

HYDROMETALLURGICAL PROCESSING OF ANODE SLIMES OBTAINED FROM THE ELECTROLYTIC REFINING SOLDERING SCRAP

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Abstract. The anode slime generated as a by-product during the electrorefining of tin in hydrochloric acid solutions should be processed to recover the included tin, tin oxides and the alloying elements. The most frequently used lead-free soldering alloy contains significant amounts of silver and copper, which elements report to the slime. The metallic tin is leached with boiling hydrochloric acid, and the residue is digested in nitric acid. The leaching efficiency was examined as a function of time, temperature and liquid/solid ratio. It was found that more than 80% of the soluble tin content of the slime can be dissolved with ~ 10M HCl in 4-5 hours in a boiling reactor, while silver is retained, however copper also tends to dissolve with tin under these conditions. The remaining copper and all the silver was efficiently dissolved with boiling cc. HNO₃ in less than 2 hours. The obtained solutions are suitable for metal extraction by standard methods.

1. Introduction

As the lead-free soldering alloys applied in the modern electronic industry tend to produce more dross during the wave soldering technology, the recycling of the included metallic values are becoming increasingly important. These alloys are more aggressive towards the copper material of the PCB surface and also their oxidation resistance is lower. The most widely used type of such alloys are the SAC materials, containing considerable amounts of silver, making the recovery even more imperative. During wave soldering, an oxidized dross is generated at the surface of the tin melt. It is removed periodically by skimming and it contains a large amount of entrapped metal. The metallic component can be separated by re-melting the primary dross and after skimming, the molten metal can be cast into anodes that are dissolved electrolytically. Recovery of pure tin from the electrolyte is achieved by cathodic reduction. Tin recovery is dictated by a high market price and a shrinking primary supply. Silver and copper, as more noble elements, can also be separated efficiently by electrorefining, as they are accumulated undissolved at the surface of the cast anodes, forming a thick layer of slime together with separated metallic and non-metallic particles. Extensive investigations [1,2] have resulted in the development of a new technology [3] applying inexpensive HCl-SnCl₂ electrolyte solutions combined with either current reversing (PCR) technology or some electromechanical system to compact the loosely deposited dendritic metal at the cathode [4,5]. The generated argentiferous slime can be removed periodically from the surface of the anodes and this by-product needs

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processing to recover silver and tin, and eliminate the residue from the main process of electrorefining.

Because of uneven anodic dissolution, a large amount of tin particles drop from the anode surface, thus the formed slime layer contains metallic tin, which can be dissolved in boiling and concentrated hydrochloric acid [1], although it may take considerable time. This should be the first step of a hydrometallurgical processing of the slime, as silver and copper are less likely to dissolve in this medium. They can be leached from the residue with concentrated nitric acid. The feasibility and the selectivity of these subsequent leaching steps need to be investigated by examination of the anodic slime structure and leaching experiments.

2. Experimental procedure

The examined anode slime material was prepared by electrolytic refining of anodes cast from a tin alloy exceptionally enriched in copper by fractional crystallization of the ordinary SAC305 alloy bath. The general composition of the anode was 9% Cu, 3% Ag, the balance made up by tin. Electrolysis was carried out with 100, 500 and 1000 A/m² anodic current densities in stationary solutions of 1 M HCl and 10 g/dm³ Sn. The electrolysis process, the produced anodic slime layer and the anode surface are illustrated by the pictures in Fig. 1. However, the lowest current density experiment was carried out in a different cell of semi-industrial scale. The slime layer was removed from the anode surface by scraping, as shown in Fig. 2a. The collected material was rinsed with water and dried at 110 °C in an oven, followed by fine grinding in an achat mortar (Fig. 2b). Samples of the slime powder (20 g) were taken and mixed with usually 200 cm³ hydrochloric acid of 10 mol/dm³ concentration in a closed reactor vessel (2c) equipped with a water cooled reflow condenser (Fig. 2d) to exhaust the evolved hydrogen gas.

