Initial stages of the copper electrocrystallization from a sulfuric acid electrolyte: Chronoamperometry at a platinum ring-disk electrode

3 **AUTHORS**, INCLUDING:

A.I. Danilov

Russian Academy of Sciences

53 PUBLICATIONS **411** CITATIONS

SEE PROFILE

Initial Stages of the Copper Electrocrystallization from a Sulfuric Acid Electrolyte: Chronoamperometry at a Platinum Ring–Disk Electrode*

A. I. Danilov, E. B. Molodkina, and Yu. M. Polukarov

Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 117915 Russia

Received February 1, 2000

Abstract—Initial stages of the copper electrocrystallization on platinum from a sulfuric acid electrolyte are studied by measuring potentiostatic current transients (the chronoamperometry method) on a rotating and stationary ring–disk electrode. The number of active centers and the copper nucleation rate are shown to substantially depend on the electrochemical pretreatment of the electrode. The mechanism governing the formation of intermediate species (ions Cu^+) during the nucleation of a new copper phase and the deposit dissolution is analyzed.

INTRODUCTION

The electrochemical nucleation processes have an important fundamental and applicational value because they to a considerable extent determine physicochemical properties of electroplated coatings and their ability to protect corroding metals from the action of aggressive media. The effect of oversaturation on the porosity of a growing layer with the crystal nucleation occurring by the Stransky–Krastanov mechanism was first considered in [1]. The mechanism of the copper electrocrystallization on platinum draws the researchers attention because of several factors. The process begins from the construction of an adlayer comprising co-adsorbed atoms of copper and anions. At sufficiently high cathodic overvoltages, three-dimensional nuclei form (the Stransky–Krastanov mechanism). A further growth of the nuclei leads to the formation of an islet or compact coating. The stage discharge of copper ions in conjunction with the stage electrocrystallization process, on the whole, allow this system to be used as a modeling one when studying complex electrochemical processes. In recent years, the development of technologies intended for the formation and investigation of nano-size objects (monolayers, nano-size phases), which underlie modern micro- and nanoelectronics, has taken on great significance. This is one more reason for intensive research into the kinetics and mechanism of the formation and growth of a new phase nuclei.

Initial stages of the process of copper electrodeposition from electrolytes containing large amounts of acids have been studied sufficiently comprehensively

([2–19] and references therein). Solutions of pH > 2 are used much less frequently [4, 5, 14, 20–22]. There are only a few works that have been devoted to studying processes of three-dimensional nucleation [5, 14, 21] and the formation of adlayers [4, 14, 21, 22]. It was shown that, in low-acidity electrolytes, the discharge of copper ions accelerates and the number of intermediate species (ions Cu^+) formed during the deposit discharge is much smaller than that in acid solutions, which points to a change in the discharge mechanism [4, 5, 14, 20, 23]. However, the available information on the copper electrodeposition is insufficient for a clear understanding of the nucleation mechanism; therefore, this process calls for thorough examination.

An electrochemical treatment of the electrode surface substantially affects the kinetics of the copper adlayer formation and the nucleation and growth of three-dimensional copper nuclei in potentiodynamic conditions [4–6, 11–15]. Of importance are the acidity and the anion composition of the electrolyte. Preliminary data on the kinetics of the copper electrodeposition from such solutions as 0.5 M H_2SO_4 + 0.01 M $CuSO_4$ of pH 0.3 and 0.5 M Na_2SO_4 + 0.01 M $CuSO_4$ of pH 3.7 were obtained in [5] using cyclic voltammetry on a ring–disk electrode (RDE). The latter method is convenient for studying a stage discharge of ions and observing semi-quantitative effects during the metal electrocrystallization. In this work, we investigate how an electrochemical pretreatment of platinum affects the copper nucleation kinetics in a sulfuric acid electrolyte of pH 0.3 in potentiostatic conditions. In subsequent communications, we will consider the effect the solution acidity and the support nature have on the copper nucleation rate at platinum and glassy carbon.

---

* Dedicated to the ninetieth anniversary of Ya.M. Kolotyrkin's birth.

EXPERIMENTAL

The experiments were performed on a rotating or stationary platinum RDE (Tacussel, France). The disk diameter was 4 mm, the internal and outer ring diameters were 4.4 and 4.8 mm, respectively. The ring's collection coefficient was $N = 25 \pm 5\%$. We employed a platinum auxiliary and a mercury sulfate reference electrodes. All the potentials in the paper are referred to a normal hydrogen electrode.

The 0.5 M H_2SO_4 + 0.01 M $CuSO_4$ and 0.5 M Na_2SO_4 + 0.01 M $CuSO_4$ solutions were prepared from reagents of the "p.a." purity (Merck, Germany) and Milli-Q water with a resistivity of 18 Mohm cm and an organic impurity content of less than 10 ppb (Millipore, USA). The dissolved oxygen was removed by bubbling argon of extra purity grade.

A standard state of the platinum surface was obtained by cycling the potential of a stationary electrode in the potential region 0.27 to 1.25 V for a sufficiently long time. The potential scan rate V was 100 mV s^{-1}. Once a standard state was reached, a current transient was recorded at a proper potential. The deposit amount was determined by integrating a cathodic current transient or an anodic pulse of a cyclic voltammogram (CVA). For the electrode used, a charge of 0.09 μC corresponds to one effective monolayer (EM) of copper provided the space distribution of copper on the platinum surface is ignored.

To monitor the concentration of univalent copper in the near-electrode layer in the reaction $Cu^+ - e = Cu^{2+}$, the ring electrode potential was maintained at 0.8 V. The procedure is described in detail elsewhere [4–6, 11–15]. The explanations will be given below when required.

