Impact Milling of Printed Circuit Board Waste for Resource Recycling and Evaluation of Liberation using Heavy Medium Separation

Shigeki Koyanaka¹, Hitoshi Ohyá¹, Jae-chun Lee², Hiroyuki Iwata¹ and Shigehisa Endoh¹
¹National Institute for Resources and Environment
²Korea Institute of Geology, Mining and Materials

Abstract

The authors evaluated the degree of liberation of printed circuit boards ground by impact milling to recover valuable materials. Wastes of two board types were ground with a swing-hammer-type impact mill. Heavy medium separation using tetrabromoethane was employed to separate the ground materials into the sink product, containing mainly copper, and the float product, consisting mainly of epoxy resin and glass fiber. The degree of liberation was evaluated with heavy medium separation. The sink product was larger than the float product. When processing boards whose surfaces are fully plated with copper foil we attained a degree of liberation for copper in the sink of up to 95%, which was higher than the degree of printed circuit board liberation. By contrast, the copper content of the float product was quite low at less than 1%. Thus, non-copper materials are easily liberated, and non-copper materials with few impurities can be obtained from printed circuit board wastes.

1. Introduction

Factory shipments of personal computers and other kinds of electronic information equipment are increasing at a blistering pace, which is indicative of the fast-growing information society, and it is anticipated that the amounts of discarded equipment will likewise increase rapidly. The 1997 quantities have been calculated at 1,230,000 desktop computers and 430,000 laptop computers, while the weight of PCs discarded in 2002 is anticipated to be about 200,000 tons for the year.¹,² Electronic information equipment contains many valuable materials, but a characteristic of such equipment is that they consist of about 10% printed circuit boards, which are made by copper foil wiring on epoxy reinforced with material like glass fibers, and resins such as phenol, combined in a laminated structure. Because copper accounts for about one-third to one-half, it is apparently possible to recover from electronic appliances an amount of copper equal to several percent of that used in the printed circuit boards.² Furthermore, the electronic components mounted on circuit boards use gold, platinum, and other precious metals, which can also be recovered.³,⁴ Major computer makers are setting up their own recovery and resource reclamation systems for discarded PCs and other items, but overall most junked equipment is disposed in landfills.⁵ This gives rise to concerns about soil contamination by the lead and other hazardous substances in circuit boards, making it urgent to set up systems for resource reclamation.

In view of the foregoing, the authors tried applying the shape separation technique in a process for recovering the copper from scraps produced when manufacturing printed circuit boards, and from discarded boards.⁶-¹⁰ In this attempt we focused on the nature of materials used in printed circuit boards, i.e., metals, consisting primarily of copper, become spherical particles when impact milled because of their great ductility and malleability, while the plastics and glass fibers making up the boards become non-spherical particles because they undergo brittle fracturing. This demonstrated that the efficient recovery of copper can be accomplished. And because the composition ratio of recovered materials is important for the reuse of copper, we also examined the recovered copper's liberatability and the dependence on milling conditions of the amount of solder contained in the recovered materials.¹⁰

Therefore, to increase the reclamation of materials other than copper, such as plastics and glass, this
report explores the liberation of plastics and glass, and the relationship between impact milling and the intermixing of plastics and glass with metals.

2. Experimental Apparatus and Method

2.1 Experiment Samples

Our experiment used the two types of circuit boards described in Table 1 as samples. Sample 1 was glass fiber-reinforced unpatterned scrap from the printed circuit board manufacturing process. This sample therefore had no electronic components mounted. Copper content was about 60%.

Table 1 Copper Printed Circuit Boards Used in Experiment

|                  | Sample 1 | Sample 2                  |
|------------------|----------|---------------------------|
| Unpatterned board| 60 wt%   | 24 wt%                    |
| Board thickness  | 1.5 to 1.8 mm | 1.8 mm                  |
| Copper film and board | Copper films plated on both sides of glass/epoxy resin board | Laminated glass/epoxy resin board with four copper film layers |

2.2 Experimental Method

Fig. 1 illustrates the experiment procedure. Samples were milled as described in previous reports. They were first cut into 2- or 3-cm pieces by hand, then coarse cut to under 3 mm with a cutting mill (a model VM16 vertical cutting mill made by Orient Co., Ltd.). These pieces were milled with a swing-hammer type impact mill (high-speed hammer mill 1018-LA made by Tokyo Atomizer Co., Ltd.) under appropriate milling conditions (1 mm mesh, 4,000 to 10,000 rev. min⁻¹), and the product was used as the analysis sample.

