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Electrodeposition of Ag from nitrate solutions: Part I. Effect of phosphate ions on morphology

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The initial steps of silver deposition from nitrate solutions on silver and platinum substrate were studied. The formation of boulders was observed on both substrates, their growth onto platinum being the more regular. A compact Ag-surface film was not produced under the applied conditions, even after prolonged deposition. Instead, growth of (i) independent large Ag grains occurred at lower overpotentials and (ii) dendrites formed at higher overpotential values. In the presence of phosphate in unstirred solutions 2D and/or 3D dendrites were formed at lower and higher overpotentials, respectively. Increase in electrolyte temperature above 25 °C was found to cause dendrite coarsening, even at lower overpotentials. In stirred solutions compact Ag-surface films were deposited over a wide range of overpotentials, showing different structural features depending on the applied overpotential.

Keywords: *morphology of Ag-electrodeposits*, *nitrate solution*, *phosphate ions*, *silver electrorafination*

List of symbols

r	radius of zone of zero nucleation probability
E	cell voltage
E_k	critical voltage for nucleation to occur
r	radius of nucleus hemispherical drop
f	numerical factor accounting for deviation of geometry
j_0	exchange current density
j_l	limiting diffusion current density

1. Introduction

Traditionally, silver is produced by an electrorefining process from nitrate solutions giving small Ag crystallites. The latter are used as Ag-powder or, preferably, are transformed into compact metal by a suitable smelting/casting procedure [1–3].

Normally, direct formation of compact Ag deposits, as is the case in Cu electrorefining or Zn electrowining, is preferable. Simpler and cheaper operation, as well as a higher degree of purification, due to the substantially reduced deposit surface area, are among the expected advantages of compact Ag-deposit electrorefining. To explain why silver deposited from nitrate solution forms dendrites both crystalographical and electrochemical aspects of silver electrocrystallization are considered.

Compact Ag-layers are not deposited due to the inadequate nucleation. According to Milchev [4], a wide nucleation exclusion zone exists around each Ag nucleus growing on a foreign substrate, so that the nucleus surface density is low. As a result, the subsequent growth of these nuclei produces rough and uneven deposits. Their shape varies according to the value of the applied overpotential. Granular or dendritic Ag is deposited at lower and higher overpotentials, respectively [5]. It was shown elsewhere that the high value of the silver exchange current density is a possible explanation of this phenomenon [7, 8].

To check the possibilities for compact silver deposition from nitrate solutions, the following work was undertaken:

(i) Determination of the morphology of Ag-deposits produced at constant overpotentials and from unstirred nitrate solutions without additives, as a reference.
(ii) Study of the effect of some additives, stirring and/or impulse current regimes, as measures leading to smooth deposit morphology.

To produce a continuous Ag-film over the whole substrate, different additives were tested in a preliminary study. It was found that addition of small amounts of phosphate ions to the nitrate solution substantially changes the morphology of the deposits [6]. Consequently, the goal of the second part of the study is to elucidate how the added phosphate anions, affect the morphology of the Ag-deposits.

2. Experimental details

Silver was deposited onto stationary Pt and Ag wire electrodes from 0.1–0.5 M $AgNO_3$ in $100\,g\,dm^{-3}$ $NaNO_3$ solutions and on to stationary Ag-wire electrodes from 0.5 M $AgNO_3$ in $100\,g\,dm^{-3}$ $NaNO_3$ + 3, 6 or $12\,g\,dm^{-3}$ H_3PO_4 solutions. Copper was deposited on to stationary Ag wire electrodes from 0.1 M $CuSO_4.5H_2O$ + 0.5 M H_2SO_4. An open cell was used. Experiments were conducted at 25 °C and 50 °C. In some cases, where stated, magnetic stirring at 350 rpm was applied. Analytical grade chemicals were used, together with doubly distilled water.

Deposition was carried out under potentiostatic conditions at 40 to 140 mV overpotential. Counter and reference electrodes were of pure silver. Polarisation curves were taken, or constant quantities of electricity ($2-120\,mA\,h\,cm^{-2}$) were passed through the cells at given overpotentials. The morphologies of the deposit were photographed using scanning electron microscopy (Joel T20).

