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# Influence of some additives on Cu layer formation in underpotential and overpotential regions in acidic $\text{CuSO}_4$ solution. 8. Initial stages of Cu electrocrystallization onto polycrystalline Pt in the presence of polyethylene glycol (M. W. 3000)

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The initial stages of electrocrystallization of Cu were investigated on a polycrystalline Pt electrode in 0.1 M  $\text{CuSO}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution without or with polyethylene glycol (M. W. 3000) by a potentiostatic step technique. The experimental current transients were correlated with the predicted ones calculated using a new general equation for the current transients proposed by Heerman and Tarallo (*J. Electroanal. Chem.*, **470**, 70 (1999)). It was shown that the chronoamperometric transients corrected according to this equation can be treated as evidences for the electrocrystallization of Cu via 3D progressive nucleation with diffusion-controlled growth. The influence of PEG was supposed to be associated with the blocking action. Analysis of the chronoamperometric transients also showed that PEG did not change the character of Cu electrocrystallization.

**Key words:** copper, platinum electrode, sulphate solution, electrocrystallization, initial stages, polyethylene glycol

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## INTRODUCTION

The initial stages of electrocrystallization of metals (M) onto foreign substrates (S) are commonly accepted to exert a significant action on the overall process of the formation of an overlayer, especially that of small thickness. Taking into account a widespread application of various additives for affecting the properties of M deposits, it is of great interest to investigate the initial stages of electrocrystallization of M on a foreign substrate in the presence of additives of most technological and commercial application.

One of the primary areas of interest in practical M plating is the use of the additives as brighteners. Concerning the deposition of bright Cu coatings from acidic  $\text{CuSO}_4$  solutions, polyethylene glycols (PEGs) are found to be one of the main constituents of the brighteners having currently the widest application [1, 2].

A series of studies of the mechanisms of action of additives in the electrodeposition of M layers including Cu have already been made. These mechanisms have been reviewed in several papers (for a

general review see, e.g., [3–8] and, particularly, for Cu [4, 6, 8]). Over the years, the most commonly proposed mechanism of action of additives in M deposition processes is a simple blocking action in which the additive adsorbs on the electrode and blocks one of the steps in the formation of the M deposit [6–8].

Electrochemical and laser Raman spectroscopic measurements [9] showed that PEGs and chloride ions act cooperatively to inhibit Cu deposition onto a Cu substrate. This finding was not only confirmed using an EQCM technique, but it was shown that a synergistic interaction of PEGs and  $\text{Cl}^-$  occurred in inhibiting the deposition of Cu as well [10, 11]. Furthermore, PEGs were supposed to form surface complexes with  $\text{Cu}^+$  [12] and also complexes with both  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  in the bulk of solution [13]. The initial stages of Cu electrodeposition in a presence of a complex additive for bright Cu plating containing PEGs were investigated in [14, 15]. Despite the fact that a wealth of electrochemical information on the effect of PEGs in the Cu plating process has been obtained in the past, no attempt was made to study

the initial stages of Cu electrocrystallization in the presence of a sole PEG.

In this paper, the initial stages of electrocrystallization of Cu onto a smooth polycrystalline Pt electrode from acidic  $\text{CuSO}_4$  solution containing PEG (M. W. 3000) were investigated using a conventional potential step technique.

## EXPERIMENTAL

Chemicals used were  $\text{H}_2\text{SO}_4$  (highest purity),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  recrystallized additionally and polyethylene glycol (M. W. 3000) (Merck). Solutions were prepared with double-distilled water. The experiments were performed using the unstirred 0.1 M  $\text{CuSO}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  solutions without or with PEG.

Before and between the experiments, solutions were deaerated with argon (AGA, Sweden) for 1 h. The deposition was performed at a constant temperature of  $25 \pm 0.1$  °C.

The electrochemical experiments were carried out in a conventional three-electrode cell using a PI 50-1 potentiostat (Belarus) interfaced through a homemade analogue to digital converter with a PC (Siemens) and a PR-8 programmer (Belarus). The experimental data acquisition was in a numerical form with time resolution of 20 ms per point.

