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PHYSICO-MECHANICAL PROPERTIES OF METALLIC PARTS ELECTROCHEMICALLY PRINTED USING COPPER NITRATE ELECTROLYTE

The process of electrochemical 3D printing of copper parts using a concentrated copper nitrate electrolyte has been investigated. It was established that in a nitrate copper plating electrolyte with a copper nitrate concentration of 500 g/l, it is possible to obtain locally electrodeposited metal parts with a compact fine-crystalline structure and an average profile height of 150 µm. The working current densities of electrochemical printing in this case were 2.45…2.7 A/dm^2. It has been shown that reducing the speed of movement of the working electrode (anode) leads to an improvement in the uniformity of metal deposition along the entire trajectory of movement and the reduction of the crystals size of the metal deposit. This is obviously a consequence of a change in the current mode of electrodeposition.

It was established that on the surface with initial parameters of microroughness (Rz(1)=1.128 Ra(1)=0.2925) during electrochemical 3D printing, a metal structure with roughness parameters – Rz(1)=95.72 Ra(1)=16.32 has been formed. The formation of a compact but at the same time a highly rough metal structure makes the application of the electrochemical 3D printing method promising in the production technology of printed circuit boards and in the field of microelectronics as a whole.

The micromechanical tests of samples of electrochemically printed copper deposits showed the following. The microhardness of the electrochemically printed copper deposit is approximately 30% higher, but the plasticity coefficient and Young's modulus acquire values close to the corresponding parameters of hydrometallurgical copper. This indicates that the method of obtaining metal objects by electrochemical 3D printing does not contribute to a significant deterioration of the elasticity of the obtained material.

Key words: *copper deposits, electrochemical 3D printing, nitrate electrolyte, microhardness, Young's modulus, coefficient of plasticity.*

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ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ ЕЛЕКТРОХІМІЧНО НАДРУКОВАНИХ ІЗ ЗАСТОСУВАННЯМ НІТРАТНОГО ЕЛЕКТРОЛІТУ МІДНЕННЯ МЕТАЛІЧНИХ ОБ'ЄКТІВ

Досліджено процес електрохімічного 3D-друку мідних об'єктів із застосуванням концентрованого нітратного електроліту міднення. Встановлено, що в нітратному електроліті міднення з концентрацією нітрату міді 500 г/л є можливим отриманням локально електроосаджених металічних виробів із компактною дрібнокристалічною структурою та середньою висотою профілю 150 мкм. Робочі густини струму електрохімічного друку при цьому становлять 2,45…2,7 А/дм^2. Показано, що зменшення швидкості руху робочого електрода анода призводить до поліпшення рівномірності осадження металу по всій траєкторії руху та подрібненням кристалічної структури металевого осаду. Це, очевидно є наслідком видозміни струмового режиму електроосадження.

Встановлено, що на поверхні з початковими параметрами мікрошорсткості (Rz(1)=1,128; Ra(1)=0,2925) при електрохімічному 3D-друці формується металічна структура із параметрами шорсткості – Rz(1)=95,72; Ra(1)=16,32. Формування компактної проте водночас шорсткої поверхні металевої структури робить перспективним застосування методу електрохімічного 3D-друку в технології виробництва плат друкованого монтажу та й в галузі мікроелектроніки в цілому.

Проведені мікромеханічні випробування зразків електрохімічно надрукованих осадів міді показали наступне. Мікротвердість електрохімічно надрукованого осаду міді є приблизно на 30% вищою, проте коефіцієнт пластичності та модуль Юнга набувають значень, близьких до відповідних параметрів гідрометалургійної міді. Це свідчить про те, що спосіб отримання металічних об'єктів електрохімічним 3D-друком не сприяє значному погіршенню еластичності отримуваного матеріалу.

Ключові слова: *мідні осади, електрохімічний 3D-друк, нітратний електроліт, мікротвердість, модуль Юнга, коефіцієнт пластичності.*

Formulation of the problem

Prospects for the use of copper nitrate electrolyte in the field of electrochemical 3D printing are its high performance and low throwing power, which can provide higher printing accuracy and precision of the obtained metal structures [1]. Among the main problems that may appear when using nitrate electrolytes is the control of the morphology of the electrodeposited structures, since there is a high tendency to the formation of coarse-crystalline dendrite-like deposits, which can be controlled by introducing special additives [2]. It is also important to optimize electrolysis parameters in order to achieve the necessary physical-mechanical and electrical properties of the obtained metal parts.

