

Recycling of silver-plated brass for production of high purity copper and ultrafine silver powder for electric contacts

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The paper presents an improved process for recycling of silver-plate brass housing. Silver and copper are recovered with a purity of 99.99 % and 99.90 %, respectively, with the aim of obtaining materials of higher value using additional procedures based on the same process and equipment. The novel approach with subsequent electrorefining yields copper of 99.99 % purity with BS EN 1978:1998 (Cu-CATH-1) quality and is referred to as LME grade A. Additional processing of silver results in superfine, micro-sized Ag powder with particle size from 0.14 to 1.13 μm and purity of 99.999 %. Copper electrorefining tests were performed using 1.50 dm³ of synthetic electrolyte in a 2 dm³ electrolytic cell. Effects of current density and electrolyte composition were investigated. Optimal current density for the first and second refining was 120 A/m² and 200 A/m², respectively. Additional refining of silver was performed by chemical reduction from an aqueous solution. Optimal results were obtained with ascorbic acid as a reduction agent in concentration of 0.1 mol/dm³ and polyvinylpyrrolidone as a protective agent in concentration of 2 % by mass. The investigation results could be adopted into production.

Key words: recycling, copper, electrorefining, silver, micro-sized powder.

INTRODUCTION

Recycling of silver-plated brass has some specific issues when compared with conventional e-waste (waste electrical and electronic equipment, WEEE) processing. The recovery fundamentally aims at separating the three main metals in the material: copper, zinc and silver. The main goal of the present investigation was to obtain materials of higher value and to lower the cost of waste processing. Another result that was planned and realized was to obtain materials that can be reused with the same or similar purpose. Although the process of metal separation has been already applied in production [1], small changes in the process could yield copper and silver of higher purity.

Additional electrorefining (ER) leads to standard electrolytic copper quality, 99.99 %, with no more than 65 ppm of total impurities, of which maximum 25 ppm of silver [2]. Even higher purity of copper (99.999%) could be obtained from copper previously refined by electrolysis. Silver refinement is a common process and easily achieves 99.99 % metal purity. The disadvantage of the basic

hydrometallurgical process of refinement is that non-uniform, relatively coarse silver powder is obtained. ER could produce silver of uniform particle size of about 30 μm [3].

A hydrometallurgical process could be developed using a flexible technology with a full range of extractive metallurgic methods, such as pyro-, electro-, and hydrometallurgic processes. Pyrometallurgy is used barely for separation but primarily for anode casting. ER has given positive results in copper and zinc separation from pure brass [1]. It can be performed as either electrowinning or classical ER. Since no source of fresh electrolyte is available, combination of the two methods is used. Copper concentration decreases since the anodic dissolution compensates only part of the copper deposited on the cathode. Frequent corrections of the electrolyte are thus necessary. The process used in the study is basically a combination of EW and classical ER. Optimal parameters are similar to those in ER but with lower current density and higher concentrations of copper at the start of the process. Lower concentrations of copper and higher current densities have been used for similar recycling processes [4] but they were not confirmed. Subsequent ER was performed with a higher

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current density, 200 A/m² and with higher concentrations of Cu²⁺, sulfuric acid and additives. Possibilities of using higher current densities are indicated in several papers [5–7] but the research leaves only a small margin for it owing to the relatively high content of silver in the cathode copper of the second ER. The primary goal was to obtain copper of 99.99 % purity, but the results indicated the possibility of obtaining copper of higher purity in two consecutive electrolytic refining runs. Copper of 99.999 % purity could be recovered with lower current densities only from the first cathodic cycle in an experiment with three cathodic cycles.

Fine silver powder is extensively used in various industries for different applications. Despite the high purity of silver (99.99 %) obtained by classical chemical reduction of AgNO₃ with hydrazine hydrate, the aim of the research was to obtain fine particles for general industrial use with possibility of reuse. Synthesis of silver nanoparticles is a well-developed process for small size production and is of interest for mass-scale production. Silver nanoparticles can be prepared using different methods which could be categorized as [8]:

- 1) Chemical reduction from aqueous solutions;
- 2) Non-aqueous chemical reduction;
- 3) Electrochemical reduction;
- 4) Photoinduced or photocatalytic reduction;
- 5) Irradiation reduction;
- 6) Ultrasonic assisted reduction;
- 7) Microwave assisted synthesis;
- 8) Microemulsion methods and
- 9) Biochemical methods.

Subject of the present research was the production of micro-sized uniform spherical Ag powders that are commonly used in electrically conductive pastes, solid oxide fuel cells, chemical catalysts, etc. [9]. At first electrical contact alloys were considered. Because of their high electrical and thermal conductivity, silver alloys are frequently used materials in the industry. They also have high corrosion resistance, excellent solderability, resistance to abrasive wear, mechanical strength and reasonable price [10–12]. Alloying elements (Cd, Mg, Sn, C, W and Ni) are selected in order to improve the mechanical properties without significantly increasing the electrical resistance. The oldest and best known alloy of this type is Ag-CdO which meets the above requirements [10]. However, while using the electrical contacts of Ag-CdO, dissociation of CdO in Cd (vapor state) and O₂ occurs, which, due to the toxicity of cadmium, is considered extremely harmful to human health [13]. For environmental

reasons and toxicity of the material, there is interest to find a suitable replacement for Ag-CdO. The most promising material is Ag-SnO₂ [11, 14]. Its potential as substitute for Ag-CdO contacts is virtually complete for direct current applications, but not complete for alternating current. It is known that the functional properties of Ag-SnO₂ electrical contact materials can be improved by the addition of metal oxide components which increase the dispersion of the main oxide (SnO₂) in the silver matrix and contribute to the activation of the sintering process [15–16]. The influence of SnO₂ nanoparticles and the method of their introduction into the silver matrix on the microstructure and physical properties of the material have been examined. The highest hardness has been registered for the sample prepared using soluble starch as a template [17].

