Abstract
The dependences of the electrical conductivity of the methanesulfonate copper plating electrolyte on the concentrations of acid and copper methanesulfonate have been established. It has been shown that an electrolyte with a composition of 0.6 M Cu(CH₃SO₃)₂ + 0.6 M CH₃SO₃H is characterized by maximum copper ion concentration and high electrical conductivity. The study of the morphology of the copper coatings obtained in different hydrodynamic modes showed that smooth fine-grained deposits, well adhered to the base can be obtained from stirred methanesulfonate electrolyte in a range of current densities of 1 to 7 A/dm².

High-quality deposits from a quiescent electrolyte are obtained at current densities below 3 A/dm². X-ray analysis of copper coatings deposited from a methanesulfonate electrolyte showed that their structure corresponds to a face-centred cubic lattice. The deposit crystallite sizes decrease with increasing the current density. The dependence of the dislocation density on the current density is antibate. Stirring of the electrolyte mitigates the impact of current density on the parameters of the structure of coating, which changes are significantly reduced. It has been shown that stirring the electrolyte affects the structurally dependent properties of the copper coatings, such as internal stress and micro hardness. Along with the diminishing crystallite sizes, an increase in the internal stress and micro hardness of the coatings is observed. Stirring, along with the expansion of the range of coating current densities can reduce the internal stress of the ones. This is an important factor for obtaining thick layers of copper.

Keywords: electrodeposition; methanesulfonate electrolyte; copper; electrical conductivity; physical and mechanical properties; morphology; structure.
ЭЛЕКТРООСАЖДЕНИЕ МЕДИ ИЗ МЕТАНСУЛЬФОНАТНОГО ЭЛЕКТРОЛИТА
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Аннотация
Установлены зависимости электропроводности метансульфонатного электролита медения от концентрации кислоты и метансульфоната меди. Показано, что электролит максимально концентрированный по ионам меди, характеризующийся высокой электропроводностью, соответствует составу 0.6 М Cu(CH₃SO₃)₂ + 0.6 М CH₃SO₃H. Исследование морфологии медных покрытий, полученных в разных гидродинамических режимах, показало, что при перемешивании метансульфонатного электролита можно получить гладкие мелкокристаллические осадки, хорошо сцепленные с основой в диапазоне плотностей тока 1–7 А/дм². Качественные осадки из покоящегося электролита получаются при плотности тока ниже 3 А/дм². Рентгеновский анализ медных покрытий, осажденных из метансульфонатного электролита, показал, что их структура соответствует гранецентрированной кубической решетке. Размер кристаллитов осадков снижается при увеличении плотности тока. Зависимость плотности дислокаций от плотности тока антибатическая. Перемешивание электролита сглаживает влияние плотности тока на параметры структуры покрытий, изменения которых значительно уменьшаются. Показано, что перемешивание электролита влияет на структурно-зависимые свойства медных покрытий внутренние напряжения и микротвердость. Вместе с измельчением кристаллитов происходит повышение внутренних напряжений и микротвердости покрытий. Использование перемешивания, наряду с расширением диапазона плотностей тока осаждения покрытий, позволяет снизить их внутренние напряжения. Это важный фактор при получении толстых слоев меди.

Ключевые слова: электроосаждение; метансульфонатный электролит; медь; электропроводность; физико-механические свойства; морфология; структура.

Introduction
Obtaining electrolytic copper deposits is one of the most demanded branches of electropolating industry, both in terms of quantity and quality. The main features of copper coatings are ductility, low stress and good adherence to the base or other coatings. Due to this, they are used as a sublayer for the deposition of other metals [1] and as a material for electroforming [2]. In the printing industry, copper coatings are applied to printing rollers. Due to its high electrical conductivity and solderability, copper serves as the main current-carrying layer in the manufacture of printed circuit boards [3], where more than 90% of the produced electrolytic copper foil is used. In addition, the electrodeposited copper foil is used as a negative electrode collector in lithium-ion batteries [4].

