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Electrodeposition of silver powder by pulsating and reversing currents

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The effect of the shape of the current wave and frequency in silver deposition by pulsating and reversing currents on the morphology of powder particles were investigated. The possibility of obtaining particles with different properties, depending on conditions of electrolysis, was demonstrated.

Notation

j_{av}	average current density
j_L	limiting diffusion current density
j_0	exchange current density
p	anodic/cathodic time ratio
η_A	overpotential amplitude
$2.3\eta_0$	slope of the cathodic Tafel line

1. Introduction

It has been shown that powdered metal deposits with controlled grain size and morphology can be obtained in the pulsating overpotential deposition of metals [1–5]. It is easy to use pulsating overpotential deposition in laboratory size cells, but difficulties arise on a practical scale because of the demands for a higher power and a high speed potentiostat. It is easier to obtain pulsating or reversing currents, and because of this, the deposition of metal powders with desired properties obtained by these means may have greater practical importance than by use of pulsating overpotential.

The purpose of this paper is to show the effects of parameters determining the current wave and frequency on the grain size and morphology of silver powder particles.

2. Experimental details

Deposition was carried out from a non-stirred electrolyte containing $10\,\mathrm{g\,dm^{-3}}$ $AgNO_3$ and $100\,\mathrm{g\,dm^{-3}}$ $NaNO_3$ at pH $= 0.8 - 1.5$ [3] on a graphite electrode with constant, pulsating and reversing currents. The experimental set up was the same as reported earlier [2, 3]. The temperature was $(25 \pm 1)°$C. The counter electrode was of pure silver. In all experiments the initial average current density was $11.5\,\mathrm{mA\,cm^{-2}}$ and the quantity of silver corresponded to $25\,\mathrm{mAh\,cm^{-2}}$. In pulsating current deposition the frequency of pulsation was varied from 1 to 1000 Hz at pause to pulse ratio 1, and pause to pulse ratios used were 1, 2 and 5, with pulse duration of 10 ms. In reversing current deposition cathode current densities used were $20.7\,\mathrm{mA\,cm^{-2}}$, $25.8\,\mathrm{mA\,cm^{-2}}$, $28.7\,\mathrm{mA\,cm^{-2}}$ and $103.5\,\mathrm{mA\,cm^{-2}}$; anodic current densities were $2.8\,\mathrm{mA\,cm^{-2}}$, $5.7\,\mathrm{mA\,cm^{-2}}$, $6.9\,\mathrm{mA\,cm^{-2}}$ and $34.3\,\mathrm{mA\,cm^{-2}}$. Anodic to cathodic pulse ratios were 1, 1 : 5 and 5 : 1 with a cathodic pulse duration of 10 ms.

In some experiments powder fell spontaneously from the electrode, and in others the powder was removed by tapping the electrode. Subsequently it was washed with distilled water and ethanol, and photomicrographs were taken at a magnification of 50.

3. Results and discussion

The polarization curve for silver deposition is shown in Fig. 1. It is characterized by a well defined limiting diffusion current density plateau. Metal powders in galvanostatic deposition are obtained at current densities larger than the limiting diffusion value [6]. Because of this the current density used was 1, 1 $j_L \approx 11.5\,\mathrm{mA\,cm^{-2}}$. Typical powder particles obtained in constant current deposition are shown in Fig. 2. They are larger and less dendritic than those obtained in constant overpotential deposition [3], regardless of the larger initial current density. This is due to decreasing deposition overpotential during the deposition process caused by increasing electrode surface area and decreasing real current density [7].

