International Journal of Research Studies in Science, Engineering and Technology
Volume 2, Issue 7, July 2015, PP 88-95
ISSN 2349-4751 (Print) & ISSN 2349-476X (Online)

Effect of the Pulse Current and Capasitance Device on Copper Derosition

Gologan V.F.*, Bobanova Zh.I., Ivashku S.Kh., Pasincovschi E.A.

Institute of Applied Physics, Academy of Sciences of Moldova, str. Academiei 5,
Chisinau, MD 2028, Republic of Moldova
vgologan@mail.ru

Abstract: *The purpose of the present work was to study the effect of the pulse and pulsating currents on the cathode polarization, the spectrum of the variable current components, and the morphology of copper coatings. Those currents were obtained from a single-phase thyristor (with full-wave rectification) and a three-phase one (with the formation of the current shape by a thyristor), with a capacitance device connected in series to the galvanic circuit. As a result, it was found that the type of the power source and parameters of the device have a strong influence on the deposition process and the coating morphology.*

Keywords: *capacitance device, spectrum of variable current components, power source, morphology.*

Both theoretical and experimental studies have demonstrated that current (voltage) fluctuations in the system of the power source – bath, which are generated by the power source, galvanic process, and other elements of the electric circuit, have a significant effect on the kinetics of deposition and properties of coatings [1 – 5].

In order to change the dynamic state of the system of the power source – bath, an additional element was connected in series with the power source, which consisted of an induction (L) and a capacitance (C) connected in parallel [6].

A lot of investigations have demonstrated that by selecting the power source parameters (L and C) it is possible to significantly influence the cathode polarity, the spectrum of variable components, the structure and physical-chemical properties of coatings, as well as to ensure the raise of the process efficiency due to the increase of the current yield and density [4, 5].

When a pulse current source is used, it is possible to use only the C unit with various ways of capacitor connections, since they ensure the necessary current conductivity.

This is why the present study is dealing with the establishment of a possibility to control the galvanic process by varying the capacitance value of the device at the deposition of Cu coatings while using both pulse and pulsating currents.

1. Experimental Methods

In order to establish the effect of the pulse and pulsating currents of the process of Cu deposition, a single-phase thyristor - controlled rectifier (with full-wave rectification) and a three-phase thyristor (with a power of 60W). The pulse waveform was set by the adjustment of the thyristors and was not changed during the experiments. The required capacity was provided by the electrolytic capacitors connected in parallel, which were set on aluminum plates connected in series to the power source. The plates were connected in parallel, including heteropolar connections.

The Cu deposition was carried out with the sulfate electrolyte (g/l) of $CuSO_4 \cdot 5H_2O$-200, H_2SO_4-50, the current density 0.1 and 0.2kA/m^2, and the solution temperature 20°C. The deposition was plated on the polished copper surface of the samples with a diameter of 20mm.

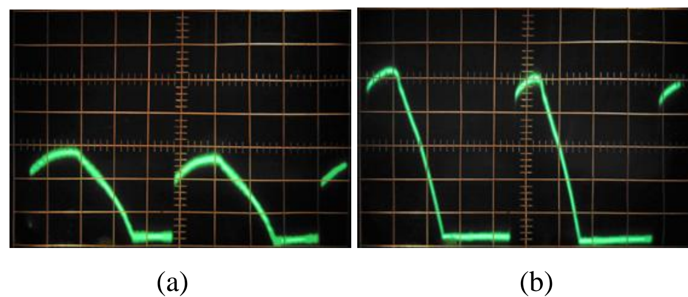
Polarization curves were taken by a rectifier via a compensation method in the galvanic regime with an exposure of 30 seconds at each setting in the stationary electrochemical cell ES-2 on the just-deposited copper on a platinum cathode with the surface area of 0.01dm^2 [7]. An EVL-1M1 type saturated silver-chloride electrode was used as a reference electrode. The current value was set by the resistance device and measured by an M 209 type voltmeter. Another voltmeter of the type V7-27A/1 was used to measure the cathode potential.

