Electrodeposition by rubbing. The method of calculating the modes and the development of the high-speed copper plating process

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Abstract. Taking into account the processes carried out during electrodeposition by rubbing, high-speed copper electrolytes have been developed: low-acid and nitrate sulfate. There are proposed modes for anode-tools with area of 1 cm², 3.75 cm² and 4.43 dm², allowing for application of matte, semi-slush and shiny copper coatings with maximum speed up to 16 μm/min. A procedure has been created for calculating the permissible cathode current density and the required rate of electrolyte supply by dipping and jet methods. The effect of the area of anodes – tools on the maximum permissible cathode current density is determined. The effect of cathodic current density in high-speed copper plating electrolytes on current output and the rate of copper coating application has been established.

1. Introduction

The electrodeposition by rubbing method uses electrolysis. For this purpose the part is attached to the negative pole of the rectifier, whereas the anode tool is wrapped with a cloth, impregnated with electrolyte, attached to the positive pole and rubbed onto the covered part of the part. The main difference between the method of electrodeposition by rubbing and the galvanic method is the absence of a galvanic bath, the function of which is performed by a porous material impregnated with an electrolyte. Pollution of wastewater and ambient air are reduced due to the small volumes of used electrolytes.

Electrodeposition by rubbing is a mobile, portable method that allows for coating deposition to various parts, including large ones. Coatings are deposited with electrodeposition by rubbing at a high speed: nickel at a speed of up to 15 μm/min, zinc up to 10 μm/min, cadmium up to 9 μm/min, chromium up to 60 μm/min, iron up to 33 μm/min. With electrodeposition by rubbing it is easier to apply selective (local) coatings [1–7]. The maximum copper plating speed of 25 μm/min was indicated in [8], herewith in 10 minutes of electrodeposition by rubbing, a coating with a thickness of 100 to 250 μm was obtained on the sample; accordingly, when determining the copper plating speed by weight gain, this would be about 17.5 μm/min. Electrodeposition by rubbing has disadvantages. The process of electrodeposition by rubbing, as a rule, has a low level of mechanization and automation. It is required to have a large number of anode tools for various parts. During electrodeposition by rubbing, coatings may be uneven. The coating rate depends on the ratio of the areas of the working...
surface of the anode tool and the area of the coated part area. There are fewer electrolytes for electrodeposition by rubbing, and electrolyte compositions, as a rule, are not disclosed. There are no methods for calculating the permissible cathodic densities and electrolyte feed rate and there is no data on the influence of the area of the anode tool on the process of electrodeposition by rubbing. In this regard, in order to eliminate some of the above shortcomings, this research was carried out using copper plating, one of the most popular processes. Electrolytic copper coatings can be applied to steel, as well as to titanium, molybdenum, aluminum, copper, zinc and alloys based on them. Electronically rubbed copper coatings can be used to improve solderability, increase electrical conductivity, restore worn parts, protect against corrosion (for example, in multilayer coatings), for local protection of steel parts from cementation, nitration, boriding and other purposes [9–15].

2. Experiment: materials and methodic

For electrodeposition by rubbing, anode tools with a working area of 1 cm², 3.75 cm² and 443 cm² were used. The conductive part of the anode tools was made of 08H18N10T stainless steel containing 0.8% carbon, about 1% titanium, 10% nickel, and an increased chromium content of 18%. It is these last two elements that increase the chemical resistance of steel to the greatest degree. The speed of movement of the anode instruments was maintained from 7 to 9 m/min. The ratio of the cathode (coated) surface to the anode (area of the anode tool) was maintained equal to two. Electrolytes were prepared using distilled water and chemically pure chemicals. To supply electrolytes, dipping and jet methods were used.

Samples were made from unalloyed carbon steel coated with copper in a pyrophosphate electrolyte. For electrodeposition by rubbing the anode tool with an area of 4.43 dm², samples with a size of 400×700×0.5 mm were used, and for electron rubbing with the rest of the anode tools – 40×60×1 mm. Before coating, the samples were polished, degreased with Viennese lime (a mixture of calcium oxide 90% and magnesium oxide 10%), decapitated in a 20% sulfuric acid solution, washed first with tap water and then with distilled water.

