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INNOVATIONS IN WEEE RECYCLING

# Pyro-Refining of Mechanically Treated Waste Printed Circuit Boards in a DC Arc-Furnace

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**Abstract**

This paper presents the results of theoretical assessment and a preliminary experimental investigation of the modified pyrometallurgical processing of metallic granulate obtained after mechanical treatment of waste printed circuit boards (WPCBs). The studied two-step process included oxidation of metallic granulate followed by pyrometallurgical refining in a DC arc-furnace. In the investigated process, the oxygen bounded in metal oxides, obtained during the oxidation annealing of granulate, was used as a "solid" oxidizer for subsequent pyrometallurgical refining in a DC arc-furnace. According to the obtained results, the Cu content in the produced metallic phase (anodic copper) was 98.4% and is suitable for further electro-refining process. In addition, over 94% of Au was concentrated in metallic phase, suggesting that a high Au yield could be attained. However, owing to the distribution between slag phase and filter product, only 60% of Ag was collected in the metal phase. In-between metal and slag is the metal-oxide phase, containing Cu with metals impurities, such as Sn and Pb, which was obtained as well, and could be further treated using conventional processes for additional metal valorization. The investigated concept would allow substitution of the long-lasting oxygen blowing process and application of complicated pyrometallurgical reactors and create a feasible alternative for lower operating capacities.

**Keywords** WPCBs · Metallic granulate · Recycling · Pyrometallurgy · Oxidative refining

## Introduction

From the perspective of chemical composition, waste electronic and electrical equipment (WEEE) represents a specific non-standard raw material containing valuable precious metals and some toxic and hazardous metals and materials. Since the majority of these highly valuable metals in WEEE are contained in waste printed circuit boards (WPCBs), their importance for metal recycling is increasing, not just from the point of environmental protection, but also from the aspect of resource efficiency and sustainable use of resources [1].

Owing to the high material and components variety, the WPCBs recycling is a very complex and demanding process, which consists of pre-processing and end-processing operations [2]. During the pre-processing stage, various mechanical operations are performed in order to separate metallic and non-metallic materials, allowing more efficient conducting of subsequent pyro- or hydrometallurgical refining stages. Although mechanical treatment may cause dissipation of precious metals in various fractions, a low quality of certain WEEE materials leads to higher costs in further treatment, which is why an interaction between mechanical pre-treatment and metallurgical end-processing should be enabled [3, 4]. This is particularly important in case of low-grade WPCBs, originating from large and small household appliances, where the unfavorable material composition (high non-metallic, Fe, Al, Si and low Ag and Au content) imposes the necessity for material composition upgrade, through an intensive mechanical treatment [5].

Pyrometallurgy represents a dominant end-processing method for the WPCBs recycling. Owing to a high content

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of copper, WPCBs are processed through the so-called black copper route, in which recycling is integrated into the primary copper production process [6]. During the processing, a joint stream of primary material and WPCBs go through a series of pyrometallurgical refining steps, starting from smelting (reduction stage), converting and fire refining (oxidative stage), and ending in anodes electro-refining and anode slime processing (combined pyro-hydro-electrometallurgical processing) [7]. The main advantages of this route are an increased valorization rate of precious metals and energy savings. More specifically, during the smelting, precious metals from WPCBs are collected in the molten copper, while burning of plastics promotes energy savings and partial replacement of the reducing agent. However, the process heat balance generally limits the amount of WPCBs that could be processed, as it may highly affect efficiency of refining operations in the converter [8]. Furthermore, the addition of WPCBs into the production process can introduce different elements in different concentrations, which are not usually found in primary raw materials, consequently making the process control far more difficult. In general, during the first stage of the refining process, a partial oxidation of molten copper with gaseous oxidizing agent is performed. In the next stage of the process, the oxidized copper reacts with metal impurity, in accordance with Eq. (1), transferring the oxidized impurity to the slag or gaseous phase [9].

$$Cu_2O_{(l)} + Me_{(l)} = 2Cu_{(l)} + MeO_{(s,l,g)}. \quad (1)$$

Accordingly, the distribution of elements during the black copper processing route could be divided into three groups with respect to the value of the equilibrium constant of the major refining reaction, presented in Eq. (1). The elements with values of $K$ less than $10^{-2}$, such as Ag, Au, Pt, Pd, Se, Te, or Tl, are difficult to oxidize, and rather dissolve in molten copper ending up in the anode slime. The elements with $K$ values higher than $10^{3}$, such as Fe, Si, Al, Ca, Ti, Cr, Mn, or Mg will easily oxidize and will be mostly found in the slag phase. Finally, the elements with intermediate values of $K$, like Pb, Sn, Ni, Co, Bi, As, or Sb may cause problems, as they are distributed in all three phases (dissolved in metal, oxidized to slag, or volatilized and collected in filter products) [10, 11].

