Extraction of Tin from Lead Free Solder Dross

by

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Sn-Pb	Tn-Lead
Sn-In	Tin-indium
Sn-Ag	Tin-Silver
Sn-Cu	Tin-copper
Sn-Bi	Tin-bismuth
Sn-Zn	Tin-zinc
Cu	Copper
Al	Aluminium
Ni	Nickel
HCl	Hydrochloric acid
$C_6H_5O_7$	Citric acid
NiC_2O_4	Nickel oxalate
$Pb(C_2H_3O_2)_2$	Pb-acetate
PbC_2O_4	Pb-oxalate
$Pb_3(C_6H_5O_7)_2$	Pb-citrate
$C_2H_2O_4)$	Oxalic acid
$Sn_2Sb_2S_5$	Antimony sulphide

ICP	Inductively couple plasma
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectroscopy
LOI	Loss on Ignition
XPS	X-ray phoelectron spectroscopy
Wt.%	Weight per cent

Pengekstrakan Bijih Timah dari Bahan Buangan Pateri Bebas Plumbum

ABSTRAK

Tin dioksida (SnO_2) boleh wujud dalam bentuk perak kristal dan boleh diekstrak daripada pelbagai bijih lain dalam bentuk sulfida yang kompleks seperti stannite, cylindrite, franckeite, canfieldite, dan teallite. Pembuangan bahan buangan pateri tanpa plumbum adalah minimum serta tidak terurus dan kuantitinya meningkat setiap tahun. Bahan buangan ini perlu dilupuskan dengan cara yang betul, jika tidak ia boleh menyebabkan masalah alam sekitar. Jumlah sisa buangan yang besar ini boleh dijadikan sumber baru untuk penghasilan timah di negara ini. Timah sangat penting dalam pelbagai aplikasi seperti elektronik industri pembungkusan, automotif dan pembungkusan makanan. Dalam kajian ini, timah akan di diekstrak menggunakan asid hidroklorik, asid sitrik dan asid oksalik dalam rawatan larut lesap menggunakan pelbagai parameter disebabkan oleh kesan negatif kaedah konvensional seperti peleburan pada suhu tinggi, rawatan haba dan penuangan. Parameter yang mempengaruhi kadar kecekapan yang dicadangkan adalah seperti suhu, masa kacau, pH dan jenis asid. Keputusan optimum kaedah larut lesap telah berjaya menggunakan 0.3 Molar asid hidroklorik dengan masa pengacauan selama 12 jam pada suhu 60 °C. Proses penulenan SnO_2 diteruskan dengan kaedah elektrolisis kimia. Kadar kecekapan perolehan timah yang paling diperolehi selepas 8 jam elektrolisis dalam larutan timah klorida pada suhu bilik mencapai kadar kecekapan sebanyak 99.3% dan grafit digunakan sebagai anod. Ketulenan timah yang terhasil mencapai piawaian 99.7 % timah tulen β-Sn0.785 (PDF 01-075-9188) selepas 8 jam proses penulenan. Analisis mikrostruktur menggunakan SEM-EDX menunjukkan Sn yang terbentuk adalah dendrit yang kasar. Berdasarkan permukaan timah melalui ujian XPS, Sn yang tulen boleh diperolehi menggunakan kaedah penulenan. Keputusan Inductively Coupled Plasma (ICP) menunjukkan bahawa kepekatan Sn di dalam larutan berkurangan dari proses larut lesap kepada proses penulenan dengan kadar 22000 mg / L kepada 4000mg / L.

