

New method of the determination of specific surface of copper obtained by the electrodeposition

The specific surface of electrodeposited copper was determined using recently proposed way for the estimation of the real surface area of metal deposits. The obtained values of the specific surface of copper deposits were correlated with the corresponding morphologies of copper deposits.

Key words: electrodeposition; copper; specific surface of copper deposit.

1. INTRODUCTION

The specific surface of the electrodeposited metal, S_{sp} , is given by Eq. (1):

$$S_{sp} = \frac{S}{m} \quad (1)$$

where S represents the surface area of a deposit and m , mass of a metal obtained by electrodeposition process.

The mass of electrodeposited metal, m can be easily calculated using Faraday's law. According to Faraday's law, mass of the electrodeposited metal, m , is given by Eq. (2):

$$m = \frac{\eta_1 \int_0^t Idt}{n_e F} M \quad (2)$$

where n_e is the number of electrones involved in the metal deposition reaction, M is the atomic mass of the deposited metal, F is the Faraday constant, η_1 current efficiency of the electrodeposited metal and $\int_0^t Idt$ is the quantity of passed electricity.

On the other hand, the determination of real surface area of metal electrodeposits can represent problem because there is no unique and corresponding technique which would enable it. The real

surface of some metal deposits can be determined by the STM and AFM techniques (using the option *surface area diff.*, in the accompanying software package) but the application of these techniques is only suitable for compact and relatively smooth deposits. In order to solve this problem *in situ*, the new and relatively easy way for the estimation of real surface area has been developed recently in our research group [1, 2]. This method is based on the measurement of currents before and after electrodeposition at the corresponding overpotential and it will be presented later in Experimental. The determination of real surface of disperse deposits is especially difficult owing to very high and developed surface area of this deposit type.

For that reason, the aim of this work will be to estimate the possibility of determination of the specific surface of the electrodeposited metal by the use of this new method for the estimation of real surface area of metal deposits by measuring the active part of it. The obtained values of the specific surface will be correlated with the corresponding morphologies of metal deposits.

2. EXPERIMENTAL

Copper was potentiostatically deposited from 0.15 M CuSO_4 in 0.50 M H_2SO_4 , in an open cell, and at a room temperature of $(18.0 \pm 1.0)^\circ\text{C}$. Doubly distilled water and analytical grade chemicals were used for the preparation of the solution for electrodeposition of copper. Reference and counter electrodes were of a pure copper. The electrodepositions of copper were performed at overpotentials of 550, 700, 800 and 1000 mV, with different quantities of the electricity.

The electrodeposition processes and the determination of the real surface area of metal

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deposits were performed using experimental procedure described in Refs. [1, 2] in the following way: copper substrates (S_0) are covered with a thin copper film by electrodeposition at an overpotential of 300 mV during 2 min. After a relaxation of the diffusion layer for 15 min, the current at overpotential of 50 mV, I_0 , is recorded, being proportional to the original electrode surface area S_0 . The overpotential is then adjusted to the desired value and deposition is carried out. After the determined quantity of electricity had been reached, the overpotential is decreased to 50 mV and after relaxation of the diffusion layer for 15 min, the current, I_η , corresponding to the surface S generated during electrodeposition, is determined. The surface area of the deposit is then calculated using the equation (3).

$$S = S_0 \frac{I_\eta}{I_0} - S_0 = S_0 \left(\frac{I_\eta}{I_0} - 1 \right) \quad (3)$$

Copper deposits were examined by the scanning electron microscope (SEM) – model JOEL T20.

3. RESULTS AND DISCUSSION

The overpotentials of 550 and 700 mV belonging to the plateau of the limiting diffusion current density, while the overpotentials of 800 and 1000 mV were for 50 and 250 mV outside the plateau of the limiting diffusion current density [3].

According to Eqs. (1) – (3), the specific surface of the electrodeposited metal, S_{sp} , can be given by Eq. (4):

$$S_{sp} = \frac{S_0 \left(\frac{I_\eta}{I_0} - 1 \right)}{\frac{\int_0^t I dt}{n_e F} M} = \frac{n_e F S_0}{\eta_l M} \frac{1}{\int_0^t I dt} \left(\frac{I_\eta}{I_0} - 1 \right) \quad (4)$$

In this case, the number of electrons involved in the electrodeposition reaction, n_e is 2, the atomic mass of copper (M) is 63.54 g/mol and Faraday constant, F , is 96485 As/mol. In this investigation, the original electrode surface before electrodeposition, S_0 , was 0.50 cm².

