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### THE USE OF PULSE ELECTROLYSIS FOR COPPER PLATING ON STEEL AND CAST IRON BASES FROM CITRATE ELECTROLYTE

Process of electrochemical deposition of copper on a steel and iron substrate from citrate electrolytes was investigated. It is determined that the material of cathode greatly influences the kinetics of copper plating process. Influence of pulse electrolysis on a range of working density of current, a current efficiency of copper and porosity of coatings were investigated. It is determined that application of a pulse mode increases a range of working density of current and improves quality of the received coatings.

**Introduction.** Quality of copper coatings on steel depends on the temperature and solution composition, the electric current density of deposition and the difference of the equilibrium potential of copper electrode  $E_1$  and stationary potential of steel electrode  $E_2$ . When a potential difference is equal  $E_1 - E_2 > -0.5$  V, there is a fast cementation. Under such conditions there emerge foam coatings with poor adhesion and cohesion. In acidic solution of copper (II) sulfate the difference  $E_1 - E_2$  is about 0.8 V, therefore the copper-coatings on steel are of poor quality. It is impossible to get smooth homogeneous copper coatings with good adhesion on steel and iron from a solution of copper (II) salts due to fast cementation. If the potential difference is  $E_1 - E_2 < 0.1$  V, there is practically no cementation. Electrochemically it is possible to obtain smooth homogeneous copper coatings with good adhesion at the corresponding current density [1].

One of the methods of coating smoothing, as well as the intensification of copper plating process is nonstationary electrolysis – the deposition of metals at periodic currents of different form [2].

Under nonstationary current conditions by increasing the deposition rate and simultaneously improving the physical and mechanical properties of the coating it may be possible to intensify the process by 2–3 times compared to their deposition at direct current [3]. Improving the quality of deposit and intensification of the process, obtained by pulsed current are usually explained by two factors: the current pulsation, allowing to make even the diffusion conditions along the entire surface of the electrode, which increases the current density (the limiting current is increased by 2–8 times) and the increase of the metal deposition; non-stationary processes on the electrode with potential fluctuations not reaching its equilibrium valuation [4].

When using nonstationary current condition the process productivity and the quality of coatings depend not only on the current density and temperature, but also on the parameters of nonstationarity: on the duration of the cathodic and anodic polarization, on their ratio, on the ratio of the ca-

thodic and anodic current density, on pulse and pause duration and ratio between them [5].

**Main part.** The coatings were deposited from the electrolyte of the following composition:  $\text{CuSO}_4$  – 100 g/l,  $(\text{NH}_4)_2\text{SO}_4$  – 200 g/l, NaCl – 26 g/l, a citric acid – 48 g/l, NaOH to – pH 7.5–8.5. Polarization measurements and deposition in pulsed mode were carried out with potentiostat PI-50-1.1, as a unit of programmer PR-8 in a standard three-electrode cell ЯСЭ-2. As a reference electrode was used saturated silver chloride electrode. All potentials presented in the article have been converted into the scale of the standard hydrogen electrode. The range of working current densities was determined by the Hull cell with volume of 250 cm<sup>3</sup>. The current efficiency was determined gravimetrically. The porosity of the copper coating was determined in accordance with GOST 9.302-88.

Cathodic pulse time varied in the range of 5–100 ms, pause time – 2–10 ms.

Fig. 1 shows the cathodic polarization curves on copper, steel and cast iron electrodes, in the test electrolyte.

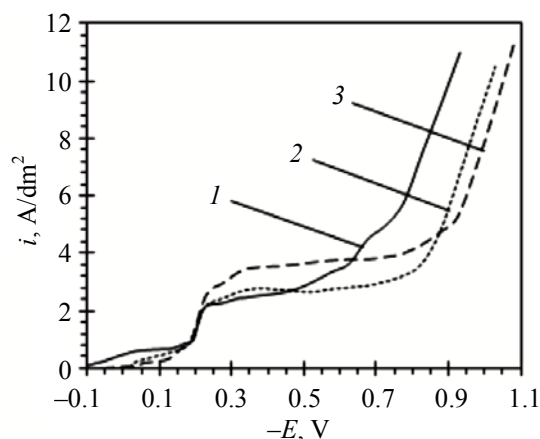


Fig. 1. Cathodic polarization curves at the cathodes of different nature:  
1 – copper; 2 – steel; 3 – iron

According to the polarization measurements the cathodic process on steel is observed at much higher cathodic polarization in comparison with

copper. This is due to the fact that the initial deposition of metal on the enthetic base requires a lot of energy, and as a result, the cathodic superpotential increases. When coating steel substrate with copper energy heterogeneity of the substrate and the deposited metal is graded and the polarization of the cathode decreases.

In the potential range from  $-0.3$  to  $-0.6$  V there is observed an area of the limiting current of  $2.2$ – $2.5$  A/dm<sup>2</sup>, which may be stipulated by the finite speed of the destruction of the complex ions at the surface of the electrode. Potential displacement of the cathode to a more electronegative values leads to an increase of the current density, which indicates a possible change of the discharge of complex copper ions and participating of particles of a different nature in the cathode process.

The electrode material has an impact on their polarization characteristics only at the initial time, when the surface is not covered with copper. However, the initial stages of copper coating formation are exceedingly important because they affect the adhesion to the surface and morphology of copper coating.

Fig. 2 presents the polarization curves that characterize the kinetics of the anodic dissolution of steel in the electrolyte without copper sulfate, and cathodic polarization curves in the electrolyte of the same composition containing copper sulfate.

