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SELECTIVE ELECTROEXTRACTION OF BASE METALS FROM LEACHING SOLUTIONS OBTAINED DURING THE RECYCLING OF WASTE PRINTED CIRCUIT BOARDS.
II. SELECTIVE POTENTIOSTATIC ELECTRODEPOSITION OF COPPER, TIN AND LEAD

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ABSTRACT. This paper presents our results concerning the feasibility of selective potentiostatic electroextraction of copper, tin and lead from leaching solutions obtained during the recycling of base metals from waste printed circuit boards. Applying this protocol, in a first stage, the concentration of Cu ions from the leaching solutions can be lowered, with acceptable efficiency, below 0.5 g/L. To avoid the contamination of Sn-Pb alloys with Cu, an intermediary step of Cu cementation on metallic Sn were proposed and tested. Finally, the potentiostatic selective electrodeposition protocol was successfully applied for the electroextraction Sn-Pb alloys. The experiments were performed in real leaching samples, using a Fisher type electrode as cathode. The obtained experimental results demonstrate that, controlling rigorously the imposed potential and corelating them with the solution composition, high purity Cu and Sn-Pb alloys deposits can be obtained, maximum contents of 99.96%, 99.83% and 82.62% being evaluated for Cu, Sn and Pb, respectively.

Keywords: *waste printed circuit boards, potentiostatic selective electroextraction, copper recovery, tin and lead alloy electrodeposition.*

INTRODUCTION

It is well known that, due to the depletion of mineral resources, the use of different wastes as secondary resources gains increased attention.

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Currently, consistent researches concerning the recycling of secondary resources are focused on the wasted printed circuit boards (WPCBs) [1], which are the base of the electronics industry. The WPCBs present a potentially high economic value, a serious concern for the environment [2], and an emerging trend towards the circular economy [3].

Copper is the major metal found in WPCBs and its recovery is therefore a top priority [4], followed by tin, lead and other metals [5]. From the ecological and economic point of view, the electrochemical recovery of metals from WPCBs presents significant advantages [6,7], it can apply highly efficient strategies [8] like the electroextraction one [9] or more complex processes [10,11], many of them based on the selective electrodeposition [12,13].

The cathodic electrodeposition represents an efficient method for the electrochemical recovery of the metals from a solution [14], extensive studies presenting different strategies and efficiencies for the Cu electroextraction [15] or the Sn-Pb alloys deposition [16,17], processes that are constantly improved [18]. Electrochemical deposition was used to obtain thin films of Cu and Sn-Pb alloy [19] which have wide applications in the industrial revolution. Starting from the results obtained during our previous research [13,20,21], this paper aimed to evaluate the feasibility of potentiostatic selective electroextraction of copper and Sn-Pb alloys from solutions resulting during the recovery of base metals from WPCBs using the leaching system KBr / HBr / Br_2. Based on the literature data [22], to prevent the contamination of electrodeposited Sn-Pb alloys with Cu, an intermediary step of Cu cementation on metallic Sn were also proposed and tested. For an accurate evaluation of process efficiency, the experiments were divided in several short time tests, the weight and the composition of the intermediary obtained deposits being evaluated. For these steps, the deposits were washed, dried, and detached from the Fisher type working electrode (WE) by mineralization with *aqua-regia* and analyzed by flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

The selective potentiostatic electrodeposition of Cu

Our previous results concerning the intense and fast selective electrodeposition of Cu from the leaching solutions demonstrated that high purity Cu deposits can be obtained, in parallel with the regeneration of the leaching solution, at high current densities [13] if the concentration of Cu ions remains over 12 g/L. Continuing the previous work, in the present paper, we proposed and tested a new protocol for the selective potentiostatic electroextraction of several metals (Cu, Sn and Pb). The main goal of the research was to evaluate the feasibility of the complete extraction of these metals from the leaching solutions.

Based on the information obtained by cyclic voltammetry and galvanostatic electrodeposition, the tests concerning the selective potentiostatic electroextraction of Cu from the leaching solutions started at imposed working electrode potentials (E_{WE}) of -0.25 V *vs.* the reference electrode (RE) [13]. As detailed in the experimental section, the initial concentration of the Cu ions in the real leaching solution sample was 12.89 g/L. When the recorded current through the WE (I_{WE}) decreased at 10% from the initial value, the experiment was stopped and the Fisher type WE was removed from the electrochemical cell, washed, dried and weighted. The obtained deposits were detached from the WE by mineralization with *aqua-regia* and the obtained solutions were analyzed by FAAS and ICP-AES to evaluate its composition. An example of images corresponding to the cleaned Fisher type electrode and of a Cu deposit obtained by electroextraction are presented in Figure 1.A and 1.B, respectively.

