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Morphology and growth of electrodeposited silver powder particles

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Abstract

The effect of overpotential pulsing and periodic current reversal on the morphology of silver powders was investigated using a scanning electron microscope (SEM). It is shown that the profile of pulses or current reversal determines the micromorphology of the electrodeposited silver particles. Generally, three forms of silver were detected: (1) dendrites, (2) equiaxial crystals (independent and/or agglomerates) and (3) rods. The shape of particle seems to be the result of an interplay between the surface energy and growth kinetics.

Keywords: Silver powder; Morphology; Overpotential pulsing; Current reversal

1. Introduction

It is well known that silver powders with different properties can be obtained by electrodeposition from a range of electrolytes by varying the operating conditions. The same effects can be also obtained by overpotential pulsing whilst keeping all other parameters unchanged. When overpotential pulsing the output current reverses from reduction to oxidation, and similar effects on the morphology and grain size of powder particles can be expected using either overpotential pulsing or current reversal. Whilst it is easy to use overpotential pulsing in a laboratory-scale cell, difficulties arise on a practical scale because of the demands for higher power and a high speed potentiostat. It is easier to obtain current reversal on a practical scale therefore deposition of silver powder by current reversal is of greater practical importance than overpotential pulsing (Popov and Pavlović, 1993).

The ability to generate silver powder with well-defined morphologies provides the opportunity for systematic studies of the relationship between properties of particles and their geometrical shape. Morphology, which is probably the most important property of electrodeposited metals, depends mainly on the kinetic parameters of the deposition process and the deposition overpotential or current density. In the application of metal powders many properties are of interest such as: the size and shape of the particles, bulk weight, flow rate, corrosion resistance, specific surface area, apparent density and quality of sintered product. In general, these properties depend on the shape and the size, which can be influenced by appropriate electrolysis regime (Popov and Pavlović, 1993; Pavlović and Popov, 2005). The aim of this paper is to describe the effect of overpotential pulsing and current reversal on the

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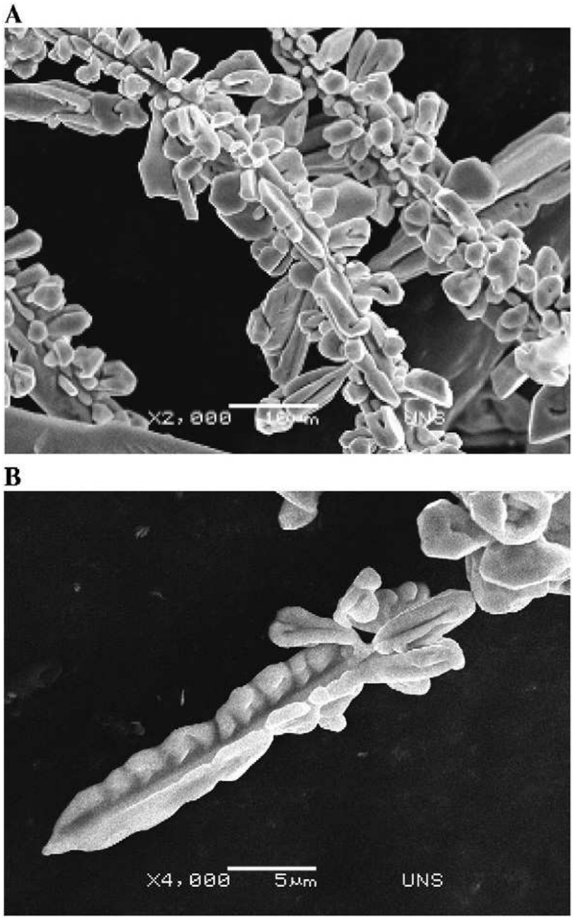

Fig. 1. SEM image. Silver powder particles obtained by square-wave pulsation overpotential ($\eta_a = 300$ mV, pulse to pause ratio 1:1, pulse duration 50 ms); (A) general view; (B) formation of secondary branches.

morphology and dimensions of silver powder particles as well as to show the limits of the current reversal technique.

2. Experimental

Silver powders were deposited from an unstirred solution containing 10 g L^{-1} $AgNO_3$ and 100 g L^{-1} $NaNO_3$ at pH = 0.8–1.5 (Pavlović et al., 1978; Popov et al., 1991a,b) onto a glassy carbon cathode by square-wave overpotential pulses ($\eta_a = 300$ mV, pulse to pause ratio 1:1, 1:2, 1:5; pulse duration 50 ms) and by current reversals ($j_c = 9$ mA, $j_a = 3$ mA, $t_c{:}t_a = 1{:}1$, pulse duration 10 ms, $j_c = 70$ mA, $j_a = 38.5$ mA, $t_c{:}t_a = 1{:}1$ pulse duration 10 ms and $t_c{:}t_a = 5{:}1$ pulse duration 10 ms). In all cases the electrode surface area was 1 cm^2. The counter and reference electrodes were of pure silver (99.9% — Aldrich) previously treated with 1:1 HNO_3. Experiments were performed at (25 ± 1) °C. The current was 810 mA/min/cm^2 in all cases. The powder was washed with distilled water and suspended in ethanol.