![Experimental Procedure](image)

We used a Ro-Tap to screen the product for 10 min, and then we checked the particle size distribution. Tetrabromoethane with a density of 2,960 kg/m³ was used to perform dense media separation, thereby separating the product into a sink product, containing mainly copper, and a float product, consisting mainly of non-copper components. Concentrated nitric acid was used to dissolve only the copper from both particle groups. We then measured the amount of copper in both groups with induced-coupled plasma-mass (ICP) analysis, and evaluated the degree of liberation.

3. Results and Discussion

3.1 Particle Size Characteristics of Milled Product

Figs. 2 and 3 show the particle size distributions of the milled circuit board products. All have about the same distributions, and the faster the hammer speed.
Here the degree of liberation $\alpha$ is defined by the following equation.

$$\alpha = \frac{W_{m,Cu}}{W_m}$$  \hspace{1cm} (1)

Where:
- $W_m$ is the particle weight recovered as sink product by heavy medium separation, and
- $W_{m,Cu}$ is the copper content of $W_m$ obtained by quantitative analysis.

It is evident from the definition that $\alpha$ is the apparent degree of liberation. In other words, the sink product conceived here is those particles with a specific gravity of 2.96 or higher, which are judged to be sink product even when nonmetals adhere to them. Accordingly, $\alpha$ will have a lower value than the true degree of liberation. As in Fig. 5, an 80 to 90% degree of liberation was achieved with sample 1 circuit board material for particles that were 100 $\mu$m or larger. Especially under high-impact milling, this particle size yielded a high liberation degree of at least 95%. Additionally, although it appears that the degree of liberation suddenly drops when particles are under 53 $\mu$m, it would seem this is for the following reasons: In general the finer the particles, the better the liberation, but when evaluating liberatability by means of heavy medium separation as in this instance, one cannot ignore the bias of dense media separation when separating fine particles. In other words, when separating comparatively large particles, the adherence of a slight bit of metal to nonmetals can be ignored, and the particles can be recovered as float product, but when particles are smaller than 100 $\mu$m, the adherence of even a little metal will make particle density relatively large, causing nonmetals to sink and be intermixed with the sink product. And as we shall discuss below, it is thought that because of a decline in the precision of

3.2 Liberatability

Fig. 5 shows the degree of copper liberation $\alpha$ from sink product subjected to heavy medium separation using tetrabromoethane with a specific gravity of 2.96.
dense media separation, the degree of liberation apparently dropped.

**Fig. 6** shows the relationship between the liberation degree for each sample as a whole and milling conditions. The degree of liberation increased in both samples as hammer speed increased. With sample 1 we achieved a liberation degree of over 95%, showing that impact force is effective for liberation. On the other hand, circuit boards with resist-processed surfaces had a somewhat lower liberation degree of about 80% owing to factors such as the complexity of their laminated structure.

**Fig. 7** shows the relationship between float product liberatability and milling conditions. In accordance with Eq. 1, the following equation defines the parameter $\beta$ of float product liberatability.

$$\beta = 1 - \frac{W_{n, Cu}}{W_n}$$

Where:
- $W_n$ is the particle weight recovered as float product with heavy medium separation, and
- $W_{n, Cu}$ is the copper content of $W_n$ obtained by quantitative analysis.

Just as in Eq. 1, $\beta$ is the apparent degree of liberation, but the float product was a particle group with a particle density of under 2.96, and the resin and glass with a slight amount of metal adhering were recovered as float product. This means that $\beta$ had a higher value than the true degree of liberation. Because the float product was a mixture of resin and glass fibers, $1-\beta$ here is the percentage of intermixed copper. Although liberation is facilitated more as impact force increases, $\beta$ was 0.98 or higher in comparison with the liberability of the copper component, and very little copper was mixed into the float product. Thus when reclaiming resin and glass, one obtains high-purity substances with little metal, which holds forth the possibility that their uses could be expanded.

**Fig. 8** plots the relationship between $1-\beta$ and particle size. Unlike the sink product, the copper intermixing rate increased as particle size grew. As noted previously, large resin and glass particles are recovered as float product even if slight amounts of metal adhere to them, indicating that liberation is inadequate. But when particles are small, those with metal adhering to them will sink, so the floating product's degree of liberation does not decrease. The reason that $1-\beta$ increases somewhat for fine particles is thought to be slight metal intermixing in the float product, which is because small metal particles sink with difficulty.

