Materials Science Forum *Online: 2004-05-15*
ISSN: 1662-9752, Vols. 453-454, pp 393-398
doi:10.4028/www.scientific.net/MSF.453-454.393

The Effect of Reversing Current on the Properties of Copper and Electrolytic Copper Powder. I. The Morphology of Powder Particles

M.G. Pavlović[1], K.I. Popov[2], Lj.J. Pavlović[1], E.R. Ivanović[3] and V.D. Jović[4]

[1]ICTM-Department of Electrochemistry, Belgrade, Serbia and Montenegro
[2]Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia and Montenegro
[3]Faculty of Agriculture, University of Belgrade, Zemun, Serbia and Montenegro
[4]Center for Multidisciplinary Studies, Belgrade, Serbia and Montenegro

Keywords: Electrolytic Copper Powder, Reversing Current, Selective Dissolution of Copper Dendrites

ABSTRACT

The selective dissolution of copper dendrites during electrodeposition by reversing current was discussed and the effects on the morphology of copper powder particles were elucidated.

1. INTRODUCTION

The morphology and crystallinity of powder particles can be varied considerably by changing the shape and frequency of the reversing current (RC) wave. In the RC deposition the particles are less dendritic and less agglomerated than the ones obtained by constant current regime. This is explained by slower growth rate, lower diffusion control and selective dissolution of the dendrite branches caused by different radii of curvature, because of the influence of surface energy on the reaction velocity during anodic process, which leads to the formation of more massive copper powder particles [1,2].

The selective dissolution of dendrite tips depends very much on the time of anodic dissolution. Hence, the morphology of particles will depend on the anodic to cathodic time ratio and the frequency of RC wave. The aim of this work is to discuss this phenomenon in a semiquantitative way.

2. EXPERIMENTAL

The experiments were performed as in previous papers [3,4], in an enlarged laboratory plastic reactor with a cell volume of 10 dm^3. Electrolytic copper powder was produced from electrolytes containing 140 g/dm^3 sulphuric acid and 15 g/dm^3 copper, at an electrolyte temperature of $(50\pm2)^0$ C. The electrolyte circulation system was designed to supply the laboratory scale cell from an electrolyte supply tank (100 dm^3).

The enlarged laboratory reactor had a circulation pump, inlet and outlet for the electrolyte, and a heat exchanger. The latter controlled the electrolyte temperature. The electrolyte was pumped from a basement storage tank to the enlarged laboratory reactor; (electrolyte circulation rate: 0,11 dm^3/min). From there, it flowed by gravity and then into the back and the top of the cell. Thus, the circulation of electrolyte in the tanks was from top to bottom, since this yields a finer, more homogenous powder than a bottom to top circulation. The electrolyte was returned to the basement storage tank by gravity.

The cell was loaded with four copper cathodes at a spacing of 30 mm, centers [each holding four vertical copper rods (120 mm long, 8 mm diameter)], and five copper anodes (120x120x10)

mm, which were hung between the cathodes. The distance between anodes was 60 mm from center to center of each anode. The electrodes in the cell were parallel with each other.

Electrolytic copper powder was deposited by reversing current. The amplitude current value was 3600 A/m^2. The anodic time was varied from 0.2 s to 2 min and the cathodic time from 1 s to 5 min.

The electrolytes were prepared using chemicals of technical grade and demineralized water.

The deposition time (brush - down interval) was 15 min.

The wet powder was washed several times with a large amount of demineralized water at room temperature, until it was free of traces of acid. It should be noted that the presence of a free acid promotes a rapid oxidation of the powder during drying. The washing of powder was carried out immediately after production in order to avoid the oxidation of copper particles. 0.1 % benzoic acid, acting as a stabilizer was added to washing water, in order to protect the powder against subsequent oxidation [5]. During the washing procedure, benzoic acid was removed.

The powder was then dried in tunnel furnaces in a controlled atmosphere (by nitrogen), at 110 - 120 ^{O}C.

The surface morphology of copper powder was studied using a JOEL T20 scanning electron microscope.

