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CURRENT MODE OF ELECTROCHEMICAL 3D PRINTING OF COPPER PARTS

The peculiarities of the use of copper nitrate electrolytes in local electrodeposition or electrochemical 3D printing systems have been studied. A model of the current mode in electrochemical 3D printing has been proposed. The possibility of obtaining electrochemically 3D printed objects with a profile height up to 100 μm with a compact fine-crystalline metal structure at a current density of 2 A/dm² in a copper nitrate electrolyte with a content of 300 g/l and with the simultaneous introduction of gloss-forming additives of the Rubin complex (KIESOW OBERFLÄCHENCHEMIE GmbH & Co) and glycine is shown.

Key words: *copper; local electrodeposition; electrochemical 3D printing; nitrate electrolyte; gloss-forming additives; current mode.*

Fig.: 7. Table: 2. References: 22.

Relevance of the research. Electrochemical 3D-printing is a promising direction in electrochemistry from an industrial and scientific point of view [1]. During this process, metal deposition takes place by layer-by-layer formation of the deposit, which leads to unique microstructural properties controlled in the printing process [2; 3]. However, the majority of current research on electrochemical 3D printing technology focuses on nano- and micro-scale objects [2-10], fewer works are devoted to the study of macro-scale objects formation [11-14]. The current mode of electrochemical 3D printing with the relative movement of the working electrode-anode assumes a non-stationary regime. By varying the parameters of the electrolysis pulse mode and studying the influence of the current mode on the morphology of the cathodic metal deposit, electrochemical 3D printing can be optimized [15; 16]. This allows for the establishment of the maximum average current density (i_m) required for forming a compact, fine-crystalline metal deposit at the appropriate speed of movement of the electrode-tool and with the selected composition of the electrolyte solution. After all, it is the i_m, which can be characterized by the ratio of the total current to the working area of the printing surface, and will determine the speed of electrochemical deposition or printing of the object as a whole.

Problem statement. The method of obtaining macroscale copper objects [12; 13] by electrochemical 3D printing is in high demand, primarily in radio electronics. For example, electrochemical printing of conductive paths for printed circuit boards allows to eliminate the stages of application of photo- or metal resist during their production. The result is an economically profitable and environmentally promising technology.

Analysis of recent research and publications. It is known that nitrate copper electrolytes allow to conduct electrodeposition at higher current densities than sulfate electrolytes, which is due to the higher solubility of copper nitrate compared to sulfate. This caused interest in the use of nitrate electrolytes in electrochemical 3D-printing technology [17]. Electrodeposition of copper from nitrate solutions leads to the formation of hard, sometimes brittle deposits [18-21]. However, in spite of this, if the electrolysis mode is chosen correctly, it is possible to obtain high-quality fine-crystalline deposits, which can also have a bright surface. At the same time, it is also necessary to maintain certain acidity of the solution at the level of pH 1...2. At a pH < 1, the reduction of nitrate ions and hydrogen can occur at the cathode. When the pH > 2, there is a possibility of deposition of the insoluble copper salts, which will cause embrittlement of the copper deposits. Electrodeposition from a nitrate electrolyte with a copper salt content of 300...500 g/dm^3 is carried out at room temperature, with an operating current density of 5...20 A/dm^2. The deposits obtained from pure nitrate electrolytes are porous and coarse-crystalline. Long-term electrodeposition of the coating leads to CuCl suspensions formation in the solution and causes the appearance of dendrites [21].

Uninvestigated parts of a common problem. All the reasons that cause the formation of dendrites, pores, and a rough branched structure are undesirable for obtaining metal objects by the electrochemical 3D-printing method. In order to eliminate dendrite formation and increase the dispersive capacity of diluted nitrate electrolytes, the introduction of organic additives [19, 20] and the use of pulse-reverse electrolysis mode [21] are proposed. However, the application of appropriate techniques for electrochemical 3D printing of macro-scale objects under the condition of a non-stationary current regime requires additional research.

Research objective. The purpose of this work is: investigation of the current mode of electrochemical 3D printing in general during the production of macro-scale objects from copper in nitrate electrolytes; investigation of the possibility of modeling the influence of the current regime on the quality of copper deposits.