In the final refining step, the main impurities that affect electro-winning process are As, Sb, Bi, Pb, and Sn [12]. Since Pb and Sn are quantitatively next in line to the major base metals (Cu, Fe, Zn), their presence in the input stream represents one of the major challenges in black copper processing route, and generally limit quantities of WPCBs that could be processed, as their presence highly impacts the quality of produced anodes and their suitability for final electro-refining step.

Considering the established industrial practice, the WPCBs recycling in the EU is dominated by several large smelters that process roughly about 300 kt of WPCBs p.a. through processes which follow the general technological steps of the black copper route [13]. Since this material represents only 10–12% of input feed, it may be concluded that the influence of impurities is overcome through their "dilution" in the input stream containing primary raw materials and a high-purity secondary copper.

However, constant changes in material composition, miniaturization of electronic devices, and recent trends toward decreasing metal content in modern electronics may represent a serious drawback for their successful operation in near future, imposing the conclusion that these operations are still far from optimized [14]. Furthermore, limited capacities of existing industrial routes for WEEE processing are challenging the metal industry to develop, design, and optimize new processes for WEEE utilization and recycling, which will be able to respond to the rising amount of WEEE in coming years [15]. Since the adjustment of existing production models generally requires huge investments and a transition period, it may be concluded that a serious gap caused by inadequate recycling capacities will be soon reached, limiting the overall resource efficiency. Therefore, the development of a new cost-effective production model suitable for lower operating capacities is urgently needed.

The major challenge in optimizing such production processes is related to development of the model that will allow subsequent production of suitable anodic metal without involvement of standard refining operations in the converter and anode furnace, which represent the major source of gaseous emissions.

This paper presents the results of theoretical thermodynamic analysis and a preliminary experimental investigation of the modified pyrometallurgical WPCBs processing. Unlike conventional processes, the pyro-refining technology investigates a possibility of using a "solid" oxidizing agent in the refining process. This way of oxidizer addition in the process of WPCB pyro-refining has not been identified in the analyzed scientific literature and industrial practice.

The two-step pyrometallurgical processing consists of oxidation of WPCBs metallic granulate, followed by oxidative refining in a DC arc-furnace. Accordingly, the internally bound oxygen generated during the oxidation annealing of WPCBs metallic granulate was used as an oxidizing agent necessary for refining reactions. By introducing a "solid" oxidizer into the system, a replacement of standard air "blowing" cycles in the converter and anode furnace would be enabled, shortening the duration of the overall refining process. The produced anodic copper with $> 98\%$ Cu would be suitable for further electro-refining processing without additional refining steps for removal of Pb and especially Sn.

## Materials and Methods

### Materials

The material used in the presented research was metallic granulate of WPCBs, obtained from a local WEEE recycler. An intensive mechanical treatment was performed through primary and secondary shredding of WPCBs, followed by a magnetic, electrostatic, and pneumatic separation, allowing a highly efficient separation of metallic and non-metallic materials. The bulk density of the used WPCBs metallic granulate was 4.55 t/m$^3$, with a granule size 97% $> 0.125$ mm.

The chemical composition was determined by X-ray fluorescence spectrometry (XRF) using a Thermo Scientific ARL Quant'x EDXRF Spectrometer. The analysis was performed using a sample cut from the middle of a cylindrical ingot, obtained by melting 1.00 kg of granulate in a medium-induction furnace under reduction conditions (at 1250 °C for 1 h). The mass difference, prior and after melting (0.17 wt%), represented the content of organic materials. The obtained results are presented in Table 1.

### Methods

A theoretical analysis and thermodynamic calculations were performed using HSC Chemistry software [16].

The amount of $Cu_2O$, as a source of oxygen needed for oxidation of impurities and their transfer toward the melt surface for slag formation, was calculated according to a stoichiometric ratio in respect to the determined chemical composition. The preparation of the oxidized WPCBs granulate was performed in a chamber electro-resistant furnace with two openings for natural circulation of ambient air. The content of $Cu_2O$ in the oxidized material was calculated in respect to the content of oxygen in the material as function of mass difference prior and after oxidation annealing and the determined chemical composition of WPCBs granulate. The oxidation was performed at 680 °C, until reaching the predefined mass difference.

