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CORROSION RESISTANCE OF ZINC GALVANIC DEPOSITS OBTAINED BY THE ELECTROCHEMICAL 3D PRINTING METHOD

The article is devoted to the implementation of the process of electrochemical 3D printing of zinc products and the determination of the effect of the method of their production on corrosion resistance. The possibility of electrochemical 3D printing of zinc objects with a fine-crystalline compact structure using high-speed sulfate plating electrolyte has been shown. The most resilient and elastic zinc deposits were obtained in the electrolyte without the addition of organic additives and when gelatin was added to the electrolyte. The use of naphthalene disulfonic acid of 1,5-disodium salt made it possible to obtain the most finely crystalline and semi-glossy zinc deposits, but the fragility of the deposits increased somewhat. Conducted studies of the corrosion resistance of printed zinc objects showed that the use of electrochemical 3D printing as a method of obtaining and introducing organic additives into the electrolyte does not lead to a decrease in the corrosion resistance of the metal.

Keywords: zinc; local electrodeposition; electrochemical 3D printing; sulfate electrolyte; surface active additives; corrosion resistance.

Table: 3. Fig.: 5. References: 18.

Relevance of the research. 3D printing is the newest additive technology that makes it possible to obtain metal products that are unique in their application and configuration complexity [1]. However, most 3D printing methods are energy-consuming, due to the presence of a stage of converting the metal into a liquid state during printing. The use of powdered metals makes this technology environmentally hazardous and explosive. Electrochemical 3D printing is a technology derived from local electrodeposition and is the most energy-efficient method of 3D printing metal products [2-6]. The advantage of electrochemical 3D printing in particular is selectivity and the absence of the need to use protective screens to limit the area of electrodeposition.

Problem statement. Most of the known sources in the relevant field of research are dedicated to the electrochemical 3D printing of metal objects from metals such as copper, nickel is somewhat less common [7]. Sources related to electrochemical 3D printing of zinc products are scarce.

Analysis of recent research and publications. The advantage of zinc as a metal in this case may be a slightly higher value of the electrochemical equivalent than for nickel and copper. This can give some advantage in the value of the metal deposition (printing) rate. In addition, similar to local electrodeposition technology, electrochemical 3D printing can be used for the purpose of manufacturing protective elements or electrodeposition of zinc-based protective coatings [8,9]. An important technological characteristic of any metal product is its corrosion resistance under appropriate operating conditions. Literary data on corrosion resistance and protective properties of various types of galvanic coatings are quite numerous. However, it should be noted that in electrochemical 3D printing, the current regime is different from that which is usually used for electrodeposition of galvanic coatings. The current mode during electrochemical 3D printing or local electrodeposition [4,6] with the movement of the counter electrode can be equivalent to the

pulse mode of electrolysis. During printing, at a certain moment in time, the working electrode (anode) is located over a certain area on a closed trajectory of its movement. As the working electrode approaches this area, the current pulse will increase, which will decrease after it moves away. As is known, the current regime, and especially the non-stationary one, can significantly affect both the crystal structure of the metal and its corrosion resistance [10, 11].

Uninvestigated parts of a common problem. The current mode can affect the process of adsorption and inclusion of surface-active additives in the metal deposit, which are used to improve the quality of cathode deposits of metals. In addition to the positive effect on the crystalline structure of the metal, surface-active additives due to inclusion in the crystalline structure of the metal can cause the process of corrosion destruction [12,13].

Research objective. The research presented in this article is devoted to the implementation of the process of electrochemical 3D printing of zinc products and the determination of the effect of the method of their production on corrosion resistance.

Research methodology

Methodology of electrochemical 3D printing on a device with a rotating electrode

Local electrodeposition - electrochemical 3D printing was carried out on the installation, the schematic diagram of which is shown in Fig. 1. An AISI 321 stainless steel plate (cathode) was placed at the bottom of the plastic vessel and connected to the negative pole of the DC source. Stainless steel was chosen to allow easy separation of the printed object from the cathode surface. The working electrode was rotated by an electric motor, the speed of rotation was 1 s^{-1} . An inert platinated titanium electrode was used as the working electrode-anode [14].