Research methodology.

Electrolyte preparation. Electrolytes were prepared by dissolving the corresponding components in distilled water. In order to improve the quality of copper cathodic deposits, chloride ions, glycine, and a complex of Rubin gloss-forming additives (KIESOW OBERFLÄCHENCHEMIE GmbH & Co) [22] were added into the corresponding electrolytes. The compositions of the electrolytes are given in Table 1.

Table 1 – The composition of the investigated electrolytes

Component	Number of electrolyte			
	1	2	3	4
$Cu(NO_3)_2 \cdot 3H_2O$	300 g/l	300 g/l	300 g/l	-
$CuSO_4 \cdot 5H_2O$	-	-	-	300 g/l
KCl	0.2 g/l	0.2 g/l	0.2 g/l	-
Glycin	-	0.5 M	0.5 M	-
Rubin *	-	-	+	+
H_2SO_4	-	-	-	32 ml/l
HCl	-	-	-	0.2 ml/l

* Gloss-forming and leveling additives (further - Rubin complex) [22]:

Rubin T200-A (serves as a base for gloss-forming and leveling) – 2 ml/l;

Rubin T200-G (the additive is intended only for assembling a new electrolyte and after cleaning the electrolyte with activated carbon) - 8 ml/l;

Rubin T200-E (increases alignment and provides high bright) – 2 ml/l.

Methodology of polarization measurements. In these experiments, a three-electrode standard cell was used to obtain polarization curves. The working electrode was a cylindrical copper electrode embedded in a Teflon tube with a working surface area of $0.05\,dm^2$. The auxiliary electrode was a copper plate, and the reference electrode was a saturated silver chloride electrode. All polarization curves were given in the scale of the saturated silver chloride reference electrode. The curves were recorded in potentiodynamic mode using a PGStat500n potentiostat, with a potential sweep speed of 2 mV/s. The digital signal from the potentiostat was transmitted to a personal computer for further recording using appropriate software.

In order to simulate the current regime during electrochemical 3D-printing, the electrodeposition of copper deposits was carried out using constant and pulse current modes. For this, a PI-50-1.1 potentiostat was used as a source of direct and pulsed currents. A copper plate of $2\times2\,cm^2$ served as a cathode, and copper plates made of copper doped with 0.03% phosphorus with a total area of $20\,cm^2$ were used as anodes. Before applying the copper coating, the samples and anodes were degreased and treated in a solution of concentrated nitric acid (1:1). The time of electrolysis was calculated to obtain 10 μm deposit thickness. After completion of electrolysis, the samples were thoroughly washed with water and dried with hot air before analyzing the morphology of the cathodic deposits.

Local electrodeposition and recording of oscillograms. The process of local electrodeposition (3D printing) was carried out on the set-up, previously described in [11], the scheme of which is shown in Fig. 1. An AISI 321 stainless steel plate was placed at the bottom of the plastic vessel and connected to the negative pole of the current source. Stainless steel was chosen to ensure separation of the printed part from the substrate after deposition. The working electrode was rotated using an electric motor, the speed of rotation was $1\ s^{-1}$. The radius of the printing trajectory along which the working electrode-anode moved was 4.5 cm, the width of the metal deposition area along the corresponding trajectory was 0.5 cm. The working electrode was a coil of platinized titanium foil connected to the positive pole of the current source. The anode was placed inside the polypropylene capillary and at a height of 1 mm above the cathode plate. The research was carried out in the range of values of average deposition current densities (i_m) of $0.5...4\,A/dm^2$. The duration of printing was 3,8 hours. The estimated profile height of the printed objects was about 100 μm. After the electrodeposition was completed, the current was turned off, the solution was drained from the vessel. The resulting object in the form of a ring was washed with distilled water, removed from the substrate, and the quality of the metal deposit was examined by optical methods.