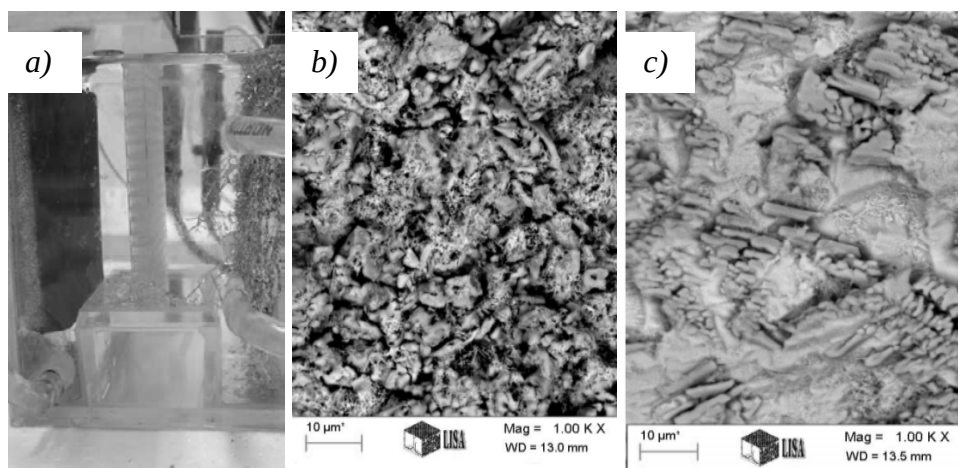


Fig.1 Production (a) and the original structure of the produced anode slime (b), on the metal substrate surface (c) (1000 A/m², 3h).

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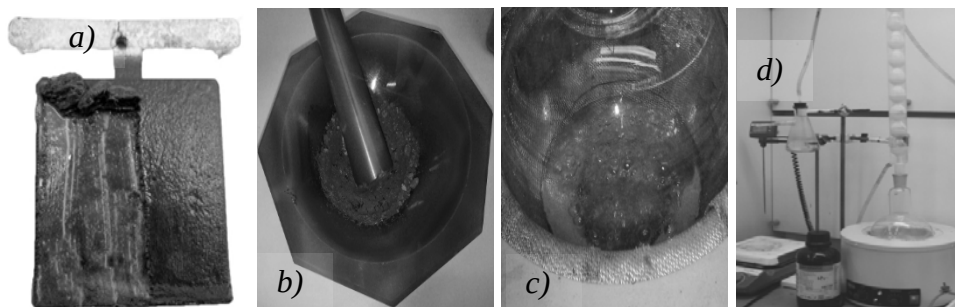


Fig. 2 Anode slime removal (a), mortar (b), leaching (c), reactor (d).

For further testing, the ground powder was mixed with different volumes of 6M HCl and heated in a simple beaker placed on a hot plate (also seen in Fig. 1d) where magnetic stirring was also applied. Solution samples of 1 cm³ volume were taken regularly during the process of leaching. The analysis was carried out for Sn, Cu and Ag and some more common elements by (Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The duration of the leaching was longer than 8 hours with the closed reactor at boiling temperature (85 ~ 90 °C). The additional experiments with the simple beaker lasted for 1.5 hours with 5, 10, 20 cm³/g liquid-to-solid (L:S) ratios and for 8 hours with the standard 10:1 ratio.

The residual material obtained from the reactor after the long lasting hydrochloric acid leaching (obtained with the 10 M HCl lixiviant applied at boiling temperature with 10:1 L:S ratio) was removed and rinsed with water, dried and weighed. Small amounts (0.5 g) of this material were leached with 50 cm³ nitric acid of 65% concentration by mass in a stirred beaker heated to 90 – 95 °C temperature. This leaching step was continued for 2 hours, leaving virtually no residue in the beaker. Solutions samples were taken and analysed, as described above.

The dried anode slime and the residue from the first leaching step were examined by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray analysis (EDX) for the physical structure and the elemental distribution, and by X-Ray Diffraction (XRD) for the phase composition.

3. Experimental results and discussion

3.1 The structure of anode slime

Produced with 1000 A/m² anodic current density for 3 hours - while the cathodic deposition still remained of acceptable visual quality - is illustrated by the SEM images of the dried and ground powder sample in Fig. 3. The residue of the anodic dissolution produced relatively large crystals of silver and copper, in virtually metallic forms, but the dispersed Sn-Ag, Sn-Cu or Sn-Cu-Ag intermetallics are also apparent. The relevant EDX spectra (Fig. 4), clearly suggest the presence of metallic Ag and Cu particles. The XRD spectrum of the sample is presented in Fig.5, revealing the clearly identified intermetallic phases of Ag₄Sn, Cu₆Sn₅ and also metallic Cu.

