

ESTABLISHING THE PATTERNS IN ANODE BEHAVIOR OF COPPER IN PHOSPHORIC ACID SOLUTIONS WHEN ADDING ALCOHOLS

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Досліджені анодні поляризаційні залежності мідного електрода у фосфатно-спиртових розчинах. Одержані залежності можна розділити на ділянки, кожна з яких відповідає протіканню певних електрохімічних реакцій у заданому діапазоні потенціалів. Перша ділянка відповідає анодному розчиненню міді, друга – формуванню на поверхні міді пасивуючої окисно-сольової плівки і дифузійному режиму розчинення металу. Після досягнення потенціалу розкладання води розчинення мідного електрода супроводжується окисленням молекул H₂O. Встановлена відповідність особливостей розчинення міді поляризаційним залежностям електрода. Електрохімічному травленню міді відповідає діапазон потенціалів електрода 0–0,8 В. Утворення окисно-сольової плівки при потенціалах 1–2 В обумовлює іонізацію міді у дифузійному режимі і приводить до переважного розчинення мікронерівностей металу з формуванням блискучої поверхні електрода. Зміщення потенціалу анода до величин, більших за 2 В, приводить до появи точкового травлення на поверхні міді внаслідок місцевого порушення суцільності пасивної плівки. Додавання до розчинів фосфатної кислоти етанолу знижує густину струму анодного розчинення міді в стаціонарній області до значень 0,2–2 А·дм⁻². Етанол сприяє одержанню блискучої поверхні міді. При c(C₂H₅OH) > 30 % ефект полірування зникає. Бутиловий спирт є ефективним інгібітором травлення міді і в його присутності j_a знижується до 0,1–1 А·дм⁻². Додаток C₄H₉OH обумовлює формування поверхні з сильним блиском і мінімальною кількістю точок травлення. При вмісті c(C₄H₉OH) > 50 % поверхня міді має значну кількість точок травлення. Інгібуюча дія гліцерину близька до дії бутанолу. Форма поляризаційної залежності обумовлюється вмістом C₃H₈O₃ у розчині. При підвищенні c(C₃H₈O₃) > 20 % полірування не відбувається і поверхня електрода має матовий вигляд. Отримані дані показують, що анодна поведінка міді залежить від природи добавки, що, залежно від необхідності, можна використовувати для розробки електролітів полірування або розмірної обробки міді

Ключові слова: електрохімічне полірування, пасивна плівка, дифузійне розчинення, пітінг, анодна поляризація, розмірна обробка

1. Introduction

Electrochemical polishing implies the dissolution of the surface layer of a metal during anode polarization in the electrolyte solution.

The result of polishing is the removal from a metal surface of the outer layer and the formation of a new surface with smooth topography, characterized by the lack of thick oxide films, foreign inclusions, and defects. The deformed layer forms at the surface during mechanical and thermal treatment to which a workpiece is exposed in order to obtain a product or semi-finished product.

Electrochemical polishing of copper is industrially used for brightening the copper coatings or treating the massive products made of copper or brass. In research, the electrochemical polishing method is employed for the size treatment of copper wire to obtain thin needles that served as cathodes in the study of the effect of electro-chemical microcontact commutation [1]. Apparently, electrochemical polishing is a necessary condition for obtaining reproducible results in the study of the long element. Such a treatment of copper conductors would make it possible to obtain a uniform metal surface, which is essential when conducting accurate measurements of the distribution of potential and current [2].

Also desirable is to perform polishing for the pretreatment of articles' surface in the case of applying multilayer coatings or coating the products with a complex composition [3–6].

Even though the first work on electrochemical polishing of copper in solutions of H_3PO_4 was performed more than 80 years ago, these solutions are a good base for creating polishing electrolytes. The attractiveness of applying a phosphoric acid is predetermined by the universality and economic efficiency of phosphoric-acid solutions. When using them, it is possible to polish not only copper but also its alloys. Copper that dissolves during anodic polarization of metal deposits at the cathode and partially precipitates at the bottom of the bath, which facilitates the regeneration of electrolyte. The scientific literature describes many compositions of solutions for electrochemical polishing of copper and its alloys, however, in most cases, similar to ferrous metals, the main component is the phosphoric acid. The difference comes down to the introduction of additives of inorganic or organic compounds that favorably influence the quality of treatment. This is the way to try to eliminate the main disadvantage – the etching of metal when the current density exceeds the limit and when potentials are higher than that of oxygen evolution.