In order to record oscillograms of changes in the potential of the cathode over time at a point on the trajectory of the working electrode of the anode, a measuring electric circuit was additionally assembled (Fig. 1). The relevant circuit consisted of a Hantek 6025 VE digital oscilloscope, which was connected to the cathode plate and a saturated chlorine-silver reference electrode. The reference electrode through two intermediate beakers and a Luggin capillary with an elastic nozzle were connected to the electric circuit at the place of potential measurement through a hole in the cathode.
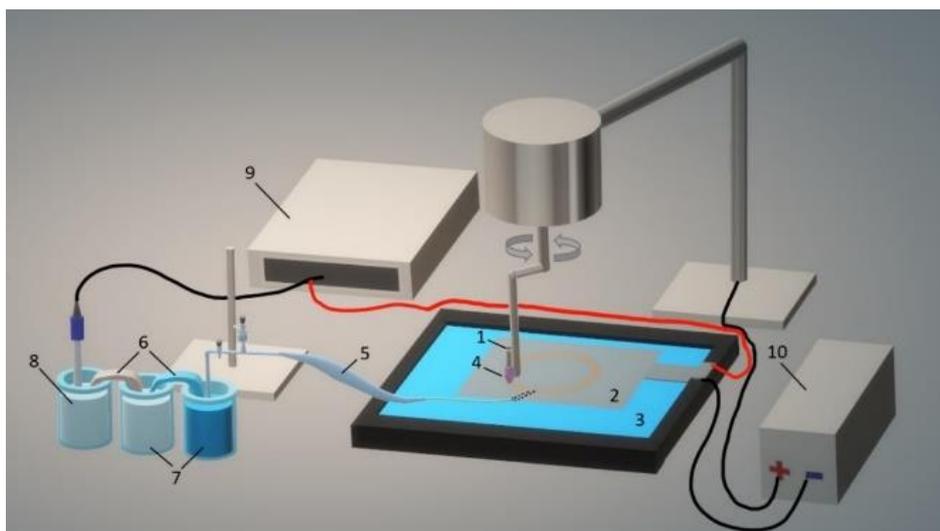
Fig. 1. Scheme of a laboratory set-up for recording oscillograms:
1 – anode; 2 – cathode-base; 3 – electrolyte; 4 – polypropylene capillary;
5 – Luggin capillary; 6 – salt bridges; 7 – intermediate beakers;
8 – cell of the reference electrode; 9 – oscilloscope; 10 – source of direct current

Research results.

Polarization measurements in copper electrolytes. Cathodic potentiodynamic polarization curves on a copper electrode were recorded in order to study the influence of the composition of the solution on the electrochemical parameters of the electrodeposition process. The results of relevant studies are shown in Fig. 2, the numbers of electrolytes correspond to those given in Table 1.
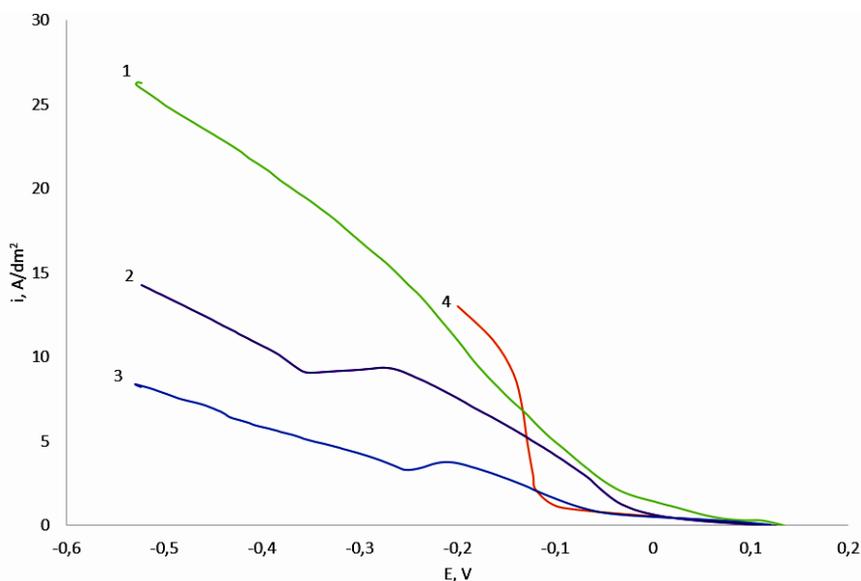

