Recovery of Tin from Wave Solder Slags generated from PCB Manufacturing

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Abstract

The recovery and purification of tin from tin solder slags are investigated by an electrorefining process in a tin(II)- sulphuric acid medium as electrolyte. Different variables which could affect to the tin deposition onto the cathode are considered: current density and electrolyte flow. Primary results are used in long term period time tin electrorefining investigations using further tin-metals alloys. The purity of the deposited tin can increases from 64.4 % to 99.93 %, being feasible the recovery of accompanying valuable metals which concentrated in the anodic slimes. Recovered tin is casting in ingots. The results obtained from this investigation are using today in the development of a demonstration tin electrorefining plant.

Keywords: Soldering waste. Tin solder slags. Tin electrorefining.

1. Introduction

One of the nowadays sources for recycling tin is the treatment of tin scrap, also so-called tin soldering scrap, materials which are produced in the tin baths and are composed by a variety of metals beside tin. Also, different tin-alloys are used as solders in the manufacture of printed circuit boards (PCBs) by wave soldering, being the various solder scraps formed by reaction of the liquid solder with the atmospheric air, they also contained a variety of metals beside tin. The price of some of these metals, i.e., tin (13,826 €/Tm), silver (500 €/kg), copper (5,618 €/Tm), lead (1,753 €/Tm), etc., and their concentrations in the scrap make of interest to investigate a technology for the recovery and profit of such metals. Pyrometallurgical refining may be one of the options, but in the case of these tin materials, the presence of accompanying metals make this option not fully advantageous due to its multi-stage characteristics, not high efficiency and high cost, against, electrorefining technologies can be the solution to save these disadvantages, primarily final purity of the electrorefined tin and the possibility of the recovery of valuable metals from the anodic slimes, and in one step.

A tin-tailored electrorefining process entails:

a) electrochemically dissolving tin from impure tin anodes into a tin(II)-suitable electrolyte, and

b) selectively electroplating pure tin from the electrolyte onto cathodes,

with two defined purposes:

1) it produces tin essentially free of unwanted impurities, and

2) it is possible to separate valuable metals and recover them as byproducts.

In the electrorefining operation, the application of an electrical potential between a tin anode and a tin cathode in a tin(II)-bearing electrolyte produces the next reactions:

i) tin is electrochemically dissolved from the anode into the electrolyte producing dissolved tin and electrons:

$$Sn^0 \rightarrow Sn^{2+} + 2e^- \quad E^0 = -0.136\ V \qquad (1)$$

ii) the electrons produced by the above reaction are conducted towards the cathode through an external circuit and power supply,

iii) the dissolved tin in the electrolyte migrate to the cathode basically by diffusion,

iv) the electrons and the dissolved tin recombine at the cathode surface to produce tin metal which plates on the cathode, accordingly to:

$$Sn^{2+} + 2e^- \rightarrow Sn^o \quad E^0 = +0.136\ V \qquad (2)$$

In equations (1) and (2) the formation of the various tin-chlorocomplexes was not considered. Tin diffuses and convect to the cathode due to two phenomena: *i)* their high concentration at the anode surface, and *ii)* their low concentration at the cathode surface.

In the particular case of tin, the electrolyte media for the above purposes are HCl, H_2SO_4 and even alkaline solutions [1-4].

This work presented data, obtained at a laboratory scale, about the purification of three tin alloys, with different compositions, using tin electrorefining in sulphuric acid medium. This medium was primarily chosen to facilitate the solutions handling and due to the lower price of this acid with respect of that of hydrochloric acid. These data are using today to develop a demonstration pilot plant.

2.Experimental

Three types of tin alloys were used in the electrorefining investigations. The composition of these alloys, and thus of the anodes, are shown in Table 1.

The electrolyte was made up by dissolving tin(II) sulphate in sulphuric acid. After near 70 hours of mixing, the mixture was filtered and a solution containing 0.22 g/L tin in 85 g/L sulphuric acid and 1 g/L thiourea (to control the crystalline growth) was used as electrolyte in further experiments.

Table 1. Composition of the tin alloys used in the investigation.

Element	Alloy 1	Alloy 2	Alloy 3
Sn	95.9	89.9	64.4
Ag	2.9	2.3	<0.05
Pb	0.32	7.4	35.5
Cu	0.79	0.47	0.13
Ni	0.036	0.021	<0.001
Sb	<0.05	<0.05	<0.05
Bi, Fe	<0.01	<0.01	<0.01
Zn	<0.002	<0.002	<0.002
Cd, In, Ge	<0.005	<0.005	<0.005

All the values in %

All the chemicals used in the investigation were of AR grade, whereas metals in solution were analyzed by AAS or ICP spectroscopies.

