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Formation of powdered copper deposits by constant and pulsating overpotential electrolysis

K. I. POPOV, D. N. KEČA, M. D. MAKSIMOVIĆ

Faculty of Technology and Metallurgy, University of Beograd, Beograd, Yugoslavia

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The possibility of electrodepositing copper powder by pulsating overpotential is shown. These powders are compared to the powders obtained by constant overpotential electrodeposition. It is also shown that the grain size and the morphology of deposited powder is a function of overpotential, and of amplitude and frequency of pulsation in constant and pulsating overpotential deposition respectively.

1. Introduction

Smooth copper deposits can be obtained in the limiting current density range by using pulsating overpotential of very high frequencies (10^4–10^5 cps). At lower frequencies rough and dendritic deposits are obtained, but more compact compared to those obtained by constant overpotential electrodeposition under similar conditions [1–3].

The purpose of this work was to try to obtain metal powder deposits by pulsating overpotential electrolysis and investigate the effect of process parameters on grain size.

2. Experimental

The deposition was carried out from 0·1 M $CuSO_4$ in 0·5 M H_2SO_4 on a platinum electrode painted with shellac, and on an aluminium electrode at room temperature by constant and sinusoidal pulsating overpotential. The experimental set-up was the same as one previously reported [3].

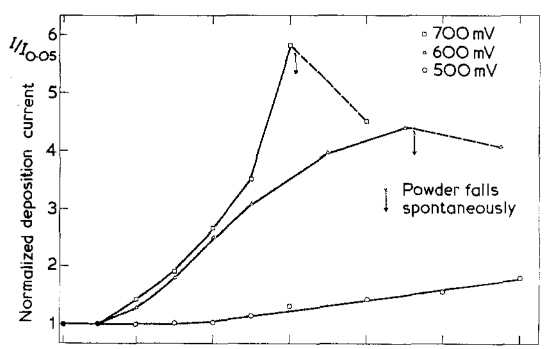

Fig. 1. Current–time relationships for copper powder deposition on an aluminium electrode at different constant overpotentials.

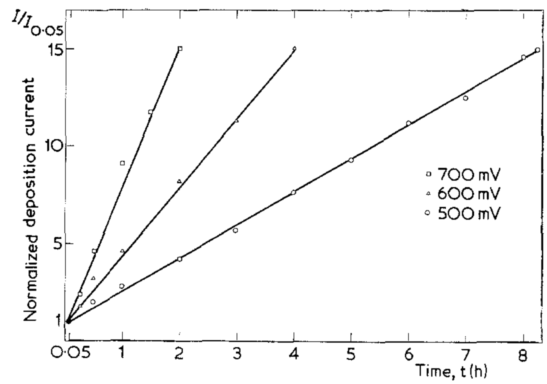

Fig. 2. Current–time relationships for copper powder deposition at different constant overpotentials on a platinum electrode painted with shellac.

Powder was removed by tapping the electrode, washed by distilled water and alcohol, and dried in air. Photomicrographs were made at a magnification of × 100.

3. Results and discussion

The current–time relationships for constant overpotential copper powder deposition on aluminium and platinum are presented in Figs. 1 and 2 respectively.* As already discussed by some authors

* In all diagrams a relative increase of current with time is shown, as the ratio of current to the current after 3 min of deposition.

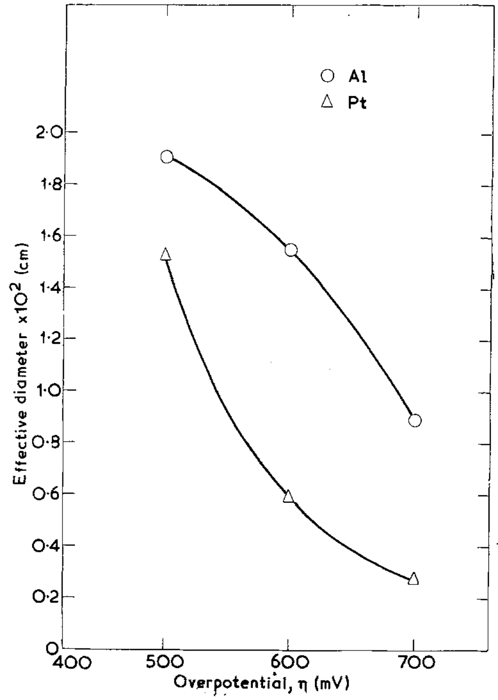

Fig. 3. Main grain size corresponding to the maxima of particle size distribution curves as a function of constant overpotential of deposition.