The laboratory tests, investigating the possibility of pyrometallurgical refining of WPCBs metallic granulate using a solid oxidizer, were performed in a laboratory high-temperature furnace with silicon carbide heaters. Different mixtures of WPCBs granulate, a solid oxidizer, and slag-forming compounds were melted at 1240 °C for 3 h, and left for cooling inside the furnace. The chemical composition of the obtained products, metallic and slag, was determined by the XRF analysis.

In order to perform a detailed metal-distribution analysis, a scaled test was performed using a semi-industrial DC arc-furnace, the power of 100 KW, a 0.4 m$^3$ working capacity, with a combined refractory lining, ordered from inside to outside: high magnesite, sinter magnesite, and corundum, equipped with an off-gas cooling system and bag filter, presented in Fig. 1. The test was performed by processing 37 kg of pre-oxidized material, using a synthetized FCS (ferrous calcium silicates) slag as a starting slag/flux system ($\sim$ 10 wt% of charge). The slag was obtained by melting a dry homogenized mixture of FeO, CaO, and quartz sand ($SiO_2$) in ratio Fe/$SiO_2$ ratio 1 and CaO 12.5%. After melting, the material was cast into a conical top-opened sand mold and kept inside for cooling. The casting temperature, 1350 °C, was measured using an immersion pyrometer.

Both the laboratory and scaled tests were performed under standard atmospheric conditions (pressure and air composition).

The efficiency of the fire refining process was determined in respect to distribution of Cu and metal impurities (Fe, Zn, Ni, Pb, and Sn) in the metal phase, slag phase, and filter products, referencing to the amount of each obtained fraction and its corresponding chemical composition. The distributing of Cu and the impurity element was calculated by the equation $C = C_{Me}/C_{tot} \cdot 100$ (%), where $C_{Me}$ represents the content of the targeted metal in the analyzed phase (metal, slag, or filter product) and $C_{tot}$ represents the total content of the analyzed element in all fractions.

In the lab scale tests, owing to the inability to collect filter products, the distribution was determined in respect to the amounts and composition of the metal and slag phase.

**Table 1** Chemical composition of mechanically treated WPCBs

| General | Metallic phase | |
|---|---|---|
| Cu (%) | 80.37 | 80.51 |
| Zn (%) | 3.00 | 3.01 |
| Fe (%) | 0.17 | 0.17 |
| Sn (%) | 10.03 | 10.05 |
| Pb (%) | 5.58 | 5.61 |
| Ni (%) | 0.31 | 0.31 |
| Ti (%) | 0.1 | 0.10 |
| V (%) | 0.06 | 0.06 |
| Mn (%) | 0.05 | 0.05 |
| W (%) | 0.04 | 0.04 |
| Sb (%) | 0.02 | 0.02 |
| Bi (ppm) | 95 | 95 |
| Ag (ppm) | 405 | 407 |
| Au (ppm) | 22 | 22 |
| Non-metallic (%) | 0.17 | |

