Electrodeposition of silver powder from nitrate electrolyte for usage in electronic

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The aim of this work was to investigate the process of electrodeposition of silver powder from nitrate electrolyte for usage in electronic. It was performed a series of experiments to test the solubility of silver powder in nitric acid and the effect of Cu^+, Pb^{2+} and Cr^{2+} ions on the properties of the silver powder. The morphology of silver powder obtained from nitrate electrolyte, was studied using the scanning electron microscope (SEM model: JOEL JSM-6610LV). Chemical composition of the silver powder was determined using the Energy Dispersive X-ray Spectroscopy (EDS). The EDS spectra for silver powder were recorded using the X-ray spectrometer, attached to the scanning electron microscope.

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1. Introduction

Silver is one of the eight precious, or noble, metals; the others are gold and the six platinum-group metals (PGM). World mine production in 2001 was 18,700 metric tons (t) and came from mines in 60 countries; the 10 leading producing countries accounted for 86 percent of the total. The largest producer was Mexico, followed by Peru, Australia, and the United States. About 25 percent of the silver produced in the world in 2001 came from silver ores; 15 percent, from gold ores and the remaining 60 percent, from copper, lead, and zinc ores [1].

The industrial uses of silver (including photography), which today account for two-thirds of world silver consumption, did not arise until the 19th and 20th centuries. A short list of some of the important uses and the dates of their introduction follows:

- Silver and silver salts have been central to the development of photography since its origins in the 1820s.
- Silver-mercury dental amalgams have been used for tooth restorations since the late 1830s.
- Mirrors of polished silver were used by the Egyptians in the third millennium B.C. The large-scale production of silvered glass mirrors through the chemical reduction of silver nitrate dates from Justus von Liebig's 1835 invention of the process.
- A patent for the electroplating of silver was granted in 1840; it was he first patent for the electroplating of any metal.
- Although Alessandro Volta had used silver and zinc as the electrodes of his "electric pile" or battery, at the beginning of the 19th century.
- Silver sleeve bearings were developed in the 1940s for use in high-performance military aircraft engines.
- Silver catalysts for the large-scale production of formaldehyde and the oxidation of ethylene are developments of the second half of the 20th century.
- Although silver was known to be an excellent conductor of electricity in the 19th century, its widespread use in switch and relay contacts and in conductors arose gradually during the 20th century [2-5].

Silver has been used for decades as a contact material in all areas of electrical engineering. Since silver is a noble metal, it creates a very thin surface layers (mostly sulfides, rarely oxides), which therefore have little impact on contact resistance. Oxides are unstable and they are reduced at a temperature of 200^0C to pure silver. Because of that silver is particularly suitable for permanently closed contacts, and therefore applied for making silver rivets or coating copper contact (galvanic or chemically deposited). However, despite good electrical properties, stability in air and relatively low cost compared to other precious metals, using pure silver is limited because of: low hardness, low melting point and sensitivity to sulfur. Silver contacts are readily banded when you turn on electric circuit. The use of silver, as contact material, becomes significant in the period of development of powder metallurgy [6].

Electrical contact materials are used as contact members in a variety of switchgear applications, such as electrical switches, contactors, circuit breakers, relays, etc. [7-9].

Ultra fine metallic powders are commonly used in electrically conductive paste, solid oxide fuel cells and chemical catalysts, etc. In the manufacture of electronic devices such as hybrid integrated circuits and multilayer components [10-12], the technology of making conductive thick film from metal powders is of considerable importance [13-14].

In the recent years investigators have applied a number of chemical approaches to control size and shape of particles and to produce the powder of metals with advanced morphology. In this regard numerous factors are considerable. Technology of synthesis and assembly of valuable nanoparticles such as silver with less than 50 micron dimensions is an important base of industry. Silver particles having fine or ultra fine size are of considerable current use in electronics chemical industry, medicine and engineering materials due to unique properties such as high electric and thermal conductivity, high resistance to oxidation, bacterial action, etc. [15-20].

So the price of the nano metal powders is 20% percent more than their bar. Hydro metallurgical methods for separating elements from an industrial waste are dividing to four processes: 1- Solvent extraction. 2- Electrolysis. 3- Ion exchange. 4- Precipitation & washing [19].

1.1 Solubility of silver powder in nitric acid

Silver is not soluble in dilute nitric acid whose concentration is less than 1% [1]. In the concentrated nitric acid solution containing dissolved silver. There are two interpretations of the mechanism of this process [21-23]:

I Mechanism:

$$Ag + 2HNO_2 = AgNO_2 + NO + H_2O \quad (1)$$

$$AgNO_2 + HNO_3 = HNO_2 + AgNO_3 \quad (2)$$

$$HNO_3 + 2NO + H_2O = 3HNO_3 \quad (3)$$

When the concentration of nitric acid reaches the equilibrium, following reaction takes place:

$$3HNO_2 = HNO_3 + 2NO + H_2O \quad (4)$$

II Mechanism

According to another interpretation mechanism of dissolution of silver in nitric acid can be represented by the following equations:

$$2Ag + 2HNO_3 = H_2O + AgNO_2 + AgNO_3 \quad (5)$$

$$AgNO_2 + HNO_3 = HNO_2 + AgNO_3 \quad (6)$$

$$HNO_2 + HNO_3 + 2Ag = 2AgNO_2 + H_2O \quad (7)$$

In this case, the primary product is silver nitrate and nitric acid acts just as a catalyst. By removing nitric acid you can prevent dissolution of silver.