Silver powders constituted of non-agglomerated micron/submicron crystalline particles with a narrow size distribution were found to be ideal for thick film conductive pastes [18]. Chemical reduction with formaldehyde in base solutions was used with similar results [19] by using silver nitrate as metal source, ascorbic acid as reducing agent and arabic gum as dispersant.

In this paper, silver particles were synthesized from silver nitrate or silver ammonium chloride, using ascorbic acid as a reducing agent and polyvinylpyrrolidone as a protecting agent, by a traditional chemical reduction method. This method was chosen because it requires no specific experimental equipment or working conditions. It may be efficiently scaled-up for mass production [20] which was the primary objective.

EXPERIMENTAL

Silver-plated brass housings were processed by a combination of pyrometallurgical, electrometallurgical and hydrometallurgical processes on laboratory and semi-industrial scale. Final products of the recycling were standard cathode copper Cu-CATH-1 (LME Grade A, European Standard EN 1978:1998) or Cu-CATH-2 grade [2] and 99.99% to 99.999% purity submicronic silver powder.

Analysis methods

Inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS)

Inductively coupled plasma optical emission spectrometer (ICP-OES, Spectro, model: Ciris Visio, detection limits: <0.0001 g/dm³) and atomic absorption spectrometer (AAS, Perkin-Elmer,

model 403, detection limits: $< 0.0001 \text{ g/dm}^3$) were used for determination of the chemical composition of silver-plated housing and final products of refining.

Scanning electron microscopy (SEM) with energy-dispersive spectrometry (EDS)

Scanning electron microscope (SEM model: JOEL JSM- 6610LV operated at 20 keV) was used for determination of the chemical composition (with EDS), particle size and morphology of the silver powder. Chemical composition was determined using energy dispersive X-ray spectroscopy (EDS). The EDS spectra for silver powder were recorded using a X-ray spectrometer attached to the scanning electron microscope. The EDS image shows the place where the chemical composition of the silver powder was determined. Granulometric composition (particle size distribution; particle size analysis for SEM) of powders were determined by SEM software ImageJ (National Institutes of Health USA). ImageJ was able to measure distances directly from the image. The morphology of the silver powder was studied using SEM imaging.

Reagents

For the electrolyte preparation and its correction the following chemicals were used: copper sulfate pentahydrate p.a. (Zorka, Serbia); hydrochloric acid p.a. (Merck, Germany); sulfuric acid p.a. (Merck, Germany), thiourea p.a. (Kemika, Croatia) and gelatin powder pharmaceutical grade, Ph. Eur. (Merck, Germany).

For silver reduction and AgCl dissolution the following chemicals were used: nitric acid p.a. (Merck, Germany), ammonium hydroxide p.a. (Zorka, Serbia), hydrazine hydrate p.a. (Merck, Germany), ascorbic acid p.a. (Merck, Germany), polyvinylpyrrolidone, PVP K30 (trade name Plasdone[®] K-29/32) was of pharmaceutical grade (USP/NF) produced by ISP, sodium dodecyl sulfate (SDS) was of pharmaceutical grade (Ph. Eur.) produced by Cognis (trade name Texapon K12 P PH). Absolute ethanol p.a. (Zorka, Serbia) for silver powder rinsing was used. Deionized or double distilled water (max. conductivity $1 \mu\text{S/cm}$) was used in all experiments.

Experimental apparatus

Electrolytic laboratory type PP cell with approximately 2 dm^3 volume (1.50 dm^3 of electrolyte) was used for electrorefining. Electrorefining was performed with common open-tank parallel-plate electrode design, using

monopolar electrodes with parallel connection. A system of three anodes and four cathodes was used. Potentiostat Bank STP 84, with 6 A maximal electric current output was used as the electric current source. For electric measurements an HP 3466a multimeter was used, with 0.025Ω external shunt for currents above 2 A.

Analytical balance (Radwag AS 220/C/2) with a maximum load of 220 g and $d=0.1 \text{ mg}$ was used for the mass measurements of each anode and cathode and of the chemicals. High-precision laboratory balance (Kern EG 620-3NM) with maximum load of 620 g and $d=1 \text{ mg}$ was used for silver brass housing measurements.

The apparatus used for anode slime treatment experiments included: temperature-adjustable magnetic stirrer, with $\pm 1.0^\circ\text{C}$ deviation, various laboratory glassware, erlenmeyer flasks and beakers from 400 to 1000 ml, Büchner (vacuum) flask and electrical laboratory drier.

Recycling methods

Electrolytic refining

Electrolytic refining of anodes obtained by melting of silver-plated brass housing is realized through three anode periods. In the electrolytic refining of copper brass anode, the electrolyte concentration of copper decreases and the concentration of zinc increases. For this reason, during the process, the concentrations of copper and zinc should be daily monitored and adjusted. Correction of electrolyte was carried out twice a day every 12 h. Complete replacement of the electrolyte at the end of each cathode period was required. Waste electrolyte could be purified by zinc cementation or electrochemically decopperised to achieve environmental regulations [21].