Extraction of Tin from Lead Free Solder Dross

ABSTRACT

Tin dioxide (SnO_2) can exist in crystalline silvery form and can be extracted from various other ores that occur in the form of complex sulfides such as stannite, cylindrite, franckeite, canfieldite, and teallite. Utilization of lead free solder dross is minimal and unmanageable, while its quantity increases annually. These wastes are needed to be disposed properly, otherwise it may cause a major environmental sustainable issue. The large amount of this waste can be a new source of tin production in this country. Tin is very important in many application such as electronic, automotive and food packaging industry. In this study, tin will be extracted using hydrochloric, citric acid and oxalic acid in leaching treatment using various parameters due to the negative effect of conventional method using pyrometallurgical method like state of the art smelters, thermal treatment and casting. Parameter affecting the recovery efficiency of the suggested method such as temperature, stirring time, pH and types of acid were investigated. Result shows that the optimum leaching conditions were achieved by using 0.3 M Hydrochloric acid for 12 hours stirring times at 60 °C. The purified solution was subjected to SnO_2 electrowinning. The most efficient recovery of tin was observed after 8 hours electrowinning, 0.5 A in tin chloride solution at room temperature with 99.3% recovery rate using graphite as anode. The achievable purity of tin nearby to 99.7% with had fulfil the standard technical requirement after 8 hours electrorefinning process with pure β-$Sn_{0.785}$ (PDF 01-075-9188). Microstructural analysis using SEX-EDX show the cathodic deposit is usually loose and rough dendrites for Sn. Thus, the result of tin surface via XPS analysis show, Sn^{2+} can be recovered using elecrorefinning treatment when concentration oxide layer was decreased. Results Inductively Coupled Plasma (ICP) show that the decreasing concentration of Sn from 22000 mg/L to 4000mg/L in solution after leaching treatment to electrorefinning treatment.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Tin oxide (SnO_2) or commonly known as metallic tin is one of the basic materials and the valuable multipurpose chemical compounds. Tin can exists in two form of allotropes referred as 'white tin' (beta (β) phase, metallic) and 'grey tin' (alpha (α) phase, semiconductor). The structure of β-Sn is body centered tetragonal with lattice parameters a= b= 0.5820 nm and c = 0.3175 nm (Abtew & Selvaduray, 2000).

Nowadays, most of SnO_2 was extracted from cassiterite. From this process, SnO_2 will be used to fulfil the requirement in its major applications such as for electronic packaging, industrial, medical system and communications. However, manufacturing of pure tin is very expensive. Malaysia's tin mines produced about 3,000 tonne/year during the past several years. Resources were depleted and ore grades were lower after more than 100 years of active mining operations. To meet the industry demand, tin concentrates from need to be improved other countries in Asia and Africa.

Solder production was the leading tin consuming sector in Malaysia, followed by tinplate and pewter. Tin also can be found as industrial wastes in the form of dust, dross, slag and etc. Solder dross is a waste product from manufacturing of printed circuit boards (PCBs) by wave soldering process. It is generated by reactions between liquid solder with air atmosphere and characterized by a large amount of metal solder (Lucheva et al., 2011).

These wastes are needed to be disposed properly, otherwise it may cause a major environmental and human health (Lim & Schoenung, 2010; Wilmoth et al., 1991). For example, tin dissolved in water take chemical reaction with organic acid in environment, forming a rather large toxicity organic tin. The main composition of lead free solder dross is tin and the elements such as nickel, silver, copper and zinc(Ma & Suhling, 2009). Thus, several recycling methods have been introduced to reclaim Sn. The methods are pyrometallurgical, hydrometallurgical and electrometallurgical method.

The main steps in hydrometallurgical consist of series of acid that removes of a substance from a solid via liquid extraction media. In this process known as leaching, the ore is washed with some suitable reagent (solvent) so that the main metal passes into its salt solution. This solution is separated and subjected to further treatment. There are many important parameters in leaching which are temperature, contact per area and solvent selection, agitation rate etc (Baral et al., 2014).

Recovery of Cu, Pb and Sn from PCBs scrap using electrochemical ion exchange and electrodeposition have been reported by Mecucci et al. (2002). Hydrochloric acid (HCl), Sulfuric Acid (H_2SO_4) and Nitric acid (NH_3) solutions are conventionally used in leaching treatment to prepare tin materials (Jha et al., 2012; Shin et al., 2014). Leaching by organic acids is the new attractive alternative eco-friendly technology for the metals removal due to the biodegradability of the organic acids. Organic acid dissolved metals by supplying both protons (i.e.,acidolysis) and metal-complexing anions (i.e., complexolysis) and metal complexing anions (Gadd, 1999).

