

The estimation of solid copper surface tension in copper sulfate solutions

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(Received 1 July 2002)

Abstract: In metal electrodeposition in the limiting diffusion current density range, the deposition current density remains constant regardless of the deposition overpotential used. At the same time, the larger the deposition overpotential is the more disperse is the formed deposit, which is characterised by an increased specific surface. The difference in the specific surface of disperse deposits obtained at two different overpotentials in the limiting diffusion current density range is correlated with the difference between the deposition overpotentials. A method for the estimation of the surface tension of solid copper in copper sulfate solutions is also proposed.

Keywords: interfacial energy copper-copper sulfate solution, specific surface of copper powder.

INTRODUCTION

It is well known that the surface coarseness during potentiostatic electrodeposition under mixed activation/diffusion control increases with increasing deposition current density.^{1,2} It also increases during potentiostatic electrodeposition at the limiting diffusion current density with increasing overpotential,^{3,4} resulting in the formation of disperse deposits. The last effect can be easily explained. In the limiting diffusion current density range, the deposition current density is practically the same, being independent of the deposition overpotential.

The deposition overpotential, η , in the region of mixed activation – diffusion control is given by:

$$\eta = \frac{b_c}{2.3} \ln \frac{j}{j_0} + \frac{b_c}{2.3} \ln \frac{1}{1 - \frac{j}{j_L}} \quad (1)$$

where b_c is the cathodic Tafel slope and j , j_0 and j_L are the deposition, the exchange and the limiting current density, respectively. The activation part of the deposition overpotential required for the charge transfer, η_a , given by Eq. (2):

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$$\eta_a = \frac{b_c}{2.3} \ln \frac{j}{j_0} \quad (2)$$

and the rest of the overpotential, η_{diff} , given by Eq. (3):

$$\eta_{\text{diff}} = \frac{b_c}{2.3} \ln \frac{1}{1 - \frac{j}{j_L}} \quad (3)$$

is due to mass transfer limitations. In the limiting diffusion current density range, Eq. (1) can be rewritten in the form

$$\eta = \frac{b_c}{2.3} \ln \frac{j_L - \Delta j}{j_0} + \frac{b_c}{2.3} \ln \frac{1}{1 - \frac{j_L - \Delta j}{j_L}} \quad (4)$$

where

$$\Delta j = j_L - j \ll j_L \quad (5)$$

Hence, if $j \rightarrow j_L$,

$$\eta_a = \frac{b_c}{2.3} \ln \frac{j_L}{j_0} \quad (6)$$

being equal to the critical overpotential for the initiation of dendritic growth⁴ and equal for all the overpotentials on the limiting diffusion current density plateau. At the same time, for $j \rightarrow j_L$

$$\eta_{\text{diff}} \rightarrow \infty \quad (7)$$

It is obvious that a very small increase in the current density, which can be neglected relative to the current density close to the limiting diffusion current density, causes a large increase in deposition overpotential. Hence, the charge transfer overpotential and the ohmic drop in the solution remain the same for all overpotentials belonging to the limiting diffusion current density plateau, regardless of the deposition overpotential. This is because both of them depend on the current density only. On the other hand, an increase of the deposition overpotential in the limiting diffusion current density range causes a strong increase of the dispersity and an increase of the specific surface area of metal deposits. Hence, it seems reasonable to assume that the difference in deposition overpotential can be related to the increase of the specific surface of the deposited metal by the relation:⁵

$$\gamma(S_2 - S_1) = (\eta_2 - \eta_1) \int_0^t I dt \quad (8)$$

where I is the deposition current, t is the deposition time, η_2 and η_1 are the deposition overpotentials being within the limiting diffusion current density range, S_2 and S_1 are the surface areas of electrodeposits obtained by quantity of electricity Q :

$$Q = \int_0^t Idt \quad (9)$$

at the overpotentials η_2 and η_1 , respectively, and γ is the surface tension of solid copper.

Eq. (8) can be rewritten in the form:

$$\gamma = \frac{(\eta_2 - \eta_1) \int_0^t T dt}{(S_2 - S_1)} \quad (10)$$

for the direct determination of the surface tension of solid copper in sulfate solutions.

