THE INFLUENCE OF THE PARAMETERS OF ELECTROLYSIS CARRIED OUT WITH PERIODIC REVERSAL CURRENT (PRC) ON THE MORPHOLOGY OF SILVER OBTAINED VIA SILVER CHLORIDE CATHODIC REDUCTION

The aim of this study was to determine the possibility to obtain compact silver deposit during cathodic reduction of AgCl with the use of periodic reversal current (PRC).

The influence of the electrolysis parameters (current intensity $I = 0.4-1.6$ A, the ratio of working to reversal periods $t_w/t_{rv} = 100/10, 100/20, 100/30$) on the silver morphology (size and shape of Ag grains).

Under the applied electrolysis conditions powder deposits were obtained, but at $I = 0.4$ A and $t_w/t_{rv} = 100/10$ a more compact deposit was produced. Cathode efficiencies of the processes were low and ranged from approx. 52% up to 85%.

Keywords: cathodic reduction of AgCl, PRC, silver powder

1. Introduction

Silver is recovered from industrial waste materials by the reduction of Ag$^+$ ions from AgCl precipitates. The cathodic reduction of silver ions is conducted in the galvanic cell with a soluble anode [1-7], and under galvano- or poten-tio-static conditions with an insoluble anode [8]. In such cases silver is obtained as a powder, with the grain size and morphology dependent on the parameters used in the process.

The cathodic reduction in the cell is carried out with zinc or aluminium as anode, and Ag/AgCl electrode as cathode.

Cathodic reduction of Ag$^+$ ions from AgCl in a galvanic cell gives a silver powder of a characteristic morphology corresponding to the structure of the initial silver chloride deposit. Spheroidal silver grains form agglomerates creating some kind of spatial structure. The size of the grains can be controlled by the appropriate selection of the electrolyte used in the cell. HCl, NaCl as well as NH$_4$Cl, NH$_4$OH, Na$_2$SO$_4$ and H$_2$SO$_4$ are used usually as electrolytes [2-7]. Silver powder obtained in a Zn|$H_2SO_4$,AgCl|Ag cell, for sulphuric acid concentrations ranging from 0.025 to 0.5 mol/dm$^3$. The average grain size of the silver powder is 1$\mu$m [7].

There are two hypotheses describing the course of Ag$^+$ ions cathodic reduction from silver chloride using electrolytes, in which AgCl is sparingly soluble. The first one assumes that chloride ions from the silver chloride surface are transferred from the silver chloride|solution phase boundary to the solution, while metallic silver depositions on the cathode silver chloride phase boundary [9]. The originating silver deposit reproduces morphology of the AgCl particles.

The second hypothesis assumes that concentration of Ag$^+$ ions in the solution is determined by the solubility product of the sparingly soluble AgCl. AgCl dissolution and reduction of Ag$^+$ ions on the AgCl particles
occur successively and, therefore, the deposit structure is reconstructed.

The application of ammoniacal solutions as electrolytes, in which AgCl is easily soluble, causes a clear change in the morphology of the silver powder. The silver grains are larger (2.9-11 µm) and have the shape of polyhedral crystallites [10]. In this case, silver is deposited from solutions of high Ag⁺ concentration.

The research of cathodic reduction of Ag⁺ ions from silver chloride with the use of an external current supply source was conducted in galvano- or potentiostatic conditions with the use of the Ag/AgCl electrode as the cathode, and the insoluble anode (graphite) [10-12]. The measurements were performed in HCl and H₂SO₄ solutions of various concentrations. The reduction of the silver ions from the AgCl takes place on the cathode, whereas oxygen is evolved on the anode. In chloride solutions, at high currents (at high anode potential), co-evolution of chlorine is also observed [2]. The advantage of this method – in comparison with the cathodic reduction conducted in the galvanic cell with a soluble anode – is that there are no problems with the management of the waste solutions, there are not any ions of metal anode in the solution. The efficiency of the AgCl reduction reached ca. 98% in average, whereas the cathodic current efficiency ranged from approx. 60% up to 100%, depending on the cathodic potential (within the range: +150 mV to -150 mV). It is understandable, because lowering the cathodic reduction potential causes an increase in the hydrogen coevolution in the total cathodic reaction.