Fig. 2. Cathodic polarization curves in copper plating electrolytes:
1 – nitrate electrolyte (№ 1); 2 – nitrate electrolyte with added glycine (№ 2); 3 – nitrate electrolyte with glycine additives and Rubin complex (№ 3); 4 – sulfate electrolyte (№ 4)

In works [19; 20] it was proposed to introduce 0.25 M of glycine into a diluted copper plating nitrate electrolyte in order to obtain bright fine crystalline deposits of copper. Given the fact that more concentrated solutions will be used in electrochemical 3D printing systems in order to intensify this process, in this work it was proposed to introduce glycine at a concentration of 0.5 M into the investigated plating electrolyte. This led to a significant inhibition of the

cathodic process and the appearance of a limiting current of 9 A/dm^2, which is associated with the active adsorption of the corresponding additive on the surface of the cathode during the electrodeposition process. In addition, the slope of the polarization curve in the range of current densities 1...9 A/dm^2 also decreased, which indicates that the introduction of glycine helps to increase the throwing power of the electrolyte (Fig. 2, curves 1, 2). Also, in the nitrate electrolyte, the synergetic effect of Rubin additives and glycine on the inhibition of the cathodic process have been established, as a result of which the slope of the polarization curve and the value of the limiting current decrease more strongly than in the case of separate introduction of the corresponding additives (Fig. 2, curves 2, 3).

In the case of comparison, the course of the polarization curves of sulfate electrolyte and nitrate electrolyte with the corresponding additives (Fig. 2, curves 3, 4) is similar in the range of current densities up to 2 A/dm^2. In addition, this value of the current density corresponds to about 50% of the limit for the nitrate solution with the addition of glycine and Rubin additives. In view of the above, in the course of further studies for galvanic and electrochemically printed copper deposits, obtained precisely at 2 A/dm^2, a comparative assessment of the morphology have been carried out.

Current mode of electrochemical 3D-printing. In the case of electrochemical 3D-printing or local electrodeposition [11] with the movement of the counter electrode (anode), the current mode will be equivalent to the pulse mode of electrolysis, since at a certain time the counter electrode (anode) is over a certain area on a closed trajectory of its movement (Fig. 3, *a*). In this area, when the counter electrode (anode) approaches it, the current pulse will increase, which will decrease after it moves away (Fig. 3, *b*). Accordingly, in electrochemical 3D printing and the movement of the electrode-tool along a closed trajectory with the same speed, with a certain approximation, the formula can be used to describe the current regime and calculate the average value of the current density i_m:

$$i_m = \frac{i_i + \tau_i}{\tau_i + \tau_p} = \frac{i_i}{1 + \dfrac{\tau_p}{\tau_i}}, \tag{1}$$

where i_i – pulse current density, τ_i – pulse duration, τ_p – pause duration.

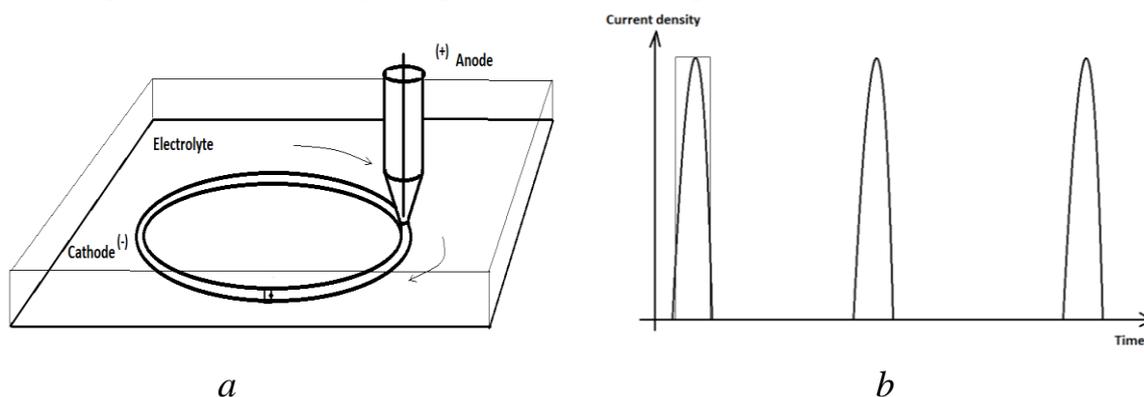*a*   *b*

Fig. 3. Scheme of the electrochemical cell of the 3D printer (a) and the theoretical graph of the change in current density over time at a certain point on the trajectory of the working electrode-anode (b)