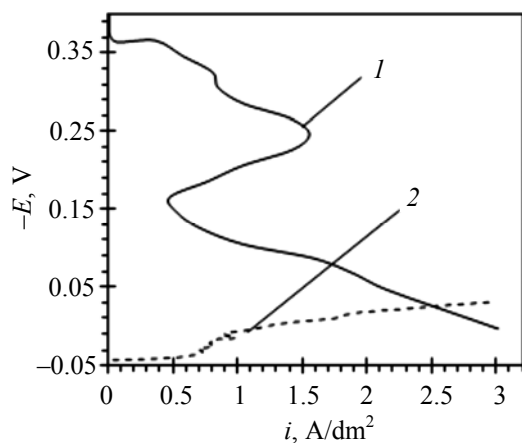


Fig. 2. The curves of the anodic (1) and cathodic (2) polarization of the sample St3

Anodic curves of iron in complex electrolyte, in contrast to the acidic, have an area of passivation, which in combination with cathodic polarization curves causes the adhesion of coatings. Cathodic and anodic polarization curves cross in the field of superpassivation, corresponding to low current of contact exchange and good adhesion of the coating to the substrate.

The results of measurements in the Hull cell allowed to detect changes in the range of working current density with different ratios of the pulse and pause duration (see the table).

#### The results of measurements in the Hull cell

$\tau_c$ , ms	$\tau_p$ , ms	$i_w$ , A/dm <sup>2</sup>
5	2	1.0–3.5
	5	1.2–5.1
	10	2.0–10.2
10	2	1.7–2.9
	5	1.3–3.9
	10	2.0–6.0
20	2	1.3–3.9
	5	2.0–4.5
	10	3.3–7.0
50	2	2.0–3.9
	5	2.4–3.9
	10	1.7–3.9
100	2	2.0–3.9
	5	1.7–3.9
	10	1.7–4.5

In the stationary mode this range was within  $1.0$ – $2.3$  A/dm<sup>2</sup>.

As the table shows, the maximum current density is reached at  $\tau_c = 5$  ms and  $\tau_p = 10$  ms. The upper limit of the current density increased by 3 times, and the range of current working densities has been expanded as well.

When determining current efficiency and porosity deposition in the stationary mode was conducted at a current density  $2$  A/dm<sup>2</sup>. Effective current density when deposited in pulsed mode was equal to  $2$  A/dm<sup>2</sup>.

Fig. 3 shows that the maximum value of the current efficiency of copper corresponds with pause duration of  $2$  ms. It is also clear that the maximum value of the current efficiency are reached at a ratio  $\tau_c : \tau_p = 1 : 2$ . The current efficiency of copper deposition in the stationary mode is  $80.91\%$ .

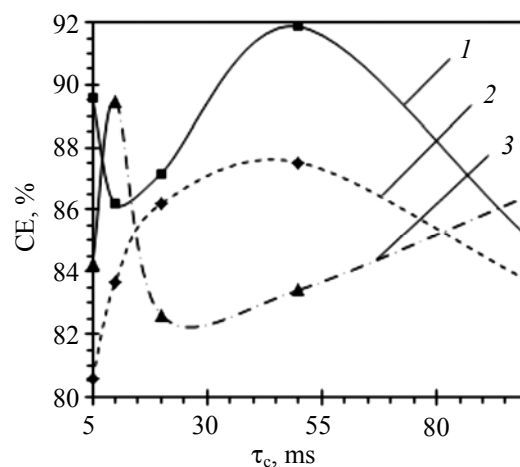


Fig. 3. The dependence of the copper current efficiency on pulse duration according to the following values of the pause duration: 1 – 2 ms; 2 – 5 ms; 3 – 10 ms

Fig. 4 shows the dependence of coating porosity on the pulse duration.

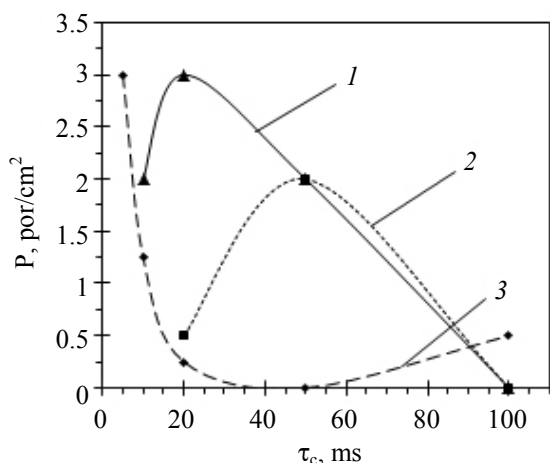


Fig. 4. The dependence of the coating porosity on the pulse duration according to the following values of the pause duration: 1 – 2 ms; 2 – 5 ms; 3 – 10 ms

As it is obvious from Fig. 4, coatings with minimum porosity are deposited at the following values of the pulse and pause duration, respectively: 50 : 10, 100 : 2, 100 : 5, 100 : 10.

Compact fine crystal shiny coatings are produced when using pulsed electrolysis. Compared with coatings obtained in the stationary current mode, these coatings have a smaller grain size of metal.

**Conclusion.** Thus, as a result of studies it has been found that the use of pulsed electrolysis when copper depositing allows to increase the operating current density significantly. At the values of pulse

and pause duration of 5 ms and 10 ms respectively, the working current density can be increased by 3 times, it greatly intensifies the process of copper deposition. At the optimum ratio of pulse and pause time it is possible to improve the quality of the obtained coatings and their properties. In particular, the current efficiency increases and the coating porosity obtained at any ratio of pulse and pause duration, compared with their properties obtained under stationary current loads decreases.

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