Analysis of the latest research and publications

In works [3,4] it was shown the possibility of obtaining metal products with a compact fine-crystalline structure and high physical and mechanical properties by the method of electrochemical 3D printing using copper sulfate electrolyte. Initial experiments using nitrate copper electrolyte [5] showed the possibility of obtaining compact electrochemically printed metal deposits with a profile height of up to 100 μm.

Formulation of the purpose of the research

Thus, the purpose of this work is to investigate the possibility of using a concentrated highly productive nitrate electrolyte in electrochemical 3D printing systems and to determine the physical and mechanical properties of electrochemically printed copper parts.

Presentation of the main research material

Research methodology. The process of electrochemical 3D printing was carried out in an electrochemical cell (Fig. 1). A cathode in the form of a plate made of AISI 321 stainless steel or M0 hydrometallurgical copper with a thickness of 3 mm was placed at the bottom of the plastic cell. Stainless steel was used when it was necessary to separate the printed element from the base after printing. The working electrode (anode) was a cylinder made of platinum-plated titanium foil, which was located in a plastic dielectric case, with the purpose of focusing the electric field in the appropriate place under the working electrode. This ensures precision metal deposition or electrochemical printing. Before conducting the experiment, an electrolyte solution with a volume of 1 L was poured into the cell, the level of the electrolyte was 20 mm above the cathode. The electrochemical cell was placed in the upper part of the 3D printer. In all experiments, the distance between the edge of the dielectric case of the anode and the surface of the cathode of the substrate was 1 mm [3-5].

The investigation of the electrochemical 3D printing process of copper parts was carried out using a nitrate electrolyte with a copper (II) nitrate concentration of 500 g/l. In this study, similar to [3-5], “square” type objects with a side length of 1.9 cm were printed. The estimated height of the printed object was 200 μm. The movement of the working electrode along the appropriate trajectory was provided by a specially developed Travis 3D printer program. After deposition, the current was turned off, the solution was drained from the vessel. The printed object was washed with distilled water and dried with warm air.

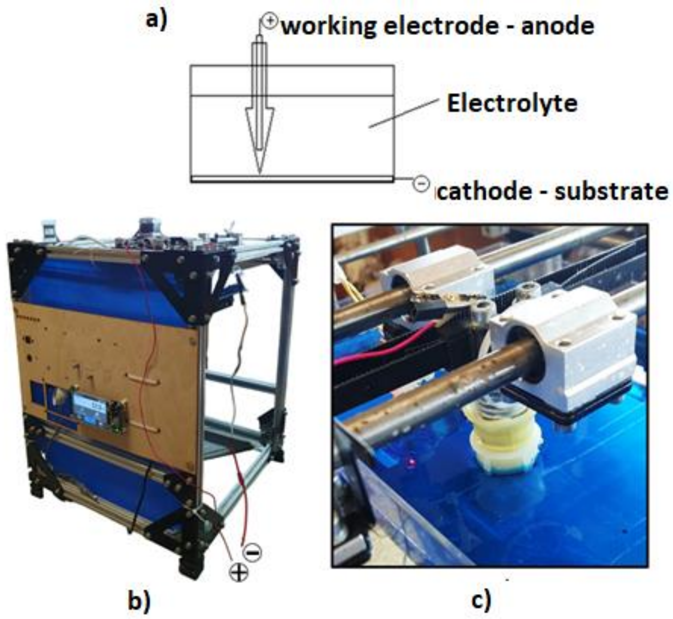


Fig. 1. Photo of the electrochemical 3D printing installation: a) schematic image of the electrochemical cell; b) electrochemical 3D printer; c) electrochemical cell and working electrode of an electrochemical 3D printer

Micromechanical tests of printed objects were carried out on the universal microhardness-scratch tester "Micron-gamma" by the method of continuous pressing of the indenter. The load on the Berkovich indenter is carried out by a linear non-contact electromagnetic loader with a maximum force of 50 N [4, 6, 7]. In order to determine the micromechanical characteristics, the electrochemical 3D printing of the studied objects was carried out on a copper base made of M0 hydro-electrometallurgical copper, which served as a reference sample.

