



# The processing of eWaste. Part 1: The preparation and characterization of a metallic alloy derived from the smelting of printed circuit boards

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## Synopsis

A brief overview is given of the issues regarding the processing of waste electrical and electronic equipment (WEEE). The printed circuit board component of WEEE is an exceptionally complex feed to possible recycling processes.

Scrap printed circuit boards were selectively smelted at 1 200°C to produce a metallic alloy. Iron and aluminium were found not to be part of the alloy. The alloy was characterized by SEM-EDS, and three phases were identified: alpha and delta bronzes, and a lead-rich phase. Calculations show that about 56 mass per cent of the alloy is the alpha phase, 35 per cent delta phase and 9 per cent lead phase.

A simplified approach using appropriate binary phase diagrams was used to derive a phase composition for the alloy. This was further backed by FactSage calculations, which showed that the simplified approach was appropriate for this alloy. The experimental findings and theory were found to agree well.

## Introduction

The disposal of waste electrical and electronic equipment—the so-called eWastes—has been recognized worldwide as an important issue. This is due to concerns about the leaching of hazardous metals such as chromium, mercury and cadmium from electronic and electric wastes in landfill. In more developed countries such as the United States of America and Western Europe the problem of eWaste has grown to the extent where legislation has been enacted, such as the Waste Electrical and Electronic Equipment (WEEE) legislation of the EU (European Union Directive 2002/96/EC).

Worldwide there is also an increasing appreciation of the limited nature of economically exploitable primary metal resources<sup>1</sup>. Hence there is more pressure for reclaiming metal values from obsolete items through appropriate recycling. Such secondary sources have not, in general, featured strongly in the South African base metals industry. So far the country has had access to adequate primary ores especially in precious metals, but also in

many base metals. In addition, while tonnages are relatively small, scrap material is often of unknown composition, and thus it requires additional chemical analysis, and possibly special treatment.

Obsolete scrap is often complex, requiring disassembly and identification of component materials. For instance, as copper is an undesirable element in steel, wiring harnesses and small electric motors need to be stripped from scrapped cars before the steel can be smelted. Alternatively, scrapped items can be shredded complete, or after partial disassembly to provide adequate liberation of various materials. This makes the separation problem more difficult, however.

In the case of electrical and electronic waste equipment it is necessary to remove items such as electrolytic capacitors which can contain dioxins when they have been in use, as well as batteries. Printed circuit boards (PCBs) can often be removed fairly intact after a simple disassembly process. This is worthwhile doing as they generally contain sufficient gold and other precious metals to make recovery economically viable.

A typical PCB consists of a glass reinforced thermosetting epoxy resin base, or a sheet of phenolic resin impregnated paper material. These are normally impregnated with bromine based fire retardants that result in an off-gas handling problem if the base material is subjected to high temperatures. The board will have one or more layers of thin copper material defining the conductive interconnects between electronic components. Components of various types are connected to the copper tracks by soldered connections. The solders have generally been 60–40 tin-lead types. Due

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to environmental considerations, there is a movement to replace the lead based solders by lead-free solders. These solders have higher tin contents than the older lead-tin alloys, which will increase the total material footprint<sup>2</sup>, and thus the need for recycling.

Boards may have contact fingers or other connectors that have gold plating to ensure reliable, corrosion-free electrical contacts. Precious metals such as silver, platinum and palladium may be used for special electrical contacts. A number of other materials and components are generally present such as a variety of thermoplastic polymers, steel fasteners, batteries, fans, etc. The electronic components themselves generally are complex in terms of their physical structure and the variety of materials used.

The PCBs are thus complex, heterogeneous assemblies containing many materials, including precious metals. However, the levels at which even the precious metals are present are high compared to normal ores. Table I illustrates analyses for PCBs, a personal computer and for electronic scrap. Boards vary considerably in their metal contents, depending on the application and the technology used, so the values in the table should be regarded as indicative.

In many respects metal recovery from scrap PCBs would parallel normal ore processing techniques. Firstly comminution would be required to obtain suitable liberation. Physical separation methods could be used to obtain one or more metallic concentrates. Steel components could be removed through magnetic separation, for instance. The metallic concentrates may go to pyrometallurgical methods of extraction such as smelting or sweating (which may obviate comminution). Alternatively, or in conjunction with the pyrometallurgical methods, hydrometallurgical methods could be used.

An alternative route is to use the PCB material directly as feed to a smelting furnace, where the polymeric materials would burn and so decrease the external energy input. Extensive treatment of the smelting product and off-gases is required. One example of such an integrated plant is Umicore in Belgium (see e.g. [www.umicore.com](http://www.umicore.com)).

