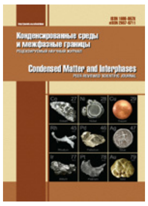

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Electrochemical reduction of nitrate ions on copper coatings of various roughness under conditions of mixed transport and kinetic control

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Abstract

Objectives: In this work, the influence of electrode surface roughness on the kinetics of the non-stationary electrochemical process of cathodic reduction of nitrate ion under conditions of mixed transport-kinetic control under potentiostatic polarization conditions is established.

Experimental: The research was carried out on two copper coatings obtained by galvanostatic deposition from a copper sulfate electrolyte, which was supplemented with various organic additives to vary the roughness of the synthesized copper coatings. The kinetics of the electrochemical reduction of nitrate ions on the obtained copper coatings were studied by transient electrochemical methods of voltammetry and chronoammetry in an aqueous deaerated solution of 10 mM KNO_3 + 100 mM H_2SO_4. Potentiostatic measurements were performed at a cathodic potential of -470 mV, corresponding to a mixed transport-kinetic control. The surface roughness of the synthesized copper coatings was evaluated using atomic force microscopy and underpotential deposition of lead monolayer.

Conclusion: Based on the previously developed theoretical model of the electrochemical process occurring in a mixed transport-kinetic mode on a rough electrode, an approach is proposed for estimating the main parameters of the kinetic stage, taking into account normalization to the real surface area, using the example of the electrichemical reduction of nitrate ions on copper coatings of various roughness. Within the framework of this approach, it was found that a rougher copper coating is characterized by higher values of the heterogeneous constant of the rate and density of the exchange current, which indicates an increase in the electrocatalytic activity of copper in the reaction under study during the transition to electrodes with increased roughness.

Keywords: Surface roughness, Copper coating, Nitrate ion, Electrochemical reduction, Mixed kinetics, Atomic force microscopy, Voltammetry, Chronoamperometry

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1. Introduction

Surface roughness is an important property of solid electrodes. The generally accepted quantitative characteristic for its estimation is the roughness factor $f_r = S_{real}/S_{geom}$, which is equal to the ratio of the true (S_{real}) to the visible area (S_{geom}) of the electrode surface [1, 2]. The roughness effect is not purely geometric, since the formation of a rough (morphologically heterogeneous) surface can lead not only to an increase in surface area, but also to the appearance of new active reaction and adsorption centers on it [3], changes in the kinetic parameters of the electrode reaction [4, 5], changes in corrosion resistance [6–8] and double-layer characteristics [9]. As a consequence, for a correct assessment of the electrocatalytic activity and adsorption capacity of the electrode, it is necessary to normalize the extensive parameters of the kinetics of the electrode reaction (current, impedance, admittance), double electric layer (differential and integral capacitance) and adsorption to the roughness factor when calculating them. Otherwise, the claimed “increase in electrocatalytic activity” may simply be the result of an increase in surface area without any real catalytic effect.

In this case, the procedure for finding the current density as a measure of the rate of the electrode process occurring on a rough electrode is generally not trivial, since it depends on the nature of kinetic constraints. So, if the limiting stage of the electrochemical reaction is charge transfer, then the current density $i = I/S_{real} = I/(S_{geom} \cdot f_r)$ should be calculated by dividing the current I by the true area of the electrochemically active electrode surface. Considering that electrocatalytic processes controlled by the charge transfer stage are mainly carried out on highly developed, dispersed electrodes, the main problem in this case is the determination of the roughness factor f_r [10], but not the task of calculating the rate of the electrode process.

In the case of diffusion-controlled processes, the procedure for taking into account the roughness factor becomes significantly more complicated, since their rate, generally speaking, should be normalized not to the surface area of the electrode, but to the surface area of the diffusion front [11]. At the same time, in the non-stationary mass transfer mode, the geometry of the diffusion front changes over time: it repeats the profile of the electrode surface at short times and is almost completely smoothed out at sufficiently long times. This is explained by the fact that during the initial period of the process, the thickness of the diffusion layer d is very small and does not exceed the size of the micro-dimensions, whereas during the propagation of the diffusion front deep into the phase, on the contrary, it becomes so large that the diffusion flux practically ceases to be sensitive to the roughness of the electrode surface [12].

The most difficult situation is when a non-stationary electrochemical process takes place in the mode of mixed transport and kinetic control. In this case, the contributions of the stages of charge transfer and mass transfer to the kinetics of the electrode process are comparable, and their ratio varies over time. Such processes play a special role in the formation of metal coatings, including in microelectronics, when it is necessary to carry out uniform electrodeposition of metal onto the surface of a rather complex micro- and/or macrogeometric profile.

In [13], a mathematical model was constructed of the process occurring at potentiostatic polarization in the mode of mixed diffusion-kinetic control on an electrode with an average surface roughness ($1 < f_r \leqslant 3$) of a harmonic, fractal, or irregular profile. The simulation results showed that the i,t-chronoamperograms of rough and flat electrodes are related by a ratio $i(t)_{\text{rough}} = i(t)_{\text{flat}} \cdot \varphi(k, D, f_r, \lambda, t)$ in which $\varphi(k, D, f_r, \lambda, t)$ is a roughness function. It depends in a complex way on the roughness factor f_r, the average size of the irregularities λ, as well as on the ratio of the heterogeneous rate constant k of the electrode process (charge transfer stage) and the diffusion coefficient of the electroactive reagent D, varying over time from $\varphi = f_r$ to $\varphi = 1$.

