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The effect of reversing current deposition on the apparent density of electrolytic copper powder

K. I. POPOV[1#], LJ. J. POPOVIĆ[2], E. R. IVANOVIĆ[3], V. RADMILOVIĆ[1] and M. G. PAVLOVIĆ[2]

[1]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, YU-11000 Belgrade,* [2]*ICTM – Department of Electrochemistry, Njegoševa 12, YU-11000 Belgrade and* [3]*Faculty of Agriculture,University of Belgrade, Nemanjina 6, 11080 Zemun – Belgrade, Yugoslavia*

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The possibility of depositing copper powders with different apparent density by changing the shape of reversing current wave is shown. The morphology and crystallinity of powder particles can be varied considerably by changing shape of the reversing current wave and, hence, the apparent density of powders. The relation of apparent density with particle morphology and structure was illustrated.

Keywords: reversing current, apparent density, electrolytic copper powder.

INTRODUCTION

It is well known that the reversible potential of a surface with a radius of curvature r would depart from that of a planar surface by the quantity ΔE_r according to:

$$\Delta E_r = \frac{2\gamma V_m}{Fr} \tag{1}$$

where γ is the surface tension and V_m the molar volume of deposited metal.[1] For example, this makes the equilibrium potential of a spongy deposit 7–10 mV more cathodic than that of zinc foil.[2,3] As a result of this, the formation of spongy deposits can be completely prevented by pulsating overpotential electrodeposition,[4] as can the branching of dendrities,[5] due to the faster dissolution of electrode protrusions with lower tip radii relative to ones with larger tip radii or to the flat surface during the pause. Recently, a semi-quantitative analysis of this effect was also been performed.[5] In this way, globular copper powder particles can be obtained[6] and even monocrystalline ones of silver.[7] A similar effect was obtained in the reversing current deposition of metal powder,[8,9] but the analytical approach is not yet available.

It was shown in a previous paper[10] that the apparent density of electrochemically obtained copper powder depends strongly on the structure of the powder particles. The

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more dendritic particles that are deposited, the smaller is the apparent density of powder. Also copper powders with different apparent densities were obtained by changing the conditions of the deposition process[10] such as: electrolyte composition (acid and copper content), electrolyte temperature, electrolyte circulation rate, current density and brush-down interval.

On the other hand, as was earlier pointed out,[11] the same effects can be expected by changing the parameters which determine the shape of the deposition reversing current wave, the other deposition conditions remaining unchanged. The aim of this paper is to show the morphologies of powder particles and apparent densities of copper powders obtained by different regimes in reversing current (RC) deposition, as well as the apparent densities of the powders.

EXPERIMENTAL

Copper powders were deposited by reversing current. The amplitude current value was 3600 A/m^2. The anodic times were varied from 0.2 s to 2 min and the cathodic time from 1 s to 5 min. The brush-down interval was 15 minutes, and all other parameters were the same as in a previous paper.[10]

The powders were treated in the same way as in the previous paper.[10]

The photomicrographs of the powder particles were taken under magnifications: ×200, ×1000 and ×3500 using a JOEL T20 microscope.

RESULTS AND DISCUSSION

The SEM photomicrographs of copper powder particles obtained using different reversing current regimes are shown in Figs. 1–6. Particles of considerably different grain size and morphology were obtained.