The microrelief of the surface was studied on a non-contact interference profilometer "Micron-alpha". This approach makes it possible to register the topography of the surface by processing a sequence of interference data (pictures) under partially coherent illumination, which are recorded by a digital camera during the displacement of the reference (reference) mirror [8].

Results and their discussion. Electrochemical 3D printing of the "square" objects under study was carried out with a linear speed of movement along a given trajectory of 1.5 cm/s and 3 cm/s, the average height of the obtained objects is 150 µm. Images of the obtained objects are shown in Fig. 2, 3, and the morphology of their cathodic deposits is shown in Fig. 4.

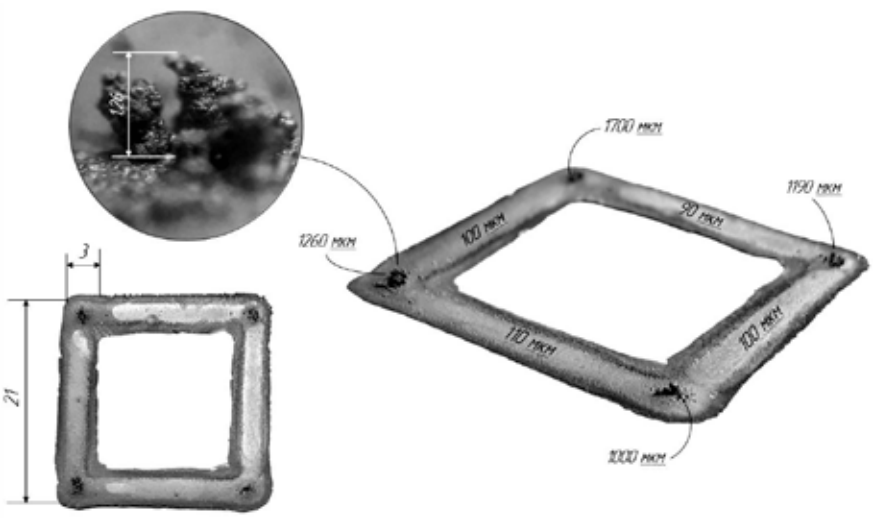


Fig. 2. Electrochemically printed "square" part with an anode movement speed of 3 cm/s. The average current density during printing is 2.7 A/dm^2

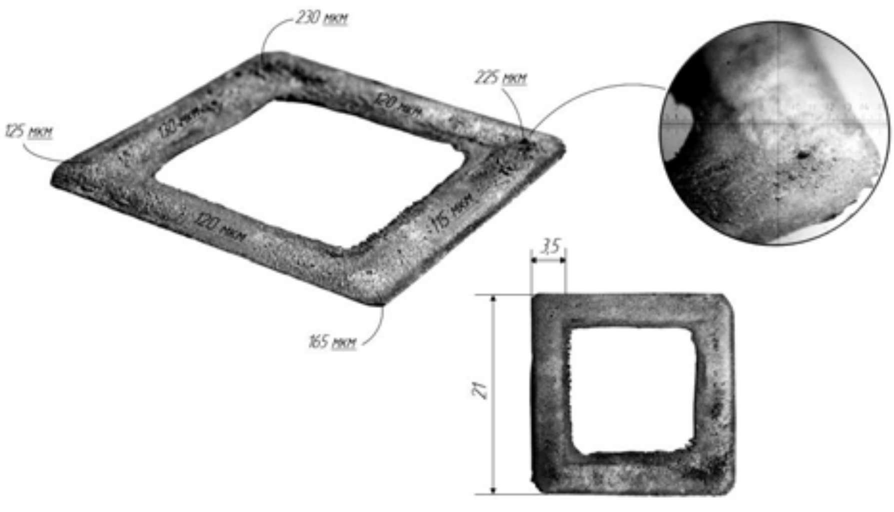
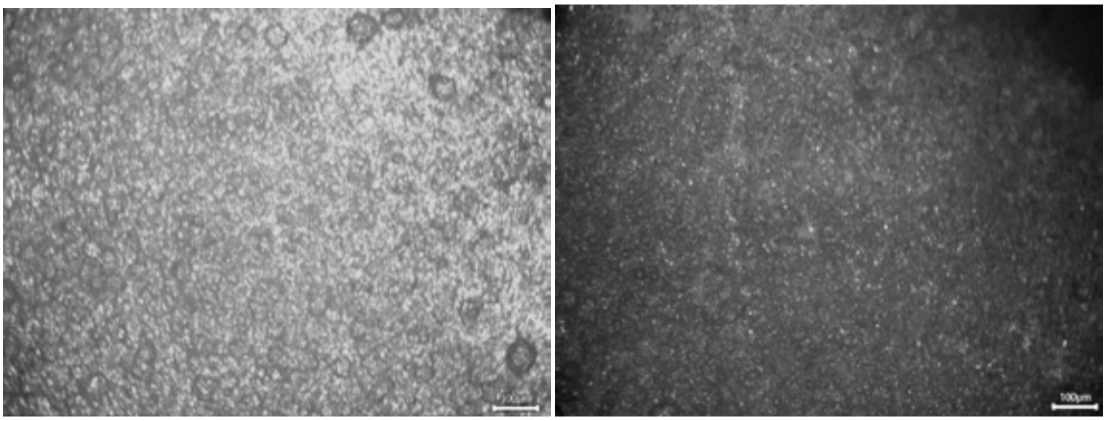