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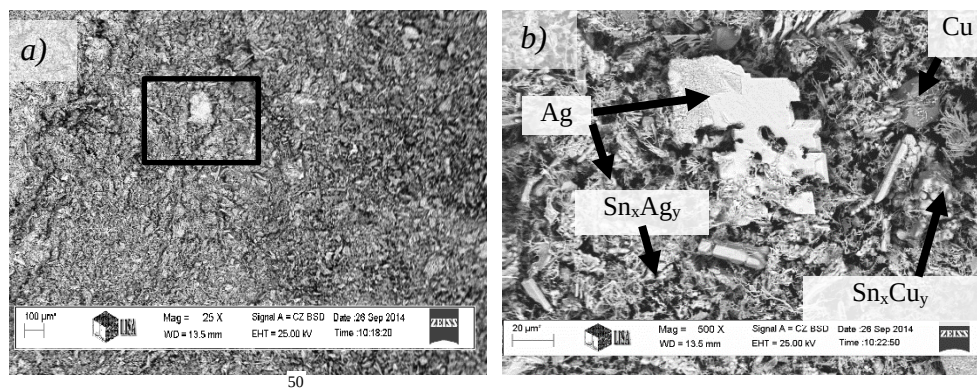


Fig. 3 The SEM images of the dried and ground anode slime sample produced by an electrolysis of 3h with 1000 A/m^2 , a – low magnification, b – high magnification of the marked area.

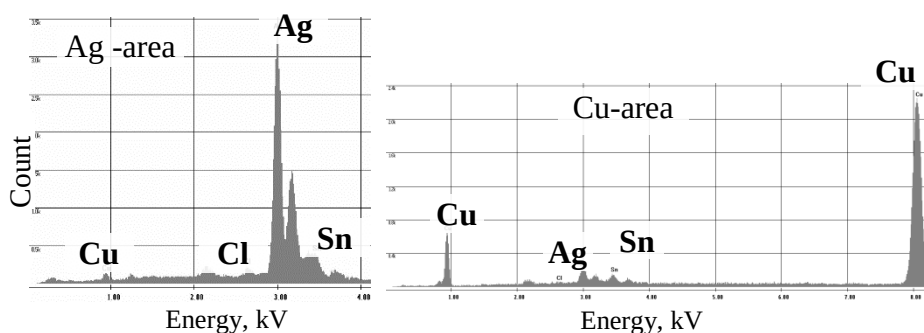


Fig. 4 The characteristic EDX spectra of the anode slime produced in 3h with 1000 A/m^2 .

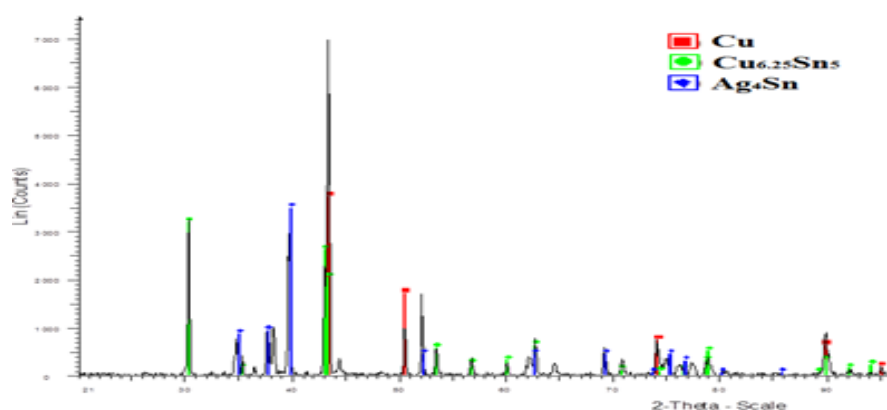


Fig. 5 The XRD spectrum of the anode slime sample produced (3h electrolysis with 1000 A/m^2).

Similar results were obtained for the anode slime powders produced with 500 and 100 A/m² anodic current densities. Figure 6 shows the SEM images and the overall EDX spectrum for the slime powder obtained with 3h electrolysis applying 500 A/m² anodic current density.

