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# Preliminary studies on hydrometallurgical tin recovery from waste of tin stripping of copper wires

# Wstępne badania hydrometalurgicznego odzysku cyny z odpadów procesu odcynowania drutów miedzianych

**Abstract**

This paper presents the results of tin leaching and electrowinning from $SnO_2$ waste originating from the industrial process of tin stripping of copper wires. The sludge was leached by acids (sulfuric, hydrochloric, tartaric, oxalic) and sodium hydroxide at various temperatures (40–80°C). The highest efficiency of tin leaching (12–18%) was obtained in an oxalic solution, while the lowest effectiveness (0.2–0.5%) was found for sulfuric acid. Tin leaching was accompanied by a transfer of copper residues to the solution. The electrowinning stage was realized under potentiostatic and galvanostatic conditions using oxalate solutions. Cyclic voltammetry was applied to select the potentials for the selective deposition of metals.

**Keywords:** electrolysis, leaching, tin, tin(IV) oxide, waste

**Streszczenie**

W artykule przedstawiono wyniki uzyskane w trakcie ługowania i elektrolitycznego odzysku cyny z odpadów $SnO_2$ pochodzących z przemysłowego procesu usuwania cyny z drutów miedzianych. Szlam ługowano w roztworach kwasów (siarkowego, solnego, winowego, szczawiowego) i wodorotlenku sodu, w różnych temperaturach (40–80°C). Najwyższą skuteczność ługowania cyny (12–18%) otrzymano w roztworze szczawianowym, podczas gdy najniższą wydajność (0,2–0,5%) stwierdzono w przypadku kwasu siarkowego. Ługowaniu cyny towarzyszyło przejście pozostałości miedzi do roztworu. Elektrolityczny odzysk metali został zrealizowany w warunkach potencjostatycznych i galwanostatycznych z zastosowaniem roztworu szczawianowego. Warunki potencjałowe selektywnego osadzania metali wytypowano, opierając się na badaniach metodą woltamperometrii cyklicznej.

**Słowa kluczowe:** elektroliza, ługowanie, cyna, cyny (IV) tlenek, odpady

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## 1. Introduction

Tin is widely used as protective layers on steel packages for food products, a component of solders, and coatings on copper wires, cables, and tubes (preventing the formation of copper oxides and sulfides) [1–3]. In recent years, there has been a growing interest in research into the recovery of tin from various waste materials and solutions [4–12]; it is estimated that about 15% of the tin produced worldwide originates from secondary sources [13]. The recycling of tinned copper scrap, spent copper circuit board, and obsolete electric cables is not a simple process. Direct casting of tinned copper results in an increase in tin content in the copper melt, making it unable to reuse for the production of new materials with the desired properties. For example, a tin content of about 5 wt% decreases the conductivity of metallic copper by about 25% [14]. Therefore, tin stripping is required before the final treatment of copper scrap.

Removal of tin from the copper surface is generally performed via hydrometallurgical methods (chemical or electrochemical) using baths of various compositions [4]. Depending on the tin-stripping method and conditions of the process, the metal is oxidized to Sn(II) or Sn(IV) compounds. Usually, acid solutions are used for tin dissolution, but soluble Sn(II) salts are easily oxidized with air to Sn(IV) and precipitate as $SnO_2$, forming a suspension with particle sizes within a range of 0.02–1 μm [8]. Tin(IV) oxide is known as hardly soluble compound, resistant to the lixiviates commonly used for hydrometallurgical treatment. Kerr [5, 8] proposed filtrating $SnO_2$ from the stripping solution, washing with water, and dissolving in hot HCl (followed by tin electrowinning) [5]. Harangi and Kekesi [11] converted $SnO_2$ into a soluble form by carbothermic reduction followed by leaching the reduced material with boiling 6M HCl. McKesson [12] recommended the addition of sodium hydoxide into the spent stripping solution to transform $SnO_2$ into soluble stannate and stabilizing the Sn(IV) ions by the addition of a gluconate complexing agent.

The present paper shows a hydrometallurgical treatment of waste originating from the stage of tin stripping from chopped copper wire in a recycling plant. The detinning step was performed in a $CuSO_4$-$H_2SO_4$ solution. Dissolution of the tin coating resulted in the formation of $SnO_2$ sludge in an acid sulfate bath. The sludge was filtered, washed a few times with demineralized water, and leached in acid and alkaline solutions at various temperatures. The process was followed by an electrochemical analysis of tin electrowinning. The obtained results allowed us to determine the best conditions for further optimization of the process for effective tin recovery.

## 2. Experimental

The sludge used in this research was industrial waste produced during tin stripping from spent copper wires. The stripping bath consisted of sulfuric acid and copper sulphate.

