

Ewa Rudnik, Dawid Wincek

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 SnO₂ 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 SnO₂ pochodzących z przemysłowego procesu usuwania cyny z drutów miedzianych. Szlam ługowano w roztworach kwasów (siarkowego, solnego, winowego, szczawianowego) 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 voltamperometrii cyklicznej.

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

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 SnO₂, 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 SnO₂ from the stripping solution, washing with water, and dissolving in hot HCl (followed by tin electrowinning) [5]. Harangi and Kekesi [11] converted SnO₂ into a soluble form by carbothermic reduction followed by leaching the reduced material with boiling 6M HCl. McKesson [12] recommended the addition of sodium hydroxide into the spent stripping solution to transform SnO₂ 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 CuSO₄-H₂SO₄ solution. Dissolution of the tin coating resulted in the formation of SnO₂ 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_{Kα}).

20-g portions of the sludge were leached in the acid and alkaline solutions (200 cm³): 2M sulfuric acid H₂SO₄, 4M hydrochloric acid HCl, 2M tartaric acid H₆C₄O₆, 1M oxalic acid H₂C₂O₄, 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 H₂C₂O₄ 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-cm³ 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 α was calculated according to the following formula:

$$\alpha = \frac{C_{\text{Sn}} v}{0.788 \cdot m_s} 100\% \quad (1)$$

where:

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

v – volume of the lixiviant,

0.788 – initial tin content in the sludge (78.8 % in SnO₂),

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 cm²), platinum plate (0.8 cm²) as the counter electrode, and silver chloride as the reference electrode (Ag/AgCl). The volume of the solution (not agitated) was 20 cm³. 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 cm²) 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/dm². Two platinum plates (each 25 cm²) were used as cathode and anode. Electrolysis was performed using the oxalate solution (150 cm³) 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:

$$Z = \frac{Ult}{m} \quad (2)$$

where:

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

Cathodic current efficiencies η were also determined:

$$\eta = \frac{m}{m_t} \cdot 100\% \quad (3)$$

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

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

where:

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

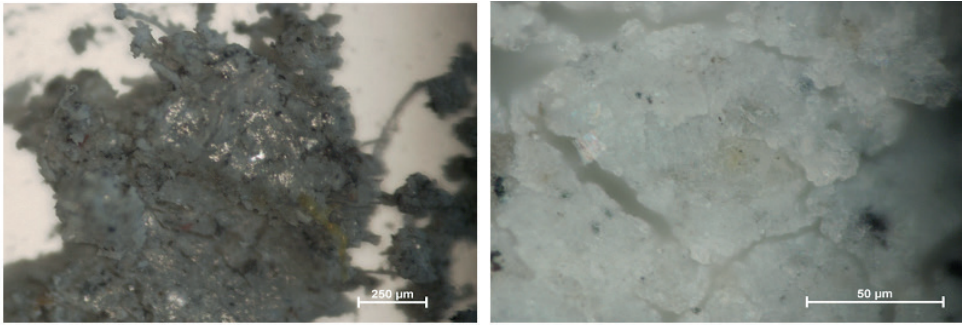


Fig. 1. Morphology of sludge originating from tin stripping from copper wire

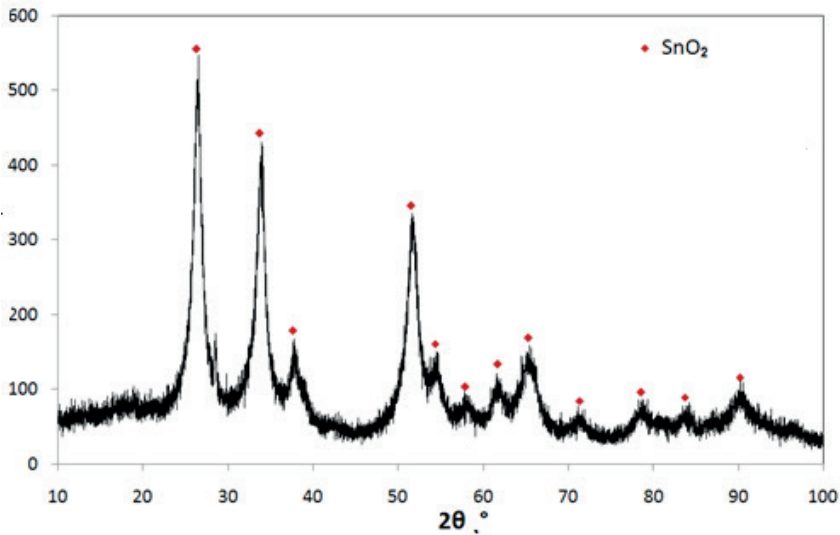


Fig. 2. X-ray diffraction pattern of sludge

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 amorphous Sn(OH)_4 is quite soluble.

The latter transforms to SnO₂ within a month:



Reliable thermodynamic data concerning the stable complex formation of Sn(IV) with inorganic ligands are quite limited, but among them are chloride SnCl_n⁴⁻ⁿ (n = 1–6) and sulfate Sn(SO₄)₂²⁺ 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(H₄C₄O₆)₂²⁻ and oxalate Sn(C₂O₄)₃²⁻ complexes.

Under alkaline conditions, the formation of Sn(OH)₅⁻ and Sn(OH)₆²⁻ as soluble tin(IV) species are proposed [16].

The discussion above shows that the leaching of SnO₂ may be improved by the formation of soluble complexes of Sn(IV). Therefore, some acids (H₂SO₄, HCl, H₆C₄O₆) were selected with concentrations corresponding to 4M H⁺. The one exception was 1M oxalic acid, since the application of 2M H₂C₂O₄ was accompanied by its crystallization (H₂C₂O₄ solubility is 1.6M at 25°C). The alkaline lixiviate was represented by strong base NaOH.

Leaching of SnO₂ 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 H₂SO₄, 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/dm³, 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/dm³; 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/dm³ and 4.7 g/dm³, 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/dm³, 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 SnO₂ 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 H₂SO₄ and HCl solutions, where final Cu(II) concentrations were 2.1–2.6 g/dm³ and 1.9–2.7 g/dm³, respectively. Tartaric acid was not so effective (1.4–1.9 g/dm³ Cu(II)), while final Cu(II) concentrations were below 0.03 g/dm³ in the presence of NaOH and H₂C₂O₄. This confirms the selection of oxalic acid as a good selective leachant for tin.

