J.Serb.Chem.Soc. *68* (8–9)649–656(2003)
JSCS – 3073

UDC 531.3:546.883+546.11:543.44
Original scientific paper

The current efficiency during the cathodic period of reversing current in copper powder deposition and the overall current efficiency

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(Received 14 February 2003)

Abstract: The current efficiency during the cathodic period of reversing current in copper powder deposition was determined by measuring the quantity of hydrogen evolved. The diagrams from which the instantaneous and average current efficiencies for copper deposition can be extracted for any deposition time up to 30 min are given. A procedure for the calculation of the overall current efficiency is proposed.

Keywords: reversing current (RC), copper powder deposition, current efficiency in RC copper powder deposition.

INTRODUCTION

The current efficiency in copper powder electrodeposition is a very important parameter from the energetic point of view, as well as from the point of view of the powder deposition rate. In general, it is known that the current efficiency in copper electrodeposition decreases with increasing deposition current density, concentration of sulphuric acid and increases with increasing copper concentration, electrolyte solution flow rate and temperature.[1–3] Data concerning powder electrodeposition in the reversing current regime is not available in the literature at this moment. It is obvious that the number of possible reversing current powder deposition regimes is very large and that it is impossible to measure the current efficiency for each of them in a classical way.

Some powders are very active and react with the electrolyte as soon as they are formed. It is recommended that they be removed from the bath and dried as soon as possible. Clean oxide-free copper surfaces have a strong tendency to oxidize, especially when exposed to air or high relative humidity. Copper powders have a high chemical activity because of their large surface area and a readily react with oxygen in the air either to form surface oxides or to burn spontaneously. This is because the surface of a copper powder undergoes oxidation in air which

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can cause errors in the determination of the powder mass.[4–10] Hence, it seems that it would be much better to determine the current efficiency in copper powder electrodeposition by measuring the volume of hydrogen evolved as described earlier.[11]

The aim of this work was to develop a method which would permit the determination of the current efficiency in copper powder electrodeposition by a reversing current using the results of a small number of experiments.

EXPERIMENTAL

The copper powder electrodeposition was carried out galvanostatically at room temperature on a stationary platinum wire electrode from an electrolyte containing 15 g/dm^3 copper and 140 g/dm^3 sulphuric acid. In all cases the electrode surface area was 0.63 cm^2. The deposition time was 30 min. The hydrogen evolved was measured in a cell provided with a marked burette, and results are given in N cm^3. The currents in the galvanostatic deposition were the average amplitude values of the current during the reversing current deposition.

The powder was removed from the cathode, washed in destilled water, dried under a purified nitrogen atmosphere and then weighed.

The measurements were made at the following current densities: 771, 1028, 1285, 1542, 1800, 2400, 3000 and 3600 A/m^2.

The electrolyte was prepared from p.a. chemicals and demineralized water.

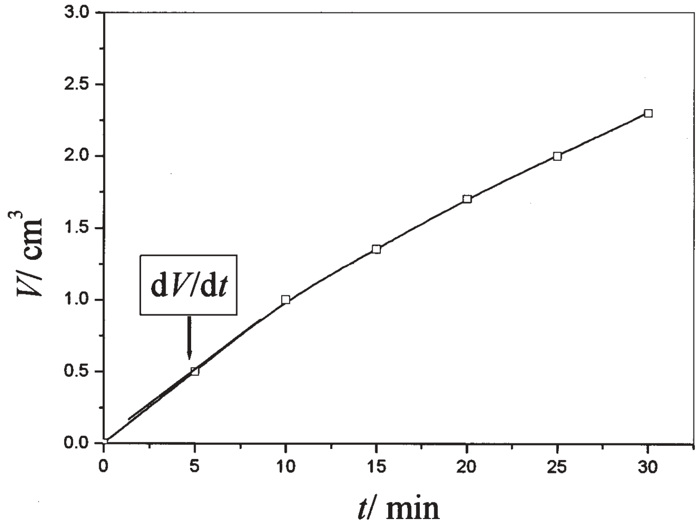

Fig. 1. The volume of hydrogen evolved as function of time and the determination of d*V*/d*t*.