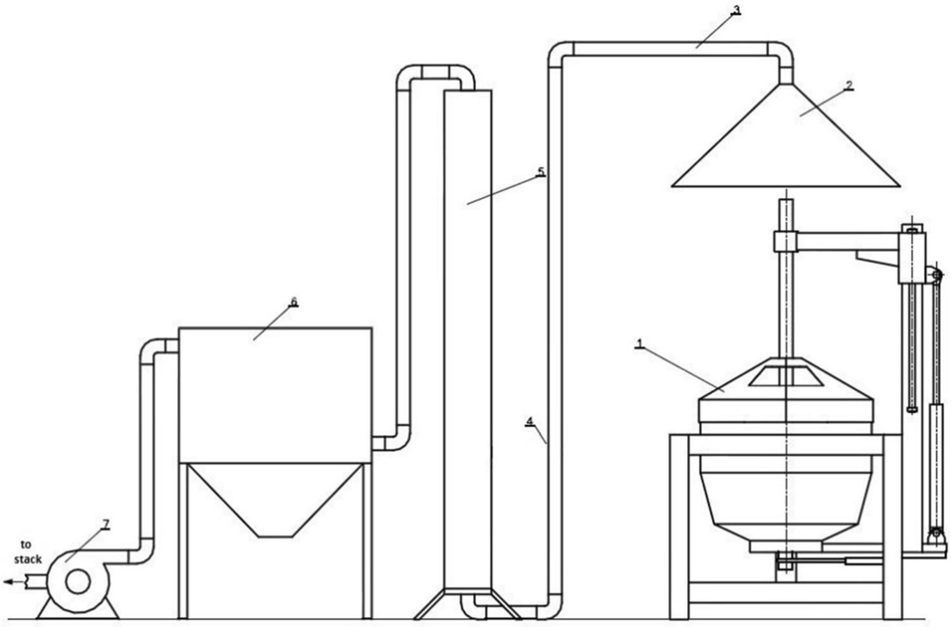

**Fig. 1** Semi-industrial DC plasma furnace: *(1)* DC plasma furnace, *(2)* Hood, *(3)*, *(4)* Off-gas pipeline, *(5)* Cooling tower, *(6)* Bag filter, *(7)* Fan

## Results and Discussion

### Thermodynamic Analysis

The distribution of elements in the metal or slag phase and filter products was analyzed from the equilibrium calculations using the HSC Chemistry software. The major impurities (Fe, Zn, Pb, Sn, Ni, Mn, Ti, W, V, Sb, and Bi) are divided into three groups based on their stability in the presented system. The thermodynamic analysis of refining reactions of each of them in accordance with Eq. (1) and their expected distribution between metal, slag, and filter products are presented in Table 2. Group 1 is excluded from the table and consists of precious metals which are the most stable, with $K < 10^{-2}$ and $\Delta G > 0$.

As presented, the high value of equilibrium constant ($K$) for reactions of Fe, Sb, Mn, V, W, and Ti with $Cu_2O$ suggests that all these metals will be easily oxidized and transferred to the slag phase. Conversely, the intermediate values of $K$ for reactions of Zn, Pb, Sn, Bi, and Ni with $Cu_2O$ suggest that these metals may be distributed within the metal or slag phase, or in the filter products.

These conclusions generally correspond to the available experimental and thermodynamic data, and studies of the distribution of various elements between the FCS slag and Cu melt [11]. According to the available data, during the Cu smelting process, Sn will be distributed between the metal, slag, and filter products phase and its distribution is dependent on oxygen partial pressure ($P_{O2}$). Accordingly, at higher $P_{O2}$, Sn will be segregated to the slag phase in the form of a highly stable $SnO_2$. At lower $P_{O2}$, $SnO_2$ will be reduced to volatile SnO, and as such will be mainly transferred to filter products [11].

Considering the distribution of Pb, apart from $P_{O2}$, the Pb distribution is also dependent on slag basicity. As in the previous case, it is reported that the Pb distribution has a linear correlation to $P_{O2}$, meaning that Pb is either segregated in the slag phase as PbO, reduced to the metallic phase as Pb, or volatilized to filter products [11]. However, in the FCS system, a part of the oxidized Pb tends to form stable silicates in the slag phase, in accordance with the reactions in Eqs. (2)–(6).

$$2\mathrm{Pb} + \mathrm{O_2(g)} = 2\mathrm{PbO} \quad \Delta G^{\theta}_{1573} = -147.71\ \mathrm{kJ} \tag{2}$$

$$2\mathrm{Pb} + \mathrm{O_2(g)} + 2\mathrm{SiO_2} = 2\mathrm{PbSiO_3} \quad \Delta G^{\theta}_{1573} = -195.59\mathrm{kJ} \tag{3}$$

$$\mathrm{PbO} + \mathrm{SiO_2} = \mathrm{PbSiO_3} \quad \Delta G^{\theta}_{1573} = -23.94\mathrm{kJ} \tag{4}$$

$$2\mathrm{PbO} + \mathrm{SiO_2} = \mathrm{Pb_2SiO_4} \quad \Delta G^{\theta}_{1573} = -26.20\mathrm{kJ} \tag{5}$$

$$4\mathrm{PbO} + \mathrm{SiO_2} = \mathrm{Pb_4SiO_6} \quad \Delta G^{\theta}_{1573} = -76.83\mathrm{kJ}. \tag{6}$$

As presented, all possible reactions of PbO with $SiO_2$ are spontaneous, which is why the majority of Pb may be expected to be transferred to the slag phase, either as PbO or in the form of silicates $Pb_xSiO_y$.