For electrodeposition by rubbing, AC rectifiers with current stabilization and short circuit protection were used. The installation diagram of the electrodeposition by rubbing and anode tools are presented in [16, 17]. The thickness of the coatings, the deposition rate, and the current efficiency were determined by the gravimetric method (by weight gain) on an analytical balance with an accuracy of 0.1 mg. The adhesion strength of the coatings (adhesion) was tested by the method of applying grooves.

3. Results and discussion

Considerable attention was paid to the development of high-speed copper plating electrolytes. In electrodeposition by rubbing, the slowest stage of the electrochemical process, as well as in a galvanic bath, is the delivery of ions of electrodeposited metals to the surface of the cathode (part). In this regard, the developed by us electrolytes for electrodeposition by rubbing have a high concentration of copper ions. This is justified, because in electrodeposition by rubbing small volumes of electrolytes are used, compared with the volumes of electrolytes used in galvanic baths. In addition, in order to use high cathodic current densities, it is important to use effective buffer additives to prevent alkalinization in the cathode region, which can occur as a result of reaction (1) and lead to the copper hydroxides precipitation. In electrodeposition by rubbing, mainly insoluble anodes are used, which are close to the cathode. In this regard, the electrolyte may be acidified due to the formation of hydroxonium. Moreover, if the current efficiency of reaction (3) is equal to 100% or close to 100% at the anode, then, in addition to hydrogen evolution, a metal ion reduction reaction takes place at the cathode (2). On the other hand, reaction (1) proceeds directly on the surface of the cathode, and hydroxonium forms in the anode space and diffuses to the cathode. The final pH in the cathode space will depend on the ratio of the rates of the above processes, on the initial pH of the electrolyte and on the diffusion rate of the ions. Therefore, we need a high buffer capacity of the electrolyte in both acid and alkali.
\[ 2H^+ + 2e = H_2 \]  
\[ Me^{n+} + ne = Me \]  
\[ OH^- + 4e = 2H_2O + O_2 \]

Considerable attention should be paid to the choice of additives: shine-forming, inhibitory, accelerating, wetting. Many of them can significantly increase the rate of deposition of copper coatings, improve the quality of coatings, contribute to the production of shiny coatings [18–23], and this was taken into account when developing electrolytes. It is important that the electrolyte has high electrical conductivity, does not strongly corrode the metal base, does not emit toxic substances during operation, and has a low sensitivity to impurities. The following acidic electrolytes are used for applying copper coatings in electroplating and electrolyte: sulfate, fluoroborate, silicofluoride, nitrate, citrate, tartrate, trilonate, chloride, iodide, sulfamide and others. However, these electrolytes are more expensive, more harmful and more sensitive to impurities, in comparison with sulfate and nitrate electrolytes. The remaining acidic and alkaline copper plating electrolytes did not attract our attention due to the inability to conduct electrodeposition at high speeds. The most common copper plating electrolytes are sulfate. Copper sulfate electrolytes are simple in composition, stable in operation and have a low cost. It is known that sulfuric acid in sulfate electrolytes of copper plating increases the electrical conductivity of the electrolyte, prevents the hydrolysis of copper salts, however, the solubility of copper sulfate decreases with increasing sulfuric acid. Since reaction (3) proceeds during electrodeposition by rubbing, leading to an increase in acidity at the insoluble anode close to the cathode, an electrolyte with a lower concentration of sulfuric acid and a higher content of copper sulfate can be used accordingly. A lower concentration of sulfuric acid can also be used due to the constant updating of the cathode space with new portions of fresh electrolyte. Such a low-acid sulfate electrolyte is electrolyte 1; its composition is shown in table 1. Glossy coatings can be applied from this electrolyte when a shine-forming BS-1 additive is added to its composition with a concentration of 4 to 6 g/l. BS-1 additive is a stabilized mixture of aqueous solutions of safranin dye and dipropanedisulfonic acid disulfide. In addition to the shining effect, additives of the BS series (BS-1, BS-2) increase the scattering ability, the permissible cathode density. Copper coatings, electrodeposited from electrolytes containing only organic additives, have low ductility. To increase the ductility, sodium chloride with a concentration of 0.03–0.1 g/l is introduced into the electrolytes. In addition, chloride ion in sulfate electrolytes increases the cathode current density [24]. Nitrate electrolytes are of interest for electrodeposition by rubbing because of the high solubility of copper nitrate and a significantly higher limiting current density in comparison with other copper plating electrolytes. However, it is known that during electrodeposition of copper from copper nitrate solutions it is not possible to obtain high-quality coatings. The coatings are obtained friable with dendrites at the edges of the cathode due to the fact that in addition to copper precipitation during the electrolysis on the cathode, reactions of reduction of nitrate ions to nitrite ions and ammonium ions occur. These reactions reduce current efficiency by up to 20% and degrade the quality of coatings. Nevertheless, in the presence of inhibitors that suppress the reaction of reduction of nitrate ions, it is possible to obtain matte and even shiny copper coatings. Inorganic additives (chlorine ions, pyrophosphate and others) increase the current output of nitrate electrolytes to 100%. Organic compounds: acetic acid, citric acid, aminoacetic acid and trilon B, as a rule, increase the current efficiency to a lesser extent. However, citric acid and trilon B contribute to shiny coatings [25, 26]. Electrolyte 2 is a copper plating nitrate electrolyte in which the addition of XX chloride-quinonic and citric acid perform such functions. For the preparation of electrolyte 2, nitric acid copper was used, and for the preparation of electrolyte 1, copper sulfate was used. The range of copper ion content in electrolytes was established with a 20% decrease in copper concentration from the maximum for each specific electrolyte. Most often, it is precisely such a decrease in concentration as a result of copper production during electrodeposition with an insoluble anode rubbing that does not lead to a
deterioration in the quality of the coatings, the concentration of copper sulfate from 200 to 250 g/l is
given in the classic sulfate electrolyte of copper plating, i.e. with a difference of 20%.

