Recovery of Metals from Waste Electrical and Electronic Equipment (WEEE) by Anodic Dissolution

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The recovery of metals from a multi-component alloy obtained by crushing and melting of PC mainboard scraps has been investigated. The anodic dissolution of the alloy was carried out in a electrolysis cell (1500 mL capacity) with two symmetrical stainless steel cathodes (70×60×0.5mm) and a central cast anode, immersed in an acidic electrolyte containing 150 g/L H_2SO_4 *and 120 g/L* $CuSO_4 \cdot 5H_2O$ *respectively. The temperature of the electrolyte during the process was 60 °C. Depending on the electrolysis parameters (current density, cell voltage), cathodic deposits of Cu (99 wt %) and Cu-Sn alloy (with 8-10 wt % Sn) were obtained. It was observed that Pb, Sn as well as precious metals (Au, Ag) were concentrated in the anodic slime. The experiments performed have demonstrated the possibility of separating/recovery of metals from the multi-component alloy which resulted from waste electrical and electronic equipment, by anodic dissolution.*

Keywords: WEEE recycling, WPCBs, anodic dissolution, copper recovery, Cu-Sn alloy

The rapid development of the global economy and especially of the electric and electronic industries requires increasing quantities of nonferrous metals and mainly of metals which are considered as critical from the point of view of the natural resources. For this purpose, the processing of electrical and electronic wastes (WEEEs) resulting from the industry represents a major technological challenge and at the same time a major opportunity, taking in consideration two aspects: (*i*) the protection of the environment through the treatment of the toxic elements contained in WEEEs; *(ii)* the recovery of the useful metals present in the wastes and the provision of alternative sources of valuable metals for the industry [1-3]. In the category of WEEEs with obsolete lifetime, the electronic devices such as computers and mobile phones represent a special class. Printed circuit boards (PCBs), as a main WEEE component, have a contents of 40% metals, 30% organic substances, 30% ceramics and they may be a very important source of nonferrous (Cu, Al, Fe, Ni, Pb), rare and precious (Au, Ag, In, Sr, Ta, etc.) metals. The mounting support represents approximately 23% of the weight of PCBs [4, 5]. The elements with the highest economical value are Cu and Au [1, 3, 4]. In an ordinary personal computer the contents of copper (20%) and gold (250 g/t) in a printed circuit board are much higher that the ones existent in an exploitable ore, respectively 20-40 times higher for Cu and 25-250 times for Au [4,5]. The heterogeneous composition and complex structure of these wastes make their processing and recovery of the contained metals to be a technical and technological challenge, especially concerning the efficiency of the processes, but also in regard to environmental protection (emissions of toxic gaseous compounds). The conventional methods for processing WEEEs are pyrometallurgical, hydrometallurgical or combined methods, all applied after a prior treatment through physical-mechanical methods. The hydrometallurgical treatments are generally more flexible in terms of the process progress. At a smaller scale they may present a better control of the processes leading to the obtaining of higher efficiencies for the recovery of metals. Hydrometallurgical processes include an initial step of solution extraction of metals through acid or alkaline leaching, followed by a step of refining the solution through various methods, such as: precipitation, cementation, absorption, ion exchange, electrolysis or solvent extraction. For the recovery of useful metals from PCBs, the most frequently used leaching agents are: cyanides, halides, thiourea, thiosulfate, HNO_3, NaOH, aqua regia, etc. [6-9]. Most of the hydrometallurgical routes for processing PCBs use oxidative leaching with H_2SO_4, in the presence of H_2O_2 as oxidizing agent, followed by solution refining [1,4,9]. The use of nitric or hydrochloric acids was studied intensively, but because of the severe environmental regulations and the corrosive nature of these reagents, they cannot be considered as appropriate, compared to the sulphuric acid which is less hazardous [10]. The use of electrochemical methods for processing PCBs presents the advantages of reducing the reagent consumption and of increasing the recovery efficiency for valuable metals and it have a mitigated impact on the environment [11-13]. The various electrochemical techniques for the recovery of base metals from PCBs, described in the literature, are based on two major steps which can be carried out in a single cell: 1) anodic generation of the oxidizing agents for increasing the rate of metal dissolution; 2) cathodic electrolysis of the dissolved metals for separation and recovery. Research studies [14] have underlined the possibility of recovering 93% gold and 97% copper from mobile phone wastes, in the presence of chlorine generated electrochemically *in situ*. The application of the same method in the processing of PCBs