Nitric acid reacts with urea:

$$2HNO_3 + CO(NH_2)_2 = CO_2 + 2N_2 + 3H_2O \quad (8)$$

Thus by adding urea to nitric acid it is possible to remove the silver catalyst decomposition reaction and thus prevents the silver dissolution.

1.2 Influence of cations (Cu, Pb and Cr) on electro-crystalisation of silver from nitrate solution

Electrolytes for obtaining metal coatings, metal powders and for electrolytic refining of metals, contains various additives, include organic colloids: dextrin, gelatin, thiourea and others. The application of these organic additives is based on the results of their influence on electro-crystallization of metal on the cathode. However, it is observed that non-organic additives, namely, various metal cations affect the appearance and shape of dendrites. Paper [21] shows the results of research on effects of small amounts of several metal ions on shape of silver dendrites obtained at the silver cathode in a solution of silver nitrate.

Cations were added in the form of their nitrate salts or anodic dissolution. The electrolyte was an ammonia solution 0.25-1 M of silver nitrate. The concentration of cations was in the range 0.01- 0.1 g/dm3. Experiments were carried out at constant current density. Silver cathode surface was 1-3 mm2 and current intensity was 6-25 mA. Research was including effect of: Cu, Cd, Fe, Cr, Zn, Cd and Zn mixture and Ni on electro-crystalisation of silver from nitrate solution. The results showed that the metal cations have a significant influence on the shape of crystals of silver and that this influence depends on the type of cations [24].

2. Experimental work

2.1 Apparatus and reagents

Experiments were carried out with the aim to investigate the effect of ions: Cu, Pb and Cr on the external appearance, chemical composition and grain size composition of silver powder.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Produced by: Spectro, Model: Ciris Visio, Detection limit: < 0, 0001 g/dm^3) and Atomic Absorption Spectrophotometer (AAS, Produced by: Perkins & Elmer, Model: 403, Detection limit: < 0, 0001 g/dm^3) in ordered to obtain exact chemical composition of electrolyte and silver powder.

Granulometric composition of powders was determined by sedimentation balance produced by ″Sartorius″, Germany.

The morphology of silver powder obtained from electrolytes with Cu$^+$, Pb^{2+} and Cr^{2+}, was studied using the scanning electron microscope (SEM model: JOEL JSM-6610LV operated at 20 keV).

Chemical composition of silver powder was determined using the Energy Dispersive X-ray Spectroscopy (EDS). The EDS spectra for silver powder were recorded using the X-ray spectrometer, attached to the scanning electron microscope.

In two experiments silver powder was dissolved in diluted nitric acid. First, the two samples of 100 ml of 0.5% nitric acid were measured. In both probes 0.2 g of silver powder were added. In one of the probes 0.5 g of urea was added. Prepared probes were left for 5 hours. After 5 hours, solutions were filtered and in both NaCl were added. After adding sodium chloride, the solutions remained completely clear in both samples.

In a second experiment of 100 ml of 3.0% nitric acid were measured and the solubility of silver was examined. Quantitative determination of silver in both experiments showed that the total content of silver in the 100 ml of 3% nitric acid, in which urea is added, was C_{Ag}=0,0205 g/dm^3. In the second sample, in which was added about 0.5 g of urea, there was not the silver in solution. Two apparatuses were used electrolytic cell with a rotating cathode in the aim to examine the influence of cations on the properties of silver powder.

In Fig. 1 are shown scheme of apparatus and in Fig. 2 electrolytic cell used in experiments.

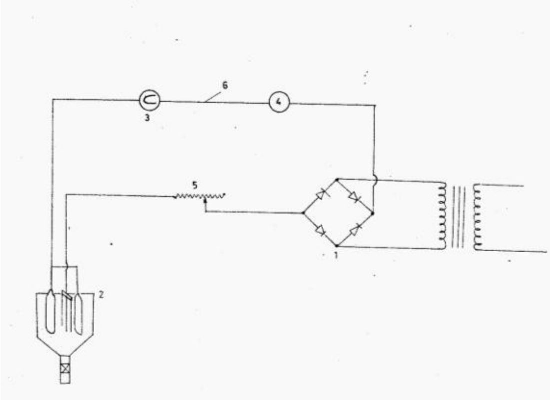


Fig. 1. Scheme of the apparatus.

Improvised apparatus consisted of laboratory glass cup V=250 ml (2) and the electrolysis bath in which silver powder as a voluminous precipitate separates at the cathode during the experiment. Silver was stripped from the electrode by hand using glass rod. Stripping from the cathode is carried out at regular intervals in order to obtain the homogeneous powder.

If one considers that the time between the cathode powder shudder 30-45 seconds, it is clear that shudder with powder by hand using a glass electrode sticks, limiting the duration of the experiment. That is reason the second series of experiments performed on the apparatus in which the powder with a shudder the cathode is automated. That is reason that the second series of experiments were preformed on apparatus with automated stripping process.

Bath has a shape of square container (1) with funnel bottom (2). This type of dish bottom facilitates the extraction of powder, which accumulates in the bath during the electrolysis. Pipe (3) has the valve (4) and is used to drain the powder suspension and the electrolyte. Bath is made of PVC (d = 4 mm). It is composed of several elements that are connected by welding. With the four holders (5), bath is attached to a metal frame (6). Cooler (7) regulate the temperature of the electrolyte. Anodes (8) are casted from the refined silver, 70×115×5 mm dimensions, weight 500-550 grams. Anode casting mold was made of sheet steel that is a specially designed for this purpose. Anodes are attached to copper rods (10) by copper loops (9), which rely on anode rails (11). Cathodes are made from steel rods, 130 mm in length, and fixed for cathodic rail (12). The distance between two adjacent bars was 15 mm. Each cathode bar has, at one end, the coil with which is connected with the cathodic rail so that the number of cathode rods can easily be changed and therefore the size of the cathode surface.