The silver powder of high purity is obtained in the cathodic reduction of the Ag⁺ ions from the AgCl in the cell with a soluble anode or in the electrolysis process with an insoluble anode.

The possibility of employing the cathodic reduction for the conservation of copper, silver, and lead objects, originated from excavations, has been proved. Such objects made of silver are usually covered with corrosion products, the main component of which is silver chloride. The cathodic reduction and the so-called consolidating cathodic reduction are used in the conservation works. The latter was used for the first time in the British Museum for the restoration of the silver parts of the lyre of Ur [12]. The basis of the consolidating reduction is the cyclically repeated stages of dissolution and deposition. Pulsating current was applied.

As an example of the use of this method, the restoration of the chalice and the paten from the tomb of Bishop Maur in the Wawel Cathedral in Kraków, Poland, can be mentioned, which was carried out in the Archaeological Museum laboratory in Kraków, [13]. The consolidating cathodic reduction was conducted with the use of a platinum gauze as the anode. The electrolyte was a 3% NaOH solution, and the cathodic current density was 10 mA/dm². Under these conditions the consolidation process of the individual chalice parts lasted for 25 days. Then the restored fragments were glued with an ultra-fine glass fibre and polyester resin. As a result of consecutive conservation procedures, the obtained shape of the chalice and the paten was probably very similar to the original.

The effects of the conservation works described above are presented in Fig. 1. They show a very high effectiveness of the consolidating method of the AgCl cathodic reduction with the application of pulsating current.

![Fig. 1. The silver chalice from the Wawel Cathedral; a – as it was in 1989, b – after the consolidating reduction and gluing of the restored parts](image-url)
The study presented here shows the results of the AgCl cathodic reduction using the PRC technique. The objective of the investigation was to obtain the silver as a compact deposit.

During the research, the AgCl cathodic reduction process took place for a relatively long time ($t_w$), and then the current direction was being changed for a short time ($t_{rv}$) (with this change the anode becomes the cathode, and vice versa). The main parameters affecting the process course are: the ratio and the sum of the working ($t_w$) and the reversal ($t_{rv}$) periods of current flow.

Within the periods of the cathodic current direction, the Ag$^+$ ions from the AgCl, are reduced, and this leads to a presence of the metal particles (coming from the reduction) on the sample surface. Within the relatively short periods of the anodic current direction, the metallic silver remaining on the surface is partly dissolved. The metal ions appearing in the solution due to the short anodic period are then deposited during the cathodic periods. It enhances consolidation of the deposit.

The application of PRC leads to a decrease in the process efficiency. This is understandable because part of the metal that is deposited in the cathodic process is anodic dissolved in the period of the reversed current flow.

A review on pulse and reverse techniques for electrodeposition of individual metals and alloys was reported by Chandrasekar and Malathy Pushpavanam [14].

Under industrial conditions, the PRC technique is used in the process of the copper electrorefining from sulphate electrolytes. In this case, the application of PRC leads to the obtaining of a cathodic deposit of a more smooth surface. This is because in the periods of a reversed current flow, the ‘tops’ of the unevenness are dissolved first. In addition, the passivation of the copper anodes is prevented to a large extent [15].

2. Experimental

The AgCl deposit was the initial material. Silver chloride was hot precipitated from a silver nitrate by means of the 50% excess of 1 M hydrochloric acid (with reference to the stoichiometric amount). The obtained AgCl deposit was filtered off, washed with distilled water, and wet spread on the cathode surface. A graphite electrode of a geometrical area of 24.62 cm$^2$ was the cathode, while a platinum gauze was the anode. AgCl specimens containing 2 g of silver were prepared.