Chemical refining of anode slime

Anode slime from copper electrorefining process consists mainly of silver (approx. 60%) with copper, lead, iron, cadmium and other impurities. Chemical refining could produce silver powder of 99.99% purity. This hydrometallurgical process has several stages, and is based on anode slime dissolving in dilute nitric acid, followed by precipitation with sodium chloride. The final stage is silver/lead separation by hydrazine reduction from ammonia solution. Recrystallization of silver is required to obtain a smaller particle size.

RESULTS AND DISCUSSION

Silver-plated brass housing in a quantity of 1846.574 g was the starting material for recycling. At the start, it was melted in an induction furnace.

Reducing atmosphere in the furnace was provided to prevent oxidation and evaporation of silver. Nine anodes with total mass of 1833.3833 g were made by casting. Anode dimensions were 60×80×5 mm. The chemical composition of the silver-plated brass and the anodes was different (Table 1). However, the differences are very small and are mainly due to metal evaporation, since refining does not take place during the anode casting. Nevertheless, even with small evaporation, higher silver concentration is obtained in the casted anodes.

Table 1. Chemical composition of silver-plated brass housing and brass anodes obtained from it

Composition, %	Silver-plated brass housing	Casted brass anodes
Copper (Cu)	59.41	59.53
Zinc (Zn)	34.85	33.77
Lead (Pb)	2.17	2.02
Cadmium (Cd)	0.018	0.023
Silver (Ag)	2.42	2.75
Iron (Fe)	0.64	0.97
Nickel (Ni)	0.38	0.56
Tin (Sn)	0.12	0.10
Silicon (Si)	0.00	0.28

Electrolytic refining

Metal recovery and separation start with the electrolytic refining. It is the first step of the process. The main goal of electrolysis is to obtain high-purity copper from the material with recovery as close as possible to 100%. The process is essentially brass electrolysis, since about 93% of the anode consists of copper and zinc. The electrolytic process is based on the large difference in the standard electrode potentials of copper and zinc. The potential difference between the copper and zinc half-cells is 1.10 V. It is more than enough for metal separation but due to the heterogeneous composition and variable concentration of ions in the electrolyte, several issues should be considered. The most important aspect is the constant increase in zinc concentration simultaneously with the reduction of copper concentration in the electrolyte. This affects the composition of the electrolyte as an important technological parameter and has to be adjusted during operation. Current density is important for both the quality of the cathode and the anode slime composition.

Electrolytic refining (ER) was realized in three independent experiments similar to the anodic periods in industrial-scale process. The first anodic period had two consecutive cathodic cycles, the second anodic period had three cathodic cycles and the third had two cathodic cycles. The first and second anodic periods had identical current density for determination of the influence of the electrolyte

composition and the third had higher current density for determination of the influence of that parameter. Refining the same anode material on a larger scale in a pilot plant requires minimum two and preferably three cathodic cycles to obtain copper purity higher than 99% to eventually 99.9% [1]. In large-scale production (refining) three cathodic cycles result in better cathode copper quality. However, two cathodic cycles were found as the optimum compromise, since one cycle leads to a high concentration of zinc that exceeds the experimentally determined maximum level to obtain copper of 99% purity while more than two cycles raise the expenses and are very demanding in industrial conditions because of the need of handling a lot of material. Finally, the number of cathodic cycles primarily depends on the required quality of copper; higher purity like 99.99% or 99.999% could be obtained only by re-refining using two subsequent electrorefining processes. This is cost-effective especially if the copper cathode from the last (second or third) cathode cycle is used. Variable concentrations of copper and zinc in the electrolyte require their constant monitoring and correction of the electrolyte composition based on analysis. Electrolyte corrections require a daily addition of 10 g of copper sulfate pentahydrate and 10 ml of concentrated sulfuric acid.

First experiment (anodic period)

For electrolytic treatment three brass anodes with total weight of 613.7987g were used in one electrolytic cell. Cathode starting sheets were made from "grade A" (purity of 99.97% or more) copper sheets with dimensions 80×60×0.5mm. The process duration was 140 h: 80 h for the first cathodic period and 60 h for the second cathodic period. The first period is longer on purpose, as is the usual practice in electrorefining of copper with two cathodic cycles. Organization of electrodes in the cells was cathode - anode - cathode, so that the cell had 4 cathodes and 3 anodes with parallel configuration. The last two cathodes were placed next to the cell wall and had only one active side, so the anode and cathode surfaces were practically identical. Inter-electrode axial distance was 20 mm, current level was maintained in the range of 3.45 to 3.60 A which corresponds to a current density of 120 to 125 A/m². Electrolyte temperature was maintained within 55±2 °C. Circulation system for the electrolyte was provided. Due to the specifics of the process, the composition of the electrolyte was determined on every 24 h from the beginning of each cycle and at the end, as shown in Table 2.