The current efficiencies for the copper electrodeposition at overpotentials of 550, 700, 800 and 1000 mV are experimentally determined using procedure for the measurement of the hydrogen

evolution described in Ref. [3]. At the overpotential of 550 mV, the current efficiency for the copper electrodeposition was 100 % [3]. The current efficiency for the copper electrodeposition at the overpotential of 700 mV was ≈ 98.0 % [3]. At overpotentials of 800 and 1000 mV, the hydrogen evolution takes place, and consequently, current efficiencies for the copper electrodeposition are considerably smaller than those observed at lower overpotentials. At the overpotential of 800 mV, the current efficiency for the copper electrodeposition was 89.2 %, while at the overpotential of 1000 mV, this value reached up to a value of 70.0 % [3].

Current I_η and I_0 are obtained in the way described above.

The estimated values of the specific surface of the electrodeposited copper in the way described above are given in Tables (1) – (4) in APENDIX I.

The dependence of the specific surface of the electrodeposited copper on the quantity of the electricity is given in Fig. 1. Two groups of the dependences of the specific surface of the electrodeposited copper on the quantity of the electricity can be observed from this Figure.

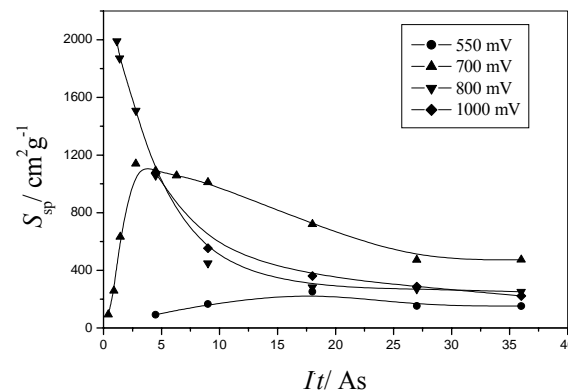


Fig. 1. The dependence of the specific surface of the electrodeposited copper on the quantity of the electricity.

The first one is observed for overpotentials of 550 and 700 mV at which the hydrogen evolution does not exist (550 mV) or it is very small (700 mV). The characteristic of this group is maximum of the specific surface which is a function of the quantity of the electricity. The increase of the overpotential led to the decrease of the quantity of the electricity needed to reach maximum of the specific surface.

The analysis of SEM microphotographs of copper deposits obtained at these overpotentials showed that maximum values of the specific

surface correspond to the formation of cauliflower structures. Figure 2 shows the copper deposit obtained at the overpotential of 550 mV with the quantity of the electricity of 18.0 As (Fig. 2a) and the copper deposit obtained at the overpotential of 700 mV with the quantity of the electricity of 4.5 As (Fig. 2b).

The decrease of the specific surface with the increase of the quantity of the electrodeposited copper is accompanied by the formation of dendritic forms. Figure 3 shows the copper deposit obtained at the overpotential of 550 mV with the quantity of the electricity of 36.0 As, and can be seen from this Figure that the formed copper dendrites are relatively alone (Fig. 3a) and this deposit represents a mixture of cauliflower and dendritic forms (Fig. 3b).

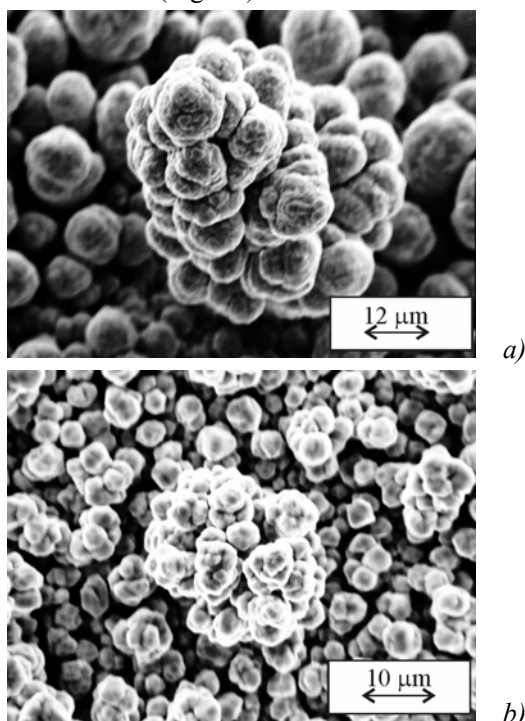


Fig. 2. Copper deposits obtained at the overpotential of: a) 550 mV; the quantity of the electricity: 18.0 As, b) 700 mV; the quantity of the electricity: 4.5 As

On the other hand, copper deposits obtained at the overpotential of 700 mV with quantities of the electricity larger of 4.5 As showed purely dendritic forms (Fig. 4). Copper dendrites were consisted of corn-cob – like elements, and the whole electrode surfaces were covered with dendritic forms after the electrodeposition with quantities of the electricity larger of approximately 10.0 As.