The range of electrode processes occurring in the mode of mixed transport-kinetic control is very wide. For instance, the complex process of cathodic reduction of the nitrate ion is very sensitive morphologically and structurally [14–19]. The cathodic reduction of NO_3^- ions is of great practical importance due to the need to control the nitrate content in aqueous media, as well as a method for obtaining nitrogen-containing compounds, primarily ammonia as a starting substance in the production of nitrogen fertilizers. In this work, the process of the electrochemical reduction of NO_3^- ions is considered as a model for detecting the effect of surface roughness of the electrode.

Among the transition metals of the IB-group, copper exhibits the highest activity and selectivity in the cathodic reduction of nitrates [20], with ammonium ion being the main product in an acidic medium [21]. To vary the roughness of a copper electrode, our work uses the method of electrodeposition from sulfate electrolytes of copper plating, the introduction of organic additives into which makes it possible to obtain coatings with variable roughness [22].

The study of the role of roughness in the catalytic activity of electrodeposited copper coatings is complicated by the fact that the process of the cathodic reduction of NO_3^- ions is multielectron and multistage. As a consequence, the identification of a purely catalytic effect requires the determination of the kinetic parameters of the electrochemical stage, primarily the heterogeneous charge transfer rate constant. The transient electrochemical methods can be used to find the kinetic current. The potentiodynamic method (chronovoltammetry) allows us to identify the general kinetic patterns of the cathodic process involving the nitrate ion, as well as the potential range of its electroreduction. In turn, the potentiostatic method (chronoamperometry) makes it possible to evaluate the contributions of the diffusion and electrochemical stages to the overall rate of the process. In this paper, these problems are solved under conditions of mixed transport-kinetic control using a previously developed theoretical model of the electrode process on a geometrically inhomogeneous electrode surface of medium roughness [13]. Such electrodes can be used as electrochemical sensors to determine the concentration of nitrate ions in aqueous media.

The aim of the work is to establish the influence of the medium roughness of the electrode surface on the kinetics of the non-stationary electrochemical process of cathodic reduction of nitrate ion under conditions of mixed transport-kinetic control under potentiostatic polarization.

The tasks of the work are as follows:

1. To synthesize copper coatings with different roughness by electrodeposition and to determine the main microscopic and integral parameters of their surface morphology.
2. To determine the range of electroreduction potentials of the nitrate ion in an acidic sulfate medium on the obtained copper coatings under the potentiodynamic conditions of cathodic polarization, to establish the general nature of the kinetic limitations of the process and to determine the conditions for the implementation of mixed transport-kinetic control.
3. To identify the role of the roughness of synthesized copper coatings in the kinetics of cathodic reduction of NO_3^- ions under conditions of mixed transport-kinetic control.

2. Experimental

The studies were carried out on two copper coatings with a thickness of ~1 μm obtained by galvanostatic deposition at a current density of -15 mA/cm^2 from acidified solutions of copper sulfate onto a carbon-metal electrode (NTF Volta LLC). To vary the morphological state of the copper coatings, various organic additives were introduced into the sulfate solution of copper plating [22] (Table 1): polyethylene glycol of various molar weights (PEG-1500, PEG-4000), disodium salt of 4,4-dithiobenzenedisulfonic acid (DTBS) and 2-aminobenzothiazole (ABT). A copper plate was used as an auxiliary electrode during electrodeposition, and the silver chloride reference electrode (OOO NPP Tomanalit) was located in a separate vessel, which was connected to the cell by an electrolytic bridge filled with agar-agar with a saturated solution of potassium nitrate.

Table 1. Composition of solutions for galvanostatic deposition of copper coatings

Coating	Composition
No. 1	156 g/l $CuSO_4{\cdot}5H_2O$ + 10 g/l H_2SO_4 + 50 mg/l HCl + 0.5 g/l PEG-1500
No. 2	156 g/l $CuSO_4{\cdot}5H_2O$ + 10 g/l H_2SO_4 + 50 mg/l HCl + 0.12 g/l DBTA + 0.5 g/l PEG-4000 + 0.5 g/l ABT

Before coating, the surface of the carbon-metal electrode was standardized by sequential polishing on a velvet fabric with a diamond suspension, reducing the grain size (1.5, 1.0, 0.5 microns) to a mirror surface. After polishing, the electrode was washed twice with distilled water (bidistillate). Next, to clean its surface from abrasive particles and degrease it, it was sequentially placed in an ultrasonic bath for 3 minutes, first in a container with acetone and then with bidistillate, after which the surface of the electrode was dried using filter paper.

The kinetics of the model reaction of the electroreduction of nitrate ion on the obtained copper coatings was studied by transient electrochemical methods of voltammetry and chronoammetry. Cathodic polarization curves were recorded over a range from an open-curcuit potential value to –700 mV at various potential scan rates (from 10 to 100 mV/s). Chronoamperometric measurements were carried out at a cathodic potential of –470 mV, corresponding to the implementation of a mixed transport-kinetic control, recording current decay curves for 1000 s. A working solution of 10 mM KNO_3 + 100 mM H_2SO_4 was deaerated with chemically pure argon directly in an electrochemical cell for 90 minutes before the experiment. Electrochemical measurements were carried out in a three-electrode glass cell with undivided cathode and anode spaces. The reference electrode was a silver chloride electrode (OOO NPP Tomanalit), an auxiliary graphite electrode.