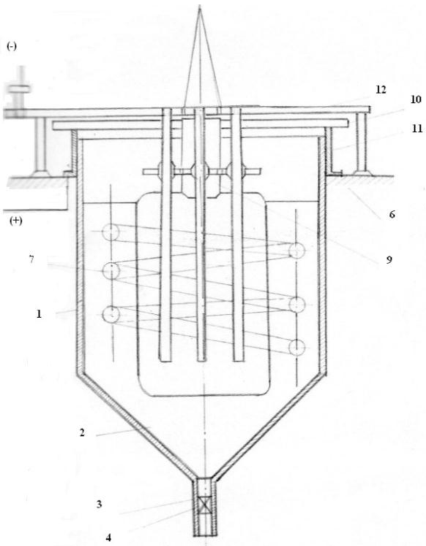


Fig. 2. Electrolytic cell with the cathode in the form of rods.

2.2 Preparation of solution for electrodepositon of silver powder

The chemical composition of the used electrolyte was: 0.1M $AgNO_3$, 0.1M $NaNO_3$ and 0.05M HNO_3.

Electrolyte temperature was 25°C.

Different metal ions were added to the electrolyte in the form of nitrate. Their concentration varied within the limits of 0.01-0.1 g/dm^3.

Current density is maintained constant and was 20 A/dm^2, while the intensity of current through cell was 8,0 A. The active cathode area was 40 cm^2 and anode area was 150 cm^2 (Pa/Pk = 3.5).

Silver powder was stripped on every 30 seconds. Electrolyte volume was 1.5 dm^3. After 30 minutes, by a power supply was interrupted, suspension of silver powder and nitrate electrolyte is discharged through the drain pipe in the receiving vessel in which the powder was completely participated and can be easily separated from the electrolyte by decantation. The powder was rinsed with water until negative reaction on the Cu^{2+} ions (test with ammonium hydroxide until the flush water in the trial shows no blue color) and finally with ethyl alcohol in order to shorten the drying time. Powder is dried at room temperature.

3. Results and discusion

3.1 Investigate the effect of ions: Cu, Pb and Cr on silver powder

Results of testing the solubility of silver powder in diluted solutions of 100 ml of nitric acid are given in Table 1.

Table 1. Solubility of silver powder in diluted solutions of nitric acid.

C_{NHNO_3} (%)	G_{Ag} (g)	$G_{CO(NH_2)_2}$ (g)	t (h)	C_{Ag^+} (g/dm^3)
0.5	0.2	-	5	-
0.5	0.2	0.5	5	-
3	0.2	-	5	0.0205
3	0.2	0.5	5	

From the results shown in Table 1 can be concluded that the urea completely destroys nitric acid, which performs the catalytic dissolution of silver and points to the possibility of adding urea to the nitrate electrolyte for a silver powder production in order to reduce corrosion, and also would like this increased the current efficiency obtaining a powder of silver by electrolysis of acid silver nitrate solution; also, this would increase current efficiency in obtaining silver powder by electrolysis of acid solutions of silver nitrate.

- **Influence of the Cu^+ ions**

The content of copper in silver powders obtained by the electrolytic electrolytes at different concentrations of copper is given in Tables 2 and 3 respectively.

Table 2. The content of copper in silver powders depending on the content of copper in the electrolyte (improvised apparatus).

Cu in electrolyte (g/dm^3)	Cu in silver powder (%)
0	0.005
0.01	0.009
0.05	0.018
0.10	0.018

Table 3. The content of copper in silver powders depending on the content of copper in the electrolyte (bath with cathodes in the form of bars).*

Cu in electrolyte (g/dm^3)	Cu in silver powder (%)
0	0.005
0.02	0.018
0.04	0.007
0.06	0.009
0.08	0.014
0.10	0.013

* For each concentration of copper in the electrolyte, two samples are made

Graphic representation of sedimentation analysis are shown in Figs. 3 - 6 (for the experiment with improvised apparatus - I experiment) and in Fig. 7-12 (for the experiment with the apparatus in Fig. 2- II experiment).

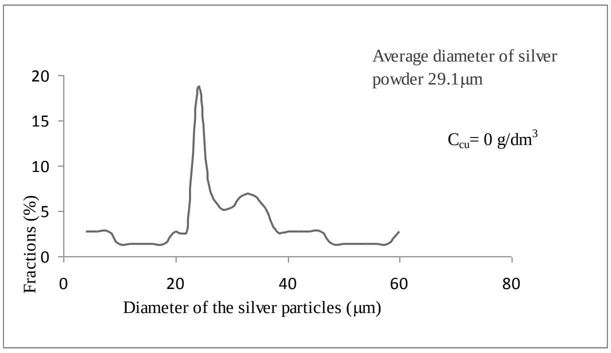


Fig. 3. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0 g/dm^3 (I experiment).

