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Enhancement of leaching copper by electro-oxidation from metal powders of waste printed circuit board

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ABSTRACT

Oxidation leaching copper from metal powders of waste printed circuit boards (PCBs) was conducted at room temperature in sulfuric acid solution. The result showed that the copper in metal powders was oxidized by Cu^{2+} to form $CuCl_2{}^-$ in the presence of chloride ion without electrochemical oxidation. Then, $CuCl_2{}^-$ was oxidized into $CuSO_4$ by oxygen derived from the air insufflated into leaching solution. The leaching rate of copper reached 100%. The whole reaction took 5.5 h because it was limited by the low solubility of the air in water. In the electro-oxidation conditions, the chloride ion was electro-oxidized into ClO^-, which oxidized $CuCl_2{}^-$ into $CuSO_4$ and ClO^- was reduced into Cl^- itself again at the same time. Since Cl^- was recycled in the solution not only as a complexing agent but also as an oxidant, which made the reaction speed up to 3.5 h to reach 100% leaching rate. Leaching solution was concentrated to crystallize $CuSO_4{\cdot}5H_2O$, and crystal liquor was reused to leach copper from metal powders.

1. Introduction

The production of printed circuit boards (PCBs) is the base of the electronic industry as it is the essential part of almost all Electrical and electronic equipment (EEE). Nowadays, the new technological innovation continues to accelerate the replacement of equipment, leading to a significant increase in waste PCBs [1].

However, PCBs contain nearly 28% metals that are abundant non-ferrous metals such as Cu, Pb, and Sn, etc. The purity of precious metals in PCBs is 10 times more than that of rich-content mineral. The hazardous materials may seriously pollute the environment if they are not properly disposed. Therefore, the recycling of PCB waste is an important issue, not only from the aspect of waste treatment, but also with respect to the recovery of valuable metals [2–8].

Mechanical/physical processing is a method of recycling processes for waste PCBs. the mechanical recycling process may increase the content of metal scraps. Since no water or chemical additive is associated with this method, there is no wastewater problem in this type of operation. High-grade metals can be recovered. It is researched and applied widely at home and abroad. But recovered metals may also need further purification before they can be utilized [9–14].

In this study, a new process technology with small environment pollution for further purifying copper from recovered metals of waste PCBs treated by mechanical method was investigated. The objective of the research was to try to recover valuable metal copper by leaching process using H_2SO_4, Cl^- and the air. Our interest was focused on the reduction of the environmental impact, the enhancement of leaching copper efficiency by electro-oxidation and the recovery of valuable metals such as copper [15].

2. Experimentals

100 kg waste PCBs were pretreated by mechanical process and were separated into two parts: about 25 kg recovered metal powders with high copper content and non-metallic plate. Fig. 1 showed that waste PCBs were pretreated into metal powders with high copper content. The chemical compositions of metal powders were shown in Table 1. Furthermore, concentrated sulfuric acid, sodium chloride and copper sulfate were used in the experiment. These reagent purities were of analytical grade.

The metal powders separated from waste PCBs were used to recover copper by recycling leach process, as presented in Fig. 2. Leaching of metal powders with high copper content was carried out at room temperature (about 298 K) in dilute sulfuric acid solution. Chloride ionic was taken as complex agent and Cu^{2+} and air were taken as oxidants.

The leaching solution was put into anode region of electrolysis device to enhance leaching reaction rate of metal powders, as shown in Fig. 3. The anode material was graphite, and cathode

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Table 1
Chemical compositions of metal powders from waste PCBs.

Element	Cu	Sn	Pb	Zn	Ni	Fe
Content (%)	86.1	2.23	1.28	<0.02	0.039	0.16
Element	Al	Ag	Pd	Mn	Au	Other
Content (%)	0.27	0.019	0.011	0.0052	0.0079	9.86

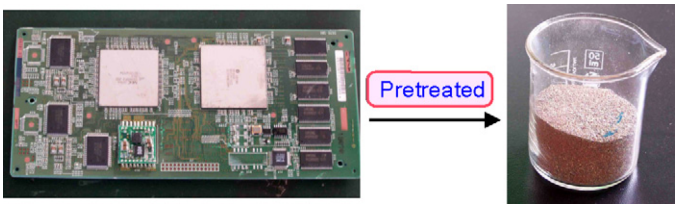

Fig. 1. Waste PCBs pretreated into metal powders with high copper content.

material was stainless steel. Anion exchange membrane was used to separate anode region and cathode region.