The effect of pause to pulse ratio on the morphology and particle grain size is illustrated by Fig. 3. This can be explained in the following way. It is easy to show that for a pulsating current, in steady state conditions,

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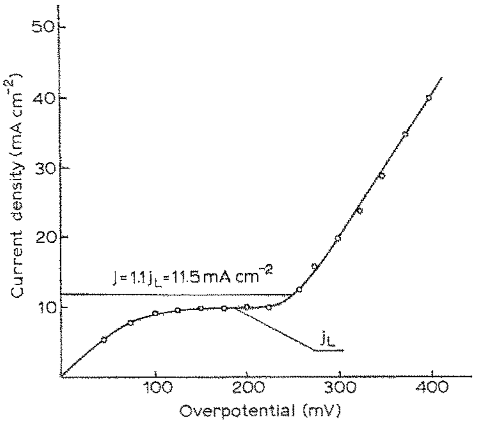

Fig. 1. Polarization curve for silver deposition from an electrolyte containing $10\,g\,dm^{-3}$ $AgNO_3$ and $100\,g\,dm^{-3}$ $NaNO_3$.

the overpotential amplitude and pause to pulse ratio are related by the equation:

$$\eta_A = \eta_0 \ln(j_{av}/j_0) + \eta_0 \ln\left(\frac{1}{1 - j_{av}/j_L}\right) + \eta_0 \ln(p + 1) \qquad (1)$$

meaning that deposition during 'on' periods is carried out at overpotentials larger than in d.c. conditions at the same average current densities. In this way increasing p leads to a decreasing size of particles, these being deposited at higher overpotentials.

The effect of frequency in pulsating current deposition is illustrated by Fig. 4. Deposition at lower frequencies results in smaller particles, while at higher frequencies the deposited particles are the same shape and grain size as in deposition at constant current. The last effect is due to the smearing effect of the double layer capacity on the faradaic current wave [5].

The effect of reversing current on the morphology and powder particle size is illustrated by Fig. 5. It is seen that the morphology of the silver particles is different to those obtained in d.c. and pulsating current deposition. The powder particles are not needle-like. This is due to the Kelvin effect during the anodic periods; the points of dendrites with lower tip radii are dissolved faster than those with larger tip radii, because of their more negative standard potential [8]. This effect is more pronounced in the case of very high anodic current amplitude values. In this case an additional effect is possible: the dendrite root can 'burn' during the anodic period, which results in very low particle grain size.

