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The effect of pulsating overpotential on the morphology of electrodeposited silver powder particles

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The effects of overpotential amplitude, frequency and pulse-to-pause ratio in silver deposition by square-wave pulsating overpotential on the morphology of powdered particles were investigated. These results were compared with those obtained in constant overpotential electrolysis. The possibility of obtaining powder particles, with different properties, depending on conditions of electrolysis was demonstrated.

1. Introduction

It was shown in the recent papers [1, 2] that powdered copper deposits with controlled grain size can be obtained in the constant and pulsating overpotential deposition of copper. The purpose of this paper is to try to extend this procedure to the deposition of powdered silver deposits.

2. Experimental

A deposition was carried out from an electrolyte containing $10\,g\,dm^{-3}$ $AgNO_3$, $100\,g\,dm^{-3}$ $NaNO_3$, at pH = 0·8–1·5 [3] on a graphite electrode with constant and square-wave pulsating overpotential. The temperature was 25·0 ± 0·1° C. The experimental set-up and procedure were the same as earlier reported [1, 2]. The counter and reference electrodes were of pure silver.

In constant overpotential electrolysis the overpotential of deposition was varied from 140 to 200 mV. In pulsating overpotential deposition the frequency of pulsation was varied from 1 to 100 Hz at the overpotential amplitude of 200 mV. For the constant frequency of pulsation (1 Hz), the amplitude was varied from 160 to 200 mV. The pulse-to-pause ratio was also varied from the ratio 1 : 1 to 1 : 5 with pulse duration of 50 ms at the overpotential amplitude of 200 mV.

Some experiments have been performed at an amplitude of 160 mV with a 1 : 5 pulse-to-pause ratio. The pulse duration was again in this case 50 ms.

In all experiments powder fell spontanously from the electrode. Subsequently it was washed, with distilled water and ethanol, and microphotographs were taken under the magnification of x 100.

3. Results and discussion

The current–time relationship for the deposition of silver at a constant overpotential of 200 mV is presented in Fig. 1. Similar plots were obtained for the depositions at all constant overpotentials. The powder particles obtained in such a deposition are shown in Fig. 2. The shape of the current–time relationship and the morphology of particles in constant overpotential deposition can be explained in the following way. It is seen from Fig. 2 that dendritic powder particles probably originate by the cracking of tree-like dendrites growing on the electrode. They interweave during their growth and the whole deposit falls off at the same time when the weight of the tree-like dendrites becomes too large for the strength of the dendrite stalks. A fall of deposit is indicated by a fall in the deposition current.

Fig. 3 shows the current–time relationships for pulsating overpotential deposition at the frequency

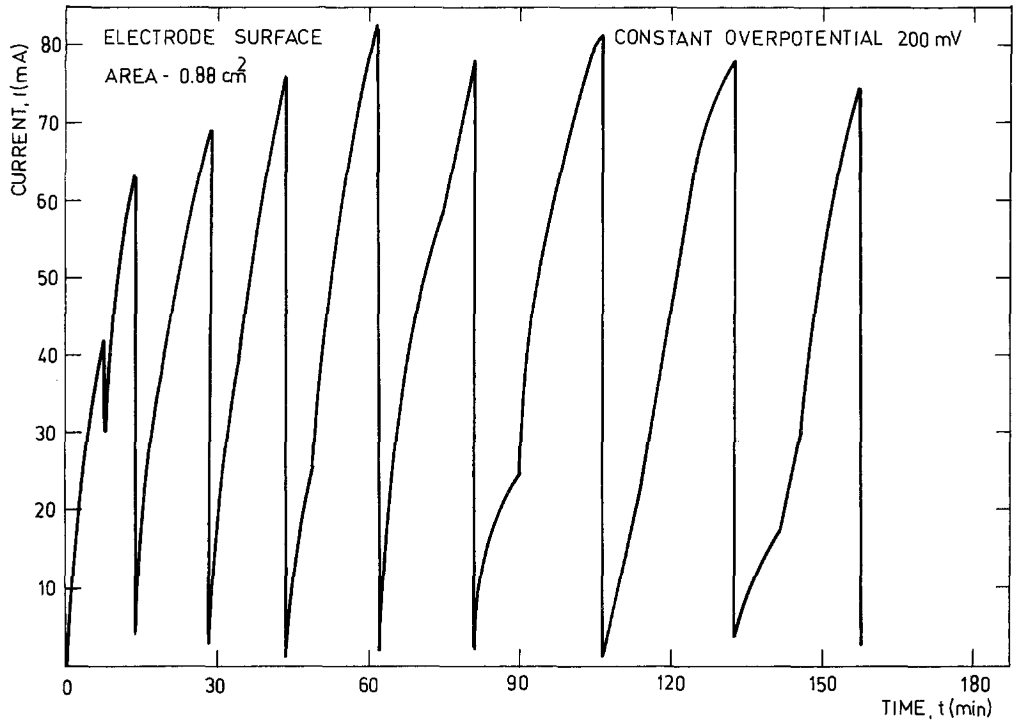


Fig. 1. The current–time relationship for silver powder deposition at a constant overpotential of 200 mV. Electrode surface area 0·88 cm^2.