The main experimental equipments include exposures oxygen machine, magnetic stirrer and DC power supply. The compositions of samples were analyzed by ICP spectrometer. Concentration of hypochlorous acid was analyzed by chemical method.

3. Experimental results

3.1. Leaching copper without electro oxidation

Leaching copper from metal powders was carried out at room temperature (about 298 K), and there are many factors influencing its leaching rate such as concentration of sulfuric acid, aerobics pump number, leaching time, NaCl and $CuSO_4$ quality.

Fig. 4a shows the curve of copper leaching rate for different qualities of NaCl. Leaching rate of copper from metal powders increases with the increase in NaCl, and its leaching rate reaches the maximum when 12 g NaCl is added. Fig. 4b shows the curve of copper leaching rate in the aerobics pump number condition. The copper leaching rate increases with the increase in aerobics pump number in the initial stage, which can improve the concentration of dissolved oxygen. Fig. 4c shows the curve of copper leaching rate for different qualities of $CuSO_4 \cdot 5H_2O$. The copper leaching rate increases with the increase in Cu^{2+} concentration. The copper in 20 g metal powders is extracted completely with 9 g $CuSO_4 \cdot 5H_2O$. Fig. 4d shows the curve of copper leaching rate for different volume of H_2SO_4. The copper leaching rate increases with the increase in added volume number of H_2SO_4. The best result shows that copper leaching rate reaches 100% when H_2SO_4 (98%) is added to 18 ml. On the contrary, its leaching rate decreases when the volume of added H_2SO_4 is more 24 ml.

Fig. 5a shows the curve of copper leaching rate for different time. The copper leaching rate increases with the increase in leaching time, and it takes 5.5 h to extract copper from metal powder completely. Fig. 5b shows the curve of copper leaching time for different solid–liquid ratio. The leaching time increases with the decrease in solid–liquid ratio. Therefore, the best condition of leaching copper from metal powders is 20 g metal powders, solid–liquid ratio of 1/15, two aerobics numbers, 12 g NaCl, 9 g $CuSO_4 \cdot 5H_2O$, 25 °C and a leaching time of 5.5 h.

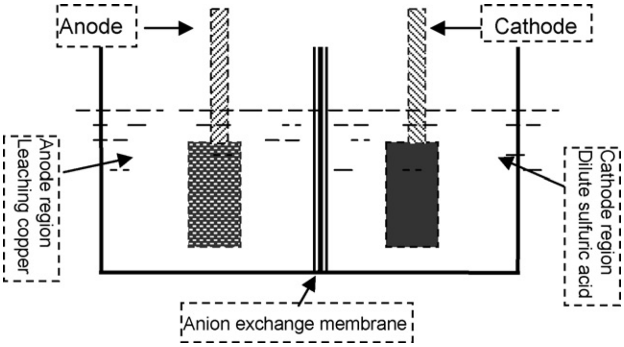

Fig. 3. Experimental equipment sketch of electro-oxidizing to leach copper.

3.2. Leaching copper in the presence of electro oxidation

Fig. 6(a) shows the curve of copper leaching rate for different NaCl mass in the presence of electro oxidation. The concentration of hypochlorous acid synthesized by electrochemical methods in NaCl solution increases with the increase in NaCl quality. Fig. 6(b) shows the curve of copper leaching rate for different current density. The result denotes that leaching rate is improved by the increase in current density. Fig. 6(c) shows the curve of copper leaching rate for different time under the enhancement of electro oxidation. The copper leaching rate reaches 100% in about 3.5 h. Leaching time of electro-oxidation enhancement is 2.0 h less than that without electro oxidation. Fig. 6(d) shows the curve of copper leaching rate versus solid–liquid ratio. The leaching rate decreases with the increase in solid–liquid ratio.