Fig. 3. Electrochemically printed "square" part with an anode movement speed of 1.5 cm/s. The average current density during printing was 2.45 A/dm^2

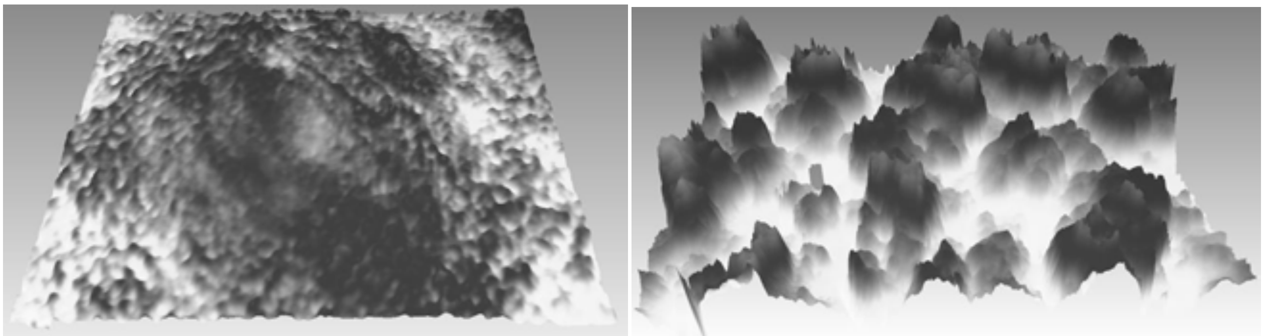
Conducted studies of electrochemical 3D printing of "square" parts indicated the following. Parts with a fine-crystalline compact metal structure were obtained. However, it was found that excessive metal deposition is observed in the corners (Fig. 2, 3). This phenomenon is related to the peculiarities of the movement of the working electrode, in particular with the deceleration when passing the corner. A decrease in the speed of movement, which is also accompanied by an increase in its uniformity, causes a decrease in the manifestation of excessive deposition and the removal of dendrites from the corresponding places on the received object. Also, as can be seen from Fig. 4, a decrease in the speed of movement leads to the formation of a finer crystalline structure of the surface of the metal deposit and the elimination of spherulites. This, in particular, may be associated with a change in the current regime, in particular with a decrease in the frequency of pulses and current pauses.



a b

Fig. 4. Morphology of electrochemically printed copper parts, speed of anode movement, cm/s: a – 3; b – 1.5

3D relief modelling and determination of the surface roughness of the obtained electrochemically printed samples on a copper substrate are shown in Fig. 5.



a b

Fig. 5. 3D models of the surface of the hydrometallurgical copper base (a) and a fragment of the electrochemically printed copper deposit (b)

As can be seen from Fig. 5. during electrochemical 3D printing, a deposit with a columnar structure is formed. The roughness of the surface of the sample of hydroelectrometallurgical copper base has the following parameters: Rz(1)=1.128; Ra(1)=0.2925. For the electrochemically printed sample: Rz(1)=95.72; Ra(1)=16.32. Considering the possible application of the investigated production method, the formation of a compact and, at the same time, rough metal structure is beneficial. In particular, the adhesive properties of the conductive pattern obtained by electrochemical 3D printing will be improved at the stage of its installation on the dielectric base according to the technology of printed circuit board production by the "transfer" method. Also, due to the increase in the specific surface area of the metal conductor, heat transfer can be improved.