Besides that tin also assimilated from waste using organic acid for example citric, oxalic and gluconic acid. Organic acids acid producing fungi *Aspergillus niger* have been used to recover Pb, Cu, Zn and other metals from fly ash (Bosshard, R.Bachofen, et al., 1996). Thus, it is shown that citric acid leaching treatment is significantly useful and effective to dissolve zinc oxide. The reaction of zinc and citric acid reaction as in Eq. 3 (Demir, 2006):

$$3ZnO(s) + 2C_6H_8O_7\,(aq) \rightarrow 3Zn_2+ + 2C_6H_5O_7(aq) + 3H2O \qquad (1)$$

Although organic acid are promising leaching agents, there are some restrictions in the selection of the organic acids beneficiation method which had some drawbacks that should be taken into consideration(Ma & Suhling, 2010). The advantages of organic acid leaching are very selective, acid plants have low capital cost, the method has few environmental hazards, leaching does not affect phosphate minerals, organic acid can be recycled and etc.

As a conclusion, many researchers have concluded that preliminary leaching of Sn with a solution of Hydrochloric acid (HCl) proved to be effective in substantially removing most of the metallic impurities(Jha et al., 2012). However, the strong acid is significantly hazardous to the environment and human society. The strong acid leaching treatment also has an economic problem due to a necessary use of expensive materials with corrosion resistance to strong acids, water rinsing of solder dross, and a special disposal treatment of used strong acid.

1.2 Problem Statement

Extensive research have been carried out to extract tin from wastes such aselectronic waste, solid waste and tin plates due to industrial application of tin. In previous studies, pyrometallurgical method consist smelting, roasting, converting and refining was carried out on electronic waste to recover nonferrous metals as well as precious metals from electronic waste. Pyrometallurgical processes have been proven to be more efficient for the extraction metals such as Ti, Zr, Nb, Ta, Mo and etc (Gonzalez et al., 2004). However, state of the art smelters are highly depended on the investment. Furthermore, this thermal process usually produces polluting emissions and causes the loss of metals from scrap during combustions (Havlik et al., 2011; Ojeda et al., 2009b). Therefore, hydrometallurgical process will be studied with organic acid as a leaching reagent.

1.3 Objectives

The prime objective of this project is:

a) To study the possibility in developing new method to extract tin from solder dross by using acid leaching method.

b) To study the effect of optimum parameter and further investigate the proof of concept for a better and more reliable high volume process.

c) To study the properties of tin in solder dross extracted from hydrometallurgical method.

1.4 Scope of the study

In this project, hydrochloric acid, citric acid and oxalic acid was used as a leaching reagent. The parameter that will be varied are concentration of acid solution, temperature and stirring time. The tin obtained will be characterized based on characterization based on the chemical contents, morphology and the effect of acid concentration, leaching temperature and reaction time of solder dross.

CHAPTER 2

LITERATURE REVIEW

2.1 Tin

Tin is a basic raw material that is widely used in many applications such as electronic packaging, automotive and sports industry. Tin is a chemical substances with the symbol Sn. Tin can exist in two phase which is beta (β) phase in metallic form and alpha (α) phase in semiconductor. Tin is a very soft metal and good in ductility. Tin can be found in various application and can be produce in various shaped (Figure2.1).

Tin is alloyed with other metal to enhance the hardness and mechanical workability, or to improve the electrical properties (Evans, 1994). Tin generally can be extracted from tin ore. It is also found in small grain or particle in mineral and rock fragments (Falcon, 1989).

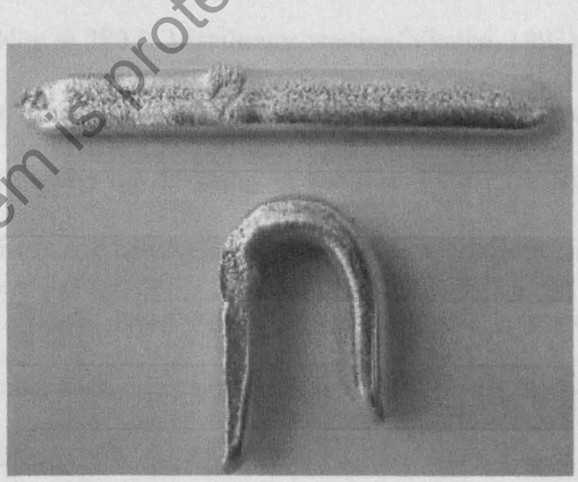

Figure2.1: A molten and a bent tin bar (R., 2006)