Table 2. Chemical composition of the electrolyte for the first anodic and both cathodic periods

Concentration, g/dm ³	First cathodic cycle					Second cathodic cycle			
	Start, 0h	24h	48h	72h	End, 80h	Start, 0h	24h	48h	End, 60h
Cu	37.05	33.18	32.09	30.44	29.11	36.93	34.84	33.26	31.47
Zn	0	21.56	44.20	67.18	73.57	0	21.83	43.66	54.43
H ₂ SO ₄	180.5	177.2	178.3	181.6	175.9	180.2	184.0	182.4	172.8
Ag, ppm	0	0	0	0.8	1.6	0	1.2	1.8	2.7
Fe	0	0	0	1.08	1.46	0	0	0.87	1.82

Voltage measurements were done and cell voltage ranged within the limits of 180 - 220 mV. The obtained copper cathode had purity of 99.63 % by weight for the first cathodic cycle and 99.56% for the second one. Silver content was 0.058 % and 0.077 %, respectively. The corresponding concentrations of zinc were 19 ppm and 24 ppm.

Second anodic period

For electrolytic treatment three brass anodes with total weight of 610.2755 g were used in the electrolytic cell. The process duration was 144 h. All three cathodic periods were of 48 h and the end of ER was adjusted for their equalization. Configuration of the electrodes in the cells was identical to that in the first anodic period. Current level was maintained in the same range with corresponding current density of 125 to 150 A/m². Electrolyte temperature was 55±2°C. Circulation of electrolyte was provided. The composition of the electrolyte was determined on every 24 h and is shown in Table 3. Voltage measurements were

done and cell voltage ranged within the limits of 175 - 210 mV. The purity of the obtained copper cathode for all three cycles is shown in Table 4

It is obvious that the fresh electrolyte directly influences the purity of cathode copper.

Third anodic period

For electrolytic treatment three brass anodes with total weight of 609.3091 g were used in one electrolytic cell. The process duration was 106 h: 60 h for the first cathodic period and the remaining 46 h for the second cathodic period. The first period was longer, as in the first experiment with two cathodic cycles. Organization of electrodes in the cells was the same as in the previous two experiments. Current level was maintained in the range of 4.60 to 4.75 A which corresponds to a current density of 160 to 165 A/m². Electrolyte temperature and other parameters were the same as in the previous two anodic periods. Sampling of the electrolyte was also identical and its chemical composition is shown in Table 5.

Table 3. Chemical composition of the electrolyte for the second anodic and all three cathodic periods

Concentration, g/dm ³	First cathodic cycle			Second cathodic cycle			Third cathodic cycle		
	Start, 0h	24h	48h	Start, 0h	24h	48h	Start, 0h	24h	48h
Cu	37.02	34.04	30.43	37.05	36.32	29.64	36.89	38.80	33.67
Zn	0	22.00	43.68	0	21.75	44.11	0	21.59	42.90
H ₂ SO ₄	180.0	181.2	178.6	180.3	182.2	176.5	179.7	176.0	173.4
Ag, ppm	0	0	0.8	0	0	2.3	0	0.6	1.5
Fe	0	0	0	0	0	0	0	0	0

Table 4. Chemical content of the copper cathode in the second anodic period

Concentration of metals, ppm	First cathodic cycle	Second cathodic cycle	Third cathodic cycle
Copper (Cu), %	99.95	99.92	99.89
Silver (Ag)	166.7	297.4	432.5
Zinc (Zn)	3.0	4.8	10.5
Lead (Pb)	86.3	98.1	134.9
Cadmium (Cd)	< 1.0	< 1.0	1.1
Tin (Sn)	28.4	27.6	39.8
Nickel (Ni)	41.6	49.9	58.2
Iron (Fe)	72.5	121.7	144.3

Table 5. Chemical composition of the electrolyte for the third anodic and both cathodic periods

Concentration, g/dm ³	First cathodic cycle				Second cathodic cycle		
	Start, 0h	24h	48h	Stop, 60h	Start, 0h	24h	48h
Cu	37.01	37.50	35.66	33.13	36.95	38.23	34.74
Zn	0	29.86	59.39	74.22	0	30.27	57.88
H ₂ SO ₄	180.1	182.0	177.2	170.6	179.6	181.3	174.5
Ag, ppm	0	0	2.0	3.3	0	0	2.8
Fe	0	0	1.31	2.02	0	0	1.50

The correction of the electrolyte required an addition of 15.0 g of copper sulfate pentahydrate and 15.0 ml of concentrated sulfuric acid per day. Larger correction of electrolyte composition was necessary due to the higher current density. Cell voltage ranged within the limits of 190 - 235 mV. The obtained copper cathode had a purity of 99.37 % by weight for the first cathodic cycle and 99.25 % for the second one. Silver content was 0.094 % and 0.135 % respectively. Concentrations of zinc were 33 ppm for the first cathodic cycle and 41 ppm for the second. When comparing the results with those of the first anodic period, a direct influence of current density is clear.

Second stage of electrolysis

Since "grade A" purity of copper was not achieved in any of the three experiments, cathode copper was used as anode for subsequent electrorefining to produce copper metal of 99.99% purity or more. Electrorefining is a very efficient process and could reduce impurities by an order of magnitude but rarely more, especially when copper has high a concentration of silver - a metal with higher allowed concentration in cathode copper [2]. Therefore, the cathode copper with the second maximum purity (obtained in the second cathodic cycle of the second anodic period) was refined. The starting electrolyte was synthetic (p.a. chemicals) and all impurities came from the anode, in this case cathode copper with Cu-CATH-2 quality. Cathodes from the second cathodic cycle were used.