It should be noted that for a certain object, which will be produced by electrochemical 3D printing, the parameters of the current mode, that is, the pulse amplitude, duration of pulse and pause, will acquire a certain value, and will depend on the length of the trajectory and the speed of movement.

In order to confirm the above hypothesis, during the electrochemical 3D printing of the object "ring" made of copper, the oscillograms of potential change over time were taken in the studied copper electrolytes, which are shown in Fig. 4-7. The numbers of electrolytes correspond to those given in Table 1.

As can be seen from Fig. 4–7, the oscillograms of the change in time of the cathode potential during electrochemical 3D printing have a predicted appearance with a parabolic pulse shape. Obviously, the current pulses at the corresponding point on the trajectory of the counter electrode (anode) will have a corresponding shape.
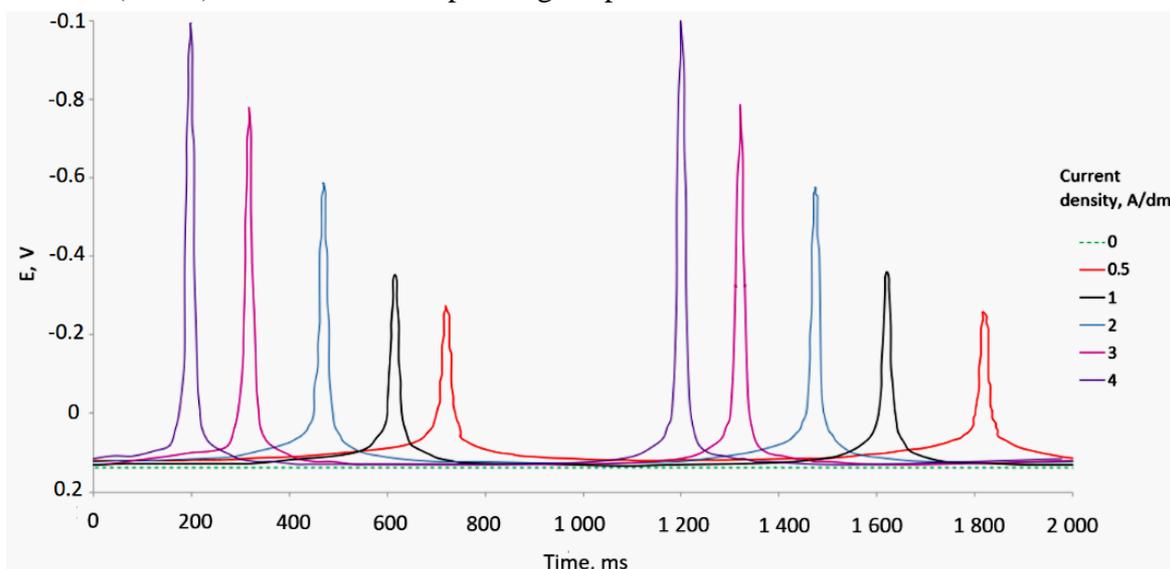