The working electrode was a vertical polycrystalline Pt disc (99.99% purity) with an exposed area of 1.0  $\text{cm}^2$ . The real surface area was estimated from a hydrogen adsorption/desorption  $I/E$  profile in 0.5 M  $\text{H}_2\text{SO}_4$  taking a specific charge of 210  $\mu\text{C cm}^{-2}$ . The roughness factor ( $f$ ) was found to be equal to  $2.1 \pm 0.1$ .

The counter electrode was a Pt sheet with an area of 4  $\text{cm}^2$ . The reference electrode was a Pt spiral coated with electrolytic Cu. In order to check the stability of this electrode and also in the case of  $\text{Cu}^{2+}$ -free acidic solution, a mercury/mercurous sulphate electrode (MSE) ( $E = +0.682$  V) was used as the additional reference electrode. All potentials ( $E$ ) were recalculated with respect to the standard hydrogen electrode (SHE).

The preparation of the working Pt electrode involved a mechanical and electrochemical pre-treatment. Prior to the first use, the Pt electrode was initially mechanically polished using fine emery papers with decreasing grades and then finally polished using 1.0  $\mu\text{m}$  alumina. Thereafter it was cleaned with an organic solvent and a hot 1.0 M NaOH solution, dipped further into a mixture HCl +  $\text{HNO}_3$  for 20 s and rinsed with distilled water. The electrochemical pre-treatment was carried out before each series of experiments and was as follows: (i) activation in the 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte by  $E$  cycling between +0.10 and +0.90 V at a scan rate  $\nu =$

$= 0.05$  V  $\text{s}^{-1}$  until the  $I/E$  curves typical of a clean Pt surface in both the “hydrogen” and “oxygen” regions were obtained; (ii)  $E$  was further cycled in the narrower region, between +0.30 and +0.90 V, for no less than 3 min; (iii) the cycling was stopped during an anodic half-cycle at +0.90 V and then the supporting solution was replaced by the deaerated working solution.

The  $I/t$  traces were recorded starting with  $E_{\text{start}} = +0.30\text{V}$ , at which the working Pt electrode was held for 3 min (the current reduced to a value of  $5 \pm 0.5$   $\mu\text{A cm}^{-2}$ ) to various overpotentials  $\Delta E = E_{\text{dep}} - E_{\text{eq}}$ , where the Nernstian potential  $E_{\text{eq}}$  for a couple  $\text{Cu}/\text{Cu}^{2+}$  was +0.292 V.

In the text and Figures, the values of  $I$  are given with respect to the geometrical area of the Pt electrode.

## RESULTS AND DISCUSSION

Potentiostatic current transients for Cu deposition onto the polycrystalline Pt electrode from acidic  $\text{CuSO}_4$  solution in the absence (Fig. 1) and in the presence of PEG (M. W. 3000) (Fig. 2) were recorded as a function of the overpotential  $\Delta E$ . The experimental current transients exhibit a shape which is generally close to that for a nucleation process, *i.e.* after a decay of a sharp electrode double-layer charging current reaches a current maximum,  $I_{\text{max}}$ , as the discrete hemispherical diffusion zones of each of the growing nuclei begin to overlap at the time  $t_{\text{max}}$ . Then, as these zones overlap, hemispherical mass transfer gives way to a semi-infinite linear diffusion effectively to a planar electrode. The current transients corresponding to the higher  $\Delta E$  show a current decay with the  $I$  vs.  $t^{-0.5}$  dependence typical of a semi-infinite linear diffusion (Cottrell condition).

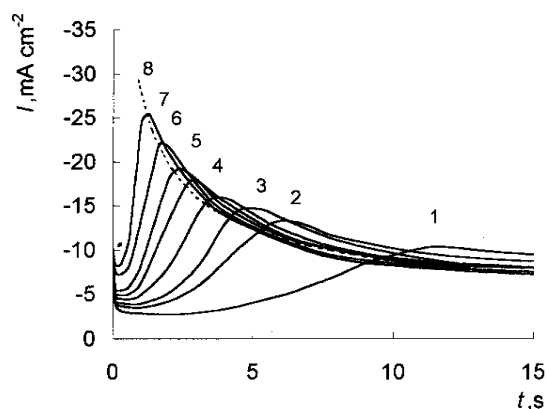


Fig. 1. Experimental potentiostatic current transients for Cu electrocrystallization on Pt at different overpotentials in 0.1 M  $\text{CuSO}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  at 25 °C.  $\Delta E$ : 1 – 0.210, 2 – 0.220, 3 – 0.225, 4 – 0.230, 5 – 0.235, 6 – 0.240, 7 – 0.250 and 8 – 0.260 V. Dotted line represents a Cottrellian dependence calculated at  $D = 6.5 \cdot 10^{-6} \text{cm}^2 \text{s}^{-1}$  (from the data obtained with a Cu RDE)