[4–7], current–time relationships are known to reflect the development of a disperse deposit in potentiostatic metal electrodeposition. A larger relative increase of current in the same time of deposition indicates the formation of a more disperse deposit. Hence, considering the current–time relationships, a decrease of particle size with increase of overpotential is indicated. The relation-

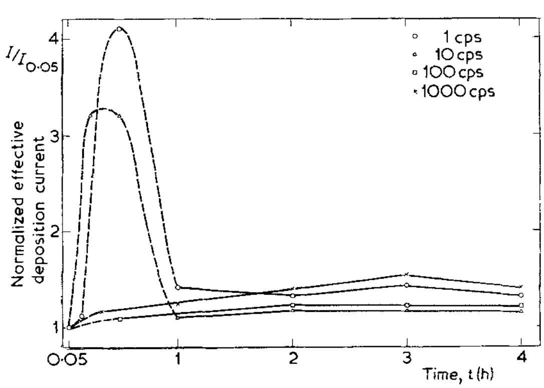

Fig. 4. Effective current–time relationships for copper deposition by sinusoidal pulsating overpotential at different values of frequency of pulsation on an aluminium electrode for an overpotential amplitude of 700 mV (effective overpotential 350 mV).

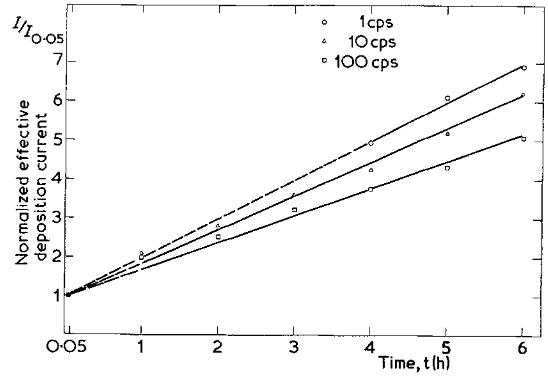

Fig. 5. Effective current–time relationships for copper powder deposition by sinusoidal pulsating overpotential on a painted platinum electrode at different values of frequency of pulsation for an overpotential amplitude of 600 mV (effective overpotential 300 mV).

ship between the mean grain size corresponding to the maxima of particle size distribution curves and overpotentials is presented in Fig. 3. These results are in accordance with literature data [8].

In pulsating overpotential deposition on aluminium, powder was not obtained, but a rough compact deposit was obtained. This can be seen from Fig. 4. The current–time relationships exhibit a maximum in the first stage of deposition. The decrease of current with increase of electrolysis time indicates that after some time of deposition the powder particles coalesce and hence the specific surface area decreases. On the painted platinum electrode powder deposits were obtained in all cases. Effective current–time relationships for copper powder deposition by pulsating overpotential are shown in Figs. 5 and 6, for pulsating over-

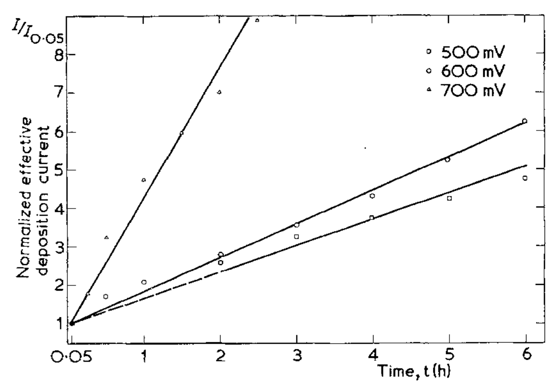

Fig. 6. Effective current–time relationships for copper powder deposition by sinusoidal pulsating overpotential on a painted platinum electrode for different values of overpotential amplitude at a frequency of pulsation of 10 cps.