Anyway, the values of S_{sp} obtained at 700 mV before initiation of the dendritic growth, i.e. with

low quantities of the passed electricity, are similar to those obtained at 550 mV but with larger quantities of the electricity. Besides, the farther increase of S_{sp} with the increasing quantity of the electricity before dendritic growth initiation is because of the decrease of size of deposit grains. After formation of precursors of dendrites and dendrites the S_{sp} strongly increases and remains approximately constant up to quantity of electricity at which the overlap of dendrites begins. At larger quantities of electricity the S_{sp} value decreases up to constant value, which probably corresponds to the established front of dendritic deposit growing to the bulk of the solution.

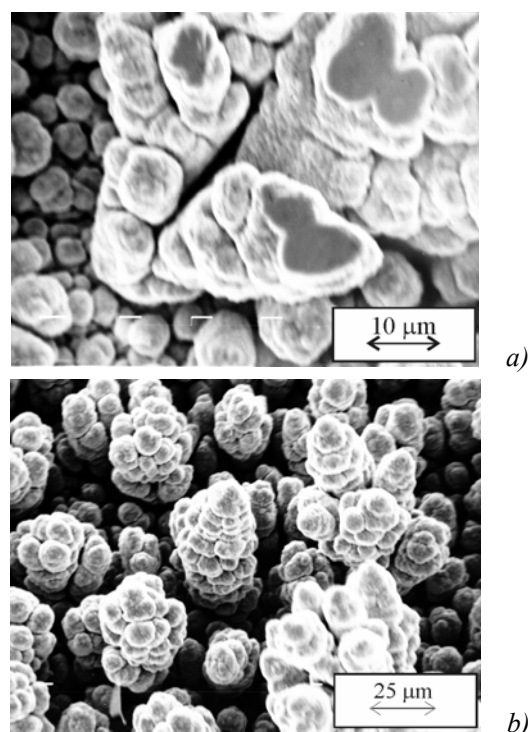


Fig. 3. The copper deposit obtained at the overpotential of 550 mV with the quantity of the electricity of 36.0 As: a) x 2000, b) x 750.

The second group of the dependences of the specific surface of the electrodeposited copper on the quantity of the electricity is obtained for the overpotentials of 800 and 1000 mV. As mentioned above, the hydrogen evolution takes place during the electrodeposition at these overpotentials. It can be seen from Fig. 1 that there is not maximum the specific surface in a function of the quantity of the electrodeposited metal. The specific surface of the electrodeposited copper decreased with the increase of the quantity of the electricity. This is due to the overlap of the agglomerates of grains in prolonged electrodeposition. At low deposition times

S_{sp} is very large. Also, it can be observed from Fig. 1 that there is not essential difference between the specific surfaces obtained at the overpotential of 800 mV and ones obtained at 1000 mV. SEM analysis of copper deposits obtained at these overpotentials showed that copper deposits were a very porous, with large craters or holes formed of the attachment of the hydrogen bubbles (these copper structures can be denoted as "honeycomb" structures [3]). The typical copper deposits obtained at overpotentials of 800 and 1000 mV are shown in Fig. 5. From this Figure can be noticed that morphologies of these copper deposits consisted of copper grains grouped in small aggregates. However, copper dendrites are not formed during electrodepositions at these overpotentials.