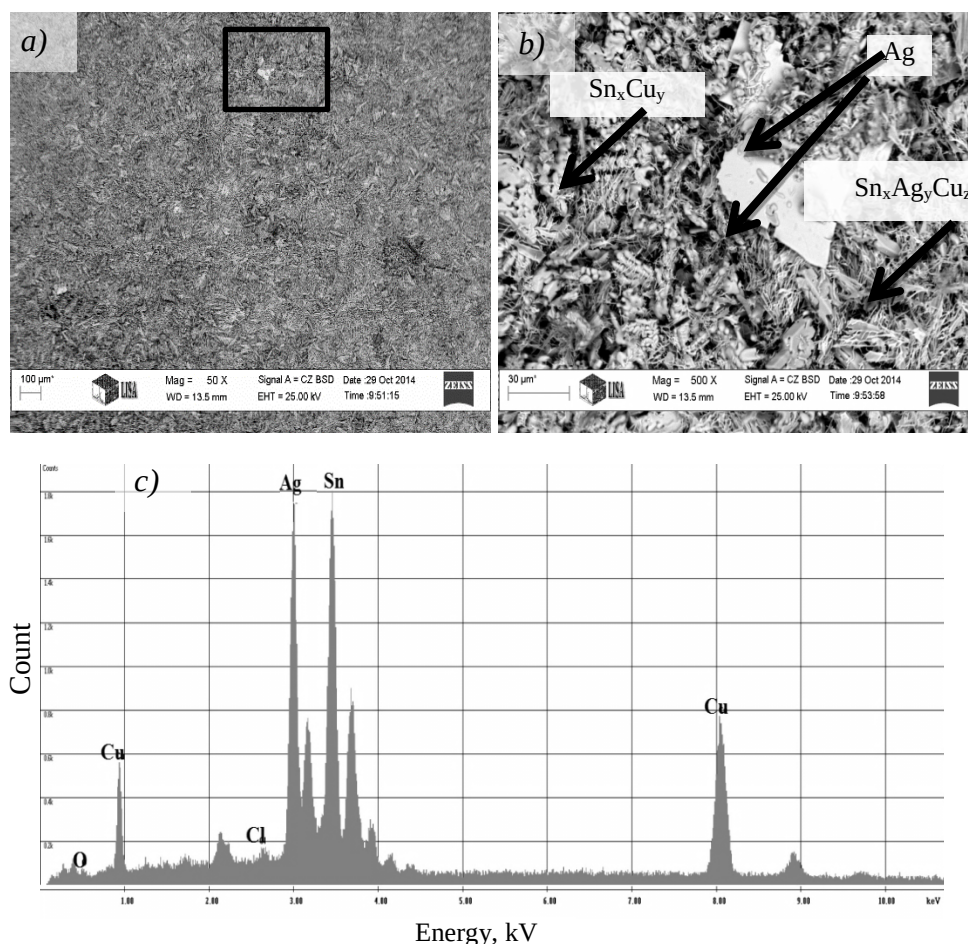


Fig. 6 The SEM images and the overall EDX spectrum of the dried and ground anode slime sample produced in 3h electrolysis with 500 A/m², a – low magnification, b – high magnification of the marked area, c - the characteristic EDX spectra of the examined area.

The amount, the structure and the composition of the produced slime layer primarily depends on the type of the soldering alloy scrap refined, however it is also affected by the potential developing during the anodic dissolution. It is in direct correlation with the applied anodic current density and the average thickness of the slime layer impeding the free dissolution process. At lower currents the preferred crystallographic orientation will dissolve faster [6], thus rougher structures may develop. In this case, the impurities of higher electrode potential may be more efficiently retained in the metal matrix. At high

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current densities, on the other hand, the anodic overpotential will be higher, resulting in a more uniform dissolution pattern and more intensive drop out of metallic particles from the surface, causing higher rate of slime generation. At higher potentials the dissolution process may produce Sn(IV) ions primarily, which can react with the tin particles in the slime layer to form Sn(II) ions [1]. Thus the metallic tin concentration may decrease and the noble metal concentration increases. At low HCl concentrations, however, the Sn(IV) ions may lose their stability and cause $\text{SnO}_2 \cdot \text{H}_2\text{O}$ type precipitation to accumulate in the slime.

3.2 The leaching behaviour of the anode slime

Samples were examined in two steps. Application of hydrochloric acid at the first stage targeted the selective removal of the metallic tin component from the collected slime. The analysis of the anode slime samples obtained with different current densities is given in Table 1. The indicated values, however can be considered only approximate because of the difficulties caused by the refractory nature of the material. In order to analyse the powder, it needed a complex pre-treatment by digestion in aqua regia, followed by high temperature alkaline fusion of the residue with KNaCO_3 and NaBO_4 and a final dissolution in hydrochloric acid. The ICP analysis of the solution fractions needed a careful selection of the proper conditions. Despite all the precautions taken, some loss of components during these steps may have affected the results.