The algorithm for conducting experimental research was as follows. The stainless steel cathode was polished using polishing cloth wheels, degreased and placed on the bottom of the vessel. An electrolyte solution with a volume of 1 liter was poured into the vessel, the level of the electrolyte was 10...15 mm above the substrate. The edge of the dielectric body of the anode was placed at a height of 1 mm above the substrate. After that, with the help of an electric motor, the cathode began to rotate and a current with a density of $2...4 \text{ A/dm}^2$ was supplied. After the end of the experiment, the current was turned off, and the solution was drained from the vessel. The locally electrochemically printed object in the form of a ring was washed with distilled water, removed from the substrate and examined.

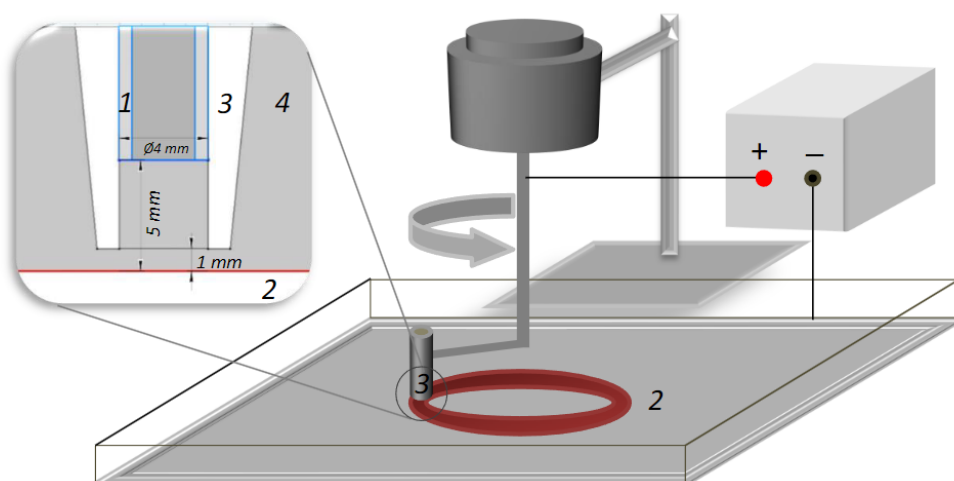


Fig. 1. Schematic diagram of the laboratory installation:
1 – platinated foil (anode); 2 – stainless steel base (cathode);
3 – polypropylene capillary; 4 – electrolyte [14]

Methodology of corrosion tests. Corrosion resistance of printed zinc objects was evaluated with polarization and electrochemical impedance measurements.

The rate of corrosion was determined by the method of direct polarization. For this, anodic and cathodic polarization curves were obtained on fragments of printed part with a scanning rate of 2 mV/s. As a working solution, 3.5% sodium chloride was used. Polarization curves were recorded in a conventional three-electrode cell. A platinum electrode was used as an auxiliary. The rate of corrosion was determined graphically by finding the intersection of the extrapolated linear sections of the polarization curves plotted in semi-logarithmic coordinates.

The measurement of electrochemical impedance was carried out in order to determine the polarization resistance of the studied samples using a digital potentiostat VersaSTAT 3 AMETEK. The frequency range of alternating current was $10^5 \dots 5 \cdot 10^{-2}$ Hz. In order to measure the electrochemical impedance, special two-electrode probes were developed, which were made from fragments of printed zinc objects (Fig. 2). The working surface area of the sensor is 0.9 cm^2 . The distance between the working area of the sensor was 2 mm. The non-working surface of the fragments was covered with a layer of electrically insulating lacquer coating. Before measurements, the sensors were kept in the working solution for corrosion tests for 0.5...1 h.