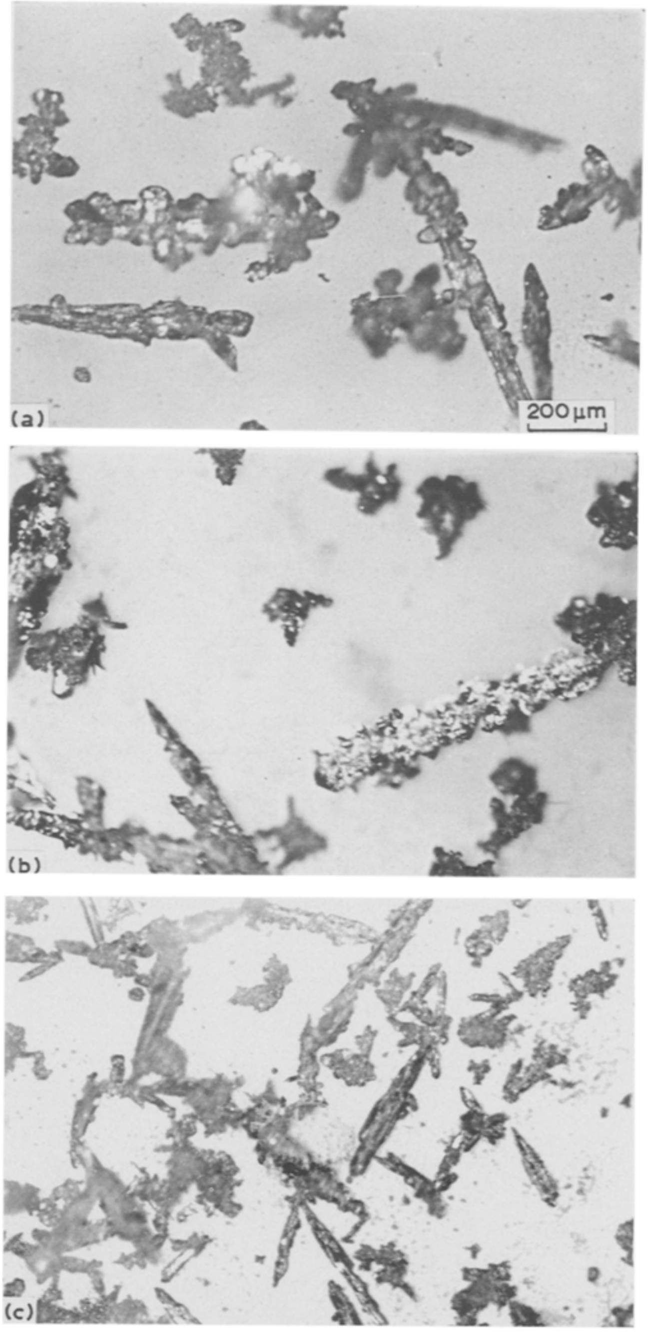

Fig. 3. Silver powder particles obtained by pulsating currents at different pause to pulse ratios. Average current density: $11.5\,mA\,cm^{-2}$. Pulse duration 10 ms. Pause to pulse ratios: (a) 1, (b) 2, (c) 5.

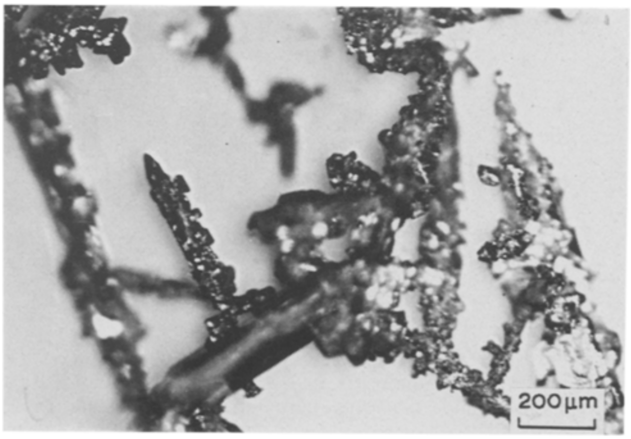

Fig. 2. Silver powder particles obtained in constant current deposition. Current density $11.5\,mA\,cm^{-2}$.

Powder particles originate by the cracking of tree-like dendrites growing on the cathode [3]. They interweave during their growth and the whole deposit falls off when the weight of the tree-like dendrites becomes too large for the strength of the dendrite stalks. A detachment of deposit is indicated by an increase of deposition overpotential.