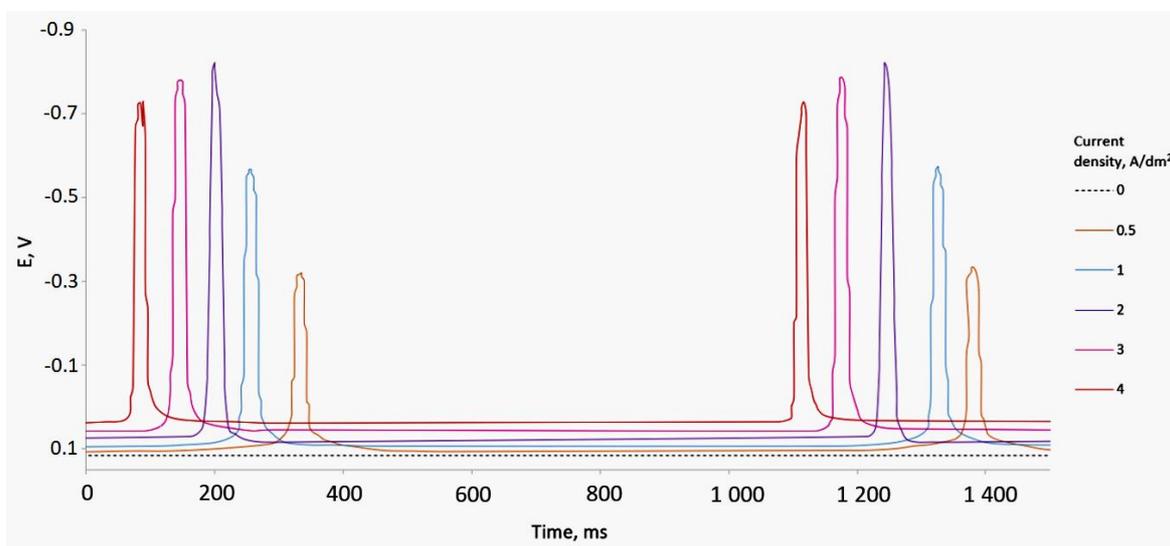*Fig. 4. Oscillograms of potential pulses in nitrate electrolyte without additives (№ 1)*

*Fig. 5. Oscillograms of potential pulses in a nitrate electrolyte |
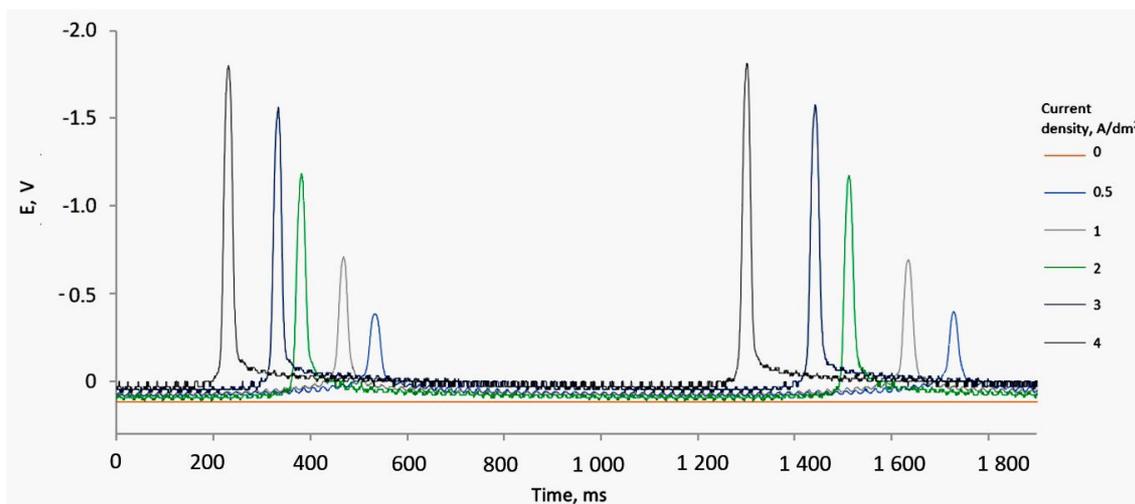with the addition of glycine (№ 2)*