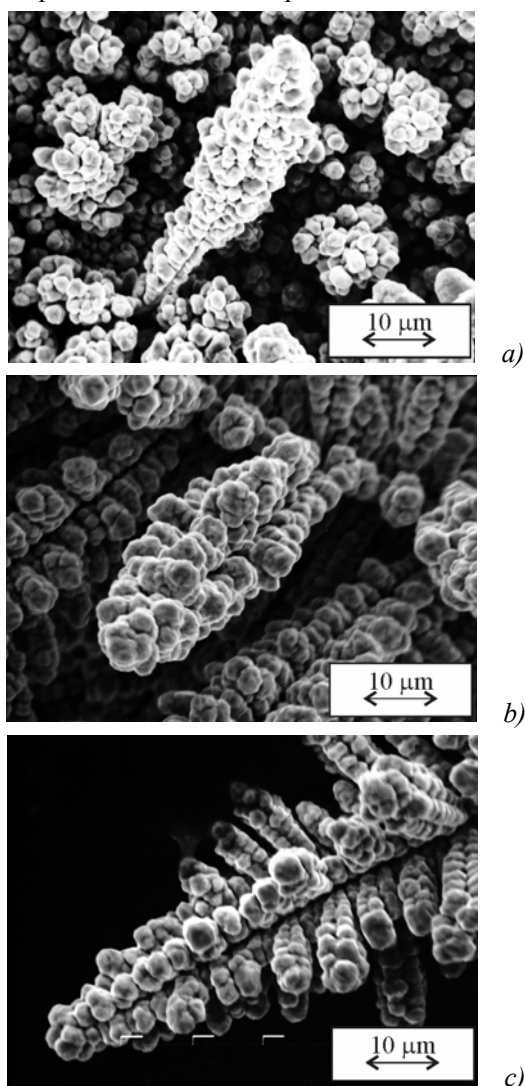


Fig. 4. Copper deposits obtained at the overpotential of 700 mV. The quantity of the electricity: a) 9.0 As, b) 18.0 As, c) 36.0 As.

Figure 6 shows the dependence of the specific surface of the electrodeposited copper on the overpotential of the copper electrodeposition for different quantities of the electricity. It can be seen from this Figure the existence of maximum of the specific surface of the electrodeposited copper at the overpotential of 700 mV for all examined quantities of the electricity except for the quantity of the electricity of 4.5 As. Hence, according to this method, dendritic deposits showed to have the largest electrode surface area.

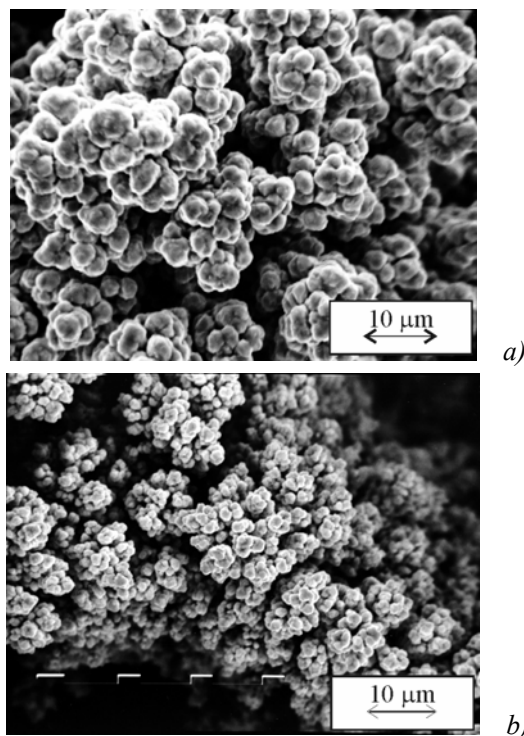


Fig. 5. Copper deposits obtained with the quantity of the electricity of 36.0 As and at the overpotential of: a) 800 mV, b) 1000 mV. Magnification: $\times 2000$.

The decrease of the specific surface with the increase of overpotentials of the electrodeposition from 700 to 800 mV can be explained by the change of the hydrodynamic conditions in the near electrode layer by the evolved hydrogen. The range of overpotentials between 700 and 800 mV represents transient region of overpotentials when the hydrogen evolution becomes an enough intensive to effect on the electrodeposition process, i.e. to change hydrodynamic conditions in the near electrode layer. Then, the electrodeposition takes place at overpotential which is effectively lower than the specified one and, for that reason, copper morphologies obtained at overpotentials of 800 and 1000 mV are similar to ones obtained at lower

overpotentials before the initiation of dendritic growth [3].

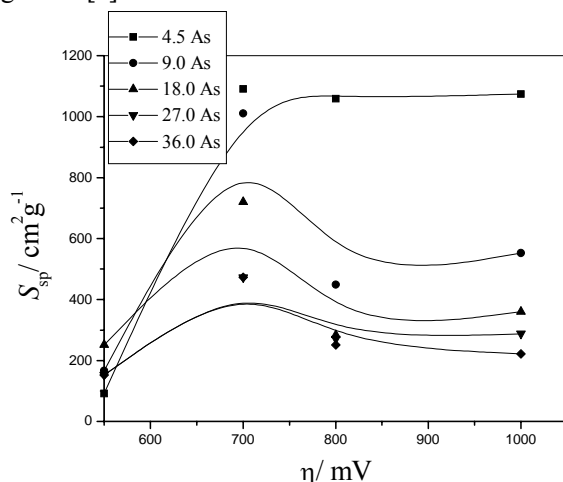


Fig. 6. The dependence of the specific surface of the electrodeposited copper on the overpotential of the copper electrodeposition.