Figure 6 shows the overpotential-time relationship

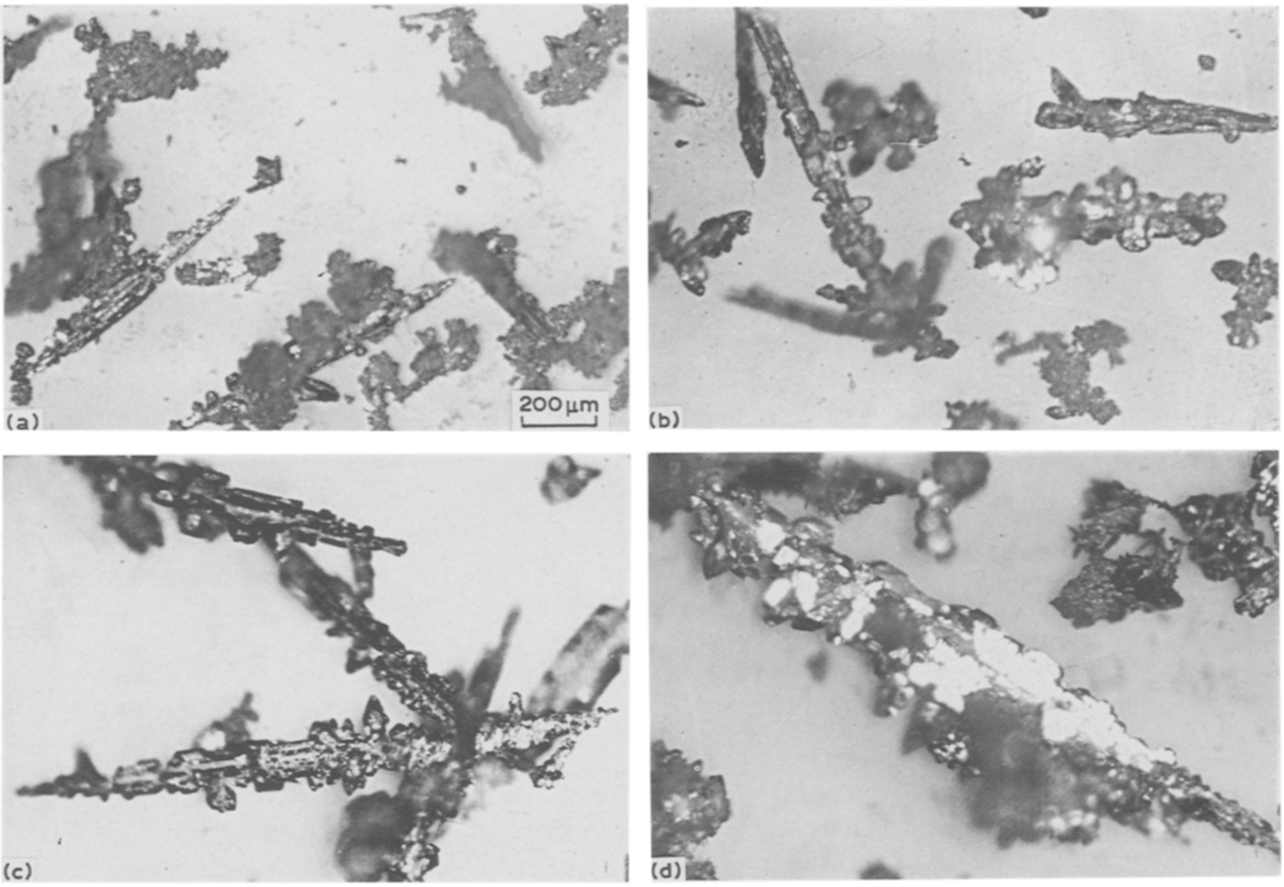

Fig. 4. Silver powder particles obtained by pulsating currents at different frequencies. Average current density 11.5 mA cm^{-2}. Pause to pulse ratio 1. Frequencies: (a) 1, (b) 10, (c) 100, (d) 1000 Hz.