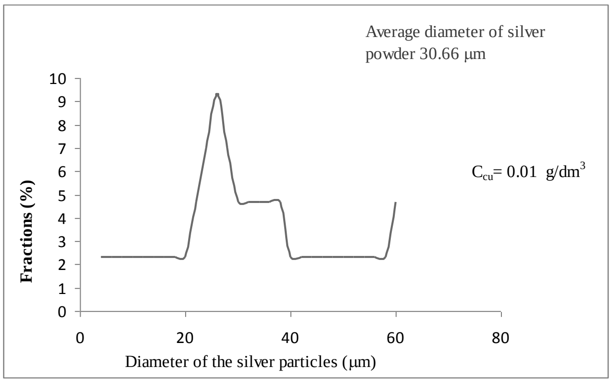


Fig. 4. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.01 g/dm^3 (I experiment).

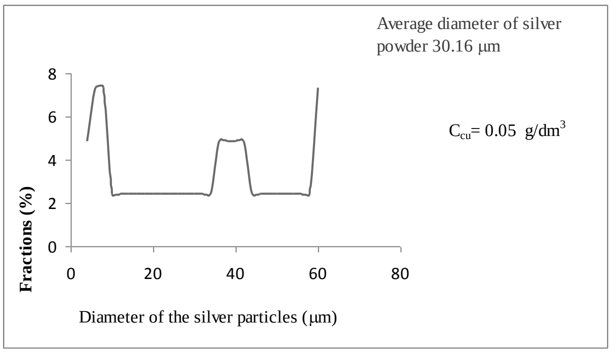


Fig. 5. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.05 g/dm^3 (I experiment).

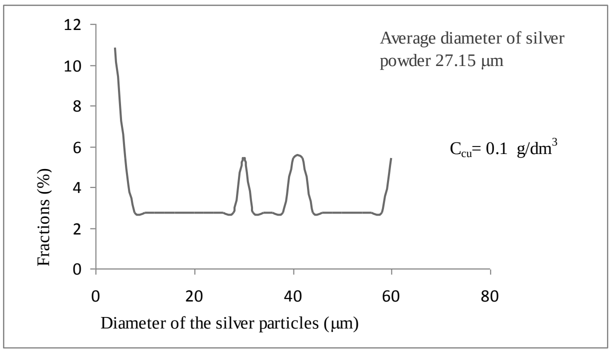


Fig. 6. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.1 g/dm^3 (I experiment).

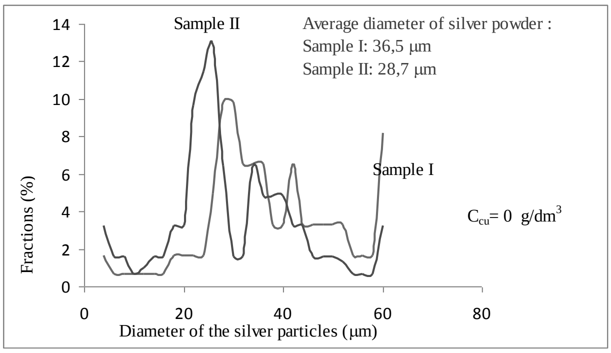


Fig. 7. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$= 0 g/dm^3 (II experiment).

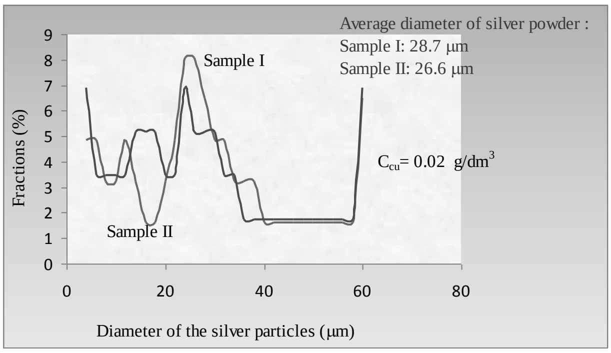


Fig. 8. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.02 g/dm^3 (II experiment).

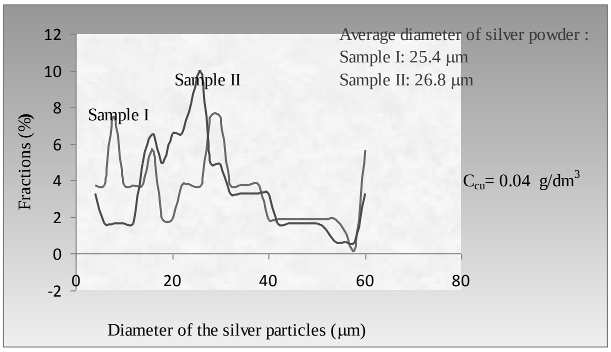


Fig. 9. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.04 g/dm^3 (II experiment).

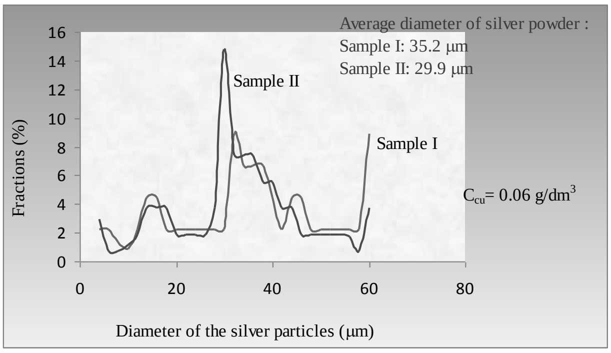


Fig. 10. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.06 g/dm^3 (II experiment).

