ELECTROLYTIC RECOVERY OF TIN FROM ELECTRONIC COMPONENT INDUSTRIAL WASTE[1]

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Abstract

The manufacture of components for the electro-electronic industry, such as capacitors and resistors, generates waste from leftovers and process non-conforming parts (e-scrap). Among these residues there are pieces of tinned copper-plated iron wire. The present work aims at studying the possibility of electrolytic recovery of tin from this residue in a basic aqueous medium at room temperature. Using a solution of sodium hydroxide as an electrolyte, and a predetermined voltage, recovery of metal with good purity was effective. A thermodynamic study of the dissolution and deposition of the tin under the process conditions, made with the aid of the thermodynamic software tool FactSage, preceded the work.

Key words: Electrolytic tin; E-scrap; Thermodynamics.

RECUPERAÇÃO ELETROLÍTICA DE ESTANHO A PARTIR DE RESÍDUOS DA FABRICAÇÃO DE COMPONENTES ELETRÔNICOS

Resumo

A fabricação de componentes para a indústria eletro-eletrônica, tais como capacitores e resistores, gera resíduos provenientes de sobras de processo e de peças não-conformes (sucata eletrônica). Dentre estes resíduos têm-se pedaços de arame de ferro cobreado e estanhado. O presente trabalho tem como objetivo estudar a possibilidade de recuperação eletrolítica do estanho deste resíduo em um meio aquoso básico, na temperatura ambiente. Utilizando-se uma solução de hidróxido de sódio como eletrólito e uma voltagem pré-estabelecida, foi efetivada a recuperação do metal com uma boa pureza. Um estudo termodinâmico da dissolução e deposição do estanho nas condições do processo, feito com o auxílio da ferramenta computacional FactSage, precedeu o trabalho.

Palavras-chave: Estanho eletrolítico; Sucata eletrônica; Termodinâmica.

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[1] *Technical contribution to 67th ABM International Congress, July, 31th to August 3rd, 2012, Rio de Janeiro, RJ, Brazil.*

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1 INTRODUCTION

Technological development has led to a continuous introduction of products from the electro-electronic industry in the market. This fact leads to the rapid obsolescence of older equipment, which have shortened their life cycle,(1) creating the necessity of making a greater amount of new electronic circuits for these products.

Electronic circuits are composed mainly of printed circuit boards (PCB) that provide the physical support for electronic components (mounted later), conductive tracks and electronic components. Like several other studies,(2-5) which have been made in recent years with the aim of recovering metals from electrical and electronic industry waste – mainly precious and non-ferrous metals – an earlier study by this group research, used the residue from the manufacture of these boards as an object of research.(6)

The manufacture of electronic components such as capacitors and resistors – an essential part of the circuit –, in turn, also generates waste from processing and parts out of specifications. Among the wastes are the disposed tinned copper conductor wires. These circuit elements located on the ends of the electronic components have the function to conduct electricity and to promote the coupling of the parts, by welding, with the printed circuit boards.

Many of these terminal conductors are made of tinned copper. Today, for reasons of cost, may also be composed of a core of ductile iron or low carbon steel with a prior electrolytic copper cover. Subsequently, on the copper layer, an electrolytic deposit of tin is made. The function of the tin layer on the conductor is centered on the use of some good properties like high electrical conductivity and good chemical resistance to atmospheric agents presented by this metal at room temperature. In addition, tin has the property of forming bonds with most metals – which provides a good coupling of electronic components to the printed circuit board by soldering with Sn/ Pb alloy.

Tin is a relatively scarce metal and its mineral deposits are mostly low grade. Due to shortage and demand for various applications, its value has remained high in recent years. Because of this, the recovery of metal tin scrap unites the economic interests to the environmental concern – considering that this is a non-renewable natural resource.

Several studies have been developed in recent years aiming at the *hydrometallurgical* recovery of tin, with lead or copper from electronic waste.(7-9) However, if they are put into operation, some of these processes are likely to generate solid or liquid waste to be treated. This fact, in an industrial environment – given the interest in enforcement of environmental legislation and a focus on cleaner production – can be crucial to the practical and economic viability.