3. Results and discussion

3.1. *Deposition of silver on foreign substrate*

In Fig. 1(a) and 1(b) the morphology of silver electrodeposited from 0.1 M aqueous $AgNO_3$ on to a Pt substrate is shown. As expected, deposits formed at lower overpotentials (e.g., 40 mV) are boulder-like with well defined crystallography, while dendrites, or their performs were seen when higher overpotentials (e.g., ≥ 70 mV) were applied.

According to Markov *et al.* [7] when metal crystallites or drops nucleate or grow on to a foreign substrate, in their immediate vicinity zones of zero nucleation probability exist. Nucleation under these conditions occurs under the influence of the external electrical field. The growth of nuclei causes deformations in the field, resulting in an overpotential drop in the screened surface segments. When the overpotential is lower than the minimum value for nucleation, further nucleation is impossible. It was shown that for a hemispherical drop on a flat substrate, nucleation is impossible inside a zone of radius *r*, defined as

$$r = f\frac{E}{E - E_k}\rho \qquad (1)$$

When $E \gg E_k$, the zone radius, *r*, approaches the effective value of the drop size. This explanation is valid only for a processes controlled by resistivity, for example, for deposition of metals having high exchange current densities, as is the case with silver [8, 9].

At cathodic overpotentials higher than 60 mV, the number of nuclei formed on a Pt substrate and, consequently, the number of Ag grains rapidly increased. Nevertheless, due to the grain shape, formation of Ag surface film is still impossible. It should be pointed out that flat dendrites are visible in Fig. 1(b). Dendrites are electrode surface outgrowths formed under activation control, while the deposition on the remaining (flat) surface takes place mainly under diffusion control [10].

To start dendritic growth, two requirements are necessary: (i) the overpotential must be higher than some critical value and (ii) precursors leading to dendritic growth must exist [11].

Upon increasing the Ag^+ ion concentration in the electrolyte, the critical overpotential value for dendritic growth becomes higher [12]. In 0.5 M $AgNO_3$ solution dendritic growth on Pt starts at 120 mV (as compared with 70 mV in 0.1 M $AgNO_3$, Fig. 1b).

At the same time, according to Markov [13], the increase in silver ion concentration makes the nucleation exclusion zone wider. Accordingly, the number of Ag grains is lower than in more dilute Ag^+ solutions. The situation is further complicated by the fact that, in more concentrated Ag^+ solution, dendriteless Ag deposition is feasible at higher overpotentials, corresponding to higher nucleation rates. As a results, it is possible that the grain number will increase.

3.2. *Deposition of silver onto its own surface as substrate*

Deposition of Ag on to Ag as substrate occurs under different conditions but, in principle, is similar to that