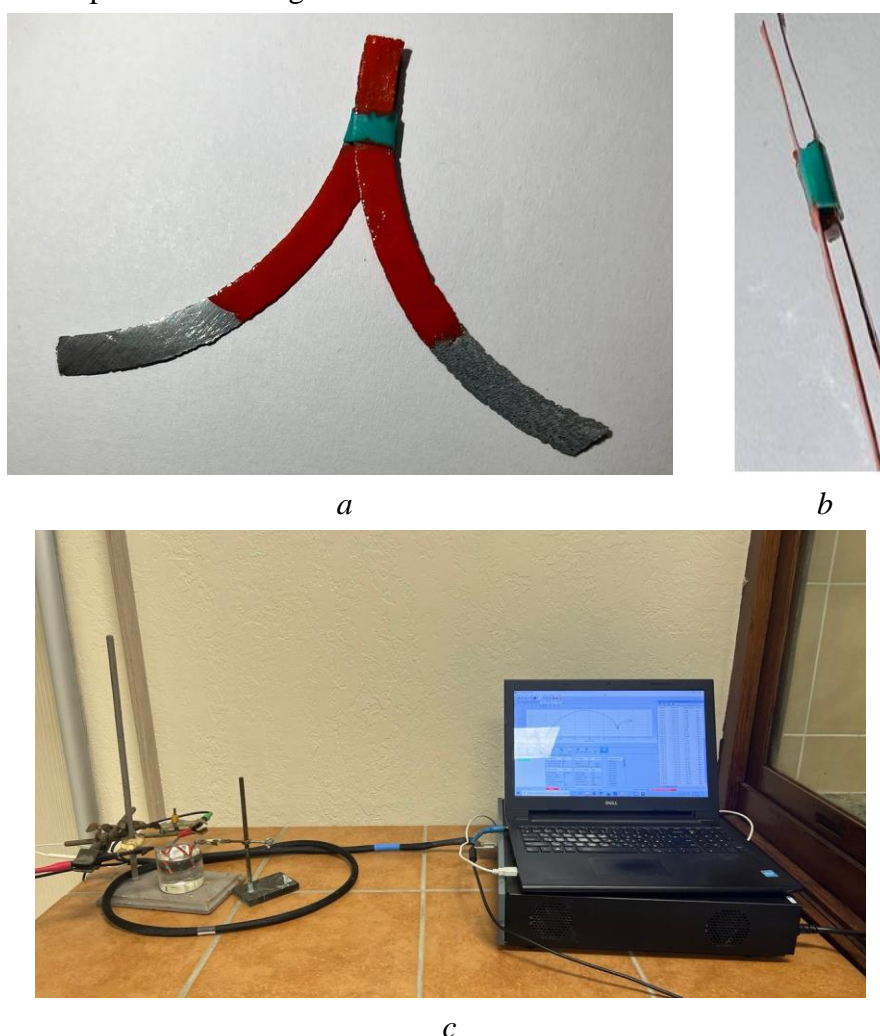


Fig. 2. A probe from fragments of an electrochemically printed zinc object "ring" (a, b) and an electrochemical impedance measurement setup using AMETEK's VersaSTAT 3 digital potentiostat (c)

Research results of electrochemical 3D printing of the "ring" object. At this stage of research, local electrodeposition (electrochemical printing) of zinc objects "ring" with a thickness of $180 \dots 240 \text{ }\mu\text{m}$ was carried out. Sulfate electrolyte was chosen for the research because

it is relatively environmentally safe. In addition, this electrolyte is highly productive due to the possible zinc sulfate content of about 600 g/l [15]. The pH value in the electrolyte was maintained in the range of 3.5...4.5. For this purpose, 30 g/l of ammonium sulfate and 20 g/l of aluminum-potassium sulfate were added to the electrolyte. Such well-known additives for zinc plating electrolytes as thiourea, gelatin, OP-10, naphthalene disulfonic acid, 1,5-disodium salt were introduced into the electrolyte in order to improve the structure and appearance of cathode deposits. The composition of the electrolytes and the duration of the process for each experiment, as well as the measured thickness of the obtained objects are shown in the Table 1.

Table 1 – Composition of electrolytes and research conditions





№	Electrolyte composition, g/l	Duration of the process, min	Current densities, A/dm ²	Calculated thickness, μm	Measured thickness, μm
1	ZnSO ₄ ·7H ₂ O – 600; (NH ₄) ₂ SO ₄ – 30	215	2,4	147	200
2	ZnSO ₄ ·7H ₂ O – 600; (NH ₄) ₂ SO ₄ – 30; gelatin – 0,1	210	2,4	142	180
3	ZnSO ₄ ·7H ₂ O – 600; (NH ₄) ₂ SO ₄ – 30; naphthalene disulfonic acid of 1,5-disodium salt – 2	320	2,6	238	240
4	ZnSO ₄ ·7H ₂ O – 600; (NH ₄) ₂ SO ₄ – 30; naphthalene disulfonic acid of 1,5-disodium salt – 2; ОП-10 – 0,25; KAl(SO ₄) ₂ ·12H ₂ O – 20	260	3,0	222	220