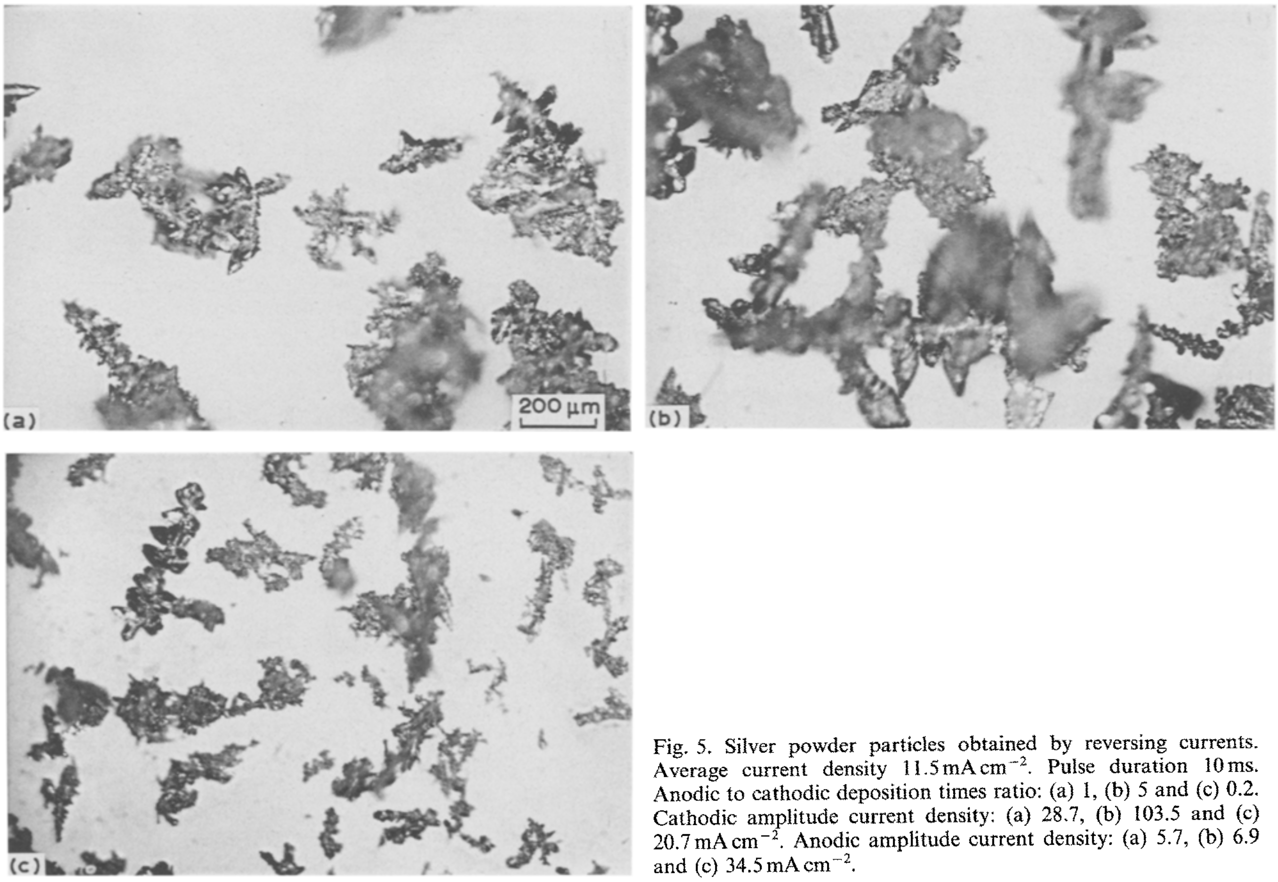

Fig. 5. Silver powder particles obtained by reversing currents. Average current density 11.5 mA cm^{-2}. Pulse duration 10 ms. Anodic to cathodic deposition times ratio: (a) 1, (b) 5 and (c) 0.2. Cathodic amplitude current density: (a) 28.7, (b) 103.5 and (c) 20.7 mA cm^{-2}. Anodic amplitude current density: (a) 5.7, (b) 6.9 and (c) 34.5 mA cm^{-2}.

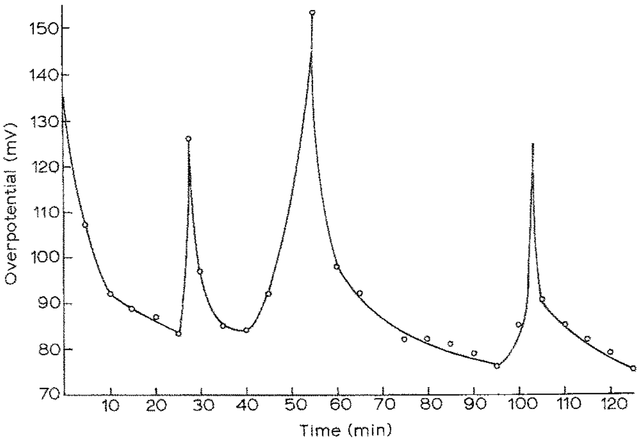

Fig. 6. The overpotential against time relationship for silver powder electrodeposition by constant current. Current density 11.5 mA cm^{-2}.

