Journal of Mining and Metallurgy, Section B: Metallurgy

# THE PARTICLE SIZE DISTRIBUTION (PSD) AS CRITERIA FOR COMPARISON OF SILVER POWDERS OBTAINED BY DIFFERENT METHODS OF SYNTHESIS AND BY CONDITIONS OF ELECTROLYSIS

Lj. Avramović <sup>a</sup>, M. Bugarin <sup>a</sup>, D. Milanović <sup>a</sup>, V. Conić <sup>a</sup>, M.M. Pavlović <sup>b</sup>, M. Vuković <sup>c</sup>, N.D. Nikolić <sup>b\*</sup>

<sup>a</sup> Mining and Metallurgy Institute, Bor, Serbia

<sup>b</sup> University of Belgrade, ICTM-Department of Electrochemistry, Belgrade, Serbia

<sup>c</sup> University of Belgrade, Institute for Multidisciplinary Research, Belgrade, Serbia

(Received 02 October 2017; accepted 05 October 2018)

#### Abstract

Silver powders produced by both electrochemical (galvanostatic (DC) and potentiostatic (POT) regimes of electrolysis) and chemical processes were examined by scanning electron microscope, and particle size distribution (PSD) of the obtained particles was done. In the DC regime, the current densities of  $-14.4 \text{ mA cm}^2$  for the nitrate (NIT; powder denoted with DC(NIT)) and  $-13.05 \text{ mA cm}^2$  for the ammonium (AM; DC(AM)) electrolytes were applied. In the POT regime, the used overpotentials were -90 mV (NIT(90)) and -150 mV (NIT(150)) for the nitrate, and -625 mV (AM(625)) and -925 mV (AM(925)) for the ammonium electrolytes. Reduction with hydrazine was used for chemical synthesis (powder denoted with HYD). On the basis of SEM and PSD analysis, Ag powders were grouped into three groups. In the first group DC(AM), AM(925) and HYD powders with the (8.4–8.9 %) volume ratios were placed. In the second group were AM(625) and DC(NIT) powders with the (6.5–6.6 %) volume ratios. NIT(90) and NIT(150) powders with the volume ratios of (5.2–5.7 %) made the third group. The obtained volume ratios were correlated with the morphology of synthesized particles in order to perceive advantages and lacks of powder production via electrochemical and chemical routes.

Keywords: Silver; Powder; Electrolysis; Chemical synthesis; SEM; PSD

# 1. Introduction

Silver powders attract attention because of their high technological significance. They are widely used in silver paints, conductive pastes and resins, as solid lubricants, in electronics for printed circuit boards and contacts, as a component of batteries as well as being a catalyst for a number of homogeneous chemical reactions used on the industrial scale [1–3]. Also, Ag powders find application as electrode material in ceramic capacitor and silicon solar cells [4–6].

The use of silver powders strongly depends on the particles shape that is dependent on the methods of their preparation. Various routes are used for the synthesis of silver powders and they can generally be divided into chemical and electrochemical processes [1]. Finely divided Ag powders are produced by electrolysis from the cyanide [1] bath with morphology of particles completely different from those obtained from the nitrate electrolytes [7–10]. Electrolysis from a sulphate electrolyte gives Ag particles of the average size of about 200–500  $\mu$ m, with a tendency to decrease with the addition of

titanium ions [11]. Although electrolysis from aqueous electrolytes is most often used way for the synthesis of Ag powders, molten salt electrolysis has also been used [12, 13].

Non-electrochemical processes for the synthesis of Ag powders involve a wide spectrum of methods. For example, Ag powders consisting of irregular particles in the range  $2-30 \,\mu\text{m}$  can be produced by the mechanical decomposing and mechanochemical reductions of silver oxide [14]. The Ag powders obtained through water atomization process represented the mixture of spherical, spheroidal and irregular particles [4]. A wet-chemical method is also used for synthesis of Ag powders, and the microsized, uniform spherical particles with rough surfaces [15], as well as Ag nanoparticles were obtained [16].

Aside from the methods used for the synthesis of Ag powders, the morphology of the particles depends on the composition and kind of the solutions, the presence of complexing, buffering and reducing addition agents, temperature, cathode used, etc. [9, 17–19]. For example, globular powders are formed via galvanic deposition on flat aluminium substrate in

DOI:10.2298/JMMB171002020A



<sup>\*</sup>Corresponding author:nnikolic@ihtm.bg.ac.rs

the alkaline solutions (pH 10), while powders consisting of dendritic particles were obtained under the same conditions in the acidic solution (pH 2) [17, 18]. The same shape of the particles is obtained via the same reaction on Cu substrate, indicating that pH solution plays a more crucial role on the morphology of the particles than the nature of metal substrate [17]. Various reducing agents, such as hydrazine hydrate [20, 21], formaldehyde [6, 17, 18], ascorbic acid [22] are also used for the synthesis of Ag powders at the submicro and micro levels. Agglomerates of the spherical-like particles of a rough surface morphology are obtained in the alkaline solution with ascorbic acid as a reducing agent [17, 18]. In the acidic solutions platelets or geometric crystals of individual particles of silver were obtained with the same reducing agent [17, 18]. On the other hand, agglomerates composed of globular Ag particles were obtained with formaldehyde as the reducing agent.