3.3. Experimental result of mother liquor cycles

Fig. 7 shows the curve of mother liquor cycles versus quality of added NaCl with electro-oxidation enhancing. The result denotes that NaCl is added into the solution of cycle leaching to compensate its consumption. Fig. 8 shows the curve of mother liquor cycles versus crystal purity of $CuSO_4 \cdot 5H_2O$. The grade of its crystal

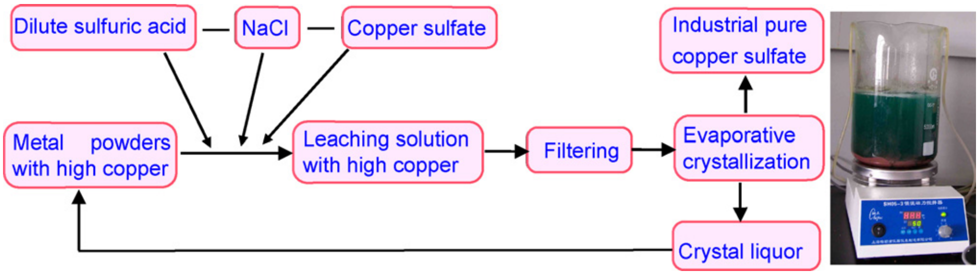

Fig. 2. Process and equipment of leaching copper from metal powders without electro-oxidation.

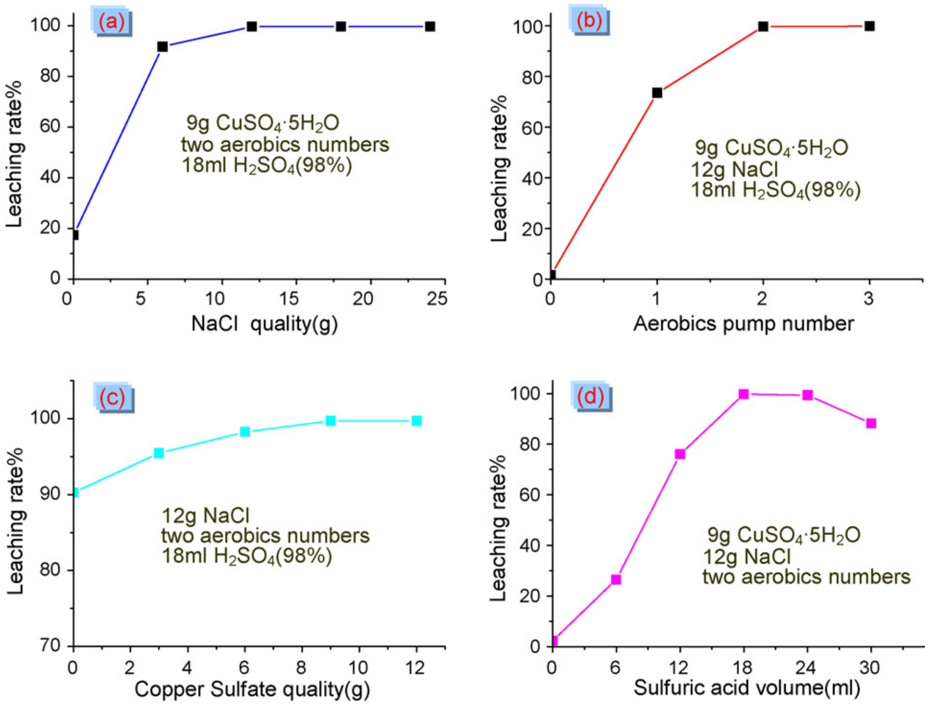

Fig. 4. Copper leaching rate impacted by NaCl quality, copper sulfate quality, aerobics pump number and H_2SO_4 volume (300 ml leaching solution, temperature: 25 °C, leaching time: 5.5 h, 20 g metal powders).

purity still reaches 98.5% after cycle leaching of 5 times. The pictures of crystal and powder $CuSO_4{\cdot}5H_2O$ products are shown in Fig. 9.

4. Discussion

In the case of recovering copper from metal powders of waste PCBs, acid leaching process is carried out in sulfuric acid solution using Cu^{2+} ionic and the air oxidant under chloride ion catalyzing condition. In the acid leaching of copper, it is well known that the yield of metallic elements depends on the acid concentration, leaching time and oxidant. From the results of Fig. 4a–d and Fig. 5a and b, it is indicated that the copper leaching rate increases with the increase in sulfuric acid volumes, aerobics pump number, leaching time, NaCl, $CuSO_4$ quality and decrease in solid–liquid ratio. Their reaction mechanisms are listed in Eqs. (1)–(6).