### Slag System Design

As one of the very important aspects of all pyrometallurgical processes, in this case slag was given special attention. Slags protect metal, but at the same time, if designed correctly, remove undesirable impurities. In the presented

**Table 2** Thermodynamic data of elements in liquid Cu at 1300 °C using HSC Chemistry

| Reaction | Equilibrium constant (*K*) | $\Delta G^{\theta}_{1573}$, kJ | |
|---|---|---|---|
| $Pb + Cu_2O = PbO + 2Cu$ | $1.06 \times 10^{-1}$ | 29.778 | Group 2 (most volatile metals) |
| $Bi + 3Cu_2O = Bi_2O_3 + 6Cu$ | 1.67 | − 6.767 | |
| $Ni + Cu_2O = NiO + 2Cu$ | 33.24 | − 45.826 | |
| $Zn + Cu_2O = ZnO + 2Cu$ | $1.54 \times 10^{2}$ | 54.609 | |
| $Sn + Cu_2O = SnO + 2Cu$ | $3.69 \times 10^{2}$ | − 77.319 | |
| $Fe + Cu_2O = FeO + 2Cu$ | $3.76 \times 10^{3}$ | − 107.666 | Group 3 (metals oxidized readily) |
| $Sb + 3Cu_2O = Sb_2O_3 + 6Cu$ | $7.85 \times 10^{5}$ | − 177.525 | |
| $Mn + Cu_2O = MnO + 2Cu$ | $1.27 \times 10^{7}$ | − 213.888 | |
| $V + Cu_2O = VO + 2Cu$ | $1.22 \times 10^{8}$ | − 243.530 | |
| $W + 3Cu_2O = WO_3 + 6Cu$ | $3.74 \times 10^{9}$ | − 288.270 | |
| $Ti + Cu_2O = TiO + 2Cu$ | $2.14 \times 10^{11}$ | − 341.185 | |

research, a ferrous calcium silicate (FCS) slag was used, with the main constituents FeO, CaO, and $SiO_2$. This slag was expected to have transitional properties between iron silicate slag and calcium ferrite slag. A homogenous slag with low viscosity at the process temperature should enable a high mass-transfer, ensuring high reaction rates.

The slag system was chosen to be in Olivine area of the ternary phase diagram presented in Fig. 2, with a liquidus temperature around 1100 °C, with $Fe/SiO_2$ ratio 1, and CaO 12.5%.

## Oxidation Stage

Considering the obtained thermodynamic data and expected distributions of different metals presented in Table 2, the segregation of impurities into the slag phase is dominantly a function of $P_{O2}$, requiring an excessive presence of oxygen during the fire refining process. In this respect, a preliminary test and investigation of the process feasibility was performed introducing the excessive amount of $Cu_2O$ with respect to the required amount for major refining reactions, and was set to 100 wt% excess.

The calculation of the required amount of $Cu_2O$ for oxidation of major impurities was performed in accordance with stoichiometric ratios of reactions presented in Eq. (1) and the chemical composition of the material presented in Table 1. Therefore, the determined required amount of $Cu_2O$ for oxidation of major impurities is 1.757 kmol, which corresponds to mass of 250 $g_{Cu2O}/kg_{material}$.

Accordingly, in the oxidation stage, the WPCBs granulate was oxidized until reaching the level of 9.30 wt% of oxygen, which corresponds to excess of cca. 100% of $Cu_2O$.

## Fire Refining Tests

### Laboratory Tests

A series of laboratory tests were performed in order to verify the proposed concept and test the slag system. The first four experiments were performed using $Cu_2O$, p.a. as a source of the “solid” oxidizing agent, and the fifth experiment was performed using an oxidized WPCBs granulate.

Varied slag systems were as follows: exp 1-no slag, exp 2-FCS, exp 3-$CaO/Na_2CO_3$, exp 4-borax, and exp 5-FCS. Table 3 presents the material balance of the laboratory tests.

Based on the measured masses and chemical compositions of the obtained products, overall distributing (*C*) of Cu, Sn, and Pb in metal and slag was calculated in accordance with Eq. (7), and presented in Table 4.

$$C_{\mathrm{Mi}}(\mathrm{phase}) = \frac{\%_{\mathrm{Mi\_phase}} \times \mathrm{Mass}_{\mathrm{phase}}}{\%_{\mathrm{Mi}} \times \mathrm{Mass}_{\mathrm{INPUT}}}. \qquad (7)$$

Mi = Cu, Sn, Pb

As it could be seen from Table 4, tests 2, 4, and 5 indicated the highest Cu efficiency, but with respect to the removal of Sn and Pb, tests 2 and 5 were the most efficient. The obtained results proved on a laboratory scale that the designed slag system is the most effective in the present case. In addition, the comparison of tests 2 and 5 with the same slag system indicates that the better results are obtained using oxidized WPCBs granulate than $Cu_2O$ p.a. quality.