Depending on the field of application, copper coatings must have certain mechanical and physico-chemical properties. The desired properties are imparted to the coatings by varying the electrolyte composition and electrolysis parameters [5–8]. In particular, copper coatings obtained by electroforming and hydro electrometallurgical processing should be homogenous and free from dispersed or dendritic formations on the surface [9]. At the same time, these coatings have a considerable thickness; to reduce the time of their growth, the deposition current density should be increased. The latter, however, is limited by permissible concentrations of copper ions in the electrolyte. A traditional electrolyte used in electroforming and hydrometallurgy is a sulfate electrolyte containing copper sulfate and sulfuric acid. An increased concentration of copper ions in this electrolyte is limited by a rather low solubility of copper sulfate. Moreover, increased concentration of sulfuric acid needed for increasing the electrical conductivity of the electrolyte causes a further decrease in the copper sulfate solubility. Copper methanesulfonate electroplating electrolytes are good substitutes for sulfate electrolytes [10]. Methanesulfonate electrolytes have several advantages, such as high solubility of salts, the lack of sanitary restrictions on the concentration of methanesulfonate anions in wastewater, high electrical conductivity. Great prospects for the use of methanesulfonate electrolytes in modern electroplating cause researchers to pay more attention to these systems [11–16].

The kinetics of copper electrodeposition on glassy carbon from methanesulfonate and sulfate electrolytes was studied in [17, 18]. It was found that the overpotential of copper deposition in the methanesulfonate electrolyte is significantly lower than that in the sulfate electrolyte. It was shown in [19] that copper coatings obtained from the methanesulfonate electrolyte have finer crystallites in comparison with coatings deposited from the sulfate electrolyte. It was found that the use of gelatine as an organic additive to copper methanesulfonate electroplating electrolyte provides the deposition of glossy copper coatings. Therefore, copper methanesulfonate
electroplating electrolytes enhance the prospects for hydrometallurgical copper production and the technology of applying copper coatings. The solubility of copper methanesulfonate in water is one and a half times higher than that of copper sulfate [20], which allows to use the more concentrated solution and, consequently, to increase the current density of copper deposition. An important fact is that the lead and tin methanesulfonate have high solubility [20]. This allows to use the methanesulfonate electrolytes to produce copper by the processing of electrical scrap. Based on the foregoing, it seems relevant to study the properties of copper methanesulfonate electroplating electrolytes, as well as copper coatings obtained from them.

**Experimental**

Certified reagents of the ‘purissimum’ grade were used in the study: methanesulfonic acid (70%) and copper methanesulfonate (36%) manufactured by BASF. To measure the electrical conductivity of the electrolytes, a digital E 7-8 L.C.R. meter was used. The volume of the cell was 100 ml; the volume of the solution – 30 ml; the area of the platinum electrode – 1 cm².

The electrodeposition of copper coatings was carried out at a temperature of 293 K in a two-electrode cell. A BVP Electronics rectifier was used as a direct current source. The cathode material was made of 6 cm² copper foil. A 500 μm thick copper plate with an area of 12 cm² served as the anode. The working current densities were, A/dm²: 1, 2, 3, 5 and 7. Prior to the electrolysis, the cathode was prepared as follows: a 2x3 cm copper plate was degreased with soda and washed with distilled water. After that, the plate was activated for a minute in acid solution of the following composition: 2 mol/L of H₂SO₄, 0.5 mol/L of HNO₃. The sample was rinsed with distilled water.

The internal stress of 25 μm copper coatings was determined by the flexible cathode method, which is based on measuring the cathode deformation during the applying of the coating. The cathode surface was insulated on the one side with a duct tape so that during the electrolysis an electrodeposited coating was applied to the one side of the sample. The copper foil bends under the action of internal stress arising in the deposit. The bend deflection was determined by comparing the projections of the sample before and after electrolysis.

The equation for calculating the internal stress \( \sigma \) (MPa) has the form [13]:

\[
\sigma = \frac{E_k d_l (d_k + d_{oc}) \cdot z}{3l^2 d_{oc}} \tag{1}
\]

where \( E_k \) are the modulus of elasticity of the cathode plate material, MPa; \( d_k \) – cathode thickness, m; \( d_{oc} \) – thickness of the copper deposit, m; \( l \) – length of the working part of the cathode, m; \( z \) – the cathode edge deviation after electrolysis compared to the initial position, m.

The Vickers microhardness of the copper coatings was measured using a PMT-3 device, at a coating thickness of 25 μm. The microhardness was measured using a regular tetrahedral diamond pyramid as an indenter with an apex angle of 136 °. The pyramid was smoothly squeezed into the sample at a load of \( P = 50 \) g. The microhardness was determined by the formula [12]:

\[
H = \frac{1854 \cdot P}{l^2} \tag{2}
\]

where \( l \) is diagonal length of the indentation of a diamond pyramid, microns.

Surface morphology was studied using a Supereyes B008 optical microscope.