The morphology of the deposits was investigated using a scanning electron microscope.

3. Results and discussion

In all investigated samples three main types of particles appear: dendrites, equiaxed crystals (independent and/or agglomerates) and rods.

The representative morphology obtained by overpotential pulsing is shown in Fig. 1 and is clearly dendritic. It is known that 2D dendrites are formed at lower overpotentials, whereas 2D and/or 3D dendrites appear at higher overpotentials (Dimitrov et al., 1998). Crystals with octahedral facets (George and Vaidyan, 1981) developed at tips and sides of primary and secondary branches (3D dendrites) of particles are

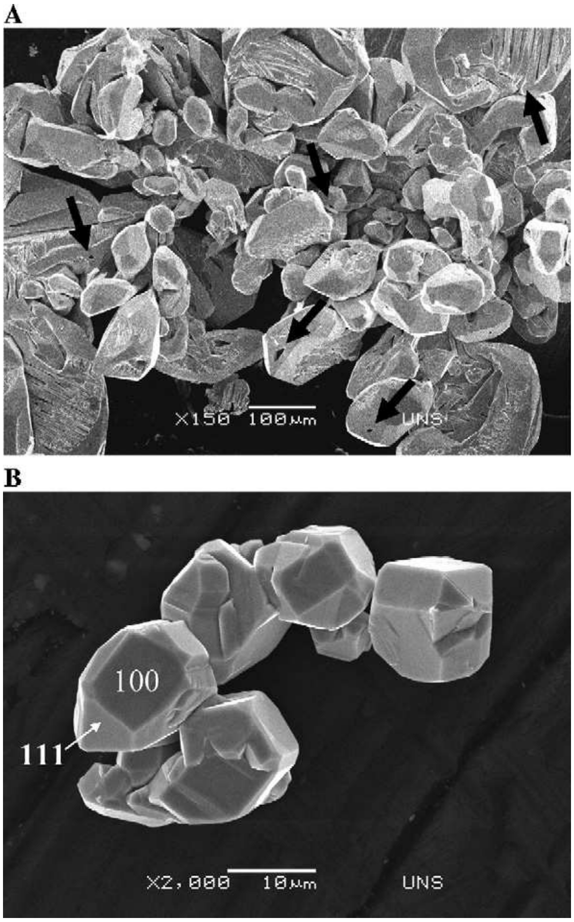

Fig. 2. SEM image. Silver powder particles obtained by square-wave pulsation overpotential; (A) $\eta_a = 300$ mV, pulse to pause ratio 1:2, pulse duration 50 ms; (B) $\eta_a = 300$ mV, pulse to pause ratio 1:5, pulse duration 50 ms.

noticed in this sample (Fig. 1A). Dendrite particles may significantly vary in size which is illustrated by the length of central stems ranging from 30 to 250 μm. It should be mentioned that the formation of dendrites passes through several stages. An early stage of nucleation of the secondary branches (precursors) is shown in Fig. 1B.

The effect of increasing the pause between pulses can be seen in Figs. 1 and 2. The increasing pause duration (pulse to pause ratio 1:1→1:2→1:5) leads to a formation of smaller particles with more regular crystal structure. The particles have large surface areas and often agglomerate as a result of attractive forces and the tendency of the system to minimize the total surface energy (Fig. 2A,B). It was proposed that agglomeration appears as a result of the interweaving of growing dendrites (Popov et al., 1990). In the case of more compact and less branched particles it is obvious that there are fewer possibilities to interweave. The agglomerates in Fig. 2A are composed of irregular sizes and shapes many of which exhibit defects as indicated by the dark arrows. When the pulse to pause ratio was 1:5 the agglomerates were composed of well-defined silver crystals (Fig. 2B).

The surface energies associated with different crystallographic planes vary with $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$ being the general sequence (Wang, 2000). The forms of silver crystals are defined by the octohedral {111} and cubic {100} faces. It was reported that {111} faces appear first as triangular facets (Radmilović et al., 1998). The final form of crystals will obviously depend on the relative rate of growth of cubic and octahedral faces. The particles formed are crystallographically perfect with no surface defects.