EXPERIMENTAL

The electrodepositions of copper were performed potentiostatically from: 0.10 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$, 0.15 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$ and 0.20 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$ onto a stationary platinum wire electrode ($S_0 = 0.45 \text{ cm}^2$) in an open cell at room temperature (18.0 ± 1.0 °C). The polarization curve was determined and different quantities of copper were deposited at different overpotentials by the following procedure.

The platinum substrate was covered with a thin copper film by deposition at an overpotential of 300 mV for 2 min, and after allowing the diffusion layer to relax for 15 min, the current at an overpotential of 50 mV $I_{50,0}$ was recorded, being proportional to the surface layer of the electrode (0.45 cm^2). The overpotential was then adjusted to the desired value and deposition was carried out. After the required quantity of electricity had been reached, the overpotential was decreased to 50 mV and, after relaxation of the diffusion layer for 15 min, the current, $I_{50,\eta}$, corresponding to the surface S generated during the deposition, $I_{50,\eta}$ was determined as well as the surface area S from:

$$S = S_0 \frac{I_{50,\eta}}{I_{50,0}} \quad (11)$$

During the depositions $I-t$ dependences were recorder and the quantity of electricity was determined by graphical integration.

RESULTS AND DISCUSSION

The polarization curves for copper deposition are presented in Fig. 1, from which the positions of the deposition overpotentials on the limiting diffusion current density plateaus can be seen, the results of the surface tension estimations are given in Table I for copper electrodeposition from 0.10 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$. Table II for copper electrodeposition from 0.15 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$ and Table III for copper electrodeposition from 0.20 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$.

It can be seen from Table I–III that the agreement between the results of different determinations is good. The calculated average values of the surface tensions were $(2.8 \pm 0.4) \text{ J cm}^{-2}$ for 0.10 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$, $(2.7 \pm 0.3) \text{ J cm}^{-2}$ for 0.15 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$ and $(2.9 \pm 0.5) \text{ J cm}^{-2}$ for 0.20 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$.

TABLE I. Estimated values of the surface tension: 0.10 M CuSO₄ + 0.50 M H₂SO₄

Number of measurement	$It/A\ s$	η_2/mV	η_1/mV	S_2/cm^2	S_1/cm^2	$\gamma/J\ cm^{-2}$
1.	8.64	650	400	1.69	0.576	1.94
2.	8.64	600	400	1.35	0.576	2.23
3.	8.64	650	400	1.38	0.519	2.51
4.	8.64	600	400	1.23	0.519	2.43
5.	8.64	650	400	1.28	0.589	3.12
6.	8.64	600	400	1.22	0.589	2.74
7.	12.96	650	400	1.64	0.543	2.95
8.	12.96	600	400	1.48	0.543	2.77
9.	12.96	650	400	1.53	0.532	3.25
10.	12.96	600	400	1.49	0.532	2.71
11.	12.96	650	400	1.69	0.589	2.94
12.	12.96	600	400	1.54	0.589	2.72
13.	17.28	650	400	1.95	0.630	3.27
14.	17.28	600	400	1.52	0.630	3.88
15.	17.28	650	400	2.07	0.459	2.68
16.	17.28	600	400	1.92	0.459	2.37
17.	17.28	650	400	2.01	0.658	3.20
18.	17.28	600	400	1.77	0.658	3.11