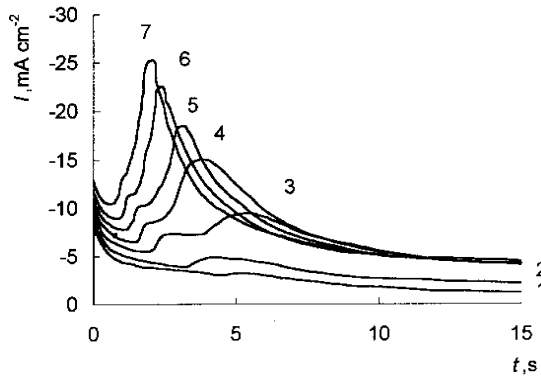


Fig. 2. Experimental potentiostatic current transients for Cu electrocrystallization on Pt at different overpotentials in 0.1 M CuSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 · 10<sup>-5</sup>M PEG (M. W. 3000) at 25 °C.  $\Delta E$ : 1 – 0.250, 2 – 0.260, 3 – 0.270, 4 – 0.280, 5 – 0.290, 6 – 0.300 and 7 – 0.320 V

The time  $t_{\max}$  depends on  $\Delta E$  and decreases as the applied  $E$  is made more negative (Figs. 1, 2).

However, the current transients recorded here (Figs. 1, 2) cannot be strictly analyzed using the 3D nucleation with diffusion-controlled growth models [16, 17], which considered only the limiting cases of instantaneous and progressive nucleation, since the descending parts of the  $I/t$  curves intersected instead of converging into one.

More general theory which should be valid for any value of the nucleation rate has been proposed for the first time by Scharifker and Mostany [18]. A different solution to this problem has later been proposed by Sluyters et al. [19]. Both models are based on the concept of planar diffusion zones and the use of Avrami's theorem to account for overlap.

Recently, Heerman and Tarallo [20] have proposed a new equation for the 3D nucleation with diffusion-controlled growth in which some limitations of the earlier models [16, 19] were taken into account. This new equation has been written as:

$$I(t) = zFDc(\pi Dt)^{-0.5}(\Phi / \Theta) \cdot (1 - \exp(-\alpha N(\pi Dt)^{0.5} t^{0.5} \Theta)) \quad (1)$$

where  $I(t)$  is the current density at the time  $t$ ,  $\Phi = 1 - [(\exp(-At) / (At)^{0.5})]_0^{(At)^{0.5}} \exp(\lambda^2) d\lambda$ ,  $\Theta = 1 - (1 - \exp(-At / At))$ ,  $\alpha = 2\pi(2M D c / \rho)^{0.5}$ ,  $N$  is the density of active sites,  $A$  is the nucleation rate constant,  $M$  and  $\rho$  are the molar mass and the density of the deposited metal, respectively. As may be seen from Eq. (1), such nucleation parameters as  $N$  and  $A$  became separated. Furthermore, according to this equation, the general run of a current transient depends not only on the nucleation rate  $AN$ , as in the cases considered earlier (see, e.g., in [16, 17]), but also on which parameter,  $A$  or  $N$ , changes with increasing  $\Delta E$ .

Since Eq. (1) is rather complicated and no analytical solution of its fast derivative  $dI(t) / dt = 0$  is available, the dependences of  $I_{\max}$  and  $t_{\max}$  on the parameter  $\beta = N\pi k D / A$ , where  $k = (8\pi c M / \rho)^{0.5}$ , were calculated numerically. By analogy with [18], on the basis of such calculations the dependences  $b \cdot t_{\max}$  vs.  $\log \beta$  (Fig. 3) and  $I_{\max} \cdot t_{\max}^{0.5} / a$  vs.  $\log \beta$ , where  $b = N\pi k D$  and  $a = z F D^{0.5} c / \pi^{0.5}$ , (Fig. 4) were obtained. From the data presented in Figs. 3 and 4 the nucleation parameters  $N$  and  $A$  can be obtained. It was established that the calculated values of these parameters which may fit the experimental values of  $I_{\max}$  and  $t_{\max}$  in the current transients presented in Fig. 1 should be as follows:  $N \approx 10^6 \text{ cm}^{-2}$ ,  $A = 0.01 \pm 0.005$  (for curve 1),  $0.05 \pm 0.01$  (for curve 2),  $0.2 \pm 0.05$  (for curve 5),  $0.5 \pm 0.1$  (for curve 7) and  $2 \pm 0.5 \text{ s}^{-1}$  (for curve 8). Then, the current transients calculated according to Eq. (1) using these quantities (Fig. 5) were obtained to be quite close to the corresponding experimental current transients (Fig. 1).