The current due to pulsing is anodic and dissolution will occur. The dissolution of a protrusion is more rapid than dissolution of a flat surface. Consequently, branching of dendrites and the formation of agglomerates can be prevented by using overpotential pulsing. The faceted surfaces of silver powder particles can be explained by the adatoms in unstable positions dissolving faster than atoms in the lattice encouraging smooth deposition. This is possible only in overpotential pulsing electrodeposition (Popov et al., 2002) and because of this the experiments with overpotential pulsing are included in this paper. Besides, the deposit from Fig. 2B can be taken as a reference for regular forms of silver powder particles. It is necessary to note that the current wave in overpotential pulsing forms spontaneously according to overall deposition conditions (Popov et al., 1991a,b, 1997), being practically optimal at high pause to pulse ratios. Unfortunately, the overpotential pulsing electrodeposition is difficult to perform in practical systems, and current reversal as an approximation of the current wave in overpotential pulsing case could be used.

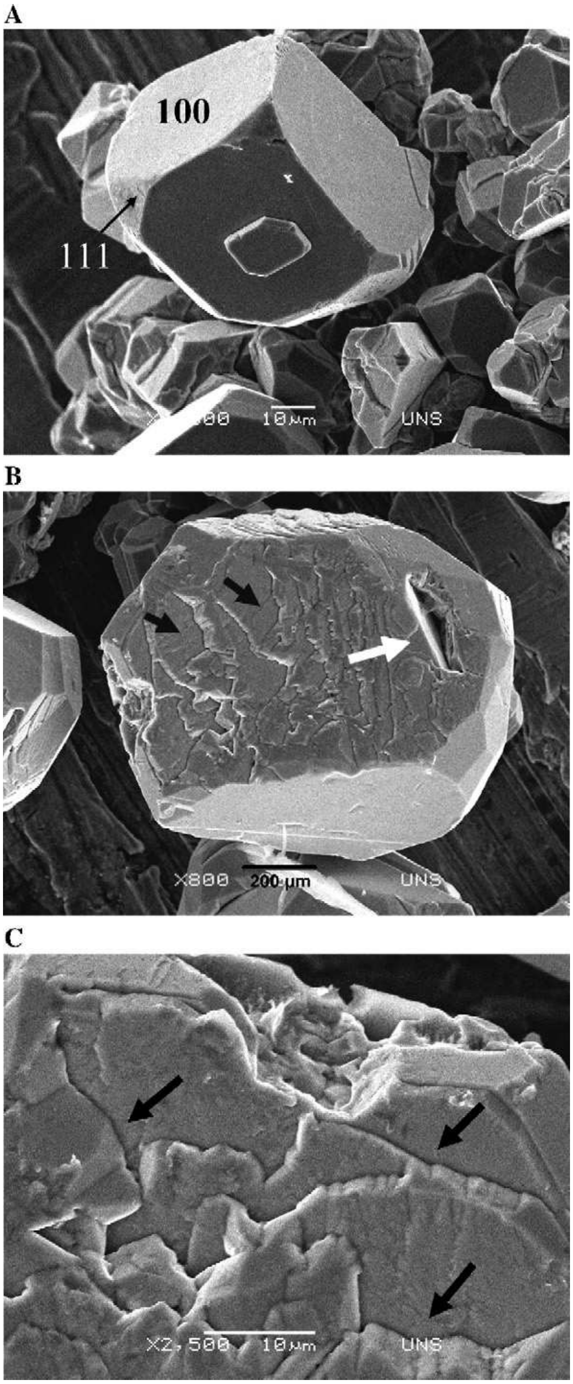

Fig. 3. SEM image. Silver powder particles obtained by current reversals (j_c=9mA, j_a=3 mA, t_c:t_a=1:1, pulse duration 10 ms, average current density: 3 mA cm^{-2}); (A) regular crystal; (B) crystal with rough surface; (C) detail of surface in (B).

The shape of a crystal is usually determined by the relative rates of advance of close-packed faces. Close-packed faces grow relatively slowly since atoms can only be added at kink sites, while high index faces grow more rapidly. Since the rapid disappearance of the high index faces is a consequence of their high growth rate, then the total growth rate will be determined by the growth of the close-packed faces. At extremely low growth rates when the solution and the crystal are nearly in equilibrium, the shape of faces will be determined by the requirement that the total surface energy of crystals is minimized (Cabrera and Velmilyea, 1958).

The effect of periodic millisecond current reversal on the morphology and powder particle size is illustrated in Figs. 3, 4 and 5. It may be seen that the morphology of the silver particles is different to those obtained in square-wave overpotential pulsing. The cubic crystal (in Fig. 3A) is defined by two forms of faces, six of which are of the {100} type, having a square shape, and eight are of the {111} type, developed by cutting away the original corners of the cube ($R \approx 0.7$). In most cases, however, the shape seems to be the result of interplay between the surface energy and growth kinetic effects. It appears that crystals often grow by laterally extending 0.1–1 μm thick layers and such layers have been observed on metal crystals formed by electrodeposition. The growth planes of layers are the closest packed atom planes of the crystal lattice (Barton and Bockris, 1962; Wranglen, 1960). Typical very rough {111} and smooth and flat {100} surfaces of silver particles are shown in Fig. 3B,C. This result is in accordance with the result reported by Yu and Scheffler (1996). The detail of a {111} surface is illustrated in Fig. 3C (steps are indicated by black arrows in Fig. 3B,C). The regular silver crystals are finished with smooth surfaces, but some surfaces have defects such as deep rectangular holes (Fig. 3B, white arrow). Regardless of this it can be concluded that at low current densities small monocrystals of silver powder particles can be obtained by current reversal deposition.