All solutions were prepared with water of analytical quality (GOST R 52501-2005) using a Livam UPVA-5 system (electrical conductivity 0.8–1.0 μS/cm) using reagents of analytical grade.

Electrochemical studies were performed on IPC-compact or P-20X potentiostats. The potentials are given relative to a standard hydrogen electrode. The current density is calculated per unit geometric surface area of the electrode.

The morphological state of the surface and quantitative parameters of the microgeometry of synthesized copper coatings were evaluated using atomic force microscopy (AFM) data. The AFM method was performed using a Solver P47PRO device in a semi-contact scanning mode of a sample using HA_FM composite cantilevers (resonant frequency 74.025 kHz, elastic constant of the cantilever console 3.5 N/m, radius of the probe tip curvature was 10 nm). AFM images were obtained at three different 10x10 mm^2 scan zones. The roughness parameters were found according to the statistical processing of AFM data in the Gwyddion software package.

The area of electrodeposited copper coatings was determined by the underpotential Pb monolayer deposition (UPD Pb) in an argon-deaerated solution of 1 mM $PbCl_2$ + 1 mM $HClO_4$ at a potential scan rate of 10 mV/s in accordance with the procedure described in [23]. 10 cycles were recorded in the range of potentials from 130 to -320 mV, and after stabilization of the voltammogram (Fig. 1), a charge corresponding to the deposition of a monolayer of lead was found:

$$Q_{\mathrm{UPD,Pb}} = \frac{1}{V}\int_{E_1}^{E_2} i(E)\,dE\,, \tag{1}$$

where $Q_{\mathrm{UPD,Pb}}$ is the charge, mC/cm^2; V is the potential scan rate, mV/s; $i(E)$ is the current density at a given potential; E is the potential, mV.

The roughness factor was calculated using the formula:

$$f_{\mathrm{r}} = \frac{Q_{\mathrm{UPD,Pb}}}{Q_S}\,, \tag{2}$$

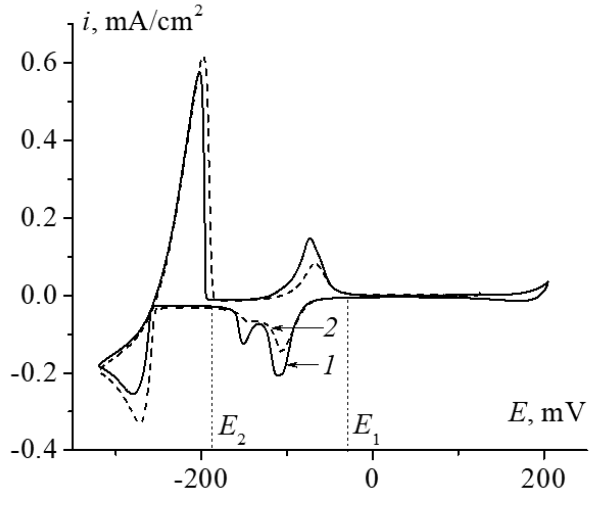


Fig. 1. Cyclic voltammograms obtained for coatings No. 1 (*1*) and No. 2 (*2*) in a solution of 1 mM $PbCl_2$ + 0.01 M $HClO_4$ at a scan rate of 10 mV/s

where Q_s is the charge required to form a monolayer of lead, which was assumed to be equal to ~250 mC/cm^2 [23].

3. Results and discussion

3.1. Morphology and roughness of electrodeposited copper coatings

Fig. 2 shows surface images, as well as 3D and 2D profiles of synthesized galvanic copper coatings obtained by atomic force microscopy. It can be seen that both coatings are morphologically heterogeneous, while the maximum height of irregularities for coating No. 1, deposited from a solution with the addition of polyethylene glycol PEG-1500, is higher than for coating No. 2, obtained from an electrolyte containing a complex of organic additives. This is consistent with the data from [22], in which scanning electron microscopy confirmed the smoothing of the surface of an electroplated copper coating deposited from a sulfate solution in the presence of PEG, DTBS, and ABT. A visual comparison of the morphology of the obtained coatings is confirmed by the analysis of quantitative parameters characterizing the surface roughness (Table 2). Indeed, the average and root mean square (RMS) roughness decreases by about one and a half times during the transition from coating No. 1 to No. 2, while the average distance between neighboring irregularities, on the contrary, increases. This is reflected in a decrease in the ratio of the total area of the scanned zone to its projection, which is indicated in Table 2 by f_r(AFM). However, this value, which is quite close to unity, turned out to be significantly underestimated compared to the roughness factor f_r(UPD) obtained by the electrochemical method. This can be explained by the fact that the atomic force microscopy method allows us to characterize the roughness of a relatively small area of the electrode surface limited by the AFM scanning area (in this work, 10×10 μm^2 = 10^{-6} cm^2). While electrochemical methods make it possible to determine the surface area of the electrode as a whole. The geometric area of the working electrode in operation is 0.07 cm^2, which exceeds the size of the AFM scanning site by $7\cdot10^4$ times. As a result, the AFM method makes it possible to register irregularities at the nano and micro levels, but it cannot, in principle, detect morphological irregularities on a larger scale that exceed the size of the scanning zone, which, however, contribute to the result of electrochemical measurements of the electrode area. At the same time, the previously detected decrease in the degree of morphological disorder during the transition from coating No. 1 to No. 2 continues in both cases of f_r(AFM) and f_r(UPD).