A spectrum analyzer SK 4-56 was used to assess the influence of the capacitance device (CD) on the process of Cu deposition, with the account of the noise spectrum in the system power source – galvanic bath. The current shape was followed with oscilloscopes S 1-15 and GDS-1072-U.

A scanning electron microscope TESCAN and an optical one NEAAPOT were used to investigate the surface of the coatings. An X-ray diffractometer DRON-3 was used to analyze the texture of the coatings [8].

2. Results and Discussions

Our investigations have revealed that certain values of the capacitance provoke distortion of the pulse from the power source: the oscillograms show an increase of its amplitude and of the pause (Fig. 1).



(a) (b)

Fig1. *Source current wave (I = 100mA, X = 2ms/unit, Y = 0.05 V/unit): a – without CD, b-with CD: capacitance of C = 35200μF.*

The polarization curves demonstrate that in this case there is also a shift of the electrode potential: at C = 35200μF and current density 0.1kA/m2 it was displaced into the positive area at 75 mV (Fig. 2).

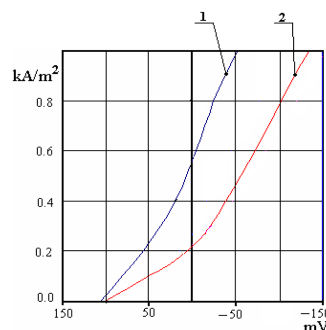
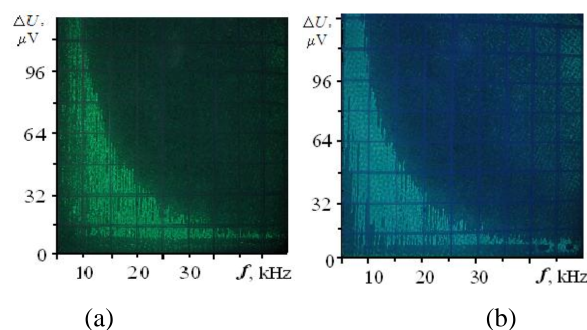


Fig2. *Influence of cooper deposition on cathode potential: 1 – C = 35200μF; 2 – without CD.*

A significant change of the electrode potential was observed when connecting C, at the current density 0.2kA/m^2 and further on. This shift of the potential at the current density given above and other electrolysis conditions was not observed when a single-phase power source with a full-wave rectification and a three-phase rectifier with an induction-capacitance device were used, which testifies to a higher activity of the electrochemical process even at small currents (20mA).

Studies of the variables in the circuit, where an active resistance was used but not a bath, have demonstrated that the power source used in the present research is a strong 'noise' generator. When compared to the values obtained with a single-phase rectifier with full-wave rectification and a three-phase one, at a current of 100mA, the frequency variables were going up from 3-5 up to 40-50 kHz (Fig. 3a).



(a) (b)