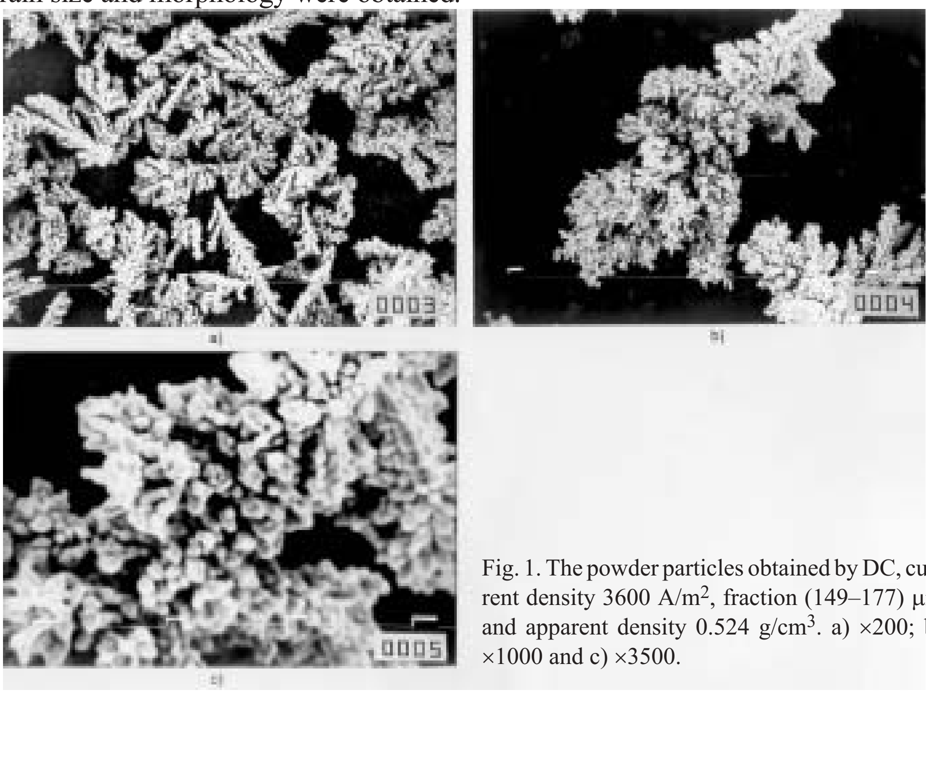


Fig. 1. The powder particles obtained by DC, current density 3600 A/m^2, fraction (149–177) μm and apparent density 0.524 g/cm^3. a) ×200; b) ×1000 and c) ×3500.

The SEM photomicrographs of the powder particles obtained by direct current (DC) are presented in Fig. 1. The powder particles on the "macrolevel" are branched (Fig. 1a) and very disperse on the "microlevel" (Figs. 1b and c). This leads to a very small apparent powder density (0.524 g/cm^3). The same magnifications but with reversing current are shown in Figs. 2–4. As expected, the particles are "shaved" (×200) by the anodic current flow on the "macrolevel" and the structure on the "microlevel" (×1000 and ×3500) is more dense, which results in a considerable increase of the apparent density of the copper powders.

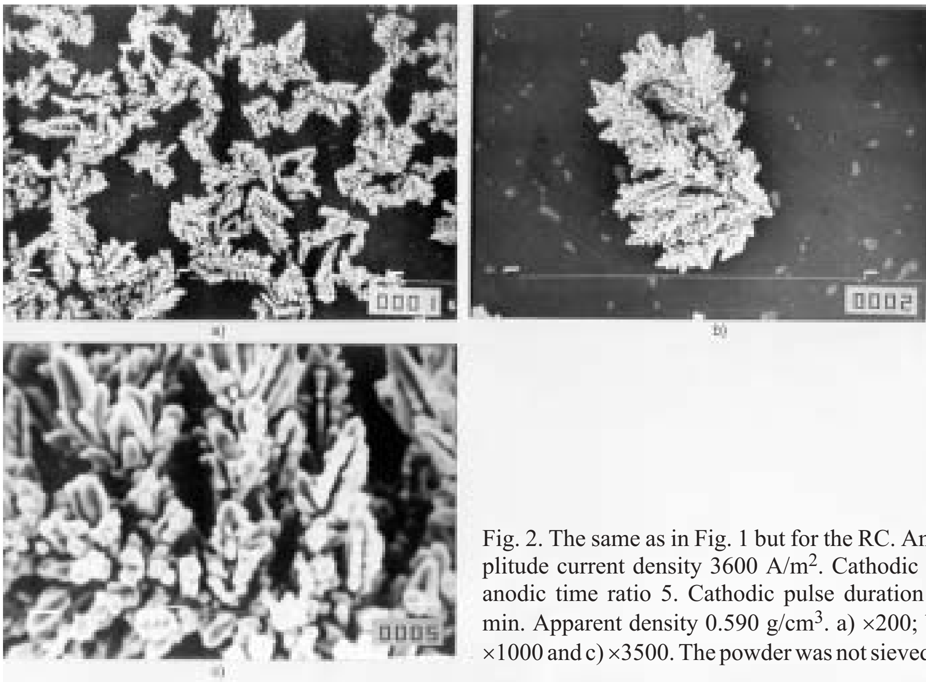
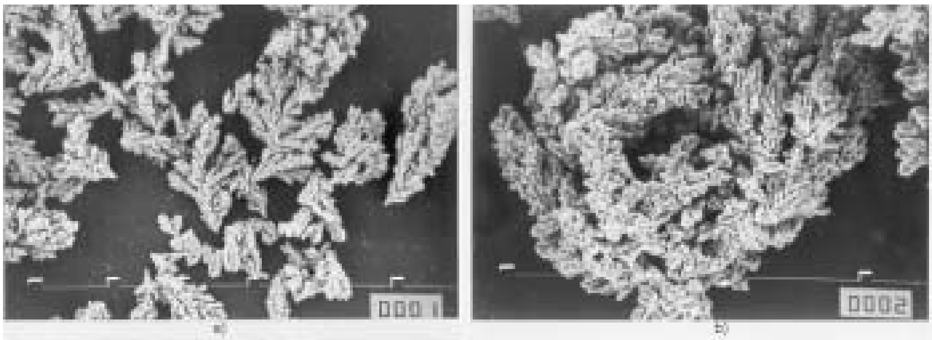