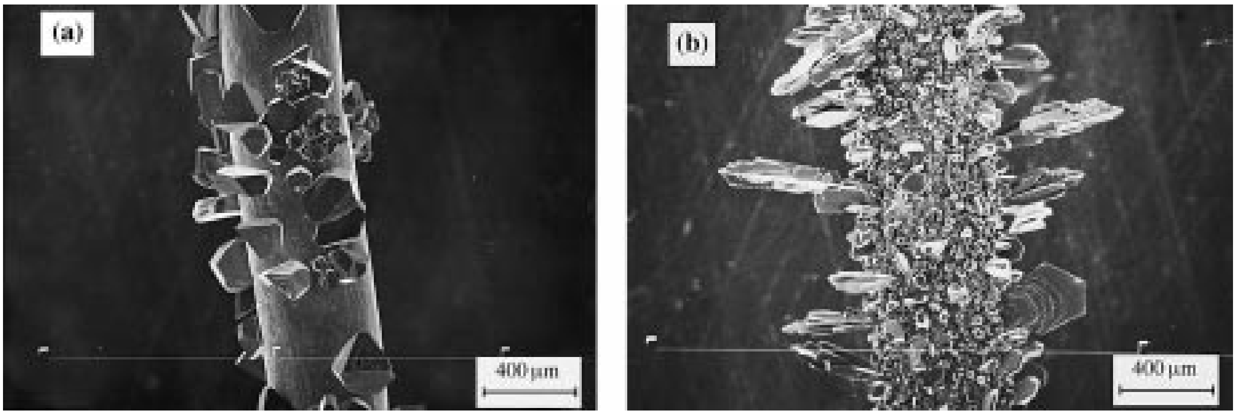

Fig. 1. Silver electrodeposits obtained potentiostatically onto stationary platinum wire electrodes. Quantity of electricity $2\,mAh\,cm^{-2}$. (a) 0.1 M $AgNO_3$ + $100\,g\,dm^{-3}$ $NaNO_3$, 40 mV; (b) 0.1 M $AgNO_3$ + $100\,g\,dm^{-3}$ $NaNO_3$, 70 mV.

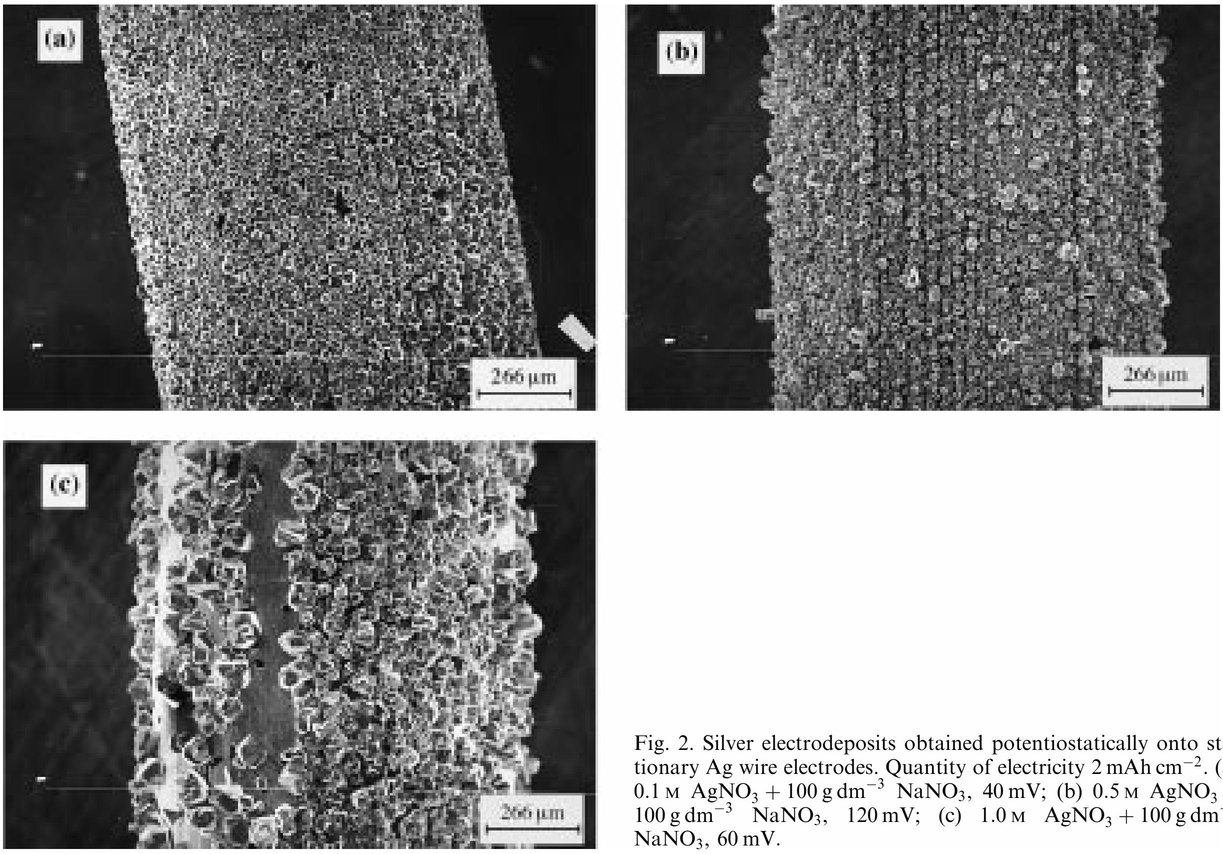

Fig. 2. Silver electrodeposits obtained potentiostatically onto stationary Ag wire electrodes. Quantity of electricity 2 mAh cm^{-2}. (a) 0.1 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$, 40 mV; (b) 0.5 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$, 120 mV; (c) 1.0 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$, 60 mV.