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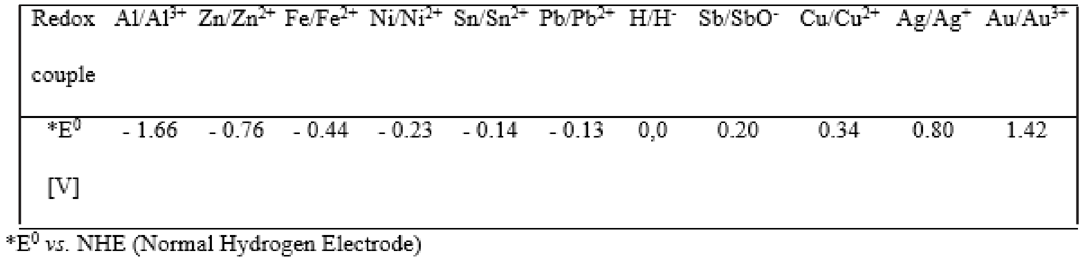

Redox couple	Al/Al^{3+}	Zn/Zn^{2+}	Fe/Fe^{2+}	Ni/Ni^{2+}	Sn/Sn^{2+}	Pb/Pb^{2+}	H/H^{-}	Sb/SbO^{-}	Cu/Cu^{2+}	Ag/Ag^{+}	Au/Au^{3+}
*E^0 [V]	- 1.66	- 0.76	- 0.44	- 0.23	- 0.14	- 0.13	0,0	0.20	0.34	0.80	1.42

*E^0 *vs.* NHE (Normal Hydrogen Electrode)

Table 1
STANDARD ELECTRODE POTENTIALS OF SOME METALS PRESENT IN WEEEs [20]

made possible the total recovery of copper [15]. In the same manner, in other studies, the copper from PCBs was recovered by direct electrochemical oxidation, with simultaneous cathodic deposition of copper, but instead of chlorine or other hazardous reagents, less dangerous acid electrolytes (for instance H_2SO_4) were used, mediated by the Fe^{3+}/Fe^{2+} redox couple [16-18]. An alternative to this method for the simultaneous recovery of copper and the separation of a residue with a high gold content is the use of an acid ferric chloride solution in chemical and electrochemical reactors connected in series, which allowed the simultaneous generation of Fe^{3+} and the dissolution of metals without additional leaching agents [13]. Another technological method is the recovery of copper from PCBs which is obtained in the shape of metallic powders, through a process of acid leaching in H_2SO_4 in the presence of Cu^{2+} ions and air as oxidizer, using the Cl^- ion which forms $CuCl_2$ (as a complex intermediate product) [19].

Recently, studies have been carried out to investigate anodic dissolution, a new and very promising method for the recovery of metals from WPCBs. This method consists of the direct extraction of copper through an electrochemical process without a prior chemical dissolution.

In general, the anodic dissolution of the metal will begin when the anodic potential will be higher than the reversible electrode potential of the respective metal. The standard electrode potentials for the metals in WEEE are given in table 1.

For the anodic dissolution of an alloy, the concentration of the metal with the more positive potential must exceed a certain percentage in the alloy composition or the dissolution order can be changed. For example, in a metallic alloy which contains the metals Me_1, Me_2, Me_3, placed in a decreasing order of the standard potentials, if the current density is low enough, the following situations can occur: 1*)* Me_1 dissolves almost certainly if its proportion in the alloy is much higher than that of the other metals; 2*)* Me_1 and Me_2 are the only ones dissolved, if the proportion in Me_2 is much higher than that of the other metals; 3*)* Me_1, Me_2, Me_3 are dissolved together if the proportion of Me_3 is much higher than that of the other metals.

It is understandable that in cases 2) and 3) Me_1 cannot dissolve alone, because, being in small quantity, its particles are absorbed in Me_2 and Me_3 and it cannot be approached until these metals are dissolved.

An increase of the current density induces the dissolution of metals, which, according to their position in the series of standard potentials, should not dissolve. Simultaneously to the anodic dissolution process, a phenomenon of cation reduction takes place at the cathode leading to the formation of metallic atoms which are deposited as a crystalline lattice on the cathode surfaces. Since in the case of the anodic dissolution of multi-component alloys the electrolyte will contain various types of metallic cations, the first cation to be reduced will belong to the noblest metal.