No special adjustment of the process was necessary. Minor corrections of the electrolyte composition were: higher concentration of Cu^{2+} ions, 40–45 g/dm^3 and H_2SO_4 , 200–220 g/dm^3 while the concentrations of additives (thiourea, gelatin and chloride ions) were not significantly higher than is normal for the process. As silver was the main impurity, chloride ions concentration was monitored and kept in the narrow limits of 50 mg/dm^3 , as silver chloride is not favorable for the further recovery and refining of silver. Thiourea and gelatin were of initial concentration of 10 mg/dm^3 and 5 mg/dm^3 of both were added per day; current density was set to 200 A/m^2 partly because of equipment limitations but essentially near the optimal level although higher values are also possible. Results confirmed that there was not much room for increasing this parameter. Temperature was a little bit higher than in the previous electrorefining and was kept at 60 ± 2 °C. There was only one cathodic cycle.

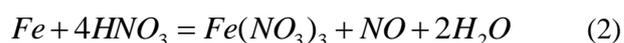
The obtained copper cathode had a purity of 99.99% with 13 ppm of silver. This purity meets

the requirements of BS EN 1978:1998 standard (LME Grade A) [2].

Hydrometallurgical refining of anode slime

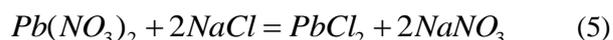
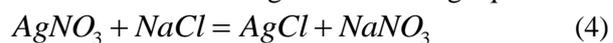
Anode slime with 57.81% silver content was refined by the technological process shown in Figure 1. Anode slime also contained lead, iron, cadmium and other contaminants. The goal of anode slime refining was to obtain silver with purity of 99.99% in powder form which can be used in sinter metallurgy and especially for electrical contact alloys.

The first phase of the anode slime processing is its dissolution in dilute nitric acid (1:1 vol.). The solution contains silver and many impurities like iron, nickel, copper, zinc and lead. During sludge dissolution, the following reactions (1) to (6) occurred:



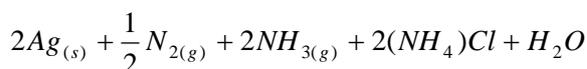
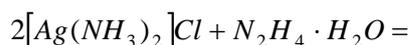
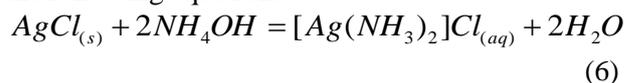
where M are metals giving two-valent nitrates: Cu, Pb, Zn and Ni.

Silver was separated from the impurities in the nitrate solution by precipitation with sodium chloride. Lead is also precipitated as a chloride with silver. Precipitation of silver and lead in the form of chlorides occurs through the following equation:



The white precipitate after the above reactions is a mixture of lead and silver chlorides. It was washed with hot water until a negative reaction for the Pb^{2+} ions (test with SO_4^{2-}).

Silver chloride was dissolved with the addition of ammonium hydroxide (12.5% mass) and reduced to elemental silver by hydrazine hydrate, according to the following equations:



The obtained silver powder was filtered, rinsed with distilled water and 96% ethanol (absolute ethanol or high purity 2-propanol) and dried at 110 °C for two hours.

