 600 °C (c).

X-ray phase studies (Fig. 5) and thermograms of the samples indicated that the surface layers of copper undergoes two successive phase transformations during oxidation: first, copper is oxidized to copper oxide Cu_2O (I), then copper oxide (I) transforms into copper oxide CuO (II). Copper oxidation processes occur unevenly, their rates increase in some temperature intervals, and they are accompanied by the heat release (Fig. 4).

The change in the enthalpy (ΔH) determined from the DSC curves (Fig. 4), for foils of two types turned out to be different. For foils grown without the mechanical activation, these changes at temperatures 350-413 °C and 500-580 °C are 12.9 kJ / kg and 5.65 kJ / kg, respectively. For foils grown using mechanical activation, the change in enthalpy ΔH at

temperatures of 220-360 °C is 15.6 kJ / kg, and at temperatures of 500-580 °C it is 10.8 kJ / kg. At temperatures about 0.5 T_{melt} of copper, in foils consisting of microcrystals with pentagonal symmetry (PPs), CCs with high growth steps, and DCs the enthalpy change is larger.

The difference in the enthalpy change and the shift in the peaks (Fig. 4) indicate that in the addition to intense oxidation during the heating of copper foils, relaxation processes are also realized, probably due to the presence in the material of a high concentration of crystalline defects of growth origin (Figs. 2, 3b).

To test this hypothesis, we analyzed in details the change in the morphology of the surface of copper foils grown with mechanical activation before and after calorimetric studies, see Fig. 6. Microscopic investigation of the surface of foils and crystals in them showed that during the oxidation of copper at temperatures about 600 °C, whiskers and a significant concentration of surface pores can be observed (Fig. 6b). An analysis of changes in the morphology of the surfaces of PPs and CCs, which have high growth steps, made it possible to detect partial smoothing of the lateral faces of the pyramids and cones (Fig. 6b). Smoothing was more noticeable for steps of lower depth and height.

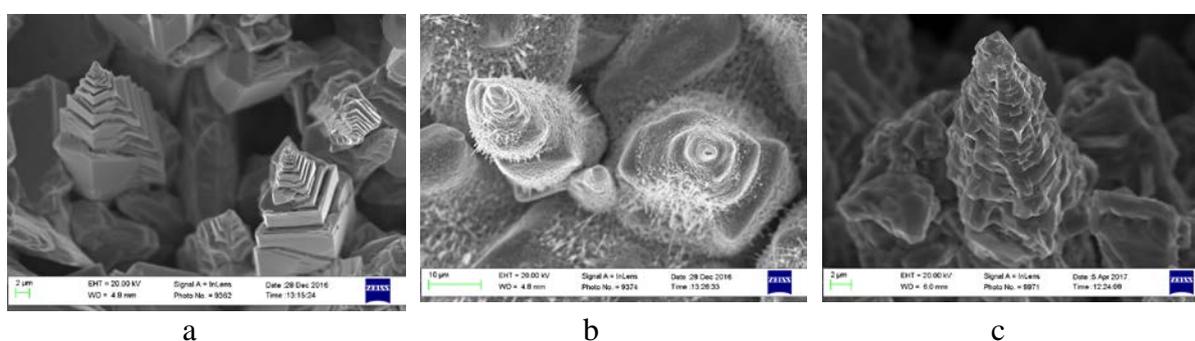


Fig. 6. SEM photomicrographs of copper electrodeposited in a mode with mechanical activation. Surface morphology: a) initial; b) after heating to 600 °C in oxygen; c) after heating to 600 °C in nitrogen.

Exoeffects fixed by DSC thermograms (Fig. 4 and Fig. 7) indicate the operation of several processes simultaneously occurring in temperature range 250-600 °C. Processes that cannot occur in a vacuum or an inert atmosphere realized in temperature fields and an oxygen-containing medium. The heat release in copper samples during annealing in the oxygen-containing atmosphere is associated with phase and structural transformations. In particular, such transformations include the formation of copper oxides Cu_2O and CuO , surface nanopores, and growth of CuO nanowhiskers [17-19]; the fusion of growth steps, the formation of internal cavities, degradation of defects in the crystalline structure, evolution of the initial dislocation and disclination-fragmented structures formed during electrocrystallization (Fig. 2 and Fig. 3b).