The diagram of the measurement system is shown in Fig. 2. The time adjuster, which controlled the direction and time of the flow of current, is the key component of the system. It was connected to two DC power supplies. A digital ammeter, which allows controlling of current intensity during the process, was connected to each power supply. Electrodes were also connected to the time adjuster. A glass vessel, where the process took place, contained 1 dm$^3$ 0.5 M sulphuric acid. The electrolyte was stirred by a magnetic stirrer. During the process, potential of the C|AgCl,H$_2$SO$_4$ electrode was measured versus the saturated calomel electrode by using a METEX MXD – 4660A digital multimeter that was connected to a PC recording the data. The readings’ precision was ±1 mV. The measurements were carried out at temperature 20±1°C.

![Fig. 2. Diagram of the measurement system](image)

A series of the electrolyses was carried out at the constant ratio of the working to reversal period $t_w/t_{rv} = 100/10$ and at the various values of the current intensity: 1.6, 0.8, and 0.4 A.

The next series were carried out by using current intensity of 0.4 A, at various ratios of $t_w/t_{rv} = 100/10$, 100/20 and 100/30.

Microphotographs of the specimens’ surface were then taken by using a HITACHI S-4700 and NORAN Vantage scanning microscope.

The values of the average size of silver powder grains was determined, based on the computer analysis of the structures obtained, by means of a scanning microscope.

The silver was washed with boiling ammonia to remove the residues of unreduced AgCl, if any, and then dried and weighed on an analytical balance with a precision of 10$^{-4}$ g, which enabled the determination of the cathode efficiencies.

3. Results and discussion

3.1. C|AgCl, H$_2$SO$_4$ electrode potential dependence on time

Figure 3 shows an example of the electrodes’ potential dependence on the time of the electrolysis. The values of the potential during the working period (time forward $t_w$, when the C|AgCl,H$_2$SO$_4$ is the cathode) are
illustrated by the lower part of the graph. Its course was found to be very similar to the curves $E = f(t)$ obtained in a Zn|H₂SO₄,AgCl|Ag cell [7].

A plateau is observed on the curve, corresponding to the process of Ag⁺ ions reduction to silver (range I):

$$Ag^+ + e \rightarrow Ag$$  (1)

Then, the cathode potential shifts gradually towards more electronegative values. Silver ions and hydrogen ions are reduced in this range (range II):

$$2H^+ + 2e \rightarrow H_2$$  (2)

A sudden potential drop to values that correspond to H⁺ ions reduction on silver (range III) indicates the completion of the silver reduction process. It is noteworthy that, because of the PRC technique used, in range III a reduction of Ag⁺ ions, formed in the reversal period, is observed.

According to the Faraday’s law it is possible to calculate the amount of silver dissolved during one reversal period. For the highest current intensity ($I = 1.6$ A) and $t_{rv} = 10$ s (in individual cycle), the mass of dissolved silver amounts to 0.0179 g, which corresponds to $1.658 \times 10^{-4}$ mol/dm³. It should be mentioned that silver forms along with sulphuric acid (VI) a sparingly soluble salt, Ag₂SO₄. From the solubility product it is possible to calculate the concentration of silver ions, at which the deposit will precipitate. For the applied concentration of sulphuric acid (VI) it amounts to 0.034 mol/dm³. The comparison of those values leads to the conclusion that no Ag₂SO₄ precipitation occurs.

In the periods of reversal current ($t_{rv}$) (C|AgCl,H₂SO₄ electrode becomes the anode), the upper part of the graph corresponds to changes of potential during the electrolysis. The course of the $E = f(t)$ curve is similar to the cathodic part, but the increase in potentials corresponds to the end of the process. Anodic dissolution of silver (silver oxidation to Ag⁺ ions) occurs during the entire reversal period.