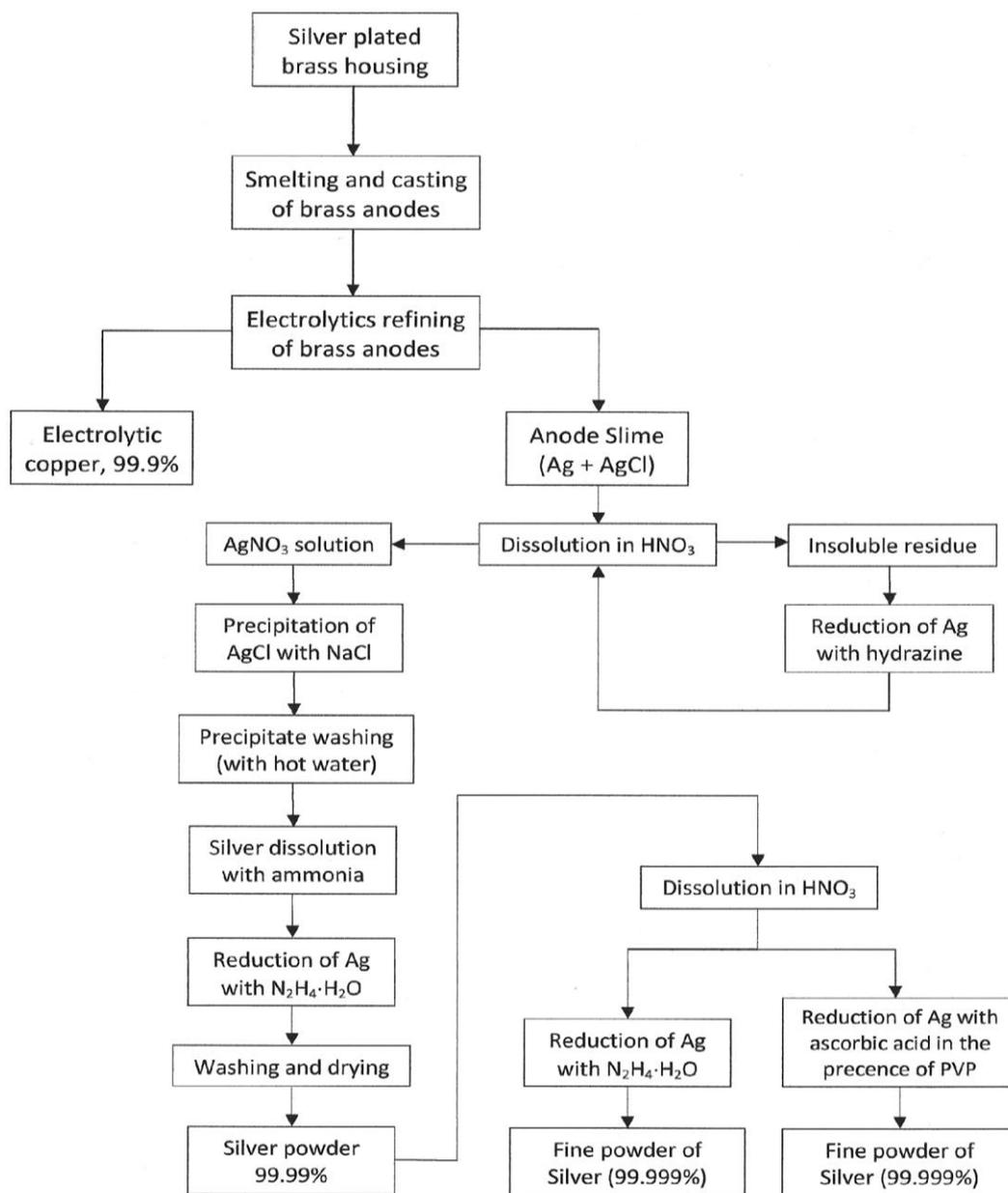


Fig. 1. Flow sheet of anode slime processing

Morphology and size of the silver particles

Classical chemical reduction could result in microsized silver crystals, especially when re-precipitated at an appropriate pH. Reducing agent (hydrazine solution) should be added slowly, drop by drop, with vigorous mixing. The obtained silver powder particles were under 5 μm , non-uniform [1], some particles reaching up to 50 μm [18]. Traditional electrochemical methods easily produce uniform but coarse particles with an average size of about 30 μm [3]. Certainly, there are a number of ECh methods for obtaining silver nano particles, as discussed above, but they have specific requirements and are not suitable for mass production.

For the synthesis of nano silver particles a variety of chemical reduction methods were developed.

Wet-chemical reduction route is preferred due to the controllable size and shape of the particles obtained [9]. Various reducing agents and templates or protecting agents are used depending on the required particle morphology [8]. The same principles with little modification of the conditions lead to micro sized Ag particles. Ascorbic acid is a commonly used reducing agent [22-24] for preparation of fine silver powder, silver microcrystals and silver nanoparticles. Ascorbic acid (AA) has been chosen as reducing agent due to the positive experience in gold and silver reduction

on its usage. Silver ions are reduced to metal silver by ascorbic acid (C₆H₈O₆) according to the following reaction [25]:



This easily controlled process yielding high purity metals was a real alternative for hydrazine for all but very dilute solutions.

The morphology of the silver microcrystals is affected by the modifiers used in the reduction process. They are mainly surfactants or polymers and are used to prevent particles from aggregation. Polyvinylpyrrolidone (PVP) is a most commonly used protecting agent not only in chemical reduction but in other methods as well [8]. Therefore, PVP was selected for this investigation. It is common for the nanoparticles production that ascorbic acid reaction with AgNO₃ is performed in dilute solutions (10⁻² mol/dm³ or less for both) but for obtaining of fine microcrystals a higher concentration is used, like: 0.2 M of AgNO₃ and AA [22] or 60 g/dm³ AgNO₃ and 40 g/dm³ AA [26]. For reduction by formaldehyde (CH₂O) the concentrations of AgNO₃ are even higher (up to 0.865 M) [9].

In this research, concentration of 0.1 M of both, silver nitrate and AA was used. The concentration was set conservatively to be between ideal for nanoparticles and microcrystal structure. Detailed influence of different parameters was not investigated since the main goal was the production on a moderate scale in a pilot plant.

Fine silver powder preparation

After silver reduction with hydrazine hydrate (HH) from nitric acid solution, fine powder with purity of 99.99 % was obtained. Reduction was performed with an excess of reduction agent. The hydrazine/silver molar ratio was 5:1. For the preparation of fine silver powder, silver was recrystallized after dissolution in nitric acid and evacuation of the nitrous oxides from the solution. Two methods for silver reduction from the solution were used: by HH and by AA. Reduction with HH was used as a control method. In both cases silver with purity of 99.999 % was obtained, but the use of HH without a protecting agent gave less uniform and larger particles.

Table 6. Statistical analysis of the particle sizes given in Figure 2

Reduction agent and type of reduction	Average particle size, μm	Corrected sample standard deviation, μm
Hydrazine, one reduction	0.800	0.391
Hydrazine, two consecutive reductions of silver	0.627	0.271
Hydrazine reduction followed by ascorbic acid reduction in presence of PVP	0.423	0.210

Starting solution was 0.1 M AgNO₃ and the solution was thermostated at 25.0±0.5°C. Reductions were performed by dropwise adding the reduction solution. Reduction solutions were of the same volume as the AgNO₃ solution and the reducing agent/silver molar ratio was 2:1 in both cases (0.1 M AA and 0.1 M HH).