The sludge was filtered, washed with water, and dried at 95°C for 96 h. The initial material was observed under an optical microscope (Nikon) and analyzed using an X-ray diffractometer (MiniFlex II Rigaku, $Cu_{K\alpha}$).

20-g portions of the sludge were leached in the acid and alkaline solutions (200 $cm^2$): 2M sulfuric acid $H_2SO_4$, 4M hydrochloric acid HCl, 2M tartaric acid $H_6C_4O_6$, 1M oxalic acid $H_2C_2O_4$, and 2M sodium hydroxide NaOH. Leaching was carried out for 3 h at temperatures within a range of 40–80°C. The solution was agitated with a magnetic stirrer at a rate of 300 rpm. Additional leaching was performed in 1M $H_2C_2O_4$ at 80°C using 5-g and 10-g portions of the sludge. After leaching was completed, the remaining (undissolved) sludge was filtered, washed with water, dried, and weighed.

During leaching, 5-$cm^3$ samples of the solution were taken every 20 min, and the concentrations of copper and tin ions were determined using atomic absorption spectrometry (Solaar M5 Thermo Elemental). The efficiency of tin leaching $\alpha$ was calculated according to the following formula:

$$\alpha = \frac{C_{Sn} v}{0.788 \cdot m_s} 100\% \tag{1}$$

where:

$C_{Sn}$ – the final tin concentration in the solution,

$\nu$ – volume of the lixiviant,

0.788 – initial tin content in the sludge (78.8 % in $SnO_2$),

$m_s$ – mass of the leached sludge.

To determine the conditions of tin electrowinning, the oxalate solution obtained during leaching (10 g, 80°C) was used for electrochemical analysis. A typical three--electrode cell was used: glassy carbon as the working electrode (0.198 $cm^2$), platinum plate (0.8 $cm^2$) as the counter electrode, and silver chloride as the reference electrode (Ag/AgCl). The volume of the solution (not agitated) was 20 $cm^3$. Cyclic voltammetry was performed at a scan rate of 10 mV/s from the initial potential of 0.2 V to values within a range from –0.3 V to –0.8 V (vs. Ag/AgCl), where the scan was reversed. Potentiostatic electrodeposition on the platinum substrate (0.8 $cm^2$) was realized at the potentials within a range from –0.5 V to –0.8 V. Potentiostat (PGSTAT 302N Autolab) was used.

Galvanostatic electrodeposition was realized at a constant cathodic current density of 1 A/$dm^2$. Two platinum plates (each 25 $cm^2$) were used as cathode and anode. Electrolysis was performed using the oxalate solution (150 $cm^3$) obtained from the leaching stage (5 g, 80°C). The solution was agitated with a magnetic stirrer at a rate of 300 rpm. Total electrolysis time was 8 h. Every 30 minutes, the cathode was removed from the solution, washed, dried, and weighed. Electrolysis voltage *U* was monitored.

Energy consumption $Z$ was calculated using the following formula:

$$Z = \frac{UIt}{m} \tag{2}$$

where:

$I$ – current intensity,
$t$ – electrolysis time,
$m$ – mass of the cathode deposit.

Cathodic current efficiencies $\eta$ were also determined:

$$\eta = \frac{m}{m_t} \cdot 100\% \tag{3}$$

where: $m_t$ – theoretical mass of the cathode deposit calculated as follows:

$$m_t = \frac{Q \cdot 100\%}{F\left(\frac{2 \cdot \%_{\mathrm{Cu}}}{M_{\mathrm{Cu}}} + \frac{4 \cdot \%_{\mathrm{Sn}}}{M_{\mathrm{Sn}}}\right)} \tag{4}$$

where:

$Q$ – total electrical charge,
$F$ – Faraday constant,
$\%_{\mathrm{Cu}}$, $\%_{\mathrm{Sn}}$ – copper and tin weight percentages in the cathodic deposit, respectively, $M_{\mathrm{Cu}}$ and $M_{\mathrm{Sn}}$ – molar masses of the metals.

The chemical composition of the cathodic deposits was determined by means of an X-ray spectrofluorometer (Rigaku), while the phase composition of the deposits was determined using an X-ray diffractometer (Rigaku).

# 3. Results and discussion

## 3.1. Sludge

Before hydrometallurgical treatment, the tin sludge was washed with water to remove the soluble copper and acid residues. Figure 1 shows the morphology of the waste. It was gray slime with some small pieces of copper wire very randomly visible in the bulk of the sludge. XRD analysis of the waste (Fig. 2) confirmed that the main component of the sludge was $SnO_2$. No metallic copper or copper sulfate remainings were detected.