on a foreign substrate (Fig. 2a and b). In this case, nucleation is also a prerequisite for the deposition process to start, but the critical overpotential value, E_k, is much lower than on a Pt substrate. The higher grain density seen in Fig. 2a and b confirms this. According to Eq. 1, the zone radius, r, is smaller than on Pt substrate, so that the number of grains on a Ag substrate is higher. However the silver deposited onto a silver substrate was not in the form of surface film.

If the grain numbers in Fig. 2 for the same deposition overpotentials are compared at increased Ag^+ ion concentration, fewer grains are formed due to the wider nucleation exclusion zone.

In solutions of higher Ag^+ content, proper deposition can be performed at higher overpotentials, where higher nucleation rates exist. The nucleation density is influenced by both Ag^+ ion concentration and cathodic overpotential value. According to Fig. 2, 0.5 M $AgNO_3$ is a sufficient concentration for silver surface film deposition. In this case silver can be deposited with high current densities, due to relatively high Ag^+-ion concentration and higher overvoltage, that is, conditions resulting in the formation of a large number of smaller grains.

Despite these favourable circumstances, formation of polycrystalline deposits of surface films of Ag on Ag did not take place even when more metal was deposited (see Fig. 3(a) and (b)). Single grains became bigger, but still grew separately, with the deposit morphology being practically uninfluenced by the

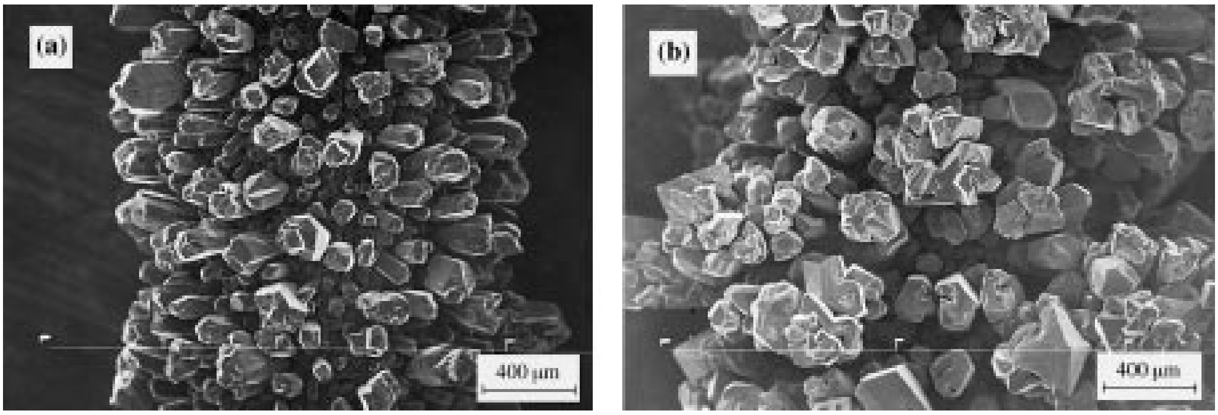

Fig. 3. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$ onto stationary Ag wire electrodes. Quantity of electricity 20 mAh cm^{-2} for (a) and 100 mAh cm^{-2} for (b). Overpotentials: (a) 100 mV and (b) 100 mV.