Table 1. Compositions of copper plating electrolytes for electrodeposition with rubbing.

| Components                  | 1   | 2          |
|----------------------------|-----|------------|
| Copper (ions)              | 64–82.5 | 112–140 |
| Sulfuric acid              | 20–30 |            |
| Citric acid                | 20–40 |            |
| Sodium Chloride            | 0.03–0.1 |       |
| Shine-forming BS-1 additive| 4–6  |            |
| Additive XX (ml/l)         | 30–50 |            |

For electrodeposition with rubbing, various feed rates of electrolytes are recommended, as a rule,
selected experimentally. In this regard, a methodology was developed for calculating the supply of
electrolyte. First of all, it is necessary to determine the feed rate of electrolyte, which compensates for
the production of copper ions during electrodeposition with rubbing. To do this, we calculate the
allowable decrease in the concentration of copper ions $\Delta C$ in each electrolyte, based on the
composition of the electrolytes. So for electrolyte 1, the maximum concentration is 82.5 g/l, and the
minimum is 64 g/l, respectively, for electrolyte 1 this value is $\Delta C = 0.0185$ g/ml, for electrolyte 2
$\Delta C = 0.028$ g/ml. The mass of electrodeposited copper and $m$ removed from the electrolyte can be
calculated by the formula (4).

$$m = K_e \cdot I \cdot \eta \cdot \tau$$  \hspace{1cm} (4)

Taking into account formula (4), it is possible to propose formula (5) for calculating the rate of
compensatory supply of electrolyte ($G_c$, ml/cm² min), which does not allow the generation of ions of
an electrodeposited metal below the allowable by prescription.

$$G_c = \frac{K_e \cdot I \cdot \eta \cdot \tau}{\Delta C \cdot S} = \frac{K_e \cdot I}{\Delta C \cdot S} = \frac{K_e \cdot D_c}{\Delta C}$$ \hspace{1cm} (5)

In formulas (4) and (5), $m$ is the mass of electrodeposited copper, $K_e$ is the electrochemical
equivalent in g/A min, $I$ is the current strength in A, $\eta$ is the current output in fractions of a unit, $\tau$ is
the electrolysis time in minutes, $G_c$ is the electrolyte feed rate, which compensates for the production
of ions of the electrodeposited metal, ml/cm²·min, $\Delta C$ is the decrease in the concentration of the
electrodeposited metal, g/ml, $S$ is the cathode (coated area) area in cm², $D_c$ is the cathodic current
density in A/cm².

