

## The Effect of Periodically Changing Regimes on the Electrodeposition of Silver Powder

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The effect of different deposition regimes (constant and reversing currents, constant and pulsating overpotential), on the powdered and dendritic silver electrodeposits morphology were investigated. The morphology of electrodeposited silver powder was studied utilizing a scanning electron microscope. The results obtained in constant regimes were compared with those obtained in pulsating and reversing regimes. The size of dendrites decreased strongly with increased overpotential or current. It was also shown that the agglomeration of silver dendrites in spongy-like agglomerates was strongly decreased by pulsating overpotential electrodeposition or reversing current. The possibility of obtaining powder particles, with different properties, depending on conditions of electrolysis was demonstrated.

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**Keywords:** Silver powder; dendritic growth; reversing current; electrodeposition, morphology

### 1. INTRODUCTION

Almost any material can be made into powder, but the method selected for fabrication of the powder depends on specific material properties. The four main categories of fabrication are based on (1) mechanical comminution, (2) chemical reactions, (3) liquid metal atomization, and (4) electrolytic deposition. In addition to these major techniques, several specialty techniques are used for special materials [1].

Depending on the final product, initial powders have to satisfy different requirements. These include physical (size and particle-size distribution, state of the surface), chemical (basic metal and admixture content, chemically bound, adsorbed or dissolved gas contaminants), and technological

properties (apparent density, flowability, stability, compressibility, corrosion resistance, etc.). At the same time, the physical, chemical, and technological properties of metal powders strongly depend on the method of powder fabrication. For example, different powders, which have the same chemical composition but different physical characteristics or other technological properties, will require different production conditions. On the other hand, the favored production method is determined also by economical aspects, that is, by the price of the powder, the price of the treatment alteration, the quantity of ingredients, and the possibility of obtaining the powder with all necessary physical, electrical, and magnetic characteristics [1-3].

All metals that can be electrodeposited exhibit a tendency to appear in form of powders at current densities larger than a certain critical value. A powder formed by the electrolytic technique is often dendritic or spongy in shape although considerable control of particle size and shape is possible. The specific properties of the powder depend on the electrolytic bath conditions during deposition and on the subsequent processing steps. Moreover, it should be noted that there is a possibility of electrodeposition of metal powders with controlled grain size, morphology, and crystal structure of the particles by using electrodeposition at periodically changing rate [1-3].

Morphology is probably the most important property of electrodeposited metals. It depends mainly on the kinetic parameters of the deposition process and the deposition overpotential or current density. For the application of metal powders, many of their properties are of interest. 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, they depend on the shape and the size, which can be influenced by appropriate electrolysis regime [1-3].

Copper deposits obtained at high current densities and overpotentials are very important from a technological point of view. It has been stated that the open and porous structures of copper deposits obtained at high current densities were ideally suited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors [4], while the extremely high surface area is relevant for evaluating some electrochemical reactions. For example, it was known that copper shows a high activity for the nitrate ion reduction [5] as well as for the reaction in which nitrate is reduced to ammonia in high yield in aqueous acidic perchlorate and sulphate media [6]. Having in mind a potential high technology significance of copper deposits obtained at high overpotentials, it is necessary to better recognize the effect of this process on electrodeposition of copper under these conditions [7]. For that reason, one of the aims of this paper is to examine the effect of this process on silver electrodeposition at overpotentials on the plateau of the limiting diffusion current density or higher ones.

The various phenomena related to silver electrodeposition under various experimental conditions, producing different deposit morphologies (mostly dendritic), have been extensively studied [8-12]. The purpose of this paper is to give an analysis of the effects of the shape of current or overpotential waves in electrodeposition at a periodically changing rate, on the morphology of silver powder particles. It is well known that the electrodeposition of metal powders by pulsating overpotential produces particles of changed morphology relative to those obtained in classic potentiostatic deposition [1-3]. It is also known that it is easy to use pulsating overpotential deposition in the laboratory-scale cell but difficulties arise on a practical scale because of the demands for higher

power and a high-speed potentiostat. The output current for input pulsating overpotential is a reversing current [13], and similar effects on the morphology and grain size of powder particles can be expected in deposition by pulsating overpotential and by reversing current. However, it is easier to obtain reversing currents on a practical scale and the deposition of silver powder by reversing current is of greater practical importance than pulsating overpotential deposition.