Table. 1 Elemental analysis of the examined anode slime samples

Current density of production, A/m^2	Elemental analysis, % (by mass)								
	Ag	As	Bi	Fe	Ni	Pb	Sb	Cu	Sn
100*	3.36	0.0000	0.0086	0.2627	0.0002	0.0047	0.0096	34.21	46.10
500	6.15	0.0042	0.0005	0.0217	0.0075	0.0053	0.0265	25.5	43.74
1000	11.75	0.0025	0.0001	0.0096	0.0045	0.0062	0.0182	22.06	36.04

* Produced in a semi-industrial cell

Applying the analytical results of the slime samples and those of the solution samples taken during the leaching experiments, the relative masses of the dissolved metals could be determined. Figure 7 shows that tin may be dissolved to a great proportion from the anode slime with 10 M HCl in a reactor 4 – 5 hours boiling.

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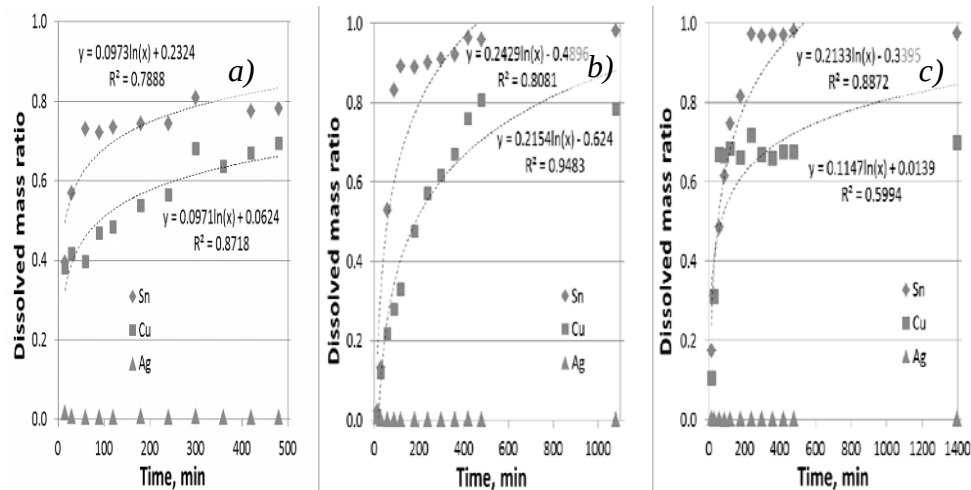


Fig. 7 Efficiency of leaching the anode slimes produced with different (a – 100 A/m², b – 500 A/m², c – 1000 A/m²) current densities in 10 M boiling HCl.

As the reaction vessel was not isolated from the ambient air, the dissolution of copper is also seen to take place to a similarly high degree. However, silver is virtually perfectly retained in the solid residue. Figure 8 shows that leaching in simple beakers - covered by hour glasses - with the azeotropic concentration of HCl solution without intensive boiling can be also efficient for dissolving tin, but leaving most of the copper content behind undissolved.

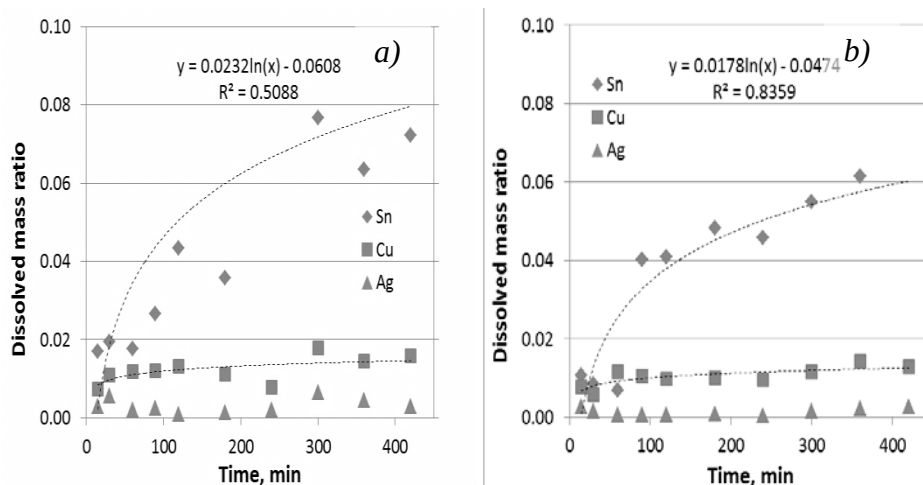


Fig. 8 Efficiency of leaching the anode slimes produced with different (a – 500 A/m², b – 1000 A/m²) current densities in 6 M HCl at 80°C temperature in glass beakers.