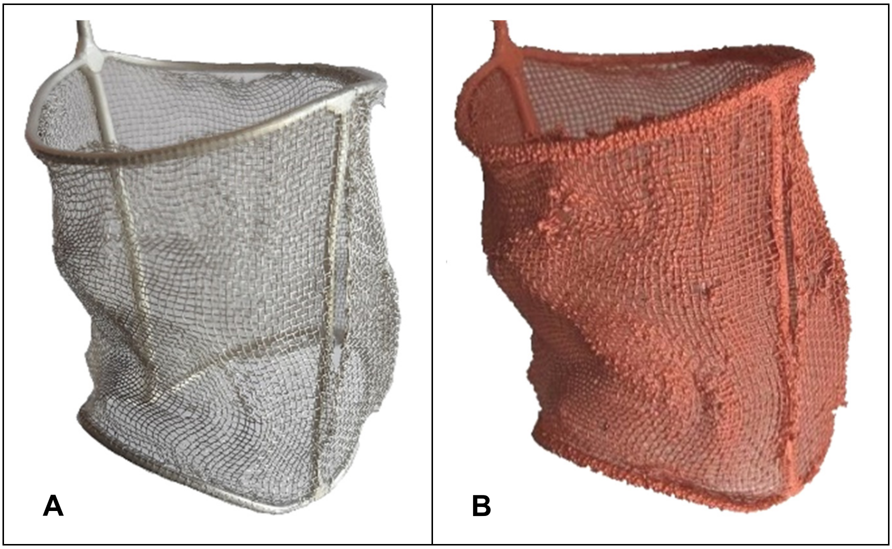

Figure 1. Example of images of the clean Fisher type electrode (A) and of the copper deposit obtained after electrodeposition (B).

Afterwards, the imposed E_{WE} was progressively switched to more negative values of -0.3 and -0.35 V/RE The main electrical parameters recorded during the selective potentiostatic electrodeposition of Cu are presented in Figure 2, where U_T, E_{CE}, pH and ORP represent the instantaneous values of the voltage at the electrochemical cell terminals, counter electrode (CE) potential, pH and oxidation/reduction potential, respectively. Also, the mean and/or individual values of the operational and efficiency parameters evaluated from the experimental data are presented in Table 1, were C_{EF} and W_S represent the current efficiency and the specific electricity consumption, and $E_{WE,M}$, $I_{WE,M}$ and ORP_M represent the average values of E_{WE}, I_{WE} and ORP, respectively. [Cu] stands for the Cu ions concentration in the leaching solutions.

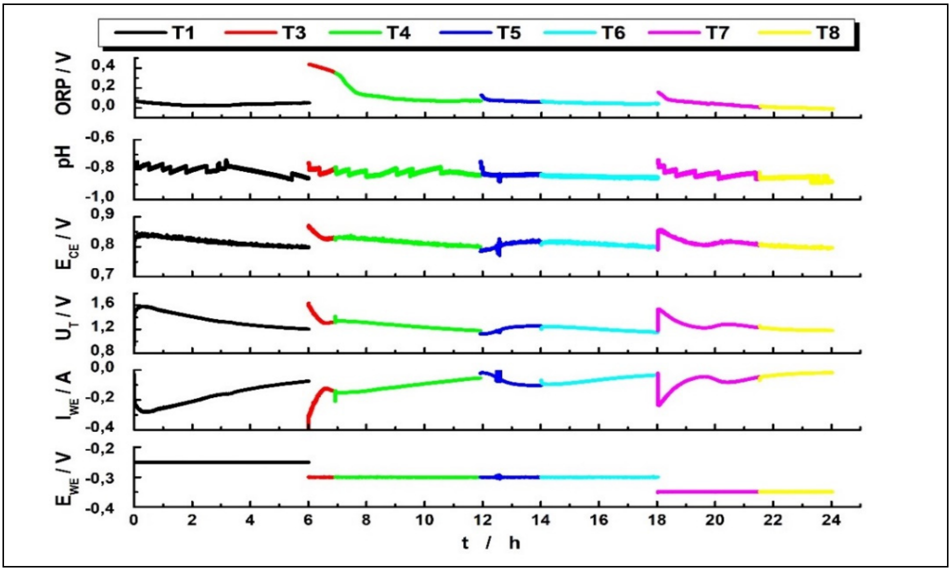

Figure 2. The evolution of the electrochemical and electrical parameters during the potentiostatic selective electrodeposition of Cu from the leaching solution.