The next stage of the research was the comparison of the micromechanical characteristics of the electrochemically printed copper deposit with the industrial material – hydroelectrometallurgical copper. Diagrams of the indentation of the Berkovich indenter for both studied materials are shown in Fig. 6.

The obtained appearance of the indentation diagrams reflects the influence of the method of obtaining on the physical and mechanical properties of the studied copper samples. Accordingly, the maximum average value of the indenter insertion depth for hydroelectrometallurgical copper is 3.2 µm, and for electrochemically printed copper – 2.8 µm.

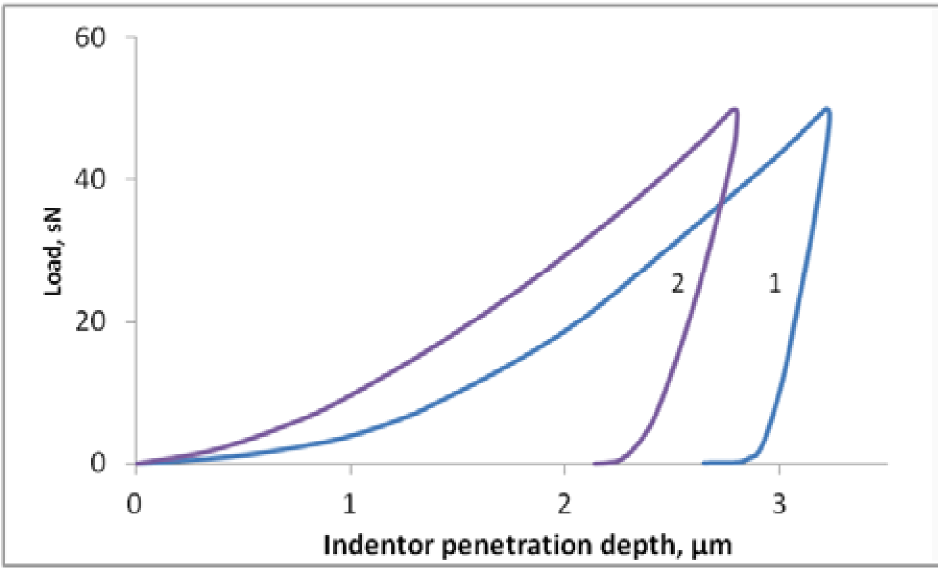


Fig. 6. Indentation diagram of hydroelectrometallurgical copper sample (1) and for electrochemically printed copper deposit from nitrate electrolyte (2)

On the basis of the obtained implementation diagrams, the Meier microhardness, Young's modulus, and plasticity coefficients for the studied copper samples were calculated and averaged, which are given in Table 1.

Table 1

Micromechanical parameters of the studied copper samples

Hydro-electrometallurgical copper			Electrochemically printed copper deposit from nitrate electrolyte		
HM, GPa	E, GPa	K_{elast}	HM, GPa	E, GPa	K_{elast}
2,16	114,4	0,918	3,20	98,9	0,880

As can be seen from Table 1, the microhardness of the electrochemically printed copper deposit is approximately 30% higher than that of hydroelectrometallurgical copper, which is associated with the formation of a pronounced columnar structure of the deposit (Fig. 5.a). However, plasticity coefficients and Young's modulus of both electrochemically printed and hydrometallurgical copper samples are close in value. Thus, the method of obtaining metal objects by electrochemical 3D printing does not contribute to a significant deterioration of the elasticity of the obtained material.

Conclusions

The possibility of obtaining copper metal parts using the electrochemical 3D printing method with a compact fine-crystalline structure using nitrate copper electrolyte has been shown.

It has been shown that a decrease in the speed of movement of the working electrode leads to an increase in the uniformity of the metal deposit, but the precision of printing decreases.

It was established that in terms of plasticity coefficient, electrochemically printed copper deposits in nitrate electrolyte are close to hydroelectrometallurgical copper. The formation of a compact copper deposit with a rough surface is a positive characteristic from the point of view of the use of electrochemical 3D printing in the production technology of printed circuit boards.

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