Figure 1 showed the installation used in this investigation.

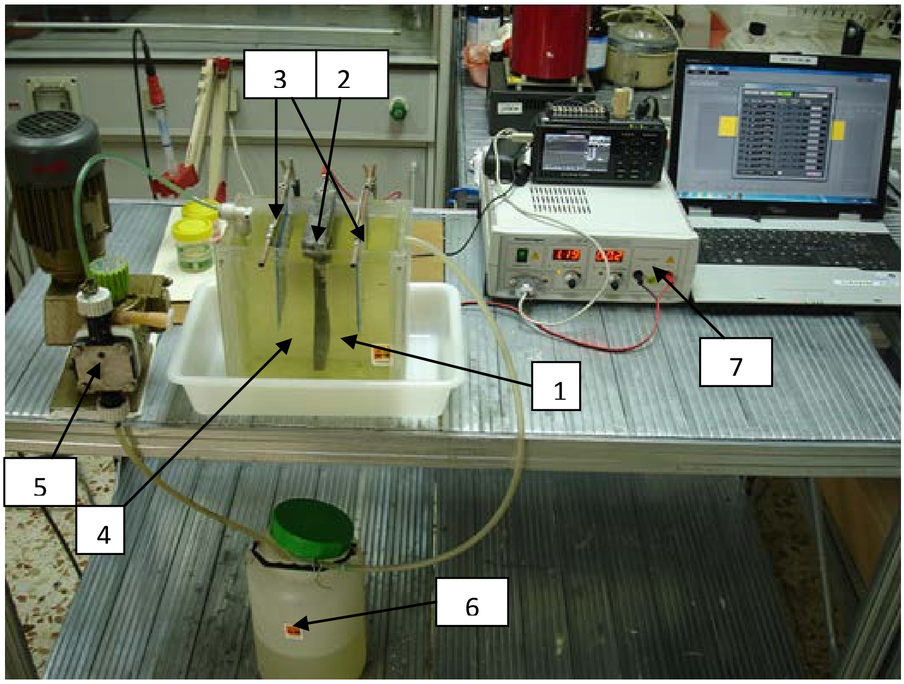

Figure 1. General view of the device used for tin electrorefining experiments.

It consists in an electrolytic cell (1) in which the anode (2) and two cathodes (3) were immersed in the electrolyte (4) which was pumped (5) from the storage tank (6) to the cell. A power station (7) was used to supply current to the system, where the anode and the cathodes were connected by copper bars.

Whereas the cell was filled with 3.84 L of electrolyte, the anodes had the composition shown in Table 1, with dimensions of 14x11x2.5 cm with a weight around 3 kg; the cathodes with a dimension of 15x11x0.1 cm and 200g weight had 99.83 % tin content, and they were separated from the anode near 4 cm, because previous experiments showed that less distance produced dendrites, and bigger ones produced non-uniform tin deposits. Based in the cathodes dimensions, the cathodic area facing the anode was of 330 cm^2.

3. Results and discussion

3.1. Electrorefining of alloy 1

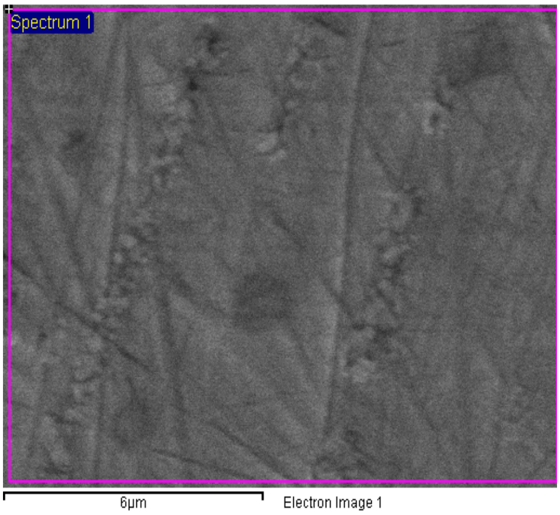

Figure 2 showed an aspect of this alloy, mainly composed of tin, silver and copper.

Figure 2. Micrography of alloy 1.