*Fig. 6. Oscillograms of potential pulses in a nitrate electrolyte
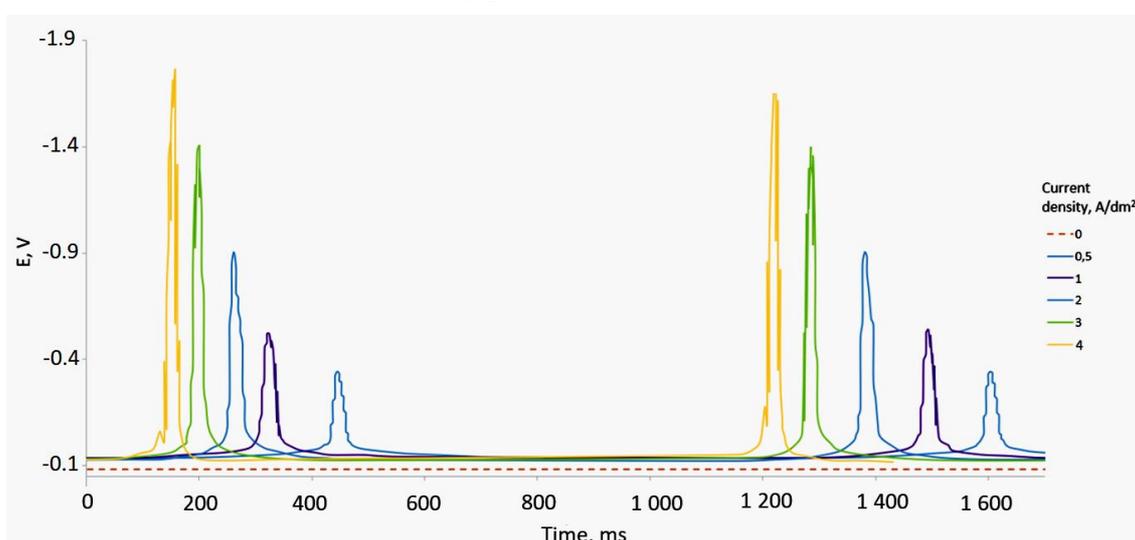with the addition of glycine and Rubin additives (№ 3)*

*Fig. 7. Oscillograms of potential pulses
in a sulfate electrolyte with the addition of Rubin (№ 4)*

Based on the oscillogram data, the maximum values of the cathode potentials (Ei), which are reached at the moment of the current pulse, are determined and are shown in Table 2. Given the simplification of model calculations and the description of the current mode as a unipolar pulse with a rectangular pulse shape (Fig. 3 b), using formula (1), the maximum values of the pulse current densities ii, which correspond to the potentials Ei, were calculated.

Table 2 – Basic parameters of the current mode of electrochemical 3D printing

Electrolyte number according to Table 1				i_m, A/dm^2	i_i, A/dm^2
1	2	3	4		
E_i, V					
-0.26	-0.33	-0.40	-0.33	0.5	5.5
-0.34	-0.58	-0.69	-0.52	1.0	11.0
-0.57	-0.81	-0.12	-0.90	2.0	22.0
-0.78	-0.79	-0.16	-1.40	3.0	33.0
-1.0	-0.73	-0.18	-1.76	4.0	44.0

From the analysis of the oscillograms (Fig. 4–7), it can be seen that the time interval between the sharp growth and the almost complete attenuation of the potential pulse is approximately 100 ms. The maximum pulse current densities ii of electrochemical 3D printing, which correspond to the values of $i_m \geq 0.5$ A/dm2, go beyond the polarization curves, that is, they exceed the values of the limiting current densities for the stationary copper electrodeposition process (Fig. 2). In fact, at the moment of the current pulse, there is a high probability of side processes that can significantly affect the quality of copper deposits. Therefore, in order to verify the possibility of modeling the current regime using a pulse potentiostat, comparative studies of the influence of the composition of the solution and the current regime on the morphology of copper cathode deposits were conducted under the following conditions:

1) during electrodeposition in a conventional galvanic cell using a pulsed current mode, which is close to the current mode in electrochemical 3D printing ($\tau_i = 0.1$ s, $\tau_p = 1$ s);

2) directly in the process of electrochemical 3D printing on a device with a rotating anode. The results of relevant studies are given in Table 3.