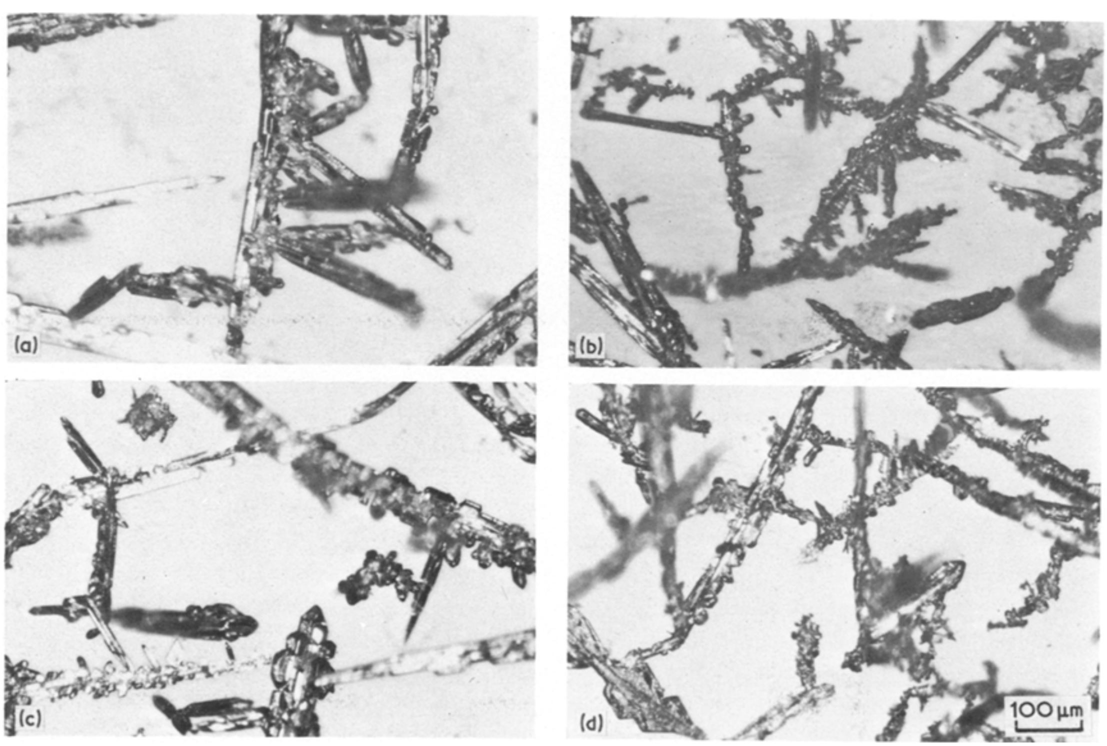


Fig. 2. Silver powder particles obtained by constant overpotential electrolysis at different overpotentials of deposition: a) 140 mV; b) 160 mV, c) 180 mV, d) 200 mV.