$$Cu + Cu^{2+} = 2Cu^{+} \tag{1}$$

$$Cu^{+} + Cl^{-} = CuCl \quad CuCl + Cl^{-} = CuCl_2{}^{-} \tag{2}$$

$$4CuCl_2{}^{-} + O_2 + 2H_2O = 2[Cu(OH)_2{\cdot}CuCl_2] + 4Cl^{-} \tag{3}$$

$$4CuCl + O_2 + 2H_2O = 2[Cu(OH)_2{\cdot}CuCl_2] \tag{4}$$

$$[Cu(OH)_2{\cdot}CuCl_2] + H_2SO_4 = CuSO_4 + CuCl_2 + 2H_2O \tag{5}$$

$$CuSO_4 + 5H_2O = CuSO_4{\cdot}5H_2O \tag{6}$$

Here, copper sulphate is added as a kind of oxidant into initial leaching solution, which provides Cu^{2+} to oxidize the copper into Cu^{+} such as in Eq. (1) Sodium chloride is added to provide Cl^{-}, and Cu^{+} which is from the copper oxidized is formed into $CuCl_2{}^{-}$ complex compound with Cl^{-} such as in Eq. (2). So the copper powders are dissolved into the leaching solution. After air insufflated into leaching solution, O_2 oxidant makes $CuCl_2{}^{-}$ converse into $[Cu(OH)_2{\cdot}CuCl_2]$ as shown in Eqs. (3) and (4). In sulfuric acid solution, $[Cu(OH)_2{\cdot}CuCl_2]$ can produce copper sulphate as shown in Eq. (5), which is crystallized to $CuSO_4{\cdot}5H_2O$. Then, mother liquor

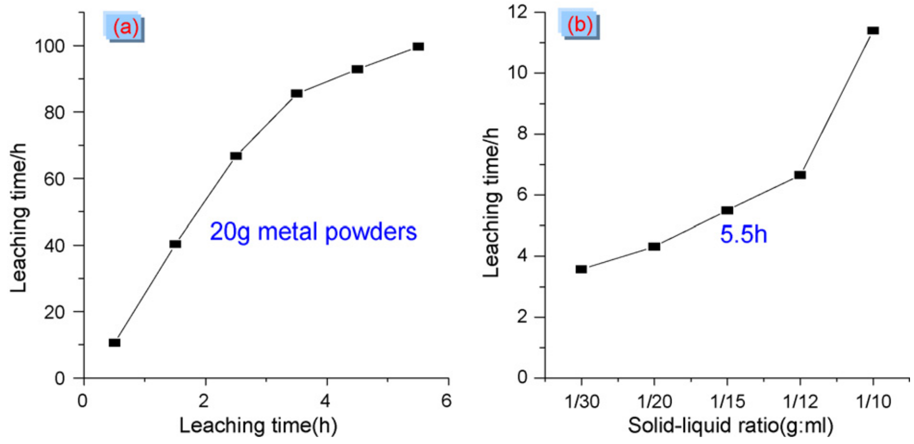

Fig. 5. Copper leaching rate impacted by leaching time and solid–liquid ratio (300 ml leaching solution, temperature: 25 °C, 12 g NaCl, two aerobics numbers, 18 ml H_2SO_4, 9 g $CuSO_4{\cdot}5H_2O$).