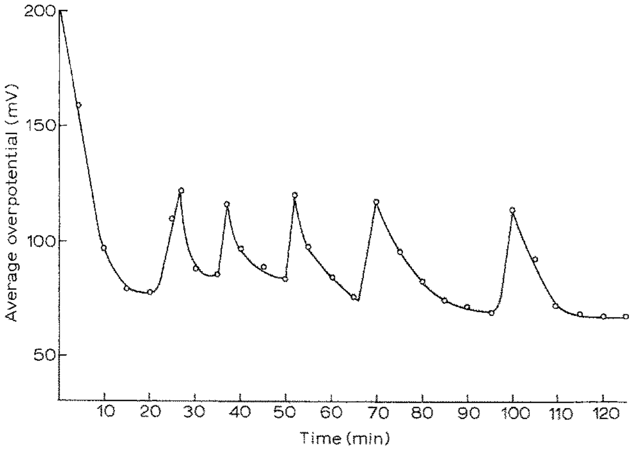

Fig. 7. The average overpotential against time relationship for silver powder electrodeposition by pulsating current. Average current density 11.5 mA cm^{-2}. Pause to pulse ratio 1. Pulse duration 10 ms.

for deposition at a constant current. It is seen that deposit detaches after relatively long deposition periods, which results in the formations of large particles. In the pulsating current case, as seen from Fig. 7, the deposition times are shorter, i.e. deposit detaches after shorter times. This is due to the thinner dendrite stalks and results in the formation of smaller particles.

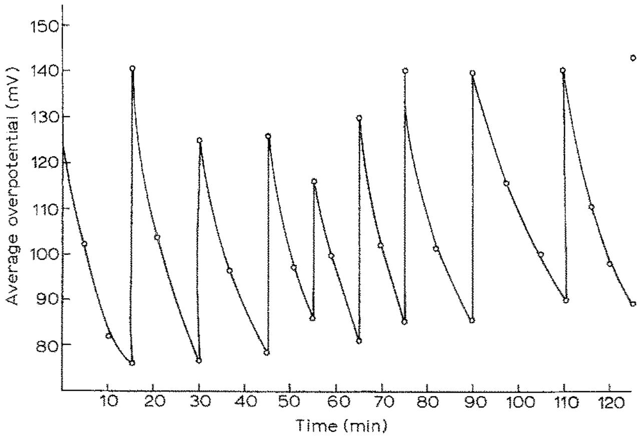

Fig. 8. The average overpotential against time relationship for silver powder electrodeposition by reversing current. Average current density 11.5 mA cm^{-2}. Anodic to cathodic deposition times ratio 1. Pulse duration 10 ms. Cathodic amplitude current density 28.7 mA cm^{-2}. Anodic amplitude current density 5.7 mA cm^{-2}.

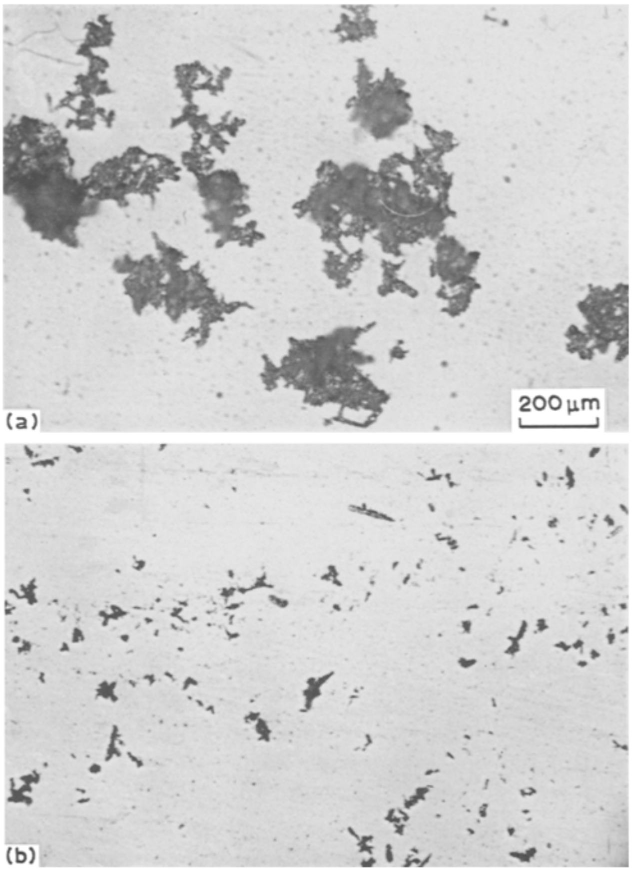

Fig. 9. Disperse silver deposits obtained by electrolysis with constant current density of 11.5 mA cm^{-2}. Electrode tapping time 5 min. (a) Agglomerates of silver dendrites before treatment with water stream. (b) Silver powder particles after treatment with water stream.

