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Formation of powdered copper deposits by square-wave pulsating overpotential

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Copper powder deposits were obtained by square-wave pulsating overpotential electrolysis and by constant overpotential electrolysis. It is shown that the particle grain size and the morphology of deposited powders are functions of amplitude overpotential, frequency of pulsation and pulse to pause ratio in pulsating potential deposition, and of overpotential in constant overpotential deposition.

1. Introduction

In a recent paper [1] it was shown that powdered copper deposits with controlled grain size can be obtained in constant and sinusoidal pulsating overpotential deposition. It was shown that morphology and particle grain size are functions of overpotential in constant overpotential electrolysis, while in the case of sinusoidal pulsating overpotential these parameters were functions of amplitude overpotential and frequency of pulsation.

Similar effects can be expected in square-wave pulsating overpotential electrodeposition. In this case, besides the amplitude of the overpotential and frequency of pulsation, the pulse to pause ratio can also be varied.

It was the purpose of this work to investigate the effect of these parameters in the square-wave pulsating overpotential deposition of powder on powder morphology and particle grain size.

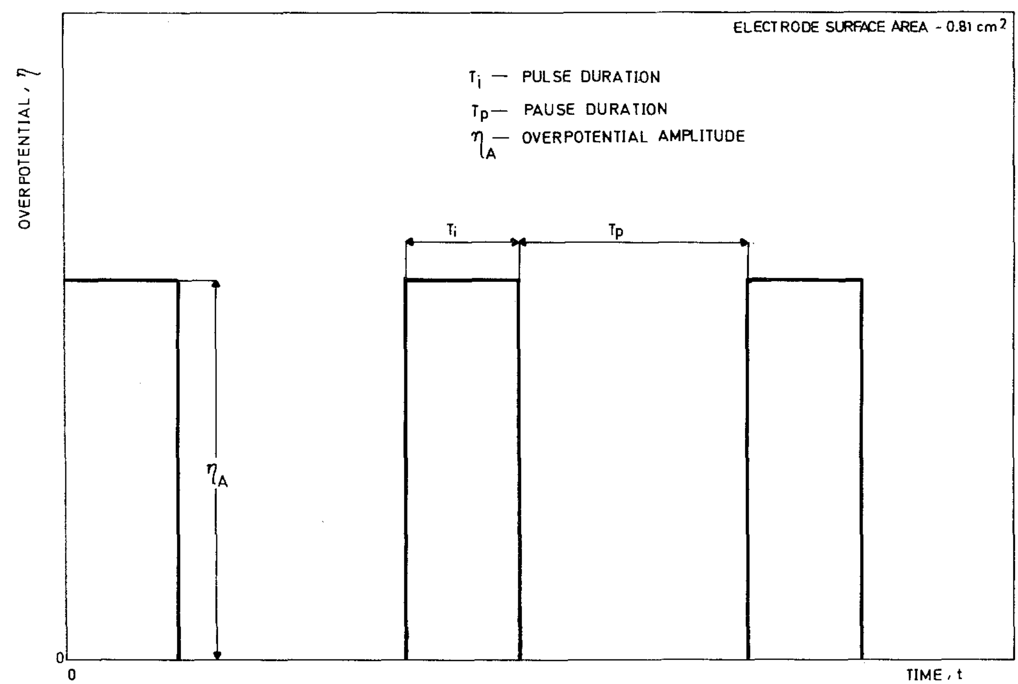

Fig. 1. The shape of the input pulsating overpotential.

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 at 25·0 ± 0·1° C, with constant and pulsating overpotential. The square-wave pulsating overpotential was potentiostatically applied to the cell. The shape of the applied pulsating overpotential is shown in Fig. 1. The ratio between the pulse and pause has been varied from 2 : 1 to 1 : 5 with an overpotential amplitude of 600 mV and pulse duration T_i = 5 ms. The effect of frequency was investigated with an overpotential amplitude of 600 mV.

The experimental set-up was the same as the one previously reported [2]. Powder was removed by tapping the electrode, washed by distilled water and alcohol and dried in air. The photomicrographs of powder were made at a magnification of x 100.

The particle size–distribution curves were plotted on the basis of effective diameters calculated for 500 different particles in each case.

