Copper Recovery from Printed Circuit Board by Carbonization

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In an attempt to raise the copper grade of Printed Circuit board (PCB) by removing other components, carbonization treatment was investigated. The crushed PCB without surface-mounted parts was carbonized under nitrogen atmosphere. After screening, the char was classified by size into oversized pieces, undersized pieces and powder. The copper foil and glass fiber pieces were liberated and collected in undersized fraction. The liberation of copper foil from the oversized pieces was also investigated. The copper foil was liberated easily from glass fiber by stamping treatment. Liberation rate of copper foil was high at high carbonized temperature. The experimental results indicated that 90% of oversized char was liberated and the copper foil recovery from PCB carbonized at 1073 K was 110 kg/t. The copper recovery from char powder by flotation was also investigated. 15% of the copper grade and 80% of the copper recovery were obtained.

Key Words : Carbonization, Printed Circuit Board, Recycling, flotation

1 INTRODUCTION

Recently, it has been required to recycle valuable resources from wastes to conserve limited resources. Especially Waste Electrical and Electronic Equipments (WEEEs) should be recycled because they have many kinds of valuable materials. Most WEEEs include Printed Circuit Boards (PCBs). In Japan, about 30 million m² per year of PCB has been produced [1]. PCBs are normally separated from WEEEs and picked up by hand and sold to non-ferrous metal users because PCBs include high grade of copper and other precious metals such as gold, silver and palladium [2]. However, PCB also has impurities such as silicon, aluminum and calcium, which become slag materials during a non-ferrous smelting process, and other harmful elements such as lead, bromine and antimony. Low grade PCBs are sold after removal of invaluable parts or sometimes landfilled without any treatment.

Copper foil and glass fiber form multi-layered structure in PCB. PCB is produced by heating and pressurizing multi-layered copper foil and glass fiber impregnated by epoxy resin. Copper foils are so closely attached with glass fiber that it is difficult to separate copper foil from PCB.

Metal recovery from PCB has been studied by several methods such as crushing, separation method and leaching method [3-7]. Glass fiber recovery has also been studied [8].

Pyrolysis of PCB has been also studied but these studies were mainly investigated about the pyrolysis gas and char constituent [9-12]. In this paper, carbonization treatment was studied to remove glass fiber from low grade PCBs. Carbonization is a pyrolysis treatment of solids in absence of oxygen. Resins in PCB are pyrolyzed and metals are not oxidized by carbonization. It is therefore expected to recover copper efficiently in post process.

2 EXPERIMENTAL METHOD

2.1 Carbonization and separation

PCBs of 4 to 20 mm in size, which were crushed by using a biaxial shear cutter and rotor crusher, were used for experiment. Surface mounted parts were removed from crushed PCBs. 100 g of crushed PCB was spread over a stainless tray made of SUS430 and set in an electric furnace with 17 L of furnace volume. PCBs were heated with 50 K/min. of heating rate and carbonized at prescribed temperature for 1 hr. 15 L/min. of nitrogen gas was blown into the furnace to keep oxygen concentration at 2.5% due to air leakage into the furnace. PCB char was air-cooled after carbonization.

PCB char was screened by sieves and weight ratio with each particle size was measured. From char pieces with size over 4 mm,

Figure 1. Experimental flowsheet

copper foil, glass fiber and other parts were hand-picked and recovery of copper foil was measured.

Separation tests were conducted for different parts in which copper foil and glass fiber keep multi-layered form. The aim was to liberate copper foil with cutter mill, ball mill and stamp mill. 20 g of multi-layered parts was tested with each test. Parts with the size over 4 mm were screened after separation test and liberated copper foil and glass fiber were hand-picked to measure each weight.

After measuring the weight, several elements such as copper, silicon and calcium were analyzed with wavelength-dispersive X-ray fluorescence spectrometer (XRF, Rigaku Supermini) and copper grade and recovery were calculated. Figure 1 shows the experimental flow.

2.2 Flotation

For the powder of PCB char carbonized at 1073 K with size under 0.5 mm, copper upgrade was investigated by flotation. Chemical compounds of the char were identified by X-ray diffraction (XRD) analyzer (Rigaku MiniFlex). Element distributions on the char surface were investigated under scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer (Hitachi S-4200/KeveX Super Dry).

Char was ground with pestle and mortar to prepare powder of particle size under 150, 75 and 44 μm . Flotation reagents were 0.5 mol/L sulfuric acid and 1 mol/L sodium hydroxide as pH adjuster, sodium hydrogen sulfide (NaHS, purity 70%) as activator, Potassium Amyl Xanthate (PAX, purity 90%) as collector and Methyl Isobutyl Carbinol (MIBC) as frother. The dosage of MIBC was 1.4 kg/t. NaHS and PAX are dissolved in ionic exchanged water to obtain 5 mass% and 1 mass% solution.