RESULTS AND DISCUSSION

The current transients that correspond to the nucleation of three-dimensional nuclei of a metallic phase are usually represented by chronoamperograms having each one or several maximums. A stepwise variation of the electrode potential leads to the emergence of the current of charging the electrical double layer (EDL). In the case of the copper electrocrystallization on platinum, the next process intermediate the charging of a pseudocapacitance (accumulation of metal atoms) and the accumulation of univalent copper ions in the near-electrode layer [4, 5, 13, 14]. These processes give rise to a first sharp maximum ($t < 1$ s) in a current transient. Depending on the magnitude of the cathodic overvoltage $\eta = E_{eq} - E$, copper nuclei form on the layer of adatoms at one rate or another. The current of the nuclei growth depends on the cathode overvoltage, the active surface area of the deposit, and the magnitude of the flow of electroactive ions towards the electrode–solution interface. If the crystallite growth occurs under a diffusion control or a mixed control, the chronoamperogram usually displays a second, smoother maximum.

The maximum corresponds to the overlapping of hemispherical zones where concentrations of discharging ions is lower. Afterwards, the crystallite growth occurs in the conditions of a non-steady-state diffusion, and the current decreases with time in accordance with the equation

$$I = SzFc(D/\pi t)^{1/2}. \tag{1}$$

Here, S denotes the geometrical surface area of the electrode, z is the ion charge, F is Faraday's number, c is the concentration, D is the diffusion coefficient, and t stands for the time. To the first approximation, the dependence of the steady-state nucleation rate J on η is described by the equation [24]

$$J = KN\exp[(n_c + \alpha)zF\eta/RT], \tag{2}$$

where K is a constant weakly dependent on the overvoltage, N is the number of active centers of the support at which nuclei form at a given overvoltage, η, n_c is the number of atoms in a critical nuclei, and α is an electrochemical transfer coefficient.

One can describe the current transients and calculate the nucleation parameters (J, N, n_c) from the coordinates of the maximum, using a number of mathematical models [25–28]. However, in each particular case, the applicability of a model must be proved experimentally [11, 12].

Consider the effect an electrochemical pretreatment exerts on the copper nucleation kinetics in a stagnant electrolyte. Figure 1 shows current transients for the copper deposition at overvoltages of 30 mV (curves 1, 3, 5) and 70 mV (curves 2, 4, 6). The polarization programs for the electrode (the potential variation with time) are shown in the insert in Fig. 1. The cathodic currents are positive. In all the experiments, cycling the potential in the region 0.27 to 1.25 V ensured that a standard state of the electrode surface was obtained (when measuring the current, the scatter of experimental points did not exceed 1 to 2 μA). This means that the differences observed in the shapes and heights of the current transients at identical overvoltages η are due to variations in the interface state occurring in the course of the potentiostatic pretreatment. The deposit dissolution occurred in an anodic pulse of CVA from the deposition potential to 1.25 V, at $V = 10$ mV s^{-1}. Subsequently, the electrode potential was cycled in the region 0.27 to 1.25 V at $V = 100$ mV s^{-1}.

Curves 1 and 2 were recorded after the electrode was kept for 10 s at the equilibrium potential $E_{eq} = 0.25$ V of the Cu/Cu^{2+} pair. Ten seconds were sufficient enough for the formation of a complete monolayer of copper adatoms. Curves 3 and 4 were recorded after a prolonged (500 s) polarization at 0.25 V. The elevated copper deposition currents testify that a large number of crystallization centers are present on the platinum surface. Current transients 1–4 have no clearly pronounced maximums at $t > 1$ s, because a voltammogram is the sum of partial current transients corre-

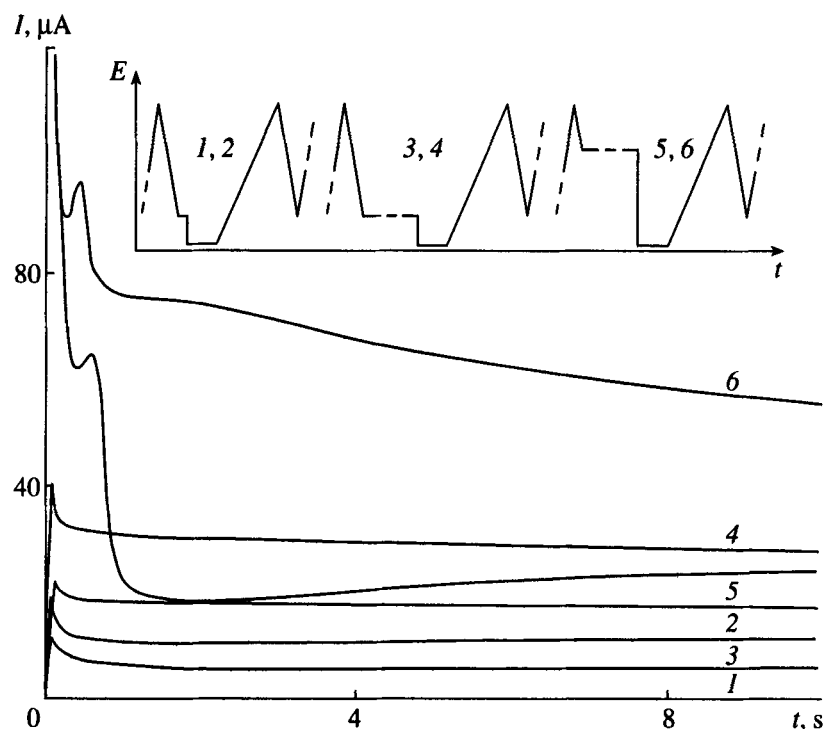**Fig. 1.** Potentiostatic transients of the copper deposition current on a stationary platinum electrode in 0.5 M H$_2$SO$_4$ + 0.01 M CuSO$_4$, obtained at overvoltages of (*1, 3, 5*) 30 and (*2, 4, 6*) 70 mV after pretreatments consisting of the electrode exposure at (*1, 2*) 0.25 V for 10 s, (*3, 4*) 0.25 V for 500 s, and (*5, 6*) 0.7 V for 500 s; inset shows the polarization program.