Table 3. Image of copper deposits obtained at an average current density of 2 A/dm2 by various methods

Electrolyte number according to Table 1	The sample was obtained by pulsed current mode electrodeposition	Electrochemically printed object "ring"	Enlarged image of the "rings" fragment
1	2	3	4
1	CE = 89,31 %		
2	CE = 79,26 %		
3	CE = 75,15 %		

End Table 3

1	2	3	4
4	CE = 99,81 %		

As can be seen in Table 3, in the pulse mode in the nitrate electrolyte without additives, dark precipitates were obtained, and the current efficiency (CE) is less than 100%. This may indicate the course of side processes of reduction of nitrate ions, accompanied by alkalization of the near-cathode layer and the formation of copper (I) oxide, which is consistent with the data [19, 20]. The introduction of glycine into the nitrate electrolyte does not suppress the process of electroreduction of nitrate ions, since the current efficiency decreases even more. However, due to the possible binding of monovalent copper into a complex, the quality of the deposits improves. The Rubin additives under the conditions of non-stationary current regime act as a brightener and in combination with glycine makes it possible to obtain semi-bright fine crystalline deposits of copper. In general, the similarity between the morphology of the deposits obtained in both cases allows to assume the adequacy of the proposed method of modeling the current mode of electrochemical 3D printing using a pulsed potentiostat.

Conclusions. Based on oscillograms of the cathode potential change in time, it was shown that the current mode of electrochemical 3D printing with relative movement of the working electrode - anode corresponds to the unipolar pulse mode.

It is shown that Rubin gloss forming additives (KIESOW OBERFLÄCHENCHEMIE GmbH & Co) provide fine crystalline bright copper deposits in both sulfate and nitrate electrolytes using stationary and pulsed electrolysis modes.

For electrochemical 3D printing of copper objects from nitrate electrolyte with copper nitrate content of 300 g/L, the addition of glycine at a concentration of 0,5 M is proposed to improve the quality of cathode deposits. Significant improvement of morphology and obtaining bright copper deposits is achieved by simultaneous addition of Rubin and glycine additives to the electrolyte.

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СТРУМОВИЙ РЕЖИМ ПРИ ЕЛЕКТРОХІМІЧНОМУ 3D-ДРУЦІ ВИРОБІВ ІЗ МІДІ

Досліджено особливості використання нітратних електролітів міднення в системах локального електроосадження або електрохімічного 3D-друку. Запропоновано модель струмового режиму у електрохімічному 3D-друці, яка визначає його подібність до уніполярного імпульсного струмового режиму. Розраховані величини максимальної густини струму в імпульсі при електрохімічному 3D-друці, які відповідають значенням середньої швидкості осадження більшим за 0,5 А/дм2, перевищують значення граничних густин струму для стаціонарного процесу електроосадження

міді в досліджуваному нітратному електроліті. На основі порівняльного дослідження морфології поверхні мідних осадів, отриманих при електроосадженні з використанням імпульсного режиму електролізу в стаціонарній комірці та отриманих в комірці з обертовим анодом, показана можливість моделювання струмового режиму при електрохімічному 3D-друці за допомогою імпульсних програмнокерованих джерел струму. Встановлено, що добавки Rubin (KIESOW OBERFLÄCHENCHEMIE GmbH &Co) у сульфатному електроліті міднення зберігають бликоутворюючий ефект при використанні нестаціонарних режимів електролізу. Виявлено, що введення в нітратний електроліт міднення гліцину не пригнічує процес електровідновлення нітрат-іонів, оскільки вихід за струмом є таким же, я в базовому електроліті без добавки і становить близько 80 %. Забезпечення формування більш дрібнокристалічної структури осаду при введенні 0,5 М гліцину може бути пов'язане зі зв'язування в комплекс одновалентної міді. Показана можливість отримання електрохімічно надрукованих об'єктів з висотою профілю до 100 мкм із компактною дрібнокристалічною структурою металу за густини струму 2 А/дм2 в нітратному електроліті міднення з вмістом нітрату міді 300 г/л та при одночасному введенні бликоутворюючих добавок Rubin та гліцину.

Ключові слова: *мідь; локальне електроосадження; електрохімічний 3D друк; нітратний електроліт; бликоутворюючі добавки;струмовий режим.*

Рис.: 7. Табл.: 2. Бібл.: 22.