Fig. 2. The same as in Fig. 1 but for the RC. Amplitude current density 3600 A/m^2. Cathodic to anodic time ratio 5. Cathodic pulse duration 5 min. Apparent density 0.590 g/cm^3. a) ×200; b) ×1000 and c) ×3500. The powder was not sieved.

The particles obtained using current waves characterized by a cathodic, t_c, to anodic, t_a, time ratio 5 are shown in Figs. 2–4. It is interest to note that the deposition time has an appreciable effect on the structure of particles. Namely, the structure of powder particles obtained by cathodic times 5 min, 5 s and 1 s are quite different with increasing compactness of the particles as well as increasing apparent density with decreasing deposition time of the powder. This dependence will be analysed in further studies, but, for instance, it is important to conclude that an increase in the compactness of powder particles leads to an increase of the apparent density of the powders. This is in perfect agreement with the results of a previous paper.[10]

Increasing the anodic dissolution time leads to a further increase of the apparent density of the copper powders and to a decrease of the dendritic character of the powder particles, as is shown in Figs. 5 and 6.

The effect of increasing the anodic dissolution time is less pronounced in the minute range than in the second one, as can be seen from Figs. 5 and 6. In the second range,



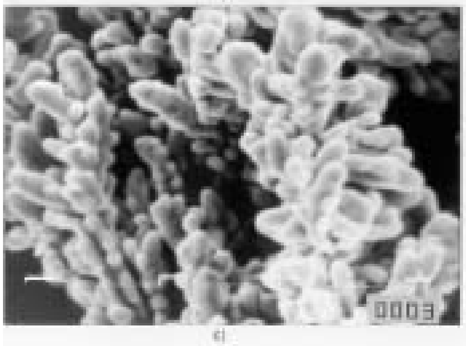
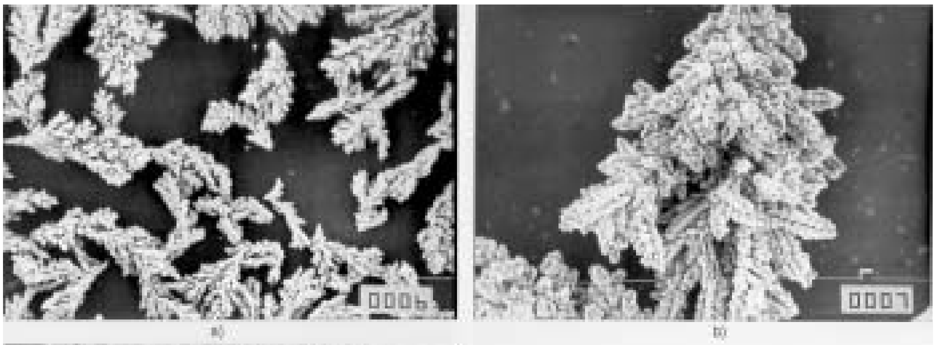


Fig. 3. The powder particles obtained by RC. Amplitude current density 3600 A/m^2. Cathodic to anodic time ratio 5. Cathodic pulse duration 5 s. Apparent density 0.652 g/cm^3. a) ×200; b) ×1000 and c) ×3500. The powder was not sieved.