Tin is uniformly distributed, whereas silver and copper formed agglomerates of different morphologies, mainly Sn/Ag and Sn/Cu.

Experiments performed during 24 h, at various current densities (54.5-109.1 A/cm^2) and electrolyte flow of 10 L/h, showed that as this variable increased, the quality of the deposit also increased in terms of compactness and homogeneity.

The tin composition of the resulting deposits varies from 99.90 % at 68.2 A/m^2 to 99.95 % at 109.1 A/m^2, with rates of tin deposition ranging from 0.44 to 2.15 g/h for current densities of 54.5 to 109.1 A/m^2, respectively.

Varying the electrolyte flow from 2.5 to 10 L/h, it was shown, that an increase of this variable produces a decrease in the rate of tin deposit in the cathode, i.e. 2.15 g/h at 10 L/h against 2.39 g/h at 2.5 L/h, attributable to a lesser residence time of the electrolyte solution in the cell as the flow increases, though the purity of the deposit varies, 99.95 % at 10 L/h and 99.93 % at 2.5 L/h. Other parameters used in these series of experiments were: current density 109.1 A/cm^2 and experiment running time 24 h.

Taking into account the above results, it was shown that the best parameters for the electrorefining of this alloy are: current density 109.1 A/m^2 and electrolyte flow of 5 L/h., and with this fixed parameters, experiments were run for large period time. The results of these series of experiments were summarized in Table 2.

Table 2. Results obtained in the electrorefining of alloy 1.

Test	Time, h	Tin purity, %	Tin deposition, g/h
1	144	99.96	2.33
2	149	99.96	2.39
3	192	99.96	2.23

Regarding the formation of anodic slimes, which is inherent to all the electrorefining operations, in the present case, they presented the composition showed in Table 3 after near 850 h of the whole operation, with a production of 0.10 kg of slimes for every kg of purified tin.

Silver can be recovered from the slimes by a leaching-cementation operation [5].

Table 3. Composition of the anodic slimes formed in the electrorefining of alloy 1.

Element	%
Sn	41.1
Ag	34.2
Cu	9.1
Pb	0.9

3.2. Electrorefinign of alloy 2

This alloy formed by tin, silver and lead presented the morphology shown in Figure 3.

Tin is the main element, being lead concentrated in given zones of the material. Silver is distributed in a heterogeneous form.

In this case, all the experimentation was carried out in a sole test, which was run for near 860 h, with the operational parameters fixed by the main results derived from the tests carried out with alloy 1. Thus, the operational parameters were: current density 109.1 A/m^2, electrolyte flow: 5 L/h, separation between the anode and each cathode 4 cm.

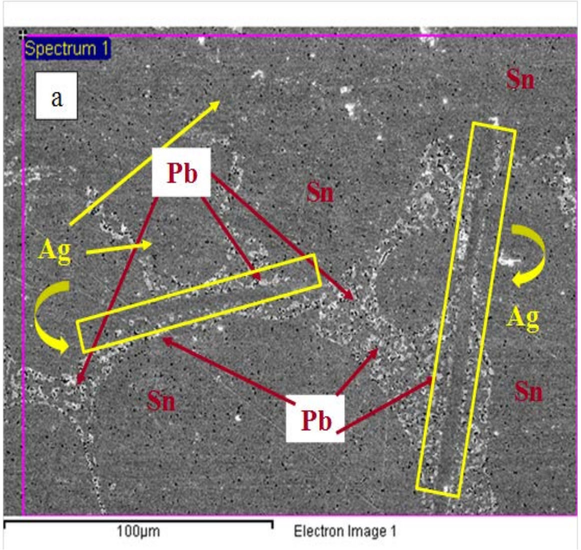

Figure 3.SEM image of alloy 2.

Table 4. Composition of the anodic slimes formed in the electrorefining of alloy 2.

Element	%
Pb	49.9
Sn	15.1
Ag	13.5
Cu	3.8

After the running time, the deposited tin was analyzed for a 99.93 % tin content and less than 0.05 % for lead and 0.005 % of silver and copper. The rate of tin deposition was 2.89 g/h, whereas the anode slimes had the next composition (Table 4), with a production of 0.19 kg of slimes for kg of deposited tin. XRD analysis of the slimes showed that they were composed by Sn-Ag-Cu intermetallics and $Cu_{6.26}Sn_5$, lead is present as anglesite ($PbSO_4$), being the presence of SnO_2 also detected. Figure 4 showed a typical image of the as-obtained slimes.