sponding to the nucleation and growth of crystallites on polycrystalline platinum whose surface is nonuniform with respect to energy (a similar situation was analyzed in [11]). Each of the partial current transients may correspond to the nucleation at centers with different activity, the nucleation occurring at different rates. As a result, the density of the nuclei distribution over the electrode surface may substantially differ at the support grains of different orientation. The overlapping of diffusion zones of growing copper crystallites will occur at different time instants, and the maximum in the net *I* vs. *t* curve will be smoother.

Curves *5* and *6* were recorded after the electrode was kept for 500 s at a potential of 0.7 V. This potential value corresponds to a region where insignificant amounts of adatoms of copper and oxygen undergo co-adsorption. The copper oxides that form here are active centers for the two-dimensional growth of an adlayer and the formation of three-dimensional nuclei of metallic copper at more negative potentials [6, 15]. The maximum at *t* < 1 s characterizes a phase transition of the co-adsorption lattice adatoms/anions into a monolayer Cu(1 × 1) [15]. At high overvoltages, the monolayer forms more rapidly (curve *6*), and the shoulder (inflection) at *t* ≈ 2 s corresponds to the instant when the diffusion zones of growing copper islets start to overlap. The increase in the current with time at η = 30 mV at *t* > 2 s (curve *5*) points to a more intensive (compared

with curves *1–3*) nucleation at a larger number of active centers of the support.

Figure 2 shows a series of current transients for the copper deposition at overvoltages of 25–250 mV following a 10-s period of keeping the electrode at the equilibrium potential. There are no clearly pronounced nucleation maximums (*t* > 1 s). Therefore, any quantitative estimation of the number of active centers and the nucleation rate would be meaningless.

The shape of the current transients substantially alters if a potentiostatic nucleation pulse is imposed almost immediately after the termination of the cathodic run of CVA. Figure 3 shows a number of current transients for the electrode pretreated at 0.27 V for 0.5 s. Under these conditions, the total coverage of the platinum surface by copper adatoms amounts to approximately 0.7 monolayers. It seems quite probable that the coverages of portions of a polycrystalline electrode with different crystallographic orientations may substantially differ. This means that the most active portions of the surface are completely covered by a monolayer of copper adatoms, while the less active portions are covered only partially. The difference in the coverages is due to the fact that the portions in question have different adsorbability towards atoms, anions, oxygen, and water molecules. Once the potential is displaced jumpwise into the region of cathodic overvoltages and the EDL is charged, the formation of metallic nuclei and their growth occur at the active centers. On
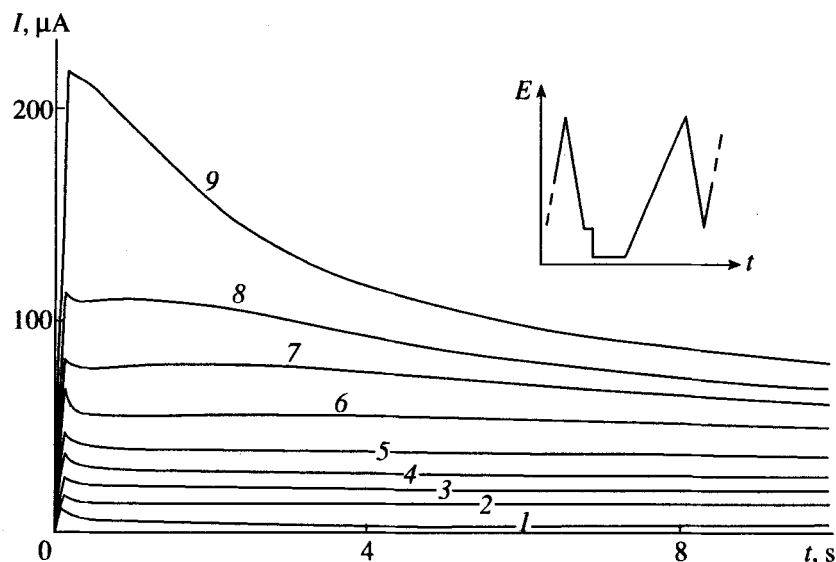
Fig. 2. Potentiostatic transients of the copper deposition current on a stationary platinum electrode in 0.5 M H$_2$SO$_4$ + 0.01 M CuSO$_4$, obtained after a pretreatment of the electrode at 0.25 V for 10 s; cathodic overvoltages are as follows: (*1*) 25, (*2*) 50, (*3*) 75, (*4*) 100, (*5*) 125, (*6*) 150, (*7*) 175, (*8*) 200, and (*9*) 250 mV; inset shows the polarization program.
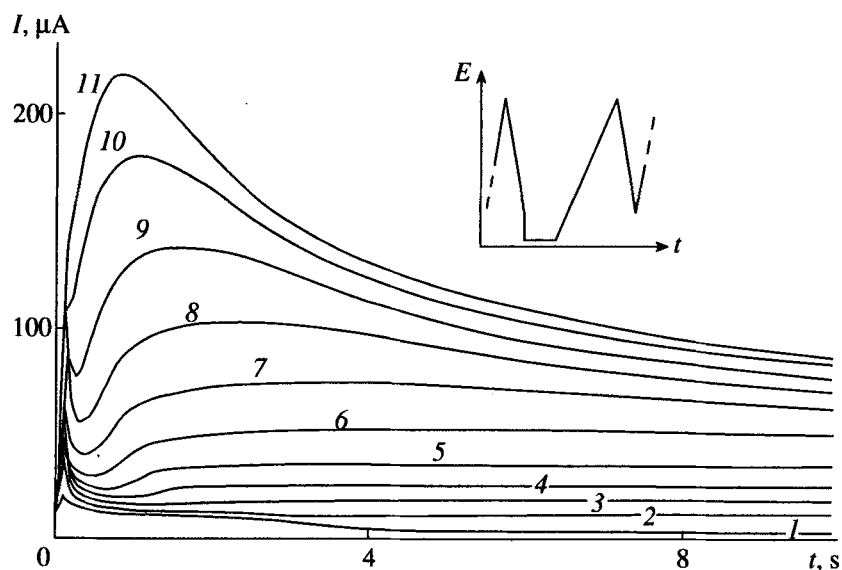
Fig. 3. Potentiostatic transients of the copper deposition current on a stationary platinum electrode in 0.5 M H$_2$SO$_4$ + 0.01 M CuSO$_4$, obtained after a pretreatment of the electrode at 0.27 V for 0.5 s; cathodic overvoltages are as follows: (*1*) 25, (*2*) 50, (*3*) 75, (*4*) 100, (*5*) 125, (*6*) 150, (*7*) 175, (*8*) 200, (*9*) 225, (*10*) 250, and (*11*) 275 mV; inset shows the polarization program.