The *electrolytic* processes for recovery or purification of metals, on the other hand, have the potential to be environmentally friendly. This is due to the use of a ‘cleaner’ energy (at least at the point of use) and to the use of the same electrolyte solutions in a number of recovery cycles. This results in less generation of waste for treatment, purification or correct landfill. Moreover, in contrast, the availability and cost of electrical energy and the need for high efficiency of the recovery process must be taken into consideration.

Under these circumstances, even in view of the good price of tin on the LME, compared to other methods, its recycling through conveniently adjusted electrolytic processes can offer economic and environmental advantages.

In view of the foregoing, the present work aims at studying the possibility of electrolytic recovery of tin, in a basic medium, experimentally, from a residue consisting of pieces of tinned wire (residue from the manufacture of electronic components or e-scrap). A thermodynamic study, performed with the assistance of a computational thermodynamic tool, evaluating dissolution and deposition of tin on the process conditions, was undertaken prior to the experimental work.

2 MATERIALS AND METHODS

2.1 Electronic Scrap

The present study employs a residue from the manufacture of industrial electronic components. The residue consists of pieces (tips) of soft iron wire, approximately 3.0 cm long, electrolytically coated with copper and tin. The residue consists of left over from processing or non-compliant material (Figure 1).

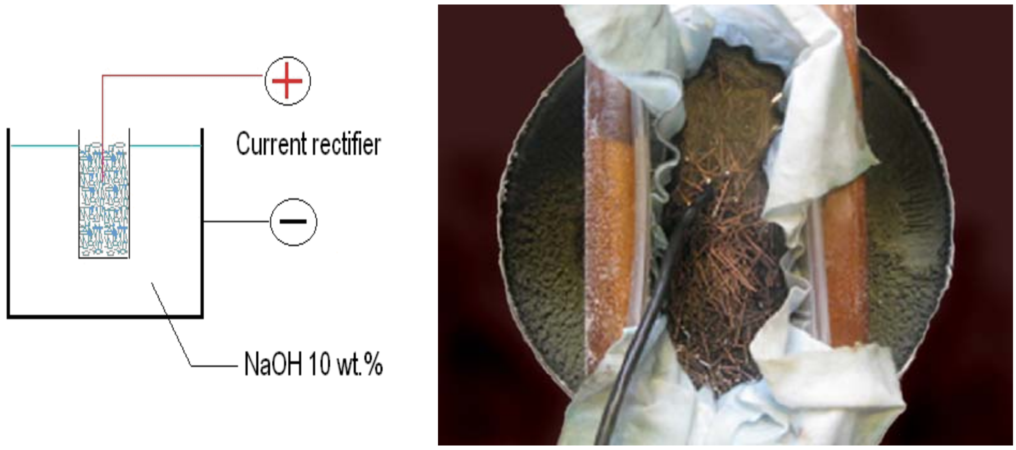
Figure 1. Waste of tinned copper wire.

2.2 Thermodynamic Process Analysis

A thermodynamic evaluation of the recovery process of the tin residue was made with the aid of computational thermodynamics.
The commercial software used in this work is called FactSage, version 6.2. It has been described by BALE in the literature.(10) The following database allowed performing the simulation: Fact53 – FactSage compound database (2010). This database contains properties of solid phases, the aqueous phase containing dissolved substances and ions and also constituents of the gaseous phase.
In the simulations, the establishment of the fundamentals for the treatment of the residue on theoretical grounds was tried. The main conditions applied to the aqueous thermodynamic system aim to reflect those of the experimental process, so that electrochemical reactions of dissolution and deposition of tin and other substances subject of this study can be examined. The tin oxides have been removed so that the strong tendency of superficial oxidation of the metal does not mask the results of the simulations.
The simulations were limited to the temperature of 25°C. In the system, besides the presence of 1 kg of water, there was 10 g NaOH, 10 g of 10 grams of copper and tin.

2.3 Experimental Methodology for Electrolytic Tin Recovery

To remove and recover the tin residue, an electrolytic dissolution and precipitation procedure with an aqueous basic solution (pH > 7) was used. This medium is very convenient, because it inhibits the reaction of dissolution of other metals present in the system. For the tests, a stainless steel vat of about eight inches in diameter connected by means of a wire to the negative pole of a current rectifier was used. The container, therefore, had the function of the cathode of the electrolytic cell (Figure 2a).