The goal of this work is to extend the use of pulsating overpotential or reversing current for the elimination of agglomeration during silver powder deposition i.e. to investigate the effect of different deposition regimes on the morphology of electrodeposited silver powder particles.

## 2. EXPERIMENTAL

Silver powder was deposited from a solution containing  $10 \text{ g dm}^{-3}$   $\text{AgNO}_3$  and  $100 \text{ g dm}^{-3}$   $\text{NaNO}_3$  at  $\text{pH} = 0.8\text{-}1.5$  [8,9,11] onto a glassy carbon cathode by constant and square-wave pulsating overpotential, and by constant and reversing currents. In all cases the electrode surface area was  $1 \text{ cm}^2$ . The counter and reference electrodes were of pure silver (99.9%-Aldrich) previously treated with 1:1  $\text{HNO}_3$ . Experiments were performed at  $(25 \pm 1) ^\circ\text{C}$ . Double-distilled water and analytical grade chemicals were used. The counter electrode was laid by the wall of the  $100 \text{ cm}^3$  cylindrical cell, and the cathode was vertical and stationary and it was placed in the middle of the cell.

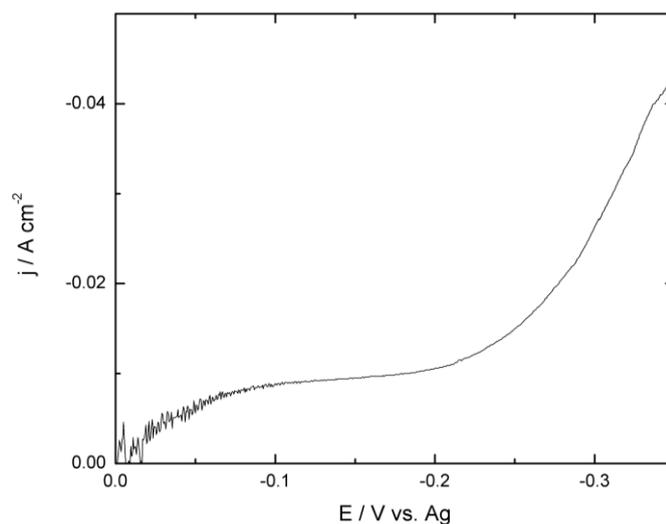
The quantity of electricity  $810 \text{ mAmin/cm}^2$  was passed through the cell in all cases. The powder was washed with distilled water and suspended in ethanol.

The morphologies of the deposits were investigated using scanning electron microscopy (SEM, JEOL T-20 microscope) at 20 kV, (SEM JEOL 6460LV) at 25 kV and Tescan VEGA TS 5130MM.