One of the methods\* for distinguishing between the models for instantaneous and progressive 3D nucleation is to compare the experimental transients given in the dimensionless form  $(I / I_{\max})^2$  vs.  $t / t_{\max}$  to the calculated ones [17] – for instantaneous nucleation:

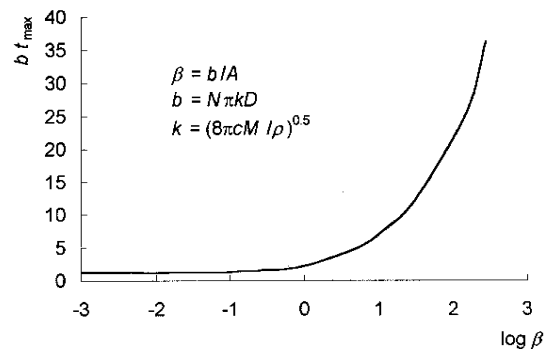


Fig. 3. Dependence of  $b t_{\max}$  on  $\log \beta$  obtained in a numerical manner by solving the first derivative  $dI(t) / dt = 0$

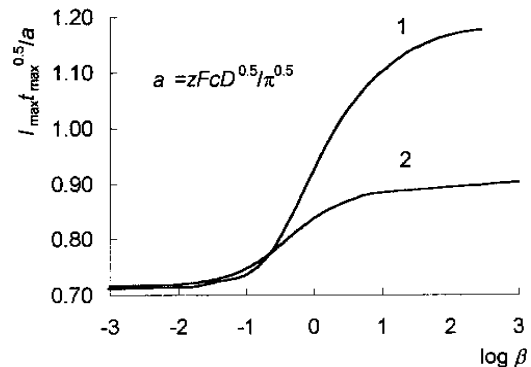


Fig. 4. Plots  $I_{\max} \cdot t_{\max}^{0.5} / a$  vs.  $\log \beta$  obtained by: 1 – numerical solution of the system of equations – Eq. (1) [20] and  $dI(t) / dt = 0$ ; 2 – according to the model by Scharifker and Mostany [18]

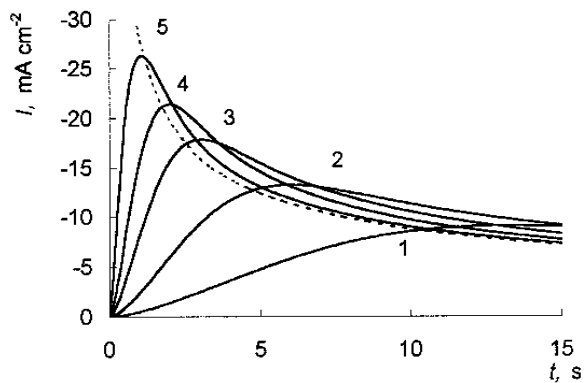


Fig. 5. Potentiostatic current transients for Cu electrocrystallization on Pt calculated from Eq. (1) at  $D = 6.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $c = 0.1 \cdot 10^{-3} \text{ mol cm}^{-3}$ ,  $N = 10^6 \text{ cm}^{-2}$  and  $A$ : 1 – 0.01, 2 – 0.05, 3 – 0.2, 4 – 0.5 and 5 –  $2.0 \text{ s}^{-1}$ . Dotted line represents a Cottrellian dependence

$$\frac{I^2}{I_{\max}^2} = 1.9542 / (t / t_{\max}) \{1 - \exp[-1.2564 (t / t_{\max})]\}^2 \quad (2)$$

and for the progressive nucleation:

$$\frac{I^2}{I_{\max}^2} = 1.2254 / (t / t_{\max})^2 \{1 - \exp[-2.3367 (t / t_{\max})^2]\}^2 \quad (3)$$

As has been shown in [18], analysis of the current transients in this form can be possible for the general case as well. However, a sufficient agreement between the experimental and calculated data will be observed only if the nucleation has a distinct character, either purely instantaneous or purely progressive.