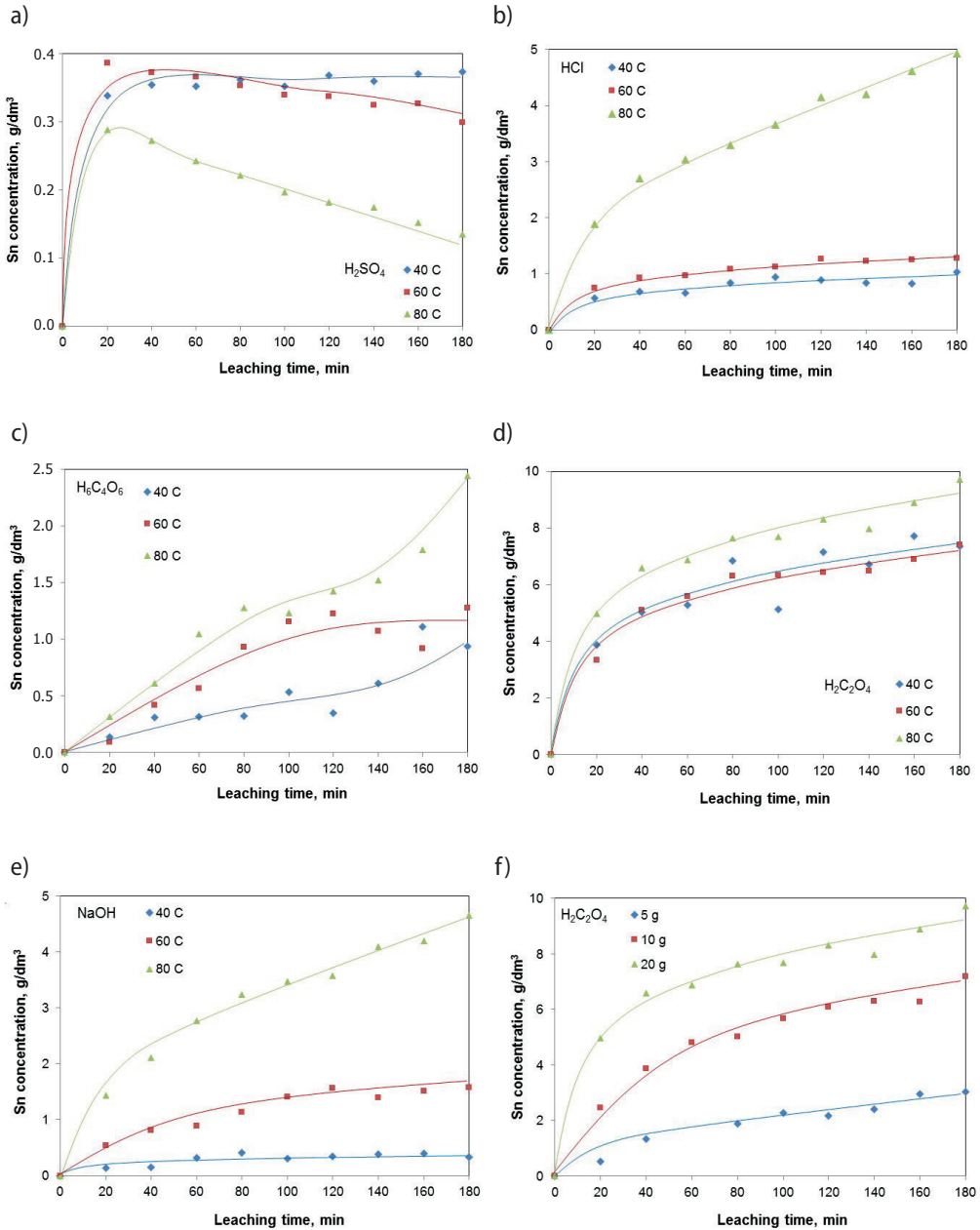


Fig. 3. Influence of leaching time and temperature on tin concentration in the solution ($s/l = 20 \text{ g}/200 \text{ cm}^3$): a) sulfuric acid; b) hydrochloric acid; c) tartaric acid; d) oxalic acid; e) sodium hydroxide; f) oxalic acid (80°C , 200 cm^3)