3. Results and discussion

All copper powdered deposits obtained corresponded to the quantity of electricity of 80 mA h. The current–time relationships for copper powder deposition by constant overpotential and by square-wave pulsating overpotential with an overpotential amplitude of 600 mV for different frequencies of pulsation are presented in Figs. 2 and 3. The results obtained with the overpotential

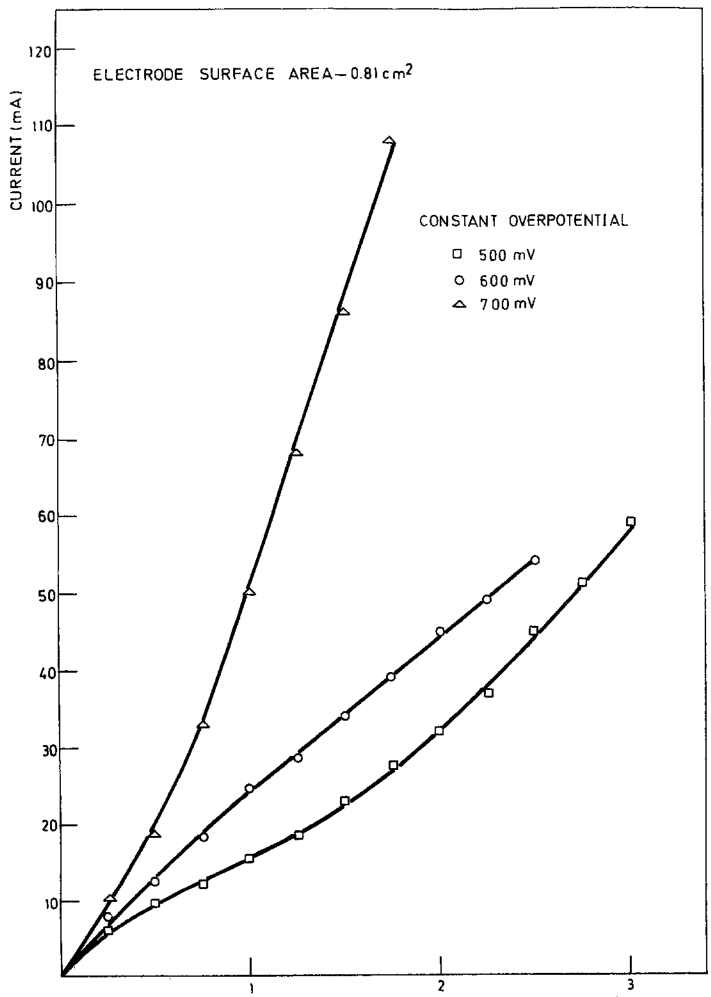

Fig. 2. Current–time relationships for copper powder deposition at different constant overpotentials.