the less active portions of the electrode surface, the formation of an adlayer continues; the nucleation starts only after this process is completed. It will be remembered that the copper electrocrystallization process on platinum occurs via the Stransky–Krastanov mechanism and that the three-dimensional nuclei of phase copper form on a monolayer of adatoms: see curves *5* and *6* in Fig. 1 and [13–15]. At low overvoltages (curve *1*, Fig. 3), the current step (*t* < 4 s) is due to the continuing growth of the monolayer of adatoms. Once this process is completed, the current corresponding to

the metallic-phase growth slightly increases (*t* > 10s; about four effective monolayers of copper are deposited for 100 s).

Such a pretreatment of the electrode (Fig. 3, insert) probably leads to a state of the platinum surface in which activities of some surface portions differ rather heavily. The nuclei that formed at the most active centers rapidly grow and create around themselves zones with reduced concentrations of copper ions and zones of an ohmic potential loss [29, 30]. This hampers the nucleation process at the neighboring portions. As a

result, the nucleation occurs at centers of approximately the same (maximum) activity; the centers are distributed more or less uniformly over the electrode surface. In this case, diffusion zones of growing crystallites overlap almost simultaneously, and the current transient has a clearly pronounced maximum.

For a given series of the I vs. t curves, the number of active centers and the nucleation rate may roughly be estimated from the coordinates of maximums I_m and t_m, using models described in [25, 26]. Such estimates may be viewed only as a first approximation [11, 12], because the real number of copper nuclei on platinum determined with the aid of electron microscopy is higher than the number of active centers calculated with these models by several orders of magnitude. Regretfully, we are unaware of any ideal theoretical models.

The current of the growth of hemispherical crystallites control by diffusion obeys the equation [26]

$$I = SzFc(D/\pi t)^{1/2}$$
$$\times [1 - \exp\{-\pi NkD(t - [1 - \exp(-J_1 t)]/J_1)\}], \quad (3)$$

where J_1 is the specific (per one active center) nucleation rate, $k = (8\pi c V_a)^{1/2}$, and V_a is an atomic volume. The total nucleation rate $J = J_1 N$. For a maximum current $(dI/dt = 0)$, one can write a set of transcendental equations [26] which may be solved under the following condition:

$$0.7153 < (I_m/SzFc)(\pi t_m/D)^{1/2} < 0.9034. \quad (4)$$

Dimensionless parameters 0.7153 and 0.9034 correspond to limiting cases of an instantaneous and a progressing nucleation [25, 26]. In the former case, the number N of centers where the deposit grows is determined by the number of sites on the support that are suitable for the nucleation at a given overvoltage. In the latter case, the nucleation rate J of crystallites is commensurate with their growth rate. In the model [25], the instantaneous nucleation is described by equations

$$I = SzFc(D/\pi t)^{1/2}\{1 - \exp[-\pi NkDt^2]\}, \quad (5a)$$

$$(I/I_m)^2 = 1.9542(t/t_m)^{-1}$$
$$\times \{1 - \exp[-1.2564(t/t_m)]\}^2, \quad (5b)$$

$$N = 1.2564/(\pi kDt_m), \quad (5c)$$

$$N = 2.4552 I_m^2/[k(zFDcS)^2] \quad (5d)$$

and the progressing nucleation, by equations

$$I = SzFc(D/\pi t)^{1/2}\{1 - \exp[-2\pi JkDt^2/3]\}, \quad (6a)$$

$$(I/I_m)^2 = 1.2254(t/t_m)^{-1}$$
$$\times \{1 - \exp[-2.3367(t/t_m)^2]\}^2, \quad (6b)$$

$$J = 3.5048/(\pi kDt_m^2), \quad (6c)$$

$$J = 16.5339 I_m^4/[kD(zFcS)^4], \quad (6d)$$

when processing current transients within this model, one must bear in mind that quantities I_m and t_m depend on the cathode overvoltage and the process mechanism. Using criteria (4) and comparing experimental current transients with modeling curves (5b) and (6b) in the $(I/I_m)^2$, vs. (t/t_m) dimensionless coordinates, one can estimate the nucleation mechanism. Then, one can calculate either N or J with equations (5c) and (5d) or (6c) and (6d).