During the study of the process of electrochemical 3D printing using sulfate electrolyte, it was established that electrochemical printing with obtaining a compact, fine crystal structure of metal is possible at an average current density of 2,4...3 A/dm² (Table 2). When trying to obtain objects at higher current densities, the growth of dendrites began on the zinc surface, which is related to the used current regime, which is different from the stationary one. It was also established that the most elastic zinc deposits were obtained in the electrolyte without the addition of organic additives and when 0.1 g/l of gelatin was added to the electrolyte. However, in the corresponding electrolytes, zinc deposits were coarser and more prone to dendrite formation. Accordingly, this explains the fact that the experimental thickness is greater than the calculated one (Table 1). When using naphthalene disulfonic acid of 1,5-disodium salt at a concentration of 2 g/l, the most finely crystalline and semi-glossy zinc deposits were obtained, but the fragility of the deposit increased to some extent. Additive OP-10 was applied to eliminate pitting and shells in the metal deposit, which were the result of a parallel process - the hydrogen evolution.

The study of the corrosion properties of electrochemically printed metal deposits was conducted using fragments of the "ring" objects obtained in experiments № 1...4 (tables 1 and 2). Samples of hydroelectrometallurgically obtained zinc plates were used as reference samples.

Polarization curves were obtained for the studied samples in order to find instantaneous values of the corrosion rate. A fragment of an electrochemically printed object served as the working electrode. The area of the working surface, not insulated with varnish, of all the studied samples was 0.4 cm². Corrosion diagrams, built on the basis of the obtained polarization curves, are shown in Fig. 2.

Table 2 – The influence of the current mode on the quality of the metal deposit of electrochemically printed "ring" objects

	№ of experiments from table 1	
	1	2
Electrochemically printed zinc objects		
		

The results of corrosion tests of the obtained "ring" objects
Corrosion diagrams

It can be seen from the obtained polarization curves (Fig. 3) that all investigated zinc galvanic deposits are actively dissolved in the investigated sodium chloride solution when anodic polarization is applied. On the cathodic polarization curve, the limiting current of electroreduction of oxygen is observed, which smoothly transitions to the next process of hydrogen release. Corrosion potential E_c and corrosion rate were determined using the obtained corrosion diagrams. The results of determining the corrosion rate and corrosion potential are shown in Table 3.

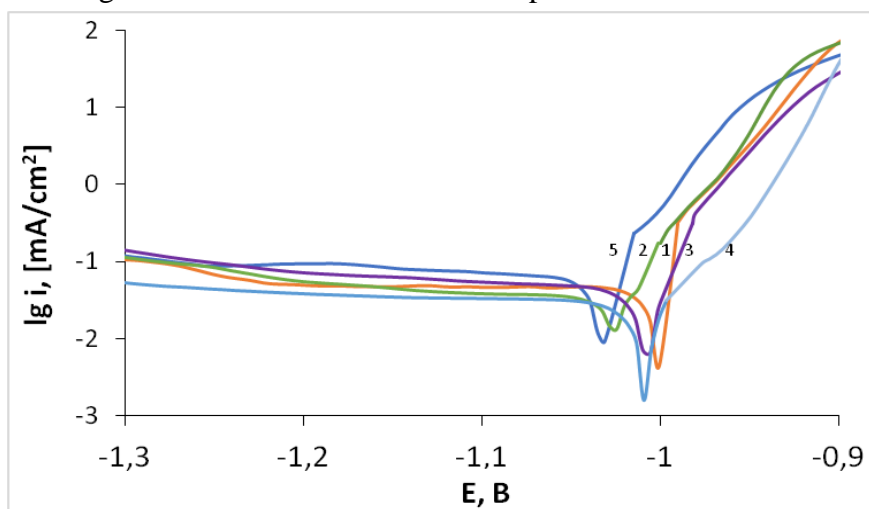


Fig. 3. Corrosion diagrams for samples of zinc deposits in a 3.5% sodium chloride solution: 1 – electrochemically printed in sulfate electrolyte without additives; 2 – electrochemically printed in a sulfate electrolyte with the addition of gelatin; 3 – electrochemically printed in a sulfate electrolyte with the addition of naphthalene disulfonic acid 1.5 disodium salt; 4 – electrochemically printed in a sulfate electrolyte with the addition of naphthalene disulfonic acid 1.5 disodium salt and OP-10; 5 – hydrometallurgical zinc