Table I

### Approximate material compositions of typical printed circuit boards, a typical personal computer, and typical electronic waste

Material	Approx. material composition, mass%		
	PCB <sup>3</sup>	Computer <sup>4</sup>	eWaste <sup>5</sup>
Non-metallic	70		
Refractory oxides		25	30
Plastics		23	30
Copper	16	7	20
Solder	4		
Lead		7	2
Tin		1	4
Iron, ferrite	3	20	8
Nickel	2	1	2
Aluminium		14	2
Zinc		2	1
Silver	0.05	0.02	0.2
Gold	0.03	0.002	0.1
Palladium	0.01	0.0003	0.005
Other (Bi, Sb, Ta etc.)	<.01		

For local processors the cost of establishing such a refinery to treat secondary materials only is probably prohibitive. With an extensive local industry dealing with primary feed materials, it would seem advantageous to process suitable secondary materials together with the primary feeds. As the main metal in PCBs is copper it might be possible to make impure anodes, that could be accommodated in normal copper electrorefining, from eWaste by smelting. Aspects of this route were studied in the work reported here.

## Experimental

Waste computer motherboards were broken into smaller pieces and placed in a suitable alumina crucible. This was heated to 1 200°C in 20 minutes in an induction furnace under an argon atmosphere, and held at temperature for 25 minutes. By using a temperature of 1 200°C, the dissolution of iron and steel was minimized while plastics were charred and non-metallics collected as a slag. Cooling to room temperature under the argon atmosphere followed. A number of rods with diameter 3 to 4 mm were machined from the alloy ingot for use as electrodes.

Surface characterization of the electrodes was done using either a suitable optical microscope, or a Jeol JSM 6300 scanning electron microscope with Noran EDS (energy dispersive X-ray spectroscopy) facilities. Before surface characterization the electrode was washed thoroughly with distilled water. When analysing samples with the SEM, the samples were dried under high vacuum to remove entrained water. When EDS was used for phase analysis, typical counts were of the order of a few thousand.

## Results and discussion

Figure 1 illustrates a typical SEM backscatter image of the alloy electrode surface. The surface is clearly rather inhomogeneous with several segregated alloy phases visible. Three different phases may be seen. The alloy compositions of these phases were characterized using the EDS facility.

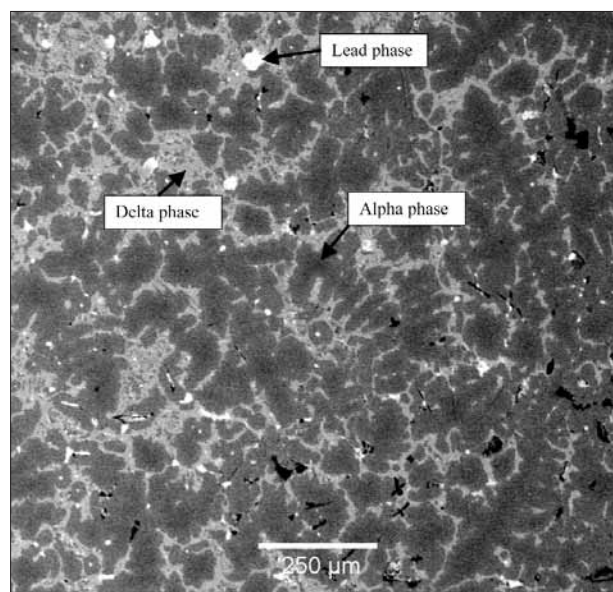


Figure 1—Backscatter image of the alloy surface, 30 keV

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The mid-grey phase in Figure 1 appears to be a high tin content bronze with a composition of about 63 mass per cent copper, 32 per cent tin and 3 per cent zinc. The darker phase has a lower tin content, having a composition of about 75 per cent copper, 13 per cent tin and 8 per cent zinc. The white phase is lead rich, with a composition of about 88 per cent lead, 6 per cent copper and 4 per cent bismuth. Of the precious metals gold seemed to associate mainly with the 13 per cent tin content bronze phase, and silver distributed in a ratio of about 60:40 between the lead rich and tin rich bronze phases. Nickel was distributed in a ratio of about 60:40 between the high tin and lower tin bronze phases. For the detailed analyses see Table II, below.