For the real current transients occurring under our experimental conditions ($S = 0.1256$ cm^2, $C = 0.01$ M Cu^{2+}) and the reference value of the diffusion concentration $D = 7.5 \times 10^{-6}$ cm^2 s^{-1}, condition (4) is not met. Hence, no calculation of the process parameters is possible in the model [26]. For curve *11* in Fig. 3, the diffusion coefficient estimated with equation (1) is somewhat smaller, specifically, $D = 2.8 \times 10^{-6}$ cm^2 s^{-1}. In reality, one can determine the product $SzCD^{1/2}$, rather than the diffusion coefficient D. However, quantities z, C, and S are presumably known to within a sufficiently high accuracy. One of the two possible reasons for the difference between calculated and experimental values of D involves the fringing effects. The point here is that equation (1) is valid for an infinitely large, plane electrode. The other may be the slow charge transfer or, in other words, the case of mixed kinetics (diffusion + discharge) instead of a purely diffusion control.

The maximum number of current transients in the series that is partially presented in Fig. 3 may meet condition (4) at $D = 2.4 \times 10^{-6}$ cm^2 s^{-1}. These are the curves obtained at $\eta = 200$–275 mV with an increment of 5 mV. At lower values of the diffusion coefficient, one can calculate nucleation parameters J_1 and N for some current transients recorded at lower overvoltages, but in a narrower overvoltage range. Under these conditions, it seems reasonable to expect a larger contribution of the charge transfer kinetics. Thus, the diffusion coefficient acts as a fitting parameter that allows one to process experimental data in the framework of an idealized model. However, one should not forget that the estimates thus made are approximate. To our minds, there are two main reasons for the discrepancies between the model and the experiment. One is the energy nonuniformness of the electrode surface. The problem is that the model described in [26] is based on the assumption that the quantity J_1 is invariant in time and space and that the nucleation rate depends only on the overvoltage η and the activity of the nucleation centers $a(\eta)$. In reality, however, at a constant potential of the electrode, on different sites of the electrode surface, $a \neq$ const and $J_1 \neq$ const either. The other reason is connected with deviations from a purely diffusion control of the copper crystallite growth: according to our estimates, the deposit grows in the conditions of mixed kinetics.

Figure 4a compares theoretical curves with experimental current transients. The theoretical curves, which were

calculated with equation (3) at $D = 2.4 \times 10^{-6}$ cm^2 s^{-1}, are represented by solid lines. The experimental current transients were recorded at overvoltages of 200, 225, and 250 mV. The values of N and J_1 required for constructing modeling curves, were calculated from the coordinates of maximums in the real I vs. t dependences. As seen, the experimental points satisfactorily match theoretical curve 1 at $\eta = 200$ mV. At higher overvoltages, the discrepancies are more noticeable (curves $2, 3$). Here, the measured current is higher than the limiting current of a non-steady-state diffusion. This effect may be due to a mixed control of the crystallite growth and to a contribution of parallel processes at centers whose activity is different.

Figure 4b illustrates the results of calculations of the number of active centers (curve 2) and the copper nucleation rates (curves $1, 3$). The calculations were performed using the model [26], at $D = 2.4 \times 10^{-6}$ cm^2 s^{-1}. Attention is drawn to the fact that values of J_1 decrease with increasing the overvoltage (curve 1). A similar pattern occurs at other values of the fitting parameter D. This result is meaningless from a physical viewpoint and testifies that the model described in [26] is invalid for this particular experimental system. Using it, one cannot obtain correct quantitative estimates of the nucleation parameters.

Figure 5 shows how the copper amount Q, expressed in units of EM, depends on the cathode overvoltage at different pretreatments of the electrode. The copper amount was calculated by integrating the current transients depicted in Figs. 1–3, for the first ten seconds of the deposition. As seen, the maximum copper electrocrystallization rate occurs at the electrode that was kept for a long time at 0.7 V. Compare curves $1–4$ at a constant overvoltage below 100 mV (at short time intervals, the crystallite growth rate is chiefly determined by the overvoltage and the charge transfer kinetics, and the diffusion limitations are not too large). The comparison suggests that the most probable reason for the change in the deposition rate is a change in the number of active centers on the support occurring during the electrode pretreatment. This conclusion conforms to the data of [4–6, 15].

To determine how the intermediate species (ions Cu$^+$) and the mass transfer process affect the formation kinetics of the copper phase, we performed experiments on RDE. The metal was deposited after keeping the electrode for 0.5 s at 0.27 V at different overvoltages (Figs. 6a, 6b). The deposition process was discontinued upon passing the cathodic charge $Q_c = 4.5$ μC (an automatic integration of an I vs. t curve and a transition to the deposit dissolution), which corresponds to 50 effective monolayers of copper. The program governing the polarization procedure and the data recording process ensured that the electrode rotation (500 rpm) was switched on during the pretreatment stage at 0.27 V (Fig. 6, curves $1'–5'$) or 0.2 s prior to replacing the cathodic overvoltage by the anodic one
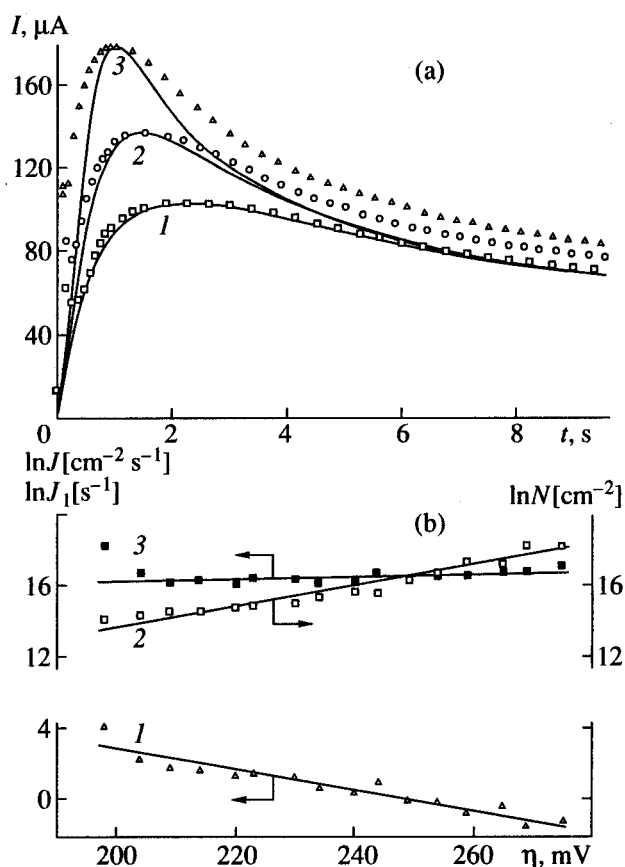