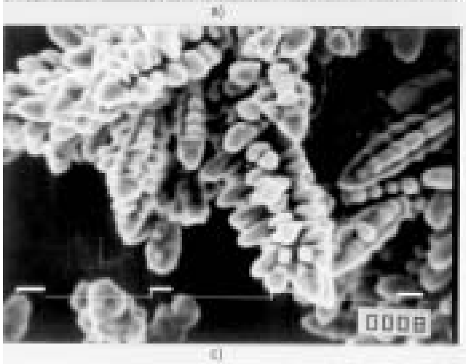


Fig. 4. The powder particles obtained by RC. Amplitude current density 3600 A/m^2. Cathodic to anodic time ratio 5. Cathodic pulse duration 1 s. Apparent density 0.772 g/cm^3. a) ×200; b) ×1000 and c) ×3500. The powder was not sieved.

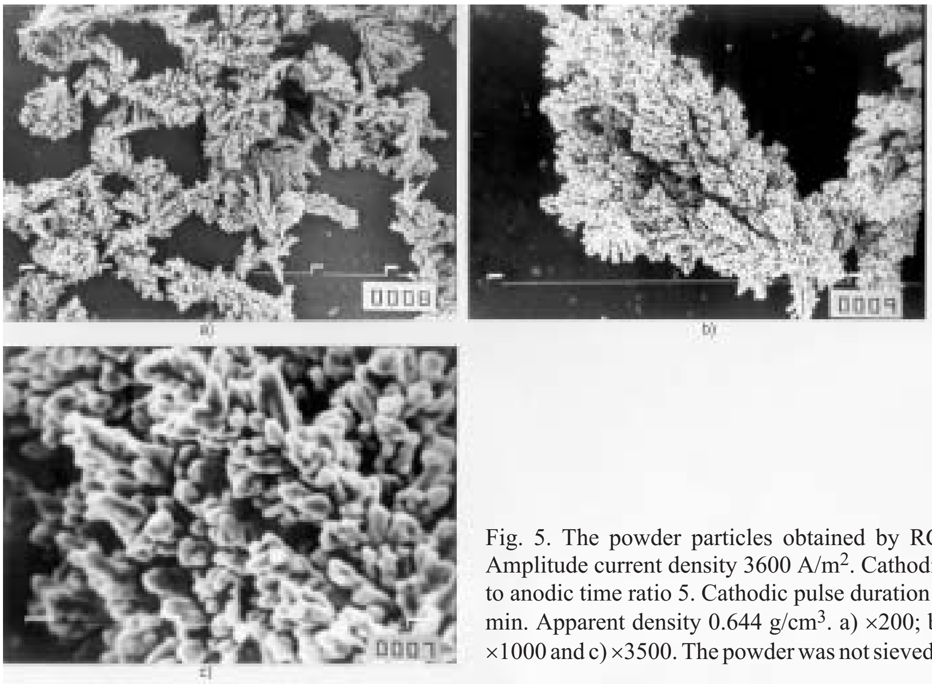


Fig. 5. The powder particles obtained by RC. Amplitude current density 3600 A/m^2. Cathodic to anodic time ratio 5. Cathodic pulse duration 5 min. Apparent density 0.644 g/cm^3. a) ×200; b) ×1000 and c) ×3500. The powder was not sieved.