We use the formula (5) to calculate the compensatory feed rate of copper plating electrolytes. To
ensure the supply rate of electrolyte with a margin, to a first approximation, we will make calculations
by taking the current efficiency as 100% or in fractions of a unit of 1. The calculation results are
presented in table 2.

Table 2. Effect of electrolyte composition and cathodic current density ($D_c$, A/cm²) on the
compensating feed rate of electrolyte $G_c$ in ml/min·cm².

| Electrolyte | $D_c = 0.05$ A/cm² | $D_c = 0.2$ A/cm² | $D_c = 1.0$ A/cm² | $D_c = 2.0$ A/cm² |
|-------------|--------------------|-------------------|-------------------|-------------------|
| 1           | 0.053              | 0.21              | 1.05              | 2.1              |
| 2           | 0.035              | 0.14              | 0.7               | 1.4              |
As can be seen from the data presented in table 2, the higher the cathodic current density is, the faster the generation of copper ions in the cathode space occurs, accordingly, a higher electrolyte feed rate is required. Naturally, the smaller the initial maximum concentration of copper ions in the electrolyte, respectively, the smaller is the allowable interval for decreasing the concentration of copper ions $\Delta C$, the larger should be the supply of electrolyte at the same current density. Therefore, the feed rate of electrolyte 1, ceteris paribus, is higher than electrolyte 2. The easiest way to supply electrolyte is by dipping an anode tool wrapped in cloth or other porous material into the electrolyte. Usually, it is one dipping per minute. In this case, the fabric or other porous material must have sufficient water absorption (electrolyte absorption), high wear resistance and good capillary properties, which ensure the movement of the electrolyte from the non-working zone to the cathode space. To increase the wear resistance and the volume held by the electrolyte fabric, combinations of fabrics were used taking into account their properties. For the manufacture of anode tools, we used a thin terry cloth with electrolyte absorption of 0.07 ml/cm$^2$ and a synthetic fabric made of polyester fibers (crimp) with electrolyte absorption of 0.02 ml/cm$^2$. Terry cloth was used for the first layer of fabric touching the conductive part of the electrode-tools, and the most wear-resistant fabric, crimp, was used for the second layer touching the cathode surface. It is possible to increase the electrolyte absorption of the anode tool using holes, recesses, and grooves on the anode tool. In particular, holes with a diameter of 4 mm were drilled on the largest of our anode tools with an area of 4.43 dm$^2$. It is easier to use the dipping method to provide the required electrolyte feed rate for small anode tools, the smaller the anode tool, the easier it is to provide the required electrolyte feed rate by dipping. This is due to the fact that the ratio of the working area of the anode tool to the area of the fabric used for small anode tools is much larger. So for the manufacture of a large anode tool with an area of 4.43 dm$^2$, a two-layer fabric of 7.09 dm$^2$ was required. This was enough to create a two-layer coating on the working surface of the anode tool and fixing the fabric on the conductive part. For the manufacture of the anode instrument with an area of 1 cm$^2$, 20 cm$^2$ of a two-layer fabric was required. Thus, the ratio of the tissue area to the working area of the anode tool for the large electrode tool was 1.6, and for the small one was 20. Accordingly, this ensures a better supply of fresh batches of electrolyte to the cathode reaction zone. To calculate the feed rate of the electrolyte with a two-layer fabric on the anode tools, we use the formula (6).

\[
G_a = \frac{(W_1 + W_2) \cdot S_T}{\tau}
\]  

In the formula (6) $G_a$ is the absorption rate of electrolyte supply using tissues, ml/min; $W_1$ and $W_2$ – electrolyte absorption of two types of tissue, m/cm$^2$; $S_T$ is the area of the two-layer fabric used to make the anode tool, cm$^2$; $\tau$ is the time interval between two electrolyte feeds, min. We take one minute, because after a minute a new supply of electrolyte was made by dipping. Using formula (6), we calculate the feed rates of electrolytes by tissues for various tissue combinations for anode instruments with an area of 1 sm$^2$, 3.75 cm$^2$ and 443 cm$^2$. Considering that for the manufacture of an anode tool with an area of 1 sm$^2$, fabrics with an area of 20 cm$^2$ were used, for an anode tool with an area of 3.75 cm$^2$ fabrics with an area of 28 cm$^2$ should be used. The results of these calculations are presented in table 3.