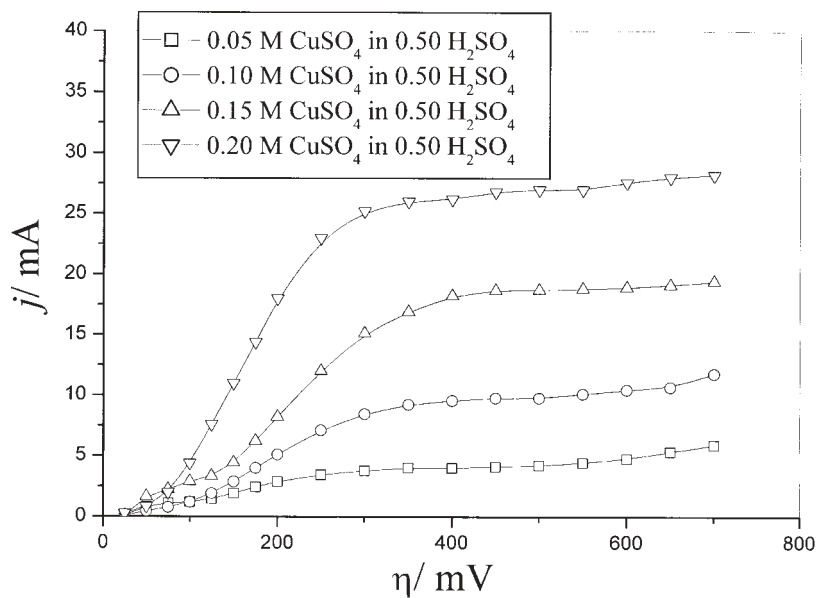


Fig. 1. Polarization curve for the cathodic process of copper deposition from: 0.05 M CuSO₄ in 0.50 M H₂SO₄ (□), 0.10 M CuSO₄ in 0.50 M H₂SO₄ (○), 0.15 M CuSO₄ in 0.50 M H₂SO₄ (Δ) and 0.20 M CuSO₄ + 0.50 M H₂SO₄ (∇), onto platinum electrode at room temperature.

TABLE II. Estimated values of the surface tension: 0.15 M CuSO₄ + 0.50 M H₂SO₄

Number of measurement	$It/A s$	η_2/mV	η_1/mV	S_2/cm^2	S_1/cm^2	$\gamma/J cm^{-2}$
1.	8.64	600	400	1.03	0.450	2.98
2.	8.64	600	400	1.30	0.450	2.40
3.	8.64	650	400	1.54	0.450	2.40
4.	8.64	600	400	1.11	0.450	2.62
5.	8.64	650	400	1.41	0.450	2.25
6.	8.64	650	300	1.41	0.480	3.25
7.	8.64	600	450	1.11	0.540	2.27
8.	8.64	650	400	1.30	0.550	2.88
9.	8.64	600	400	1.19	0.550	2.70
10.	4.32	650	400	0.970	0.540	2.51
11.	4.32	650	400	0.95	0.510	2.46
12.	12.96	650	400	1.80	0.770	3.15
13.	12.96	600	400	1.69	0.770	2.82
14.	12.96	650	400	1.875	0.814	3.05

TABLE III. Estimated values of the surface tension: 0.20 M CuSO₄ + 0.50 M H₂SO₄

Number of measurement	$It/A s$	η_2/mV	η_1/mV	S_2/cm^2	S_1/cm^2	$\gamma/J cm^{-2}$
1.	8.64	650	400	1.55	0.490	2.04
2.	8.64	600	400	1.27	0.450	2.22
3.	8.64	650	400	1.49	0.500	2.18
4.	8.64	600	400	1.62	0.500	2.61
5.	8.64	650	400	1.41	0.525	2.44
6.	8.64	600	400	1.08	0.525	3.11
7.	12.96	650	400	1.80	0.712	2.98
8.	12.96	600	400	1.50	0.713	3.29
9.	12.96	650	400	1.73	0.571	2.80
10.	12.96	600	400	1.56	0.571	2.62
11.	12.96	650	400	1.61	0.612	3.24
12.	12.96	600	400	1.48	0.612	2.99
13.	17.28	650	400	1.93	0.727	3.59
14.	17.28	600	400	1.65	0.727	3.75
15.	17.28	650	400	1.91	0.467	2.99
16.	17.28	600	400	1.64	0.467	2.95
17.	17.28	650	400	1.80	0.658	3.78
18.	17.28	600	400	1.72	0.658	3.25

The results obtained can be verified in the following way. It is well known that at deposition overpotentials larger than some critical value the formed deposit is not compact, but powdery and characterised by a very large surface area.⁶