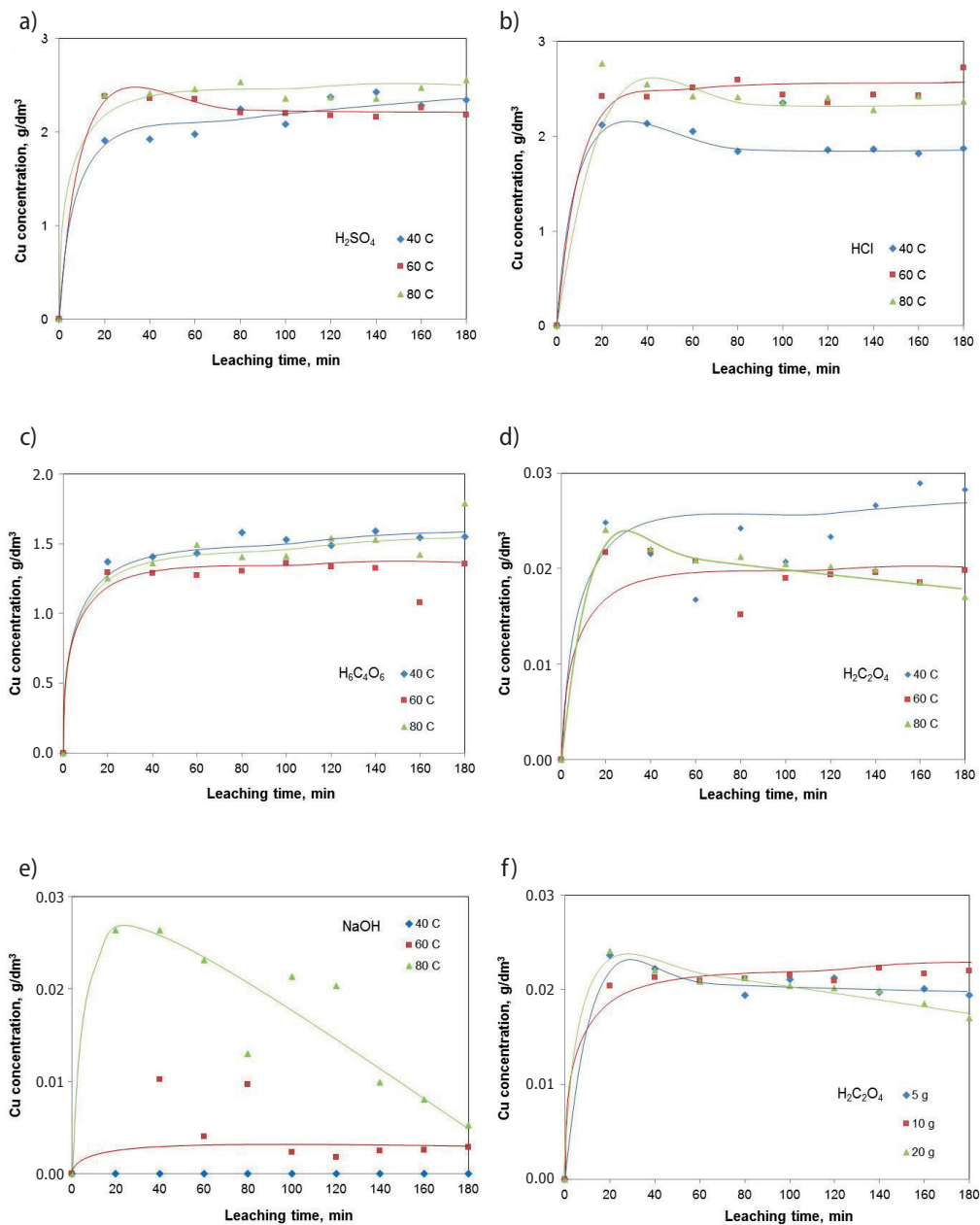


Fig. 4. Influence of leaching time and temperature on copper concentration in the solution ($s/l = 20 \text{ g}/200 \text{ cm}^3$): a) sulfuric acid; b) hydrochloric acid; c) tartaric acid; d) oxalic acid; e) sodium hydroxide; f) oxalic acid (80°C , 200 cm^3)