However, the efficiency of tin leaching is considerably lower as the HCl concentration is decreased from 10 to 6 mol/dm³ and boiling is less vigorous. The effect of changing the liquid to solid ratio was also examined. For this purpose, relatively short experiments were carried out utilizing the glass beaker option. The results summarized in Fig. 9 show that the L/S ratio in the 5 – 20 cm³/mg range does not affect the leaching rate of tin, however the application of the lowest volume ratio may efficiently depress the dissolution of copper.

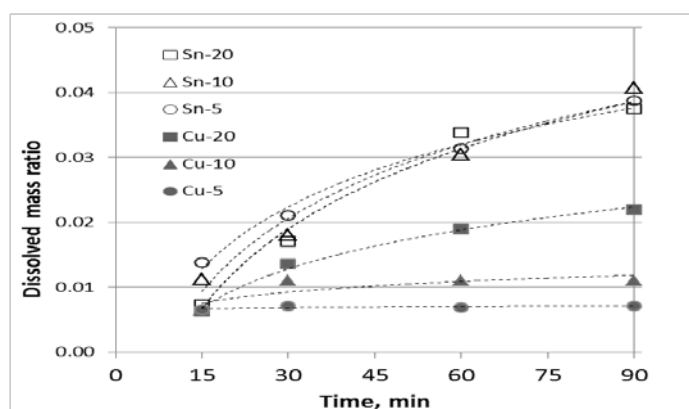


Fig. 9 Efficiency of leaching the anode slimes - produced with 500 A/m² current density - in 6 M HCl at 80°C temperature in glass beakers with L/S ratio of 5, 10 and 20 cm³/mg.

The reaction depends on the exchange of electrons at the surface of the metal particles with hydrogen ions. Without any additional oxidising effect this process is impeded by the slightly negative electrode potential of tin and the high (approx. -0.75V at 1 mA/cm²) overpotential of hydrogen on the tin surface [7]. This is slightly changed by the alloying elements. [8]. Still the component of the anode slime most soluble in HCl is tin. The higher rate of dissolution from the slime produced with higher current densities indicates that more metallic tin particles drop out from the surface of the anode during operation. As shown in Table 1, increasing the current density gradually decreases the total tin concentration in the anode slime, proving the assumption that the enhanced generation of the Sn(IV) ions result in a more intensive con-proportionation reaction with the metallic tin particles as the ions are diffusing through the slime layer. Therefore more metallic tin is solubilized in a secondary process. The higher anode potential may also cause the formation of oxidised tin species, which – unless precipitation occurs because of dropping acid concentration in the cell – may readily dissolve in the subsequent leaching. The similar decrease in the copper concentration of the slime as the anodic current density is increased indicates that Sn(IV) ions may also react with the metallic copper content of the slime layer. As the solubility of silver is much lower and its redox potential is more positive, this effect is not seen in the silver concentration of the slimes. Rather, the higher rate of secondary dissolution of Sn and Cu causes higher silver concentrations in the slimes produced at higher current densities.

The residue of the slime produced with 500 A/m² anodic current density after the intensive 10M HCl leaching step in the reactor is shown by the SEM image and the corresponding EDX spectrum in Fig. 10.

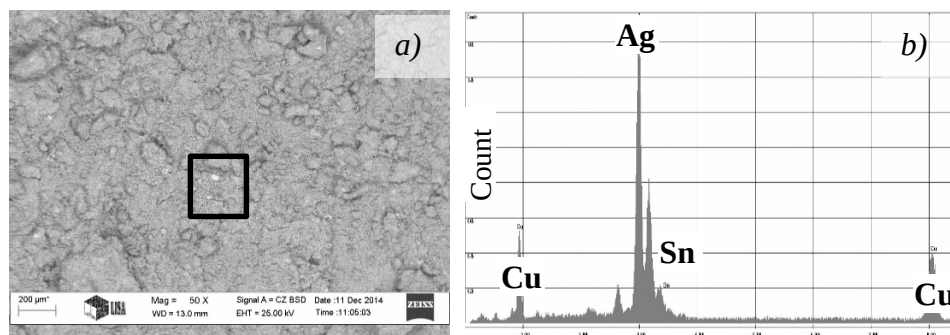


Fig. 10 Solid residue of the anode slime - produced with 500 A/m² anodic current density – after boiling in 10 M HCl (a – SEM image, b – EDX spectrum).