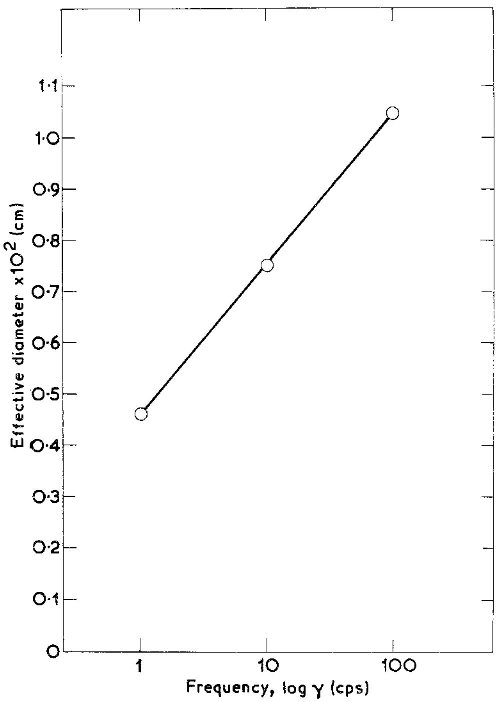

Fig. 7. Main grain size corresponding to the maxima of particle size distribution curves for sinusoidal pulsating overpotential deposition on a painted platinum as function of frequency (effective overpotential 300 mV).

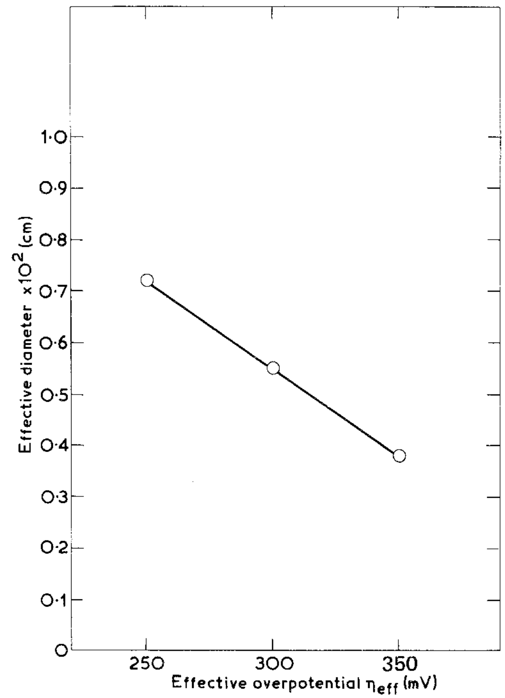

Fig. 8. Main grain size corresponding to the maxima of particle size distribution curves for sinusoidal pulsating overpotential deposition on a painted platinum as a function of effective overpotential. Frequency of pulsation 10 cps.