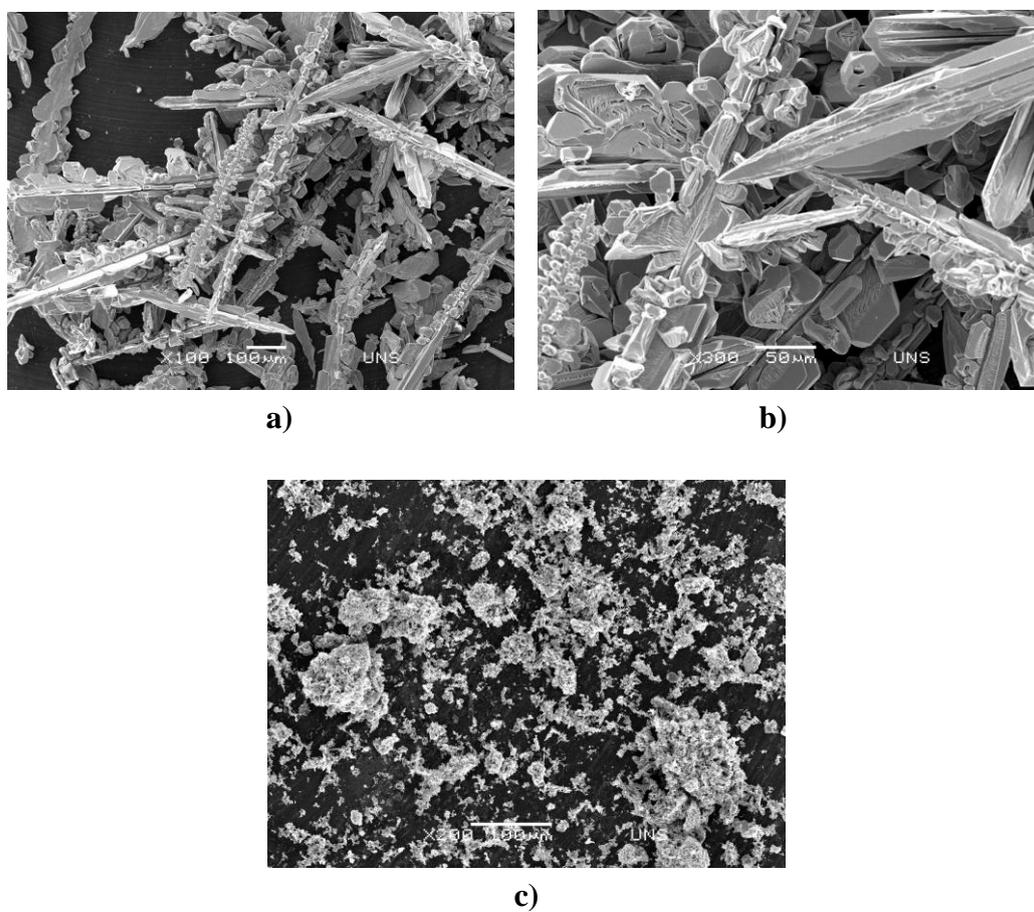
## 3. RESULTS AND DISCUSSION

The polarization curve for silver deposition is shown in Figure 1. It is characterized by well-defined limiting diffusion current density plateau.

Typical deposits obtained in deposition by constant overpotential are shown in Figure 2. Disperse deposits were obtained at all overpotentials used (100 mV, 300 mV and 440 mV). It is known that increasing overpotential leads to the formation of a more dispersed deposit characterized by decreased particle size [2,3]. Single, nonbranched dendrites were obtained at 100 mV (Figure 1a). The dendrites obtained at 300mV were occasionally branched and some interweaving of the growing dendrites started, producing spongy-like agglomerates at 440 mV (Figure 1c). Inspection under higher magnification clearly showed that the structure of spongy agglomerates is also dendritic, but dendrites are more than ten times shorter than those obtained at lower overpotentials. These dendrites were branching in only one plane, which means they are 2D [14].