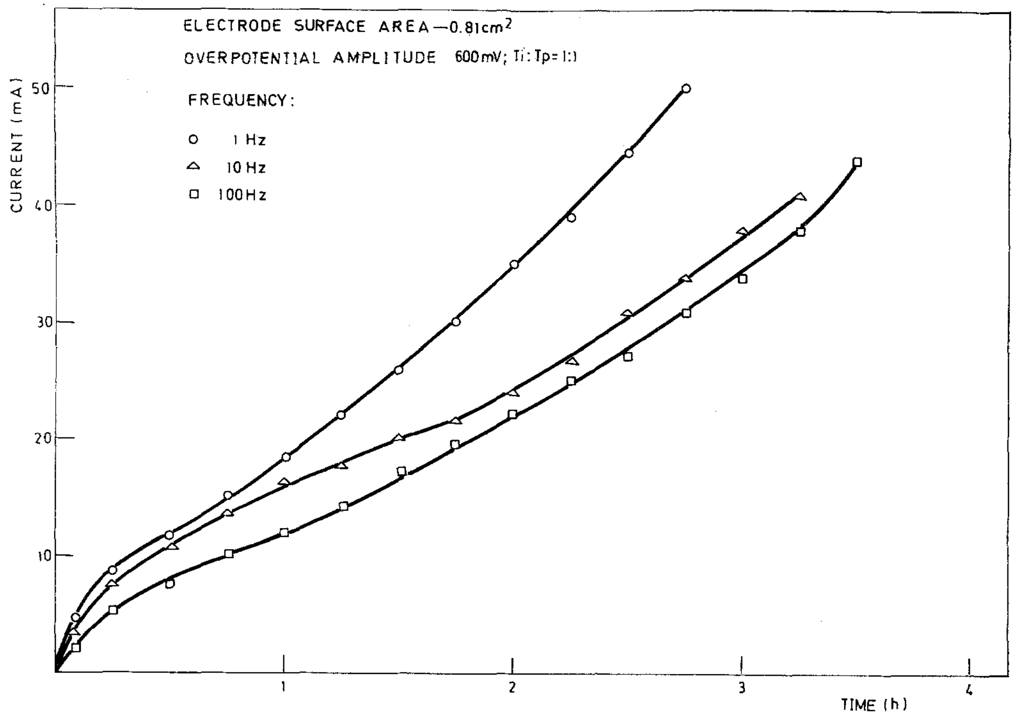

Fig. 3. Current–time relationships for copper powder deposition by square-wave pulsating overpotential at different values of pulsation frequency for an overpotential amplitude of 600 mV.

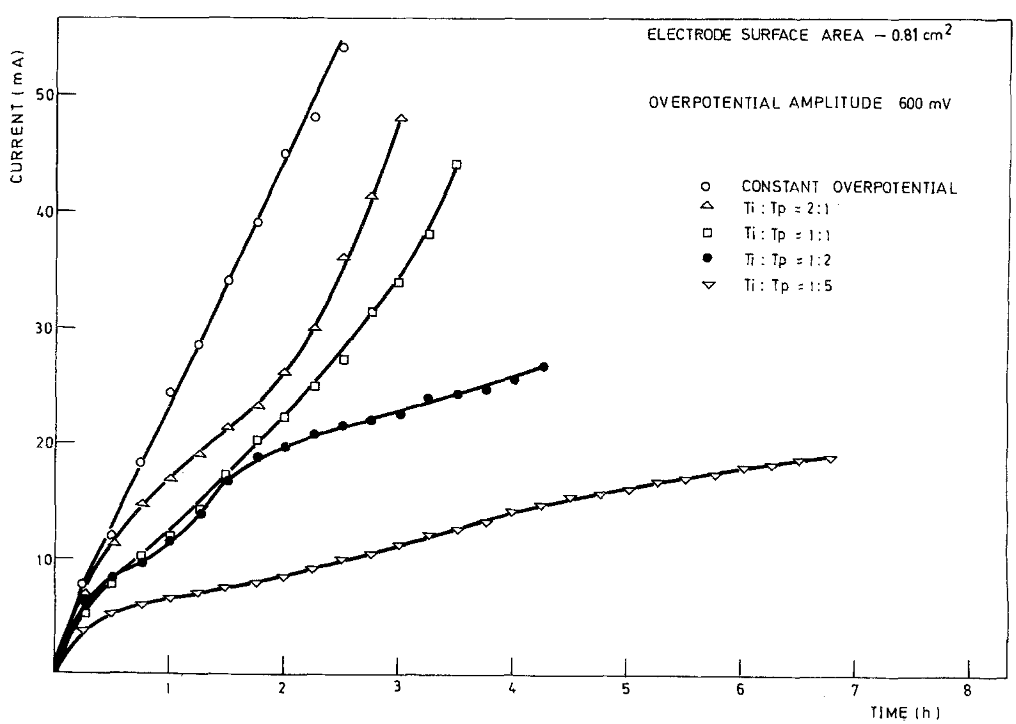

Fig. 4. Current–time relationships for copper powder deposition by square-wave pulsating overpotential at different pulse to pause ratios for an overpotential amplitude of 600 mV.