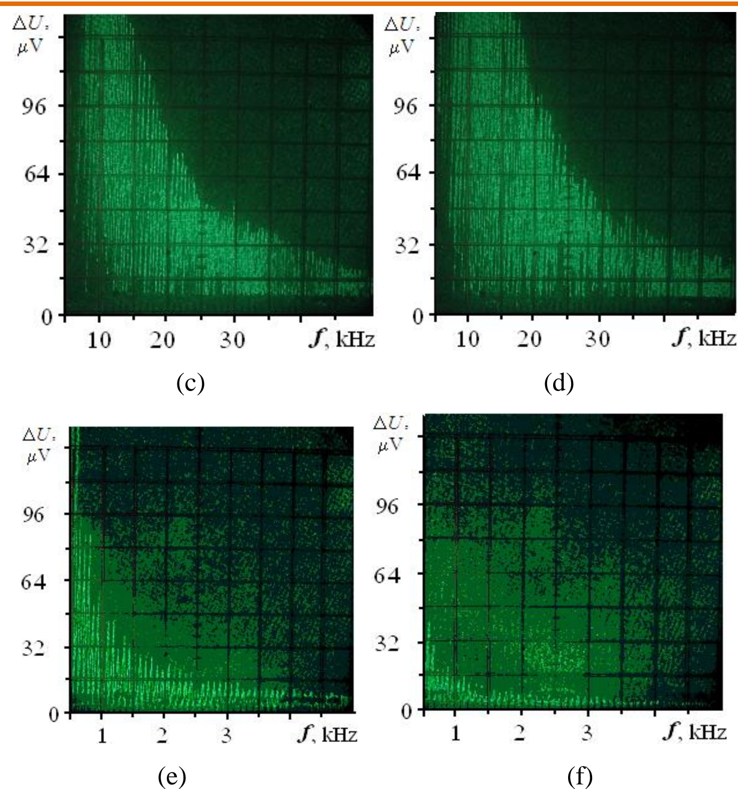
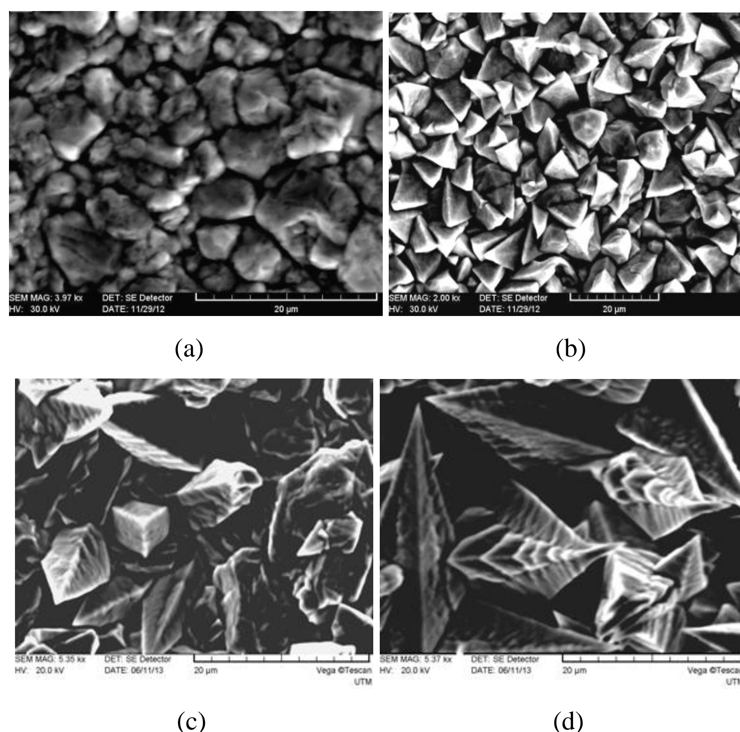


Fig3. *Spectra of alternating-current for deposition of cooper (I=100mA): a – source of current; b – source of current and bath; c – source of current and C = 35200μF (without bath); d – source of current and C = 17600μF (without bath); e – source of current (without bath), C = 35200μF (I = 20mA); f – source of current (I = 20mA)*

Inclusion of a bath had no significant effect on the formation of the spectrum in the galvanic circuit (Fig. 3b). There was a significant effect when a capacitance device was included in the circuit but not a bath (Figs. 3c and 3d). At a current of 20mA (current density 0.2kA/m^2) and C = 35200μF, the spectrum was also more developed than in the experiments without a capacitance device, which, probably affected the cathode polarization (Figs. 3e and 3f).

The conditions of the electrolysis used here had a strong influence on the coatings morphology (Fig. 4).