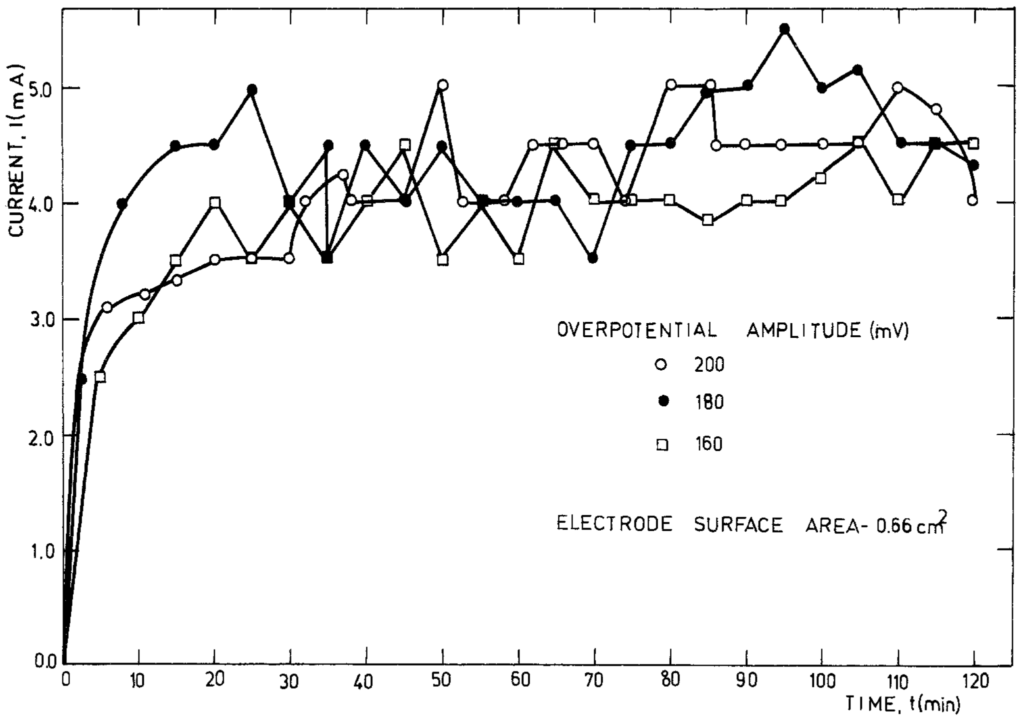
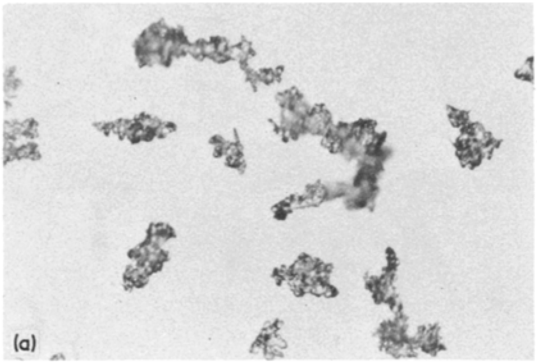
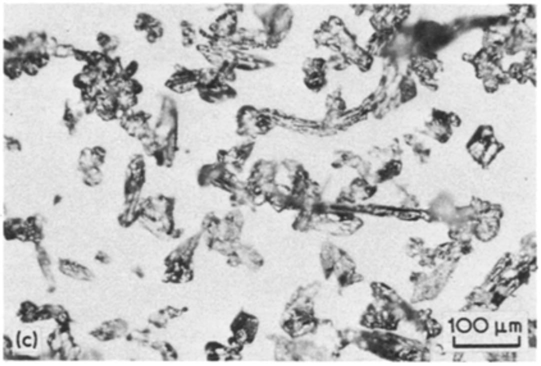


Fig. 3. The current–time relationships for silver powder deposition by pulsating overpotential at frequency of 1 Hz for different values at overpotential amplitude. Electrode surface area 0·66 cm^2.





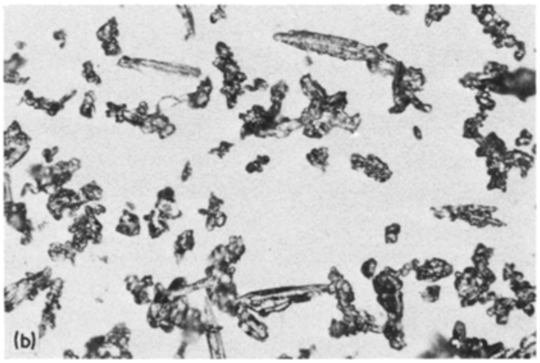


Fig. 4. Silver powder particles obtained by pulsating overpotential electrolysis at different values of overpotential amplitude: a) 200 mV, b) 180 mV, c) 160 mV, Frequency 1 Hz. Pulse-to-pause ratio 1 : 1.

of 1 Hz at different values of overpotential amplitude. The oscillations of current are smaller than those in constant overpotential deposition, indicating a growth of dendritic particles without interweaving. Similar current–time relationships are obtained in all cases of pulsating overpotential deposition. The effect of overpotential amplitude at a frequency of 1 Hz on the morphology of the