The instantaneous current efficiency of the copper powders was determined according to a literature procedure[11] in the following way: the volume of evolved hydrogen was measured after different times of copper electrolysis and the dependence of the volume of evolved hydrogen on time was plotted, as shown in Fig. 1.

From such diagrams, the overall and instantaneous current effciencies can be calculated in the following manner: the slopes d*V*/d*t* (=) (cm^3/h) were evaluated and the instantaneous current efficiencies of the evolved hydrogen η_I (H$_2$) were determined according to Eq. (1):

$$\eta_{\mathrm{I}}(\mathrm{H_2}) = \frac{\frac{\mathrm{d}V}{\mathrm{d}t} \cdot \frac{1}{\mu_{\mathrm{H_2}}}}{I} \cdot 100, \text{ in (\%)} \tag{1}$$

and the instantaneous current efficiencies for the electrodeposition of copper powders, η_I (Cu) according to Eq. (2)

$$\eta_I\,(C_u) = 100 - \eta_I(H_2),\ \text{in}\ (\%) \tag{2}$$

where: V – volume of evolved hydrogen, I – current, t – time, and

$$\mu\,(H_2) = \frac{V}{zF}\,(=)\,\frac{\text{cm}^3}{\text{Ah}} \tag{3}$$

The average current efficiencies were determined in the following way: the volume of evolved hydrogen is given by Eq. (4):

$$V_{H_2} = \mu_I\,(H_2)\,I_{H_2}\,t \tag{4}$$

and

$$I_{H_2} = \frac{V_{H_2}}{\mu(H_2)\,t} \tag{4a}$$

The current I will be:

$$I = I_{Cu} + I_{H_2} \tag{5}$$

i.e.,

$$I_{Cu} = I - I_{H_2} \tag{5a}$$

Then, the average current efficiency for the electrodeposition of copper powder, $\eta_{i,\text{av}}$ (Cu) will be:

$$\eta_{i,\text{av}}\,(\text{Cu}) = \frac{I_{Cu}}{I}100,\ \ \text{in}\ (\%) \tag{6}$$

For instance: $j = 771\ \text{A/m}^2 = 0.0771\ \text{A/cm}^2 \Rightarrow I = 0.0771\ \text{A/cm}^2 \cdot 0.80\ \text{cm}^2 = 0.0620\ \text{A}$.

Determination of the instantaneous current efficiency

– For $t = 5$ min and $V = 0.15\ \text{cm}^3$, $\text{d}V/\text{d}t = 1.6\ \text{cm}^3/\text{h}$

$$\mu(H_2) = \frac{V}{zT} = \frac{22400\ \text{cm}^3}{2 \cdot 26.8\ \text{Ah}} = 418\,\frac{\text{cm}^3}{\text{Ah}}$$

$$\eta_I(H_2) = \frac{\frac{\text{d}V}{\text{d}t}\cdot\frac{1}{\mu_{H_2}}}{I}\cdot 100 = \frac{1.6\ \text{cm}^3\text{h}^{-1}\cdot\frac{1}{418\ \text{cm}^3\ \text{Ah}^{-1}}}{0.0620\ \text{A}}\cdot 100\ \% = 6.20\ \%$$

$$\eta_I(\text{Cu}) = 100 - \eta_I(H_2) = 100 - 6.20\ \% = 93.8\ \%$$

$$j = I/S \Rightarrow I = jS$$

Determination of the average current efficiency:

$$I_{H_2} = \frac{V_{H_2}}{\mu(H_2)\cdot t} = \frac{0.15\,\text{cm}^3}{418\ \text{cm}^3\ \text{Ah}^{-1}\cdot 0.0833\ \text{h}} = 0.0043\ \text{A} = 4.30\ \text{mA}$$

$$I_{Cu} = I - I_{H_2} = 0.0620\ \text{A} - 0.0043\ \text{A} = 0.057\ \text{A}$$

$$\eta_{i,av}(\text{Cu}) = \frac{I_{Cu}}{I}\cdot 100 = \frac{0.0057}{0.0620}\cdot 100\ \% = 93.0\ \%$$

RESULTS AND DISCUSSION

The experimental results are given in Table I. Using these data it is possible to obtain diagrams like those shown in Figs. 1 and 2.