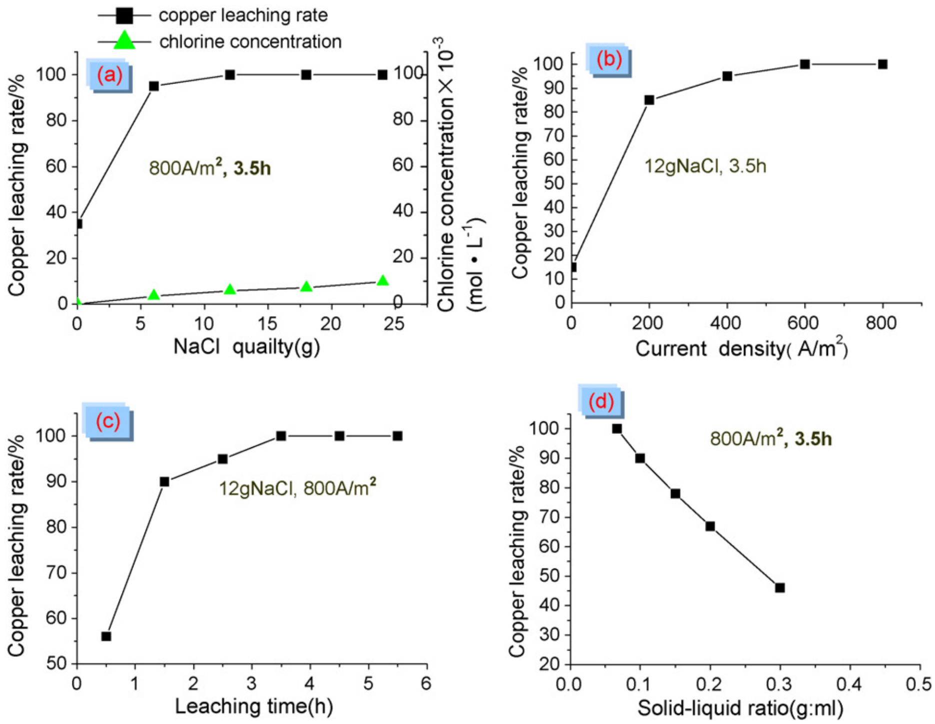

Fig. 6. Curve of copper leaching rate extracted from waste PCBs using electrochemistry (300 ml leaching solution, temperature: 25 °C, two aerobics numbers, 9 g $CuSO_4 \cdot 5H_2O$.

will provide enough Cu^{2+} and copper sulphate will not be added again.

From Eqs. (2) and (3), it is found that Cl^- plays a role as a bridge. It forms complex compound with Cu^+. After O_2 oxidized Cu^+ into Cu^{2+}, Cl^- is released from the complex compound. Then, Cl^- will return to react with Cu^+ again. So Cl^- has a cycle itself and it is not lost in the course of reaction. Cl^- plays a catalyst role in leaching copper process. Fig. 4a shows that the best value of Cl^- quality is 12 gNaCl. In addition, Cl^- cycle speed itself impacts migration and conversion rate of the copper and Cu^+ in the Eq. (1), it is shown that there is best matching between NaCl and $CuSO_4$ quality as shown in Fig. 4c. Fig. 4d shows that the copper leaching rate decreases when added sulfuric acid is more than 24 ml. This means that the solubility of copper sulfate is influenced by the increase in ${SO_4}^{2-}$, which influences copper leaching rate. The increase in solid–liquid ratio has reduced the volume of leaching solution, which will reduce the amount of dissolved oxygen and copper sulphate, the result is the decrease in the copper leaching rate such as in Fig. 5b.

Besides, the solubility of oxygen is 0.031 in a volume water at 20 °C, which limits the reaction speed of copper leaching which lasts for 5.5 h such as in Fig. 4b and Fig. 5a.

In the presence of electric field, their reaction mechanisms of anode region are listed in Eqs. (7)–(11)

$$2Cl^- - 2e = Cl_2 \tag{7}$$

$$Cl_2 + H_2O = HClO + HCl \tag{8}$$

$$2H_2O - 4e = O_2 + 4H^+ \tag{9}$$

$$ClO^- + Cu + Cl^- + H^+ = {CuCl_2}^- + H_2O \tag{10}$$

$$ClO^- + 2{CuCl_2}^- + 2H^+ = 2CuCl_2 + H_2O + Cl^- \tag{11}$$

Here, besides Cl^- cycle itself as the above described, in the electric field of anode area, Cl^- can be oxidized into Cl_2, which dissolves in water to form HClO oxidant such as in Eqs. (7) and (8). HClO oxidant plays a very important role for Cu to be oxidized into Cu^+ and Cu^+ to be oxidized into Cu^{2+}, and its reduced products is Cl^-. At

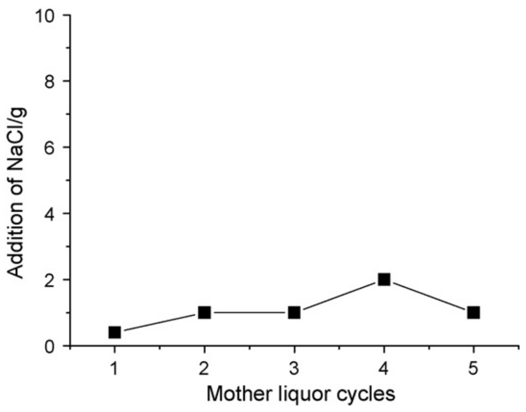

Fig. 7. Curve of mother liquor cycles versus mass of added NaCl with electro-oxidation enhancing.