**Table 3.** The feed rate of the electrolyte with tissues in ml/min ($G_{a,t}$) for anode tools of various sizes, depending on the total electrolyte absorption by tissue combinations ($W$).

| $W$, ml/cm$^2$ | Anode tool area, cm$^2$ |
|---------------|--------------------------|
|               | 1                        | 3.75       | 443       |
| 0.04 (2 layers of crimp) | 0.8                      | 1.12       | 28.4      |
| 0.09 (terry and crimp)    | 1.8                      | 2.52       | 63.8      |
Table 3 shows the rates of supply of electrolytes by tissues in ml/min, however, not all of the electrolyte supplied by the tissue manages to take part in electrochemical cathodic reactions before renewing (dipping) the anode tool in a fresh portion of the electrolyte. To determine the \( P \) – fraction (part) of the electrolyte participating in the electrolysis, we determined the permissible cathodic current density, which allows obtaining high-quality coatings.

Above this current density, the quality of the coating deteriorated; more often, a burn-out formed. The permissible current density was determined for the anode instrument with a two-layer fabric (crimp and terry cloth). The feed rates of electrolytes were determined: \( G_{cs} \) compensating for the anode tool of a certain area according to the formula (7) and \( G_{a} \) the absorption rates of electrolyte supply by the tissue by the formula (6). The ratio of these speeds allows determining the approximate share \( (P) \) of the supply of electrolyte involved in electrolysis.

\[
G_{cs} = G_{c} \cdot S_{a} \cdot \tau
\]  
(7)

In formula (7), \( G_{cs} \) is the electrolyte supply rate that compensates for the generation of electrodeposited metal for an anode tool of a certain area, ml/min; \( G_{c} \) is the electrolyte supply rate that compensates for the generation of electrodeposited metal, ml/ cm² min, \( S_{a} \) is the area of the anode tool, cm², \( \tau \) is the time interval between two electrolyte feeds, min. We take one minute, because after a minute a new supply of electrolyte was made by dipping. The results are presented in tables 4 and 5.

| \( S \) anode tool | \( D_{c}, \) A/cm² | \( G_{cs}, \) ml/min | \( G_{a}, \) ml/min | \( P, \) fraction |
|------------------|-----------------|-----------------|-----------------|-----------------|
| 1                | 0.75            | 0.79            | 1.80            | 0.439           |
| 3.75             | 0.30            | 1.2             | 2.52            | 0.476           |
| 443              | 0.10            | 46.5            | 63.8            | 0.729           |

Table 5. The influence of the area of the anode tool on the permissible cathodic current density, the feed rate of the electrolytes and the fraction of their participation in electrolysis when electrically rubbed by anode tools with a two-layer fabric (crimp and terry cloth) for electrolyte 2.

| \( S \) anode tool | \( D_{c}, \) A/cm² | \( G_{cs}, \) ml/min | \( G_{a}, \) ml/min | \( P, \) fraction |
|------------------|-----------------|-----------------|-----------------|-----------------|
| 1                | 1.00            | 0.70            | 1.80            | 0.389           |
| 3.75             | 0.40            | 1.06            | 2.52            | 0.421           |
| 443              | 0.14            | 43.4            | 63.8            | 0.680           |

As can be seen from the data presented in tables 4 and 5, the smaller the area of the anode tool, the higher cathodic current densities can be used. When using electrolyte 2, for the anode tool with an area of 1 sm² \( D_{c} = 1 \) A/cm², and for the anode tool with an area of 443 sm² it is only 0.14 A/cm², since for large anode tools the concentration polarization is higher. For a large anode instrument, the proportion of used electrolyte feed is about 0.7.