(a) (b)

Figure 2. (a) Schematic diagram of the process; (b) cell upper view.

Inside the vat is suspended a rectangular perforated basket, made of polyethylene, electrically isolated, with approximate dimensions: 18 cm length by 8 cm wide and 17 cm height. In this basket, on a screen of synthetic fabric, the residue of tinned copper was deposited. The residue contained in the basket was connected to the positive pole of the rectifier through a copper conductor, thus serving as an anode (Figure 2b). The distance between the anode and cathode was varied, ranging 3 cm to 8 cm, because of the geometry of vat and basket.

As electrolyte an aqueous NaOH solution with a concentration of 10 wt.% was used.

The used voltage was 0.5 V and current of about 0.8 A. Maximum rated capacity of rectifier used was 15 A. The tests, carried out in batch, were performed at room temperature, around 25°C. Each test lasted 24 hours and used 2 kg of residue.

As mentioned, the residue containing tin is used as soluble anode of the electrolytic cell. Thus, tin dissolved through anodic oxidation is deposited electrolytically in the vat of stainless steel (cathode). In Figure 2b (top view of the experimental setup during the final phase of testing), spongy tin can be seen deposited on the walls of the cell vat.

The metal recovered was analysed in their main elemental constituents using optical emission spectroscopy (EOS).

3 RESULTS AND DISCUSSION

Initially the simulation results of the tests based on chemical thermodynamics are presented. Subsequently, the experimental results regarding the recovery of tin from two tests with the tinned wire waste are presented.

3.1 Thermodynamic Analysis

The simulation of the Sn dissolution and electrolytic deposition tests was based on an aqueous system subject to an atmosphere which is varied from an oxidizing to a reducing state.