### Scaled Test

The fire refining test in a pilot-scale DC arc-furnace, using oxidized WPCBs granulate, was performed in accordance with the regime presented in Table 5.

**Fig. 2** Phase diagram FeO–$SiO_2$–CaO with indicated used slag composition (color figure online)

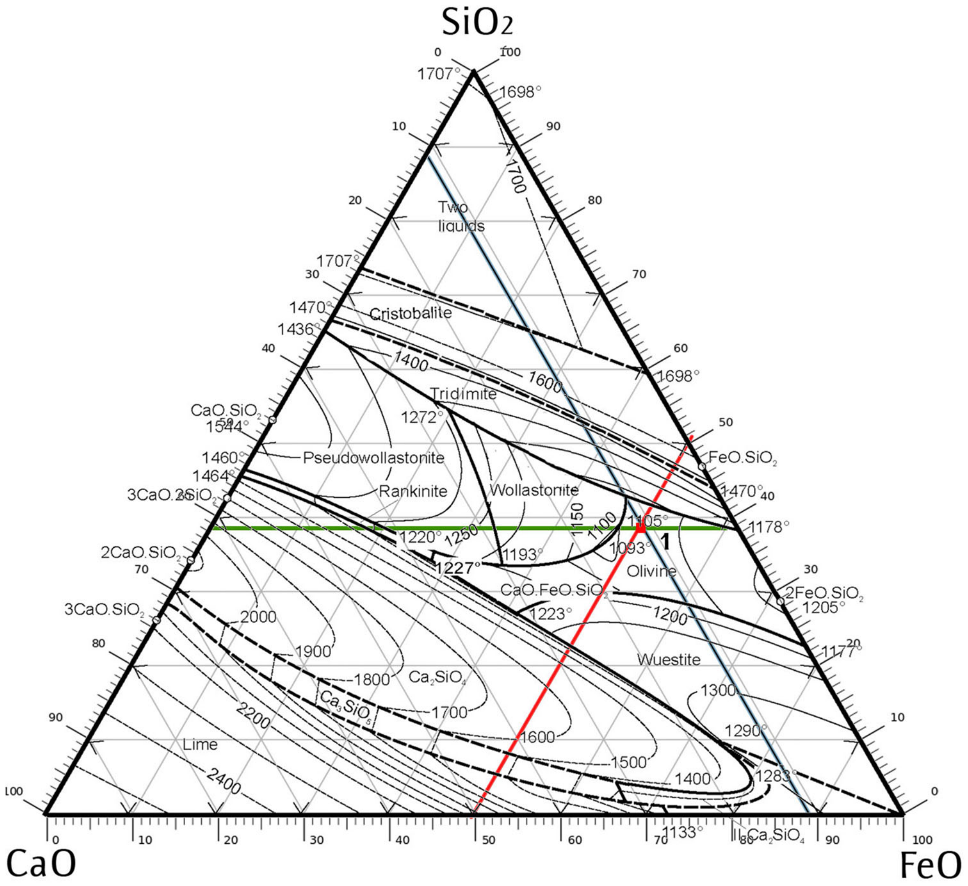

**Table 3** Laboratory tests of fire refining of the oxidized WPCBs granulate

| | Exp1 | Exp2 | Exp3 | Exp4 | Exp5 |
|---|---|---|---|---|---|
| Input (g) | | | | | |
| WPCB granulate | 500 | 500 | 500 | 500 | – |
| Oxidized granulate | – | – | – | – | 500 |
| $Cu_2O$, p.a. | 71.5 | 71.5 | 71.5 | 71.5 | |
| CaO | – | 7.14 | 42.8 | – | 6.25 |
| Fe | – | 25 | – | – | 21.87 |
| $SiO_2$ | – | 25 | – | – | 21.87 |
| $Na_2CO_3$ | – | – | 14.29 | – | – |
| Borax | – | – | – | 9 | – |
| Output (g) | | | | | |
| Metal | 484 | 552 | 236 | 465 | 386 |
| Slag | 92 | 72 | 396 | 38.5 | 156 |