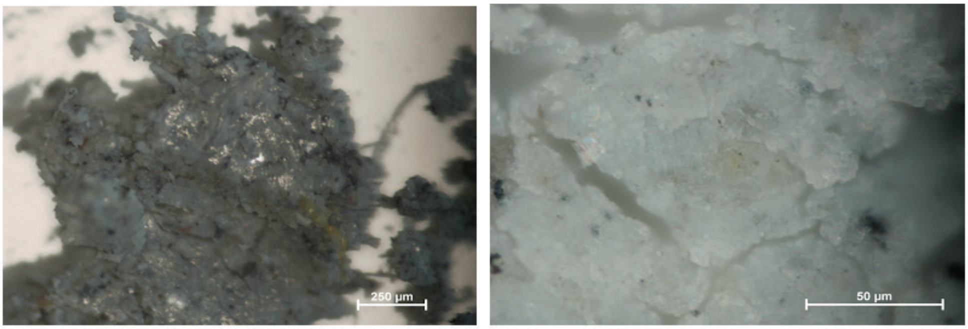

*Fig. 1. Morphology of sludge originating from tin stripping from copper wire*

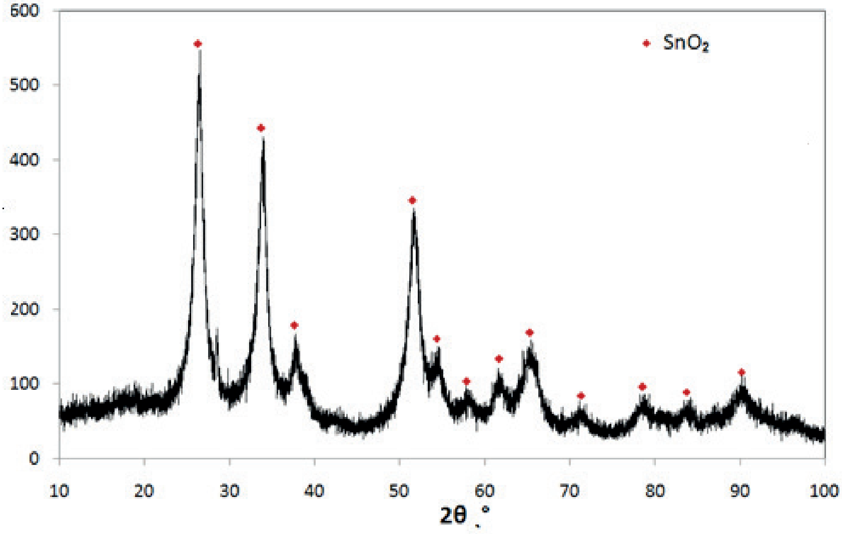

*Fig. 2. X-ray diffraction pattern of sludge*

## 3.2. Leaching

Tin exists in several oxidation states, but only the +II and +IV states are important in its aqueous chemistry [15]. The +IV state is particularly stable in natural environments, but relatively little quantitative information exists on the solubility of $SnO_2$. It is accepted that the solubility of tin(IV) oxide in water is low; i.e., $10^{-8}$–$10^{-7}$ M in a pH region of 2 to 7 [16]. In strong acid or base, tin(IV) solubility increases; however, it should be noted that crystalline $SnO_2$ (cassiterite) and precipitated $SnO_2$ are quite insoluble, while a badly defined, freshly precipitated amorphic $Sn(OH)_4$ is quite soluble.

The latter transforms to $SnO_2$ within a month:

$$Sn(OH)_4 \text{ solid} \rightarrow SnO_2 + 2H_2O \tag{5}$$

Reliable thermodynamic data concerning the stable complex formation of Sn(IV) with inorganic ligands are quite limited, but among them are chloride $SnCl_n^{4-n}$ (n = 1–6) and sulfate $Sn(SO_4)^{2+}$ species.

Tartaric and oxalic acids are carboxylic acids that have the tendency to form complexes with metal ions [17]. Oxalic acid is the only possible compound in which two carboxyl groups are joined directly; hence, it is one of the strongest acids among the organic compounds. Tin(IV) forms stable soluble tartrate $Sn(H_4C_4O_6)_2^{2-}$ and oxalate $Sn(C_2O_4)_3^{2-}$ complexes.

Under alkaline conditions, the formation of $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ as soluble tin(IV) species are proposed [16].

The discussion above shows that the leaching of $SnO_2$ may be improved by the formation of soluble complexes of Sn(IV). Therefore, some acids ($H_2SO_4$, HCl, $H_6C_4O_6$) were selected with concentrations corresponding to 4M $H^+$. The one exception was 1M oxalic acid, since the application of 2M $H_2C_2O_4$ was accompanied by its crystallization ($H_2C_2O_4$ solubility is 1.6M at 25°C). The alkaline lixiviate was represented by strong base NaOH.