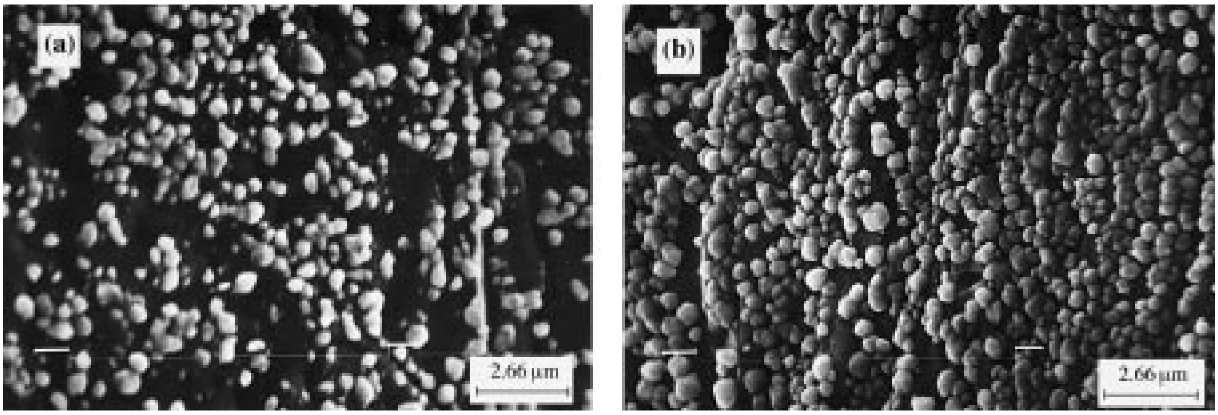

Fig. 4. Copper electrodeposits obtained potentiostatically from 0.1 M $CuSO_4$ + 0.5 M H_2SO_4 onto stationary Ag wire electrodes. Deposition thickness: (a) 200 monolayers and (b) 800 monolayers.

overpotential values or the duration of deposition. Such coarse grains adhere poorly to the substrate and are easily detached from it, giving a dispersed but dendriteless deposit.

In Fig. 4 formation of a Cu-surface film on a silver substrate is shown in order to compare it with silver deposition. In this case the nucleation exclusion zone, like that in the Ag case, does not exist around the copper grains [14, 15], and the Cu surface film is almost complete, even at $200\,mA\,s\,cm^{-2}$. This value corresponds approximately to the average deposition thickness of ca 800 Cu monolayers (Fig. 4b).

This difference between Ag and Cu behaviour is probably due to the different values of their exchange current densities. Measures such as lowering the j_0 for silver deposition or increasing the value of the j_l/j_o ratio, which was suggested as determining the morphology of metal deposits [16], are to be considered. Increase in this ratio can be achieved by stirring, adding substances that adsorb at the electrode (e.g. addition of small amounts of specific anions), and similar procedures.

A general feature of the morphology of silver deposited from nitrate solutions containing phosphate as additive is its dendritic nature. 2D dendrites were formed at lower overpotentials, and 2D and/or 3D dendrites at higher overpotentials (Fig. 5). In the absence of phosphate ions Ag-boulders were formed instead, as shown in Figs. 1 and 2.

Phosphate ions also increase the nucleation density, probably, by making the nucleation exclusion zones much smaller. In such case the crystallization overpotential is of minor influence and activation control becomes dominant [7], probably due to the lower exchange current density. However, the exchange current density is still high enough for dendritic growth to occur, even at relatively low overpotentials.

It was shown elsewhere [17], that the higher the j_l/j_o ratio the higher the value of the critical overpotential for dendritic growth to start.

The value of j_l/j_o may be varied by changing the temperature and/or the hydrodynamic regime in the cell. The rise in temperature from 25 °C (Fig. 5) to 50 °C (Fig. 6) causes lower nucleation density and stronger dendritic growth, probably due to the faster increase in j_o with temperature than that of j_L. The opposite effect may be expected with reduced temperature together with faster electrolyte circulation. Instead of dendrites obtained in stationary conditions (Fig. 5) stirring helped agglomeration of crystals (Fig. 7). Their orientation coincides with the electrical