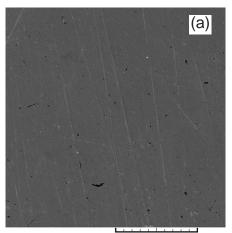
The properties defining the behaviour of the powders as collection of particles are known as the decisive characteristics, and they are: the specific surface, the apparent density, the flowability, and the particle size distribution (PSD) [9]. These properties have been analyzed in detail for electrolytically produced copper powders [23-28], and there is no data dealing with the analysis of Ag powders. In this study, regarding the high technological significance of Ag powders, we analyze the particle size distribution (PSD) of electrolytically and chemically produced powders, and correlate it with the morphology of the particles. The constant regimes (both potentiostatic and galvanostatic) of electrolysis and the two types of electrolytes (the nitrate and the ammonium ones) are used for the synthesis via electrochemical route. Reduction with hydrazine was used for the chemical synthesis of Ag powders. The electrochemical and chemical routes for the synthesis of Ag powders are mutually compared and the advantages and lacks of these methods are discussed.

## 2. Experimental

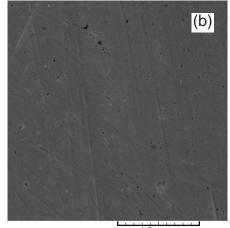
For electrolytic production of silver powders, the both galvanostatic (DC mode) and potentiostatic (POT mode) regimes of electrolysis were used. The powders were produced from solutions based on nitrate ions (0.10 M AgNO<sub>3</sub> + 2.0 M NaNO<sub>3</sub> – in the further text this electrolyte is denoted with NIT) and on the formation of complex with ammonium ions (0.10 M AgNO<sub>3</sub> + 0.50 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with NH<sub>4</sub>OH added in excess to dissolve formed precipitate – in the further text this electrolyte is denoted with AM).

The synthesis of Ag powders was performed at the temperature  $22.0\pm0.5$  °C in a cylindrical cell of open type. All solutions were prepared from p.a. reagents using ultra-pure water. The current densities of -14.4

mA cm<sup>-2</sup> (for the NIT solution) and -13.05 mA cm<sup>-2</sup> (for the AM solution) were applied in the DC mode. In the POT mode, the production of Ag powders was performed at overpotentials of -90 and -150 mV (the NIT solution) and -625 and -925 mV (the AM solution). All electrodeposition processes were performed with an amount of the electricity of 1 mA h cm<sup>-2</sup> using AUTOLAB potentiostat/galvanostat PGStat 128N (ECO Chemie, The Netherlands). In all the experiments, Pt wire of 1.0048 cm<sup>2</sup> surface area was used as the working electrode. The surface area of Pt electrode used for Ag powder production by electrolysis is shown in Fig. 1. The counter (in both DC and POT modes) and reference (in POT mode) electrodes were of Ag. The configuration of electrodes in the electrochemical cell is described in Ref. [10]. The preparation of Pt electrode for electrolysis consisted of alkaline degreasing at 70 °C followed by an acid etching (20 % H<sub>2</sub>SO<sub>4</sub>) at 50 °C. After each



50 μm



10 μm

Figure 1. The surface area of Pt electrode used in the regimes of galvanostatic and potentiostatic electrolysis of Ag powders. Magnification: (a)  $\times$  1000 and (b)  $\times$  5000



phase, Pt electrode was rinsed with distilled water.

Production of Ag powders was performed chemically with hydrazine as the reducing agent. The procedure for preparation of Ag powder by the chemical process is given in Ref. [10].

The final treatment of the powders produced on all three ways is also given in Ref. [10].

The morphology of so synthesized powders was characterized by scanning electron microscope (Tescan digital microscopy, model VEGA3; Czech Republic). The PSD of Ag powders was obtained by use of a MALVERN Instruments Ltd, United Kingdom - MASTERSIZER 2000 device.

## 3. Results and discussion

# 3.1 Electrochemical characterization of the examined systems

In the processes of electrolysis, the metal powders the diffusion controlled obtained in are electrodeposition starting from the current density (the DC mode) or the overpotential (the POT mode) belonging to the limiting diffusion current density (l.d.c.d.) plateau [9]. In this investigation, the NIT and AM solutions were selected because they belong to completely different types of electrolyte from the electrochemical point of view. Namely, Ag is classified as the normal metal with use of the NIT electrolyte. The high values of the exchange current density are the main feature of these metals [29]. On the other hand, when electrolysis was performed from the AM solution, Ag behaves as the intermediate metal. This group of metals has considerably lower values of the exchange current density than the normal metals.