Silver can be recovered from these residues by the leaching-cementation operational sequence, leaving both tin and lead undissolved in the residue.

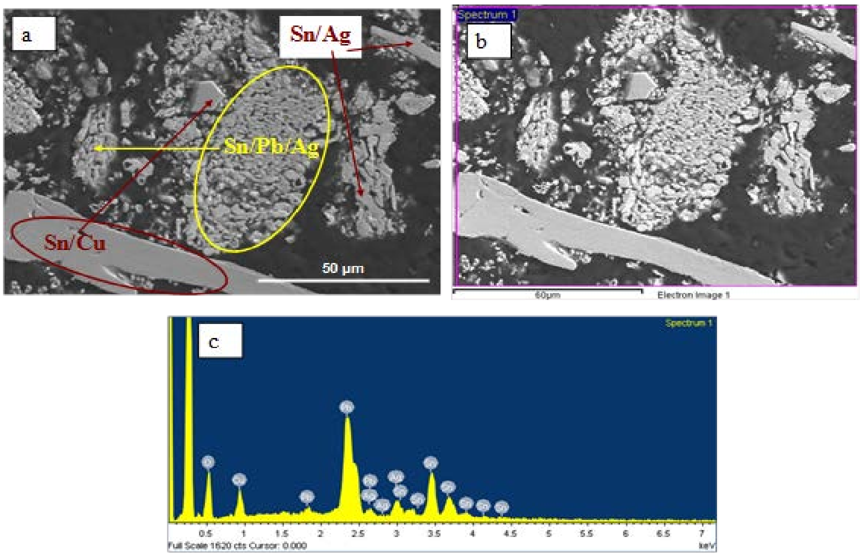

Figure 4.SEM images and EDX analysis of the anodic slimes resulting in the electrorefining of alloy 2.

3.3. Electrorefining of alloy 3

This is a microporous alloy in which tin is homogeneously distributed in the material, being lead found as globular particles (Figure 5).

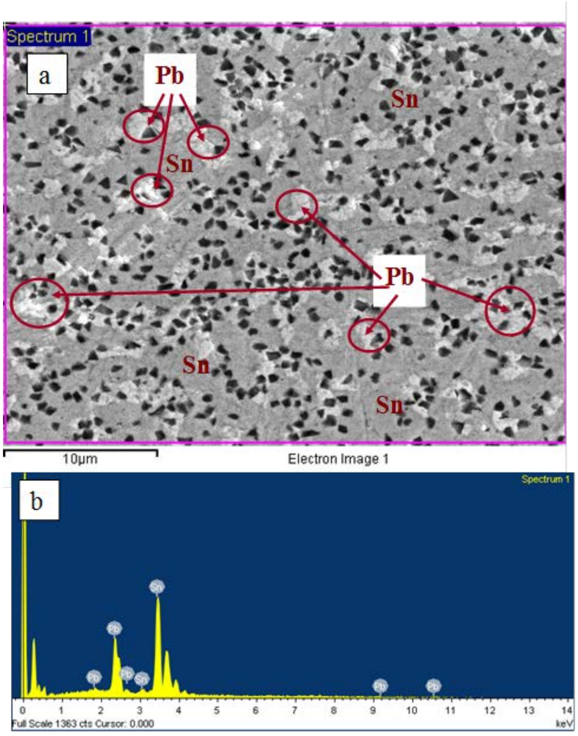

Figure 5. a) SEM image of alloy 3, b) analysis by EDX of the different phases.

In this case, the continuous running time for the electrorefining test was of 264 h, with the operational parameters fixed as in Table 5.

Table 5. Operational parameters of the electrorefining test on alloy 3.

Current intensity	Current density	Electrolyte flow	Cathodes-anode separation
120 A	109.1 A/cm^2	5 L/h	4 cm

In this test, the rate of tin deposition was of 3.86 g/h, with a final tin purity of 99.93 % in the deposited metal, and 0.002 % copper and 0.029 % lead. The material deposited in the cathodes is characterized by the formation of huge laminar tin, with no dendrites formation (Figure 6).