For anode instruments with areas of 1 cm² and 3/75 cm², the average value of this fraction is 0.43. This is due to the fact that the ratio of the area of the anode tool to the area of the tissue for the anode tool with \( S_{a} = 443 \) cm² is small – 1.6, and for other anode tools this figure is much larger. Now, using the formula (8), it is possible to calculate the real feed rates of electrolytes provided by the tissues and, subject to the conditions of the formula (9), the coating will be of high quality without burning and other defects that arise when working with \( D_{c} \) above the limit.

\[
G_{r} = G_{as} \cdot P
\]  
(8)
Formula (10) will determine at what permissible current density it is possible to electrically rub the coating using the dipping method to supply the electrolyte. For this, we determine \( D_c \) from formula (5) and replacing the compensating feed rate with the real feed rate, we obtain formula (10).

\[
D_{cd} = \frac{G_r \Delta C}{K_e \eta}
\]  

(10)

In formulas (8, 9, 10), \( D_{cd} \) is the cathodic current density when feeding the electrolyte by dipping in A/cm², \( G_r \) is the actual electrolyte supply rate provided by the tissues in ml/min, \( G_{as} \) is the electrolyte supply rate by the tissues is absorption for the anode instruments of a certain area in ml/min, \( G_{cs} \) is electrolyte supply rate, which compensates for the production of electrodeposited copper ions for an anode instrument of a certain area in ml/min, \( P \) is a fraction (part) of electrolyte that managed to take part in electrolysis, \( \Delta C \) is an allowable decrease in concentration by copper ions in g/ml, \( K_e \) is the electrochemical equivalent of copper in g/A·min, \( I \) is the current strength in A, \( \eta \) is the current output in fractions of a unit.

The dipping method can be recommended for a small anode instrument with a working area of up to about 4 cm². However, the dipping method does not allow electrodeposition with rubbing processes with high cathode current densities, especially when using a large area anode tool. Firstly, a large area anode tool is more difficult to provide with the necessary volume of electrolyte to make up for the produced copper ions by the dipping method. Secondly, when the anode tool is of smaller size, the mixing of the electrolyte in the cathode space and, accordingly, the diffusion of copper ions proceed more intensively. This leads to an increase in the limiting cathodic current density.

It is possible to significantly improve the supply and control of electrolyte supply using a jet supply of electrolyte, as well as the exchange (supply and withdrawal) of electrolyte using a pump. The last option for supplying electrolyte justifies itself in large-scale production, when it is necessary to apply thick coatings, for example, to restore worn parts. Such installations with supply and removal of electrolyte by a pump are based on metal-cutting machines. Their efficiency is very high due to the obtaining of high coating rates. However, they have a higher cost, require the use of large volumes of electrolytes and do not have mobility and portability.

Thereby, in this research the electrolyte supply was used by the dipping method and the jet-gravity method. To implement the latter, a container with an electrolyte with a volume of five liters was fixed one meter above the anode tool, the anode tool was connected to the container with a PVC polymer tube and, using a set of clamps and a tap, the necessary electrolyte supply was established. Such an electrolyte supply system made it possible to increase the permissible cathodic current density and the deposition rate of copper coatings. It is known that increasing the diffusion rate of ions of an electrodeposited metal due to mixing of the electrolyte decreases concentration polarization and increases the limiting current density and the deposition rate. In the jet method, in comparison with the dipping method, the diffusion rate of copper ions can be increased by increasing the supply of electrolyte. It was found how the feed rate of the electrolyte affects the deposition rate of copper coatings and current efficiency. The results are shown in table 6.

| \( V_j \), ml/min | \( R \), \( \mu \)m/min | \( \eta \), % |
|-------------------|------------------|-----------|
| 0.7               | 9.8              | 22.1      |
| 2.1               | 13.9             | 31.4      |
| 6.3               | 16.2             | 36.7      |
| 18.9              | 16.9             | 38.2      |
As can be seen from table 6, the coating rate increases with an increase in the supply of electrolyte by 9 times from 0.7 ml/min to 6.3 ml/min, with a further increase in the supply of electrolyte, the copper plating rate is almost unchanged. It is possible to determine the optimal jet velocity of the electrolyte supply by the formula (11).

\[ C_j = G_c \cdot S \cdot N_j \]  

(11)