Table 1. The evolution of the operational and efficiency parameters for the tests of potentiostatic selective electrodeposition of Cu from real leaching solutions.

Deposit	Test	$E_{WE,M}$ (V/RE)	$I_{WE,M}$ (mA)	t (min.)	[Cu] (g/L)	C_{EF} (%)	W_S (kWh/kg)	ORP_M (V/RE)
D1	**T1**	-0.25	-172	361	5.17	95.9	0.62	0.038
D2	**T2**	-0.25	-1.5	360	5.17	48.6	1.09	0.125
D3	**T3**	-0.30	-173	55	1.63	65.7	0.84	0.397
D3	**T4**	-0.30	-106	300	1.63	65.7	0.84	0.111
D4	**T5**	-0.30	-74	126	1.58	1.7	30.46	0.071
D4	**T6**	-0.30	-67	241	1.58	1.7	30.46	0.048
D5	**T7**	-0.35	-86	211	0.36	41.9	1.32	0.049
D5	**T8**	-0.35	-28	150	0.36	41.9	1.32	0.001

As it can be seen in Figure 2, the U_T, E_{CE}, pH and ORP values remains relatively constant, proving the stability of the electrochemical system during the progressive Cu electroextraction. Contrarily, to maintain a reasonable high value of the I_{WE}, and, consequently, an acceptable rate of Cu electroextraction, the imposed E_{WE} value must be permanently adjusted to more and more negative values, in accordance with the decrease of the Cu ions concentration in the solutions. Otherwise, the reaction of hydrogen evolution (RHE) becomes the main process, wasting electrical energy without any supplementary electroextraction of Cu. These conclusions are in excellent agreement with the C_{EF} and W_S values presented in Table 1.

Finally, it is worth to note that the concentration of the Cu ions in the leaching solution sample decreased from its initial value (12.89 g/L) up to 0.36 g/L, proving the proposed process feasibility. The attempt to continue the process under this value leads to the enhancement of the RHE and increase the risk of Sn and Pb inclusion in the Cu deposits.

For the Cu obtained deposits, their compositions were evaluated analyzing the solution (resulting by mineralization of deposits with *aqua-regia*) by FAAS, the obtained results being presented in Table 2.

Table 2. Percentage of metals (w/w) evaluated by FAAS in the deposits obtained by selective potentiostatic electrodeposition of Cu from the leaching solution.

Test	Cu (%)	Sn (%)	Pb (%)	Fe (%)	Ni (%)	Zn (%)
T1	99.78	0.22	ND	0.00	ND	0.00
T3+T4	99.91	0.00	ND	0.01	ND	0.00
T5+T6	98.76	ND	ND	0.90	ND	0.34
T7+T8	99.96	0.00	ND	0.04	ND	0.00

The data presented in Table 2 reveal that the average purity of the deposits exceeds 99.8%, proving that the selective potentiostatic electrodeposition of Cu from the leaching solution is a feasible and cost-effective technology, leading to products of excellent quality and value.

Extraction of Cu traces by cementation on metallic Sn

To recover completely the existing Cu from the leaching solutions and to avoid the contamination of the Sn-Pb alloys deposit with Cu traces, we decided to implement a step of Cu cementation on metallic Sn between the Cu electrodeposition step and the Sn-Pb alloys electroextraction stage. At this level, in the low pH values, the next reaction takes place:

$$2Cu^{+}_{(aq)} + Sn^{0}_{(s)} \rightarrow 2Cu^{0}_{(s)} + Sn^{2+}_{(aq)} \qquad (1)$$

The variation of the measured parameters is presented in Figure 3.