The absence of maximum of the specific surface of the electrodeposited copper for deposits obtained with the quantity of the electricity of 4.5 As can be explained by the absence of the formation of dendritic forms for the copper deposit obtained at the overpotential of 700 mV with this quantity of the electricity. Copper deposits obtained with this quantity of the electricity were relatively similar each others (no dendritic growth!).

Also, it is necessary to note again that copper dendrites formed during electrodepositions at overpotentials of 550 mV and 700 mV with the quantity of the electricity of 36.0 As were completely different. As mentioned earlier, copper dendrites formed at 550 mV were relatively alone, and this deposit represented the mixture of cauliflower like and dendritic forms (Fig. 3). On

APENDIX I

The values of the specific surface of the electrodeposited copper obtained at overpotentials of 550, 700, 800 and 1000 mV with different quantities of the electricity

Table 1 - The estimated values of the specific surface of the electrodeposited copper obtained at the overpotential of 550 mV

	Quantity of the electricity/ As	I_0 / mA	I_η / mA	$S_{sp}/\text{cm}^2 \text{g}^{-1}$
1.	4.5	1.60	2.10	92.19
2.	9.0	1.50	3.20	166.20
3.	18.0	1.00	4.50	251.07
4.	27.0	0.90	3.70	152.44
5.	36.0	0.90	4.80	152.29

the other hand, the copper deposit obtained at 700 mV was much ramified dendritic structure (Fig. 4). This clear difference is confirmed and by the different measured specific surfaces of these copper deposits.

Finally, it was shown by the proposed method that dendritic copper deposits had the largest electrode surface area, i.e. these deposits are with maximum of the specific surface. This is consistent with that shown in Ref. [4], where Chassaing et al. showed by impedance spectroscopy that the electrodeposition of ramified deposits is related to the large increase of the deposit surface area. In this stage, this agreement makes the proposed method to be very relevant for the estimation of specific surface of electrodeposited metal.

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Table 2 - The estimated values of the specific surface of the electrodeposited copper obtained at the overpotential of 700 mV

	Quantity of the electricity/ As	I_0 / mA	I_η / mA	$S_{sp}/\text{cm}^2 \text{ g}^{-1}$
1.	0.42	0.76	0.78	93.20
2.	0.90	0.78	0.90	258.42
3.	1.45	0.84	1.35	631.53
4.	2.80	0.90	2.80	1139.31
5.	4.50	0.96	4.00	1091.08
6.	6.30	0.87	4.60	1057.06
7.	9.0	0.72	4.95	1010.58
8.	18.0	0.84	7.90	719.65
9.	27.0	0.80	7.40	472.04
10.	36.0	0.80	9.60	473.03

Table 3 - The estimated values of the specific surface of the electrodeposited copper obtained at the overpotential of 800 mV

	Quantity of the electricity/ As	I_0 / mA	I_η / mA	$S_{sp}/\text{cm}^2 \text{ g}^{-1}$
1.	1.16	1.25	3.00	1991.76
2.	1.40	1.05	2.70	1870.84
3.	2.80	1.18	4.10	1507.96
4.	4.50	1.20	4.60	1059.05
5.	9.0	1.35	4.60	449.06
6.	18.0	1.45	5.80	283.25
7.	27.0	1.30	6.90	270.44
8.	36.0	1.10	7.00	250.84

Table 4 - The estimated values of the specific surface of the electrodeposited copper obtained at the overpotential of 1000 mV

	Quantity of the electricity/ As	I_0 / mA	I_η / mA	$S_{sp}/\text{cm}^2 \text{ g}^{-1}$
1.	4.5	1.25	4.00	1073.70
2.	9.0	1.28	4.20	553.04
3.	18.0	1.35	5.40	359.96
4.	27.0	1.35	6.20	287.41
5.	36.0	1.25	5.85	221.53

REZIME

NOVI METOD ODREĐIVANJA SPECIFIČNE POVRŠINE ELEKTROHEMIJSKI ISTALOŽENOG BAKRA

Specifična površina elektrohemijski istaloženog taloga bakra je bila određena korišćenjem nedavno predloženim načinom za procenu realne površine taloga metala. Dobijene vrednosti specifične površine taloga bakra su bile povezane sa odgovarajućim morfologijama taloga bakra.

Ključne reči: elektrohemijsko taloženje; bakar; specifična površina taloga bakra