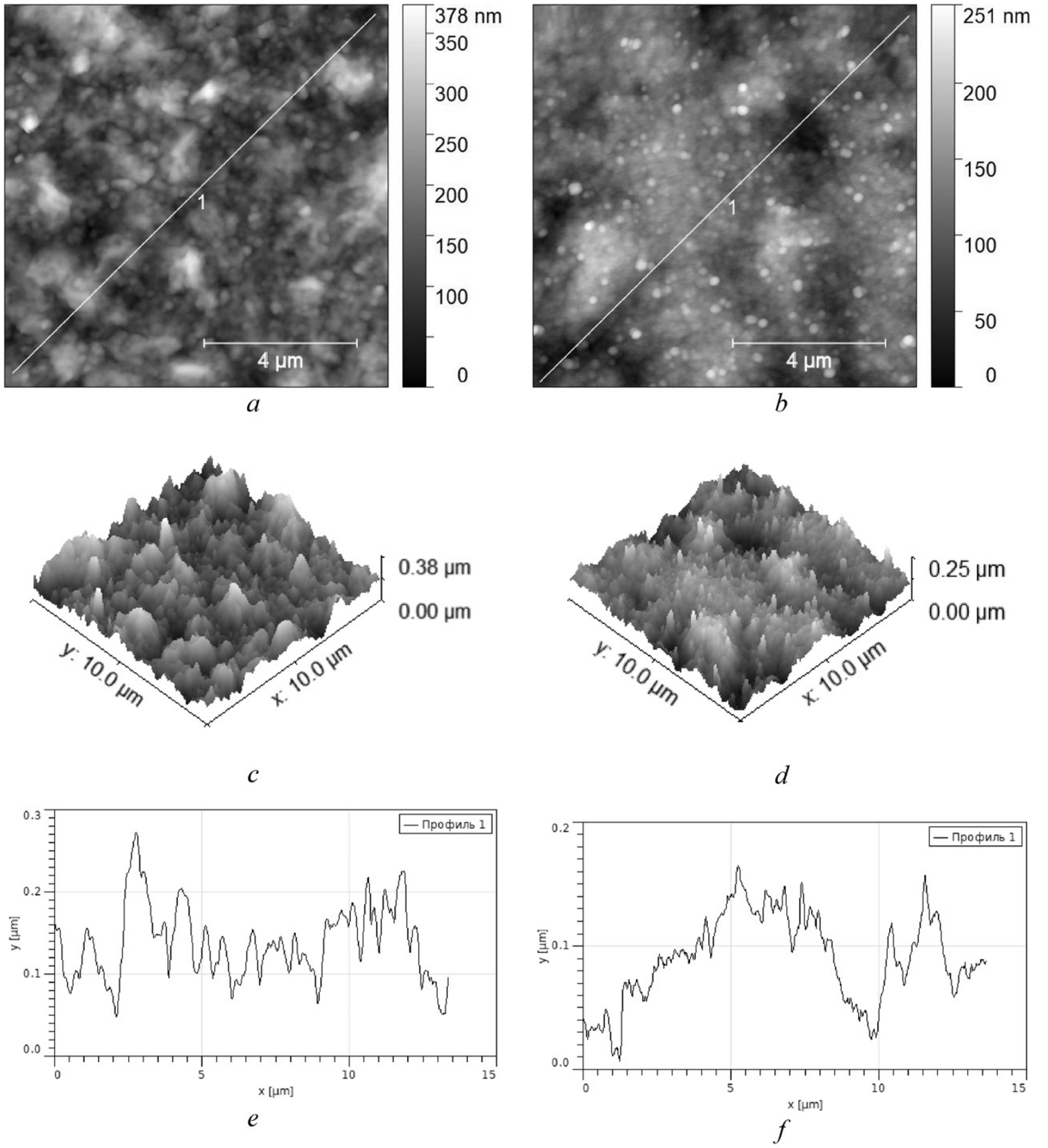
3.2. Voltammetry of electroreduction of nitrate ion on copper coatings

When potassium nitrate is introduced into a sulfuric acid solution, a maximum is recorded on the cathodic voltammograms in the range from −100 to −600 mV of both studied copper coatings (Fig. 3a). Considering that in the absence of KNO_3, the peaks on the polarization curves are not revealed in the same potential range (dotted line in Fig. 3a), the observed maximum in the voltammogram can be attributed to the process of the cathodic reduction of NO_3^- ions.