Tables 1A and 1B show the values of the C|AgCl,H₂SO₄ electrode potentials, corresponding to the plateaus in the $E = f(t)$ curves during the process of Ag⁺ ions reduction and after its completion (end plateau) for the working and reversal periods, and also give the stationary potential of the C|AgCl,H₂SO₄ electrode prior to the start of the process.

It is understandable that with the increasing current intensity, an increase in the value of the cathodic overvoltage ($\eta_K$) of the Ag⁺ ions reduction is noticed (Table 1A).

Similar dependence is observed in the case of the plateau corresponding to the potentials of the process completion. It should be emphasized that at this stage two electrode reactions are observed – the reduction of H⁺ ions and the reduction of Ag⁺ ions, which are formed during the reversal period. The values of potentials, corresponding the end of the reduction process, depend on contribution of both of these electrode reactions. Such contribution, at a constant value of the working period, depend on the reversal period duration.

Fig. 3. Dependence of potential vs. time for selected PRC electrolyses: $I = 1.6$ A, $t_w/t_{rv} = 100/10$; (meas.No. 2) I – the range of Ag⁺ ions reduction, II – the range of Ag⁺ and H⁺ ions reduction, III – the range of the reduction of H⁺ and Ag⁺ ions that appear during the reversal period $t_{III}$
TABLE 1A

The values of C|AgCl,H2SO4 electrode potentials during the electrolysis carried out by the PRC technique versus the applied current intensity \( I \)
\[ t_{w}/t_{rv} = \text{const} = 100/10 \]

<table>
<thead>
<tr>
<th>No.</th>
<th>Curr. intensity ( I )</th>
<th>Meas. time ( t_{meas} )</th>
<th>Forward time ( t_{w} )</th>
<th>Reversal time ( t_{rv} )</th>
<th>( t_{w}/t_{rv} )</th>
<th>( E_{0} )</th>
<th>working period</th>
<th>( \eta_{k} = E_{pl} - E_{0} )</th>
<th>( E_{pl,end} )</th>
<th>( E_{pl,rv} )</th>
<th>( E_{pl,end,rv} )</th>
<th>( V_{\text{, vs SHE}} )</th>
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</thead>
<tbody>
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<td>A</td>
<td>1.6</td>
<td>3960</td>
<td>3600</td>
<td>360</td>
<td>100/10</td>
<td>0.676</td>
<td>0.010</td>
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<td>0.483</td>
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<td>average</td>
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<tr>
<td>8</td>
<td>0.617</td>
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<td>-0.510</td>
<td>-0.219</td>
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<tr>
<td>9</td>
<td>0.623</td>
<td>0.091</td>
<td>-0.532</td>
<td>-0.173</td>
<td>0.252</td>
<td>0.392</td>
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<tr>
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<td>0.093</td>
<td>-0.547</td>
<td>-0.192</td>
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<td>0.343</td>
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<tr>
<td>average</td>
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</table>

\[ t_{meas} = t_{w} + t_{rv} \ [s] \]

- \( E_{0} \) = stationary potential of the C|AgCl,H2SO4 electrode
- \( E_{pl} \) = potential of the Ag\(^+\) reduction plateau
- \( \eta_{k} = E_{pl} - E_{0} \) = cathodic overvoltage
- \( E_{pl,end} \) = potential of the H\(^+\) and Ag\(^+\) reduction plateau (Ag\(^+\) ions appear in the solution after the reversal period \( t_{rv} \))
- \( E_{pl,rv} \) = potential of anodic silver dissolution
- \( E_{pl,end,rv} \) = potential of anodic silver dissolution corresponding to the process end
TABLE 1B

Values of the C|AgClH₂SO₄ electrode potentials during the electrolysis carried out by the PRC technique versus the applied ratio of the working to reversal period \( t_w/t_{rv} \) for \( I = \text{const} = 0.4 \text{ A} \)