A similar situation appears in reversing current deposition, as illustrated by Fig. 8. As can be seen from Figs 2, 3a, 5a and 6–8 shorter deposition time means smaller particles. This is in accordance with literature data [9].

The last experiments were carried out by tapping the electrode during deposition every 5 min. In the constant current case agglomerates of powder particles were obtained, Fig. 9, as in the case of some soft metals such as lead [10] and tin [11]. This is due to the fact that silver particles are very thin, having different

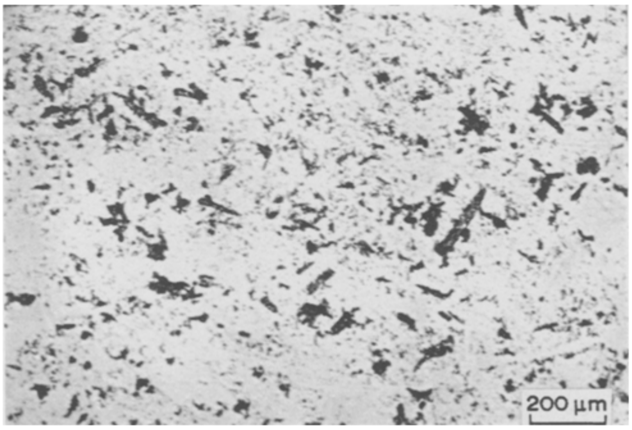

Fig. 10. Silver powder particles obtained by reversing current electrodeposition. Average current density 11.5 mA cm^{-2}. Anodic to cathodic deposition times ratio 1. Pulse duration 10 ms. Cathodic amplitude current density 28.7 mA cm^{-2}. Anodic amplitude current density 5.7 mA cm^{-2}. Electrode tapping time 5 min.

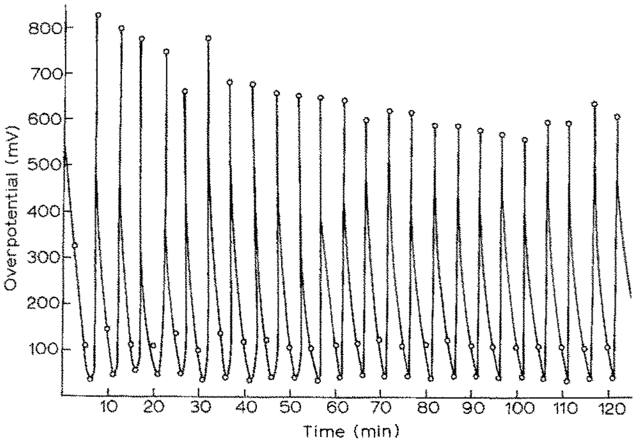

Fig. 11. The overpotential against time relationship for silver powder electrodeposition by constant current density 11.5 mA cm^{-2} and tapping time 5 min.

mechanical properties from thicker ones. After destroying the agglomerates using a water stream very fine powder particles were obtained (Fig. 9b). In the reversing current deposition there is no formation of agglomerates, but fine powder particles are obtained directly. This is in accordance with findings on lead [10] and tin [11] powder deposition by pulsating overpotential. It is also seen from Fig. 11 that overpotential jumps after detachments of deposit are more pronounced in the reversing current case, implying a better removal of powder particles from the electrode in this case.

On the basis of the above results, it is clear that the morphology and grain size of silver powder particles are strongly influenced in electrodeposition by pulsating and reversing current. The deposition of metal powders by pulsating and reversing currents on a pilot plant scale will be the object of further investigations.

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