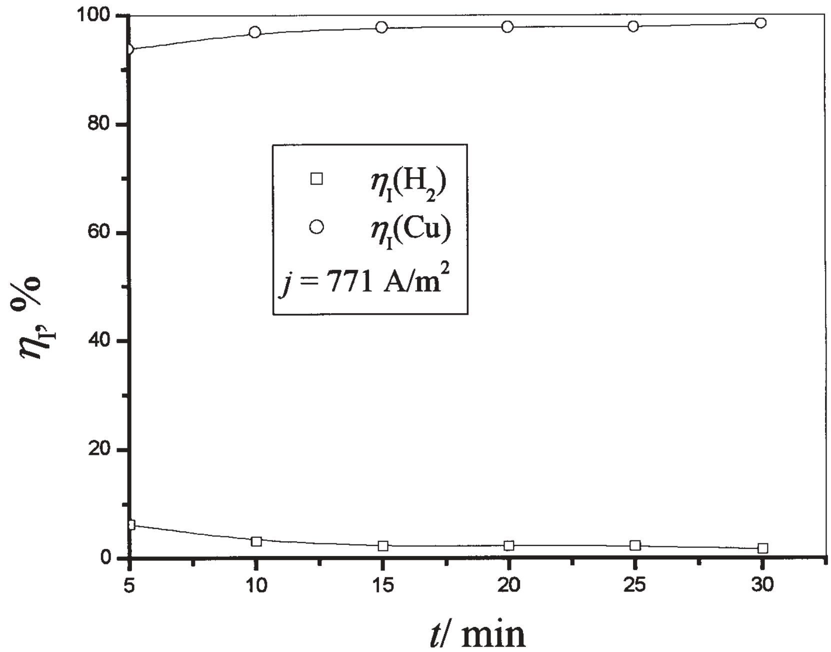

Fig. 2. The dependence of η_I(Cu), $\eta_I(H_2) - t$ for the electrodeposition of copper powder at 771 A/m^2.

In Fig. 2, the dependence of η_I (Cu), η_I $(H_2) - t$ for electrodeposition of copper powder at 771 A/m^2 is shown. It is to be noted that from such diagrams the current efficiency (average and instantaneous) can be determined for each deposition time between 0 and 30 min. It can be seen that the current efficiency for copper powder deposition increases with increasing deposition time, which is in accordance with literature data. This is because the real copper surface increases with increasing deposition time under galvanostatic conditions,[12] resulting in a decrease of the real current density.

TABLE I. Current efficiencies for copper powder deposition and the volume of hydrogen evolved at different constant current densities on a platinum electrode as a function of time