2. Literature review and problem statement

Many studies focused on instructions about the favorable impact of adding certain organic compounds (carboxylic acids or their salts, aldehydes, amines, alcohols) on the process of electrochemical polishing of copper in phosphoric-acid solutions [7–17]. The most commonly used as additives are the saturated, unsaturated and aromatic alcohols whose introduction reduces the limiting current density, prevents point etching and metal etching. It is also noted that in some cases the additives of alcohols contribute to improving the resistance of polished copper against atmospheric corrosion, which is linked to the formation of chemisorbed films of organic origin at its surface.

For example, the positive effect is observed when adding to phosphoric-acid solutions glycerin and organic acids [11], ethanol, ethylene glycol or glycerol [12], methanol [13, 14], which ensures the uniform dissolution of metal at polishing, decreases the number of etching points and reduces the limit anode current. The influence of additives of aromatic alcohols during copper electropolishing in H_3PO_4 solutions was investigated in [15]. It is shown that the introduction to polishing solutions of phenols reduces the rate of copper corrosion, which contributes to the better treatment of metal.

In studies [16, 17], the electropolishing of copper in phosphoric-acid solutions containing alcohols was investigated using a rotating disk electrode. It is shown that the introduction to the composition of electrolytes of additives of alcohols predetermines a slowdown in the rate of anode dissolution of copper and promotes a more uniform dissolution of the metal. The results obtained are explained by the fact that the introduction of alcohols reduces the concentration of water molecules in a near-anode layer, which reduces the rate of copper dissolution, which is limited by the transport of acceptor particles (water to the surface of copper) [16] or by a change in the physical characteristics of electrolyte, which alter the conditions for stirring a solution near the surface of the anode [17].

Thus, the cited studies highlight only specific cases of copper polishing regarding the treatment of products in electronic industry [11, 14], the adsorption phenomena when

investigating corrosion processes on copper [13, 15]. Of interest is the research aimed at establishing the influence of additives of alcohols on the technical indicators of polishing process, such as the relative smoothing of surface unevenness, coefficient of reflectance, specific metal removal. Many articles made use of the procedure for the rotating disk [12, 16, 17] or cylindrical electrode [15]. The results obtained are certainly interesting, however, they are not always applicable to the industrial process of polishing, which is often conducted employing the fixed anodes. The difference in the electrolyte mixing conditions in this case may affect the features of metal dissolution.

3. The aim and objectives of the study

The aim of this work is to establish the influence of alcohols on the patterns in anode behavior of copper in the solutions of phosphoric acid.

To accomplish the aim, the following tasks have been set:

- to derive the polarization dependences of copper electrode in solutions of phosphoric acid in the acidic-alcohol solutions;
- to determine, based on an analysis of the polarization dependences, conditions for the electrochemical polishing and to establish the effect of alcohols on indicators of the polishing process.

4. Procedure for deriving the polarization dependences

We used, as working electrodes, copper of grade M00 in the form of plates of rectangular shape, made from a rolled ribbon with a thickness of 0.5 mm. Preparation of the samples involved sanding with sandpaper, degreasing with a Na_2CO_3 aqueous suspension, and etching in a 10 % solution of HCl. The samples were washed with water between the cycles.

We applied, as an auxiliary electrode, a coaxially positioned cylinder made of a copper rolled tape. Ratio $S_k:S_a = 100:1$.

We measured potentials relative to the saturated second-type electrode Ag/AgCl, reversible with respect to chloride ions. To fill the electrode, we used the saturated solution of KCl. The electrode was placed in a container with the saturated solution of KCl and connected to the cell using an electrolytic key filled with a thickened solution of KCl (20 g of salt per 100 cm³ of solution). All values for the potentials are listed in the scale of a given electrode.

Stationary polarization dependences were derived using a potentiometric circuit. The circuit included the power source B5-43 (USSR), the ammeter M2038 (USSR), and the multimeter Keithley-2000 (United States). The potentiometric circuit allowed us to define conditions for polishing (values of current densities and the range of potentials). Dependences were derived under a potentiometric mode, feeding the cell with voltage in steps of 0.05 V. The values for current and potential of the electrode were recorded after maintaining the cell for 5 minutes at the predefined voltage, which made it possible to determine their established magnitudes.

The reflectivity of copper surface was determined using the photoelectric glossmeter BF5-60/60. Relative smoothing ΔR_a of the surface was determined applying the profilometer-profilograph, model 202 (Caliber).

Composition of the examined electrolytes is given in Table 1.