Fig. 4. (a) Current transients for copper deposition on platinum at overvoltages of (1) 200, (2) 225, and (3) 250 mV obtained experimentally (points) and compared with theoretical curves (solid lines) calculated with equation (3); (b) dependences of logarithms of (1) specific nucleation rate J_1, (2) number of active centers on the support N, and (3) total nucleation rate $J = J_1 N$ on the cathode overvoltage; the electrode polarization program and the current transients are given in Fig. 3.
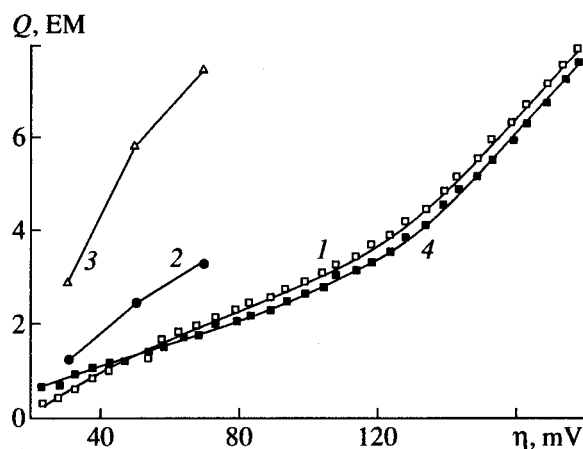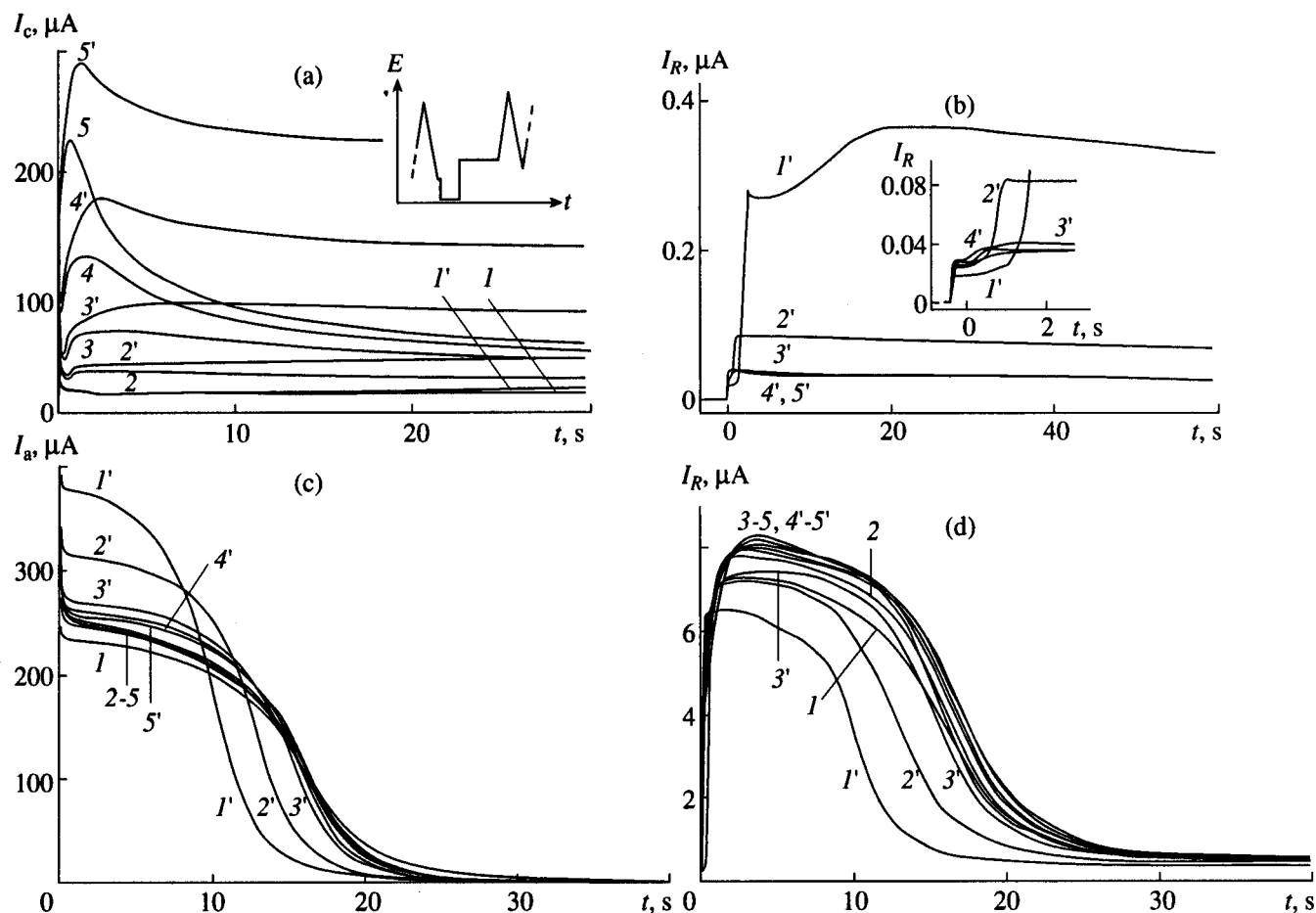