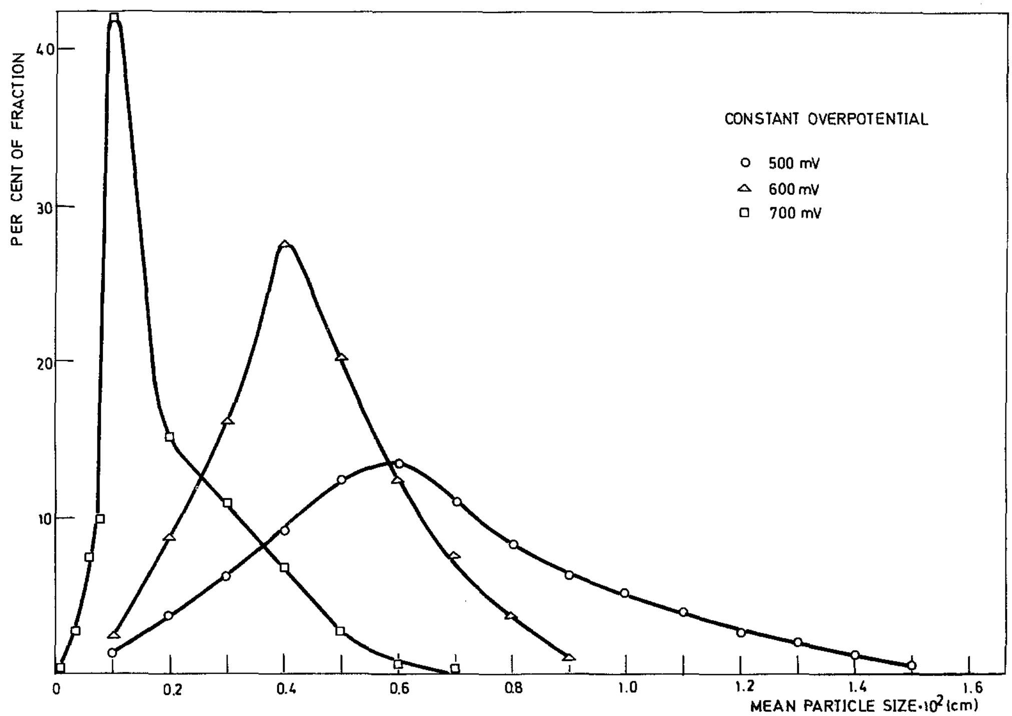

Fig. 5. Particle size distribution curves for copper powders deposited by different constant overpotentials.

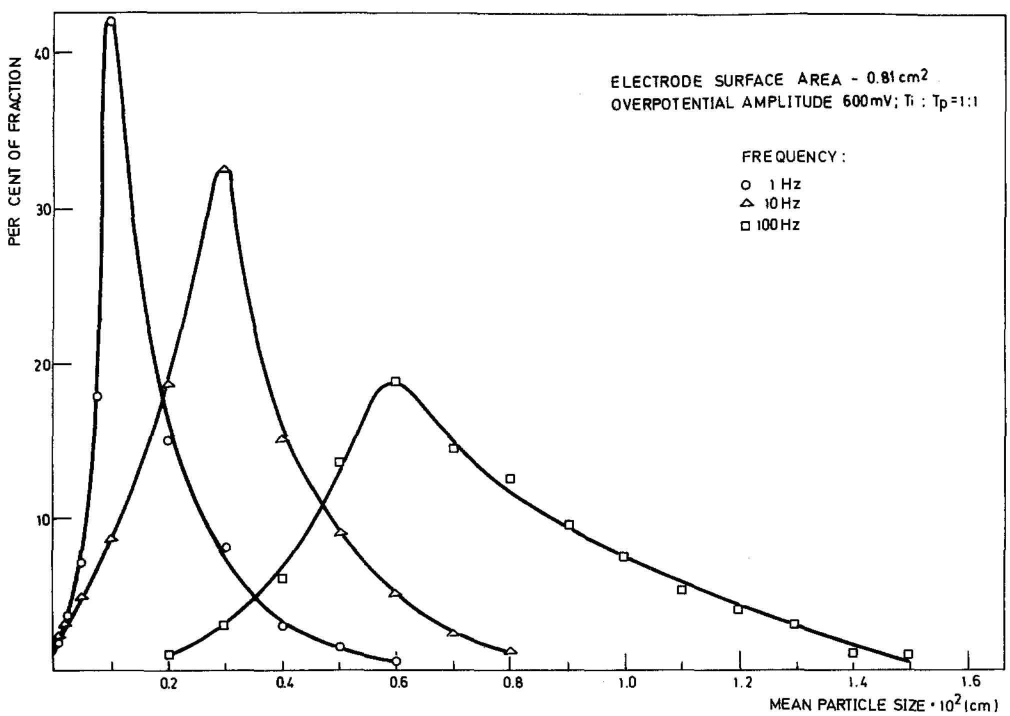

Fig. 6. Particle size distribution curves for copper powders deposited by square-wave pulsating overpotential at different values of pulsation frequency for an overpotential amplitude of 600 mV.