3. RESULTS AND DISCUSSION

The effect of frequency and anodic to cathodic time ratio on the morphology of copper powder particles is shown in Fig. 1. The micrographs presented in Fig. 1 show that the increase in frequency from a 'minute' to a 'second' range (Figs. 1a and 1b) and the decrease in cathodic to anodic time ratio from 5 to 2.5 (Figs. 1c and 1b), lead to the formation of more compact powder particles. This can be explained in the following way. The selective dissolution of dendrites, hence the powder particles, was treated quantitatively for the electrodeposition of dendrites by pulsating overpotential [6,7]. This can be extended to the RC electrodeposition as follows. The RC wave is characterized by cathodic and anodic current densities j_c and j_a and cathodic and anodic time t_c and t_a, respectively. The current densities j_c and j_a to the flat surface during the cathodic and anodic times are given by:

$$j_c = j_0\left[(1-\frac{j_{av}}{j_L})\exp(\frac{2.3\eta_c}{b_c}) - \exp(\frac{2.3\eta_c}{b_a})\right] \quad \text{..... 1}$$

and

$$j_a = j_0\left[\exp(\frac{2.3\eta_a}{b_a}) - (1-\frac{j_{av}}{j_L})\exp(-\frac{2.3\eta_a}{b_c})\right] \quad \text{.....2}$$

where η_c and η_a are the cathodic and anodic overpotentials, and j_0, j_c and j_{av}, the exchange current density, the limiting diffusion current density and the average current density, respectively. Equations 1 and 2 are valid at sufficiently high frequencies where the surface concentration is constant [8]. Assumming that during the cathodic period the anodic term in Eq. 1 can be neglected and vice versa, Eqs. 1 and 2 can be rewritten as:

$$\eta_c = \frac{b_c}{2.3}\ln\frac{j_c}{j_0}\frac{1}{1-\frac{j_c}{j_L}} \quad \text{.....} \qquad 3$$

and

$$\eta_a = \frac{b_a}{2.3}\ln\frac{j_a}{j_0} \quad \text{.....} \qquad 4$$

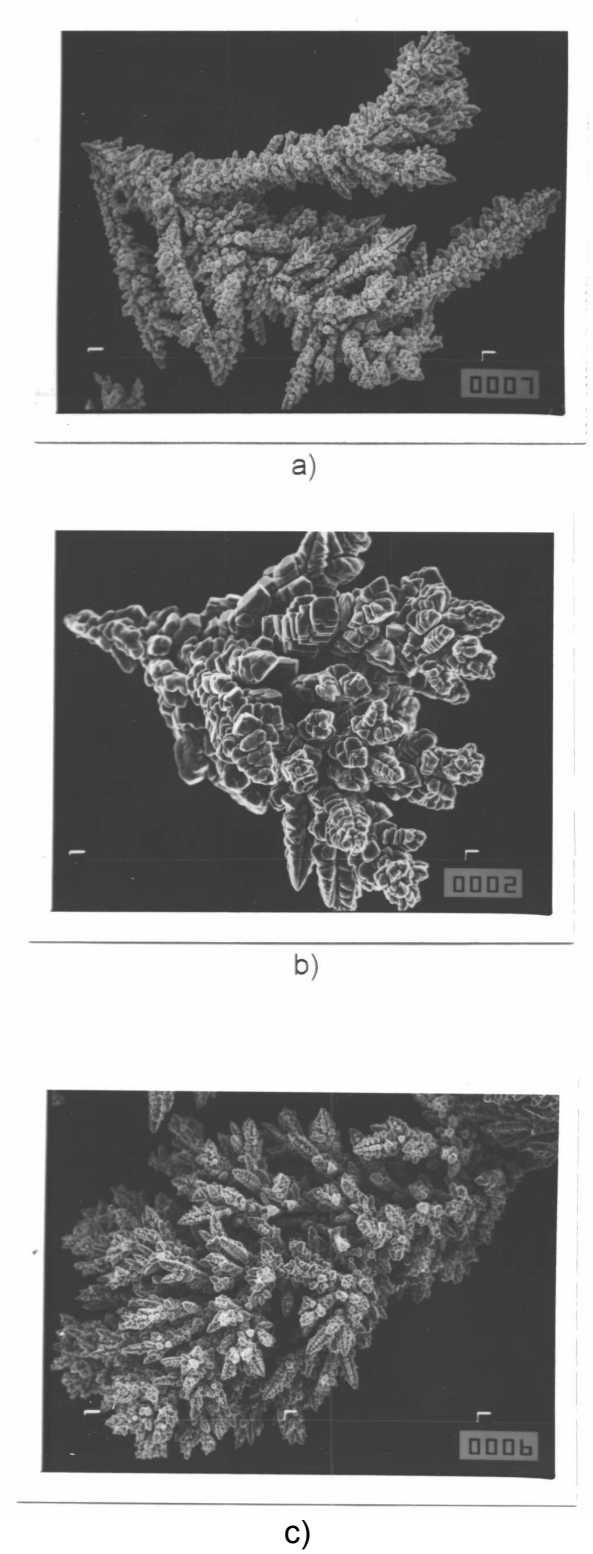


Fig. 1. SEM micrographs of powder particles obtained by RC. Amplitude current density 3600 A/m^2. a) Cathodic to anodic time ratio 2.5. Cathodic pulse duration 5 min. X1000; b) Cathodic to anodic time ratio 2.5. Cathodic pulse duration 1 s. X1000; c) Cathodic to anodic time ratio 5. Cathodic pulse duration 1 s. X500.