t/min	t/h	$V(H_2)$/cm^3	dV/dt/cm^3 h^{-1}	$\eta_I(H_2)$/%	η_I(Cu)/%	η_{av}(Cu)/%
a) j = 771 A/m^2						
5	0.083	0.15	1.6	6.2	93.8	93.0
10	0.167	0.25	0.80	3.1	96.9	94.2
15	0.250	0.30	0.60	2.3	97.7	95.3
20	0.333	040	0.59	2.3	97.7	95.3
25	0.417	0.40	0.61	2.3	97.7	96.3
30	0.500	0.45	0.45	1.7	98.3	96.5
b) j = 1028 A/m^2						
5	0.083	0.15	1.85	5.4	94.6	94.8
10	0.167	0.30	1.85	5.4	94.6	94.8
15	0.250	0.50	1.8	5.2	94.8	94.2
20	0.333	0.60	1.3	3.8	96.2	94.8
25	0.417	0.70	1.2	3.5	96.5	95.1
30	0.500	0.80	0.91	2.6	97.4	95.3
c) j = 1285 A/m^2						
5	0.083	0.38	4.3	10.0	90.0	89.4
10	0.167	0.70	3.7	8.6	91.4	90.2
15	0.250	1.00	3.62	8.4	91.6	90.7
20	0.333	1.22	2.70	6.3	93.7	91.5
25	0.417	1.45	2.22	5.2	94.8	91.9
30	0.500	1.60	2.11	4.9	95.1	92.6
d) j = 1542 A/m^2						
5	0.083	0.42	5.3	10.3	89.7	88.4
10	0.167	1.00	6.1	11.8	88.2	88.4
15	0.250	1.40	4.6	8.9	91.1	89.1
20	0.333	1.75	4.2	8.1	91.9	89.8
25	0.417	2.10	3.7	7.2	92.8	90.2
30	0.500	2.40	3.4	6.6	93.4	90.7
e) j = 1800 A/m^2						
5	0.083	0.75	8.32	13.8	86.2	85.0
10	0.167	1.40	7.47	12.4	87.6	86.1
15	0.250	2.20	7.78	12.9	87.1	85.4
20	0.333	2.70	7.13	11.8	88.2	86.5
25	0.417	3.20	5.61	9.3	90.7	87.3
30	0.500	3.70	5.43	9.0	91.0	87.7

TABLE I. Continued

t/min	t/h	$V(H_2)/cm^3$	$dV/dt/cm^3\ h^{-1}$	$\eta_I(H_2)$/%	η_I(Cu)/%	η_{av}(Cu)/%
f) $j = 2400\ A/m^2$						
5	0.083	1.10	12.9	16	84	83.5
10	0.167	2.10	12.3	15.2	84.8	84.3
15	0.250	3.15	12.0	14.9	85.1	84.3
20	0.333	4.10	11.65	14.4	85.6	84.7
25	0.417	5.00	10.2	12.6	87.4	85.1
30	0.500	5.80	9.5	11.8	88.2	85.5
g) $j = 3000\ A/m^2$						
5	0.083	1.50	18.2	18.1	81.9	82.1
10	0.167	3.10	17.6	17.5	82.5	81.5
15	0.250	4.45	16.2	16.1	83.9	82.3
20	0.333	5.80	15.2	15.1	84.9	82.6
25	0.417	7.0	14.0	13.9	86.1	83.3
30	0.500	8.15	12.9	12.8	87.2	83.7
h) $j = 3600\ A/m^2$						
5	0.083	2.2	26.5	22.0	78.0	78.1
10	0.167	4.1	22.0	18.3	81.7	79.6
15	0.250	5.5	20.0	16.6	83.4	81.7
20	0.333	7.0	18.9	15.7	84.3	82.5
25	0.417	8.6	15.3	12.7	87.3	82.9
30	0.500	10.2	16.3	13.5	86.5	83.1

It is known that the average current density in RC metal electrodeposition is given by:

$$j_{av} = \frac{j_c t_c - j_a t_a}{t_c + t_a} \tag{7}$$

where j_c and j_a, and t_c and t_a represent the cathodic and anodic current densities and cathodic and anodic times, respectively. Equation (7) is valid if both the anodic and cathodic current efficiencies are equal to 1 (which means 100 % efficiency). This is practically the case in copper plating by RC from sulphate acid baths. In copper powder electrodeposition by RC, as can be seen from Table 1, the cathodic current efficiency is less than 1. Assuming the anodic current efficiency is still equal 1, Eq. (7) can be rewritten in the form:

$$j^*_{av} = \frac{j_c t_c \eta_{i,c} - j_a t_a}{t_c + t_a} \tag{8}$$

where j^*_{av} is the effective average current density and $\eta_{i,c}$ the cathodic current efficiency.