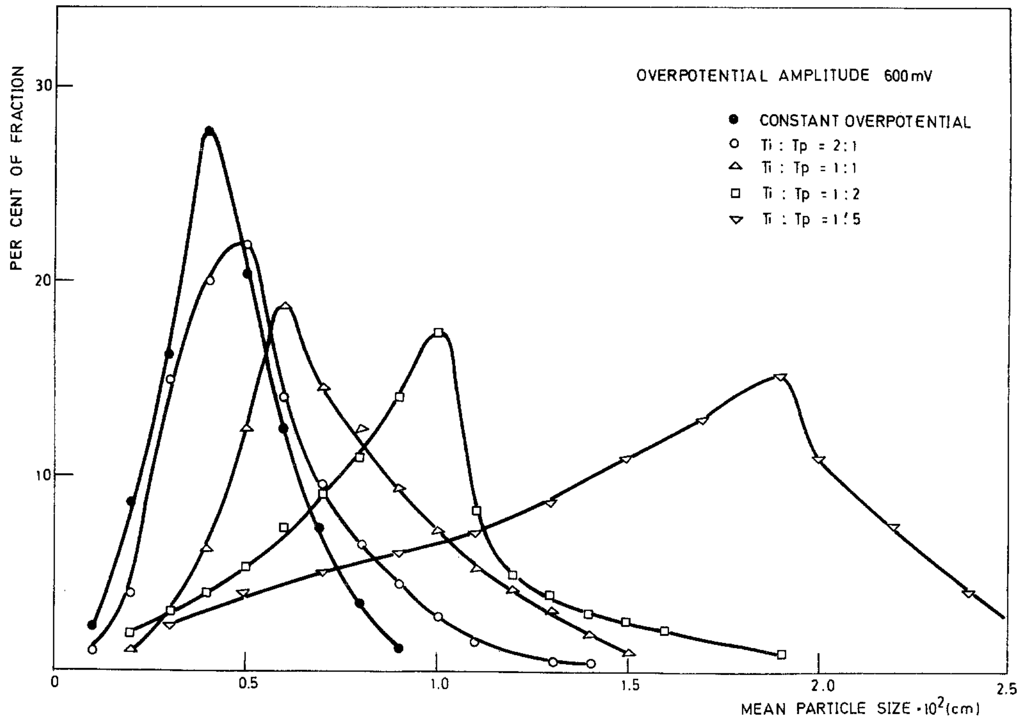

Fig. 7. Particle size distribution curves for copper powders deposited by square-wave pulsating overpotential at different pulse to pause ratios for an overpotential amplitude of 600 mV and pulse duration of 5 ms.

amplitude of 600 mV, pulse duration of T_i = 5 ms and different pause durations are presented in Fig. 4. It is seen that the current increases with time in both cases which indicates the formation of disperse deposits, the larger current corresponding to the more disperse deposit. This can be also seen from the particle size distribution curves presented in Figs. 5–7. It is interesting, that less narrow particle-size distribution curves are obtained for less disperse deposits.

The increase of frequency of pulsation, for the same value of overpotential amplitude, leads to an increase of particle size; an increase of the pause for the same pulse duration has the same effect. The effect of frequency in square-wave pulsating overpotential deposition was the same as that obtained for sinusoidal pulsating overpotential [1]. An increase of pause duration with constant pulse duration leads to a decrease in the diffusion control of deposition and to the formation of larger and less dendritic particles. This result is in agreement with earlier reported effects of different parameters which decrease diffusion control during the electrodeposition of powder [3].

The effect of the variation of pulse to pause ratio on the morphology of copper powder deposits is illustrated in Fig. 8. Thus it is possible to obtain powdered copper deposits with controlled particle grain size in pulsating overpotential electrodeposition.

The effects of the deposition overpotential on the morphology and particle grain size distribution in constant overpotential electrodeposition can be qualitatively discussed in terms of the Barton–Bockris theory of the electrolytic growth of dendrites [4]. It is known [4] that the dendrite growth velocity is maximal for some optimal value of dendrite tip radius. The optimal tip radius decreases with increase of overpotential. A difference between the maximal velocity and the actual velocities for dendrite growth, with tip radii larger than the optimal one, becomes larger with increasing overpotential. Hence, smaller particles and a more narrow particle-size distribution curves can be expected with increasing overpotential of powder deposition. The graphs in Fig. 5 confirm the above analysis.