The structure of copper coatings was investigated by XRD using a DRON-3 diffractometer. The crystallite sizes were calculated according to the Scherrer formula [21]:

\[
L = \frac{k \cdot \lambda}{(\beta \cdot \cos \theta)} \tag{3}
\]

where \( \lambda \) is the wavelength; \( \beta \) is the line broadening of the copper sample; \( k \) is an empirical constant that is approximately equal to unity; \( \theta \) is the diffraction angle.

The density of dislocations was calculated using the equation [21]:

\[
D = A \cdot \beta^2 \tag{4}
\]

where \( A \) is a coefficient that depends on the elastic properties of the material. In the case of metals with a crystal lattice of cubic type, \( A = 2 \cdot 10^{-16} \text{ cm}^2 \).

**Results and discussion**

*Study of the Conductivity of the Electrolytes.* One of the key features of electrolytes used for the electrodeposition of metals is their electrical conductivity. For example, the low conductivity of copper sulfate solutions requires the addition of sulfuric acid to the electrolyte. The electrical conductivity of these electrolytes can be enhanced by varying their acidity. The same is true for copper methanesulfonate electroplating electrolytes.

Fig. 1 shows the dependence of the electrical conductivity of methanesulfonate and sulfate electrolytes on the concentration of the copper salt and acid. An increase in the concentration of
methanesulfonic acid results in an increase in the electrical conductivity of the electrolyte. An increased concentration of copper methanesulfonate in the copper plating electrolyte, on the contrary, decreases the electrolyte conductivity. The copper salt added to the electrolyte apparently impedes the charge transfer by the hydroxonium ion through the relay mechanism. During the hydration of the ions formed as a result of salt dissociation, some of the water molecules are structured around these ions and do not take part in the transfer of the hydrogen ion. The conductivity of methanesulfonate electrolytes is rather high, although is inferior to the conductivity of sulfate electrolytes. The nature of the electrical conductivity dependence on the concentrations of the copper salt and acid is similar for methanesulfonate and sulfate electrolytes. An increase in the acid concentration is limited by the limit of copper salt solubility in water at a given temperature. When the concentration of copper methanesulfonate is 0.6 mol/L and the content of methanesulfonic acid is increased to 1 mol/L, there is reached the solubility limit of the salt, and it precipitates. Based on the data obtained, methanesulfonate electrolyte containing Cu(CH$_3$SO$_3$)$_2$ of the concentration of 0.6 mol/L and CH$_3$SO$_3$H of 0.6 mol/L was selected for further studies.

![Graph a](image1.png) ![Graph b](image2.png)

**Fig. 1.** Dependence of the electrical conductivity of methanesulfonate (a) and sulfate (b) electrolytes on the acid and copper salt concentrations

**Morphology and Structure of Copper Coatings.** Electrodeposition of copper coatings was carried out at current densities of 1 to 7 A/dm$^2$ at a temperature of 20°C in a quiescent and stirred electrolyte. As can be seen from micrographs (Fig. 2), light and homogeneous copper coatings can be only deposited from unstirred methanesulfonate electrolyte at low current densities, not exceeding 3 A/dm$^2$. With a further increase of current density, dark coarse-grained coatings are deposited that are poorly adhered to the substrate. In deposits obtained at a current density of 7 A/dm$^2$, pronounced dendritic formations are observed. Stirring of the electrolyte during the copper coating electrodeposition significantly expands the current density range, in which compact deposits are formed. The micrographs showed in Fig. 3 demonstrate that even with an electrodeposition density of 7 A/dm$^2$, the copper coatings obtained from a stirred methanesulfonate electrolyte are light and homogeneous.

It should be noted that despite a uniform macroscopic distribution of the current density on the electrode surface, the local current density at the coating depressions and protrusions turns out to be different.
The difference in the conductivity of the electrolyte and the electrode material leads to the fact that the electric field is not homogeneous on the rough surface. Equipotential surfaces deflect on the boundary, and, accordingly, the field lines are also deflected. The unevenness of the field leads to an uneven distribution of current over the surface. This is of fundamental importance in the study of the development of surface roughness during electrodeposition. Near the limiting current density, the front of the deposit growth becomes unstable, since any randomly formed protrusion starts to grow faster than the rest of the surface and do not disappear. When the current density of the copper electrodeposition is approaching the limiting values, the stability of the deposit growth front is violated; the surface roughness increases, and dendrites start to grow.
In this case, the cause of the local increase in current density is the uneven microdistribution, which results in a further increase in the local current density at the microprotrusions evolving on the rough surface. Under the conditions of the concentration polarization, the rate of the roughness growth increases with an increase in the electrodeposition current density. Stirring of the electrolyte accelerates the transport of copper (II) ions to the cathode surface and reduces the diffusion limitations of the process of their electroreduction. This positively affects the conditions of electrocrystallization; deposits, obtained in the range of current densities of 1–7 A/dm² are fine-crystalline and do not exhibit dendritic growth.