Leaching of $SnO_2$ was performed at three temperatures (40°, 60°, and 80°C). The obtained results are presented in Figure 3. The lowest leaching efficiency was observed for $H_2SO_4$, but increased temperature enhanced the hydrolysis of the dissolved Sn(IV) salt, decreasing the concentration of tin ions in the solution. Final concentrations of Sn(IV) were only 0.1–0.4 g/dm$^3$, corresponding to 0.2–0.5% of the tin leaching efficiency. Better results were found for tartaric acid, where an increase in temperature favored dissolution of the sludge. Final Sn(IV) concentrations were 0.9–2.6 g/dm$^3$; nevertheless, leaching efficiency was still very low (1.2–3.1%). Comparable results were found in the HCl and NaOH lixiviates, with the highest concentrations of Sn(IV) at 80°C: 4.9 g/dm$^3$ and 4.7 g/dm$^3$, respectively. Depending on the temperature used, leaching efficiency was within a range of 1.3–6.3% for HCl and 0.4–5.9% for NaOH. The best leaching compound was oxalic acid. The final Sn(IV) concentrations reached 7.4–9.7 g/dm$^3$, corresponding to 9.3–12.5% of tin-leaching efficiency. A decrease in the solid to liquid ratio raised the leaching effectiveness somewhat (to 15.4–18.3%). The obtained results show that a complexing agent seriously improves the dissolution of $SnO_2$ but is not effective enough if used alone. Therefore, the addition of $H^+$ originating from strong acid should be helpful.

The tin sludge was contaminated with copper, which was also dissolved during leaching. Figure 4 shows the changes of copper ions concentrations over time. A comparable action was observed in the $H_2SO_4$ and HCl solutions, where final Cu(II) concentrations were 2.1–2.6 g/dm$^3$ and 1.9–2.7 g/dm$^3$, respectively. Tartaric acid was not so effective (1.4–1.9 g/dm$^3$ Cu(II)), while final Cu(II) concentrations were below 0.03 g/dm$^3$ in the presence of NaOH and $H_2C_2O_4$. This confirms the selection of oxalic acid as a good selective leachant for tin.