Denver type flotation cell of $200 \times 10^{-6} \text{ m}^3$ was used. 5 g of powder was added in $150 \times 10^{-6} \text{ m}^3$ of deionized water while stirring by using an impeller at 350 rpm. Next, NaHS solution was added. After 15 min, PAX was added and pH was adjusted. After 15 min., MIBC was added and $1.5 \times 10^{-6} \text{ m}^3/\text{min}$. of air was introduced under the cell. The floated froth was collected for 10 min. The froth and tailing were filtered and dried at 363 K for 12 hr.

After measuring the weight, copper, silicon were analyzed with XRF (Rigaku Supermini) and copper grade and recovery were calculated.

3 RESULTS AND DISCUSSIONS

3.1 Carbonization and separation

Table 1 shows the breakdown of the char. Char with size over 4 mm was composed of copper foil, glass fiber, other parts, and multi-layered parts at any carbonized temperature. On the other hand, copper foil and glass fiber were liberated among char with size under 4 mm by visual check.

It is expected to recover copper foil efficiently from char with size under 4 mm with eddy current separator or electrostatic separator.

As a result of separation tests for multi-layered parts, both copper foil and glass fiber were pulverized when cutter mill was employed. Most parts kept multi-layered structure, when the ball mill was employed. Multi-layered parts decreased gradually with back and forth shaker, but most parts were pulverized by abrasion and copper foil hardly increased.

On the other hand, copper foil and glass fiber were liberated by stamping treatment. Figure 2 shows the result of separation test by stamping with pestle at a rate of 150 times per min. Multi-layered

parts was gradually separated into copper foil and glass fiber. It was concluded that stamping treatment was the best way for copper foil liberation.

Copper foil liberation of char carbonized at each temperature was compared. Table 2 shows the breakdown of the char after stamping treatment. Some multi-layered parts remained even at 673 K of carbonization temperature. The amount of material with size over 4 mm was decreasing with increasing in carbonization temperature. This is because char became brittle at higher carbonization temperature. Glass fiber was liberated most from the char carbonized at 873 K. Multi-layered parts were broken down most and glass fiber was selectively pulverized to powder for the char carbonized at 1073 K.

Table 3 shows the copper and silicon concentrations and distributions of each particle size and classification of the char. Up to 42% of initial copper amount was separated as copper foil at 673 K of carbonization temperature. In the same way, up to 45% of silicon was separated as glass fiber.

Figure 3 shows the copper grade of the char after glass fiber removal. Copper grade was raised from 13 to 30% at 873 K of carbonization. It was concluded that carbonization and liberation process was effective for the copper recovery from the low grade PCB.

3.2 Flotation for powder of PCB char

Copper grade of char carbonized at 1073 K with size under

Figure 2. Weight changes by stamping treatment for the char with size over 4 mm carbonized at 673 K

Figure 3. Copper grade of the char after glass fiber removal

Table 1. The breakdown of the char before stamping treatment.

Carbonization temperature	residual ratio	particle size / mm					-4/+2	-2/+1	-1/+0.5	-0.5/+0.15	-0.15
		total	Cu foil	Glass fiber	multi-layered parts	total	total	total	total	total	
K	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t
673	738	663	28	44	591	20	21	17	14	7	
773	680	573	37	107	429	7	45	26	21	10	
873	651	552	38	179	334	18	27	23	23	9	
973	653	477	44	145	288	35	31	35	47	30	
1073	654	422	31	91	300	84	46	37	42	25	

Table 2. The breakdown of the char after stamping treatment.

Carbonization temperature	residual ratio	particle size / mm					-4/+2	-2/+1	-1/+0.5	-0.5/+0.15	-0.15
		+4mm									
		total	Cu foil	Glass fiber	multi-layered parts	total	total	total	total	total	
K	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t
673	738	448	91	254	103	42	54	44	66	84	
773	680	396	74	223	99	18	82	61	80	41	
873	651	395	85	222	88	28	57	60	51	60	
973	653	272	103	159	10	43	50	45	141	100	
1073	654	189	98	91	0	89	64	51	124	137	

Table 3. Cu, Si concentration and distribution of each particle size and classification.