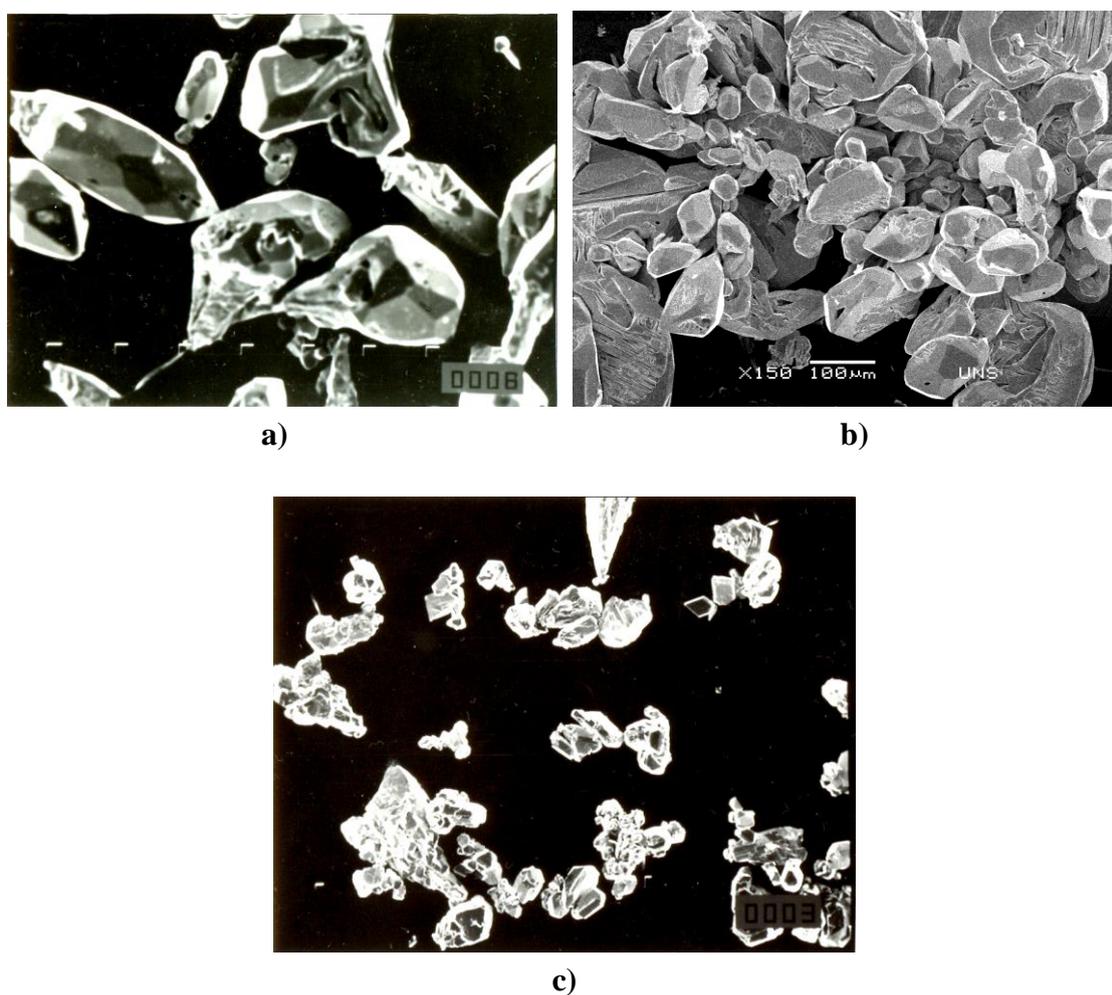


**Figure 1.** Polarization curve for silver deposition from an electrolyte containing  $10 \text{ g dm}^{-3} \text{ AgNO}_3$  and  $100 \text{ g dm}^{-3} \text{ NaNO}_3$ .



**Figure 2.** Dispersed electrodeposits of silver obtained by constant overpotential deposition at different overpotentials: a) 100 mV; b) 300 mV; c) 440 mV. Magnification: a) x 100; b) x 300; c) x 200.

The square-wave pulsating overpotential deposition was used in order to eliminate agglomerates during the deposition of dispersed deposits. It is well known that the square-wave pulsating overpotential deposition produces the particles of different morphology than the potentiostatic deposition [2]. The effect of frequency on particle grain size and morphology obtained by the square-wave pulsating overpotential deposition, millisecond range, is shown in Figure 3. 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 copper powder deposition and can be explained in the same way [15].



**Figure 3.** Silver powder particles obtained by pulsating overpotential electrolysis at different frequencies. Overpotential amplitude 300 mV, pulse-to-pause ratio 1:1. Pulse duration: a) 0.5 ms; b) 5 ms and c) 50 ms. Magnification x 150.