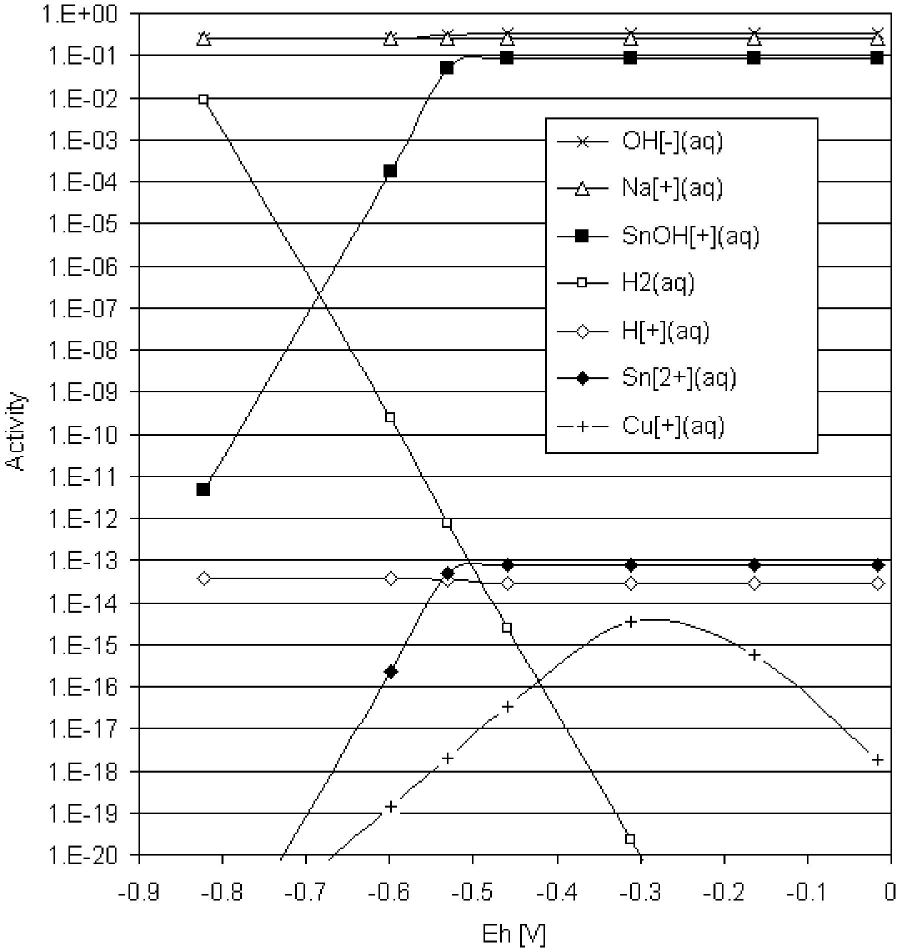


Figure 3. Activity of aqueous solutes as a function of the electrochemical potential (ref. H_2(g)).

The concentration of ions (or substances) in the aqueous solution as well as the amounts of condensed substances (phases) was determined for each of these different states of equilibrium. The corresponding values for the activities of the most abundant aqueous solutes can be seen in Figure 3 as a function of electrochemical potential of the system, E_h (reference state: H_2(g), 1 atm., 25°C).

Strictly, these concentrations correspond to specific regions of the electrolyte near the anode (anolyte) or the cathode (catholyte).

For regions where E_h value is low (cathode), the concentration of the constituents of the aqueous solution containing tin falls. In the contrary case (anode) the solution is rich in tin, indicating the dissolution of Sn metal into the electrolyte. As shown, the most abundant chemical species containing the metal is the monovalent cation $SnOH^+$ (aq.).

The amount of solids present in the system is also computed as a function of electrochemical potential (Figure 4).

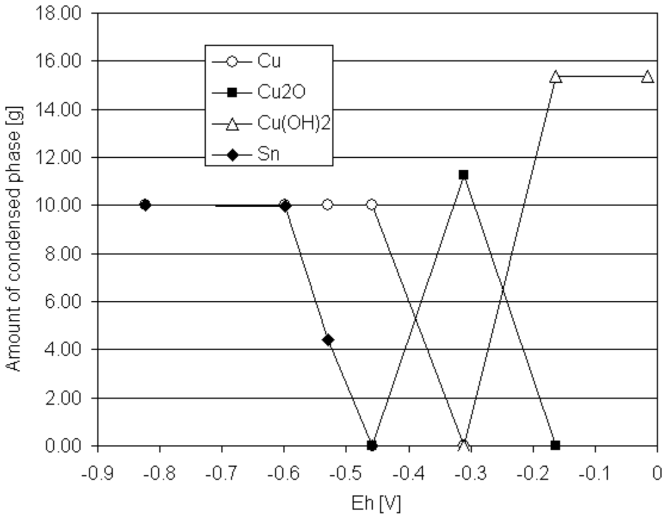


Figure 4. Amount of condensed phases as a function of the electrochemical potential (ref. H_2(g)).

As can be seen, in regions with low E_h value, Sn and Cu are in the reduced state (see the note, made further, about the presence of *copper* at the cathode). For higher potential values, while Sn vanishes (dissolved in the solution), the copper is present in the form of oxide or hydroxide, Cu_2O and $Cu(OH)_2$. This means that the copper from wire (anode) will *not* dissolve in the solution and therefore there will be *no* ions of this metal (in significant amounts) to be reduced at the cathode – as suggested before in the simulation.