3.3. Electrochemical analysis

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

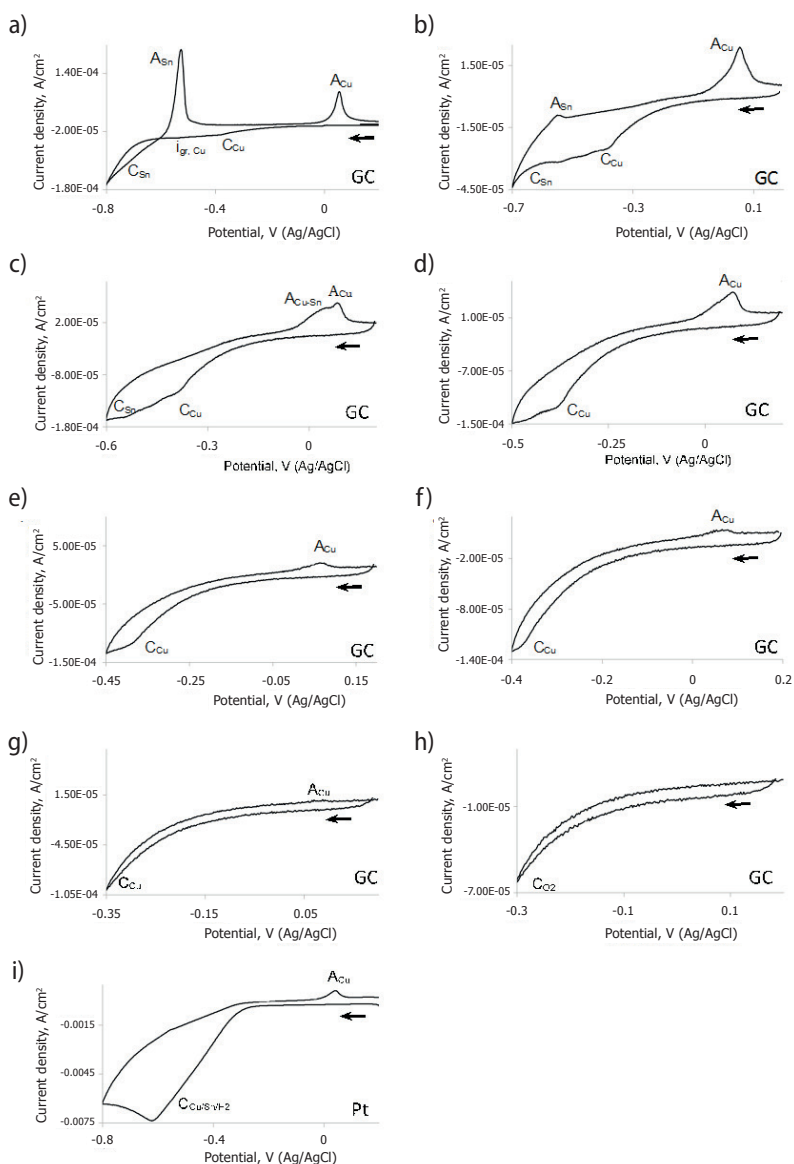


Fig. 5. Cyclic voltammograms registered in oxalate solution ($7.2 \text{ g/dm}^3 \text{ Sn(IV)}$ and $0.02 \text{ g/dm}^3 \text{ Cu(II)}$) in various potential ranges: a–h) on glassy carbon electrode; i) on platinum electrode

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)

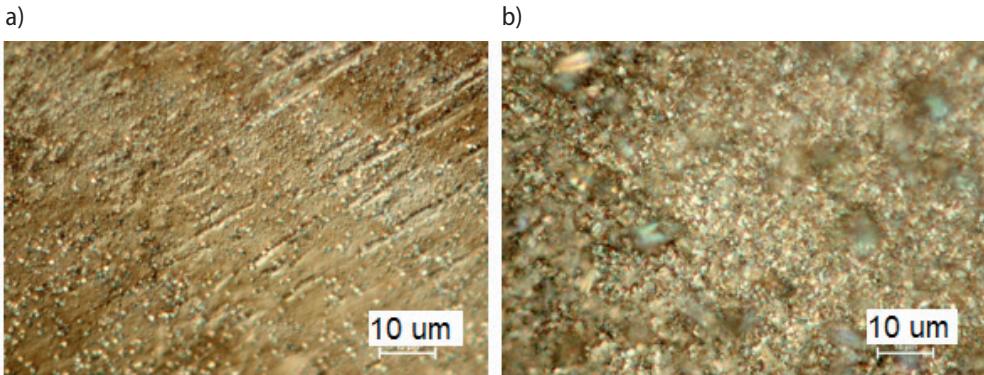


Fig. 6. Surface of cathodic deposits obtained from oxalate solution at constant potentials: a) -0.5 V ; b) -0.8 V

Galvanostatic electrowinning was also carried out from an oxalate solution containing $3.0\text{ g/dm}^3\text{ Sn(IV)}$ and $0.02\text{ g/dm}^3\text{ Cu(II)}$. 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.