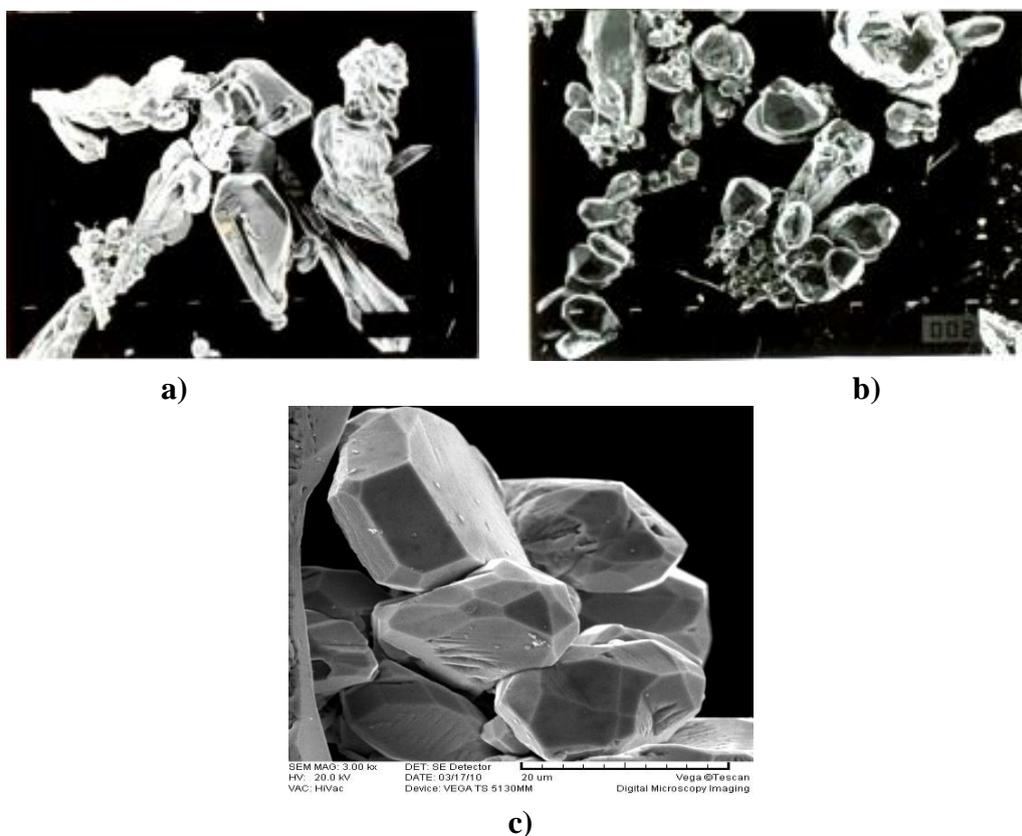
The effect of increasing the pause with the same pulse duration on the morphology and particle grain size can be seen from Figures 3b and 4. The increasing pulse duration leads to a formation of smaller particles with a more regular crystal structure. Figures. 4b and 4c show the silver powder particles obtained at 300 mV overpotential amplitude with a pulse-to-pause ratio 1:5. It is seen, that the

powder particles in this case are small, well-defined silver crystals. With the overpotential amplitude of 300 mV, starting from pulse-to-pause ratio 2, it comes to curvation of the dendrites peaks. The single grains are obtained, and the branches are becoming only the precursors. The grains with well-defined crystal planes are obtained at the pulse-to-pause ratio 5, and the agglomerates are completely eliminated.

Regardless the fact that the anodic current density during “off” periods can be neglected compared with the cathodic one during “on” periods, it has an important influence on the morphology of the powder particles. This is due to the fact that particles with lower tip radii are dissolved faster than those with larger ones. The reversible potential of a surface with a radius of curvature  $r$  would depart from that of a planar surface by the quantity [16].

$$\Delta E = \frac{2\sigma V}{Fr} \quad (1)$$

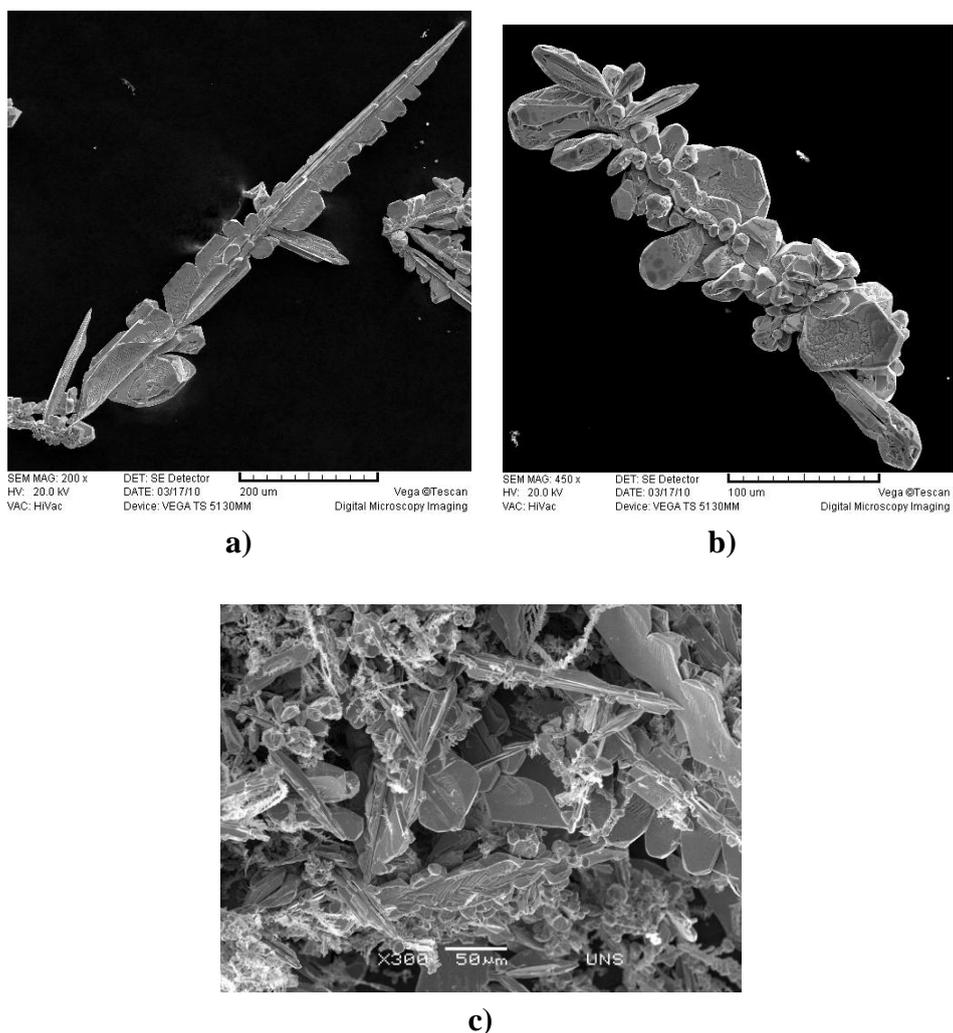
where:  $E$ -potential,  $F$ -Faraday constant,  $V$ -molar volume and  $\sigma$ -surface energy. Obviously, the tips of dendrites characterized by small tip radii dissolve faster than the flat surface in deposition by all current or overpotential wave forms that are characterized by some anodic current flow [12].