In regard to their behaviour during the anodic dissolution process, the metallic elements of the multi-component alloy can be classified as follows:

(i*)* Noble and platinum-group metals: that are nobler than Cu and thus are not electrochemically dissolved in the electrolyte and cannot impurify the cathodic deposit. During the anode dissolution they separate as fine particles and decant to the bottom of the electrolysis cell forming an anodic slime. Although under normal conditions silver is more electropositive it can still dissolve partially in the electrolyte and be deposited at the cathode simultaneously with copper. Thus chloride ions are introduced in the electrolyte to prevent the cathodic deposition of Ag by the precipitation of silver as AgCl;

(*ii)* Lead and tin, that are more electropositive (American definition) than copper and therefore are electrochemically dissolved forming $PbSO_4$ and $Sn(OH)_2SO_4$ (alkaline sulphate). The resulted compounds are insoluble in the electrolyte and deposit in the anodic slimes;

(*iii)* Fe, Ni, Co, Sb, etc. group; All these elements are also more electropositive than copper and have the tendency to dissolve electrochemically and to accumulate in the electrolyte as free ions. Their presence in the electrolyte, especially in high concentrations, can lead to the contamination of the cathodically deposited copper, either through electrolyte entrainments or by the precipitation of complex compounds. Fe^{3+} can be formed if the iron contents is too large, determining the oxidation of the cathodically deposited copper through a parasitic reaction ($Cu + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+}$), which can diminish the current efficiency of the process.

Experimental part

The WEEEs were processed through an innovative method of melting in a microwave installation, which allowed the complete separation of the organic and metallic fractions. Two anodes as plates with a size of 10 x 50 x 50 mm and a weight of 200 g were prepared from the melted and casted WEEEs. The anodic dissolution was carried out in an electrolysis cell (volume of 1500 cm^3) using two stainless steel cathodes (70 x 60 x 0.5mm), symmetrically placed versus the central anode. The anodic connection was achieved through a platinum conductor. Figure 1 presents a photo image of the multi-component alloy anode obtained by melting and casting of WEEEs.

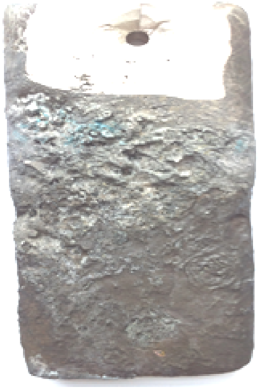

Fig. 1 Multi-component alloy anode

The dissolution was performed in an acid solution with the following initial composition: 150 g/L H_2SO_4 and 120 g/L $CuSO_4 \cdot 5H_2O$ (Cu content of 30 g/L). The temperature of the electrolyte was set at 60°C using a thermostat. The volume of the electrolyte was maintained constant (1 L) by adding bi-distilled water. During the experiments the cell voltage was between 0.35-0.4 V and the anodic current density was 0.02 A/cm^2. The process war carried out for 166 h, until the complete dissolution of the anodes. Periodically, the anodic slime samples were collected in order to study the evolution of the chemical composition.

After complete dissolution, the electrolyte was filtered and the anodic slime was washed with bi-distilled water and dried. Further, the anodic slime was melted to produce new anodes, with higher content of Au and Ag, for a second anodic dissolution. In this way, a new anodic slime rich in precious metals was obtained. The melting of the anodic slime mixed with charcoal was performed using a cylinder graphite crucible, in an electric furnace with controlled atmosphere (inert gas-Ar). A mixture of Na_2CO_3 and Borax (10 wt %) was used as protective flux. The melting temperature was 400°C and the process lasted for 60 minutes. After solidification in the crucible the metallic ingot was machined to a weight of 50 g. The second anodic dissolution was performed in the same cell and experimental conditions. The process was carried out at three current densities (0.01, 0.02 and 0.04 A/cm^2). The chemical compositions of the electrolyte, cathodic deposit and anodic slime were determined using a Spectroflame PICP analyser.

Results and discussions

The chemical composition of the anode obtained by WEEEs melting is given in table 2.

Figure 2 shows photos images of the cathodic deposits obtained after the first and the second anodic dissolutions, respectively.

Table 3 shows the evolution of the chemical composition of the anode during the anodic dissolution process. The evolution of the chemical composition of the electrolyte during the anodic dissolution process is presented in table 4.