The formation of the phases identified experimentally may be understood by reference to the phase diagrams of the materials involved. An estimated metallic composition was derived from the published<sup>3</sup> typical composition data for PCBs. It was assumed that all non-metallic materials (70 per cent) would be lost during the smelting process. Due to the smelting temperature of 1200°C, it was assumed that steel components (3 per cent) were not part of the melt. Alloy analyses (Table II) show aluminium to be present at low concentrations only, although there is a substantial amount in the PCB composition. Given the high reactivity of aluminium, it is expected to report to the slag during melting. It was thus left out as a major alloy component. The results for the major elements are shown in Table III.

As a first approximation binary phase diagrams<sup>6</sup> for the three major metal combinations were considered. The copper-lead diagram (Figure 2) shows that these metals are mutually insoluble at room temperature. Cooling of the liquid mixture from 1200°C will allow the formation of a copper solid phase

Table II

### The elemental composition of various alloy phases identified in the metal

Element	Lead phase mass %	Bronze, low tin mass %	Bronze, high tin mass %
Ag	0.8	0	0.5
Al	0.2	0.5	0.1
Au	0	0.8	0
Bi	3.5	0.9	0
Cl	0	0.2	0
Cu	6.2	74.6	62.8
Fe	0.3	0.5	0.2
Ni	0.1	1.1	1.6
Pb	87.9	0.6	0
Sn	0.4	13.0	32.0
Zn	0.6	7.8	2.8

Table III

### Estimated simplified alloy composition

Metal	Mass% in PCB	Mass% in alloy
Copper	16	70
Tin	3	13
Lead	2	9
Nickel	1	4
Zinc	1	4

and a copper-lead liquid containing about 37 mass per cent of lead at 955°C. At 955°C the solution undergoes monotectic solidification to give pure solid copper and liquid lead. At 326°C the lead solidifies.

Copper and nickel are mutually completely soluble, and the nickel is thus expected to distribute between the various copper-tin phases. Copper and zinc form an alpha bronze phase, containing up to 36 mass per cent zinc. At the low levels of zinc in this alloy, the zinc may be expected to distribute between the various copper-tin phases. Thus the system could be simplified to one containing 78 mass per cent of copper-nickel-zinc and 22 per cent of tin, and a separate one for lead.

Assuming that the copper-tin phase diagram shown in Figure 3 would approximate the behaviour of the molten mixture, the following would be expected. At about 900°C an alpha bronze phase is expected to start forming, reaching 13.5 mass per cent tin at 798°C. As the temperature further decreases, more of the alpha phase will form, as well as other phases that eventually transform to form a delta bronze phase at about 520°C. The delta phase is expected to contain 32.6 mass per cent of tin and would hence coexist with a copper-based alpha phase.

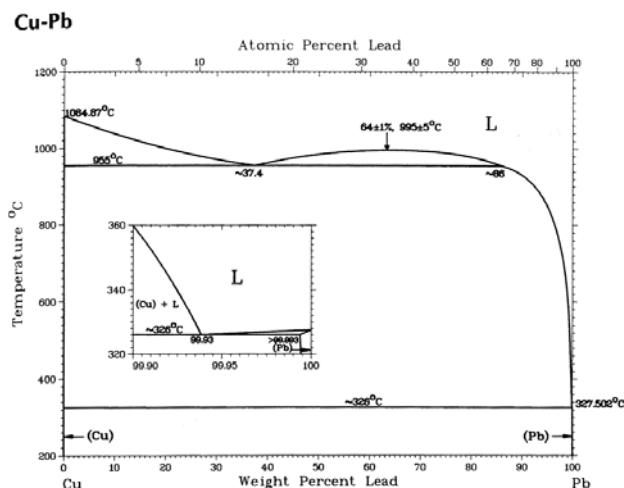


Figure 2—The binary phase diagram<sup>6</sup> for the copper-lead system

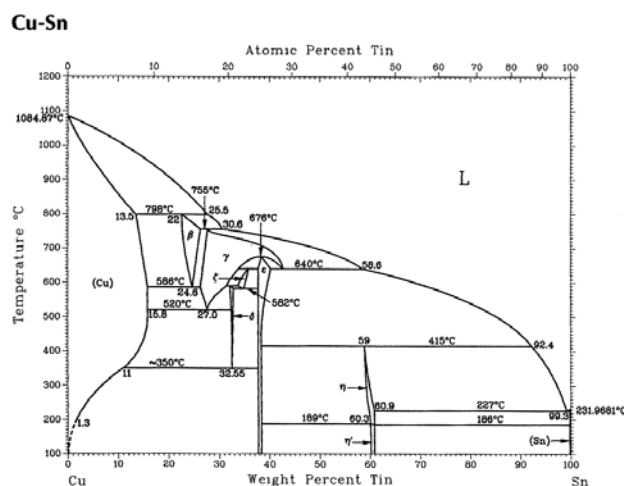


Figure 3—The binary phase diagram<sup>6</sup> for the copper-tin system

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The above simplified approach appears to give a reasonable description of the alloy that formed, as shown in Figure 1. The expected tin contents agree with the EDS results shown in Table II. The dark phase in Figure 1 is thus the alpha bronze phase, and the grey phase the delta bronze. Between these bronze grains the white lead phase is seen. Evidence of alpha bronze phase dendrite formation, as expected from the above discussion, is seen in Figure 1.