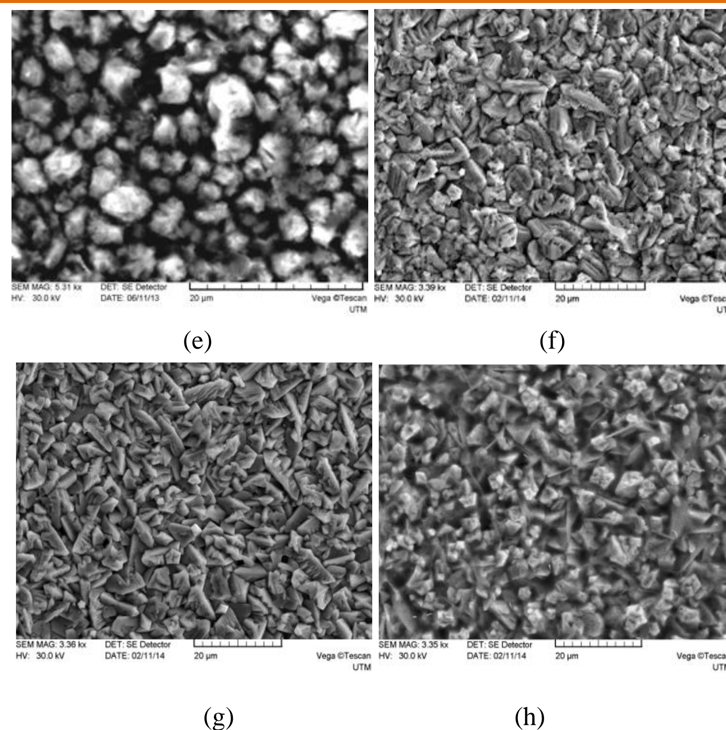


Fig4. *Morphology of cooper coating (i_k=0,2kA/m^2, time of deposition 2 hours): a –without CD; b – = 35200µF; c – C = 26000µF; d – C = 26000µF (time of deposition 4 hours); e – C = 92000µF (2 pallets of 46000µF connected in parallel with opposite polarity); f – after 4 hours of deposition); g – C = 2000µF after 4 hours of deposition; h – C = 4000µF after 4 hours of deposition.*

The coatings deposited only from the power source (i_k = 0.2kA/m^2) had the dimensions of components that were changing in the range of 5-18µm, showing their insufficient coalescence, keeping the surface growth plane (Fig. 4a).

When capacitors with C = 35200µF were connected in parallel (Fig. 4b), the morphology of the coatings greatly changed: because of a greater number of centers of crystallization, the number of crystals went up; they were mostly pyramidal. The shape of the pyramid base could be trilateral, quadrilateral, or, sometimes, pentahedral. The crystals did not splice and could have different inclinations to the base. Unlike coatings without offset of the device, these ones have not only texture at plate (110) but also a strong texture at plate (111). When the capacitance C = 26000µF was used, then the crystals were deposited not covering the entire surface, they had clear faces, whose surfaces were not continuous (Fig. 4c). At longer deposition periods, there was some growth of the crystals dimensions; however, it did not result in a significant change of their configuration (Fig. 4d).

The surface of the depositions was definitely changed when the capacity was C = 92000µF; that is, two pallets of C= 4400µF each, of the opposite polarity, were connected in parallel. Those coatings had fine aggregates, with non-splicing borders; their shape could be considered of a spheroidal type (Fig. 4e). However, the coating surface was changed when the deposition period was up to 4 hours (Fig. 4f). The dimensions and shapes of aggregates also changed. Tighter coatings were deposited at the connection of one capacitor of C = 2000µF, their aggregates were but slightly different from the previous ones (Fig. 4g). When the capacity went up to 4000µF, first pyramidal crystals were deposited and the crystals of various shapes were formed on their surfaces (Fig. 4h).