The polarization curves for the NIT and AM solutions have been already given in Ref. [10]. However, for easier understanding of the considered electrochemical systems, they are repeated in Fig. 2.

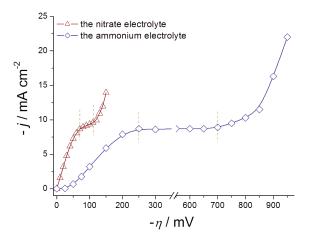
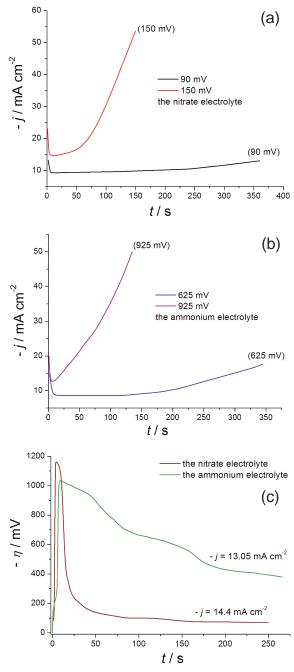


Figure 2. The polarization curves for Ag electrodeposition from the NIT and the AM solutions. According to Ref. [10]

For the AM solution, the l.d.c.d. plateau corresponds to the overpotential range 250–700 mV, with the value of the limiting diffusion current density ( $j_L$ ) of 8.7 mA cm<sup>-2</sup>. For the NIT solution, the short sloping plateau of the l.d.c.d. (70–110 mV) is observed. For  $j_L$ is taken value of 9.6 mA cm<sup>-2</sup> corresponding to the end of this plateau. Please note that plateaus of the l.d.c.d. are denoted by vertical lines at this Figure. For the



*Figure 3.* The chronoamperometric curves obtained from: a) the NIT solution, b) the AM solution, and c) the chronopotentiometric curves obtained from NIT and AM solutions



both types of solutions, the strong increase in the current density occurs after the end of the l.d.c.d. plateau.

Figure 3a shows the dependencies of the current density on the time of electrolysis obtained from the NIT solution at -90 and -150 mV. Figure 3b shows the same dependencies but obtained from the AM solution at -625 and -925 mV. Both solutions feature a strong growth of the current density with electrolysis time. This strong growth of the current density with the time clearly indicates that the formation and growth of powder particles is expected at these overpotentials [30]. The chronopotentiometric dependencies obtained from the same solutions at  $-14.4 \text{ mA cm}^{-2}$  (the NIT solution) and  $-13.05 \text{ mA cm}^{-2}$ (the AM solution) are shown in Fig. 3c. The overpotential values after the passed amount of the electricity of 1 mA h cm<sup>-2</sup> remained in the range of overpotentials enabling formation of Ag powders under these conditions of electrolysis.

# 3.2 Morphologies and particle size distribution (PSD) curves of Ag powders obtained by different methods of synthesis and by conditions of electrolysis

Fig. 4 shows the PSD curve for the particles obtained by the chemical synthesis with hydrazine as the reducing agent. In the further text, this powder is denoted with HYD. The largest volume ratio has the particles of the size of about 39.3  $\mu$ m. The SEM analysis of the obtained particles showed that the chemically synthesized particles represent aggregates made from grains like spheres as shown in Fig. 5. The average size of these grains was about 500 nm.

The PSD curves for the silver powders produced galvanostatically at -14.4 mA cm<sup>-2</sup> from the NIT and at -13.05 mA cm<sup>-2</sup> from the AM solutions are shown in Fig. 6. These powders are denoted with DC(NIT) for the powder produced in the NIT electrolyte, and

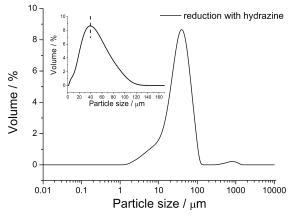
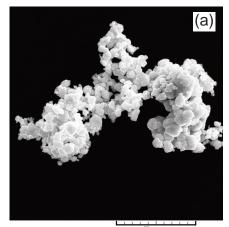


Figure 4. Particle size distribution (PSD) curve for chemically synthesized particles with hydrazine

DC(AM) for the powder produced in the AM electrolyte. The current densities of -14.4 and -13.05 mA cm<sup>-2</sup> were one and a half times greater than  $j_{\rm L}$  values for the NIT and AM solutions, respectively. Both electrolytes types give uniform distribution of particles, but the positions and the values of the maximum were different. The powder obtained by use of the NIT solution showed the largest volume ratio of the particles average size of about 31.3 µm. On the other hand, the powders produced in the AM solution had the maximum corresponding to the average size of the particles of about 19.7 µm.