<table>
<thead>
<tr>
<th>No.</th>
<th>Curr. intensity ( I )</th>
<th>Meas. time ( t_{meas} )</th>
<th>Forward time ( t_w )</th>
<th>Reversal time ( t_{rv} )</th>
<th>( t_w/t_{rv} )</th>
<th>( E_0 )</th>
<th>working period</th>
<th>( \eta_k = E_{pl} - E_0 )</th>
<th>( E_{pl,end} )</th>
<th>( E_{pl,rv} )</th>
<th>( E_{pl,end,rv} )</th>
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<td>660</td>
<td>100/10</td>
<td>0.617</td>
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<td>-0.219</td>
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<td>0.464</td>
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<td>9</td>
<td>0.623</td>
<td>0.091</td>
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<td>0.343</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

average

| 0.627 | 0.097        | ±               | ±               | ±               | ±               | ±               | ±               | ±       |
| 0.097 | 0.007        | 0.118          | 0.015          | 0.199          | 0.001           | 0.011           | 0.007           | 0.050   |

| 11  | 0.4             | 10440          | 8700         | 1740           | 100/20          | 0.640 | 0.112          | -0.528          | -0.153         | 0.272          | 0.340          |
| 12  | 0.633           | 0.105         | -0.528      | -0.146         | 0.285           | 0.462 |
| 13  | 0.660           | 0.136         | -0.524      | -0.132         | 0.258           | 0.318 |

average

| 0.644 | 0.118       | ±               | ±               | ±               | ±               | ±               | ±               | ±               |
| 0.011 | 0.013       | 0.002          | 0.009          | 0.001           | 0.011           | 0.007           | 0.003           | 0.065         |

| 14  | 0.4             | 12480          | 9600         | 2880           | 100/30          | 0.606 | 0.144          | -0.462          | -0.134         | 0.297          | 0.588          |
| 15  | 0.688           | 0.140         | -0.548      | -0.129         | 0.298           | 0.634 |
| 16  | 0.657           | 0.141         | -0.516      | -0.123         | 0.275           | 0.571 |

average

| 0.650 | 0.142        | ±               | ±               | ±               | ±               | ±               | ±               | ±               |
| 0.034 | 0.002        | 0.035          | 0.004          | 0.011           | 0.027           |

\( t_{meas} = t_w + t_{rv} [s] \)

\( E_0 \) – stationary potential of the C|AgClH₂SO₄ electrode

\( E_{pl} \) – potential of the Ag⁺ reduction plateau

\( \eta_k = E_{pl} - E_0 \) – cathodic overvoltage

\( E_{pl,end} \) – potential of the H⁺ and Ag⁺ reduction plateau (Ag⁺ ions appear in the solution after the reversal period \( t_{rv} \))

\( E_{pl,rv} \) – potential of anodic silver dissolution

\( E_{pl,end,rv} \) – potential of anodic silver dissolution corresponding to the process end

Based on Table 1b, at a constant value of the working period, the overvoltage of the cathodic reduction of Ag⁺ ions decreases with the extension of the reversal period. This is understandable because the application of a longer reversal time in turn results in an increased concentration of silver ions in the electrolyte – the process of the cathodic reduction of Ag⁺ ions is therefore easier.

3.2. Dependence of cathodic efficiency on the process parameters

The dependence of cathode efficiency on the parameters of silver electrolysis is shown in Table 2. The values of the cathode efficiencies are low and range from approx. 52 to 85%, which results from the specificity of the research method used. In the PRC measurements, the amount of silver deposited in the cathodic periods is partly dissolved in the periods of reversal current. This value depends on the sum and the ratio of time \( t_w \) and \( t_{rv} \). In case when \( t_w/t_{rv} = \text{const} = 100/10 \), cathodic efficiency decreases together with the increase of current intensity \( I \).