**Table 4** Distributing of Cu, Sn, and Pb in products of laboratory tests of fire refining

| | Exp1 | Exp2 | Exp3 | Exp4 | Exp5 |
|---|---|---|---|---|---|
| Metal | | | | | |
| Cu | 93.92 | 99.13 | 42.72 | 99.48 | 99.89 |
| Sn | 64.73 | 35.42 | 32.59 | 79.48 | 27.02 |
| Pb | 66.85 | 19.32 | 34.20 | 65.80 | 8.46 |
| Slag | | | | | |
| Cu | 6.08 | 0.87 | 57.28 | 0.52 | 0.11 |
| Sn | 35.27 | 64.58 | 67.41 | 20.52 | 72.98 |
| Pb | 33.15 | 80.68 | 65.80 | 34.20 | 91.54 |

After refining, the melt was cast into a mold and left for cooling and phase separation. After 24 h, the material was extracted out of the mold and the obtained fractions were measured. As presented in Fig. 3, in addition to the expected phases of reduced metal and slag, the intermediate phase composed of metal-oxide compounds was obtained.

The complete mass balance of the process is presented in Table 6.

The phase composition of the obtained intermediate metal-oxide phase was investigated by the XRD analysis, using a PHILIPS PW–1710 diffractometer. The obtained diffractogram is presented in Fig. 4. According to the results of semi-quantitative analysis, the dominant phase represents $Cu_2O$ (70–75%), followed by $SnO_2$ ($\approx$ 15%),

**Table 5** Schedule of performed operations

| Operation | Time (min.) |
|---|---|
| Heating of DC arc-furnace and melting of starting slag | 90 |
| Charging of material | 30 |
| Fire refining | 60 |
| Total time | 180 |

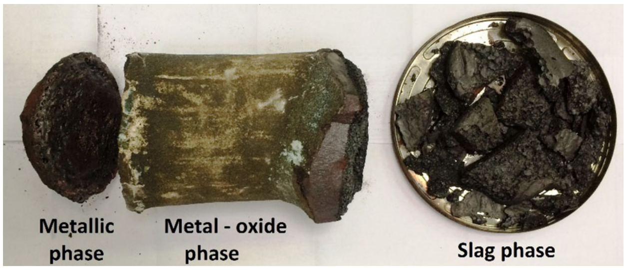

**Fig. 3** Obtained fractions after fire refining process (color figure online)

**Table 6** Mass balance of fire refining process

| | |
|---|---|
| Input | |
| Oxidized WPCBs granulate | 37.00 kg |
| FCS Slag | 4.00 kg |
| Total | 41.00 kg |
| Output | |
| Metal_red. | 7.50 kg |
| Metal_ox. | 27.33 kg |
| Slag | 3.27 kg |
| Filter products | 0.55 kg |
| Total | 38.65 kg |

FeO(OH) ($\approx$ 10%), $Pb_3O_4$ ($\approx$ 5%), FeO ($<$ 1%), and $TiO_2$ ($<$ 1%).

The distribution of Cu and metal impurities in the obtained fractions of metal, metal-oxide, slag, and filter products was determined in accordance with the mass and chemical composition of the obtained fractions, Fig. 5. The complete material balance of the oxidative refining process is presented in Table 7.

According to the presented material balance, by applying a two-stage pyrometallurgical treatment of WPCBs metallic granulate, which includes oxidation and the oxidative refining process, anodic copper (98,4% Cu) suitable for further electro-refining was obtained. In addition, the metal-oxide phase containing Cu with collected metal impurities, such as Sn and Pb, was obtained as well. This metal-oxide phase could be further treated using conventional processes, for instance, a metallothermic reduction for additional valorization of useful components and production of lead–tin bronze.