An increase in the potential scan rate V leads to an increase in the current density of the cathodic peak i_{max}, and this dependence is linearized in coordinates $i_{max} - V^{0.5}$ (Fig. 4a), which confirms the non-stationary nature of the diffusion transfer stage. Note that the obtained linear dependences are not extrapolated to the origin, which indicates the occurrence of a secondary cathodic process; the reaction of hydrogen evolution in the acid solution under study seems to be the most likely. In turn, the dependence of the peak potential E_{max} on lg$V$ is

Table 2. Roughness parameters of copper coatings

Parameter	Coating No. 1	Coating No. 1
RMS roughness (S_q), nm	53±5	32±2
Average roughness (S_a), nm	42±4	25±2
Average distance between neighbor irregularities (λ), nm	965±33	1561±107
Roughness factor f_r (AFM)	1.07±0.01	1.03±0.01
Roughness factor f_r (UPD)	2.56±0.02	1.89±0.02



a *b*

c *d*

e *f*

Fig. 2. AFM images of the surface (*a, b*), three-dimensional (*c, d*) and two-dimensional profiles (*d, e*) of copper coatings No. 1 (*a, c, e*) and No. 2 (*b, d, e*).

linear (Fig. 4b). As the scan rate increases, the peak potential becomes more negative. This indicates the irreversibility of the slow charge transfer stage of the process under study [24].

A comparison of the voltammograms on synthesized copper coatings (Fig. 3b) shows that the cathodic peak on the rougher coating No. 1 is formed at less negative potentials. The shift of the peak potential to the negative direction during the transition to a less rough coating is also confirmed by data obtained at different potential scan rates (Fig. 4a). Indeed, the $E_{\max}$–lg$V$ dependence for the coating No. 2 shifts by about 25 mV in the negative direction. Considering that the open-circuit potential practically does not change during the transition from one coating

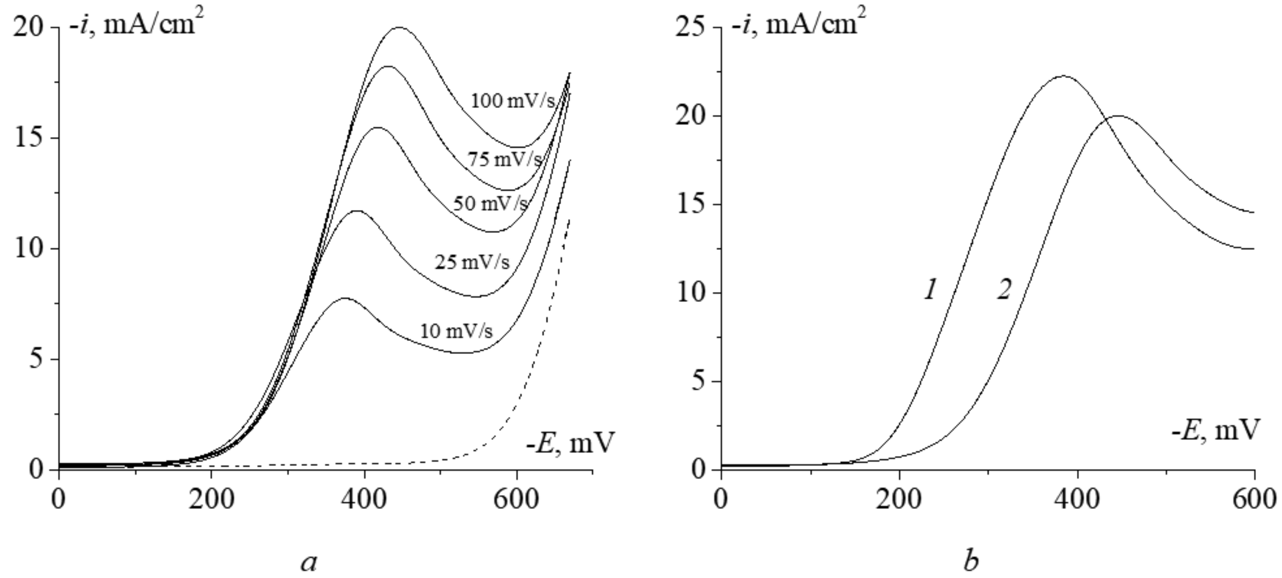


Fig. 3. Cathode voltammograms obtained in a solution of 10 mM KNO_3 + 100 mM H_2SO_4: (*a*) at different potential scan rates on copper coating No. 2; (*b*) at a rate of 25 mV/s on copper coatings No. 1 (*1*) and No. 2 (*2*). The dotted line is voltammogram obtained on copper coating No. 2 in a background solution of 100 mM H_2SO_4 at 25 mV/s