In case when \( I = \text{const} = 0.4 \text{ A} \) and \( t_w = \text{const} = 100 \text{ s} \), cathodic efficiency decreases together with increase of the time of reverse period \( t_{rv} \). This problem has been studied in detail in the paper [14].
TABLE 2

<table>
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<th>Curr. intensity</th>
<th>time of cathodic reduction</th>
<th>Cathodic reduction of Ag&lt;sup&gt;+&lt;/sup&gt; ions</th>
<th>Anodic dissolution of Ag</th>
<th>Final mass of Ag</th>
<th>Cathodic efficiency</th>
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<tr>
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<td>(t&lt;sub&gt;Ag&lt;/sub&gt;)&lt;sub&gt;C&lt;/sub&gt;</td>
<td>(m&lt;sub&gt;Ag&lt;/sub&gt;)&lt;sub&gt;C&lt;/sub&gt;</td>
<td>(t&lt;sub&gt;Ag&lt;/sub&gt;)&lt;sub&gt;A&lt;/sub&gt;</td>
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<td>0.4</td>
<td>8750</td>
<td>3.9127</td>
<td>3120</td>
<td>1.3952</td>
<td>2.5175</td>
</tr>
</tbody>
</table>

(t<sub>Ag</sub>)<sub>C</sub> – time of cathodic reduction from dependence E=F(t)
(t<sub>Ag</sub>)<sub>A</sub> – time of anodic dissolution from dependence E=F(t)
(m<sub>Ag</sub>)<sub>F.L</sub> = (m<sub>Ag</sub>)<sub>C</sub> - (m<sub>Ag</sub>)<sub>A</sub> – final mass of Ag from Faraday’s law

1) specimens obtained in the measurements 2, 4, 5, 8, 11 and 14 were assigned to other studies.

3.3. Observations of the structure

3.3.1. Dependence of a silver microstructure on the current intensity

Silver electrolysis was carried out with the application of PRC, depending on the current intensity, at a constant ratio of t<sub>w</sub>/t<sub>r</sub> = 100/10. A series of measurements was performed using the following current intensities: 1.6, 0.8 and 0.4 A. The obtained silver deposits were observed under a scanning microscope. The microphotographs are shown in Fig. 4.

The silver obtained during electrolysis at current intensity of 1.6 A (Fig. 4a) has the form of powder, which create globular interconnected grains which create agglomerates. The mean single grain size amounted to 3.33±0.63 [µm]. The grains’ surface is not uniform. It is covered with numerous ‘accretions’ of a globular shape and has a size below 1 µm. Based on microphotography, it could be presumed that the surface of the silver grains
formed during the working period of the PRC electrolysis (Ag$^+$ ions reduction from AgCl) becomes the place of the nucleation of many fine silver grains originating through the reduction of the Ag$^+$ ions present in the electrolyte after the reversal period, when the silver anodic dissolution takes place.

Reducing current intensity to 0.8 A (Fig. 4b) results in an increased grain size to 4.51±1.31µm. At the same time, the ‘accretions’ on the grains’ surface became larger and stuck together, and their contours became blurred.

The reduction of current intensity to 0.4 A in turn results in clear changes of the obtained silver microstructure (Fig. 4c). Under those conditions, a kind of framework is observed, which is formed from very densely interconnected ‘accretions’, no longer globular but now taking the shape of growing up from each other elongated irregular forms. In relatively large areas, these forms are so compactly interconnected that individual grains cannot be distinguished.

### 3.3.2. Dependence of the silver microstructure on the ratio of the working to reversal current time

In the next series, electrolyses were carried out at a constant current intensity of 0.4 A and various values of the $t_w/t_r$, ratio. Current intensity of 0.4 A was selected based on previous observations of cathodic silver deposits, which show that the most compact silver structure is obtained at this value (Fig. 4c).

The following values of $t_w/t_r$ were used: 100/10; 100/20; 100/30. The silver obtained under these conditions was observed by using a scanning microscope. The microphotographs are shown in Fig. 5.