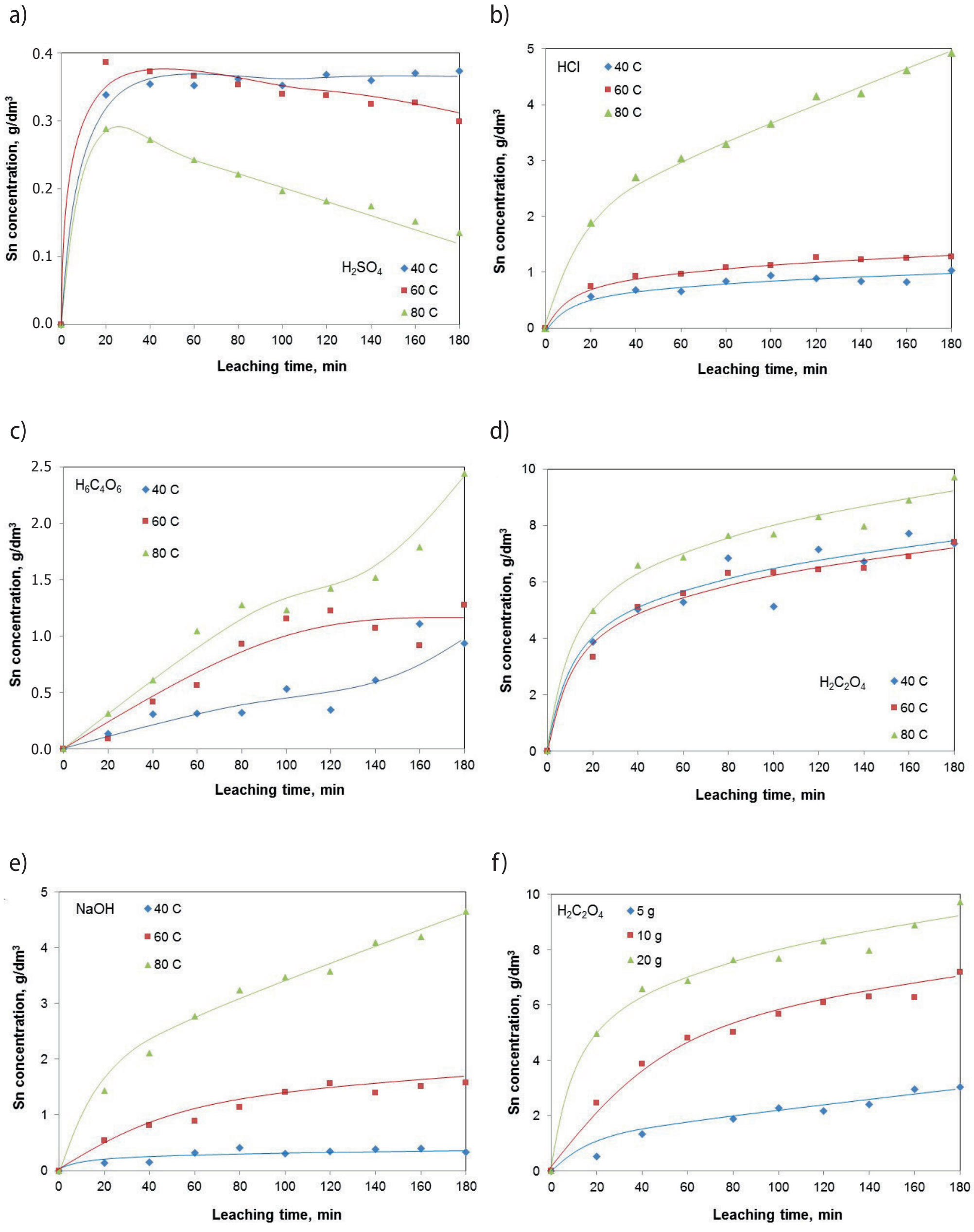

*Fig. 3. Influence of leaching time and temperature on tin concentration in the solution (s/l = = 20 g/200 cm$^3$): a) sulfuric acid; b) hydrochloric acid; c) tartaric acid; d) oxalic acid; e) sodium hydroxide; f) oxalic acid (80°C, 200 cm$^3$)*

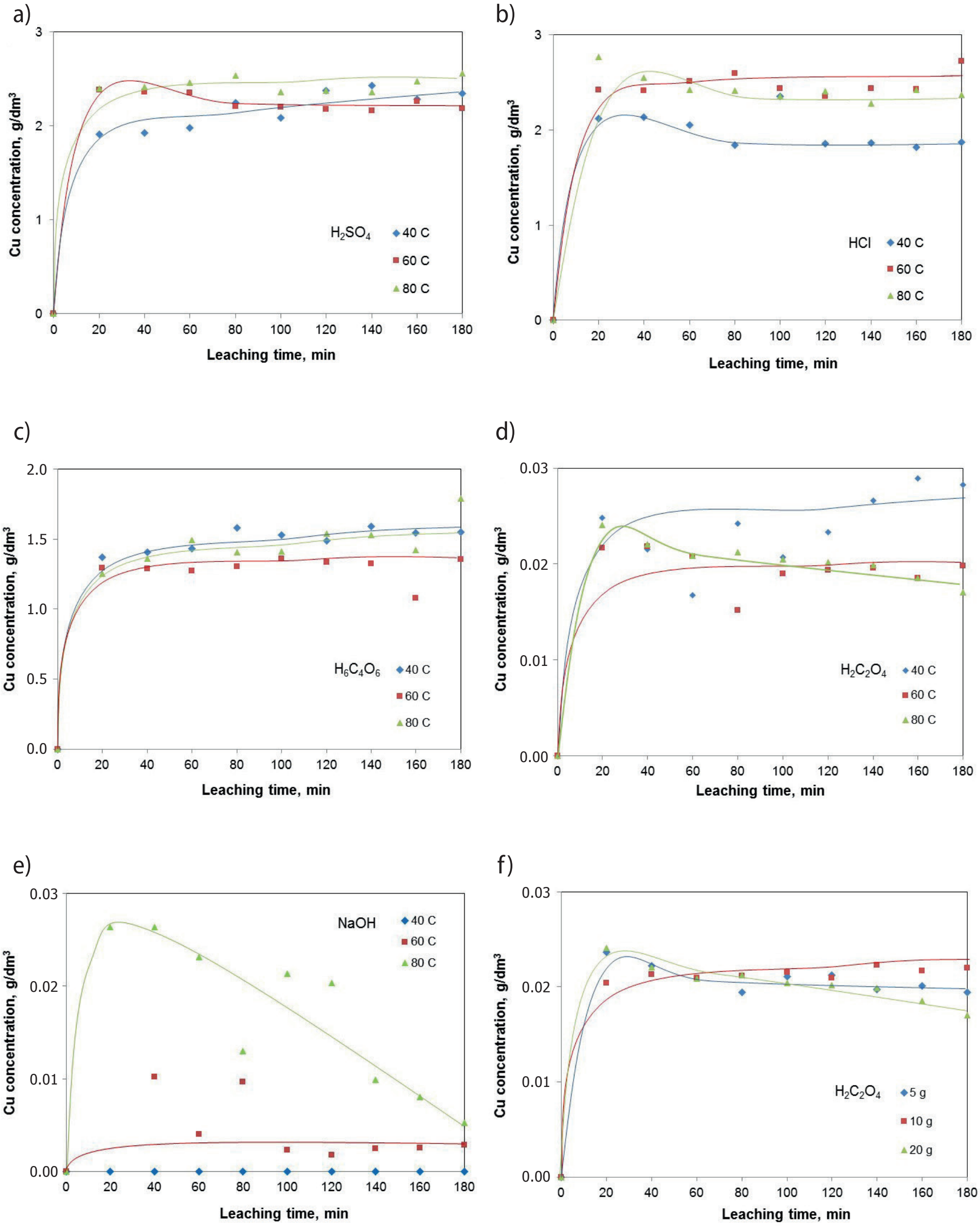

*Fig. 4. Influence of leaching time and temperature on copper concentration in the solution (s/l = = 20 g/200 cm$^3$): a) sulfuric acid; b) hydrochloric acid; c) tartaric acid; d) oxalic acid; e) sodium hydroxide; f) oxalic acid (80°C, 200 cm$^3$)*