The structure of copper coatings electrodeposited from methanesulfonate electrolyte is of face-centred cubic lattice type with a lattice parameter of 3.6105 Å (Fig. 4).

As can be seen from Fig. 5, an increase in the current density of the electrodeposition of the copper coating from methanesulfonate electrolyte leads to the crystallite fining and increase in the density of dislocations. Stirring of the electrodeposition electrolyte has a damping effect on these parameters. The decrease in the crystallite sizes and increase in the dislocation density with increasing the current density is less significant in this case (Fig. 5).

Physical and Mechanical Properties. Copper belongs to the metals with an intermediate melting temperature and is characterized by low values of internal tensile stress. During electrolysis, copper coatings tend to compress, causing the stretch of the substrate.

Fig. 6 shows the dependences of the internal stress of copper coatings on the current density of the deposition from a stirred and unstirred methanesulfonate electrolyte.

An increase in the current density of the copper coating electrodeposition leads to an increase in the values of internal tensile stress. This effect can be explained as follows. With an increase in the current density under the conditions of concentration polarization, the predominant role is played by the depletion of electrolyte layers adjacent to the growing faces, because of the ions participating in the electrochemical process. An increase in the linear crystallization rate is lower than the increase in the rate of nucleation of the centers of crystallization. As a result, the grains are becoming finer and the total grain surface is extended. Since internal tensile stress arises as a
result of a spontaneous movement of dislocations in newly formed crystals to the periphery and their annihilation at grain boundaries, the surface extension facilitates the exit of most dislocations to the grain surface. This statement is supported by changes in crystallite sizes and dislocation densities, observed during X-ray diffraction studies of the copper coatings (Fig. 4).

Copper deposits obtained under stirring are characterized by lower values of internal stress in comparison with those obtained from an unstirred electrolyte. They exhibit an almost threefold decrease in internal tensile stress. Obviously, this is due to the intensification of the transport stage of the delivery of discharging ions to the cathode surface and owing to a decrease in cathodic polarization.

The microhardness of electrodeposited coatings is one of the most important parameters characterizing their mechanical properties. Figure 7 shows the experimental microhardness dependences on the current density for copper coatings obtained from a stirred and unstirred methanesulfonate electrolyte. As can be seen from the figure, the microhardness of copper coatings, electrodeposited without stirring the electrolyte increases slightly with an increase in the current density.

A similar effect is also observed in deposits obtained from the stirred electrolyte. However, it should be noted that an increase in the current density has a greater effect on the microhardness of coatings deposited from the quiescent electrolyte. The microhardness of copper coatings electrodeposited under stirring is one and a half times lower than the microhardness of the deposits obtained without stirring.

The microhardness of electrodeposited coatings is determined by the structure and morphology of their surface. An increase in the microhardness of copper deposits with an increase in the electrodeposition current density is caused by the evolution of additional lattice defects and a decrease in the mobility of dislocations.

Therefore, a change in the conditions of electrocrystallization depending on the hydrodynamic conditions of the process is the cause of changes in the physicochemical properties of the resulting copper coatings.

**Conclusions**

The study provides a comparative analysis of the electrical conductivity of methanesulfonate and sulfate electrolytes of copper plating as a function of the acid and copper salt concentration. It has been shown that an increase in the acid concentrations leads to an increase in electrical conductivity, while an increase in the concentration of copper ions leads to a decrease in electrical conductivity. It has been established that copper methanesulfonate electroplating electrolytes have high electrical conductivity, the values of which are slightly inferior to the values of electrical conductivity of sulfate electrolytes. Based on the maximum electrical conductivity, copper methanesulfonate plating electrolyte of the 0.6 M Cu(CH₃SO₃)₂ + 0.6 M CH₃SO₃H composition has been recommended for use. It has been found that electrodeposited copper coatings obtained from the methanesulfonate electrolyte are compact and homogeneous. Fine-crystalline coatings, well adhered to the base, were obtained.
in the range of current densities of 1 to 3 A/dm² from the unstirred electrolyte and 1 to 7 A/dm² from the stirred electrolyte. It has been shown that the deposition of copper coatings from the stirred electrolyte allows to reduce the internal stress of a deposit, which is important for obtaining thick layers of copper during the electroforming. An increase in the current density of the deposition of copper coating leads to an increase in the deposit internal stress and microhardness.

Bibliography


References


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