Hence, for $S_2 \gg S_1$

$$S_2 = \frac{(\eta_2 - \eta_1) \int_0^t I dt}{\gamma} \quad (12)$$

On the other hand, the quantity of electrodeposited metal, m , is given by

$$m = \frac{A}{nF} \int_0^t I dt \quad (13)$$

assuming a current efficiency equal to 1, where A is the atomic mass of the deposited metal, n is the number of electrons in metal deposition reaction and F is the Faraday constant. From Eqs. (12) and (13), the specific powder surface S_{sp} is obviously:

$$S_{sp} = \frac{S_2}{m} = \frac{(\eta_2 - \eta_1)nF}{\gamma A} \quad (14)$$

According to Calusaru,⁶ the specific surface of copper powder is 500 – 3000 cm² g⁻¹ depending on the deposition conditions. Using the difference in the actual deposition overpotential and the overpotential of the beginning of the limiting diffusion density plateau as 0.80 V, γ determined in this way as 2.7 J cm⁻², atomic mass of copper, number of electrons 2 and $F = 96\,485$ C mol⁻¹, it is easy to calculate using Eq. (14)

$$S_{sp} = 1100 \text{ cm}^2 \text{ g}^{-1}$$

which is in fair agreement with the findings of Calusaru.⁶

It is obvious that using this value of the surface tension and Eq. (14), the specific surface of copper powder can be calculated for each deposition conditions, if the deposition overpotential and the overpotential of dendritic growth initiation from the electrolyte under consideration are known. In this way, one of the most important characteristics of copper powder is related to the deposition overpotential and hence to the deposition conditions. It can be seen from Tables I–III that there is no remarkable difference in the values of the copper surface tension determined from different solutions.

However, it seems that the lower limit of the concentration which can be used is 0.05 M CuSO₄ and the copper limit 0.20 M CuSO₄, because of the slopes of the plateaus of the polarization curves.

The results obtained are also in accordance with data concerning the energy requirements for electrolytic copper powder deposition.⁷

On the other hand, a change of the value of the surface tension with changing overpotential can be expected. For example, in the case of liquid mercury, the surface ten-

sion changes from 350 erg cm^{-2} at $+0.5 \text{ V}$ to more than 400 erg cm^{-2} at 0 V and again to 350 erg cm^{-2} at -1.0 V versus the hydrogen electrode,⁸ which amounts to a difference of about 20 % between the minimum and maximum values. In the case of solid electrodes, a number of interfacial properties change with changing potential, permitting the determination of the zero charge potential^{9,10} but without a direct relation with the surface tension of solid metal. Regardless of this, it is reasonable to assume that the differences in the surface tension of solid copper at different electrode potentials should be considerably lower than in the case of liquid mercury and that the values of surface tension determined by the procedure described in this paper can be taken as good estimations.

Acknowledgements: This work was supported by the Ministry of Sciences, Technology and Development of the Republic of Serbia under the research projects "Electrodeposition of Metal Powders at a Constant and Periodically Changing Rate" (1806/2002) and "Surface Science and Thin Films" (2018/2002). The authors are indebted to Professor D. M. Dražić for helpful discussion during the preparation of this paper.

ИЗВОД

ПРОЦЕНА ВРЕДНОСТИ ПОВРШИНСКОГ НАПОНА ЧВРСТОГ БАКРА У
РАСТВОРИМА БАКАР-СУЛФАТАК. И. ПОПОВ¹, Н. Д. НИКОЛИЋ² И З. РАКОЧЕВИЋ³

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Гранична дифузиона струја код електрохемијског таложења метала не зависи од примењене пренапетости у области пуне дифузионе контроле процеса. У исто време повећање пренапетости таложења доводи до настајања талоба веће специфичне површине. Разлика специфичне површине талоба добијене на две пренапетости у области пуне дифузионе контроле процеса је повезана са одговарајућом разликом пренапетости и предложен је метод оцене површинског напона чврстог бакра у растворима бакар-сулфата.

(Примљено 1. јула 2002)

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