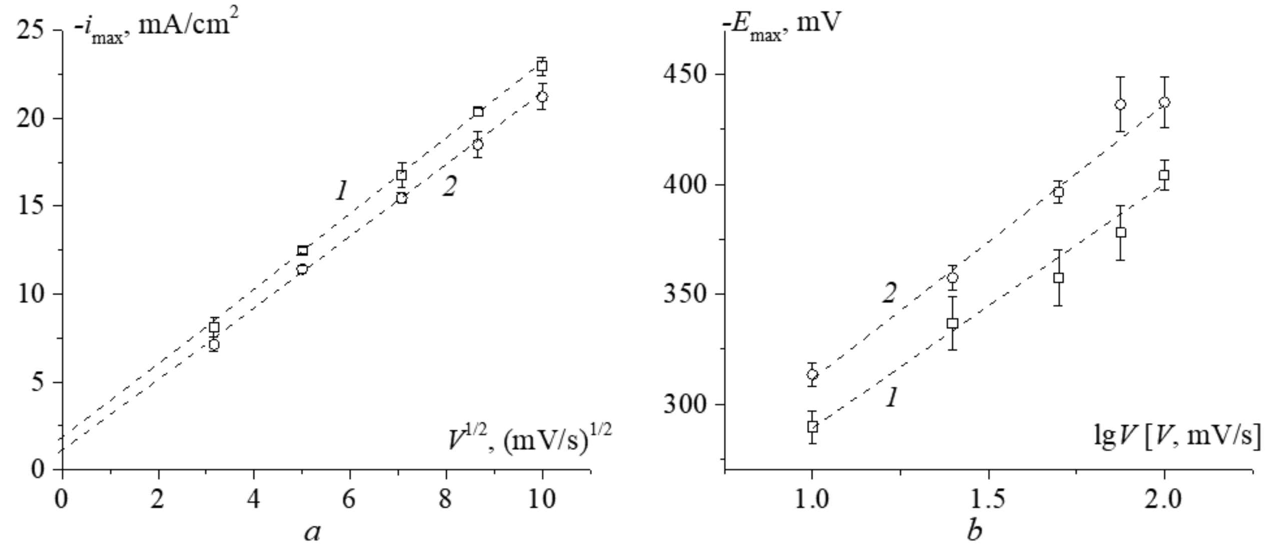


Fig. 4. Criterion dependences on the scan rate of maximum current density (*a*) and potential (*b*) of cathodic voltammograms of nitrate ion reduction in a solution of 10 mM KNO_3 + 100 mM H_2SO_4 on copper coatings No. 1 (*1*) and No. 2 (*2*)

to another, it can be concluded that the process of electroreduction of nitrate ion on a rougher coating No. 1 is characterized by a lower value of electrode polarization compared to coating No. 2.

In this case, the i_{max},$V^{1/2}$ dependences obtained for the two coatings, on the contrary, are quite close. The question arises: should the peak current density i_{max}, calculated for the geometric surface area of the electrode, be additionally normalized for the coating roughness factor? First, a preliminary estimation shows that such a correction by dividing by f_r leads to a fundamentally different result, namely, the i_{max} for the smoother coating No. 2 becomes higher than for coating No. 1, which contradicts the data on a decrease in cathodic polarization on the rougher coating No. 1. Secondly, a procedure is currently theoretically justified for the correct consideration of the roughness factor in voltammetry of only reversible [25] and completely irreversible [26] electrode processes. In the first case, the rate constant of the charge transfer stage k is very high, and the limiting stage is non-stationary diffusion transfer. A characteristic feature of this mode is the absence of dependence of the peak potential on the scan rate. Obviously, this situation is not realized in the system under study. For a completely irreversible process, on the contrary, the value of the constant k is very small, so the limiting stage is charge transfer. According to the theory of voltammetry of an irreversible process on a rough electrode [26], taking into account the roughness of the electrode surface is mandatory and amounts to dividing the current by the roughness factor only under conditions of high potential scan rates, namely, under the condition $\upsilon \gg 1$ where the dimensionless potential scan rate is determined by the expression:

$$\upsilon = (nF\lambda^2/RTD)\cdot V. \qquad (3)$$

Here F is the Faraday constant, R is the universal gas constant, T is the temperature, and D is the diffusion coefficient of the nitrate ion. In this paper, according to [27], $1.85\cdot10^{-5}$ cm^2/s is assumed. The total number of electrons involved in electroreduction was assumed to be $n = 8$. Indeed, according to the literature data [28-30] on copper surfaces in acidic solutions, the process of nitrate ion cathodic reduction is eight-electron and can be described by the following equation [31]:

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O. \qquad (4)$$

Assuming that the electrode process is completely irreversible, the estimate of the dimensionless rate for the system under study leads to values of $\upsilon = 0.002–0.02$. This means that the potential scan rates V used in the work are so low that the condition $u \ll 1$ is fulfilled, under which, according to [26], the roughness factor is not required, since by the time the peak is reached on the voltammogram, the diffusion front becomes flat. Therefore, the current density must be calculated for the geometric surface area of the electrode. Thus, the maximum currents on coatings No. 1 and No. 2 would have to coincide. However, this conclusion is valid only if a completely irreversible process is implemented, which, apparently, is not performed in the system under study due to mixed kinetic control, which causes the observed slight discrepancy in $i_{\max}$, $V^{1/2}$ dependencies (Fig. 4a).

3.3. Chronoamperometry of nitrate ion electroreduction under the mixed diffusion-kinetic control

The results of potentiostatic studies at $E = -470$ mV were used to quantify the role of morphological heterogeneity of the coatings in the mixed kinetics of electroreduction of NO_3^- ions. The choice of this value of the cathodic potential is due to the fact that, according to the results of potentiodynamic measurements, it corresponds to the maximum or decrease of the current on the voltammogram (Fig. 3a), when the contribution of diffusion mass transfer to the kinetics of the electrode process becomes significant enough, and therefore the probability of mixed kinetic control at the potentiostatic polarization is high. The shape of the current decay curves in Cottrell coordinates (Fig. 5) confirms this assumption. Indeed, at short times, the current is weakly time-dependent, which corresponds to a noticeable contribution from the kinetic stage. However, over time, a decrease in current becomes pronounced, and the rectification of the chronoamperogram in Cottrell coordinates observed at sufficiently long times indicates diffusion control of the process.