Table 3 - Corrosion characteristics of electrochemically printed zinc in a 3,5% sodium chloride solution

№ of experiments from Table.1	E_c, V	$lg i_c$	$i, mA/cm^2$	$R_p, Ohm \cdot cm^2$
1	-1,00	-1,36	0,044	1054
2	-1,02	-1,44	0,036	1147
3	-1,01	-1,31	0,049	1000
4	-1,01	-1,49	0,032	1272
5*	-1,03	-1,19	0,060	950

* hydroelectrometallurgical zinc

Also, in this work, electrochemical impedance measurements were carried out in order to identify the mechanism of the controlling stage and to determine the polarization resistance of printed deposits samples. The results of these measurements are presented in the form of Bode and Nyquist plots in Fig. 4.

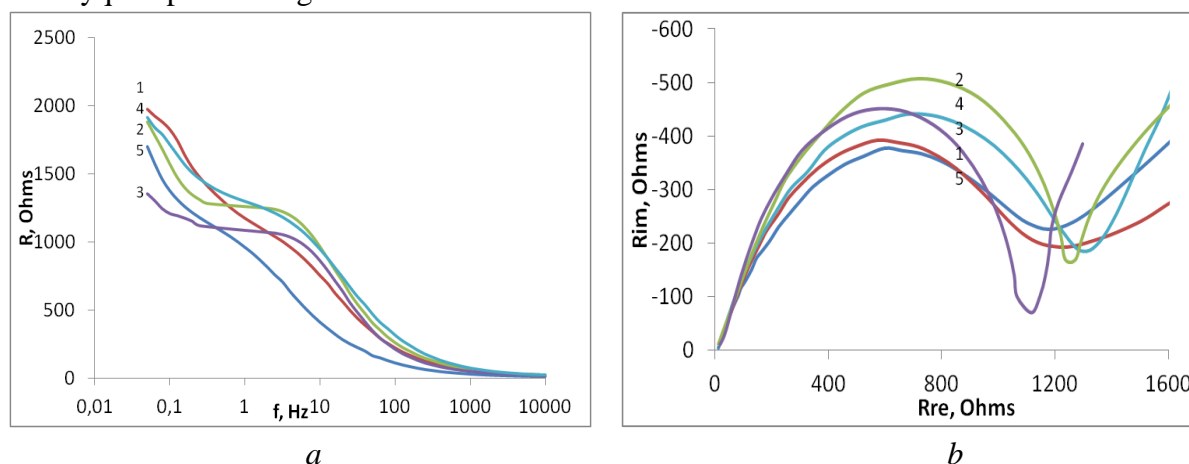


Fig. 4. Bode (a) and Nyquist (b) plots for zinc deposits in a 3.5% sodium chloride solution: 1 – electrochemically printed in a sulfate electrolyte with the addition of gelatin; 2 – electrochemically printed in sulfate electrolyte without additives; 3 – electrochemically printed in a sulfate electrolyte with the addition of naphthalene disulfonic acid 1.5 disodium salt; 4 – electrochemically printed in a sulfate electrolyte with the addition of naphthalene disulfonic acid 1.5 disodium salt and OP-10; 5 – hydrometallurgical zinc

The obtained form of the Bode and Nyquist plots corresponds to the course of the corrosion process with mixed diffusion-kinetic control (Fig. 4), which is consistent with the data [16-18] and the obtained corrosion diagrams (Fig. 3). Accordingly, the equivalent electrical circuit of the surface of the corroding zinc sample corresponds to Fig. 5 b.