The dimensionless parameter  $\beta$  determines both the growing rate of the diffusion zones and the character of nucleation. In the case of the limited value of  $N$  and the large  $A$ , the nucleation process ends rather quickly, *i.e.* before the overlap of the diffusion zones. Such a case corresponds to small values of the parameter  $\beta$  and brings the nucleation process closer to the instantaneous nucleation model. On the other hand, in the case of high  $N$  and low  $A$ , which corresponds to high values of the parameter  $\beta$ , the nucleation process proceeds according to the progressive nucleation model. It is not difficult to verify that the relationship between  $(I / I_{\max})^2$  and  $t / t_{\max}$  approaches that calculated according to Eq. (2) for  $\beta < 0.1$  and, on the contrary, to the one calculated from Eq. (3) for  $\beta > 1$ .

\* Considerations for another possible criterion for distinguishing between the models of instantaneous and progressive 3D nucleation with diffusion-controlled growth are presented in Appendix.

The data presented in Fig. 6 show that the initial stages of Cu electrocrystallization onto polycrystalline Pt from an additive-free acidic  $\text{CuSO}_4$  solution proceeds most likely through the model of progressive nucleation.

As regards the influence of PEG, it should be noted that there are some differences in the run of the experimental current transients recorded in the absence (Fig. 1) and in the presence of PEG (Fig. 2). Firstly, rather well-defined pre-waves can be easily observed in the current transients obtained in the presence of PEG (Fig. 2). It is interesting to note that the width of these pre-waves decreased as  $\Delta E$  was increased. In our opinion, appearance of such pre-waves in the potentiostatic current transients may be associated with a certain surface reduction process being most likely a discharge of adsorbed  $\text{Cu(I)-PEG}$  complex species formed as a consequence of a consecutive discharge of  $\text{Cu}^{2+}$  ions and adsorption of PEG molecules. In particular, a similar mechanism has been considered by Yokoi et al. [12].

Secondly, it was established that in the presence of PEG, the same values of  $I(t)$ , including  $I_{\max}$ , were obtained at higher  $\Delta E$  applied, *i.e.* this additive seems to show a certain inhibiting action on Cu nucleation onto Pt. This feature suggests the blocking action of PEG on the electrocrystallization of Cu. This problem will be studied in a further work.

As can be seen from Fig. 6, under the conditions of our experiments PEG did not show any more or less significant influence on the character of Cu electrocrystallization onto Pt.

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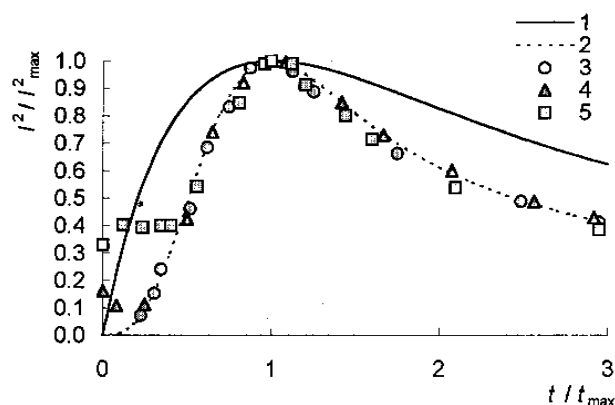


Fig. 6. Plots of  $(I / I_{\max})^2$  vs.  $t / t_{\max}$  for Cu electrocrystallization: 1 – calculated from Eq. (2); 2 – calculated from Eq. (3); 3, 4 – experimentally obtained for 0.1 M + 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $\Delta E$ : 3 – 0.230 and 4 – 0.250 V; 5 – experimentally obtained for 0.1 M  $\text{CuSO}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  +  $1 \cdot 10^{-5}$  M PEG (M. W. 3000) solution at  $\Delta E = 0.290 \text{ V}$