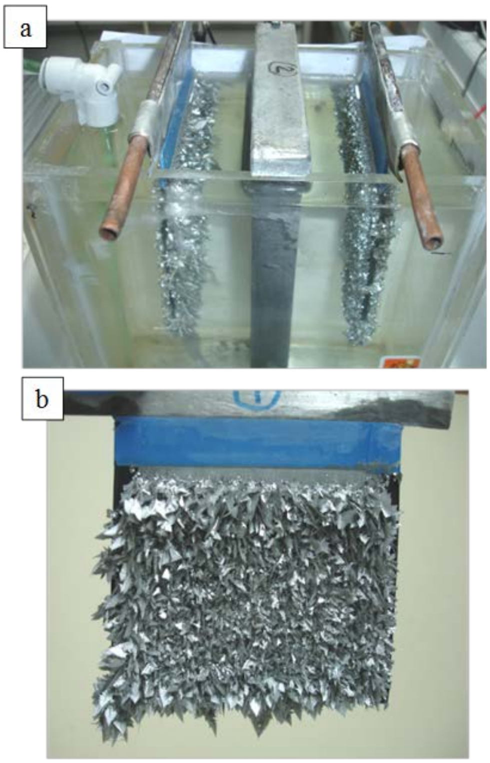

Figure 6.Tin deposits resulting in the electrorefining of alloy 3.

The anodic slimes produced (0.84 kg per kg of deposited tin) in this test showed an important lead content (76.6 % as $PbSO_4$), together with 13.0 % tin (mainly as SnO_2, but with presence of metallic tin and tin sulphate). Lead can be recovered from the slimes using a pyrometallurgical operation.

4. Conclusions

Tin is purified from the various tested alloys using an electrorefining operation with purities summarized as in Table 6.

Table 6. Tin purification in the electrorefining of the tin alloys.

Alloy	Initial tin purity, %	Deposited tin purity, %
1	95.9	99.96
2	89.8	99.93
3	64.4	99.93

Based in the results obtained from this work, a demonstration plant is now under development, and consisting in six sections: *i)* anode production, *ii)* electrorefining plant, *iii)* electrolyte circulation, *iv)* cathode production, *v)* melting and ingot casting and *vi)* anodic slimes treatment plant. A schematic flowsheet of the plant is shown in Figure 7.

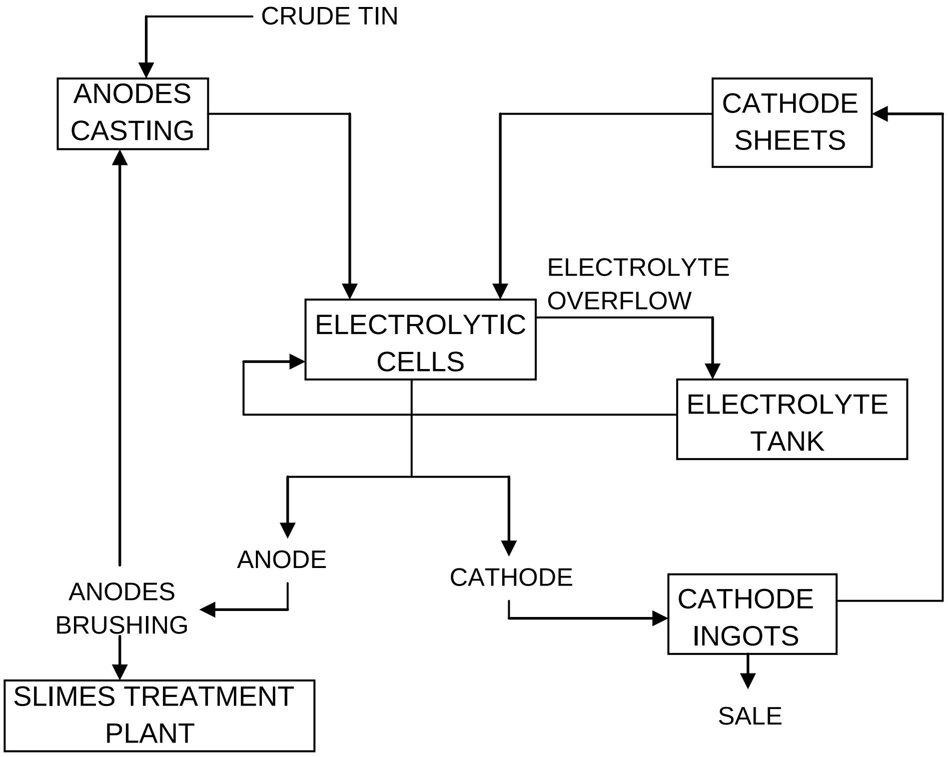

Figure 7. Schematic flowsheet of the projected tin electrorefining plant.

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