As boiling 10 M HCl dissolves most of the tin component from the anode slime, the resistant silver can become liberated. A silver rich area – marked in Fig. 10 – is shown in higher magnification in Fig. 11. The large silver particle virtually corresponds to a similar one seen in the raw anode slime in Figs. 3 and 6, however, the intensive leaching with boiling 10 M HCl has apparently converted the originally smooth surface into a porous structure by removing the soluble tin component from the agglomerate. The smaller crystals in the more heterogeneous looking surrounding area have also been transformed into a finer structure by the selective dissolution. While the leaching process with HCl is relatively slow even at high temperatures and high acid concentrations, the resulting porous structure will be advantageous for a faster reaction in the subsequent leaching step with nitric acid.

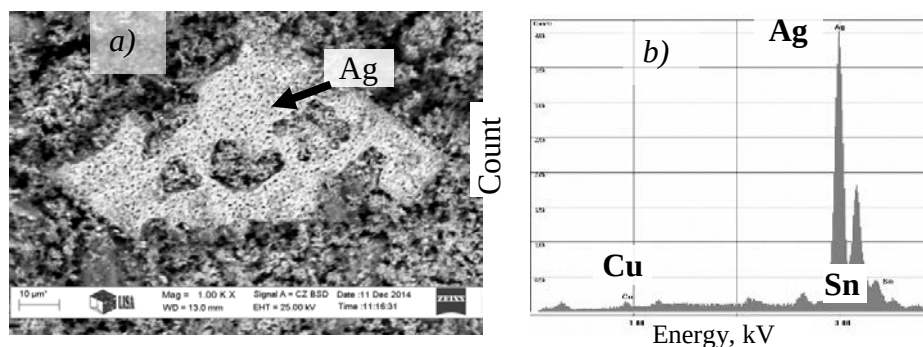


Fig. 11 Magnified SEM image (a) and a relevant EDX spectrum (b) of the residue of the anode slime after intensive leaching with 10 M HCl.

A similar picture is characteristic of the residue obtained from the slime produced with 1000 A/m² anodic current density after the HCl boiling step is shown by the SEM image and the corresponding EDX spectrum in Fig. 12.

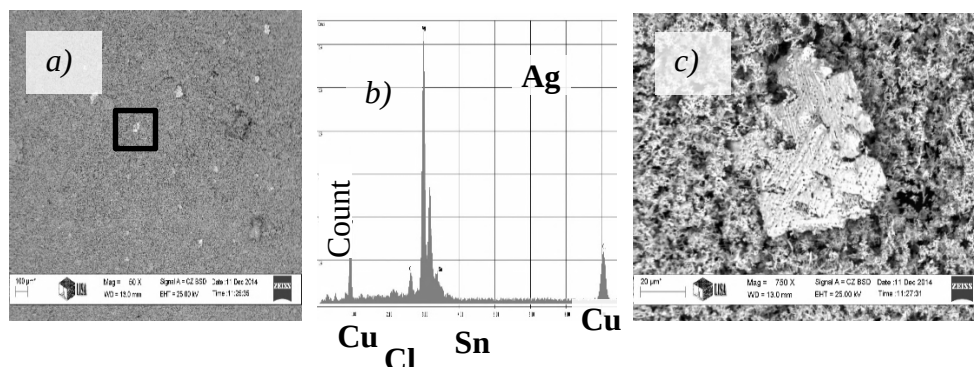


Fig. 12 Solid residue of the anode slime - produced with 1000 A/m^2 current density – after boiling in 10 M HCl (a – SEM image, b – EDS spectrum, magnified SEM image of the Energy, keV).

After the more or less selective hydrochloric acid leaching, the residue is enriched in silver, which can be efficiently dissolved in hot and concentrated nitric acid. This reaction is relatively fast because the oxidising power of nitric acid enhances the rate of electron transfer from the metallic particles of large specific surface produced by the selective dissolution in the first leaching step. As the elemental analysis of this residue was even less reliable than that of the raw slime, the results of the nitric acid leaching (Fig. 13) are given in terms of the dissolved masses of metals from the treated 0.5 g solid sample taken from the residue of the intensive HCl leaching in the reactor.