## 3.3. Electrochemical analysis

An oxalate solution containing 7.2 g/dm$^3$ Sn(IV) and 0.02 g/dm$^3$ Cu(II) was used for the further stages of tin potentiostatic electrowinning. This was preceded by an electrochemical analysis using cyclic voltammetry.

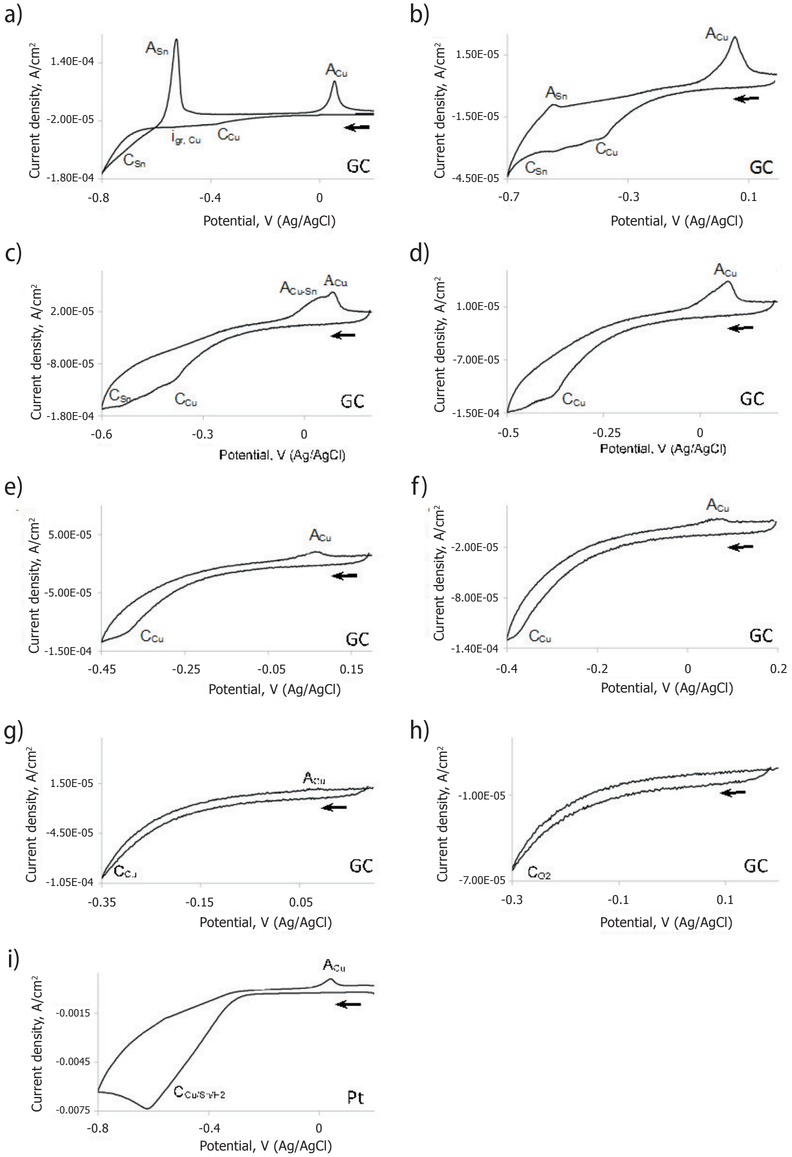

*Fig. 5. Cyclic voltammograms registered in oxalate solution (7.2 g/dm$^3$ Sn(IV) and 0.02 g/dm$^3$ Cu(II)) in various potential ranges: a–h) on glassy carbon electrode; i) on platinum electrode*

Figure 5 (a–h) shows voltammograms registered in various potential ranges on the glassy carbon (GC) working electrode. The GC substrate allows for the good separation of electrochemical reactions due to the high hydrogen overpotential (0.5 V [18]); thus, individual cathodic reactions registered during the forward scan are clearly reflected by anodic responses during the backward step. Analysis of the data shows that tin and copper can be selectively recovered from the solution. Only copper ions are reduced on the cathode if the deposition potential is between −0.35 V and −0.45 V (vs. Ag/AgCl). At a more-positive potential, the reduction of dissolved oxygen occurs solely. A decrease in the cathode potential to −0.6 V is accompanied by tin codeposition and the formation of an Sn-Cu alloy enriched in copper. Intensification of tin deposition was observed for the more-negative potentials (up to −0.8 V), where copper ions are co-reduced under a limiting current.