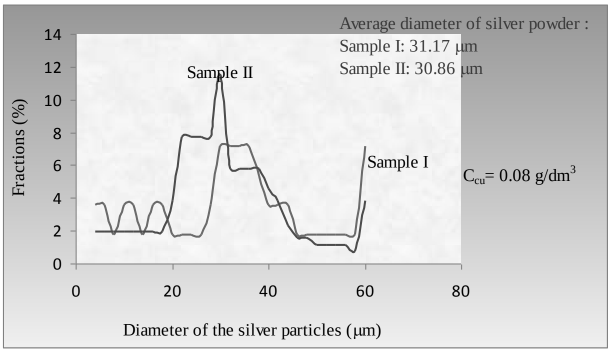


Fig. 11. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.08 g/dm^3 (II experiment).

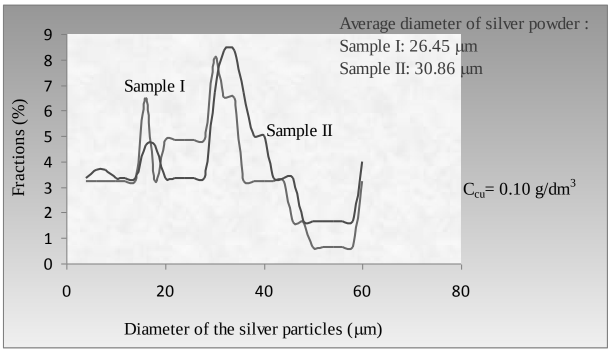


Fig. 12. Sedimentation curve of the silver powder analysis for $C_{(Cu)}$=0.10 g/dm^3 (II experiment).

From Figs. 7-12, comparation the two sedimentation curves (sedimentation fluid: alcohol), can be concluded that all curves have two maximums of which one is more pronounced. It can be assumed that the appearance of two maximums on the sedimentation curves is result of the fact that it is impossible to completely remove powder from the cathode. The stripper never removes all the powder because the length of its step through the electrolyte is less than the height of the immersed part of the cathode. For samples with $C_{(Cu)}$=0.08 g/dm^3 sedimentation curves show deviations from the other samples. This can be explained by inhomogeneous silver powder which was taking for the samples. This could be avoided by homogenization of the dried powder of silver.

- **Influence of the Pb^{2+} ions**

Lead is added to the electrolyte in the form of $Pb(NO_3)_2$. By external appearance, powders obtained from an electrolyte containing Pb^{2+} ions did not differ from the powder that is obtained from electrolyte in which Pb^{2+} ions are not added.

Series of three experiments were performed, in which the impact of Pb^{2+} addition on the properties of silver powder was examined. Results of determination of lead content in silver powder are given in Table 4.

Table 4. The content of lead in silver powders depending on the content of lead in the electrolyte (improvised apparatus).

Pb in electrolyte (g/l)	Pb in silver powder (%)
0	0
0.01	0
0.05	0
0.10	0.0056

Graphic representation of sedimentation analysis is shown in Fig. 13.

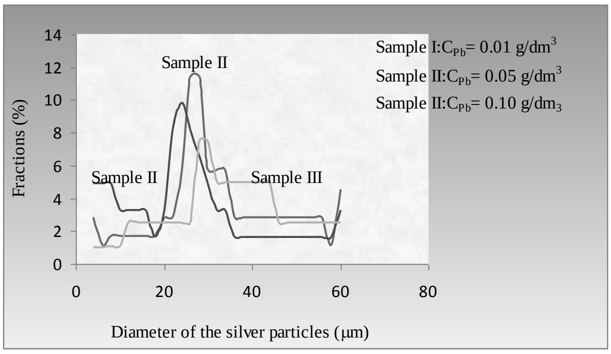


Fig. 13. Sedimentation curve of the silver powder analysis for various concentrations of Pb^{2+}.

By comparative analysis of sedimentation curves in Fig. 13 (sedimentation fluid: alcohol) it can be concluded that all curves have a maximum. The distribution of dust particles by fractions changes with the addition of Pb^{2+} ions in electrolyte for a silver powder obtaining.

- ***Influence of the Cr^{2+} ions***

Chromium(III) ions were added in the electrolyte by adding $Cr(NO_3)_3$ which was obtained from CrO_3 according to the equations:

$$CrO_3 + H_2SO_{4(20\%)} \xrightarrow{C_2H_5OH} Cr_2(SO_4)_3 \qquad (9)$$

$$Cr_2(SO_4)_3 + 12NH_4OH = 4Cr(OH)_3 + 6(NH_4)_2SO_4 \qquad (10)$$

$$Cr(OH)_3 + 3HNO_3 = Cr(NO_3)_3 + 3H_2O \qquad (11)$$

Cr^{3+} concentration in the electrolyte was 0.10 g/dm^3. The powder of silver obtained from the electrolyte containing Cr^{3+} has a dark gray color. By analytical methods it was confirmed that chrome precipitates with silver. The mass concentration of chromium in silver powder was C_{Cr}=0.015%.

Graphic presentation of the results obtained by sedimentation analysis of the powder from an electrolyte containing Cr^{3+} ions is shown in Fig. 14.