**Figure 4.** Silver powder particles obtained by pulsating overpotential at different values of pulse-to-pause ratio: a) 1:2; b) 1:5 and c) 1:5. Pulse duration 50 ms. Overpotential amplitude 300 mV. Magnification: a) and b) x 150; c) x 3.000.

In this way deposits become less dendritic and less agglomerated with the increasing “off” period and decreasing overpotential amplitude. Thus, powder particles obtained in pulsating overpotential deposition at one and the same overpotential amplitude value are more compact and less branched with increasing pause-to-pulse ratio.

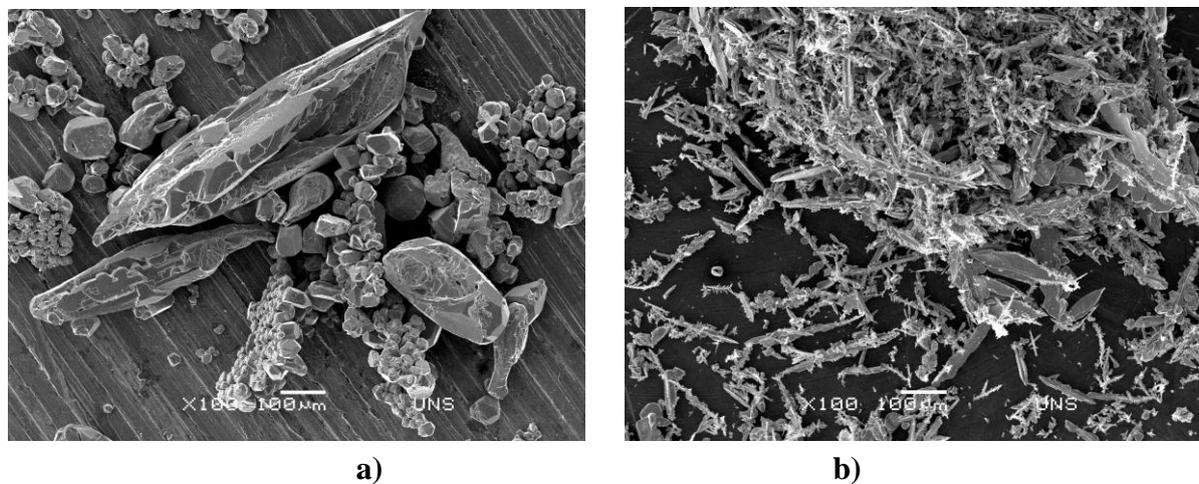
Typical powder particles obtained in constant current deposition are shown in Figure 5. They are larger and less dendritic than those obtained in constant overpotential deposition [8]. This is due to decreasing deposition overpotential during the deposition process caused by increasing electrode surface area and decreasing real current density [17].