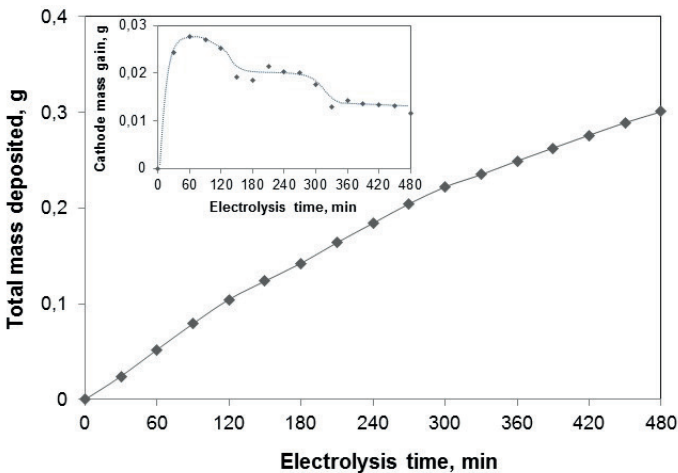


Fig. 7. Changes of cathode mass during galvanostatic electrowinning

Decreased masses of deposits were accompanied by decreased cathodic current efficiencies 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).

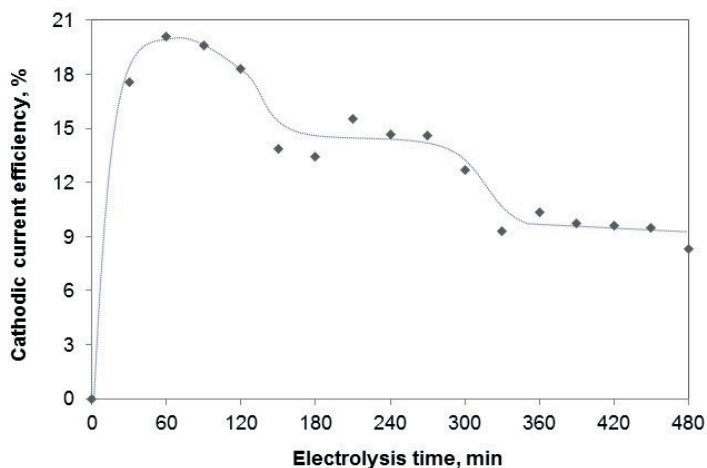


Fig. 8. Changes in cathodic current efficiency during galvanostatic electrowinning

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).

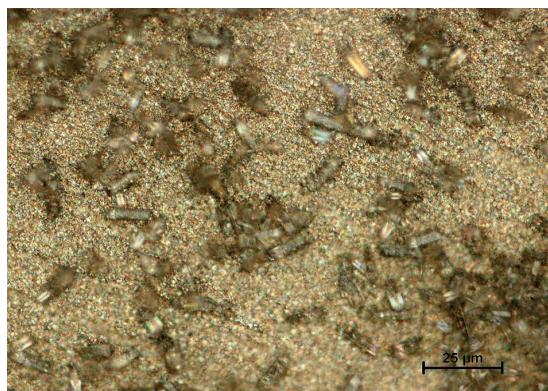


Fig. 9. Surface of cathodic deposit obtained from oxalate solution at constant current density (1 A/dm^2)

Figure 10 shows the diffraction pattern of the obtained deposit. The main component of the layer was β -Sn (white) contaminated by a $\text{Cu}_{10}\text{Sn}_3$ phase. No pure copper was detected, but peaks characteristic of tin are shifted a little, indicating the formation of an Sn-Cu solid solution.