Table 5 shows the evolution of the chemical composition of the cathodic deposit during the anodic dissolution process. The evolution of the chemical composition of the anodic slime during the anodic dissolution process is presented in table 6.

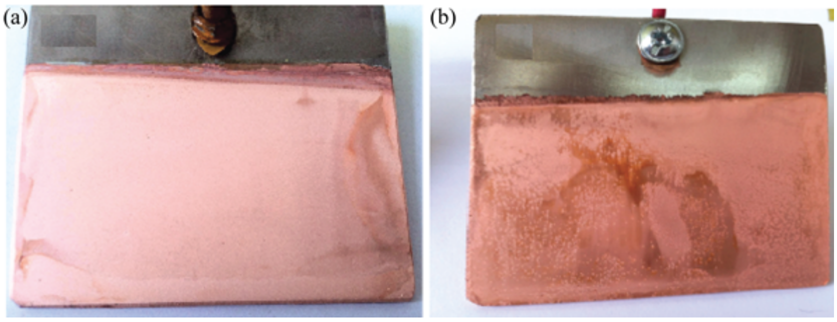

Fig. 2. Cathodic deposit from the first (a) and second (b) dissolution

Table 2

CHEMICAL COMPOSITION (wt %) OF THE PROCESSED WEEE SAMPLE

Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other metallic elements
61.9	17.8	8.9	3.65	3.6	1.75	1.5	0.23	0.056	0.16

Table 3

EVOLUTION OF THE CHEMICAL COMPOSITION (wt %) OF THE ANODE DURING THE ANODIC DISSOLUTION PROCESS

Time	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other*
0 h	61.9	17.8	8.90	3.65	3.60	1.75	1.50	0.230	0.056	0.160
40 h	57.8	23.6	8.08	9.20	0.09	0.63	0.16	0.063	0.016	0.030
80 h	56.5	22.8	7.86	11.62	0.07	0.56	0.13	0.061	0.015	0.036
120 h	60.3	24.3	8.68	5.52	0.08	0.59	0.15	0.057	0.013	0.038
166	Complete dissolution									

*Other elements: Cr, Mg, Mn, Mo, Sb, Si, Ti, Pt

Table 4

EVOLUTION OF THE CHEMICAL COMPOSITION (g/L) OF THE ELECTROLYTE (IONIC SPECIES) DURING THE ANODIC DISSOLUTION PROCESS

Time	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other
0 h	30.00	-	-	-	-	-	-	-	-	-
40 h	20.30	7.10	2.73	0.07	0.033	0.20	0.053	0.001	0.001	0.03
80 h	10.60	7.38	4.83	0.01	0.060	0.28	0.270	0.001	0.001	0.03
120 h	6.05	11.90	5.04	0.01	0.050	0.40	0.450	0.001	0.001	0.03
166 h	6.08	12.40	4.98	0.01	0.050	0.41	0.460	0.001	0.001	0.03

Time	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other*
0 h	-	-	-	-	-	-	-	-	-	-
40 h	99.77	0.12	0.01	0.01	0.01	0.01	0.01	0.006	0.001	0.05
80 h	99.74	0.12	0.01	0.03	0.01	0.01	0.02	0.007	0.001	0.05
120 h	99.47	0.40	0.01	0.03	0.01	0.01	0.01	0.009	0.001	0.05
166 h	98.64	1.15	0.01	0.08	0.01	0.01	0.02	0.013	0.001	0.06

*Other elements: Cr, Mg, Mn, Mo, Sb, Si, Ti, Pt

Table 5
EVOLUTION OF THE CATHODIC DEPOSIT CONCENTRATION (wt %) DURING THE ANODIC DISSOLUTION PROCESS

Time	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other*
0 h	-	-	-	-	-	-	-	-	-	-
40 h	6.60	30.30	0.32	40.15	0.01	0.010	0.17	0.31	0.070	0.41
80 h	6.55	25.30	0.25	45.04	0.01	0.010	0.19	0.50	0.089	0.35
120 h	6.90	25.44	0.15	44.62	0.01	0.010	0.18	0.76	0.095	0.26
166 h	13.3	10.2	0.16	44.70	0.01	0.012	0.27	0.305	0.100	0.22