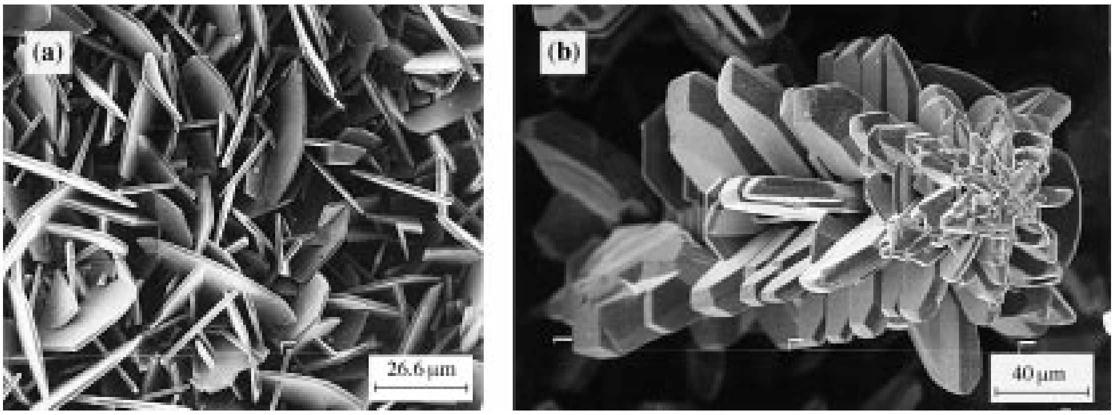

Fig. 5. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3$ + $100\,g\,dm^{-3}$ $NaNO_3$ + $6\,g\,dm^{-3}$ H_3PO_4 onto stationary Ag wire electrodes. Quantity of electricity: (a) 2 and (b) $20\,mAh\,cm^{-2}$. Overpotentials: (a) 60 and (b) 120 mV.

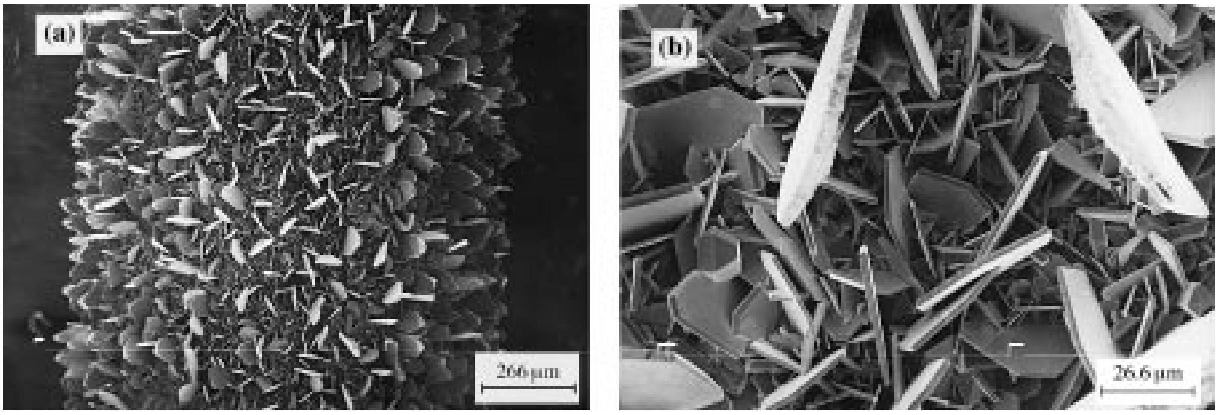

Fig. 6. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3 + 100\,g\,dm^{-3}$ $NaNO_3 + 6\,g\,dm^{-3}$ H_3PO_4 onto stationary Ag wire electrodes. Quantity of electricity 20 mAh cm^{-2}. Temperature 50 °C. Overpotential 60 mV.