Deposition of metals on a platinum substrate is accompanied by hydrogen coevolution (hydrogen overpotential on platinum is 0.15 V [18]), and individual electrochemical reactions are difficult to distinguish (Fig. 5i).

## 3.4. Electrowinning

Cyclic voltammetry enhanced the selection of potentials for metal electrowinning. Table 1 summarizes the results of the potentiostatic electrodeposition. It was found that deposition conducted at potentials from −0.5 V to −0.7 V allows for the selective recovery of copper, but the highest current efficiency was found at −0.6 V. At a potential of −0.8 V, the deposits contained more than 80% of tin. This confirms the possibility of selective electrowinning of the metals: copper should be recovered first, followed by tin.

*Table 1. Results of potentiostatic deposition of metals from oxalate solution*

| **Potential, V (Ag/AgCl)** | **Electrolysis time [min]** | **Composition of the cathodic deposits [wt%]** | | **Cathodic current efficiency [%]** |
|---|---|---|---|---|
| | | **Sn** | **Cu** | |
| −0.5 | 30 | 0 | 100 | Trace amount of deposit |
| −0.6 | 30 | 0 | 100 | 70.1 |
| −0.7 | 30 | 0 | 100 | 53.0 |
| −0.8 | 30 | 81.3 | 18.7 | 43.1 |
| −0.8 | 60 | 87.6 | 12.4 | 79.9 |

Figure 6 shows exemplary morphology of the deposits. Copper was electrodeposited as even layer (Fig. 6a), while codeposition of tin resulted in formation of “needle” like grains on electrode surface (Fig. 6b)

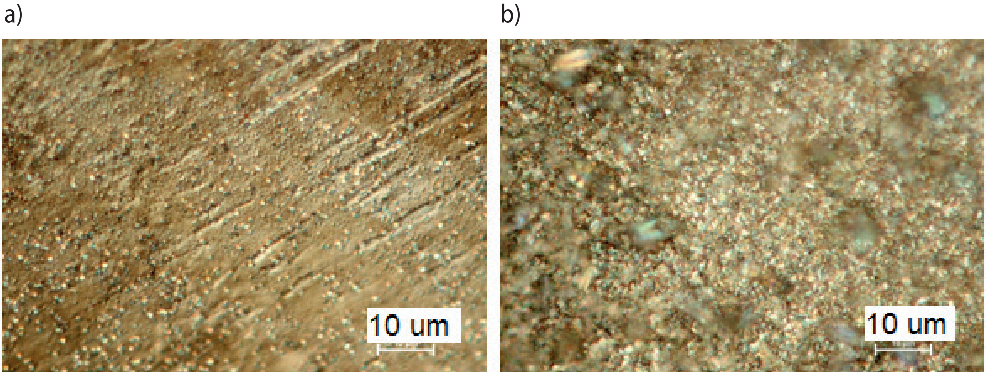

*Fig. 6. Surface of cathodic deposits obtained from oxalate solution at constant potentials: a) –0.5 V; b) –0.8 V*

Galvanostatic electrowinning was also carried out from an oxalate solution containing 3.0 g/dm$^3$ Sn(IV) and 0.02 g/dm$^3$ Cu(II). Figure 7 shows the changes in the mass of cathodic deposits during electrolysis. The mass of the cathode continuously increased, but the mass gains in each period gradually decreased due to the depletion of electrolytes with metallic ions.

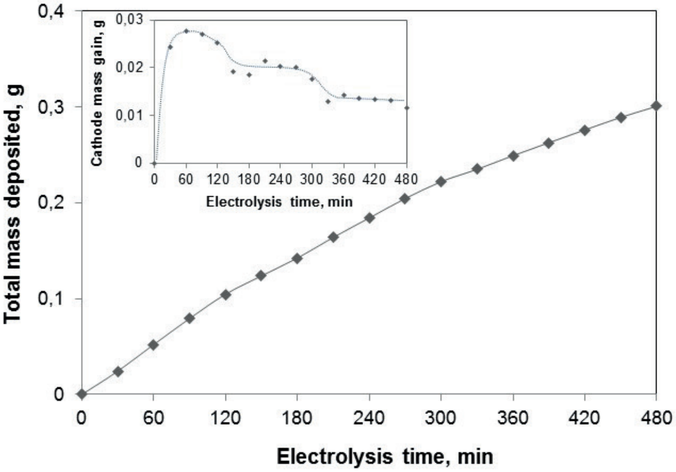

*Fig. 7. Changes of cathode mass during galvanostatic electrowinning*

Decreased masses of deposits were accompanied by decreased cathodic current efficiences from a maximal value of about 20% at the initial stages of the process (Fig. 8). This resulted in higher energy consumption, which changed from 39 kWh/kg (up to 120 min) to about 80 kWh/kg (330–480 min).