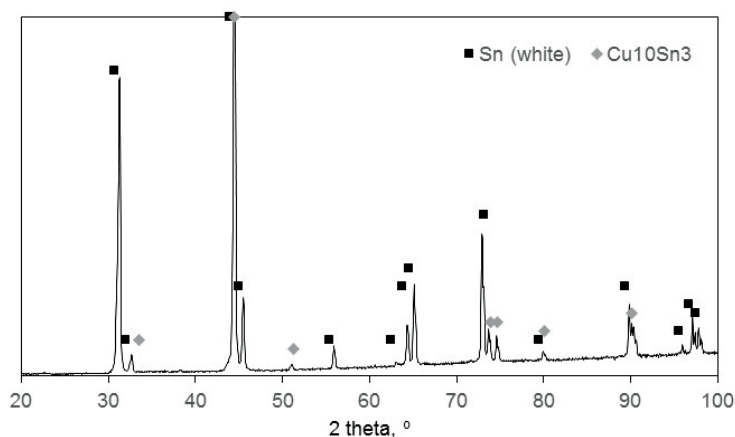


Fig. 10. XRD spectra of cathodic deposit obtained from oxalate solution at constant current density

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.

References

- [1] Schreiner H., Fidos H.: Method of producing tin layers or tin alloy layers on copper or copper alloy wires by hot tin plating, 3774427 US Patent (1973)
- [2] Delves-Broughton J., Burton V.A.C., Kempster B.A., Williams T.J.: Electroplating wire, 3947343 US Patent (1976)
- [3] Diehl P.: Process for the production of tin-plated wires, 4661215 US Patent (1987)
- [4] Rudnik E., Sikora P.: Studies on cementation of tin on copper and tin stripping from copper substrate. Archives of Metallurgy and Materials, 61, 2 (2016), 593–98
- [5] Keskitalo T., Tanskanen J., Koukkanen T.: Analysis of key patents of the regeneration of acidic cupric chloride etchant waste and tin stripping waste. Resources Conservation and Recycling, 49 (2007), 217–243

- [6] Scott K., Chen X., Atkinson J.W., Todd M., Armstrong R.D.: Electrochemical recycling of tin, lead and copper from stripping solution in the manufacture of circuit boards. *Resources Conservation and Recycling*, 20 (1997), 43–55
- [7] Li B., Pan D.A., Jiang Y.H., Tian J.J., Zhang S.G., Zhang K.: Recovery of copper and tin from stripping tin solution by electrodeposition. *Rare Metals*, 33, 3 (2014), 353–357
- [8] Kerr C.: Sustainable technologies for the regeneration of acidic tin stripping solutions used in PCB fabrication. *Circuit World*, 30, 3 (2004), 51–57
- [9] Roy S., Buckle R.: The recovery of copper and tin from waste tin stripping solution. Part II: Kinetic analysis of synthetic and real process waste. *Separation and Purification Technology*, 68 (2009), 185–192
- [10] Ryu S.H., Ahn J.W., Ahn H.J., Kim T.: Recovery of tin and copper from waste solder stripper by oxalate precipitation. *Journal of the Korean Institute of Resources Recycling*, 23, 3 (2014), 37–43
- [11] Harangi Z., Kekesi T.: Extraction of tin from oxidized soldering dross by carbothermic reduction and acid leaching. *Materials Science and Engineering*, 39, 2 (2014), 13–22
- [12] McKesson D.: Miracles in tin stripping. *Printed Circuit Fabric*, 22 (1999), 34–38
- [13] Smakowski T., Ney R., Galos K.: Bilans gospodarki surowcami mineralnymi Polski i świata. 2012. Państwowy Instytut Geologiczny – Państwowy Instytut Badawczy, Warszawa 2014
- [14] Smart J.S., Smith A.A.: Effect of certain fifth – period elements on some properties of high – purity copper. *Transactions AIME*, 152 (1943), 103–105
- [15] Pourbaix M.: Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, New York 1966
- [16] Lothenbach B., Ochs M., Wanner H., Yui M.: Thermodynamic data for the speciation and solubility of Pd, Pb, Sn, Sb, Nb and Bi in aqueous solution. Japan Nuclear Cycle Development Institute, Naka-gun, Ibaraki 1999
- [17] Sillen L.G., Martell A.E.: Stability constants of metal-ion complexes. Suppl. No. 1, Alden Press, Oxford 1971
- [18] Hampel C.A.: The encyclopedia of electrochemistry. Reinhold, New York 1964