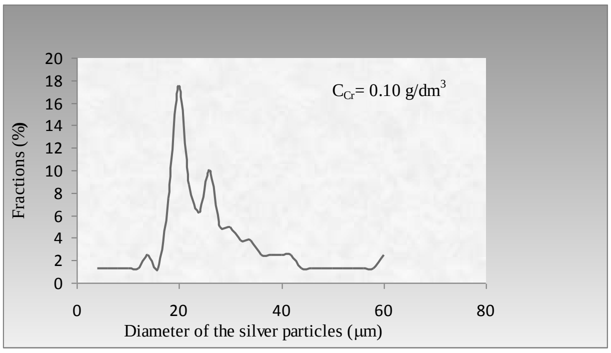


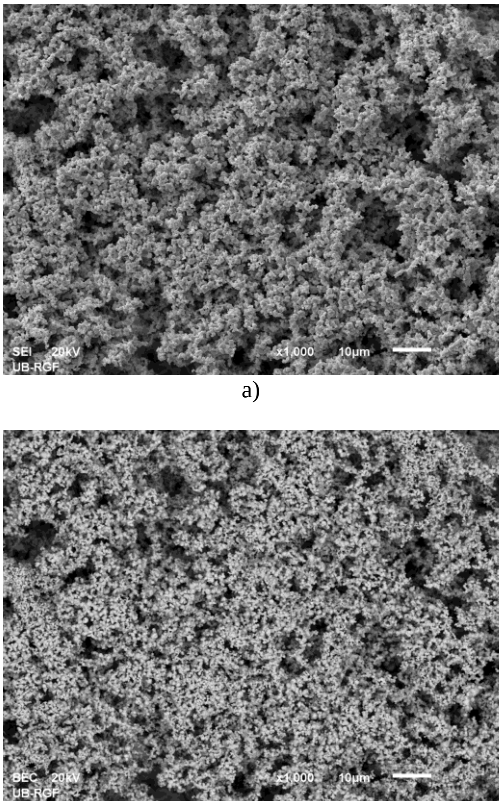
Fig. 14. Sedimentation curve of the silver powder analysis for C_{Cr} = 0.10 g/dm^3.

From Fig. 14 can be concluded that the distribution of powder particles by fractions is very similar to silver powder that is obtained from the electrolyte, which contained no inorganic additives (Fig. 2).

2.3 SEM with EDS

SEM images (back-scattered electron image-BSE and secondary electrons image-SE) of silver powder are presented in Fig. 15 for electrolyte with Cu^{2+}, in Fig. 16 for electrolyte with Pb^{2+} and in Fig. 17 for electrolyte with Cr^{2+}.

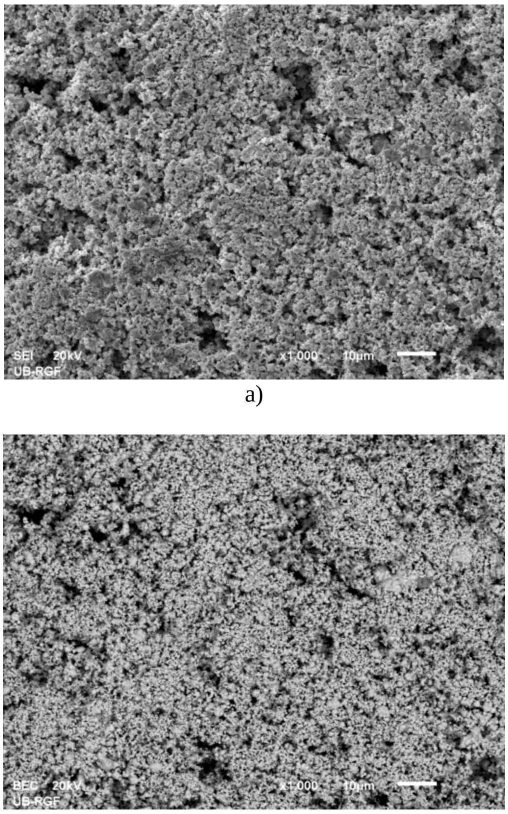
EDS images with EDS spectra of silver powder are presented in Fig. 18 for electrolyte with Cu^{2+}, in Fig. 19 for electrolyte with Pb^{2+} and in Fig. 20 for electrolyte with Cr^{2+}.



a)

b)

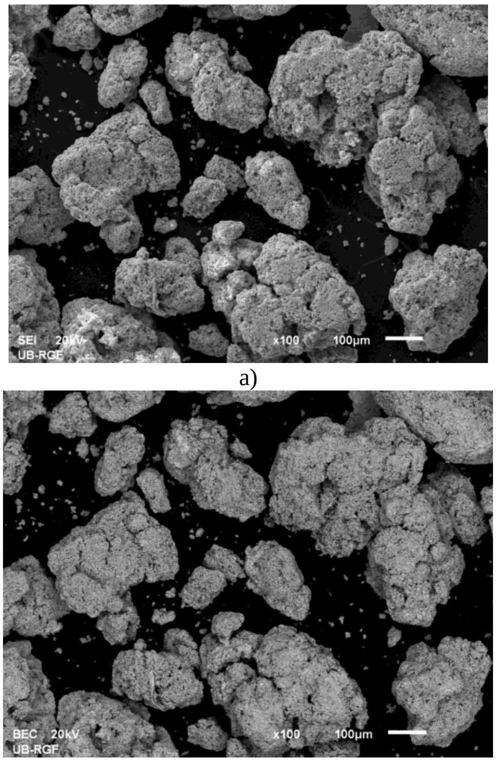
Fig. 15. SEM image of silver powder obtained from electrolyte with $C_{Cu^+} = 0.1$ *g/dm*^{3}*: a) BSE image b) SE image.*



a)

b)