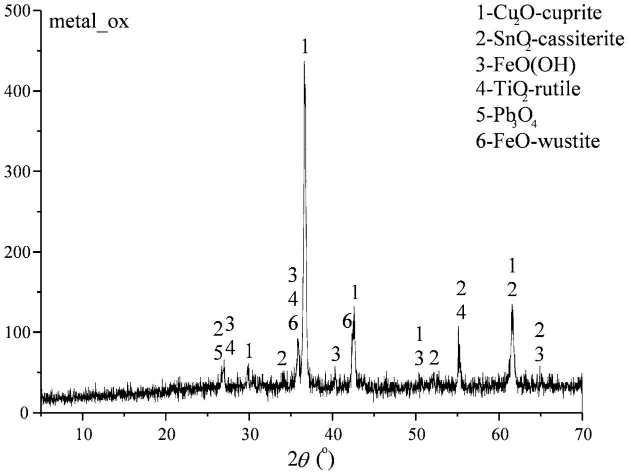

**Fig. 4** XRD pattern of intermediate metal-oxide phase

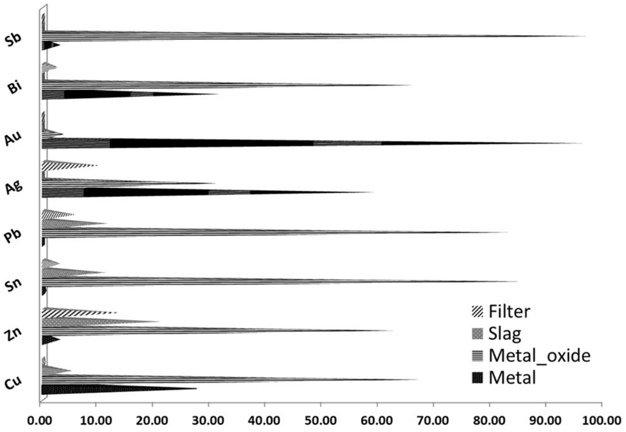

**Fig. 5** Distribution of metals in obtained products

## Conclusion

This paper presents the results of theoretical reconsideration and a preliminary experimental investigation of the modified pyrometallurgical WPCBs processing. In sum, by comparison with the traditional black copper route, the possibility of copper pyro-refining technology using a "solid" oxidizing agent has been studied. According to the preliminary results, it was determined that oxygen needed for the fire refining stage and oxidation of the main impurities (Zn, Fe, Pb, Sn) contained in WPCBs granulate could be provided using oxygen internally bound in the

**Table 7** Material balance of oxidative refining process

| | Input | | | Output | | | | |
|---|---|---|---|---|---|---|---|---|
| | WPCBs$_{9.38\%O2}$ Composition (%) | FCS slag | Total kg/*g | Metal Composition (%) | Metal_ox | Slag | Filter | Total kg/*g |
| Cu | 80.51 | 0.57 | **27.02** | 98.40 | 66.40 | 42.10 | 21.30 | **27.02** |
| Fe | 0.170 | 47.49 | **1.96** | 0.12 | 6.22 | 11.24 | 14.90 | **2.16** |
| Zn | 3.010 | 0.00 | **1.00** | 0.41 | 2.27 | 6.37 | 24.70 | **0.99** |
| Ni | 0.310 | 0.00 | **0.10** | 0.00 | 0.29 | 0.42 | 0.00 | **0.09** |
| Sn | 10.05 | 0.00 | **3.37** | 0.26 | 10.31 | 11.30 | 18.40 | **3.31** |
| Pb | 5.610 | 0.00 | **1.88** | 0.00 | 5.78 | 6.67 | 19.70 | **1.89** |
| Ti | 0.100 | 0.00 | **0.03** | 0.00 | 0.11 | 0.00 | 0.00 | **0.03** |
| Ag | 0.0407 | 0.00 | **13.6*** | 0.103 | 0.0148 | 0.00 | 0.24 | **13.01*** |
| Au | 0.0022 | 0.00 | **0.75*** | 0.0097 | 0.00 | 0.00 | 0.00 | **0.71*** |
| Bi | 0.0095 | 0.00 | **3.20*** | 0.013 | 0.0075 | 0.00 | 0.02 | **3.10*** |
| Sb | 0.0220 | 0.00 | **7.40*** | 0.003 | 0.026 | 0.00 | 0.00 | **7.30*** |

Total amounts of input/output quantities are given in bold. Values with asterisk are calculated in gram and without asterisk are calculated in kilogram

material after oxidation annealing, which precedes the oxidative refining stage in a DC arc-furnace. Moreover, the results of the scaled test and the analysis of distribution of metals in the metal phase and metal-oxide phase, slag, and filter products revealed that, with the sufficient amount of internally bound oxygen in the system, the metallic phase containing over 98% of copper could be obtained. Although around 31% of overall Bi was segregated into the reduced metal phase, Sb was dominantly transferred to the metal-oxide phase (over 97%). Additionally, the distribution of precious metals showed that through the proposed pyro-refining route, a high Au yield—over 94%—could be attained. However, in the case of Ag, owing to the distribution between the slag phase and the filter product, only 60% of Ag was collected into the metal phase. Accordingly, the presented results may be represent a strong basis for further optimization of this oxidation refining approach, which will allow a substitution of the long-lasting oxygen blowing process, application of complicated pyrometallurgical reactors, and create a feasible alternative to lower operating capacities.

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