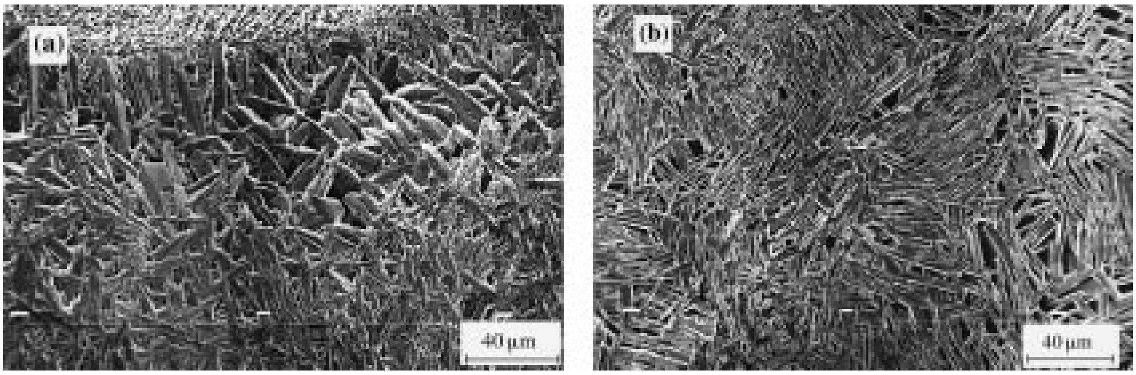

Fig. 7. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3 + 100\,g\,dm^{-3}$ $NaNO_3 + 6\,g\,dm^{-3}$ H_3PO_4 on stationary Ag wire electrodes. Quantity of electricity 20 mAh cm^{-2}. Stirring 350 rpm. Overpotentials: (a) 60 and (b) 120 mV.

field lines distributed by electrolyte stirring. The effect produced is very similar to that when zinc was deposited onto a rotating disc electrode [18].

Among the varied parameters in this study the most compact deposits were produced with overpotential of 80 mV, stirring at 350 rpm and H_3PO_4 concentration of 6 g dm^{-3}. The overall Ag single-crystal microstructure depends on several factors and varies significantly. The majority of the crystals in Fig. 6 have plate-like morphology. The broad surfaces are probably of 111 type, but under certain conditions, (e.g. change in surface composition) they can be also of the 1 1 0 type. If the broad surface is of the (1 1 0) type, then the side facets will be of (1 1 1) and (1 1 2) types. By changing j_l/j_o, the morphology of deposited silver can be altered from single particles to dendrites, typical for f.c.c. type metals. In addition to the (1 0 0) growth direction, it seems that the (1 1 0) direction of secondary dendrites is present (Fig. 6(b)). However, in order to define the dominant growth directions, more accurate dendrite crystallography must be done. The presence of surface steps, observed by close inspection of Fig. 8, reveals a ledge growth mechanism of particle coarsening. In addition to plate-like morphology, occasionally cube-octahedron and multiple twinned (MTP) silver particles are also observed. Theoretical consideration [19] on MTP particles in the size range up to 50 nm suggests that the total surface energy of these decahedral particles (5-twins) is between those of a single crystal and icosahedral MTP. This may explain why decahedral silver particles are present in Fig. 6(b) together with single-crystal particles, due to their relatively high stability.

To compare the morphology of Ag deposits formed in the course of this study with the morphology of deposits produced during a 'normal' electrorefining procedure, Ag and Cu deposits pro-

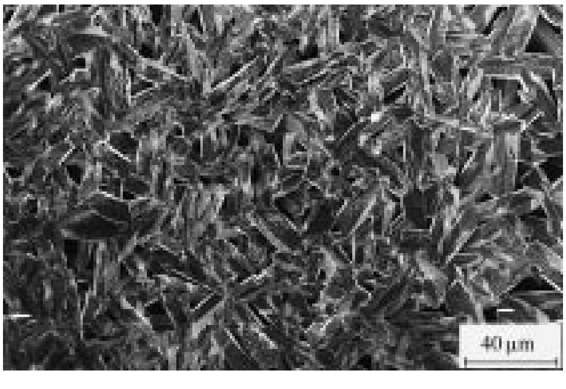

Fig. 8. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3 + 100\,g\,dm^{-3}$ $NaNO_3 + 12\,g\,dm^{-3}$ H_3PO_4 on stationary Ag wire electrodes. Quantity of electricity 20 mAh cm^{-2}. Stirring 350 rpm. Overpotential 80 mV.