3.2 Experimental Results

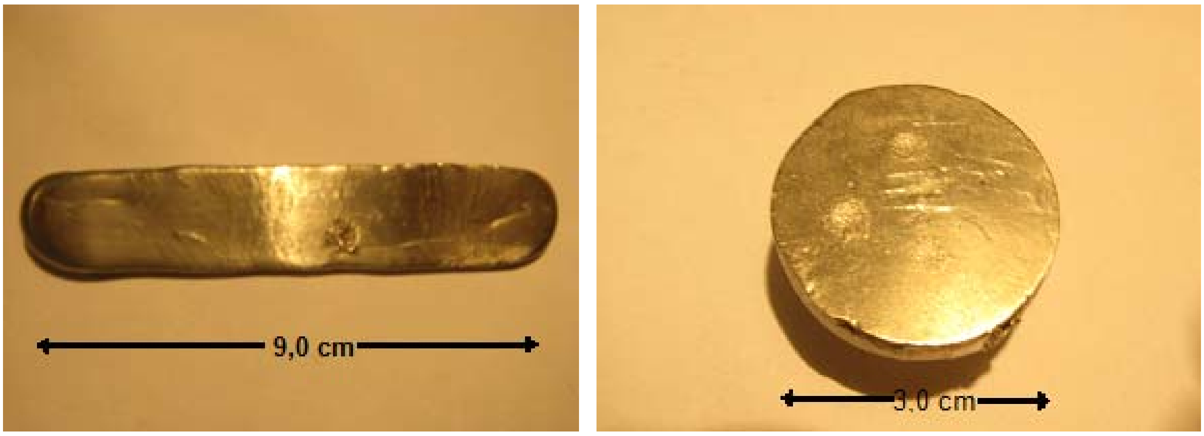
After the experimental electrolytic dissolution and deposition, a spongy mass of tin attached at the cathode was obtained. The metallic material was recovered by scraping the electrolytic vat of stainless steel. Alternatively, it can be deposited on movable iron electrodes (tin can be separated from the iron electrodes by heating them in an oven, making use of the fact that the melting point of the metal is very low, at 231.9°C).

The metallic tin, after washing with water and dried (at 60°C for 24 hours) was cast in the form of small metal ingots. The mass obtained by test is given in Table 1.

Table 1. Recovered tin mass

Test	Sn (g)
#1	44,74
#2	40,72

Figure 5a shows metallic tin from test #1, displaying the shape and dimensions of the mold (about 9 cm long by 0.35 cm thickness); whereas Figure 5b, shows the material from test #2, remelted and cast in a cylindrical steel mold (obtaining a specimen of approximately 3.0 cm diameter) more suitable for carrying out the chemical analysis.



(a) (b)

Figure 5. (a) Sn ingot from the test #1 after melting; (b) Sn from test #2 after remelting.

The chemical composition of the tin alloy obtained in the experiments can be seen in Table 2.

Table 2. Chemical composition of the tin alloy

Element	Sn	Sb	Fe	Pb	Cu	Cd	Al	Ag
wt.%	97.948	0.802	0.709	0.509	0.020	0.005	0.003	0.002

With this result, it is apparent that the tin produced has purity near 98%.

The marketed tin has ratings ranging from ‘A’ grade – which is tin with a purity exceeding 99.8 wt.% – to ‘E’ grade – or ordinary tin. It appears that under the conditions of this study, the recovered tin alloy has the E grade – a material suitable for the manufacture of alloys with other metals such as copper or aluminum.

3.3 Discussion of the Experiments

The electrolytic process used to recover the residue has the advantage of providing the metal *in a single step*. At the beginning of each reduction trial is necessary to maintain a low voltage, at around 0.3 V, considering that there is no tin dissolved in the electrolyte. Moreover, the process should be conducted so as to avoid an overvoltage – which leads to the generation of an undesirable amount of hydrogen and oxygen gases which result from the simultaneous decomposition of water from the electrolyte.

In this case, the electric efficiency is reduced, reducing the process yield, causing, at the end, the darkening of the copper layer (subjacent the tin) of the residues by the formation of an oxide of a dark color (as foreseen by the simulations).

It was not possible to determine the exact yield of the process; however, in view of the visual appearance of the waste, before and after tin recovery (Figure 6), it is clear that it is has a high level.

In the case of an industrial process using this technology, some actions can be taken so that there is an increase in the kinetics of the process. These include, for example, the use a higher electrolyte temperature and forced circulation, especially for the recovery of large waste quantities.

Figure 6. Visual appearance of the waste before tin recovery process (left) and after tin removal (right), with the typical color of copper.

4 CONCLUSIONS

The results show that it is possible to effect the electrolytic dissolution and deposition of tin covering copper wires (or steel wires coated with copper) in an alkaline medium with good chemical selectivity.

The process can be regarded as simple and of low investment. Having in sight both the high economic value of tin as well as the questions surrounding the use of cleaner technologies, this process can become very attractive.

In case of an increase in scale, complementary studies will be required to optimize the process.

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