carbonization temperature	stamping time min.	particle size		weight kg/t	concentration (mass %)		distribution (%)	
		classification			Cu	Si	Cu	Si
673	15	crushed PCB board		1000	17.0	5.5	100	100
		total		738	19.9	7.1	100	100
		-0.5mm		150	10.2	7.2	10	21
		-1/+0.5mm		44	18.1	5.8	5	5
		-4/+1mm		96	25.1	5.6	16	10
		+4mm		448	22.3	7.4	68	64
		breakdown of +4mm	copper foil	91	68.6	2.1	42	4
			glass fiber	254	4.3	9.3	8	45
			others	103	25.5	7.5	18	15
		total		651	21.0	8.4	100	100
873	5	-0.5mm		111	13.0	8.9	11	18
		-1/+0.5mm		60	27.0	7.5	12	8
		-4/+1mm		85	25.7	9.4	16	15
		+4mm		395	21.4	8.1	62	59
		breakdown of +4mm	copper foil	85	66.2	3.9	41	6
			glass fiber	222	2.8	10.0	5	41
			others	88	24.8	7.2	16	12
		total		651	21.0	8.4	100	100

Figure 4. XRD patterns of PCB char with size under 0.5mm

0.5 mm was 10%. Figure 4 shows the XRD patterns of the char with size under 0.5 mm carbonized at each temperature. The peak of Cu, Pb, SiO₂ and Sb₂O₃ were observed.

Figure 5 shows the SEM images and elemental mappings of the char with size under 0.5 mm carbonized at 1073 K. It was expected that copper particle was liberated with SiO₂ particle because copper distribution was not matched with silicon distribution. Therefore, flotation after sulfurization would be effective for the upgrade of copper.

Figure 6 shows the grade and recovery of copper in froth as a function of NaHS dosage. The flotation tests were carried out

for the powder grounded to particle size under $150\mu\text{m}$ by adding 10 kg/t PAX and adjusting pH at 6. NaHS dosage in the 5 to 50 kg/t range had little effects on copper grade and recovery. It was therefore concluded that 5 kg/t of NaHS was enough.

Figure 5. SEM images and elemental mappings of Cu, Si, Ca, by EDS

Figure 6. Effect of NaHS dosage on the flotation (particle size under $150\mu\text{m}$, pH 6, 10 kg/t PAX)

Figure 7. Effect of PAX dosage on the flotation (particle size under $150\mu\text{m}$, pH 6, 5 kg/t NaHS)

Figure 7 shows the grade and recovery of copper in froth as a function of PAX dosage. The flotation tests were carried out for the powder grounded to particle size under $150\mu\text{m}$ by adding 5 kg/t NaHS and adjusting pH at 6. The recovery of copper increased with increasing PAX dosage from 2 to 10 kg/t , but the grade slightly decreased. Thus, it was concluded that the optimum dosage of PAX was 10 kg/t .

Figure 8 shows the grade and recovery of copper in froth as a function of pH. The flotation tests were carried out for the powder grounded to particle size under $150\mu\text{m}$ by adding 5 kg/t NaHS and 10 kg/t PAX. The recovery was highest and the grade increased from 10 to 12% at pH 10. No pH adjuster was added at pH 10. Considering the grade, recovery and reagent dosage, it was concluded that optimum pH was 10.

Figure 9 shows the grade and recovery of copper in froth as a function of grinding particle size. The flotation tests were carried out by adding 5 kg/t NaHS and 10 kg/t PAX adjusting at pH 10. The grade increased with the smaller particle size, but the recovery decreased. Considering the grade and recovery, under $75\mu\text{m}$ was optimum grinding size. At this optimum condition, the copper grade increased from 10 to 15% , the copper recovery was 80% , whereas silicon and calcium removal rate were both 55% . Though this copper grade was not enough to be used as raw material for copper smelting process, the flotation was effective for the recovery of copper from the powder of PCB char.

Figure 8. Effect of pH on the flotation (particle size under $150\mu\text{m}$, 5 kg/t NaHS, 10 kg/t PAX)

Figure 9. Effect of grinding particle size on the flotation (pH 10, 5 kg/t NaHS, 10 kg/t PAX)

4 CONCLUSION

Carbonization and liberation treatment were studied for PCB to raise copper grade and remove slag components. Copper foil could be liberated from carbonized PCB by stamping treatment. Glass fibers carbonized at 1073 K were pulverized selectively. The largest amounts of glass fibers were liberated at 773 and 873 K of carbonization temperature. Copper grade was raised from 13 to 30% after removing glass fiber from the char, carbonized at 873 K. Copper grade was raised from 10 to 15% by flotation of char powder, carbonized at 1073 K with size smaller than 0.5 mm and 80% of the copper was recovered under the following conditions: particle size under 75 μm , 5 kg/t of NaHS, 10 kg/t of PAX and pH 10.

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