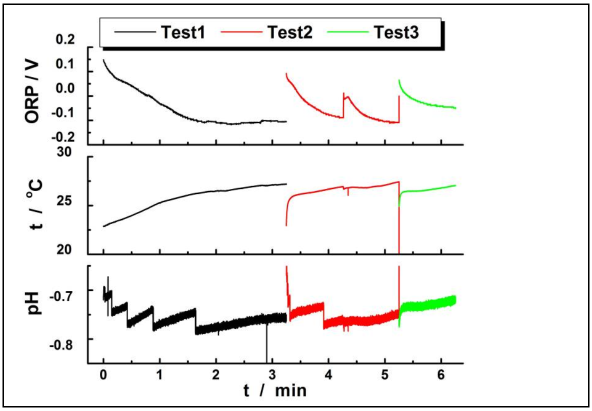

Figure 3. Evolution of pH, temperature and ORP of the leaching solution during Cu cementation on metallic Sn.

During the cementation tests, samples were collected periodically from the chemical reactor and analyzed by FAAS. The evolution of the [Cu] values during this process is presented in Table 3.

Table 3. Evolution of [Cu] during the process of Cu cementation on metallic Sn.

Time (h)	0	1	2	3	4	5	6
[Cu] (mg/L)	266.5	177.7	70.8	57.2	38.5	35.5	7.98

Based on data presented in Figure 3 and Table 3, we demonstrated that the cementation of Cu traces using metallic Sn granules is a feasible, cost-effective, and efficient method to reduce significantly the [Cu] value. Practically, after 6 hours, the [Cu] was diminished from ~250 mg/L to less than 8 mg/L, without altering the pH or the ORP of the leaching solution.

Selective potentiostatic electroextraction of Sn-Pb alloys

The measurements performed by cyclic voltammetry revealed that the electrodeposition of Sn and Pb begins at remarkably close potentials, around -0.5 and -0.55 V/RE, and depends essentially on the concentration of these ions. Consequently, the selective electrodeposition of Sn and Pb is, practically, impossible, but the deposition of the Sn-Pb alloys is favorized.

The electrochemical and electrical parameters recorded during the potentiostatic electrodeposition of Sn-Pb alloys are presented in Figure 4.

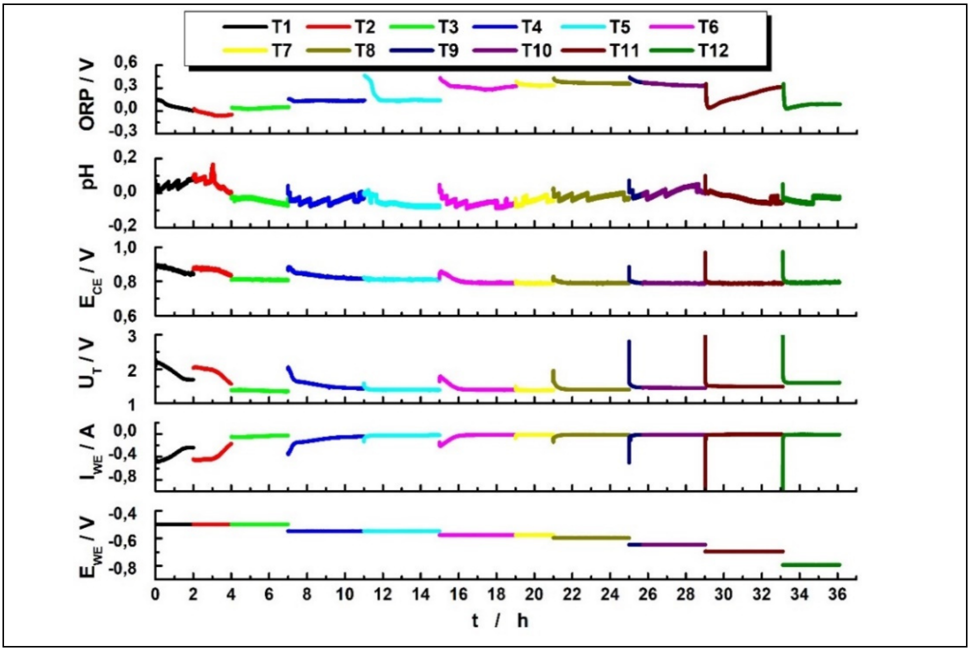

Figure 4. Evolution of electrochemical and electrical parameters during the tests of Sn-Pb alloys electrodeposition from the leaching solution free of Cu ions.