The strong difference was observed between the morphologies of the particles obtained by the galvanostatic electrolysis from these two electrolytes. The morphologies of the particles produced by the use of the NIT solution are shown in Fig. 7a–c, while those obtained from the AM electrolyte are shown in Fig. 7d–f. The mixture of the needle-like dendrites and particles of regular and irregular shapes was



5 μm

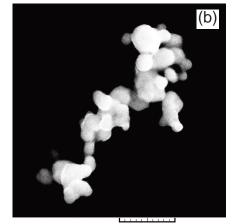




Figure 5. Morphologies of chemically synthesized Ag powder particles obtained by reduction with hydrazine. Magnification: (a) × 10000 and (b) × 35000



obtained from the NIT electrolyte (Fig. 7a–c). Unlike these shapes, the pine-like particles made of grains like spheres were obtained using AM electrolyte (Fig. 7d–f). Similar to those obtained by the chemical synthesis with hydrazine, the average size of these grains was about 500 nm.

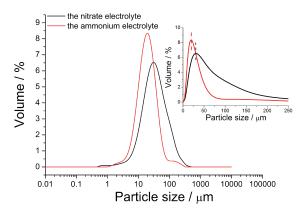


Figure 6. Particle size distribution (PSD) curves for Ag particles obtained galvanostatically by use of the NIT and the AM solutions

In the POT regime of electrolysis, silver powders were formed from the above mentioned electrolytes at overpotentials which belonged to the l.d.c.d. plateaus and at those outside these plateaus. Figure 8 shows the PSD curves obtained from the NIT electrolyte at overpotentials inside ( $\eta = -90$  mV) and outside ( $\eta =$ -150 mV) the l.d.c.d. plateau. The labels for the powders are NIT(90) for the powder obtained at -90 mV, and NIT(150) for the powder obtained at -150 mV. The shape of PSD curves was to a certain extent different from those given in Figs. 4 and 6. The two maximums are observed for the powder produced in the nitrate electrolyte at an overpotential of -90 mV: the first larger maximum corresponds to the particle size of 108 µm, while the second smaller and wider maximum corresponds to the particle size of about 780  $\mu$ m. As for as the powder produced at -150 mV, the maximum PSD curve corresponds to the particle size of 90 µm. However, there are significant volume ratios with the smaller and larger sizes of the particles than that corresponding to the maximum (Positions (A) and (B) in Fig. 8).

The explanation for these shapes of PSD curves can be found in the SEM analysis of the particles

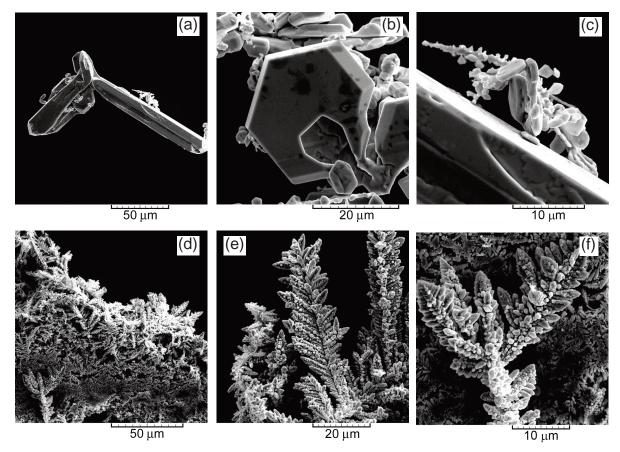


Figure 7. Morphologies of particles produced galvanostatically using: a) - c) the NIT solution, magnification:  $(a) \times 800$ ,  $(b) \times 3000$ ,  $(c) \times 5000$ ; t = 246 s, and d) - f) the AM solution, magnification:  $(d) \times 1000$ ,  $(e) \times 2000$ ,  $(f) \times 4000$ ; t = 266 s



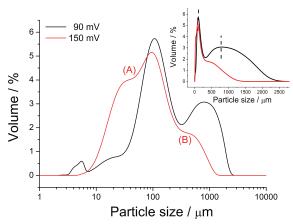
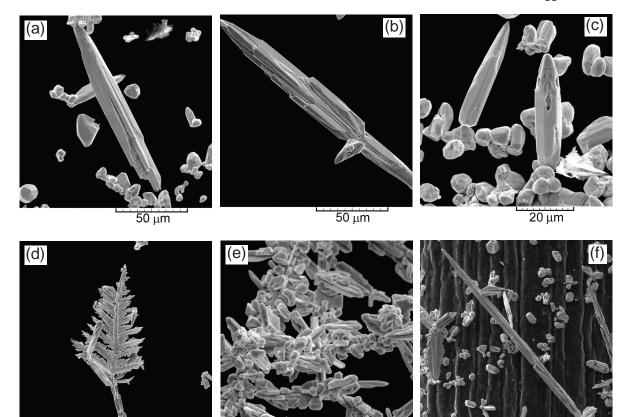


Figure 8. Particle size distribution (PSD) curves for Ag particles produced in the POT regime by use of the NIT solution at -90 and -150 mV

obtained at these overpotentials. Figure 9 shows the morphologies of the particles obtained from the nitrate electrolyte at -90 mV (Fig. 9a–c) and -150 mV (Fig. 9d–f). Similar to the galvanostatic regime of electrolysis (Fig. 7a), the needle-like dendrites were the dominant shape of the particles formed at -90 mV