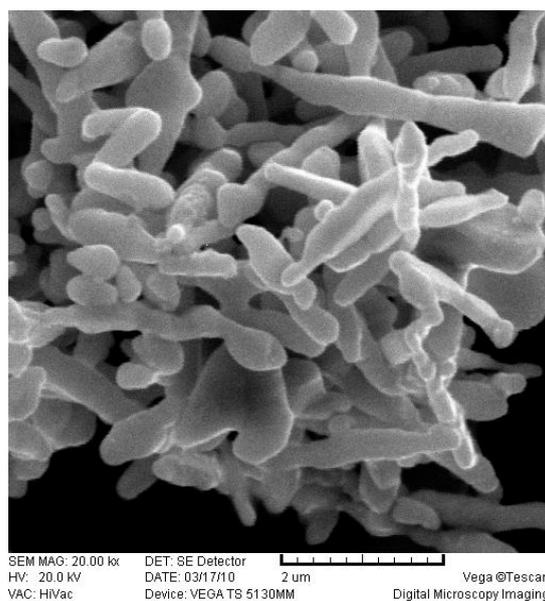
**Figure 5.** Silver powder particles obtained in constant current deposition. a) 3mA; b) 5mA and c) 10 mA. Magnification: a) x 200; b) x 450 and c) x 300.

The effect of reversing current on the morphology and powder particle size is illustrated by Figure 6. It is seen that the morphology of the silver particles is different to those obtained in direct current deposition. It is shown in Figure 6 that the increase of the cathodic (and anodic) current density leads to the formation of smaller and less dendritic silver powder particles. This is due to 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 [16]. 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.



**Figure 6.** Silver powder particles obtained by reversing currents. Pulse duration 10 ms. Anodic-to-cathodic deposition times ratio 1. Cathodic amplitude current density: a)  $9 \text{ mAcm}^{-2}$ ; b)  $30 \text{ mAcm}^{-2}$ . Anodic amplitude current density: a)  $3 \text{ mAcm}^{-2}$ ; b)  $10 \text{ mAcm}^{-2}$ . Average current density: a)  $3 \text{ mAcm}^{-2}$ ; b)  $10 \text{ mAcm}^{-2}$ . Magnification x 100.



**Figure 7.** Silver powder particles obtained by reversing current. Pulse duration 5 s. Anodic-to-cathodic deposition time ratio 1. Cathodic amplitude current density  $70 \text{ mAcm}^{-2}$ . Anodic amplitude current density  $38.5 \text{ mAcm}^{-2}$ . Average current density:  $15.75 \text{ mAcm}^{-2}$  Magnification x 20,000.

A similar but more pronounced effect to those in square-wave pulsating overpotential on the grain size and morphology of metal powder particles can be obtained in the reversing current deposition in the second range. That means if deposition is carried out at average current densities larger than the maximum for determined cathodic time/anodic time and period of function, permitting the electrodeposition of metal powders with controlled particle grain size and morphology on a practical scale. In the reversing current deposition (second range), there is no formation of agglomerates, but fine powder particles, in size of a few  $\mu\text{m}$  which are obtained directly (Figure 7).

In this way, using reversing current deposition in the second range, it is most likely possible to obtain nanoparticles of silver powder, choosing the suitable parameters of reversing current, which will be the object of further investigations.

#### 4. CONCLUSIONS

It is shown that in the constant regimes particle size significantly decreases with increasing overpotential or current. The branching of dendrites increases from needle-like, obtained at low overpotentials or currents, to a well-defined dendritic morphology tending to form agglomerates at high overpotentials or currents. In the case of square-wave pulsating overpotential regime the particles are less dendritic and less agglomerated than the ones obtained in the case of constant regime. This effect is more pronounced at lower overpotential amplitude and higher pause-to-pulse ratio. The size of particles decreases with increasing overpotential amplitude at a constant average current density. The same effect is obtained by increasing average current density at a constant anodic-to-cathodic time ratio in the case of reversing current regime. The increase of pause-to-pulse ratio and anodic-to-cathodic time ratio at a constant current density in both regimes, causes reduction of the ratio between diffusion and activation overpotential, providing more compact deposits.

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