To interpret the obtained chronoamperograms and estimate the kinetic parameters of the charge transfer stage on two copper coatings of different roughness (heterogeneous rate constant k and exchange current density $i_0 = nFkc^{\mathrm{v}}$), we used the chronoamperogram equation obtained earlier in [13] for the electrochemical process occurring on a rough electrode in the mode of mixed transport-kinetic control:

$$i(t)_{\mathrm{rough}} = \\ = nFkc^{\mathrm{v}} \cdot \exp\left(\frac{k^2 t}{D}\right)\cdot \operatorname{erfc}\left(\frac{kt^{1/2}}{D^{1/2}}\right)\cdot \varphi\left(k, D, f_{\mathrm{r}}, \lambda, t\right). \qquad (5)$$

Here $\varphi\left(k, D, f_{\mathrm{r}}, \lambda, t\right)$ is the roughness function, which is the ratio of currents across rough and flat electrodes. The analysis showed [13] that the roughness function is equal to unity $\varphi = 1$ under the condition $\left(k^2 t / D\right) \gg 1$, i.e., at long times, and this condition is facilitated by the pronounced slowness of the diffusion stage when $\left(k\lambda / D\right) \gg 1$. In another limitimg case, when $\left(k^2 t / D\right) \ll 1$, i.e.

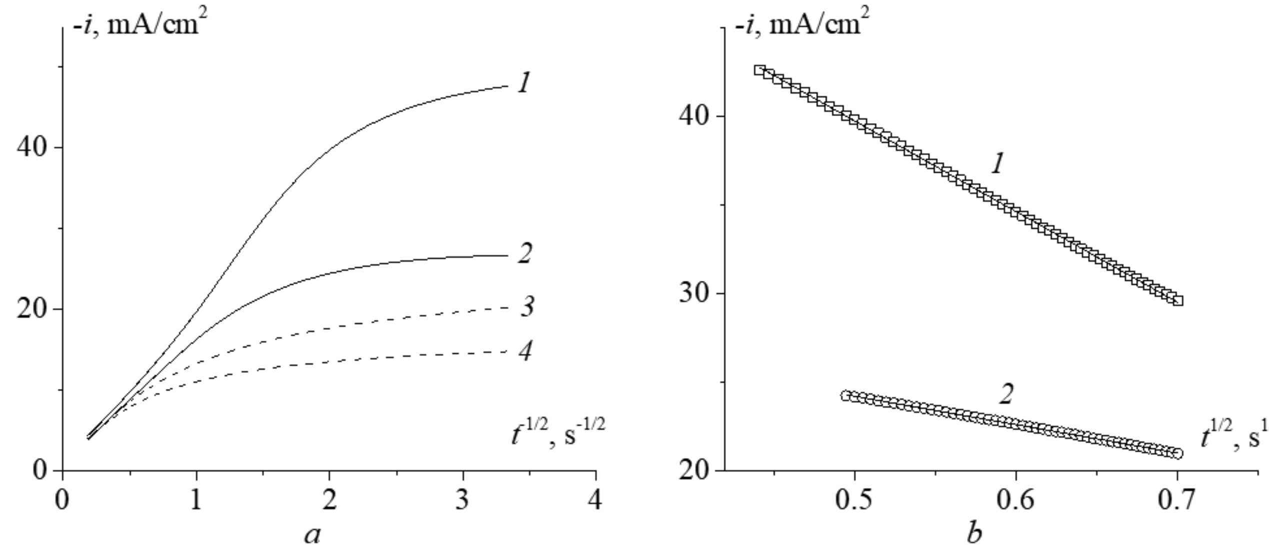


Fig. 5. (*a*) – Chronoamperograms of copper coatings No. 1 (*1*) and No. 2 (*2*) in a solution of 10 mM KNO_3 + 100 mM H_2SO_4 at a potential of -470 mV, rearranged in Cottrell coordinates. (*b*) – Initial sections of the current decay curves, linearized in the criterion $i,t^{1/2}$ coordinates

at short times, the roughness function is equal to the roughness factor $\varphi = f_r$, and the fulfillment of this condition is facilitated by the slowness of the charge transfer stage, when $(k^2t/D) \ll 1$. In the region of intermediate values, the roughness function gradually changes over time from f_r to 1 within the transition region. The position of the boundaries of this region strongly depends on the ratio of the rates of the kinetic and diffusion stages: as k decreases (the charge transfer stage slows down), the transition region shifts towards longer times and widens. Obviously, in this case, taking into account the roughness when calculating the current density is the most difficult, since it requires an estimation of the functional dependence $\varphi(k, D, f_r, \lambda, t)$.