As it can see from Figure 4, the measurements were performed at a starting E_{WE} value of -0.50 V/RE, and initial concentrations of Sn ([Sn]) and Pb ([Pb]) of 7.9 and 3.97 g/L, respectively. Further, the E_{WE} values were shifted progressively, in correlation with the decrease of [Sn] and [Pb] values concentrations, to more negative values of -0.55, -0.58, -0.6, -0.65, -0.7 and, finally, of -0.8 V/RE. As in the case of Cu electrodeposition, the modification of the applied E_{WE} value was made when the instant I_{WE} values decrease to 10% from the initial ones. In addition, the averaged and/or individual values of the operational and efficiency parameters were evaluated based on the experimental data, the obtained results being presented in Table 4.

Supplementary, Figure 4 reveals that the U_T, E_{CE} and pH values remains relatively constant, proving that the progressive electroextraction of Sn and Pb from the leaching solution do not affect the other proprieties of the electrochemical system. Contrarily, to maintain I_{WE} at reasonable high value, the imposed E_{WE} value must be permanently adjusted to more and more negative values, simultaneously with the decrease of the [Sn] and [Pb] values. Preserving the same E_{WE} for a long period leads to the enhancing of the RHE process, affecting seriously the C_{EF} and W_S values.

Table 4. The evolution of the operational and efficiency parameters evaluated for the tests of potentiostatic selective electrodeposition of Sn-Pb alloys from real leaching solutions with low Cu content.

Deposit	Test	$E_{WE, M}$ (V/RE)	t (min.)	[Sn] (g/L)	[Pb] (g/L)	C_{EF} (%)	W_S (kWh/kg)	$I_{WE,M}$ (mA)	ORP_M (V/RE)
D1	**T1**	-0.50	120	2.95	3.97	45.54	1.93	-353	0.065
D1	**T2**	-0.50	120	2.95	3.97	45.54	1.93	-384	0.038
D2	**T3**	-0.50	180	2.53	3.97	47.06	1.30	-41	0.039
D3	**T4**	-0.55	240	0.55	2.58	94.45	0.81	-100	0.134
D4	**T5**	-0.55	240	0.51	2.54	8.85	5.24	-25	0.176
D5	**T6**	-0.58	240	0.32	1.48	64.24	0.68	-43	0.315
D6	**T7**	-0.58	120	0.30	1.47	12.31	4.99	-15	0.341
D7	**T8**	-0.60	240	0.18	1.45	29.52	1.93	-16	0.369
D8	**T9**	-0.65	44	0.11	1.44	16.22	6.07	-23	0.395
D8	**T10**	-0.65	198	0.11	1.44	16.22	6.07	-11	0.345
D9	**T11**	-0.70	246	0.085	1.44	11.68	6.38	-10	0.197
-	**T12**	-0.80	180	-	-	-	-	-12	0.080

From another point of view, it is worth to note that, applying an optimized protocol for the selective potentiostatic electrodeposition of Sn-Pb alloys, the [Sn] and [Pb] values in the real leaching sample can be lowered, under acceptable efficiency conditions, below 0.1 g/L and 1.5 g/L, respectively. Interestingly, in the tested conditions, at the extremely negative E_{WE} value, of -0.8 V/RE, the deposit was, practically, absent, indicating that, at this polarization level, the entirely quantity of consumed electricity was wasted in the RHE process.

Finally, a series of images showing the obtained Sn-Pb alloy deposits are presented in Figure 5.

For better understand the deposits morphology, they were also mineralized with *aqua-regia* and the resulting solutions were analyzed by ICP-AES, the obtained results being presented in Table 5.