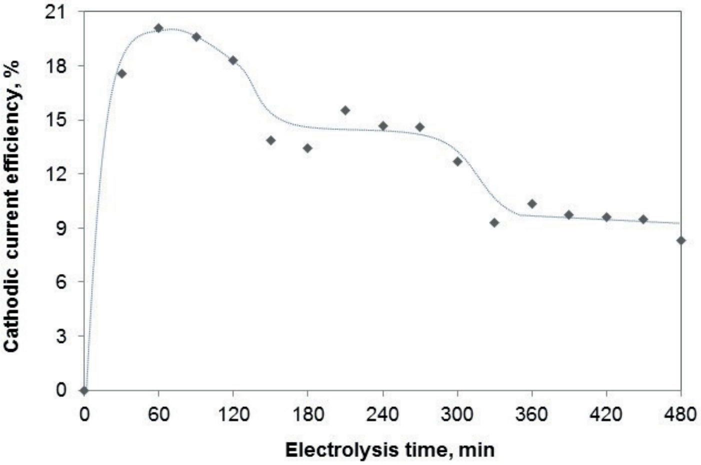

*Fig. 8. Changes in cathodic current efficiency during galvanostatic electrowinning*

Figure 9 shows the morphology of the cathodic deposit produced at constant current density. It was gray and well-adhered to the substrate, but its surface was covered with "needle" grains (characteristic of tin electrodeposits).

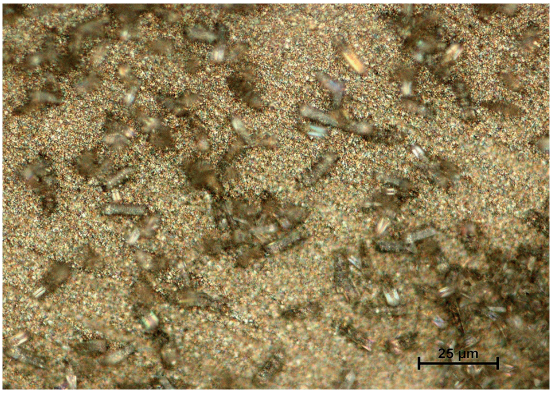

*Fig. 9. Surface of cathodic deposit obtained from oxalate solution at constant current density (1 A/dm$^2$)*

Figure 10 shows the diffraction pattern of the obtained deposit. The main component of the layer was β-Sn (white) contaminated by a Cu10Sn3 phase. No pure copper was detected, but peaks characteristic of tin are shifted a little, indicating the formation of an Sn-Cu solid solution.

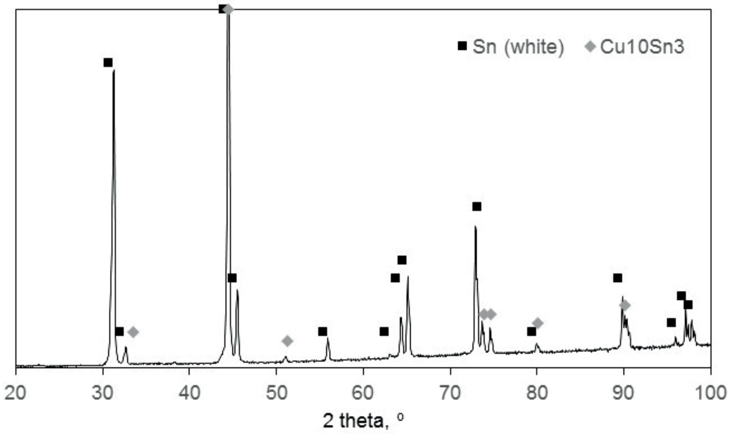

*Fig. 10. XRD spectra of cathodic deposit obtained from oxalate solution at constant current density*

## 4. Summary

A series of measurements allowed us to present the following conclusions.

- The most-effective reagent for the leaching of $SnO_2$ waste was 1M oxalic acid, while the least-effective lixiviate was 2M sulfuric acid.
- Electrowinning conducted at a constant potential higher than –0.8 V (vs. Ag/AgCl) allows for the selective deposition of copper. Tin ions are reduced only if the deposition potential is –0.8 V, and prolongation of the process increases tin content in the cathode deposit (88% after 60 min) as well as the cathodic current efficiency (80%).
- Electrowinning conducted at a constant current density yields cathode deposits of tin contaminated by copper, but at a low current efficiency (max. 20%).
- Optimization of the leaching process should be directed towards modification of the oxalate solution.

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