Assuming that

$$j_c = j_a = j_A \tag{9}$$

where j_A is the RC amplitude current density and

$$r = \frac{t_a}{t_c} \tag{10}$$

Equations (7) and (8) can then be rewritten in the forms:

$$j_{av} = j_A \frac{1-r}{1+r} \tag{11}$$

and

$$j^*_{av} = j_A \frac{\eta_{i,c} - r}{1+r} \tag{12}$$

It follows from Eqs. (11) and (12) that:

$$\frac{j^*_{av}}{j_{av}} = \frac{\eta_{i,c} - r}{1+r} \tag{13}$$

or

$$\eta_{i,RC} = \frac{\eta_{i,c} - r}{1-r} \tag{14}$$

because

$$\eta_{i,RC} = \frac{j^*_{av}}{j_{av}} \tag{15}$$

In this way, the overall current efficiency in RC copper powder electrodeposition can be calculated. It is to be noted that from the diagrams constructed using the data from Table I, the current efficiency for eight amplitude currents and any cathodic deposition time between 0 and 30 min and any anodic time can be obtained. Obviously, for other amplitude currents 771 (A/m^2) < j < 3600 (A/m^2), the current efficiencies can be estimated by interpolation.

Acknowledgement: The work was supported by the Ministry of Sciences, Technology and Development of the Republic of Serbia under the research project: "Electroceposition of Metal Powders at a Constant and Periodcally Changing Rate" (1806/2002).

ИЗВОД

ИСКОРИШЋЕЊЕ СТРУЈЕ ЗА ВРЕМЕ КАТОДНОГ ПЕРИОДА РЕВЕРСНЕ СТРУЈЕ ПРИ ТАЛОЖЕЊУ БАКАРНОГ ПРАХА И УКУПНО ИСКОРИШЋЕЊЕ СТРУЈЕ

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Одређивано је искоришћење струје за време катодног периода реверсне струје при таложењу бакарног праха, мерењем количине издвојеног водоника. Дати су дијаграми из којих могу бити израчуната тренутна и средња искоришћења струје за таложење бакарног праха, за било које време таложења до 30 минута. Предложен је поступак прорачуна укупног искоришћења струје.

(Примљено 14. фебруара 2003)

REFERENCES

1. N. Ibl, "The formation of powdered metal deposits", in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, Interscience, New York, 1962, pp. 50–55
2. A. Calusaru, *Electrodeposition of Metal Powders*, Elsevier, New York, 1979, pp. 352–355
3. A. R. Despić, K. I. Popov, "Transport controlled deposition and dissolution of metals" in *Modern Aspects of Electrochemistry*, Vol. 7, Plenum, New York, 1972, pp. 295–300
4. R. Walker, S. J. Duncan, *Surface and Coatings Technology* **27** (1986) 137
5. A. I. Levin, A. V. Pomosov, *Zh. Prikl. Khim.* **22** (1949) 592
6. R. Walker, *Met. Finish.* **71** (1973) 63
7. R. Walker, *Met. Finish.* **80** (1974) 33
8. Kunio Mori, Yoshihiro Horie, Horoshi Yamada, *Corrosion Science* **32** (1991) 1237
9. M. G. Pavlović, Lj. J. Pavlović, N. D. Nikolić, V. Bojanić, *XVII Yugoslav Symposium of Corrosion and Protection of Materials*, Book of Abstracts, Ed. SITZAMS, Belgrade, 2000, pp. 86–90 (in Serbian)
10. Lj. Radisavljević, M. G. Pavlović, N. D. Nikolić, I. D. Doroslovački, Č. Dumitrašković, *1998 Powder Metallurgy, World Congress*, p. 121, Granada, Spain (1998) Ex. Abstracts
11. K. I. Popov, M. G. Pavlović, M. D. Maksimović, S. S. Krstajić*, J. Appl. Electrochem.* **8** (1978) 503
12. M. D. Maksimović, K. I. Popov, Lj. J. Jović, M. G. Pavlović, *Bull. Soc. Chim., Beograd* **44** (1979) 547
13. K. I. Popov, M. D. Maksimović, "Theory of the effect of electrodeposition of a periodically changing rate on the morphology of metal deposits", in *Modern Aspects of Electrochemistry*, Vol. 19, B. E. Corway, J. O 'M. Bockris, Eds., Plenum Press, New York, 1989.