(Fig. 9a-c), and the maximum PSD curve corresponds to the formation of this particle type. The smaller and wider maximum at the PSD curve obtained with the particles produced at -90 mV can be probably ascribed to the formation of agglomerates of the particles of various shapes, as shown in Fig. 9a and c (see the grains around the needle-like dendrites). The three types of the particles were formed by electrolysis at -150 mV: the highly-branched 2D (two-dimensional) fern-like dendrites made of the trunk and well defined branches (primary and secondary ones) (Fig. 9d), the mass of agglomerated particles (Fig. 9e), and the very long thin needles (Fig. 9f). Although the shape of the particles corresponding to the maximum at the PSD curve cannot be clearly identified, the analysis of the particles obtained immediately after the finished process of electrolysis and before their removing from the electrode surface indicates that the maximum at the PSD curve can be ascribed to the formation of the highly-branched 2D dendrites as the most dominant form obtained at -150 mV (Fig. 9d). Then, the (A) and (B) parts at the PSD curve left and right from the maximum can be ascribed to the formation of the mass of agglomerated



50 μm

20 µm

100 μm

*Figure 9.* Morphologies of powder particles obtained potentiostatically using the NIT solution at overpotentials of: a) – c) –90 mV, magnification: (a) × 1000, (b) × 1000, (c) × 2000; t = 360 s, d) – f) –150 mV, magnification: (d) × 1000, (e) × 3000, (f) × 600; t = 150 s

particles of various shapes (Fig. 9e) and the very long thin needles (Fig. 9f).

Figure 10 shows the PSD curves obtained from the AM electrolyte at overpotentials inside ( $\eta = -625$  mV) and outside ( $\eta = -925$  mV) the l.d.c.d. plateau.

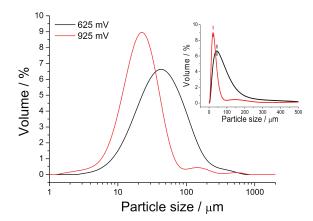


Figure 10. Particle size distribution (PSD) curves for Ag particles obtained potentiostatically using the AM solution at -625 and -925 mV

The labels for the powders are AM(625) for the powder obtained at -625 mV and AM(925) for the powder obtained at -925 mV. In both cases, the uniform distribution of particles was obtained. The increasing overpotential led to the increase of volume ratio and the shift of the maximum towards the lower particle size. The maximum of the PSD curves corresponds to the particle size of 42.4 µm for the powder produced at -625 mV and 23  $\mu$ m for that produced at -925 mV. The morphologies of the particles corresponding to these PSD curves are shown in Fig. 11. In both cases, the 3D pine-like dendrites made of grains like spheres were obtained. It can be noted from Fig. 11a that the pine-like dendrite obtained at -625 mV is shown before its removing from the electrode surface after the finished electrolysis process. Increasing overpotential leads to a ramification of the particles, so that the pine-like dendrites formed at -925 mV (Fig. 11d) were considerably more branched structure than those formed at -625 mV (Fig. 11a). The average sizes of the spherical grains of which they are constructed were: 650 nm for the particles produced at -625 mV (Fig. 11c) and 280 nm for the particles produced at -

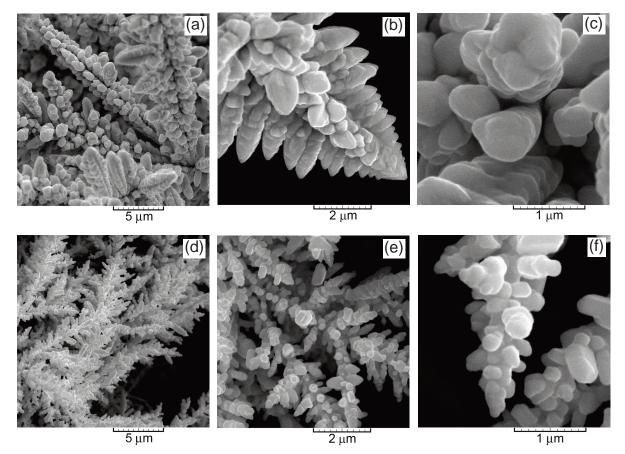


Figure 11. Morphologies of particles produced potentiostatically using the AM solution at overpotentials of: a) - c) - 625 mV, magnification:  $(a) \times 7000$ ,  $(b) \times 20000$ ,  $(c) \times 50000$ ; t = 345 s, and d) - f) -925 mV, magnification:  $(d) \times 7000$ ,  $(e) \times 20000$ ,  $(c) \times 50000$ ; t = 135 s



925 mV (Fig. 11f). Hence, the considerably decrease of the size of the spherical grains is observed with this increase of the overpotential.