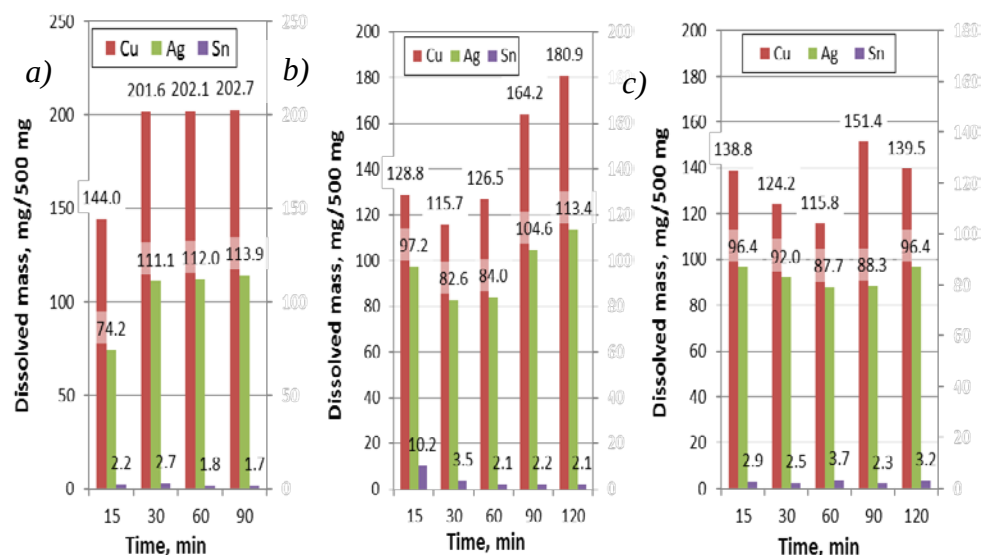


Fig. 13 Digesting the HCl -leaching residues of slimes produced with a – 100 A/m^2 , b – 500 A/m^2 , c – 1000 A/m^2 current densities with hot cc HNO_3 .

It can be seen that the tin and copper contents of the residues obtained from the high temperature 10M HCl leaching can be easily dissolved in hot and concentrated nitric acid. The lixiviated amounts of these metals are not increasing after the first 15 minutes of digestion in the reactor vessel. At the same time, the tin content of the residue from the HCl leaching is converted into a white $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ type precipitate and virtually no tin is entering the strongly oxidizing hot nitric acid solution. Finally just a minor fraction of the original slime mass is collected as a refractory precipitate. Both the tin-chloride solution from the first leaching step and the silver-copper nitrate solution from the final digestion step can be used for metal extraction by standard techniques. For producing pure tin from the hydrochloric acid solution, it is necessary to use solution purification by selective sorption in an organic phase, like controlled anion exchange by a strongly basic resin [9], or selective precipitation. Controlled potential electrowinning may also be used for a preliminary removal of copper, followed by the cathodic deposition of pure tin [2]. The silver-copper nitrate solution can be processed by precipitating silver after the addition of sodium-chloride. Silver chloride can be converted into the metal by the commonly practiced methods. Copper from the residual nitrate solution can be electrodeposited.

4. Conclusions

The anode slime produced in the electrorefining of lead-free soldering tin alloy waste materials contain high amounts of tin and the alloying elements, most commonly silver and copper. The composition of the slime may slightly differ according to the current density applied in the electrolysis utilizing the 1 M HCl – 10 g/dm³ Sn electrolyte solution earlier optimized for the electrorefining procedure. Hydrometallurgical processing of this secondary residue can be based on a two-step leaching process. The experimental results reveal that leaching with boiling 10 M HCl in a closed reactor is relatively efficient; however copper is significantly dissolved together with tin from the metallic components of the slime. A close to 90% tin recovery can be achieved within 4 – 5 hours of leaching. To assure also selectivity in leaching tin from the anodic slime, it is advisable to use the moderately aggressive conditions of gentle boiling in 6 M HCl solution and applying a L/S ratio not higher than 5 cm³/mg. While the relative amount of the applied HCl solution hardly affects the recovery of tin, it has a strong effect on the dissolution of copper. Any copper entering the hydrochloric solution together with tin requires subsequent removal by modern or conventional solution purification methods. The subsequent leaching step with hot concentrated nitric acid is efficient in dissolving silver and the remaining copper from the first residue. Separation of silver and copper from the nitric solution is straightforward by the chloride precipitation procedure. Reduction of silver chloride in aqueous media or decomposition at high temperature can result in the recovery of this valuable component. Recovery of tin from the chloride solution is possible by recently developed electrolytic processes. The final copper containing nitrate liquor can be decopperized by electrowinning. Thus the electrorefining of tin based lead-free soldering waste materials can be devised in an environmentally safe way leaving no secondary wastes behind.

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