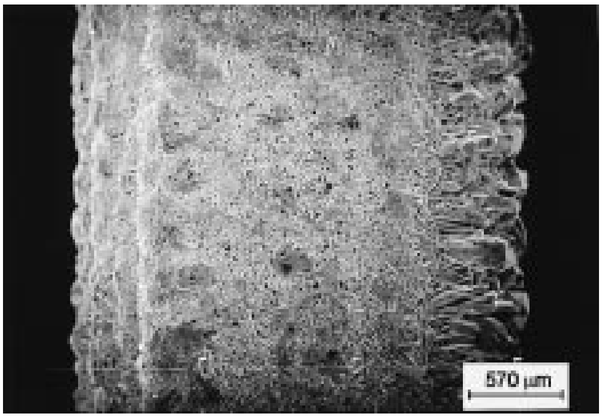

Fig. 9. Silver electrodeposits obtained potentiostatically from 0.5 M $AgNO_3 + 100\,g\,dm^{-3}\,NaNO_3 + 6\,g\,dm^{-3}\,H_3PO_4$ on stationary Ag wire electrodes. Quantity of electricity $150\,mAh\,cm^{-2}$. Stirring 350 rpm. Overpotential 80 mV.

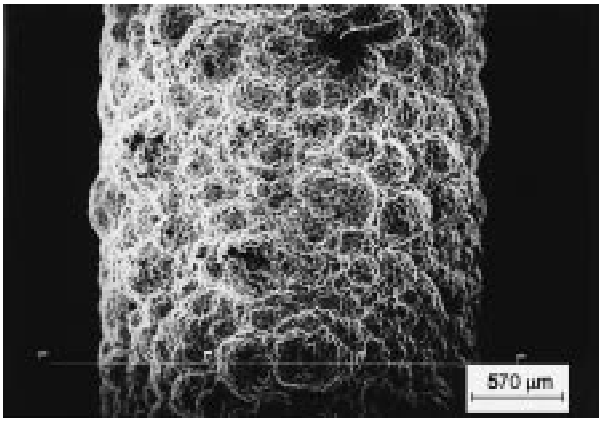

Fig. 10. Copper electrodeposits obtained potentiostatically from 0.5 M $CuSO_4 + 0.5$ M H_2SO_4 onto stationary Cu wire electrodes. Quantity of electricity $500\,mAh\,cm^{-2}$. Stirring 350 rpm. Overpotential 260 mV.

duced under prolonged electrolyses are compared in Figs. 9 and 10, copper being chosen as an example of a typical deposit with compact morphology. Proof is thus offered that deposition of a thick and compact Ag layer is possible (Fig. 9). The fine structure of silver deposits is similar to that in previous micrographs, but different from that of copper deposits (Fig. 10).

Thus, in spite of the difference in the type of crystals formed (polycrystalline and fibrous for Cu and Ag, respectively) it can be stated that optimal conditions for compact silver deposition from nitrate electrolytes were determined.

4. Conclusions

When silver is deposited from nitrate solution under conditions similar to those for electrorefining, different grain morphologies appear in the initial deposition steps. Variation of the type of substrate, deposition overpotential and Ag^+ ion concentration affects the grain shape, the grain density and the appearance of dendritic growth.

We were not able to produce compact Ag surface films under the applied set of experimental conditions. The high value of the Ag exchange current density is the probable cause of this failure. In comparison with Ag deposits, Cu deposits produced under the same electrolysis conditions are of finer structure and almost completely compact, even when much lower current quantities are applied. The exchange current density for Cu-deposition is many times lower than that for Ag-deposition and this may be the origin of the difference due to more facile onset of diffusion control in the case of Ag.

On the other hand, there is strong evidence that the addition of small amounts of phosphate ions to the traditional nitrate solution for silver electrorefining substantially changes the deposit morphology. Stirring of the electrolyte contributes further to the change in silver grain shape.

Thick and practically compact Ag layers were produced when both these modifications were applied to the silver electrodeposition process from nitrate solution.

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