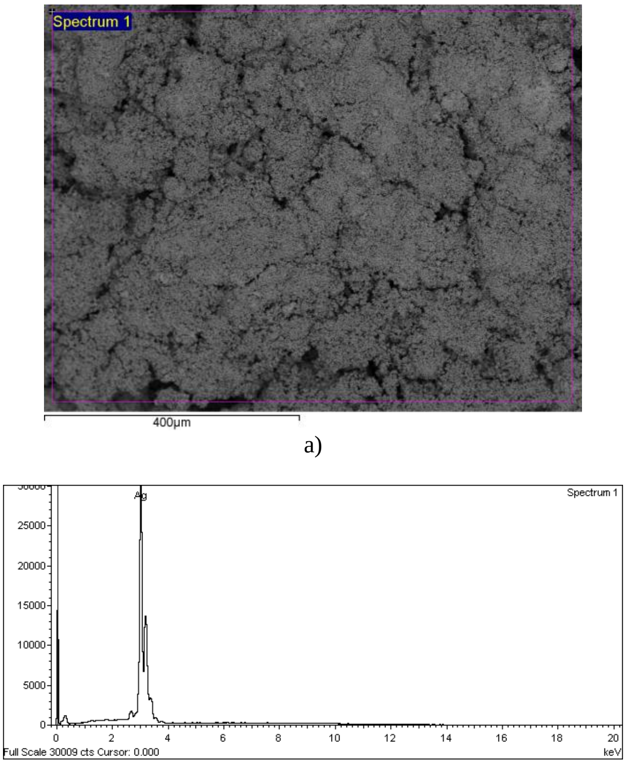
Fig. 16. SEM image of silver powder obtained from electrolyte with C_{Pb+}*= 0.1 g/dm*^{3} *: a) BSE image b) SE image.*



a)

b)

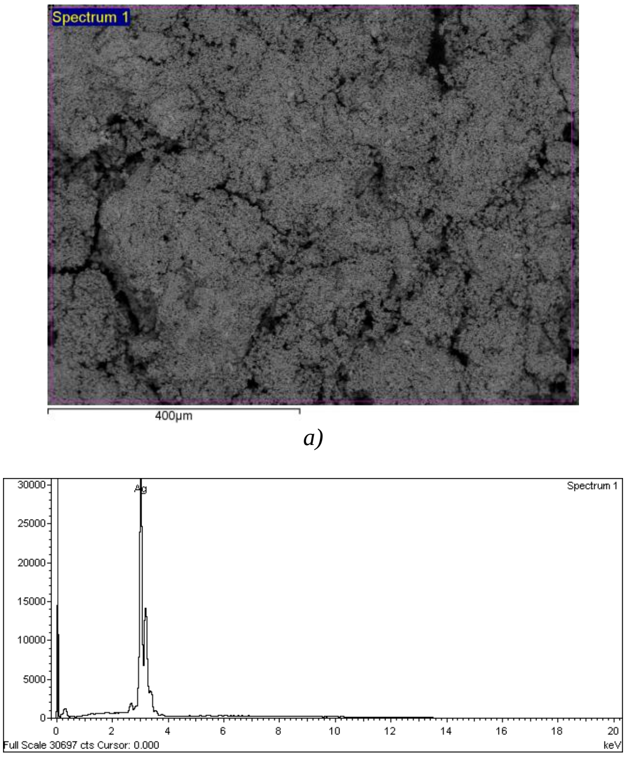
Fig 17. SEM image of silver powder obtained from electrolyte with C_{Cr+}*= 0.1 g/dm*^{3} *: a) BSE image b) SE image.*



a)

b)

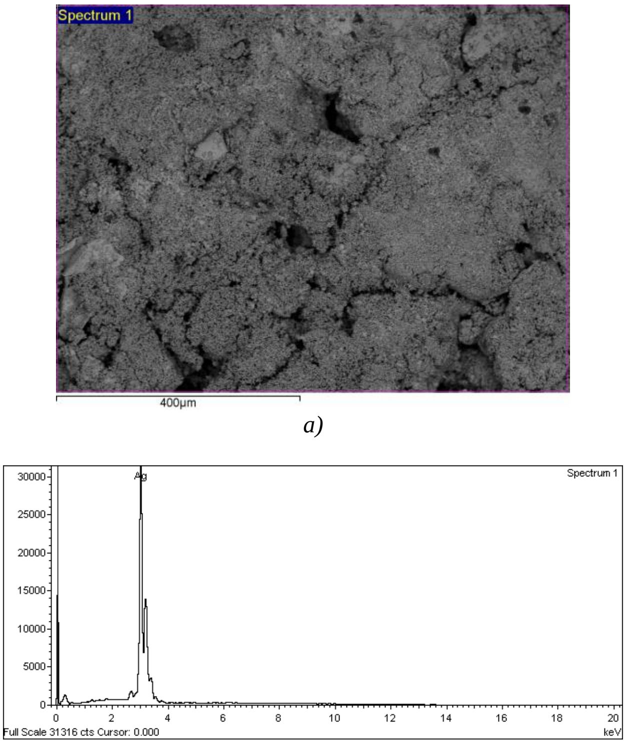
Fig. 18. EDS image with EDS spectrum of silver powder obtained at $C_{Cu^+} = 0.1$ *g/dm*^{3}*: a) EDS image, b) EDS spectrum.*



a)

b)

Fig. 19. EDS image with EDS spectrum of silver powder obtained at $C_{Pb^{2+}} = 0.1$ *g/dm*^{3}*: a) EDS image, b) EDS spectrum.*



a)

b)