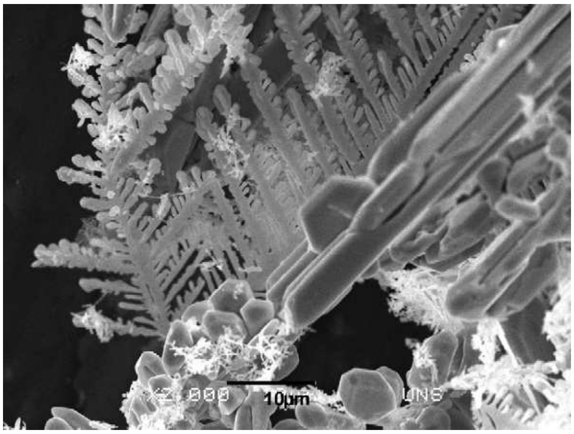

Fig. 4. SEM image. Silver powder particles obtained by current reversals (j_c=70 mA, j_a=38.5 mA, t_c:t_a=1:1, pulse duration 10 ms, average current density: 15.75 mA cm^{-2}). General view of morphologies.

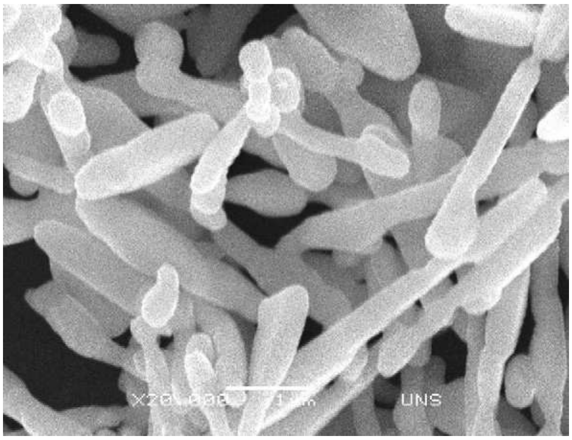

Fig. 5. SEM image. Silver powder particles obtained by current reversals (j_c=70 mA, j_a=38.5 mA, t_c:t_a=5:1, pulse duration 10 ms, average current density: 51.92 mA cm^{-2}). Rod-like particles.

As expected, increasing deposition current density produces dendritic deposits. In a sample obtained by current reversal, Fig. 4, two morphologies are obtained, such as: dendrite particles (3D dendrites) and fern-like dendrites. The branches of fern-like dendrites were very frequently seen to be inclined at 60° or 120° to each other. The branching of dendrites is repeated to several orders; e.g. Fig. 4 illustrates two orders of successive branching. The appearance of branching was previously described in the literature (Matthews et al., 1961).

Using a longer deposition time between reversals the particles were mainly in the form of rods (Fig. 5), although regular crystals and dendrites (2D, 3D and fern-like) were also formed.

On the basis of the above results it can be concluded that the effect of overpotential pulsing is similar to that of current reversal. This enables practical application of the electrodeposition of metal powders with controlled particle grain size and morphology. Current reversal in the millisecond range was examined here because the easiest way to produce current reversal electrodeposition conditions in practice is by superimposing a small amplitude alternating current onto a direct current. However, the 50 Hz frequency examined is likely to have capacitance problems on a large scale. (Popov et al., 2002; Despić and Popov, 1972).

It seems that current reversal deposition may be a suitable process for obtaining ultrafine powders (Popov and Pavlović, 1993). The results show that it is possible to change the size and morphology of particles by changing the relative lengths of cathodic and anodic pulses, and the base time period. Production of particles smaller than 1 μm will be the subject of further investigations.

4. Conclusions

The main results obtained in this study can be summarized as follows:

1. When silver was deposited from nitrate solution under square-wave pulsating overpotential and current reversal regime different types of particles were observed. Generally, three types of particles could be distinguished: dendrites (3D, fern-like), regular crystals (independent and/or agglomerates) and rods.
2. Various crystallographic forms, some of them ideal, or derivates of cube-octahedron type of morphology were obtained.
3. Some of silver particles are perfect in shape with no surface defects, but on some surfaces deep holes and fine {111} surface steps can be seen.
4. The surface crystal structure of powder particles may vary from polycrystalline shape to one characterized by well-defined crystal planes.
5. The deposition of silver powder by current reversal is of greater practical importance than overpotential pulsing.

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