The above simplified approach was also checked by appropriate calculations using the FactSage software<sup>7</sup>. A composition of 74 mass per cent copper, 13 tin, 9 lead and 4 zinc was used. As nickel forms a complete solid solution with copper at all concentrations, it was added to the copper concentration. The results obtained from the calculations, if the formation of  $\text{Cu}_3\text{Sn}$  is suppressed, is shown in Figure 4. The formation of  $\text{Cu}_3\text{Sn}$  (the epsilon phase) was suppressed, as the phase diagram shows that it will form only below 350°C. It is thus a thermodynamically stable phase at room temperature, but it will not be formed at an appreciable rate due to the low transformation temperature.

From the calculated phase stability it is expected that the final alloy material will consist of about 56 mass per cent of alpha phase and 35 per cent delta phase (' $\text{Cu}_4\text{Sn}$ ' in Figure 2), as well as 9 per cent lead phase.

### Conclusions

It was shown to be possible to selectively smelt waste printed circuit board material to give a metallic alloy. The smelt was done at 1200°C under an argon atmosphere, and then cooled to room temperature under the argon atmosphere. By using a temperature of 1200°C, the dissolution of iron and steel was minimized while plastics were charred and nonmetallics were collected as a slag.

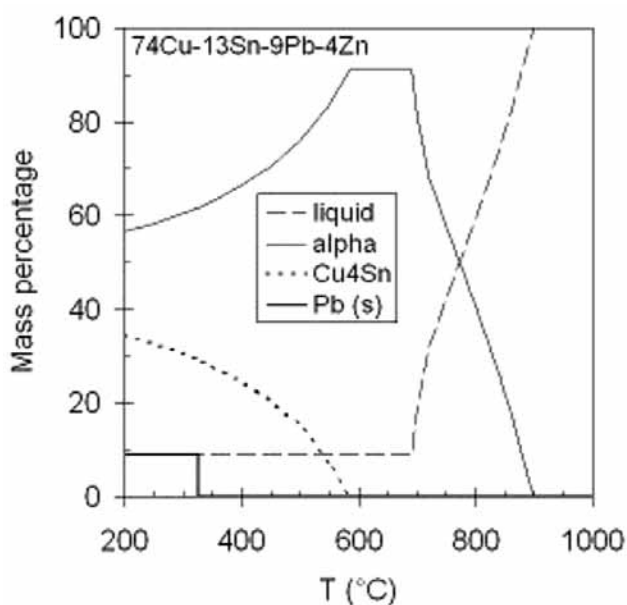


Figure 4—Calculated temperature dependence of phases in an alloy containing 74 per cent copper, 13 per cent tin, 9 per cent lead and 4 per cent zinc

A simplified approach using appropriate binary phase diagrams was successfully used to derive a phase composition for the alloy. FactSage calculations also showed that the simplified approach was appropriate for this alloy.

The alloy formed by the high temperature smelting of scrap printed circuit board materials was studied by SEM-EDS. It was shown that iron and aluminium were successfully excluded from the alloy by the selective smelting process followed. Several metallic phases were formed and identified in the alloy: a lead rich phase and two bronze phases with tin contents of 32 and 13 mass per cent. From the SEM-EDS analyses and the theoretical approaches, the phases were identified as alpha and delta bronzes, as well as a lead-rich phase. Calculations show that about 56 mass per cent of the alloy is the alpha phase, 35 per cent delta phase and 9 per cent lead phase. The experimental findings and theory were found to agree well.

The alloy that was formed through direct smelting seems to be suitable for making anodes for copper electrorefining, as it is electrically conductive and appears to have sufficient mechanical strength. However, during leaching tests<sup>8</sup> it was found that some phases leach preferentially to others. The mechanical integrity of an electrode in copper electrorefining is thus likely to be a problem during leaching.

An advantage of a selective smelting route is that iron and steel as well as aluminium are rejected, which is advantageous for subsequent hydrometallurgical processing. The very complex and heterogeneous feed material is processed by this route to a much simpler intermediate suitable for further processing.

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