Calorimetric studies carried out in an inert medium (nitrogen) allowed us to confirm this assumption (Fig. 7). In contrast to studies of foils annealed in oxygen, for foils without mechanical activation, one insignificant peak was observed on thermograms at temperatures of 300-400 °C (Fig. 7a), and for foils with mechanical activation two different exothermic peaks significantly spaced from each other on the temperature scale, were observed (Fig. 7b). Both peaks were accompanied by a significant change in the enthalpy ~ 10 -15 kJ/kg (Fig. 7b), which is not associated with the oxidative processes in copper. In our opinion, during the heating process, the annealing of low-energy defects of growth origin in the sample occurred (Fig. 3b) and this causes the appearance of the first of the exothermic peaks on the heating curves (Fig. 7). The temperature of the peak depends on the concentration and types of defects. In samples of copper foils grown with mechanical activation (Fig. 1) and without activation (Fig. 3) low-energy defects of growth origin and nonequilibrium dislocation substructures are formed (Figs. 2 and 3), which are easily annealed (the first peak) in the temperature interval 250 °C -

450 °C (Figs. 4 and 7). In the same temperature range, the growth steps are "smoothed" on crystals with a developed surface, when annealing occurs both in oxygen and in nitrogen (Figs. 4, 6, and 7). This can be caused not only by an increase in the mobility of surface atoms in temperature fields, but also by high internal stresses concentrated in the vertices and edges of the crystals. At the same temperatures, the disruption of nonequilibrium dislocation substructures begins in copper [10, 12, 13], the number of structural defects, formed during electrocrystallization, decreases, the grain size changes and the surface of the foils is transformed.

The presence of a second exothermic peak on the thermogram, shown in Fig. 7b, in the case of annealing of crystals with a fragmented structure, is probably associated with the relaxation of long-range internal stresses due to disclination defects, the stabilization of nonequilibrium high-energy structures, and the change in the shape of the crystals. An estimate of the internal stresses with the help of the heat released during the relaxation process using the technique proposed in [15] gives a value of the order of 30 MPa, which is close to the yield point of copper. Estimation of internal stresses with the help of lattice distortions also gives the value of the same order.

Summarizing the calorimetric data obtained in the study of copper polycrystalline foils heat-treated in different media, X-ray phase analysis and microscopy data (Fig. 6c), it can be said that high-energy defects are formed in copper materials obtained by electrodeposition with mechanical activation. These defects are disclination-type defects, which generate long-range elastic fields and, as a result, are the cause of the considerable elastic energy stored in the bulk of crystals. The relaxation of elastic fields is carried out both in an inert medium and in oxygen, but the relaxation mechanisms, which determines the final structure and affects the morphology of the foil surface after annealing, can be different.

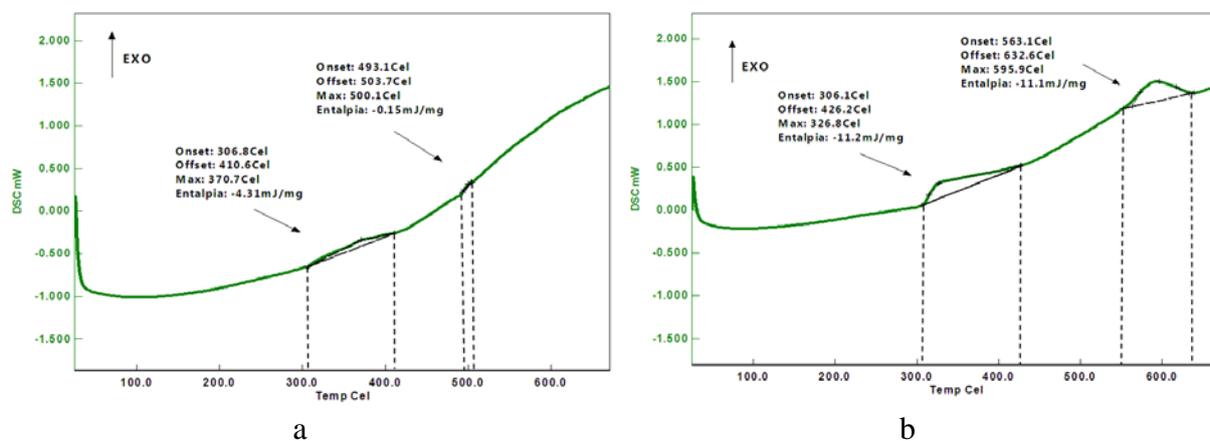


Fig. 7. Thermograms of electrodeposited copper foils annealed in nitrogen at temperatures up to 700 °C: a) without mechanical activation; b) with mechanical activation.

4. Conclusion

We have demonstrated that mechanical activation of the cathode by abrasive particles causes the formation in electrodeposited copper polycrystalline foils and coatings the high-energy disclination-type defects, crystals possessing the fifth order symmetry axes, and developed surface with polyatomic growth steps.

It has been shown that the presence of defects creating long-range elastic fields and therefore providing a large stored elastic energy, contributes and intensifies various relaxation processes in studied copper crystals. Analysis of thermograms of copper foils, X-ray diffraction and microscopic studies showed that exothermic peaks in 250-600 °C range are associated with phase and structural transformations, i.e. with copper oxidation, with formation of

nanowhiskers and nanopores on the surface of crystals, surface restructuring, annealing of low-energy defects and transformation of high-energy defects, stabilization of nonequilibrium dislocation-disclination structures that formed in the process of electrodeposition.

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