The curves for the effect of frequency on the

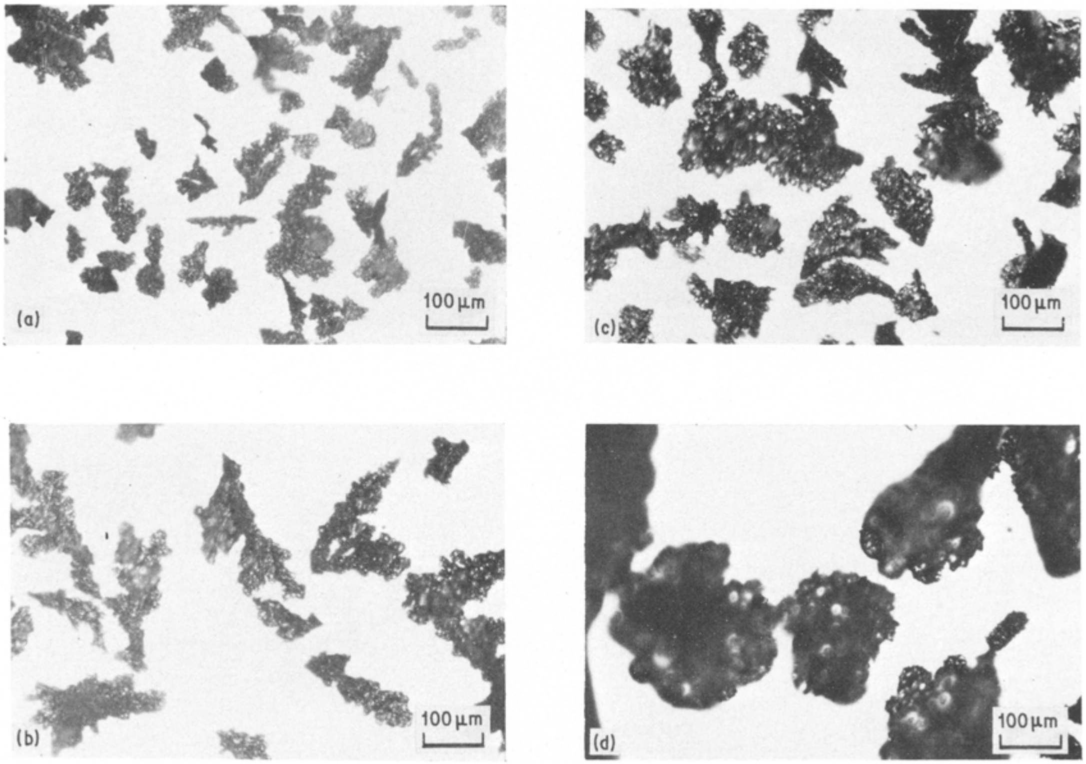

Fig. 8. Copper powders obtained by square-wave pulsating overpotential at different pulse to pause ratios for an overpotential amplitude of 600 mV and pulse duration of 5 ms for pulse to pause ratios: (a) 2:1 (b) 1:1 (c) 1:2 (d) 1:5.

particle size distribution presented in Fig. 6 can be analysed in terms of the Despić–Popov theory of the amplification of surface irregularities in pulsating overpotential electrodeposition [5]. It was shown that Nernst's diffusion layer under these conditions obeys this relationship,

$$\delta_N = K\nu^{-1/2} \quad (1)$$

where δ_N = Nernst's diffusion layer thickness, ν = frequency of pulsation and K = constant.

The difference in the supply of depositing ions between linear diffusion and, for example, spherical diffusion around tips of irregularities, can be considered to become appreciable when the diffusion layer thickness becomes of the same order of magnitude as the radius of curvature of the tips. For larger tip radii, irregularities grow according to the Barton–Bockris law [4]; at smaller radii the amplification of the irregularities obeys the mechanism of Despić and co-workers [6, 7]. Hence, the irregularities smaller than the critical ones, grow according to an exponential law [6, 7] while larger ones grow linearly [4]. A decrease of the frequency leads to an increase in this critical tip radius. In this way, at lower frequencies of pulsation, a larger fraction of the surface irregularities will grow up to the critical value according to the exponential law of amplification [6, 7] and a more narrow particle-size distribution curve is obtained. The effect of pulse ratio on particle size and morphology (Figs. 7 and 8) is due to the Kelvin effect during the pause. During the pause in square-wave pulsating overpotential the current flows in the opposite direction to that during the overpotential pulse, and smaller particles dissolve more easily than larger ones. In this way, it is possible to explain qualitatively the effects of conditions of electrolysis on the quality of copper powder deposits using the theories of dendrite initiation and dendritic growth. If this is so, it should be possible to develop a quantitative theory of metal powder deposition under potentiostatic conditions.

Acknowledgements

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