Fig. 5. Dependences of the amount of copper deposited for 10 s (integration of current transients of Figs. 1–3) on the cathode overvoltage and the electrode pretreatment consisting of its exposure at (1) 0.25 V for 10 s, (2) 0.25 V for 500 s, (3) 0.7 V for 500 s, and (4) 0.27 V for 0.5 s.

Fig. 6. (a) Potentiostatic current transients for copper deposition on (*1–5*) stationary disk electrode and (*1'–5'*) the same electrode rotating at 500 rpm, obtained at overvoltages of (*1, 1'*) 50, (*2, 2'*) 100, (*3, 3'*) 150, (*4, 4'*) 200, and (*5, 5'*) 250 mV; polarization program is shown in inset; (b) corresponding variations in the univalent copper oxidation current on the ring electrode occurring during the deposit growth; inset shows initial portions of the transients in a magnified scale; (c, d) variations in the anodic current of (c) disk and (d) ring electrodes during the dissolution of deposits at the disk potential $E = 0.3$ V.

(curves *1–5*). Thus, the dissolution of approximately the same deposit amount occurred in this experimental series in identical conditions ($E = 0.3$ V, 500 rpm, $Q_a = 3.6–3.8$ μC). Note that on RDE, the current efficiency during the deposition is below 100%, while during the dissolution, it exceeds 100% at the expense of the removal of ions Cu^+ by an electrolyte flow, especially at low overvoltages. For the chronoamperograms pertaining to the deposit dissolution, the time $t = 0$ corresponds to the instant when the electrode potential reaches 0.3 V (Figs. 6c, 6d). As seen, an intensification of the mass transfer accelerates the copper deposition process, especially at high overvoltages (Fig. 6a). At $\eta = 50$ mV, the concentration of ions Cu^+ in the near-electrode layer sharply increases (Fig. 6b, curve *1'*; $t \approx 2$ s) after the formation of a monolayer of adatoms on the disk is completed (Fig. 6a, curve *1'*; $t < 2$ s). Afterwards, the concentration passes through a maximum and steadily decreases with increasing the amount of deposited copper.

Following an increase in the cathodic overvoltage of the disk, the delay of the ring current diminishes, and the copper monolayer forms more rapidly (Fig. 6b, insert). At high overvoltages, the concentration of intermediate species during the deposit growth is much lower than that at $\eta = 50$ mV (Fig. 6b). At overvoltages of 150–250 mV, the concentration weakly depends on the time, the overvoltage, and the disk current. This suggests that, under these conditions, the platinum surface becomes covered by a virtually continuous layer of deposited copper within the first few seconds, and only an insignificant fraction of ions Cu^+ fails to undergo reduction to Cu^0 at the surface of copper crystallites. At portions of the $Pt–Cu_{ad}$ surface free of phase copper, only the reaction $Cu^{2+} + e = Cu^+$ occurs [5].

The curves describing the deposit dissolution on the disk are presented in Fig. 6c; the corresponding dependences of the ring current are presented in Fig. 6d. The deposits that are obtained at overvoltages of 50 and 100 mV on a rotating electrode dissolve much more rapidly than other deposits (Fig. 6c). The number of

ions Cu^+ formed in this case is smaller (Fig. 6d, curves *1'*, *2'*). It will be remembered that the deposit formation under these conditions occurred at an elevated concentration of ions Cu^+ (Fig. 6b); consequently, a considerable fraction of the electrode surface was free of the phase deposit [5]. The high rate of the anodic process for such coatings may be explained by the dissolution of copper islets with a large total surface area of the Cu–electrolyte interface. The coatings formed at overvoltages of 150–250 mV are more uniform, have a smaller active surface area, and dissolve slower (Fig. 6c, curves *3'*–*5'*). The deposits obtained on a stationary electrode dissolve still slower (curves *1*–*5*). Apparently, at elevated concentrations of univalent copper, a stable structure forms even at $\eta = 50$ mV (curve *1*).

It seems surprising that, at a high dissolution rate of islet deposits (Fig. 6c, curves *1'*, *2'*), the number of the formed intermediate species is considerably smaller (Fig. 6d, curves *1'*, *2'*). The concentration of univalent copper during the dissolution of the deposit formed on a stationary electrode at $\eta = 50$ mV is rather low (Figs. 6c, 6d; curves *1*). At a potential of 0.3 V, the balance between rates of reactions $Cu^0 - e = Cu^+$ and $Cu^+ - e = Cu^{2+}$ on the surface of copper crystallites and in the regions of a three-phase contact Cu–Pt–electrolyte (along the perimeter of the Cu–Pt islets) is probably different and depends on the ratio between the surface areas of copper and platinum at the electrode–solution interface. At present, we have no sufficient information to make final conclusions as to the dissolution mechanism of the islet deposits. This phenomenon calls for additional morphology investigations and for variations in the deposit amount and the dissolution potential. The hypothesis that the charge at the surface of microelements (portions of Cu and Pt) affects the rate of the electron detachment from Cu^+ seems to us the most plausible. The potential of zero charge of copper is more negative than that of platinum by approximately 100 mV [31]. At a constant potential of a platinum electrode partially covered with copper islets, the charge of copper portions is more positive. Hence, the oxidation rate of ions Cu^+ that form in regions of the three-phase contact may be higher at the more negatively charged platinum surface (local electrostatic effects).