## 3.3 Discussion of the presented results

As shown in Figs. 4, 6 and 10, the uniform distribution of the particles was obtained by the chemical synthesis with hydrazine, by the electrolysis using the NIT and AM solutions in DC mode, as well as in POT mode using the AM solution. On the other hand, the very disperse distribution of the particles was obtained in POT mode using the NIT solution. The values of the particle size with the largest volume ratio and the corresponding volume ratios are given in Table 1.

The analysis of the data from Table 1 indicates that Ag powders can be classified into three groups. In the first group are Ag powders formed galvanostatically by the use of the AM solution (DC(AM)), potentiostatically from the same electrolyte at -925 mV (AM(925)), as well as those obtained by the chemical synthesis with hydrazine (HYD). The common characteristic of these powders is a similarity of a micro structure (grains like spheres) with complete various macro structures (aggregates of grains or the pine-like dendrites). Simultaneously, the volume ratios obtained for these powders were between 8.4 and 8.9 %. The larger particle size for the chemically synthesized powder can be ascribed to the process of aggregation of particles.

In the second group can be put Ag powders produced by the galvanostatic electrolysis from the NIT solution (DC(NIT)) and by the potentiostatic electrolysis from the AM electrolyte at -625 mV (AM(625)). The common characteristic of these powders is the approximately same volume ratio (6.5–6.6 %). The diversity of shape of particles was observed at both micro and macro levels. As already mentioned, the needle-like dendrites, and the mixture of regular and irregular crystals was obtained in the

DC mode using the NIT solution (Fig. 7a–c). On the other hand, the pine-like dendrites were obtained by the POT electrolysis at -625 mV (Fig. 11a–c).

Finally, in the third group are Ag powders obtained in the POT mode using the NIT solution at both overpotentials. A wide variety of the particles characterizes this group of powders.

Hence, it is clear from the above consideration that the powders produced with the characteristics and under conditions to be placed into the first group showed the best characteristics from the point of view of the particle size distribution (PSD). It can be noticed that the processes of electrolysis from the AM electrolyte at current densities and overpotentials larger than the limiting diffusion current density showed certain advantages over the production of the powders by the chemical synthesis with hydrazine as the reducing agent. On the basis of this, all the advantages and lacks of the production of the powders by these methods can be perceived.

The electrolytic processes are very suitable ways for metal powder production because it is possibly easy to control the shape and the size of the particles by the choice of parameters and regimes of electrolysis [9]. In our case, this can be explained as follows: use of the ammonium electrolyte gave considerably better results than the use of the nitrate electrolyte. The increase of the overpotential of electrodeposition, and hence, electrolysis in the zone outside the l.d.c.d plateau led to a strong ramification of dendritic particles (Fig. 11). This ramification was accompanied by the decrease in the size of the spherical grains of which dendrites were constructed. Considering the basic nucleation law that the rate of nucleation increases with the increasing overpotential of electrodeposition [9], it follows that the further increase in overpotential (the potentiostatic regime), as well as in the current density (the galvanostatic regime) will lead to the further ramification of the dendrites, the decrease of size of the particles, and the decrease of grains of which are constructed.

 Table 1. The values of the particle size with the largest volume ratio and the corresponding volume ratios for Ag particles obtained by the chemical synthesis and under the different conditions of electrolysis\*

	the first group			the second group		the third group	
The type of Ag particles	HYD	DC(AM)	AM(925)	DC(NIT)	AM(625)	NIT(90)	NIT(150)
Particle size / µm	39.3	19.7	23	31.3	42.4	108	90
Volume ratio / %	8.6	8.4	8.9	6.5	6.6	5.7	5.2

\*HYD – the particles obtained by reduction with hydrazine; DC(NIT) – the particles produced galvanostatically using the NIT solution; DC(AM) – the particles produced galvanostatically using the AM solution; NIT(90) – the particles produced galvanostatically using the AM solution; NIT(90) – the particles produced potentiostatically using the NIT solution at –90 mV; NIT(150) – the particles produced potentiostatically using the NIT solution at –150 mV; AM(625) – the particles produced potentiostatically using the AM solution at –625 mV; AM(925) – the particles produced potentiostatically using the AM solution at –925 mV



On the other hand, the shape of chemically synthesized particles only depends on the type of reducing agent and pH, and it is difficult to control the size of the particles during chemical synthesis. Furthermore, the chemically synthesized particles show in a high degree tendency toward aggregation (as observed here) [22]. Also, chemical reduction method is a time-consuming and a complex process, as there are a number of processes involved, such as chemical reaction, separation, collection, and drying. Also, chemical reduction method has a high environmental-load because a large amount of solvent is discharged [4].

Unlike chemical processes of synthesis, the products obtained by electrolysis are very pure with a potential of easy sintering and pressing [31]. In relation to the chemical processes, the processes of electrolysis are fast and simple, and belong to the group of environmentally friendly processes. These processes require low equipment and production cost, and they take place in one-step by direct electrodeposition onto the cathode surface [32].