Composition of the examined electrolytes

No. of entry	Component	Components ratio		
1	H ₃ PO ₄	85 % H ₃ PO ₄	1:1 (H ₃ PO ₄ :H ₂ O)	1:3 (H ₃ PO ₄ :H ₂ O)
2	H ₃ PO ₄ C ₄ H ₉ OH	3:1 (H ₃ PO ₄ :C ₄ H ₉ OH)	1:1 (H ₃ PO ₄ :C ₄ H ₉ OH)	1:3 (H ₃ PO ₄ :C ₄ H ₉ OH)
3	H ₃ PO ₄ C ₃ H ₈ O ₃	3:1 (H ₃ PO ₄ :C ₃ H ₈ O ₃)	1:1 (H ₃ PO ₄ :C ₃ H ₈ O ₃)	1:3 (H ₃ PO ₄ :C ₃ H ₈ O ₃)
4	H ₃ PO ₄ C ₂ H ₅ OH	3:1 (H ₃ PO ₄ :C ₂ H ₅ OH)	1:1 (H ₃ PO ₄ :C ₂ H ₅ OH)	1:3 (H ₃ PO ₄ :C ₂ H ₅ OH)

The electrolytes were prepared using H₃PO₄ and C₄H₉OH of grade «chemically pure», C₂H₅OH and C₃H₈O₃ of grade «pure».

5. Results of studying the dissolution of copper electrode under conditions of anodic polarization

The anodic polarization dependences of the copper electrode, derived in solutions of H₃PO₄ without additives, are shown in Fig. 1, *a*. The dependences contain three regions, which correspond to certain electrochemical processes that proceed at the electrode over a certain range of potentials [16].

The initial region of the dependence is characterized by the rise of current at an electrode potential shift from

stationary value E_{st} to point *A*. In this region, the only electrode process is the dissolving of copper, which proceeds with a current output close to 100 %. The electrolysis under this mode is accompanied by the electrochemical etching of metal. Surface of the samples after 1–2 minutes of such a treatment becomes opaque and contains the sludge, which is easily removed by a filter paper.

In the region of potentials *AB*, an oxide-salt film with a complex composition forms at the surface of the electrode. The dissolution of metal occurs under the mode of limit diffusion current and has a complicated dependence on potential. The curves demonstrate a flat step or a maximum, after which the power of current decreases. The anodic output in terms of the copper dissolution current remains in this case unchanged or has a tendency to decrease. A copper surface after being treated under this mode becomes shiny.

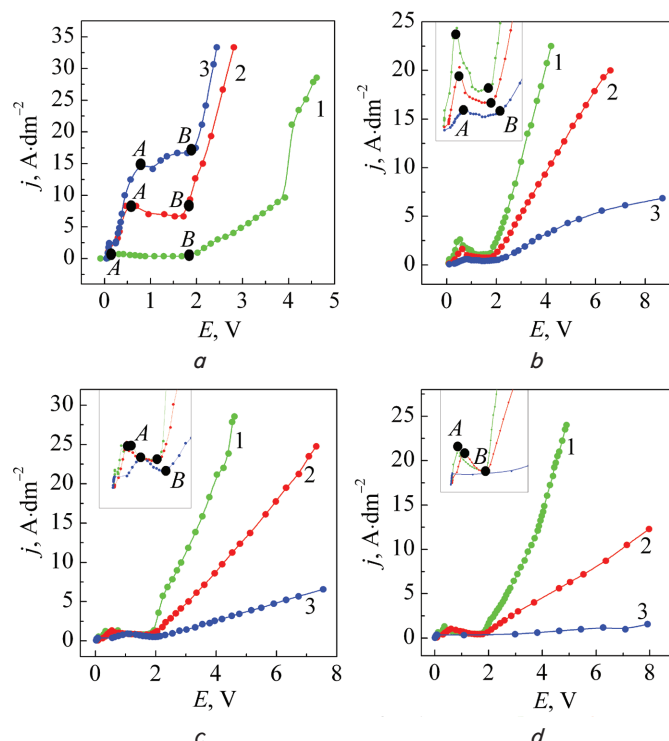


Fig. 1. Anodic polarization dependences of the copper electrode:

- a* – polarization dependences derived for solutions of H₃PO₄. H₃PO₄:H₂O, share by volume: 85 % H₃PO₄(1); 1:1(2); 1:3(3);
b – polarization dependences derived for solutions of H₃PO₄ with the addition of C₂H₅OH. H₃PO₄:C₂H₅OH, share by volume: 3:1(1); 1:1(2); 1:3(3); *c* – polarization dependences derived for solutions of H₃PO₄ with the addition of C₃H₈O₃. H₃PO₄:C₃H₈O₃, share by volume: 3:1(1); 1:1(2); 1:3(3); *d* – polarization dependences derived for solutions of H₃PO₄ with the addition of C₃H₈O₃. H₃PO₄:C₃H₈O₃, share by volume: 3:1(1); 1:1(2); 1:3(3)

Upon reaching point *B*, the surface of the electrode undergoes the process of oxidizing water molecules with the evolution of gaseous oxygen. In a given region of potentials, there occur two combined reactions on the electrode; in this case, increasing the current density leads to a decrease in the output for copper current and an increase in the output for oxygen current. The electrode surface becomes shiny. At $j_a < 20\text{--}25 \text{ A}\cdot\text{dm}^{-2}$, the surface demonstrates plots of point etching in the form of pitting. The cause of pitting is the local disruption of metal's passivity due to the action of ions-activators [17, 18], chemical dissolution of the film due to the local overheating near the surface of the anode or an oxygen bubbles delay at copper surface [16].

Increasing the content of H_3PO_4 in a solution, all other things being equal, leads to a decrease in current density, that is, it causes the higher values of the electrode polarization of the process (Fig. 1, *a*, curves 1–3). Smoothing the surface profile of the electrode proceeds better in dilutes solutions of H_3PO_4 , which confirms the relation between this process and diffusion processes around the anode. Reducing the concentration of H_3PO_4 results in its growing etching effect on metal. Etching action does not stop in more concentrated solutions if the electrolysis is carried out at high values j_a , accompanied by an intense release of oxygen. At $j_a > j_d$, a metal surface, although it becomes shiny, is covered with small point pits.

The next phase of our work was to study the anode behavior of copper in solutions of H_3PO_4 with the addition of alcohols. Polarization dependences, derived for copper in solutions containing ethanol, butanol and glycerol, are shown in Fig. 1, *b–d*.

The dependences are characterized by the presence of three conditional sections, corresponding to the dissolution of copper under stationary and diffusion regimes, as well as the progress of combined reactions on the electrode. Adding an alcohol reduces the rate of electrode processes, and the growth in its content leads to that the reduction becomes more apparent.

The polarization dependences of copper derived for solutions with the addition of $\text{C}_2\text{H}_5\text{OH}$ are shown in Fig. 1, *b*. Ethanol decreases the rate of anode dissolution of copper in the stationary region. The dissolution current density falls to $0.2\text{--}2 \text{ A}\cdot\text{dm}^{-2}$. Upon reaching the boundary of the diffusion region, the curves demonstrate a sharp maximum, followed

by a decay in current (Fig. 1, *b*, inset). The further character of curves is similar to those derived for solutions of H_3PO_4 without additives. Increasing $c(\text{C}_2\text{H}_5\text{OH}) > 30\%$ leads to the disappearance of the effect of polishing. Copper is etched and its surface becomes matte. In general, adding $\text{C}_2\text{H}_5\text{OH}$ in the concentrations not exceeding 30 % improves the gloss of copper surface, though it is negligible.

Butanol is a more effective inhibitor of copper etching (Fig. 1, *c*). The current density of electrochemical etching in its presence reduces to $0.1\text{--}1 \text{ A}\cdot\text{dm}^{-2}$. The range of potentials, corresponding to the passive state region, remains the same and is $0.8\text{--}2 \text{ V}$. Adding $\text{C}_4\text{H}_9\text{OH}$ causes a strong copper surface gloss with a minimum number of etching points. Increasing $c(\text{C}_4\text{H}_9\text{OH}) > 50\%$ is impractical because the reduction of j_a predetermines a decrease in the layer of the dissolved metal. In this case, the metal surface gloss reduces while the number of etching points grows.

The overall effect of glycerol is close to the action of butanol. Copper etching rate under stationary mode is $0.1\text{--}1 \text{ A}\cdot\text{dm}^{-2}$. The shape of dependence is determined by the content of $\text{C}_3\text{H}_8\text{O}_3$ in solution. At ratio $\text{H}_3\text{PO}_4:\text{C}_3\text{H}_8\text{O}_3$ 3:1 and 1:1 (Fig. 1, *d*), the curves demonstrate a maximum of current, which corresponds to the formation of the passive film. Increasing the ratio $\text{H}_3\text{PO}_4:\text{C}_3\text{H}_8\text{O}_3$ to 1:3 causes the disappearance of the maximum and the curve demonstrates a plot of sloping rise in current across the whole range of potentials. A metal surface after being treated in the electrolyte with the addition of glycerol has an etched matte appearance and contains the sludge that is easily removed by a filter paper.