Fig. 20. EDS image with EDS spectrum of silver powder obtained at $C_{Cr^{2+}} = 0.1$ *g/dm*^{3}*: a) EDS image, b) EDS spectrum.*

3. Conclusion

- The experiments of getting silver powder in the presence of copper cations showed that silver always have traces of copper and that the copper content in silver depends on the concentration of copper in the electrolyte.
- According to literature data, deposition of silver powder in the presence of copper, lead and chromium is accompanied by the influence of these elements on the form of silver dendrites. In our experiments the impact of these cations on the shape and size of powder particles is not proved.
- Since copper and lead can be found in anode silver and the electrolyte, and experiments have shown that they are deposited along with silver, it is necessary to have pure anodes and clean electrolyte.
- These experiments indicated the possibility of deposition of Ag-Cu alloys powder.
- From the SEM image of silver powder, obtained from the electrolyte with Cu^{2+} presented in Figure 15, for electrolyte with Pb^{2+} presented in Figure 16 and for electrolyte with Cr^{2+}., presented on Figure 17 (a-BSE image and b-SE image), it can be concluded that the distribution of grains is uniform.
- Chemical composition of silver powder obtained at $C_{Cu^{+}}$ = 0.1 g/dm^3, $C_{Pb^{2+}}$ = 0.1 g/dm^3 and $C_{Cr^{2+}}$ = 0.1 g/dm^3 presented in Figs. 17-19 (EDS image with EDS spectra), was determined by EDS. The EDS image shows a place where the chemical composition of silver powder was determined. Vapor deposition of carbon on samples is carried out in a stream of argon using the machine LEICA EM samples SC2005 (manufacturer Leica Microsystems - Germany).

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References

[1] W. C. Butterman, H. E. Hilliard, U. S. Geological Survey, Reston, Virginia 2005., http://www.usgs.gov/pubprod.

[2] Butts, Allison, The physical properties of silver, chap. 7 in Butts, Allison, and Coxe, C.D., eds., Silver—Economics, metallurgy, and use: Princeton, Van Nostrand Reinhold, 1967, p. 104-122.

[3] R. H. Hallowell, Manufacture of sterling silver hollowware, chap. 23 of Butts, Allison, and Coxe, C.D., eds., Silver—Economics, metallurgy, and use: Princeton, Van Nostrand Reinhold, 1967, p. 331-342.
[4] Silver Institute, World silver survey 2002: Washington, DC, The Silver Institute, 2002, pp. 87.
[5] Silver Institute, Traditional silver halide photography use expected to grow during decade, 2002, http://www.silverinstitute.org/news/pr05feb02.html
[6] A. Ivanović, i dr., 15th International Research/Expert Conference ”Trends in the Development of Machinery and Associated Technology” TMT 2011, Prag, 4-10 September 2011.
[7] Bharati Rehani, P. B. Joshi, P. K. Khanna, Journal of Materials Engineering and Perfomance, **19**(1), 64 (2010).
[8] G. J. Witter, in Arcing Contact Materials, Electrical Contacts—Principles and Applications, P. G. Slade, Ed., Marcel Dekker, New York, 681 (2002).
[9] P. B. Joshi, P. Ramakrishnan, Science Publishers, Enfield, NH, 165 (2004).
[10] W. Songping, Journal of Material Science: Mater Electron, **18**, 447 (2007).
[11] W. Songping, M. Shuyuan, Mater. Chem. & Phys. **89**(2-3), 423 (2004).
[12] W. Songping, Q. Haoli, L. Pu, J. Univ. Sci. Technolog. Beijing, **13**(3), 250 (2006).
[13] Wuu-Jyh Liang, Hsien-Ming Kao, Ping-Lin Kuo, Macromolecular Chemistry and Physics, 600 (2004).
[14] S. B. Rane, P. K. Khanna, T. Seth, et al. Mater. Chem. Phys., **82**, 237 (2003).
[15] M. Kargar Razi1, S. Azadi, R. Sarraf Mamoory, M. Mohammadi, International Journal of Nano. Dimension, **1**(2), 133 (2010).
[16] K. A. Khor, X. J. Chen, S. H. Chan, L. G. Yu, Mater. Sci. Eng. A, 120 (2004).
[17] S. Ivan, S. S. Branka, J. Colloid Interface Sci, 177 (2004).
[18] S. Katakam, D. S. R. Krishna, T. S. S. Kumar, Mater. Lett, 2716 (2003).
[19] G. M. Shi, J. K. Han, Z. D. Zhang, H. Y. Song, B. T. Byong-Taek Lee, Sur. Coat. Tech., 333 (2005).
[20] H. H. Nersisuan, J. H. Lee, H. T. Son, C. W. Won, Maeng, Mater. Res. Bull, 949 (2003).
[21] John Joung, Plating **54**(3), 272 (1967).
[22] A. Petica, S. Gavriliu, M. Lungu, N. Buruntea, C. Panzaru, Materials Science and Engineering B, **152**(1-3), 22 (2008).
[23] S. Gavriliu, M. Lungu, E. Enescu, F. Grigore, C. R. Ionescu, Optoelectron. Adv. Mater. – Rapid Commun. **3**(6), 634 (2009).
[24] C. Gaidau, A. Petica, C. Ciobanu, T. Martinescu, J. Optoelectron. Adv. Mater., **11**(6), 845 (2009).
[25] N. Leopold, V. Chis, I. B. Cozar, L. Szabo, A. Pirnau, O. Cozar, J. Optoelectron. Adv. Mater. **2**(5), 278 (2008).

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