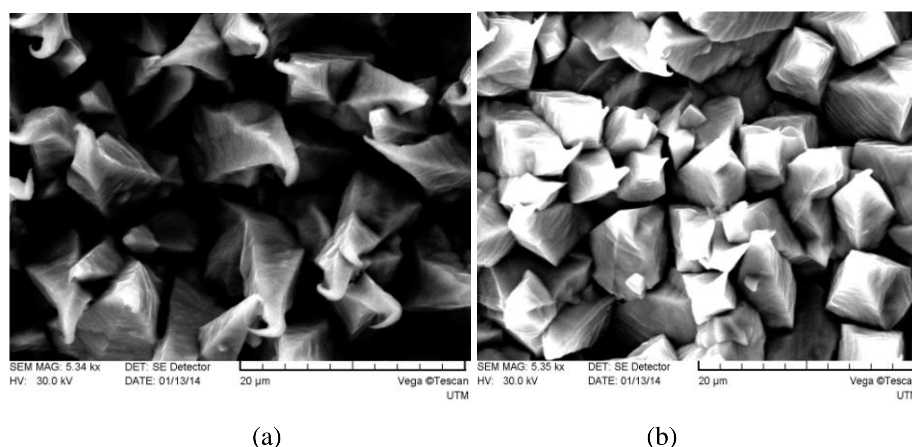
Researchers, who investigated the effect of pulsating current of various frequencies on the morphology of the crystal growth from the sulfate electrolyte of the same composition as ours, came to the conclusion that the major factor affecting the coatings morphology is the change in the ions concentration which depends on the frequency of pulses, duration of the pause, and the rate of the rotation of the disk electrode [9]. Still, they are of the opinion that the main effect on the crystal dimensions is that of the duration of the pause during which there is the decrease of the near-electrode Cu^+ ions concentration due to diffusion.

Those researchers stressed that when the duration of the pause is longer, the crystal dimensions should increase, too. It should happen because at a lower concentration of Cu adsorbed atoms the

supersaturation is reducing, hence, lower is the frequency of the crystal nucleation. In addition, variations in the Cu^+ ions concentration affected the pattern of the crystals coalescence because of a higher rate of Cu winning in wells than on bumps. At lower frequencies, faces and edges of crystals were not clearly defined. At higher frequencies, edges became more pronounced, which can be due to the fact that in the first case the continuity of the crystal edges growth is connected with the passivation of ledges on the growth layers during a pause; in this case, the dimensions of pyramids are not finally determined, because the concentration of adsorbed atoms is also lower. In the second case, passivation does not have time to occur, thus the growth goes on by the tangential distribution of layers, while keeping the stability of plane faces and edges [9].

When Cu was deposited on the pulsating current with an anodic component, the appearance of the gradient of Cu^+ ions concentration directed from the surface into the solution contributed to keeping the stable growth of the plane front, as was in the previous case, too [10]. This is why it is not possible (correct) to account for the loss of the stability of the plane front only by the increase of the Cu^+ ions concentration from the electrodes. The authors of the present paper consider that a major factor influencing nanoneedles growth is the crystal dissolution in the areas of the emergence of spiral dislocations, which are rather active growth centers; this is why by the beginning of the cathode pulse the Cu^+ ions concentration in these areas is maximal. In this case, the electrolytic process is concentrated on the protruding crystals, transforming them into separately growing needles. A continuous growth of needles is possible only in case of the maximal local concentration, since when ions are becoming dispersed, the growth stops [10].

In our case, the conditions of Cu deposition are specified by the power source type and usage of a capacitance device, while keeping the rest of the deposition requirements. Changes in the form of the pulse are not severely twisted at various device capacities. The major effect on twisting the initial pulse and the spectrum of variables is that of the volume of capacitance that determines the dynamic state of the system ‘power source – bath’, which, in turn, leads to changes in the near-cathode layer, reflected in the determination of the cathode potential. Although at various C there were small changes in the pause and the amplitude of the pulse, the coatings morphology was significantly changing. This can be connected to the changes in Cu^+ concentrations, as results of some earlier works suggest, because crystals with clear faces, without faces, and skeleton ones were grown. It is possible to assume that changes in the near-cathode layer can occur under the action of an electric field that is formed by the variable current components, which provokes shifts in the near-cathode layer thus creating conditions favorable for the formation of certain coating surfaces [11-13].