Since the SEM images showed layers of particles without clear grain boundaries, the software for granulometric analysis ImageJ was not usable. An alternative method was then used, direct measurement of the grain size on SEM images with ImageJ software (which automatically takes resolution in account). A hundred of grains for each experiment was measured from several SEM images and the result for the particle size is given in Figure 2. Since little differences were found between the smallest and the largest grain, as well in size distribution, one of the figures was taken as representative: Figure 3 for single reduction with hydrazine hydrate (HH), Figure 4 for double reduction with HH and Figure 5 for the reduction of the powder shown on Figure 3 with AA in the presence of the PVP as protecting agent.

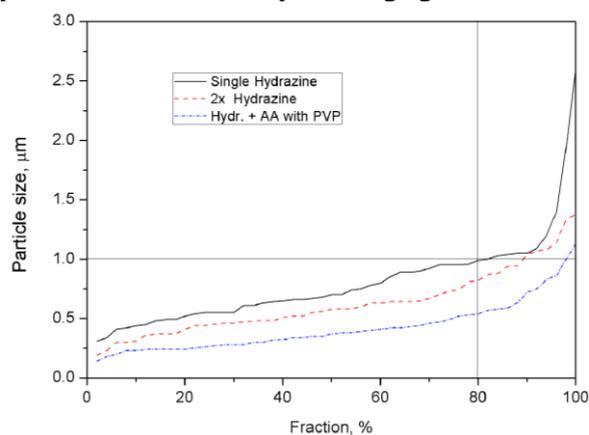


Fig. 2. Distribution of the particle size for the different reduction agents used for the reduction of Ag

The line marked with "Single hydrazine" refers to the reduction with hydrazine and the other two - to the two consecutive reductions with two different reduction agents, as pointed in the introduction.

Basic statistical data for the three sets of data are given in Table 6.

It is clear that double reduction leads to smaller size and better uniformity of the particles; if reduction by hydrazine is performed carefully, small and uniform silver grains can be obtained. The line in Figure 2 outlines that exactly 80% of the silver particles are smaller than 1.0 μm after the first reduction with hydrazine hydrate. This is due to the slow process and the great amount of the reduction agent. The obtained silver was of 99.99% purity.

Recrystallization of silver resulted in improved purity of silver and morphology of the particles. Gains in reducing the size of the particles are relatively small but the uniformity is significantly better, as shown in Figure 4.

The additive, PVP, improves the surface smoothness and compactness of the particles while the particle size is more influenced by mild reducing agents such as ascorbic acid.

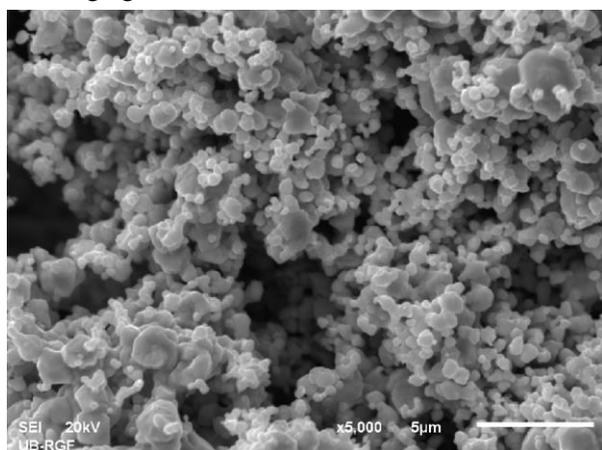


Fig. 3. SEM image of silver powder obtained by one reduction with hydrazine

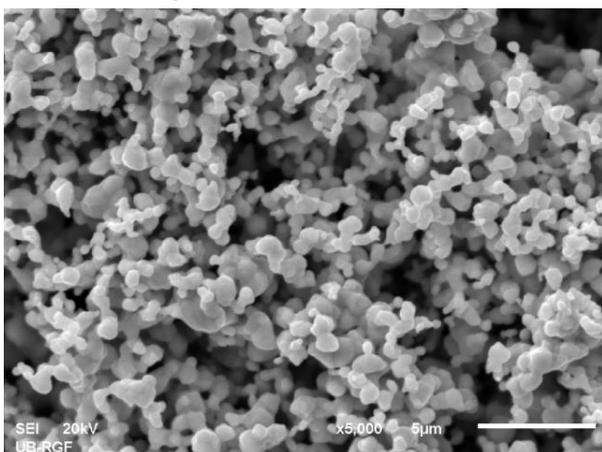


Fig. 4. SEM image of silver powder obtained by double reduction with hydrazine

First reduction with hydrazine produced very fine powder (Figure 3) which can be used in many applications including silver source for contact alloys. As Figure 2 shows, 80% of the particles are

smaller than 1.0 μm ; Figure 3 shows that there are several large and many small (even smaller than the average in Figure 4) particles, but due to aggregation larger secondary particles with fair uniformity are formed. Consecutive reduction with hydrazine is more efficient in terms of better silver purity and uniformity of the particles than in decreasing their size.