The introduction to the electrolyte composition of ethanol and butanol has a positive influence on the gloss of the surface of the metal. The point etching of the anode stops; the reflectance of the surface increases. The extent of this influence increases with an increase in the length of a hydrocarbon radical of the alcohol molecule (Fig. 2, *a*). The most intense gloss of copper surface is achieved when treating it in the electrolyte containing butanol.

The positive influence of alcohols is less pronounced when smoothing the roughnesses (Fig. 2, *b*). In this case, the relative smoothing increases with an increasing length of the alcohol molecule chain. Adding ethanol not only improves, but even worsens, the relative smoothing, compared to treatment in a phosphoric-acid solution.

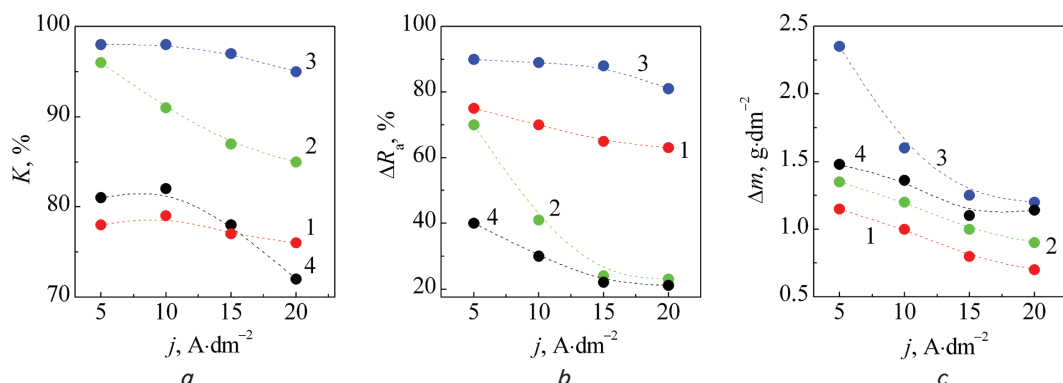


Fig. 2. Influence of alcohol additives to the phosphoric-acid electrolyte on characteristics of the process of copper polishing at a different density current: 1 – electrolyte without the addition of alcohol, 2 – with the addition of ethanol, 3 – with the addition of butanol, 4 – with the addition of glycerol. The ratio of acid to alcohol is equal to 1:1; *a* – effect of the nature of alcohol on the reflective property of metal; *b* – effect of the nature of alcohol on relative smoothing of metal's surface; *c* – effect of the nature of alcohol on specific removal of metal

This might be due to the fact that at a given concentration of the additive, the etching process is not completely suppressed, as indicated by the physical appearance of the metal's surface. A more positive effect is exerted by butanol, which correlates with its influence on the surface gloss and metal etching.

Increasing the length of the radical in a molecule of alcohol leads to the increased removal of metal (Fig. 2, c). This trend is increasingly evident with an increasing alcohol concentration in the electrolyte.

Treating copper in the solution containing glycerol does not produce the surface gloss. The relative smoothing in solutions with the addition of $C_3H_8O_3$ reaches the higher values compared to solutions with the addition of monoatomic alcohols, which causes a slight increase in the coefficient of smoothing effectiveness due to a relatively high metal removal.

6. Discussion of results of polarization measurements of the copper electrode in phosphate-alcoholic solutions

The emergence of gloss and smoothing of roughnesses at the electrochemical polishing of copper in phosphoric-acid solutions has several explanations. There are known theories that link the emergence of the effect with the dissolution of the most active regions of the anode, complicated transport of acceptor particles to the anode and the formation, at the surface of the anode, of an oxide-salt film with a complex composition. The latter theory, according to which the dissolution of microscopic protrusions occurs due to a lesser thickness of the passive film compared with its thickness in pits, was put forward a long time ago, but now it is the most common [18, 20, 22].

The dissolution of copper proceeds through the stage of film formation, which consists of a mixture of oxides of one- and bivalent copper [23–26]. It is not excluded that the film at the surface of the anode can contain oxides with a non-stoichiometric composition or consist of a mixture of copper oxides and phosphates [27–31]. It is obvious that in the case of adding alcohols they also participate in the formation of the film by adsorbing at the surface of the anode.

The role of alcohols in the process of electrochemical polishing manifests itself above all in preventing the point etching and increasing the reflectivity of the metal.