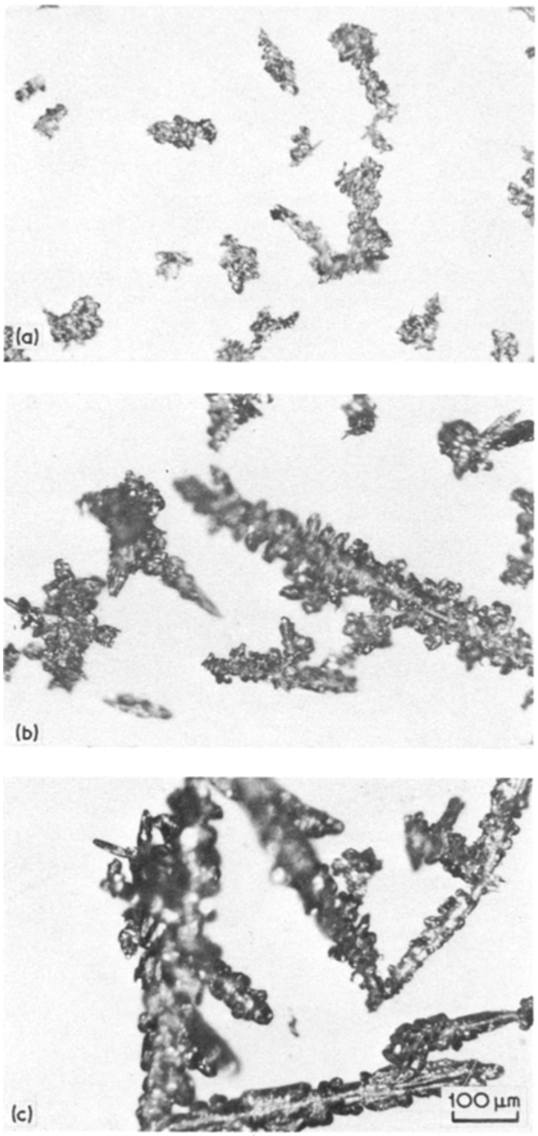


Fig. 5. Silver powder particles obtained by pulsating overpotential electrolysis at different frequencies: a) 1 Hz, b) 10 Hz, c) 100 Hz. Overpotential amplitude 200 mV. Pulse-to-pause ratio 1 : 1.

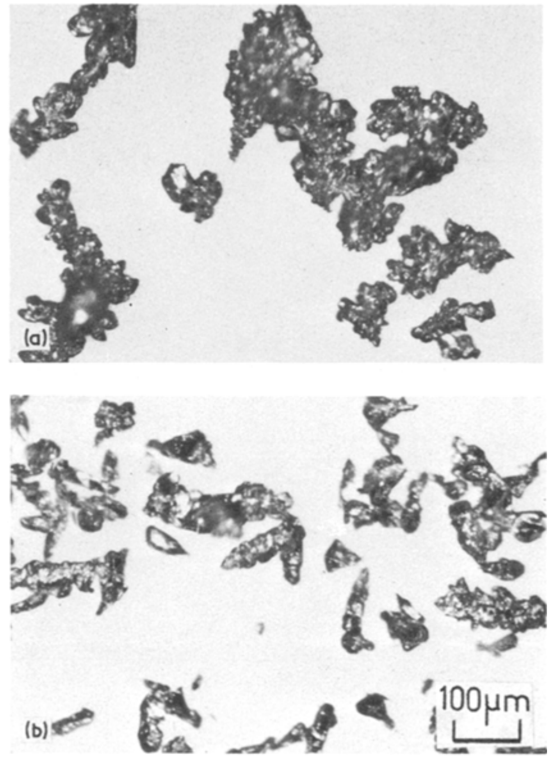


Fig. 6. Silver powder particles obtained by pulsating overpotential at different values of pulse to pause ratio: a) 1 : 2; b) 1 : 5. Pulse duration 50 ms. Overpotential amplitude 200 mV.

powder particles can be seen from Fig. 4. The overpotential amplitude does not have a large effect on the particle size. A decrease of overpotential leads to the formation of less dendritic particles. This is understandable on the basis of known effects of overpotential on the initiation and growth of dendrites [4–6].

The effect of frequency on particle grain size and morphology can be seen from Figs. 3, 4a and 5. The increase in frequency leads to the formation of larger and less branched dendritic particles. The effect of frequency on particle size is the same as in the case of copper powder deposition, and can be explained in the same way [2].

The effect of increasing the pause at one and the same pulse duration on the morphology and particle grain size can be seen from Figs. 5b and 6. The increasing pulse duration leads to a formation of smaller particles with a more regular crystal structure. Fig. 7 shows the powder obtained at 160 mV amplitude with a pulse-to-pause ratio of 1 : 5 and pulse duration of 50 ms. It is seen, that the powder particles in this case are small, well-defined silver crystals. These experiments indicate the possibility of obtaining the silver powder with different properties. The changing of the parameters of pulsating overpotential electrolysis seems to be a convenient way to study the deposition of metal powders as a function of conditions of electrolysis.

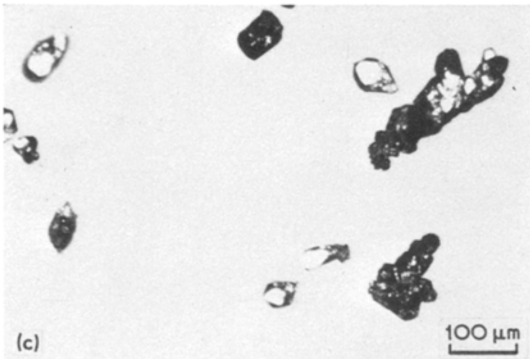


Fig. 7. Silver powder particles obtained by pulsating overpotential. Pulse-to-pause ratio 1 : 5. Pulse duration 50 ms. Overpotential amplitude 160 mV.

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