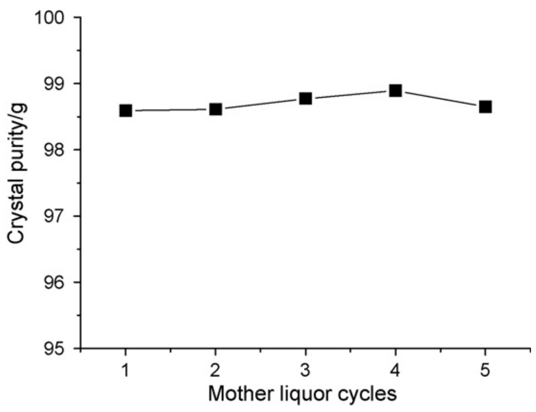

Fig. 8. Curve of mother liquor cycles versus crystal purity of $CuSO_4 \cdot 5H_2O$ with electro-oxidation enhancing.

Fig. 9. Picture of crystal and powder $CuSO_4 \cdot 5H_2O$ products.

the same time, Eq. (9) shows that active oxygen is a byproduct of anode electrochemical reaction. The above reaction speed of copper leaching limited by oxygen solubility in water is improved by the electro-oxidation HClO and O_2, that is to say, its reacting time is decreased from 5.5 to 3.5 h such as in Fig. 6c. In addition, from Eqs. (7) to (11), it is found that Cl^- has another cycle itself in the electric field, which improves cycle efficiency in the process of electro-oxidation leaching copper and decreases leaching time. Fig. 6(b) shows that leaching rate is improved by the increase in current density at first. But the solubility of chlorine in water is as low as that of oxygen, and their solubility does not increase with the increase in current density. So the copper leaching rate will no longer increase.

In addition, Cl^- ionic is slightly lost in the process of leaching copper from waste PCBs, as shown in Fig. 7. So NaCl is added into the solution of cycle leaching to compensate its consumption in regular. The grade of crystal $CuSO_4 \cdot 5H_2O$ still reaches 98% after mother liquor is cycled for 5 times.

5. Conclusions

The copper in metal powders of waste PCBs is recovered using the process of sulfuric acid leaching, in the presence of Cu^{2+} and the air oxidant, through Cl^- ionic forming $CuCl_2^-$ complex intermediate product. Leaching time is about 5.5 h for 20 g metallic powder.

Leaching solution is concentrated to produce $CuSO_4 \cdot 5H_2O$. The mother liquor is reused to leach copper from metallic powder of waste PCBs.

In the presence of electric field, Cl^- ionic in anode region is electrosynthesized by HClO oxidant, which quickens the solubility of copper. Therefore, the leaching time is shortened from 5.5 to 3.5 h for 20 g metal powders through electro oxidant.

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References

[1] P. Mou, D. Xiang, X. Pan, L. Wa, J. Gao, G. Duan, IEEE (2005) 205.
[2] Li Jia, lu Hongzhou, Guo Jie, Environ. Sci. Technol. 41 (2007) 1995.
[3] S.G. Schmelzer, H. Wolf, Aufbereit. -Tech. 37 (1996) 149.
[4] C. Jirang, E. Forssberg, J. Hazard. Mater. 99 (2003) 243.
[5] Z. Shunli, F. Eric, Res. Conserv. Recycl. 21 (1997) 247.
[6] G.-h. Gu, Y.-f. Qi, Chin. J. Nonferrous Met. 14 (2004) 37.
[7] C.-H. Lee, C.-T. Chang, K.-L. Fan, J. Hazard. Mater. 114 (2004) 93.
[8] H.-Y. Kang, Julie M. Schoenung, Res. Conserv. Recycl. 45 (2005) 368.
[9] Jirang Cui, Eric. Forssberg, J. Hazard. Mater. 99 (2003) 243.
[10] F. Veglio, R. Quaresimaa, P. Fornarib, S. Ubaldinib, Waste Manag. 23 (2003) 245.
[11] Catalog, Recovery of Metals from Electronic Scrap, Huei-Chia-Dien Company, Taiwan, 2003 (in Chinese).
[12] Jae-chun Lee, Hyo Teak Song, Jae-Min Yoo, Res. Conserv. Recycl. 50 (2007) 380.
[13] A. Bernardes, I. Bohlinger, D. Rodriguez, Proceedings of sessions and symposia sponsored by the extraction and processing division. TMS, 1997, p. 363.
[14] K. Koyama, M. Tanaka, J-c. Lee, Mater. Trans. 47 (2006 1788).
[15] Zhu, ping; Zhou,Ming. Chinese Patent 2007101049955. 2007.