The limiting factor in the application of electrolysis is a powder yield which can be produced by this process. Aside from the parameters of electrolysis, the powder yield which can be produced in the unit of time is directly proportional to the size of the cathode surface. Although the advantages of the processes of electrolysis in production of Ag powders are definitely proved in this investigation, the process of chemical synthesis like this presented here also represents a significant and representative way for the production of Ag powders. Anyway, the process which will be applied in the production of powder exclusively depends on the desired application of the produced powder.

#### 4. Conclusions

Silver powders were obtained by both electrolytic method using the NIT and the AM solutions and the chemical synthesis with hydrazine as the reducing agent. Ag powders were produced by electrolysis in the both POT and DC modes. The powders were examined by SEM and PSD analysis. On the basis of PSD analysis, the synthesized powders can be classified into three groups:

(I) powders with the volume ratios of (8.4–8.9 %): HYD, DC(AM) and AM(925) powders make this group. They consist of grains like spheres constructing either the pine-like dendrites (the particles obtained by electrolysis) or agglomerates of grains (the chemically synthesized particles).

(II) powders with the volume ratios of (6.5–6.6 %): DC(NIT) and AM(625) powders make this group. The DC(NIT) powder consists of the needle-like dendrites and the mixture of regular and irregular

crystals, while AM(625) powder consists of the pinelike dendrites.

(III) powders with the volume ratios of (5.2-5.7 %): NIT(90) and NIT(150) powders make this group. The needle-like dendrites and the agglomerates of grains are characteristic of NIT(90), while the 2D fern-like dendrites are predominant characteristics of NIT(150) powders. Aside from them, the agglomerates of grains and the very long needles are also formed at -150 mV using the NIT solution.

The advantages and lacks of Ag powders production by the electrochemical and chemical methods were also discussed.

## Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (The project No. 172046).

## References

- A. T. Kuhn, P. Neufeld, G. Butler, Surf. Technol., 16 (1982) 3-14.
- [2] R. H. Estrada-Ruiz, R. Flores-Campos, G. A. Treviño-Rodríguez, J. M. Herrera-Ramírez, R. Martínez-Sánchez, J. Min. Metall. Sect. B-Metall. 52 (2) B (2016) 163-170.
- [3] N. Talijan, V. Ćosović, J. Stajić-Trošić, A. Grujić, D. Živković, E. Romhanji, J. Min. Metall. Sect. B-Metall., 43 B (2) (2007) 171-176.
- [4] S. Arita, T. Ogihara, T. Kubo, Y. Tsubota, K. Ohshita, N. Aoyagi, R. Ueyama, M. Harada, A. Harada, Int. J. Metall. Mater. Eng., 3 (2017) 133.
- [5] J.-T. Tsai, S.-T. Lin, J. Alloys Compd., 548 (2013) 105-109.
- [6] N. Moudir, Y. Boukennous, N. Moulaï-Mostefa, I. Bozetine, M. Maoudj, N. Kamel, Z. Kamel, D. Moudir, Energy Procedia, 36 (2013) 1184-1191.
- [7] K. I. Popov, P. M. Živković, S. B. Krstić, N. D. Nikolić, Electrochim. Acta, 54 (2009) 2924-2931.
- [8] V. D. Jović, N. D. Nikolić, U. Č. Lačnjevac, B. M. Jović, K. I. Popov, in Electrochemical Production of Metal Powders, Series: Modern Aspects of Electrochemistry (S. S. Djokić, Editor), Vol. 54, Springer, 2012, pp. 63-123.
- [9] K. I. Popov, S. S. Djokić, N. D. Nikolić, V. D. Jović, Morphology of Electrochemically and Chemically Deposited Metals, Springer International Publishing, 2016, Ch. 6, pp. 205-232.
- [10] Lj. Avramović, M. M. Pavlović, V. M. Maksimović, M. Vuković, J. S. Stevanović, M. Bugarin, N. D. Nikolić, Metals, 7 (2017) 160.
- [11] E. Zh. Tuleshova, A. B. Baeshov, Russ. J. Appl. Chem., 88 (2015) 1142-1145.
- [12] I. B. Murashova, A. P. Khramov, I. V. Zotin, Yu. P. Zaikov, V. G. Zyrjanov, J. Min. Metall. Sect. B-Metall., 39 (1-2) B (2003) 137-147.
- [13] S. Xiao, G. M. Haarberg, J. Min. Metall. Sect. B-Metall., 49 (1) B (2013) 71-76.
- [14] G. R. Khayati, K. Janghorban, Trans. Nonferrous Met.



Soc. China, 23 (2013) 1520-1524.