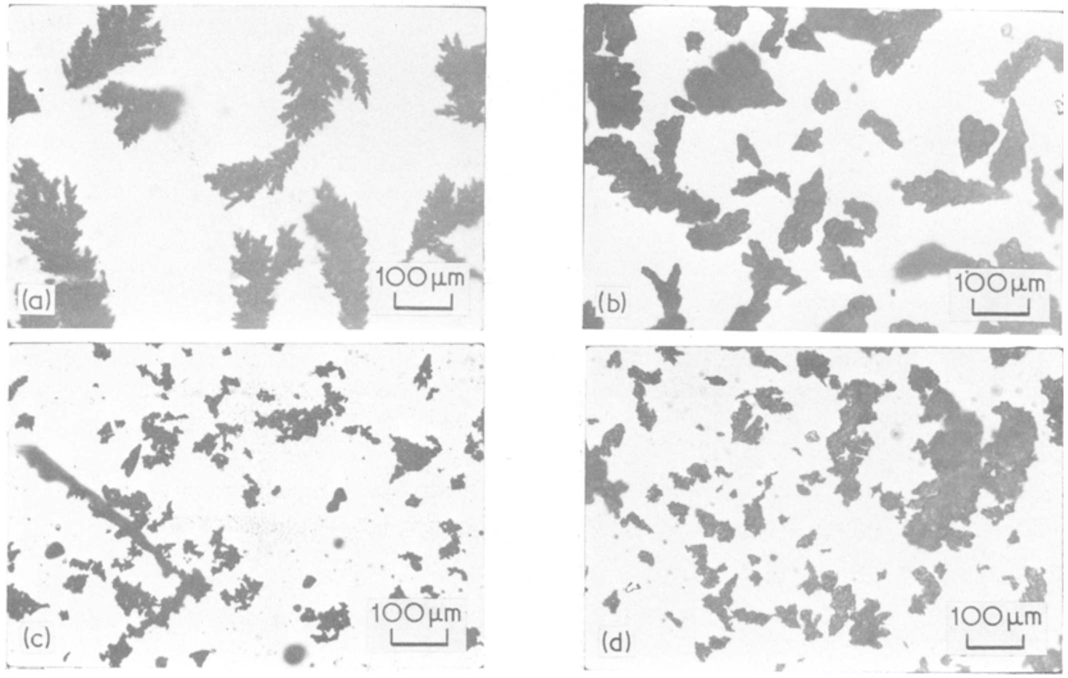

Fig. 9. Copper powders obtained on a painted platinum electrode by: (a) constant overpotential of 500 mV; (b) pulsating overpotential at a frequency of pulsation of 100 cps for overpotential amplitude of 600 mV (effective overpotential 300 mV); (c) constant overpotential of 700 mV; (d) pulsating overpotential at frequency of 1 cps for overpotential amplitude of 600 mV (effective overpotential 300 mV).

potential of amplitude value of 600 mV and different values of frequency of pulsation, and for a frequency of 10 cps and different values of amplitude overpotential respectively. In both cases a larger relative increase of current with time indicates formation of powders of smaller particle size. Hence, increasing frequency of pulsation for the same value of amplitude overpotential leads to increase of powder particle size, as well as a decrease of the amplitude value of pulsating overpotential for the same frequency of pulsation. The relationships between the mean grain size corresponding to the maxima of the particle size distribution curves and frequency and effective value of overpotential are shown in Figs. 7 and 8. These results are in accordance with earlier reported ones for effect of temperature, rate of stirring etc. on powder formation [8]. The increase of frequency of pulsation and decrease of overpotential amplitude lead to a decrease in diffusion control of deposition and to formation of larger and less dendritic particles. This is illustrated by the microphotographs presented in Fig. 9.

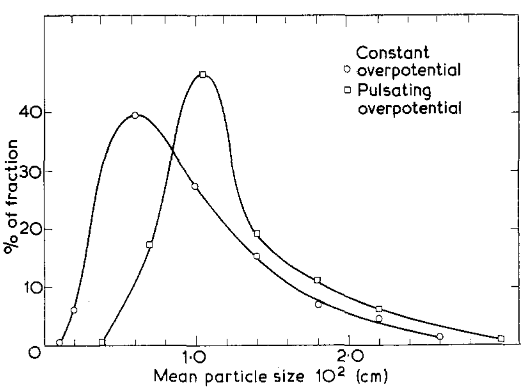

Fig. 10. Particle size distribution curves for (a) copper powder deposited on painted platinum for a constant overpotential of 600 mV; (b) copper powder deposited on painted platinum at frequency of pulsation of 10 cps for overpotential amplitude of 600 mV (effective overpotential 300 mV).

Typical particle size distribution curves are presented in Fig. 10. It is obvious that in the pulsating overpotential deposition a considerable narrower distribution curve is obtained.

From these results the possibility of obtaining a copper powder deposit with controlled particle size by changing the parameters of constant and pulsating overpotential deposition is shown.

It is obvious from [3] and results presented in this paper, that copper powder deposition by pulsating overpotential can be carried out with a much lower energy consumption compared with standard potentiostatic or galvanostatic deposition.

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