Adding alcohols could reduce the surface tension of the solution. This contributes to a reduction or even complete cessation of metal etching and increases the gloss of its treated surface. Such a relation between the quality of polishing and surface tension of the solution, observed when treating other metals, suggests that this physical-chemical characteristic directly affects the mechanism of the polishing process.

Indeed, a decrease in the surface tension of solution facilitates the detachment of oxygen bubbles from the surface of the anode and prevents point etching. Aqueous solutions of alcohols have low values of σ compared with water and solutions of phosphoric acid (Table 2).

The given values for σ indicate that the introduction to the phosphoric-acid solutions of alcohols will reduce the surface tension of the obtained mixtures, which should affect the quality of copper polishing. However, the research has shown that the magnitude of σ is only one of the factors that affect the quality of metal treatment.

Table 2

Surface tension of water, phosphoric acid, and alcohols

Medium	$\sigma \cdot 10^{-3}, N \cdot m^{-1} (20^\circ C)$
Water	72.8
Phosphoric acid (85 %)	85.2 (28 °C)
Ethyl alcohol (100 %)	22.3
Butyl alcohol (100 %)	24.6
Glycerol (50 %)	69.6

Preliminary data from Table 3 show that the introduction to the electrolyte of conventional wetting agents, for example, sulphonol or the commercially available detergent «Progress» (OOO «AMS Media», Russia), helps reduce the surface tension even to the larger degree than when adding butanol, however, the etching of copper does not stop in this case.

Table 3

Effect of additives of the surface-active substances on indicators of the copper polishing process

Additive	$\sigma \cdot 10^{-3}, N \cdot m^{-1} (20^\circ C)$	$\Delta m, g \cdot dm^{-2}$	$K, \%$	Metal surface state
Butanol, %				
25	26.5	0.50	86–99	Gloss, point etching
50	23.0	0.55	86–99	Gloss, point etching
75	20.0	0.70	96–99	Mirror shine
Preparation «Progress», $g \cdot l^{-1}$				
10	35.0	0.80	62–99	Gloss, point etching
25	29.0	0.82	62–99	Gloss, point etching
50	18.0	0.68	90–99	Gloss, point etching
Sulphonol, $g \cdot l^{-1}$				
1.0	20.0	1.0	75–80	Gloss, point etching
2.8	18.0	0.95	68–80	Gloss, point etching
5.5	16.0	0.88	70–90	Gloss, point etching

It is obvious that the specified factor does not play a decisive role by itself in the process of polishing; its positive effect is evident in the cases when an organic compound is involved in the formation of a passivating film at the surface of the anode. It might be possible that the increased hydrophobicity of an electrode surface facilitates the detachment of bubbles of oxygen off it and prevents point etching.

Of course, to better understand the nature of the effect, caused by adding the alcohols to phosphoric-acid solutions, it is necessary to conduct research into the processes of their adsorption by a copper surface. From this point of view, it might be of importance to study the capacity of a dual layer of the copper electrode, obtained under conditions of its anodic polarization. Such information would be a useful complement to the measurements of roughness, gloss and metal removal, performed during electrolysis under stationary conditions.

7. Conclusions

1. Anodic polarization dependences of copper electrode, derived for phosphoric-acid-alcohol solutions, consist of three regions, which correspond to the processes of electrochemical etching of copper, the formation of a salt-oxide film, and the composite reactions of copper dissolution and oxygen evolution. It is shown that the introduction to a phosphoric acid solution of additives of ethanol, butanol and glycerol causes a decrease in current densities over the entire examined range of potentials. This is probably due to the fact that the additions of alcohols act as diluents, reducing the concentration of water molecules in the near-anode layer, causing a decrease in the rate of copper dissolution due to a lack of acceptor particles, required for the transition of copper to solution in the form of hydrated particles.

2. The electrochemical polishing, performed under a stationary galvanostatic mode, revealed that the introduction to the composition of the bath of ethanol and butanol pre-determines an increase in gloss of the treated surface and dramatically reduces the number of etching points. The introduction of glycerol to the solution does not produce any visible effect. In addition, butanol causes surface smoothing at polishing, however, the process is characterized by an elevated metal removal. One possible explanation of the results obtained is the data on surface tension, which indicate that the addition of ethanol and butanol causes a drastic reduction in the magnitude of σ . The results obtained are interesting, however, they require further research to establish the effect of alcohols on physical-chemical characteristics of solutions and the capacity of a dual-layer, which would elucidate the results obtained.

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