In formula (11), \( G_c \) is the electrolyte feed rate that compensates for the production of ions of the electrodeposit metal \( \text{ml/cm}^2 \cdot \text{min} \); \( S \) is the area of the anode tool in \( \text{cm}^2 \); \( N_j \) – how many times it is necessary to increase the speed of the jet feed in comparison with the compensating feed rate of the electrolyte. In our experiments, \( N_j \) for the anode tool with an area of 1 \( \text{cm}^2 \) is 9–10, for the anode tool with an area of 3.75 \( \text{cm}^2 \) \( N_j = 18 \), and for the anode tool with an area of 443 \( \text{cm}^2 \) \( N_j = 32 \). These values were used to calculate the jet feed rate for other experiments. Then we determined \( N_d \), i.e., how many times \( D_{cj} \) – the permissible current density when using the jet method can be larger than \( D_{cd} \) – the permissible current density when using the dipping method to supply the electrolyte. We obtained the value \( N_d = 2.1 \). Thus, it is possible to approximately calculate \( D_{cj} \) by the formula (12).

\[ D_{cj} = N_d \cdot D_{cd} \]  

(12)

After that, the current efficiency and the deposition rate of copper coatings in electrolytes 1 and 2 were determined. The results obtained are presented in table 7.

### Table 7. The effect of the cathodic current density (\( D_{cj}, \ A/\text{cm}^2 \)) on the copper plating speed (in \( \mu \text{m/min} \)) and current efficiency (in %) in copper plating electrolytes 1 and 2 when using an anode tool of 1 \( \text{cm}^2 \). In the numerator, the copper plating speed is given in \( \mu \text{m/min} \), and in the denominator the current efficiency is given in %.

| Electrolyte | 0.5A/cm² | 1.0A/cm² | 1.5A/cm² | 2.0A/cm² |
|-------------|----------|----------|----------|----------|
| 1           | 9.2/83.2 | 11.6/52.5| 12.3/37.2| –         |
| 2           | 8.4/76.0 | 13.1/59.3| 15.9/48.0| 16.2/36.7 |

As can be seen from table 7, with an increase in the cathodic current density, the deposition rate of copper coatings increases, moreover, first up to \( D_c = 1 \text{A/cm}^2 \) more sharply, then slowly, this is due to a significant decrease in current efficiency with increasing cathodic current density. The maximum copper coating deposition rate was obtained in nitrate electrolyte 2 due to a higher initial concentration of copper ions of 140 g/l, while in electrolyte 1 this concentration was 82.5 g/l. In electrolytes 1 and 2, in the absence of shining additives, even pink-red copper coatings were deposited. Gloss depended on the cathodic current density, coating thickness, initial roughness of the sample, the type of electrolyte, and the concentration of the shiner. The degree of gloss in the presence of shiners in the sulfuric acid low acid electrolyte 1 was higher than in nitrate 2, from which semi-gloss coatings were mainly deposited. The degree of gloss decreased with increasing coating thickness and increasing cathodic current density. All coatings passed the adhesion test.

### 4. Conclusion

As a result of research work, the operating modes and compositions of high-speed copper plating electrolytes are proposed. Nitrate copper plating electrolyte, which allows applying high-quality copper coatings from semi-brilliant to matte with a maximum speed of 16 \( \mu \text{m/min} \) by the method of electrodeposition by rubbing. Low acid sulfate electrolyte is inferior to nitrate electrolyte in coating rate. However, the sulfate electrolyte is cheaper, more stable, and more reliable in operation and allows for the application of copper coatings from matte to shiny. A technique has been developed that allows calculating a combination of fabrics for the manufacture of anode tools, feed rates of electrolytes by dipping and jetting, allowable current densities to achieve high coating rates with the
rational use of electrolytes. The calculation procedure is confirmed by the experimental results. The influence of the area of the anode tools on the maximum allowable cathodic current density is established. For a small anode tool (up to about 4 cm²), electrolytes can be applied by dipping; for an anode tool with an area measured by several dm², it is better to carry out jetting of electrolyte. It was determined how the cathodic current density in copper plating electrolytes affects the current efficiency and the rate of deposition of copper coatings.

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