The positive sign is assumed for both current densities when they are considered separately.

The cathodic and anodic current densities to the tip of dendrite with radius of curvature *r* will then be given for copper deposition [8] by:

$$j_{c,t} = j_0 \left[(1 - \frac{j_{av,t}}{j_{L,t}}) \exp(\frac{2.3\eta_c}{b_c}) - \exp(\frac{2\sigma V}{RTr}) \exp(-\frac{2.3\eta_c}{b_a}) \right] \quad \text{.....} \quad 5$$

and

$$j_{a,t} = j_0 \left[\exp(\frac{2.3\eta_a}{b_a}) \exp(\frac{2\sigma V}{RTr}) - (1 - \frac{j_{av,t}}{j_{L,t}}) - \exp(\frac{2.3\eta_a}{b_c}) \right] \quad \text{.....} \quad 6$$

where $j_{av,t}$ and $j_{L,t}$ are the average and limiting current densities to the tip of dendrite, σ and V are the surface energy and the molar volume of deposited metal, and b_c and b_a are the cathodic and anodic Tafel slopes, respectively. Assumming that

$$\frac{j_{av}}{j_L} \approx \frac{j_{av,t}}{j_{L,t}} \quad \text{.....} \quad 7$$

and that the current densities on the flat part of the surface determine the deposition overpotential, it can be calculated from Eqs 3 and 4 for cathodic and anodic times, respectively. Assumming that anodic term during cathodic time and cathodic term during anodic time can also be neglected as in the case of flat surface, substitution of η_c and η_a in Eqs 5 and 6 and further rearanging give:

$$j_{c,t} = j_c \quad \text{.....} \quad 8$$

and

$$j_{a,t} = j_a \exp(\frac{2\sigma V}{RTr}) \text{.....} \quad 9$$

The equations 8 and 9 show that the cathodic current density to the tip of dendrite is the same as on the flat electrode surface, while the anodic current density to the tip of dendrite is larger than on the flat surface. This is the essence of selective dissolution in the powder electrodeposition by RC. The difference between the current density at the tip of the dendrite and on the flat surface during the anodic period Δj_a is given by:

$$\Delta j_a = j_a [\exp(\frac{2\sigma V}{RTr}) - 1] \text{.....} \quad 10$$

The change of height of surface protrusions with tip radius r and height h relative to the flat surface is given by [7] :

$$\frac{dh}{dt} = -\Delta j_a \frac{V}{zF} \quad \text{.....} \quad 11$$

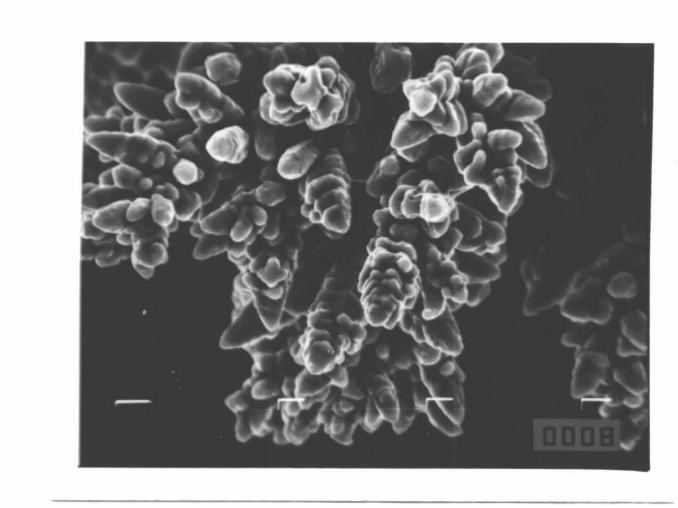
The sign minus means the decrease in the height of a protrusion with time during anodic dissolution.