They show that the extension of the reversal period from 10 to 20 seconds (in individual cycle) results in the formation of globular grains of average size equal to 1.98±1.19µm, connected in agglomerates, and covered in places with relatively clear ‘accretions’ (Fig. 5b).

In the case of an even longer reversal period of 30 seconds, the mean single grain size amounted to 0.98±0.29µm; grains were very densely covered with growth from their surface ‘accretions’ of a globular, clearly elongated shape (Fig. 5c).

It has been observed that with an increasing reversal period (10, 20 and 30 seconds in individual cycle), while maintaining a constant working period (100 seconds), the microstructure of the silver obtained clearly changes.

The case where $t_w/t_r = 100/10$ (Fig. 5a) was described above (Fig. 5a is identical to Fig. 4c).

In the case where $t_w/t_r = 100/20$ (Fig. 5b) or $t_w/t_r = 100/30$ (Fig. 5c), the globular silver grains connected in agglomerates with clear ‘accretions’ originate as a result of the cathodic reduction of Ag$^+$ ions. Their amount increases with the extension of the reversal current time. The most probable reason for the structural changes observed in silver is the fact that with the increasing reversal period the concentration of the Ag$^+$ ions in the electrolyte also grows. The nuclei of new grains, originating on silver grains as a result of Ag$^+$ reduction from AgCl in the working period, may grow easier. The higher the concentration of silver ions is in the electrolyte the easier they can grow.

Silver originating from the reduction of Ag$^+$ ions from AgCl would become the nucleation place for new silver grains, but supplying fewer Ag$^+$ ions to the electrolytic solution (shorter reversal period) would not allow these grains to grow and would perhaps lead to a denser filling of the space with new ‘accretions’, which as a result would facilitate the obtaining of a solid material.
Silver obtained at a current intensity of 1.6 A and at a ratio of working to reversal period $t_w/t_{rv} = 100/10$ (Fig. 4a) features a microstructure that is similar to the silver powder obtained in the galvanic cell (Fig. 6) [7].

The results of the measurements combined with the microstructure observations allow for the selection of the optimum conditions for obtaining silver in the form of the most compact deposit: $I = 0.4 A$; $t_w/t_{rv} = 100/10$. Fig. 7 shows a macroscopic photograph of the silver obtained under these conditions. Silver does not exist in a powder form – it is a compact deposit – a kind of brittle ‘film’.

4. Conclusion

- At a constant ratio $t_w/t_{rv} = 100/10$ with an increasing current intensity, the potential of Ag$^+$ ions reduction as well as the potential of the process end decreases. Increasing current intensity is accompanied by the growing cathodic overvoltage of Ag$^+$ ions reduction.
- The longer the reversal period is the lower the cathodic overvoltage of the Ag$^+$ ions reduction becomes.
- Cathodic efficiencies are relatively low and range from approx. 52% to 85%.
- The morphology of silver deposit strictly depends on the PRC electrolysis parameters. This is illustrated by the data shown in Table 3.
Dependence of the silver powder morphology on the PRC electrolysis parameters

<table>
<thead>
<tr>
<th>$I$, A</th>
<th>$t_w/t_r$,</th>
<th>Average grain size, $\mu$m</th>
<th>Silver deposit morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>100/10</td>
<td>3.33 ±0.63</td>
<td>agglomerates of grains covered by globular ‘accretions’</td>
</tr>
<tr>
<td>0.8</td>
<td>100/10</td>
<td>4.51 ±1.31</td>
<td>increased grain size and ‘accretions’ on the grains</td>
</tr>
<tr>
<td>0.4</td>
<td>100/20</td>
<td>1.98 ±1.19</td>
<td>agglomerates of globular grains covered by ‘accretions’</td>
</tr>
<tr>
<td>0.4</td>
<td>100/30</td>
<td>0.98 ±0.29</td>
<td>grains’ surface densely covered by globular and elongated ‘accretions’</td>
</tr>
</tbody>
</table>

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REFERENCES


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