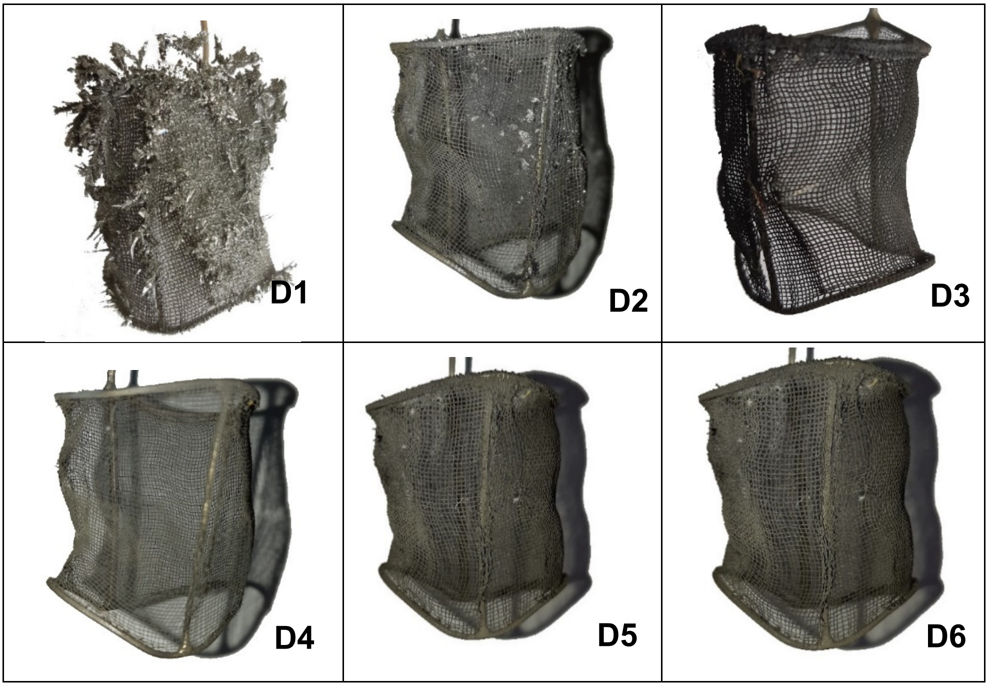

Figure 5. Images of the Sn-Pb alloy deposits obtained by selective potentiostatic electroextraction from real leaching solutions with low Cu content.

Table 5. Percentage of metals (w/w) evaluated by ICP-AES in the deposits obtained by selective potentiostatic electrodeposition of Sn-Pb alloys from the leaching solution with low Cu content.

Deposit	Cumulated tests	Cu (%)	Sn (%)	Pb (%)	Fe (%)	Ni (%)	Zn (%)
D1	**T1 + T2**	0.00	99.8	0.01	0.01	0.01	0.00
D2	**T3**	0.00	99.1	0.06	0.15	0.02	0.09
D3	**T4**	0.00	74.3	25.4	0.02	0.00	0.01
D4	**T5**	0.01	49.3	49.7	0.52	0.02	0.24
D5	**T6**	0.00	14.6	82.6	0.03	0.05	0.01
D6	**T7**	0.03	77.3	20.2	0.26	0.17	0.55
D7	**T8**	0.01	80.6	13.8	0.23	0.19	0.10
D8	**T9 + T10**	0.01	85.1	11.6	0.79	0.91	0.54
D9	**T11**	0.03	91.7	5.6	1.04	0.26	0.48

Corelating the data from Table 3, Figure 5 and Table 4, it is clear that, at high [Sn] in the solution, dendritic deposits (see D1 and D2), with extremely high content of Sn were obtained. Further, simultaneously with the decrease on [Sn] and [Pb] values, the Sn-Pb alloy deposits become smooth and compact, increasing their adherence on the cathode surface. Also, the ratio between Sn and Pb in the deposits changes significantly, depending on [Sn] and [Pb] values and the applied E_{WE}. Additionally, it is worth to note that the major impurities such as Ni, Fe and Zn, which are present in large quantities in the leaching solution and have standard reduction potentials close to the electrodeposition potentials of Sn and Pb, start to be incorporated significantly into the Sn-Pb alloy deposit only when the E_{WE} decrease under -0.65 V/RE

Finally, we conclude that the selective electrodeposition of Sn-Pb alloys, in potentiostatic mode, from leaching solutions with extremely low content of Cu, represents a feasible, efficient and cost-effective technology for the advanced recovery of Sn and Pb from WPCBs.

CONCLUSIONS

Correlating all the recorded data and the evaluated parameters during the experiments concerning the selective potentiostatic electrodeposition of Cu and Sn-Pb alloys from the leaching solution based on the KBr / HBr / Br_2 system, we concluded that the proposed and tested technologies are perfectly feasible, allowing to obtain deposits of high quality and purity, with a good commercial value, comparable with other less ecological and efficient processes cited in the literature [23].