Tin relatively is an inert metal which does not react with air, water, nitrogen, hydrogen or weak electrolytes (Hedges, 1960). Tin dioxide (SnO_2) is a very stable oxide layer. It slowly formed during ageing in air and also known as 'dross' in soldering industry. It formed as a skin on the molten tin based solder. Utilization of chemical fluxes is important to ensure good wetting of surfaces. Tin will form in two conditions such as an intermetallic compounds rather than solid solutions. The first condition is when the crystal structure of the solvent remains unchanged by addition of the solutes, where the second conditions is when the mixture remains in a single homogeneous phase (Abtew & Selvaduray, 2000).

2.2 Application of Tin

Tin is widely used in an electronic application such as a solder. Two types of solder currently used in electronic packaging industry such as leaded solder and lead free solder dross. Pb provides many technical advantages such as Pb reduces the surface tension of pure tin which is 550mN/m at 232 ºC and the lower surface tension of 63Sn-37Pb solder (470mN/m at 280 ºC) facilitates wetting(Vianco, 1993). Besides that, it can be used as solvent metal and enable for joining other constituents like Sn and Cu to form intermetallic bonds rapidly by diffusing in the liquid state. However, Environmental Protection has eliminate and restrict the use of Pb due to environmenetal and toxilogical concerns. To fulfill industry requirement, large number of Pb-free alloys containing tin as major elements have been suggested such as Sn-Au, Sn-In, Sn-Ag and Sn-Bi (Abtew & Selvaduray, 2000).

2.3 Tin extraction method

Tin can be extracted via mineral ore and secondary sources. Mineral ores are naturally occurring rocks that provide an economic starting point for the extraction and manufacture of metals for a huge variety of purposes. Two type of mineral such as solid metallic and non solid metallic. Secondary sources of tin are likely to become an even more important component of supply, especially in the United States which has no tin mines. Commonly, they recover the tin from reclaiming process. The process is made up of a series of chemical and electrical steps which separate, purify, and recover the steel and tin (Armarego & Chai, 2013).

2.3.1 Extraction from ore

Tin dioxide (SnO_2) generally can be extracted from the ore such as cassiterrite mineral and main tin bearing granite deposits (El Deeb et al., 2015).Tin granites globally host major global deposits of tin such as tungsten, uranium, lithium and other critical metals such as indium, tantalum–niobium, and the rare earth elements. However, such tin deposits are relatively uncommon on a global scale, and tend to have formed in provinces that are specific in terms of their secular and geological setting.

Generally, over 95% of historic tin production has been derived from three major areas: Southeast Asia; the Bolivian Andes; and Southwest England, Germany and the Czech Republic in Europe (Lehmann, 2006). Recovery of tin from its ores depending on the type of the ore itself, oxide or sulfide. Each type of ore should be treated by the suitable technique according to its chemical composition (Habashi, 1997a).

2.3.2 Extraction from industrial waste

Nowadays, tin production also made from industrial waste. Industrial wastes is the waste produced by industrial activity which includes any material that is rendered useless during a manufacturing process such as that of factories, industries, mills, and mining operations (Dutra, 2006; Lin & Chang, 2006). Various typed of hazardous waste generated by industries such as waste batteries, electronic waste, waste X-ray films, MSW fly ash, petroleum spent catalyst and metal finishing industrial wastes in Table 2.1. Electronic waste contains a large number of toxic elements instead of Cu, Sn, Au, Ag, Ni, Al and Zn (Tuncuk et al., 2012).