*Other elements: Cr, Mg, Mn, Mo, Sb, Si, Ti, Pt

Table 6
EVOLUTION OF THE CHEMICAL COMPOSITION (wt %) OF THE ANODIC SLIME DURING THE ANODIC DISSOLUTION PROCESS

Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other metallic elements
16.38	19.75	0.19	61.76	0.01	0.02	0.37	0.32	0.11	0.25

Table 7
CHEMICAL COMPOSITION (wt %) OF THE METALLIC ANODE OBTAINED BY THE MELTING OF THE ANODIC SLIME

As it can be observed in tables 3-6, during the metals recovery process the content of precious metals is continuously decreasing in the anode, but practically remains constant in the electrolyte and in the cathodic deposit. Very important is that precious metal content deposit is constantly increasing in the anodic slime. The chemical composition of the metallic ingot obtained after the melting of the anodic slime is given in table 7.

The chemical compositions of the electrolyte, of the cathodic deposit and of the anodic slime obtained depending on the current densities are presented in tables 8, 9 and 10.

Current density [A/cm^2]	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other metallic elements
0.1	28.64	6.63	0.57	0.001	0.01	0.34	0.11	0.001	0.001	0.18
0.2	26.31	8.75	0.82	0.001	0.01	0.37	0.12	0.001	0.001	0.25
0.4	25.18	10.66	0.86	0.01	0.01	0.18	0.37	0.001	0.001	0.23

Table 8
CHEMICAL COMPOSITION OF THE ELECTROLYTE [g/L] FOR DIFFERENT CURRENT DENSITIES

Current density [A/cm^2]	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other metallic elements
0.1	99.28	0.20	0.10	0.002	0.040	0.001	0.001	0.001	0.001	0.12
0.2	94.76	4.53	0.10	0.002	0.030	0.005	0.001	0.001	0.001	0.12
0.4	87.85	11.64	0.15	0.050	0.002	0.007	0.008	0.001	0.001	0.18

Table 9
CHEMICAL COMPOSITION OF THE CATHODIC DEPOSIT [wt %] FOR DIFFERENT CURRENT DENSITIES

Table 10
CHEMICAL COMPOSITION OF THE ANODIC SLIME [wt %] FOR DIFFERENT CURRENT DENSITIES

Current density [A/cm^2]	Cu	Sn	Zn	Pb	Al	Ni	Fe	Ag	Au	Other metallic elements
0.1	4.73	16.65	0.1	59.54	0.001	0.10	0.01	0.375	0.12	0.07
0.2	6.58	8.72	0.1	66.24	0.001	0.10	0.01	0.650	0.34	0.08
0.4	8.37	4.63	0.1	65.82	0.001	0.01	0.20	0.890	0.78	0.12

It can be observed that the Cu and Sn contained in WEEEs are accumulated mostly in the cathodic deposits, and Pb is concentrated in the anodic slime. Over 95% of the Au and Ag amount present in the wastes is found in the anodic slime (tables 7 and 10). Obviously, the current density influences the chemical composition of the cathodic deposits. Thus as at low current densities Cu with purity higher than 99% is obtained at the cathode and as the current density increases a Cu-Sn alloy is deposited. For an efficient extraction of Au and Ag with thiourea, the contents of Cu ions in the leaching solutions must be at low as possible, as they have a negative influence on the leaching of Au by decomposition of thiourea. Also, cupric ions produce the decomposition of formamidine disulfide to elemental sulphur which inhibits the dissolution of Au by passivating the surface of Au and Ag [21]. The low content of Cu and Sn in the anodic slime creates the conditions for an efficient extraction of the precious metals with thiourea.

Conclusions

The metallic complex alloy obtained by WEEE melting in microwave furnace was then successfully dissolved in an acid electrolyte by means of a two steps anodic dissolution process. A high purity Cu deposit was obtained for a low current density, while at higher current densities a Cu-Sn alloy was deposited at the cathode. The two step dissolution process of the metallic bulk allows increased concentration of the precious metals (Au and Ag) in the anodic slime. Thus, the content of Au increased from 0.056 wt % in the initial anode to 0.78 wt % in the final anodic slime and the content of Ag increased from 0.23 wt % to 0.89 wt %, respectively (tables 3 and 10). The preliminary experimental results demonstrated that high purity Cu can be efficiently separated/recovered from the WEEE metallic fraction by anodic dissolution.

Further works will include the separation of precious metals from anodic slime by extraction with thiourea.

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