The cost-effectiveness of the proposed processes can be assured by the rigorous monitoring and control of the main process parameters, such as the concentration of Cu, Sn and Pb ions, the pH and ORP of the electrolyte, and the values of the imposed E_{WE} and/or I_{WE} parameters.

In order to increase the performances of the selective potentiostatic electrodeposition of the Sn-Pb alloys, an intermediate step of Cu cementation on metallic Sn must be inserted between the Cu electroextraction and Sn-Pb alloys electrodeposition stages.

Following the presented protocols, final [Cu], [Sn] and [Pb] values below 0.01 g/L, 0.1 g/L and 1.5 g/L, respectively, can be reached under very promising conditions of profitability.

EXPERIMENTAL SECTION

Chemicals

Reagents as KBr and HBr are purchased by Fluka and Sigma-Aldrich and used as received.

The real leaching solution was obtained by mixing equal samples from different solutions resulted by the leaching of the exposed metals from 10 PC motherboards in 2.2 L of 2 M KBr + 0.5 M HBr + 1 M Br_2 solutions [21]. The ORP of the resulting mixture (1 L) was lowered by placing it over 2 kg of WPCBs, after which the solution pH was adjusted to 0.1 by addition of HBr 47%. The concentrations of the main metallic ions in the final starting solution were: 12.89 g/L Cu; 7.9 g/L Sn; 3.97 g/L Pb; 9 g/L Zn; 5.6 g/L Fe; 0.8 g/L Ni [13].

Experimental methods

The selective potentiostatic electrodeposition experiments of Cu and Sn-Pb alloys were performed in an electrochemical reactor divided using a porous ceramic membrane. As anolyte, 0.5 L samples of fresh 2 M KBr + 0.5 M HBr were introduced in the anodic compartment. The cathodic compartment was filled with 0.5 L of mixture of real leaching solutions described in the chemicals part.

The reactor was equipped with a Fisher type electrode as WE, consisting in a cylindrical Pt mesh, with $\varnothing_{EXT} \cong 25$ mm and a height of $\cong 40$ mm, fixed on a Pt wire frame with $\varnothing = 1$ mm. As CE, a rectangular graphite block with dimensions of 80 mm x 70 mm x 20 mm (height x width x thickness), was used. The WE, CE and 2 reference electrodes of Ag/AgCl/KCl_{sat} type (named further as RE) were connected to a computer controlled potentiostat (DXC236, Datronix Computer, Romania).

The measurements concerning the cementation of Cu on metallic Sn were performed in a glass cell with a volume of 400 mL, in which were introduced 300 mL of solution resulting after all the tests of selective potentiostatic electroextraction of Cu. Over this solution 26.04 g of soldering alloy Sn 97% -Cu 3% were added. The initial soldering alloy, with a diameter of 3 mm, was divided into 252 pieces with a length of approx. 5 mm, resulting an estimated grains area of approximately 120 cm^2.

Additionally, 2 laboratory multi-meters (Consort C863, Consort, Belgium) were used as galvanically insulated electrochemical interfaces with high input impedance between the data acquisition board (NI6121, National Instruments, USA) and the pH and ORP sensors (SP10T and SO50X, respectively, both from Consort, Belgium). During the experiments, the electrolyte from the cathodic compartment was stirred using a magnetic stirrer (FB 15001, Fischer Scientific).

Before each test, the WE was cleaned by immersion during 10 min. in *aqua-regia*, washed with double-distilled water and dried under nitrogen jet, and weighed using an analytical balance (XA110, RADWAG, Polonia).

After each experiment, the Fisher type WE was removed from the electrochemical reactor and the obtained Cu, or Sn-Pb alloy deposits were washed with 2 M KBr + 0.5 M HBr mixture (to avoid the precipitation of Cu, Sn and Pb ions), cleaned with double-distilled water and dried with pure acetone and pure nitrogen jet. Finally, the deposits were weighed using the analytical balance and detached from the electrode by mineralization with 28 mL of *aqua-regia*. The resulted solutions were analyzed by ICP-AES method, using a SPECTRO CIROS CCD spectrometer (SPECTRO Analytical Instruments, Germany). The concentrations of the dissolved metallic ions from the leaching solutions were measured by flame atomic adsorption spectroscopy (FAAS), using an AVANTA-PM spectrometer (GBC, Australia).

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