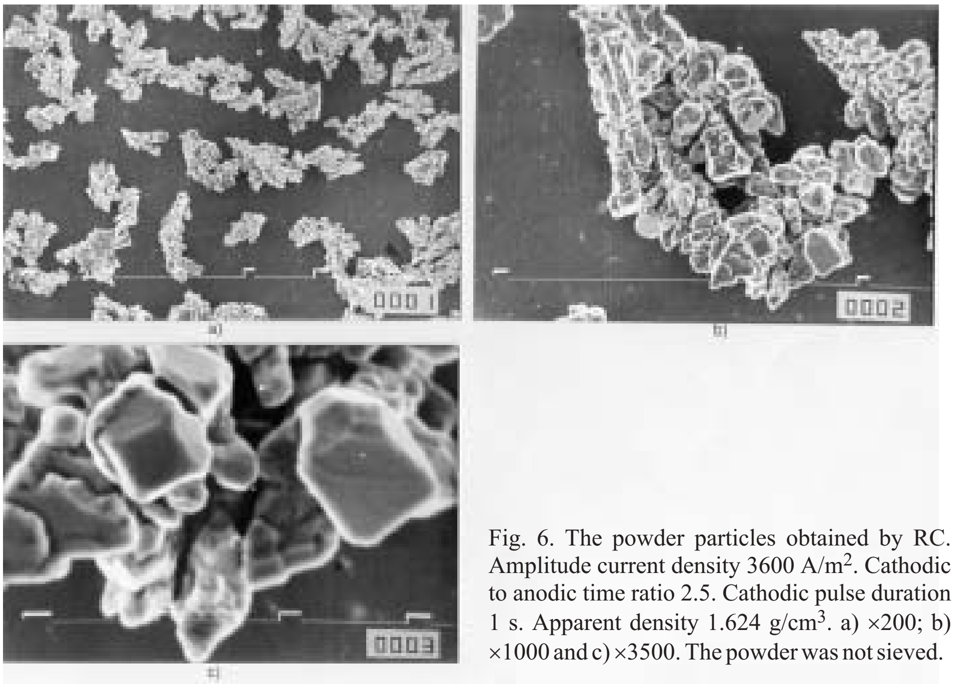


Fig. 6. The powder particles obtained by RC. Amplitude current density 3600 A/m^2. Cathodic to anodic time ratio 2.5. Cathodic pulse duration 1 s. Apparent density 1.624 g/cm^3. a) ×200; b) ×1000 and c) ×3500. The powder was not sieved.

the powder particles are agglomerates of monocrystal subparticles and the apparent density becomes 1.624 g/cm^3. The effect of deposition and dissolution times on the morphology of powder particles for pulsating overpotential (PO) deposition was discussed in a semiquantitative way.[5]

Obviously, for the RC case, this discussion can be performed on the basis of that for PO in a qualitative way. The selective dissolution of the electrode surface during the anodic time takes place only at points with very small radii of curvature, which dissolve faster than flat parts of the surface or at points with larger tip radii. In the minute range, the duration of selective dissolution must be shorter compared to the overall anodic dissolution time, because the tip radii of dendrites or dendrite branches very quickly become sufficiently large to make the effect of selective dissolution negligible and the particles dissolve uniformly. A decrease of the overall dissolution time leads to a decrease of the time in which the particles dissolves uniformly and the effect of selective dissolution is more pronounced from the point of view of the Kelvin effect, *i.e.,* the selective dissolution on the particle "macrolevel", making the particles less branched.

On the other hand, the adatoms which are not included completely in the metal lattice will be dissolved faster than those which are included in it, which has the effect of selective dissolution on the "microlevel" of the particle which results in the formation of regular crystal forms. The effect of decreased dissolution time from the minute to the second range is the same as in the case of the particle "macrolevel".

In this way it was shown that the morphology and crystalline structure of powder particles can be varied considerably by the changing of the shape of the RC current wave and, hence, the apparent density of powders. A more detailed analysis of the effect of all parameters determining the shape of an RC wave and the deposition conditions on the apparent density of copper powders will be the subject of further investigations.

И З В О Д

УТИЦАЈ РЕВЕРСНЕ СТРУЈЕ НА НАСИПНУ МАСУ ПРИ ЕЛЕКТРОЛИТИЧКОМ ТАЛОЖЕЊУ БАКАРНОГ ПРАХА

К. И. ПОПОВ[1], Љ. Ј. ПАВЛОВИЋ[2], Е. Р. ИВАНОВИЋ[3], В. РАДМИЛОВИЋ[1] и М. Г. ПАВЛОВИЋ[2]

[1]Технолошко-металуршки факултет Универзитета у Београду, Карнегијева 4, 11000 Београд, [2]ИХТМ – Центар за електрохемију, Његошева 12, 11000 Београд и [3]Пољопривредни факултет Универзитета у Београду, Немањина 6, 11080 Земун – Београд

У раду је показана могућност добијања бакарних прахова различитих насипних маса променом облика таласа реверсне струје. Успостављена је задовољавајућа веза између морфологије и структуре честица праха бакра и насипне масе праха.

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