- [15] B. An, X.-h. Cai, F.-s. Wu, Y.-p. Wu, Trans. Nonferrous Met. Soc. China, 20 (2010) 1550-1554.
- [16] J. Sopousek, J. Bursik, J. Zalesak, Z. Pesina, J. Min. Metall. Sect. B-Metall., 48 (1) B (2012) 63-71.
- [17] S. S. Djokić, in Electrochemical Production of Metal Powders, Series: Modern Aspects of Electrochemistry (S. S. Djokić, Editor), Vol. 54, Springer, 2012, pp. 369-398.
- [18] S. S. Djokić, N. S. Djokić, J. Electrochem. Soc., 158 (2011) D204-D209.
- [19] S. S. Djokić, N. S. Djokić, C. Guthy, T. Thundat, Electrochim. Acta, 109 (2013) 475-481.
- [20] D. Ghosh, S. Dasgupta, Metall. Mater. Trans. B, 39B (2008) 35-45.
- [21] S. B. Rane, V. Deshapande, T. Seth, G. J. Phatak, D. P. Amalnerkar, B. K. Das, Powder Metall. Met. Ceram., 43 (2004) 437-442.
- [22] L. Lu, I. Sevonkaev, A. Kumar, D. V. Goia, Powder Technol., 261 (2014) 87-97.
- [23] M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, V. Radmilović, K. I. Popov, J. Serb. Chem. Soc., 66 (2001) 923-933.

- [24] K. I. Popov, Lj. J. Pavlović, E. R. Ivanović, V. Radmilović, M. G. Pavlović, J. Serb. Chem. Soc., 67 (2002) 61-67.
- [25] K. I. Popov, S. B. Krstić, M. Č. Obradović, M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, J. Serb. Chem. Soc., 68 (2003) 771-777.
- [26] K. I. Popov, M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, S. B. Krstić, M. Č. Obradović, J. Serb. Chem. Soc., 68 (2003) 779-783.
- [27] K. I. Popov, P. M. Živković, S. B. Krstić, J. Serb. Chem. Soc., 68 (2003) 903-907.
- [28] N. D. Nikolić, S. B. Krstić, Lj. J. Pavlović, M. G. Pavlović, K. I. Popov, in Electroanalytical Chemistry Research Trends (K. Hayashi Editor), NOVA Publishers, 2009, pp. 185-209.
- [29] R. Winand, Electrochim. Acta, 39 (1994) 1091-1105.
- [30] N. D. Nikolić, G. Branković, U. Č. Lačnjevac, J. Solid State Electrochem., 16 (2012) 2121 – 2126..
- [31] G. Orhan, G. Hapci, Powder Technol., 201 (2010) 57-63.
- [32] M. Amiri, S. Nouhi, Y. Azizian-Kalandaragh, Mater. Chem. Phys., 155 (2015) 129-135.

# RASPODELA VELIČINE ČESTICA (PSD) KAO KRITERIJUM ZA POREĐENJE PRAHA SREBRA DOBIJENOG RAZLIČITIM METODAMA SINTEZE I USLOVIMA ELEKTROLIZE

# Lj. Avramović<sup>a</sup>, M. Bugarin<sup>a</sup>, D. Milanović<sup>a</sup>, V. Conić<sup>a</sup>, M.M. Pavlović<sup>b</sup>, M. Vuković<sup>c</sup>, N.D. Nikolić<sup>b\*</sup>

# <sup>a</sup> Institut za rudarstvo i metalurgiju, Bor, Srbija

<sup>b</sup> Univerzitet u Beogradu, Institut za hemiju, tehnologiju i metalurgiju - Centar za elektrohemiju, Beograd, Srbija <sup>c</sup> Univerzitet u Beogradu, Institut za multidisciplinarna istraživanja, Beograd, Srbija

#### Apstrakt

Prahovi srebra dobijeni elektrohemijskim (galvanostatskim (DC) i potenciostatskim (POT) režimima elektrolize) i hemijskim procesima su ispitani skenirajućim elektronskim mikroskopom (SEM) i urađena je raspodela veličine čestica (PSD). U DC režimu, primenjene su gustine struje od  $-14.4 \text{ mA cm}^2$  za nitratni (NIT; prah označen sa DC(NIT)) i  $-13.05 \text{ mA cm}^2$  za amonijačni (AM; DC(AM)) elektrolit. U POT režimu, korišćene su prenapetosti od -90 mV (NIT(90)) i -150 mV (NIT(150)) za nitratni, i -625 mV (AM(625)) and -925 mV (AM(925)) za amonijačni elektrolit. Redukcija sa hidrazinom je korišćena za hemijsku sintezu (prah označem sa HYD). Na osnovu SEM i PSD analiza, prahovi srebra su svrstani u tri grupe. U prvoj grupi se nalaze DC(AM), AM(925) i HYD prahovi sa (8.4–8.9 %) zapreminskim udelima. U drugoj grupi se nalaze AM(625) i DC(NIT) prahovi sa (6.5–6.6 %) zapreminskim udelima. NIT(90) i NIT(150) prahovi sa zapreminskim udelima (5.2–5.7 %) čine treću grupu. Dobijeni zapreminski udeli su korelisani sa morfologijom sintetizovanih čestica da bi se sagledale prednosti i nedostaci proizvodnje praha elektrohemijskim i hemijskim putem.

Ključne reči: Srebro; Prah; Elektroliza; Hemijska sinteza; SEM; PSD