Taking into account the properties of the roughness function, we obtained asymptotic relations for the chronoamperogram (5), which in two limiting cases is described by the following expressions:

$$i(t)_{\text{rough}} =$$

$$= \begin{cases} f_r \cdot nFkc^{\text{v}}\left(1 - \dfrac{2}{\pi^{1/2}}\dfrac{k}{D^{1/2}}t^{1/2}\right), \text{ if } \left(\dfrac{k^2t}{D}\right) \ll 1, & 6(\text{a}) \\ \dfrac{nFD^{1/2}c^{\text{v}}}{(\pi t)^{1/2}}, \text{ if } \left(\dfrac{k^2t}{D}\right) \gg 1. & 6(\text{б}) \end{cases}$$

It can be seen that at long times, the chronoamperogram does not include the roughness factor and is described by the well-known Cottrell equation [24], i.e. it corresponds solely to the diffusion control of the process on a flat electrode. This is confirmed by the linearization of the experimental current decay curves of both coatings at long times (Fig. 5a). Their coincidence for two coatings of different roughness is consistent with the fact that the roughness factor is not included in expression (6b), i.e. morphological heterogeneity no longer affects the rate of the electrode process in this time interval. Using formula (6b) and the slope of the linear sections of the $i,t^{1/2}$ curves (Fig. 5a), the total number of electrons involved in the process of electroreduction of the nitrate ion n » 8 was found, which is consistent with the literature data [28–31].

On the other hand, according to the ratio (6a), at short times the chronoamperogram should be linearized in the coordinates i – $t^{1/2}$, which is observed in the case of both copper coatings (Fig. 5b). Numerical comparison of expression (6a) with the initial sections of the experimental current decay curves using the roughness factor f_r (Table. 2), the total number of electrons $n = 8$ and the diffusion coefficient $D = 1.85 \cdot 10^{-5}$ cm²/s [27], the rate constant of the charge transfer stage k and the exchange current density $i_0 = nFkc^{\text{v}}$ were found (Table 3).

A comparison of the obtained values shows that the kinetic stage of nitrate ion cathodic

Table 3. Kinetic parameters of the electrochemical stage on copper coatings

Parameter	Coating No. 1 (f_r = 2.56)	Coating No. 2 (f_r = 1.89)
Heterogeneous rate constant k, cm/s	$(3.3\pm0.1)\cdot10^{-3}$	$(2.1\pm0.2)\cdot10^{-3}$
Плотность тока Exchange current density i_0, mA/cm^2	25.5±0.8	16.2±1.5

reduction on a rougher copper electrode is characterized by the higher rate constant and higher exchange current density. This indicates an increase in the electrocatalytic activity of copper in the reaction under study during the transition to electrodes characterized by a higher roughness factor.

It is important to note that this conclusion was obtained taking into account the normalization of the process rate to the true surface area within the framework of the theoretical model of chronoamperometry of an electrochemical process proceeding on a rough electrode in the mode of transport-kinetic control. Therefore, the revealed increase in the rate constant is not apparent, since it is not caused solely by a purely geometric increase in the overall surface area of the copper electrode.

Possible reasons for the increase in k and i_0 during the transition from coating No. 2 to coating No. 1 may be a change in the structure of the polycrystalline sample with the release of more catalytically active crystalline faces to the surface, an increase in the number of active adsorption centers due to an increase in the proportion of surface areas of small curvature, an increase in the concentration of surface defects of the sample. The identification of specific causes of the observed increase in the electrocatalytic activity of the copper coating was not an objective of this work and requires additional research.

The approach used in the work to determine the parameters of the kinetic stage allows us to correctly estimate the role of morphological heterogeneity in changing the electrocatalytic activity of a rough electrode, on the surface of which a complex electrochemical process takes place in the mode of transport-kinetic control. Within the framework of this approach, the contribution of the non-kinetic (diffusion) stage to the value of the rate of the process under study is quantified, and a purely geometric effect associated only with a change in the surface area of the electrode is revealed.

4. Conclusion

Two copper coatings with the different roughness factors (2.56±0.02 amd 1.89±0.02) and the size of the irregularities (the mean roughness of the coatings is 42±4 and 25±2 nm) were synthesized by galvanostatic electrodeposition from aqueous sulfate solutions with organic additives. The electroreduction of the nitrate ion in an acidic aqueous solution on both obtained coatings corresponds to the range of cathodic potentials from –100 to –600 mV relative to the standard hydrogen electrode. Analysis of characteristic parameters of voltammetry (maximum current density and peak potential) revealed the non-stationary nature of the diffusion transfer stage, the irreversibility of the slowed electrochemical stage of the process under study, and a decrease in electrode polarization on a rougher coating.

A mode of mixed transport-kinetic control of the process of nitrate ion electroreduction in an acidic medium at potentiostatic cathodic polarization has been revealed using the non-stationary chronoamperometry method. It is shown that the roughness effect does not contribute to the kinetics of the process at long times, when the non-stationary diffusion of NO_3^- ions is the rate-controlling stage.

Within the framework of the previously developed theoretical model of an electrochemical process occurring in a mixed kinetic mode on a rough electrode, it is shown that the current density recorded during the initial period of current decay should be normalized by the roughness factor. Based on this, an approach is proposed for estimating the main kinetic parameters of the charge transfer stage for a process occurring on rough electrodes in a mixed transport-kinetic mode. The approach is based on comparing the initial sections of the experimental current decay curves with an asymptotic relation describing the chronoamperogram at short times.

The application of this approach to the analysis of the data obtained for the two copper coatings synthesized in the work made it possible to establish that the heterogeneous rate constant and the exchange current density of the nitrate ion electroreduction increase with increasing roughness factor. This effect is not caused by a purely geometric increase in the true surface area of the electrode, and therefore it can be concluded that the electrocatalytic activity of copper in the reaction under study increases during the transition to rougher electrodes.

Author contributions

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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