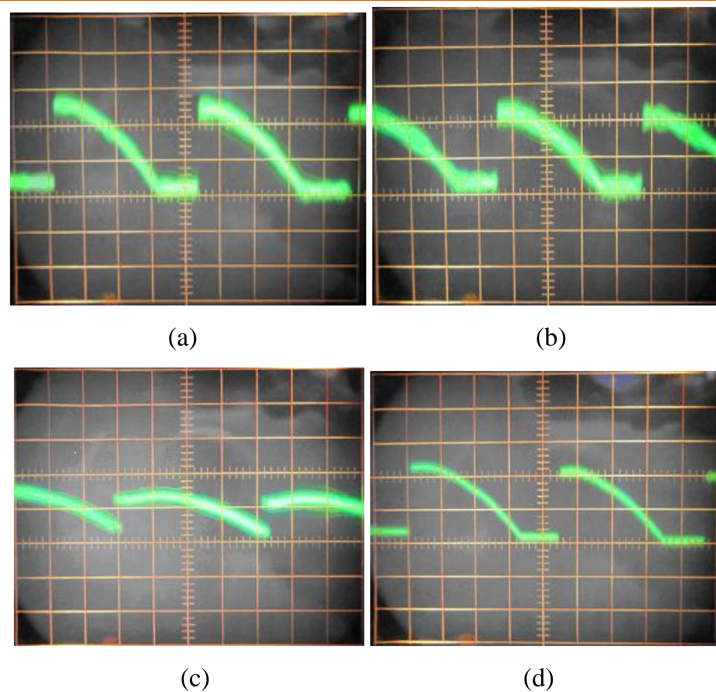


(a) (b)

Fig5. *Morphology of cooper coating (i_k=0, 2 kA/m^2, time of deposition 4 hours): a – C =4000μF (2 capacitor); b – C = 4000μF (1 capacitor)*

Changes in the concentration of Cu^+ in the near-cathode layer could be followed via the coatings deposited at C = 4000μF. Most probably, due to a high concentration of these ions at the foot of the crystal growth, starting from a certain height, they were bending either in the direction of the substrate or of the free space (Fig. 5a); or the crystal growth was beginning not on the surface of the coating (Fig. 5b).

Under certain conditions, the usual form of the crystal growth was changing (Fig.6), resembling the surface of the deposition obtained from the electrolytes with special additions [2].