CONCLUSIONS

An analysis of the experimental data presented in this work leads us to the following conclusions about the kinetics of a potentiostatic nucleation of copper crystallites on polycrystalline platinum in a sulfuric acid electrolyte.

An electrochemical pretreatment of platinum substantially affects the number of active nucleation centers. The maximum number of the crystallization centers (oxide compounds of copper) forms at potentials of about 0.7 V.

There is no doubt that the mass transfer rate substantially affects the process of copper electrocrystallization on platinum in a sulfuric acid electrolyte (the copper deposit grows more rapidly at a rotating electrode). Nevertheless, one can use the diffusion models discussed in [25, 26] only for obtaining very rough estimates of the nucleation parameters pertaining to the formation and growth of a metallic phase in this experimental system. The problem is that these models were designed for the phase nucleation on a surface uniform in terms of energy and for the deposit growth under a purely diffusion control. In reality, the nucleation in a sulfuric acid electrolyte occurs at centers of different activity, and the copper crystallites grow under a mixed kinetics control (diffusion + discharge).

In the case of dissolution of the islet deposits, the near-electrode concentration of univalent copper is lower than that in the case of continuous uniform coatings. To determine how the nature and morphology of the electrode–solution interface affects the balance between rates of individual stages of the copper oxidation process, special investigations are required.

REFERENCES

1. Popov, Yu.A., Vasil'ev, A.A., and Kolotyrkin, Ya.M., *Elektrokhimiya*, 1976, vol. 12, p. 1298.
2. Danilov, A.I. and Polukarov, Yu.M., *Usp. Khim.*, 1987, vol. 56, p. 1082.
3. Danilov, A.I., *Usp. Khim.*, 1995, vol. 64, p. 818.
4. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 2000, vol. 36, no. 9.
5. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 2000, vol. 36, no. 9.
6. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 2000, vol. 36, no. 9.
7. Tindall, G.W. and Bruckenstein, S., *Anal. Chem.*, 1968, vol. 40, pp. 1051, 1637.
8. Michailova, E., Vitanova, I., Stoychev, D., and Milchev, A., *Electrochim. Acta*, 1993, vol. 38, p. 2455.
9. Rigano, P.M., Mayer, C., and Chierchie, T., *Electrochim. Acta*, 1990, vol. 35, p. 1189.
10. Markovic, N.M., Gasteiger, H.A., and Ross, P.N., *Langmuir*, 1995, vol. 11, p. 4098.
11. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 1994, vol. 30, p. 748.
12. Smolin, A.V., Gvozdev, V.D., Danilov, A.I., and Polukarov, Yu.M., *Elektrokhimiya*, 1994, vol. 30, p. 157.
13. Danilov, A.I., Andersen, J.E.T., Molodkina, E.B., *et al.*, *Electrochim. Acta*, 1998, vol. 43, p. 733.
14. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 1997, vol. 33, pp. 313, 320.

15. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., *Elektrokhimiya*, 1998, vol. 34, pp. 1387, 1395.

16. Ikemiya, N., Miyaoka, S., and Hara, S., *Surf. Sci.*, 1995, vol. 327, p. 261.

17. Nichols, R.J., Bunge, E., Meyer, H., and Baumgartel, H., *Surf. Sci.*, 1995, vol. 335, p. 110.

18. Eliadis, E.D., Nuzzo, R.G., Gewirth, A.A., and Alkire, R.C., *J. Electrochem. Soc.*, 1997, vol. 144, p. 96.

19. Dietterle, M., Will, T., and Kolb, D.M., *Surf. Sci.*, 1995, vol. 342, p. 29.

20. De Agostini, A., Schmidt, E., and Lorenz, W.J., *Electrochim. Acta*, 1989, vol. 34, p. 1243.

21. Holzle, M.H., Zwing, V., and Kolb, D.M., *Electrochim. Acta*, 1995, vol. 40, p. 1237.

22. Zhang, J., Sung, Y.-E., Rikvold, P.A., and Wieckowski, A., *J. Chem. Phys.*, 1996, vol. 104, p. 5699.

23. Lezhava, T.I. and Meladze, K.G., *Elektrokhimiya*, 1978, vol. 14, p. 1651.

24. Milchev, A., Stoyanov, S., and Kaischev, R., *Thin Solid Films*, 1974, vol. 22, pp. 255, 267.

25. Scharifker, B. and Hills, G., *Electrochim. Acta*, 1983, vol. 28, p. 879.

26. Scharifker, B.R. and Mostany, J., *J. Electroanal. Chem.*, 1984, vol. 177, p. 13.

27. Bosco, E. and Rangarajan, S.K., *J. Electroanal. Chem.*, 1982, vol. 134, pp. 213, 225.

28. Isaev, V.A. and Baraboshkin, A.N., *J. Electroanal. Chem.*, 1994, vol. 377, p. 33.

29. Markov, I., *Thin Solid Films*, 1976, vol. 35, p. 11.

30. Milchev, A., *J. Electroanal. Chem.*, 1991, vol. 312, p. 267.

31. Damaskin, B.B. and Petrii, O.A., *Vvedenie v elektrokhimicheskuyu kinetiku* (Electrochemical Kinetics: An Introduction), Moscow: Vysshaya Shkola, 1983.