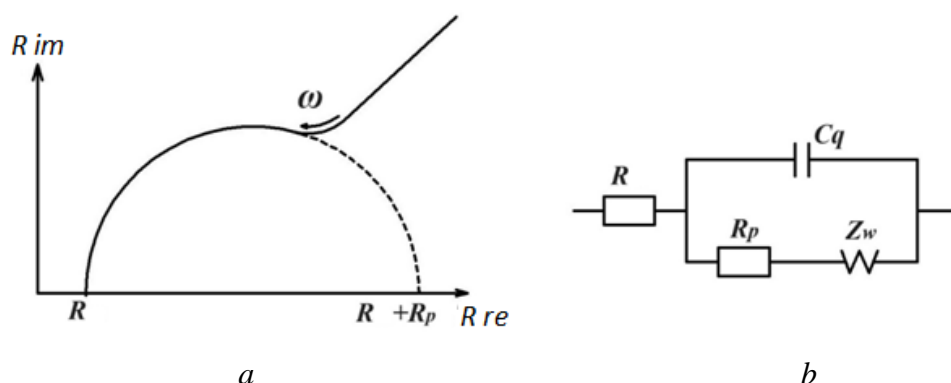


Fig. 5. The theoretical form of the Nyquist plot for diffusion-kinetic control of the corrosion process (a) and the equivalent scheme of the zinc electrode surface (b) in the process of corrosion destruction [18], where: R is the resistance of the electrolyte, R_p is the polarization resistance, Z_w is the diffusion component of the Warburg impedance, C_q is the capacitance of the double electric layer

In this case, R_p represents the difference between the resistance value at the intersection of the dotted line with the R_{re} axis ($R+R_p$) and the electrolyte resistance value R . According to the obtained Nyquist plot (Fig. 4), R_p was obtained by finding the larger root of the quadratic approximation polynomial, which is quite accurate the first section of the dependence on the Nyquist plot is approximated. The determined values of the polarization resistance in Table 3 are given taking into account the working surface area of the used probe. As can be seen from Table 3, there is a corresponding inverse correlation between the results of determining the corrosion rate and polarization resistance. In general, the results of corrosion tests indicate that the method of obtaining metallic zinc parts by electrochemical 3D printing does not cause a decrease in the corrosion resistance of the metal.

Conclusions. In the course of the conducted research, it was established that electrochemical 3D printing of zinc parts with obtaining a fine crystal structure of the metal, using a concentrated sulfate galvanizing electrolyte, is possible with the use of cathodic current densities up to 3 A/dm^2 .

Based on polarization measurements and electrochemical impedance measurement, it was established that electrochemically printed zinc parts are not inferior to hydroelectrometallurgically obtained zinc samples in terms of corrosion resistance.

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КОРОЗІЙНА СТІЙКІСТЬ ЦИНКОВИХ ВИРОБІВ, ОТРИМАНИХ МЕТОДОМ ЕЛЕКТРОХІМІЧНОГО ЗД-ДРУКУ

Стаття присвячена реалізації процесу електрохімічного ЗД-друку виробів із цинку та визначенню впливу способу їх одержання на корозійну стійкість. Показана можливість електрохімічного ЗД друку об'єктів з цинку при товщині осадуваного шару металу 180...240 мкм в інтервалі густини струму 2,4...3,0 А/дм², із дрібнокристалічною компактною структурою при використанні швидкісного сульфатного електроліту цинкування. Найбільш пружні та еластичні осади цинку були отримані в електроліті без додавання органічних добавок та при введенні до електроліту желатину. При використанні як добавка, нафталін дисульфокислоти 1,5-динатрієвої солі були отримані найбільш дрібнокристалічні та напівблискучі осади цинку, проте крихкість осадів децю зросла. З метою оцінки корозійної стійкості та визначення швидкості корозії були застосовані методи побудови поляризаційних кривих та вимірювання електрохімічного імпедансу. Для реалізації останнього із фрагментів електрохімічно надрукованих цинкових об'єктів були створені спеціальні датчики. Проведені дослідження корозійної стійкості надрукованих цинкових об'єктів у 3,5 % розчині хлориду натрію показали швидкість корозії варіюється в межах 0,03...0,06 мА/см². Вигляд, отриманих при вимірюванні електрохімічного імпедансу, діаграм Боде та Найквіста свідчить про те, що корозія надрукованих цинкових зразків відбувається зі змішаним дифузійно-кінетичним контролем. Характер зміни величин швидкостей корозії та розрахункових, на основі діаграм Найквіста, поляризаційного опору вказують на те, що використання електрохімічного ЗД-друку як способу отримання та введення при цьому в електроліт органічних добавок не призводить до зниження корозійної стійкості металу.

Ключові слова: цинк; локальне електроосадження; електрохімічний ЗД друку; сульфатний електроліт; поверхнево активні добавки; корозійна стійкість.

Табл.: 3. Рис.: 5. Бібл.: 18.