## APPENDIX

Another criterion for distinguishing between the models of instantaneous and progressive 3D nucleation may be supposed to be as follows. It has been known that, in the case of progressive nucleation, the saturation nuclear number density,  $N_{\text{sat}}$  can be estimated through the following equation [16]:

$$N_{\text{sat}} = (AN / (8 / 3) kD)^{0.5}. \quad (4)$$

The derivation of this equation was based on an assumption that new nuclei would form only on the electrode surface parts uncovered by the diffusion zones. On the other hand, it is obvious that  $N_{\text{sat}}$  cannot be larger than  $N$ . Correlating Eq. (4) with the expression of  $\beta = N\pi kD/A$ , one can find that  $N_{\text{sat}} < N$  when  $\beta > 1.178$ . This can be related as a criterion for deciding whether the nucleation is of a progressive character.

On the other hand, at  $\beta \leq 1.178$ , all active sites on the S surface can be occupied even prior to overlapping completely the diffusion zones. Under these conditions, at a constant value of  $N$ ,  $N_{\text{sat}}$  is independent of  $A$  and, consequently,  $N_{\text{sat}} = N$ . Such a process can be attributed to a quasi-instantaneous one. When  $\beta < 0.1$ , the nucleation becomes purely instantaneous.

The values of parameters  $A$  and  $N$  calculated here show that, in our case,  $\beta$  varies from 1.4 at  $A = 2 \text{ s}^{-1}$  to 270 at  $A = 0.01 \text{ s}^{-1}$  suggesting the nucleation process to be most likely progressive.

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**KAI KURIŲ PRIEDŲ ĮTAKA CU NUSODINIMUI IŠ RŪGŠČIŲ CUSO<sub>4</sub> TIRPALŲ POTENCIALŲ ZONOJE, TEIGIAMESNĖJE UŽ NERNSTO POTENCIALĄ, IR ESANT KATODINEI POLIARIZACIJAI. 8. POLIETILENGLIKOLIO (M. M. 3000) ĮTAKA PRADINĖMS CU ELEKTROKRISTALIZACIJOS STADIJOMS ANT POLIKRISTALINIO PT ELEKTRODO.**

S a n t r a u k a

Potenciostatinio įjungimo metodu buvo tirtos pradinės Cu elektrokristalizacijos stadijos ant polikristalinio Pt elektrodo 0,1 M CuSO<sub>4</sub> + 0,5 M H<sub>2</sub>SO<sub>4</sub> tirpaluose su polietilenglikolio (m. m. 3000) priedu. Eksperimentinės chronoamperogramos yra gerai aprašomos nauja bendro pobūdžio lygtimi pasiūlyta Heermano ir Tarallo (*J. Electroanal. Chem.*, **470**, 70 (1999)). Chronoamperogramų pobūdis rodo, kad Cu elektrokristalizacija ant Pt vyksta pagal progresuojantį kristalitų susidarymo modelį, o jų augimą limituoja lėta išsikraunančių jonų difuzija. PEG priedas nekeičia kristalitų susidarymo pobūdžio, bet žymiai apsunkina Cu kristalizaciją Pt elektrodo paviršiuje.

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**ВЛИЯНИЕ НЕКОТОРЫХ ДОБАВОК НА ОСАЖДЕНИЕ CU В ЗОНЕ НЕДОНАПРЯЖЕНИЯ И ПРИ КАТОДНОЙ ПОЛЯРИЗАЦИИ В КИСЛЫХ CUSO<sub>4</sub> РАСТВОРАХ. 8. НАЧАЛЬНЫЕ СТАДИИ ЗАРОДЫШЕОБРАЗОВАНИЯ CU НА ПОЛИКРИСТАЛЛИЧЕСКОЙ РТ В ПРИСУТСТВИИ ПОЛИЭТИЛЕНГЛИКОЛЯ (М. В. 3000)**

Р е з ю м е

Методом потенциостатического замыкания цепи исследованы начальные стадии зародышеобразования Cu на поликристаллической Pt в сернокислых растворах меднения без добавки и с добавкой полиэтиленгликоля (м. в. 3000). Ход хроноамперограмм хорошо описывается новым уравнением, предложенным Гирманом и Таралло (*J. Electroanal. Chem.*, **470**, 70 (1999)). Установлено, что процесс зародышеобразования является прогрессирующим с диффузионным контролем роста новой фазы. Добавка ПЭГ не меняет характера зародышеобразования, однако существенно затрудняет формирование зародышей Cu на Pt электроде.