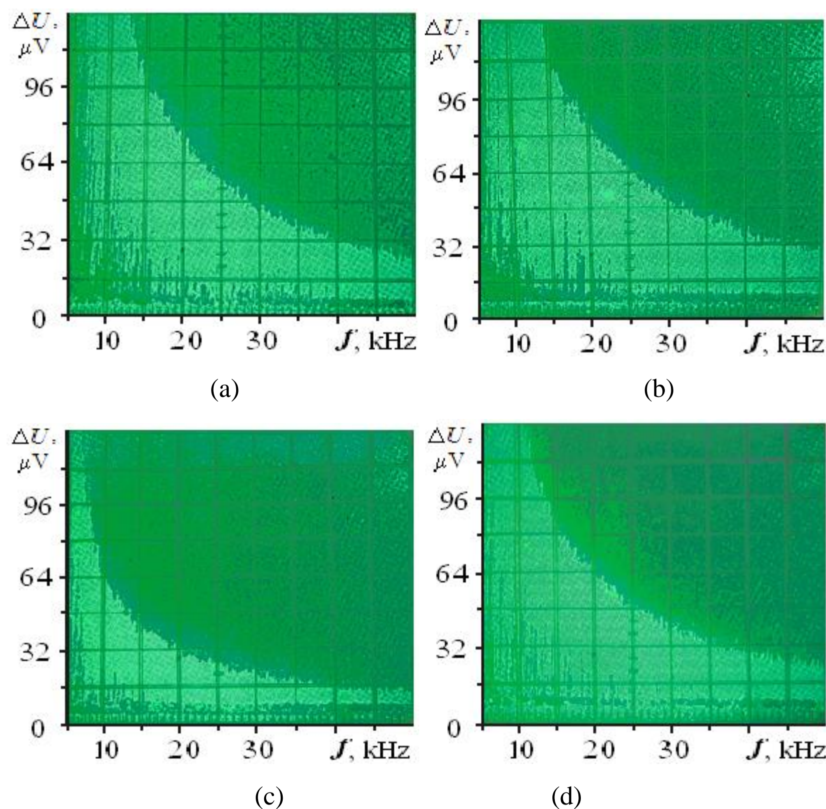


(a) (b)

(c) (d)

Fig6. *Source current wave form (3– phases), I = 100mA, X = 2ms/unit, Y = 0.05 V/unit): a – without CD, b – C=17600μF; c –17600μF (2 pallets of C= 8800μF connected in parallel with opposite polarity); d – C= 8800 μF (2 pallets of C= 4400μF connected in parallel with opposite polarity).*

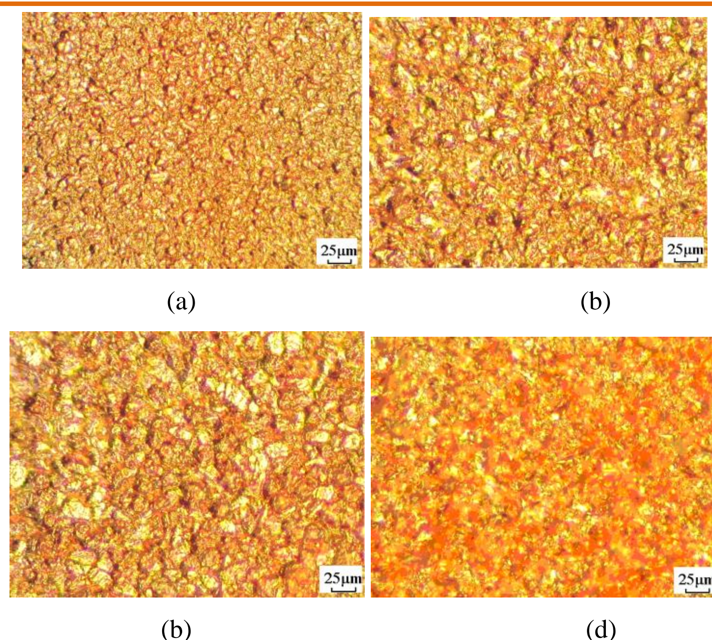
Experiments aimed at the establishment of the effect of the capacitance device on the morphology of Cu coatings were continued using a three-phase rectifier of the same capacity with a thyristor control. Thyristors were adjusted in such a way that a new phase started in the point with the zero value of the previous phase; all experiments were carried out under these conditions (Fig.7).



(a) (b)

(c) (d)

In this way, the pulsating current with a frequency of 300 Hz was produced by the power source. When a capacitance device was used in the circuit, the initial current shape was changing under certain values of C; in some, or in all, phases pauses occurred. The spectrum of the variable current components also was changing (Fig. 8).



(a) (b)

(b) (d)

Fig8. *Morphology of cooper coating (i_k=0,1kA/m^2, 4 hours of deposition): a – source of current without CD; b – C = 17600μF; c – C = 17600μF (2 pallets of C = 8800μF connected in parallel with opposite polarity); d – C = 8800μF (2 pallets of C = 4400F connected in parallel with opposite polarity).*

To analyze morphology, Cu coatings were deposited at the current density 0.1kA/m^2 (because at higher currents the functioning of the thyristors was distorted. The studies of the coatings surface revealed that the strongest effect was that of parallel connections of the capacities of two (out of 4) pallets of

C = 8800μF and two capacitors of C = 4400μF with opposite polarity. Under these conditions, the growth of the flat surface was continuous (Fig.8). The coatings deposited at the connection of two pallets with the capacitance C= 4400μF each were smoother and more fine-grained.