The substitution of Δj_a from Eq. 10 in Eq. 11 and further rearanging gives:

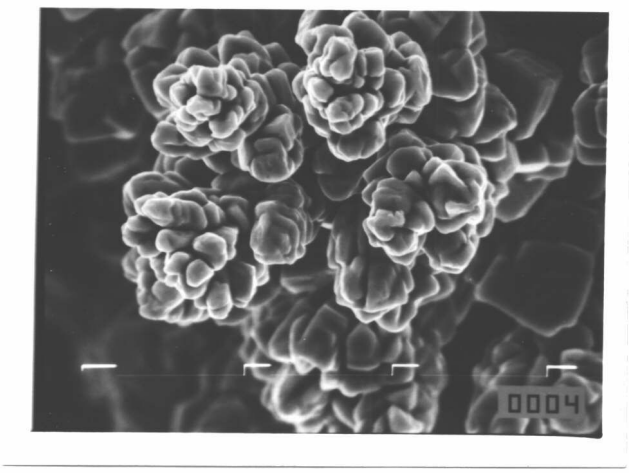
$$h = h_0 + \frac{V j_a}{zF} \left[1 - \exp(\frac{2\sigma V}{RTr}) \right] t \text{.....} \quad 12$$

were t is the duration of anodic dissolution and h_0 is the initial protrusion height, if the tip radius of the protrusion does not vary with time. The time required for dissolution of the whole protrusion during the dissolution time can be obtaining from Eq. 12 for $h = 0$ as:

$$t = \frac{zF}{V j_a} \frac{h_0}{\exp(\frac{2\sigma V}{RTr}) - 1} \quad \text{.....} \quad 13$$



a)



b)

Fig. 2. SEM micrographs of powder particles obtained by RC. Amplitude current density 3600 A/m^2. a) Cathodic to anodic time ratio 5. Cathodic pulse duration 1 s. X3500; b) Cathodic to anodic time ratio 2.5. Cathodic pulse duration 1 s. X3500.

Eq. 13 shows that when r approaches 0, then $t \rightarrow 0$, suggesting that under this condition, the tertiary dendrite arms can be completely dissolved for a relatively short dissolution time, while the primary dendrite arms do not undergo the selective dissolution, since it was observed only at very small dendrite tip radii [9,10]. Hence, at the same cathodic to anodic time ratio the increase in compactness of the powder particles can be expected with increasing frequency of RC wave, from the minute to the second range, which is illustrated in Figs 1a and 1b. On the other hand, the anodic time of 0.2 s is not sufficient to dissolve completely the tips of dendrite arms characterized with

very small tip radii (Figs. 1c and 2a), while at anodic time of 0.4 s the selective dissolution is finished (Figs. 1b and 2b).

Acknowledgement

This work was supported by the Ministry of Sciences, Technology and Development of the Republic of Serbia under the research project Electrodeposition of Metal Powders at a Constant and at a Periodically Changing Rate (1806/2002).

REFERENCES

[1] K.I. Popov, M.G. Pavlović, ¨Electrodeposition of Metal Powders with Controlled Grain Size and Morphology¨, in Modern Aspects of Electrochemistry, Vol. 24, R.E. White, J.O'M. Bockris, B.E. Conway, Eds. Plenum Press, p. 299, New York (1993).
[2] K.I. Popov, S.S. Djokić, B.N. Grgur, ¨Fundamental Aspects of Electrometallurgy¨, p. 145 Kluwer Academic/Plenum Publishers, New York (2002).
[3] M.G. Pavlović, Lj.J. Pavlović, E.R. Ivanović, V. Radmilović, K.I. Popov, J. Serb. Chem. Soc. **66**, 923 (2001).
[4] K.I. Popov, Lj.J. Pavlović, E.R. Ivanović, V. Radmilović, M.G. Pavlović, J. Serb. Chem. Soc. **67**, 61 (2002).
[5] Lj. Radisavljević, M.G. Pavlović, N.D. Nikolić, I.D. Doroslovački, Č. Dumitrašković, ¨Powder Metallurgy¨, World Congress, Extended Abstracts, p. 121, Granada, Spain (1998).
[6] K.I. Popov, M.G. Pavlović, G.Ž. Remović, J. Appl. Electrochem., **21**, 743 (1991).
[7] K.I. Popov, E.R. Stojilković, V. Radmilović, M.G. Pavlović, Powder Technology, **93**, 55 (1997).
[8] 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 Aspercts of Electrochemistry, Vol. 19, B.E. Conway, J.O'M. Bockris, Eds. Plenum Press, p. 193, New York (1989).
[9] A.R. Despić, K.I. Popov, ¨Transport Controlled Deposition and Dissolution of Metals¨, in Modern Aspects of Electrochemistry, Vol. 7, B.E. Conway, J.O'M. Bockris, Eds. Plenum Press, p. 199, New York (1972).
[10] J.L. Barton, J.O'M. Bockris, Proc. Roy. Soc. London **A268**, 485 (1962).