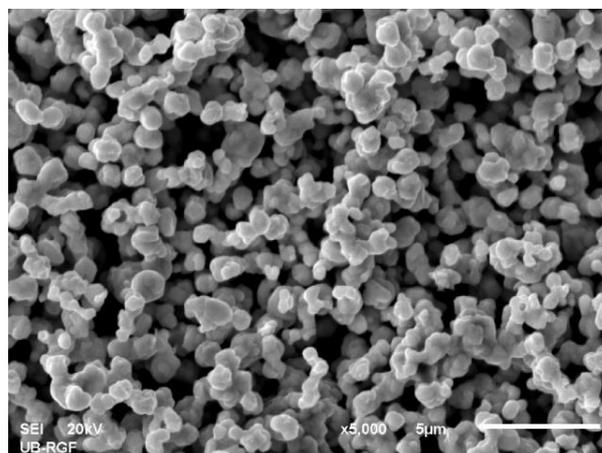


Fig. 5. SEM image of silver powder obtained by one reduction with hydrazine followed by reduction with AA in the presence of PVP

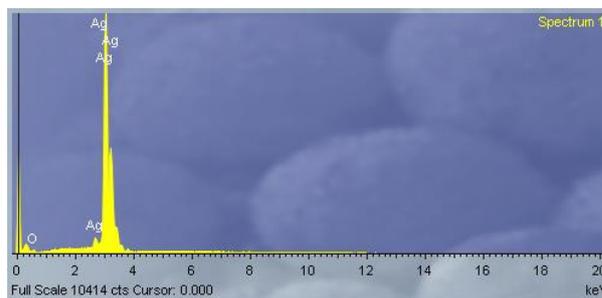


Fig. 6 EDS spectrum of the silver powder obtained by secondary reduction with AA with PVP

Reduction with AA and PVP as a protecting agent improved the morphology of the particles. They are more spherical, smaller and with much better uniformity in size ($0.423 \mu\text{m} \pm 0.210 \mu\text{m}$). The obtained powder has particles sized under micrometer. EDS analysis points to silver purity of 100.00 %; ICP-OES as a more precise method shows “5N” quality (99.999 %) with total impurities content lower than 7.3 ppm. EDS of the other two silver powders were practically the same as that in Figure 6 (100.00 % of silver) and are not shown. Purity of the silver powder, determined by ICP-OES, with one HH reduction was 99.99 % and for the double reduction with HH little higher purity was obtained than for the second reduction with AA. AAS showed only 4.8 ppm of total impurities and higher silver powder purity (99.9995 %).

CONCLUSIONS

The results presented in this paper show a possibility of recycling silver-plated brass for the production of high-purity copper and fine silver powder for electric contacts. Both investigated parameters, electrolyte composition (EC) and current density (CD), primarily need to be stable and with small variations from the optimal values (concentration of important ingredients). With increasing current density the quality of the cathode copper decreased; the optimal current density was as low as possible and technologically acceptable - about 120 A/m². The influence of electrolyte composition shows optimal Cu²⁺ and H₂SO₄ concentrations of 35–40 g/dm³ and 180±10 g/dm³, respectively. For the additional (consecutive) electrorefining the optimal parameters are slightly different: higher current density is acceptable, 200 A/m² and electrolyte composition needs adjustment, since the optimal concentrations of Cu²⁺ and sulphuric acid need to be higher, 40–45 g/dm³ and 200–220 g/dm³, respectively. The concentration of additives (thiourea, gelatin and chloride ions) should be raised.

Reduction of silver by the process shown in Figure 1 can produce micro-sized Ag powder with purity of 99.99%. Additional reduction is necessary for silver of higher purity "5N" up to 99.9995%. Reducing agents with a higher standard redox potential such as ascorbic acid and protective surface-active agents like polyvinylpyrrolidone reduce the particle size and improve its morphology. Fine submicronic Ag powder was prepared without special working conditions and the process could be useful in large-scale production.

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РЕЦИКЛИРАНЕ НА ПОСРЕБРЕН МЕСИНГ ЗА ПОЛУЧАВАНЕТО ЧИСТА МЕД И СВРЪХ-ФИН СРЕБЪРЕН ПРАХ ЗА ЕЛЕКТРИЧЕСКИ КОНТАКТИ

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(Резюме)

В работата се представя подобрен процес за рециклиране на облицовки от посребрен месинг. Среброто и медта се оползотворяват с чистота съответно от 99.99 % и 99.90 %. Целта е да се получат материали с висока стойност при същите процес и апаратура. Новият подход с последващо електрорафинаране дава мед с чистота от 99.99 % с качество по стандарта BS EN 1978:1998 (Cu-CATH-1) и се отнася към LME – степен А. Допълнителната преработка на среброто дава свръх-фин, микро-размерен сребърен прах с размер на частиците между 0.14 и 1.13 μm и чистота от 99.999 %. Изпитанията за електрорафинация за медта са проведени със синтетичен електролит с обем 1.50 dm^3 в електролизна клетка с обем 2 dm^3 . Изследвани са ефектите на плътността на тока и състава на електролита. Оптималните плътности на тока за първата и втората рафинация са съответно 120 A/m^2 и 200 A/m^2 . Допълнителната рафинация на среброто се извършва с химична редукция от воден разтвор. Оптимални резултати са получени при използване на аскорбинова киселина като редуктор с концентрация 0.1 mol/dm^3 и поливинилпирилоидон като защитен агент с концентрация 2 % (мас.). Получените резултати може да се внедрят в производството.