The carried our research allows making the following conclusions: deposition of coatings by applying pulse and pulsating currents is passible through the connection of a capacitance device in series in the galvanic system, varying the capacitance volume and the connection pattern, with a vivid effect on the mechanism of the coating deposition. The experiments conducted on Cu depositions demonstrated that the combination of a power source with a capacitance device can significantly influence the morphology of the coatings, hence, affect their structure and properties.

REFERENCES

[1] Tyagai V.A. Shumy v elektrohimicheskih sistemah (Noises in electrochemical systems). *Electrohimia*, 1975, 10 (1), 3-24.

[2] Gologan V.F., Bobanova Zh.I., Ivashku S .Kh. *Influence of the Composition of the Solution on the Process of Copper Deposition white using the Inductive-Capacitive Device*. In: Electrolysis: Theory, Types and Applications, Nova Publishers (USA). 2010, 479-492.

[3] Gologan V.F., Bobanova Zh.I., Ivashku S.Kh., Mazur V.A. and Pushkashu B.A. Features of how the parameters of an Inductance-capacitance device affect the nickel plating process. *Surf. Eng. Appl. Electrochem*. 2007, 43(5), 307-311.

[4] Gologan V.F., Bobanova Zh.I., Ivashku S. Kh. Peculiarities of chromium deposition with application of an induction-capacitance device. *Surf. Eng. Appl. Electrochem*. 2008, 44(4), 257-263.

[5] Gologan V.F., Bobanova Zh.I., Ivashku S. Kh. Influence of an induction-capacitance device on the structure and wear resistance of electrolytic chromium coatings. *Surf. Eng. Appl. Electrochem*. 2008, 44(5), 353-358.

[6] Gologan V.F., Ungurianu V.M. *Ustroistvo dlya elektrohimicheskih processov* (Apparatus for electrochemical processes). Author's Certificate of the USSR No. 1621559. Priority 15 September 1990.

[7] Vagramyan A.T., Zhamargortsyants M.A. *Electroosahdenie metallovi ingibiruyushchaya adsorbtsiya* (Electrodeposition of Metals and Inhibitive Adsorption). Moscow, Nauka, |1969, 199.

[8] Gorelic S.S., Skakov Yu.A., Rastorguev L.N., *Rentghenostrukturnyi i elektronnoopticheskii analiz* (X-ray and electronic-optical analyses). Moscow, MISIS, 2002,360.

[9] Polukarov Yu.M., Popkov Yu.A., Grishina V.V., Shemenina Z.E. Vliyanie pul'siruyuschego toka na morfologiyu rosta kristallov medi iz sul'fatnyh rastvorov (Effect of Pulsating Current on the Morphology of Growth of Cu crystals from Sulfate Solutions). *Electrohimia,* 1982, 18(9), 1224-1229.

[10] Polukarov Yu.M., Popkov Yu.A., Grishina V.V., Shemenina Z.E. Poteria ustoichivosti ploskogo fronta rosta osadkov medi pri osajdenii ih na pul'siruyschem toke s anodnoi sostavliayuschei (Loss of Stability of the Plane Front of Growth of Crystalls at their Deposition on Pulsating Current with Anodic Component). *Electrohimia*, 1982, 18(9), 1218-1223.

[11] Matsushima M., Ispas A., Bund A., Flieth W. and Fukunaka Y. Magnetic field effects on microstructural variation of electrodeposited cobalt film. *J. Solid State Electrochem*., 2007, 11, 737-743.

[12] Coey J. M. D., Rhen F. M. F. , Dunne P. and McMurry S The magnetic concentration gradient force - Is it real? . *J. Solid State Electrochem*. 2007, 11, 711-717.

[13] Bondarenko W.F., Gak E.Z. *Electromagnitnye yavlenya v prirodnikh vodakh* (Electromagnetic Phenomena in Natural Waters). Leningrad: Gidrometeoizdat, 1984, 152.