Table 2.1: Types of dangerous wastes generated by industries and metal present(Jadhav & Hocheng, 2012)

Waste type	Metal in Waste
Waste batteries	Ni, Cd,Ag
Electronic waste	Cu, Sn,Au,Ag, Ni,Al and Zn
Waste X-ray film	Ag
MSW fly ash	Cu, Zn, Ni, Al, Cr and Pb
Petroleum spent catalyst	Ni, Co, Mo
Metal finishing industrial waste	Cr,Ni,Cu,Zn,Au,Ag and Cd

Previous research shows a variety of methods in extraction of tin from industrial waste such as thermal treatment, combustion, smelting and etc. Industrial waste is the residue left after the processing of industrial products. For example electronic waste, metal finishing industry wastes, battery waste, fly ash and etc.

Hydrometallurgy, pyrometallurgy, electrometallurgy and biohydrometallugy are the recent method of extraction of tin from electronic waste (Ahn et al., 2005; Kékesi et al., 2000; Oluwole et al., 1994).

2.3.3 Solder Dross

Extraction of tin from lead free solder dross may require a separation of the metals from waste materials prior to further processing. These waste material possess toxic elements such as heavy metals, which consists of Sn, Ag, Cu, Bi and Pb which are often used in electronic industries(Yoo et al., 2012). Yoo et al. (2012) reported that the major composition of lead free solder dross includes 87.8 % of Sn, 3.09 % of Ag, 0.85 % of Cu, 0.022 % of Bi and 0.021% of Pb as shown in Table 2.2.

Table 2.2: Chemical compositions of waste lead free solder dross (Yoo et al., 2012)

Elements	Mass (%)
Sn	87.8
Ag	3.09
Cu	0.85
Bi	0.022
Pb	0.021

Lead free solders dross produce from manufacturing of printed circuit boards (PCB's) by wave soldering process. It is generated by reactions between solder with and atmosphere, this characterized by a large amount of metal solder (Lucheva et al., 2011). Wave soldering is one type of soldering method. In this method, printed circuit board (PCB) assembly passes over a continuous wave of solders. The crest of the liquid solder wave touches and wet the exposed metallization of the assembly and solder joints form upon cooling (Saleh et al., 2001). Production of lead free solder dross depends on high value of electronics assembler. For example, if the factory running two shift per day and consumes 1000 pounds of solder per month, it will generate 400 pounds of dross per month(Larry, 2015).

The resulting product is a metallic tin and a particulate material referring which consist mainly of tin oxide, with traces of copper, nickel, germanium and silver oxides depending on the composition of the solder alloy. The "Dry Black", which was formed from Sn–0.7Cu–0.05Ni solder alloys, was supplied from wave solder processing dross by Nihon Superior Malaysia. Figure 2.2shows the raw material before heat treatment of lead free solder dross also known as "Dry Black"(Henao et al., 2015).The colour of the "Dry Black" is brown and the appearance of the oxide is as shown inFigure 2.2.

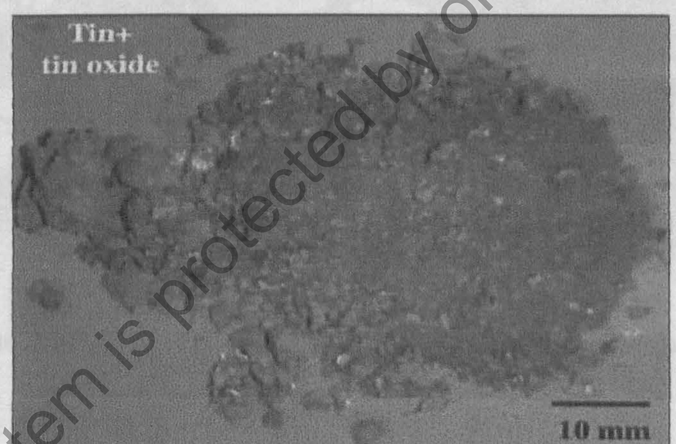

Figure 2.2:Raw "Dry Black" sample (Henao et al., 2015)

Henao et al. (2015) reported an experimental study of metallic tin recover from wave solder dross using mechanical attrition and chemical dissolution. The resulted indicates that the tin oxide covering layer was effectively reduced from the material over 53μm and the removed oxide was concentrated in particles less than this size. Moreover,