An evaluation of liberation and heavy medium separation used for printed circuit boards can be diagrammed as in **Fig. 9**. As the float product, resin and glass rather well liberated from copper are recovered, while the sink product is a mixture of well-liberated
copper, as well as resin and glass to which copper has adhered, thereby giving their particles specific gravity of over 2.9. This results in the decline of apparent liberatability $\alpha$, with the effect being especially apparent in fine particles.

4. Conclusion

In anticipation of the recovery of valuable materials from printed circuit boards, whose disposal amount is expected to increase rapidly, this paper has explored the liberation characteristics of such boards when using impact milling. We sought the apparent liberation degree of sink and float products which had undergone heavy medium separation in a dense liquid whose density was 2.96, and determined the relationship with milling conditions and other parameters. Our results produced the following conclusions.

1) Resin and glass became finer particles, and had higher liberatability, than copper. Thus even when the resin and glass are to be recycled, it is possible to recover them with very little metal mixed in.

2) Copper has a liberatability of 80% or more even from circuit boards such as those with electronic components actually mounted on them, and we demonstrated that liberatability of 90% or more is obtainable if one adjusts particle size by controlling impact force.

Acknowledgments

The authors wish to express their appreciation to Masato Miyake (who at the time of the experiment was a senior at Shibaura Institute of Technology) for this great cooperation.

Nomenclature

$Q_3$ : Cumulative undersize distribution
   (mass base) $(-)$

$v_h$ : Hammer speed
   ($\text{m s}^{-1}$)

$W_{m,cu}$ : Mass of sink product obtained by heavy medium separation using tetrabromoethane and mass of copper in the sink product measured by ICP analysis
   ($\text{g}$)

$W_{n,cu}$ : Mass of the float product obtained by heavy medium separation using tetrabromoethane and mass of copper in the float product measured by ICP analysis
   ($\text{g}$)

$X$ : Particle diameter
   ($\mu\text{m}$)

$X_{50}$ : Median diameter
   ($\mu\text{m}$)

$\alpha$ : Apparent degree of liberation of copper in the sink product defined by Eq. 1 $(-)$

$\beta$ : Degree of liberation of non-copper materials in the float product defined by Eq. 2 $(-)$

References

1) Endoh, S. "Recovery of valuable metal from spent printed circuit boards by the shape separation technique," Kinzoku, 68, 883-888 (1998).
2) "Report on resource recycling techniques of advanced wastes – Separation of metal and plastics," Clean Japan Center (1996).
3) Rokukawa, N., M. Tanaka, and H. Sakamoto. "Properties of printed wiring boards with electronic components in relation to the effective recovery of metals," Shigen to Kankyō, 1, 209-217 (1992).
4) Saito, I., M. Tanaka, and H. Sakamoto. "Research on waste treatment of advanced technology products – Recovery of valuable metals from printed wiring board wastes," Shigen to Kankyō, 4, 397-404 (1995).
5) Iji, M., S. Yokoyama, and Y. Nakahara. "Development of recycling technology of plastic wastes for electronic computers," NEC Giko, 46, no. 9, 55-61 (1993).
6) Koyanaka, S., S. Endoh, and H. Iwata. "The recycling of printed wiring board scraps using a shape sorting technique – Recovering copper components by the inclined vibrating method," J. Soc. Powder Technol., Japan, 32, 385-391 (1995).
7) Izumikawa, C., H. Sasaki, H. Ohya, S. Endoh, and H. Iwata. "Copper recycling from printed circuit board scrap by shape separation – Application of the inclined conveyor method," J. Soc. Powder Technol., Japan, 32, 378-384 (1995).
8) Koyanaka, S., S. Endoh, H. Ohya, and H. Iwata. "Particle shape of copper milled by swing-hammer type impact mill," Powder Technol., 90, 135-140 (1997).
9) Ohya, H., S. Koyanaka, S. Endoh, H. Iwata, C. Izumikawa, H. Sasaki, and P. Ditle. "Analysis of trajectory for ground printed wiring boards using shape separation," Shigen Shori Gijutsu, 44, 3-8 (1997).

10) Lee, J. C., S. Koyanaka, M. Y. Lee, H. Ohya, and S. Endoh. "Recovery of copper, tin, and lead from spent printed circuit boards (PCBs) by the shape separation method," Shigen to Sozai, 113, 357-362 (1997).

Author's short biography

Shigeki Koyanaka
Shigeki Koyanaka is a researcher at National Institute for Resources and Environment (NIRE), Japan. He received his bachelor of engineering (BE) and master of engineering (ME) in Mining Engineering from Kyoto University. He joined the Materials Handling and Characterization Division in 1993. His major research interest is physical separation of particulate solids for resource recycling. He works presently to develop new particle separation method by using laser radiation pressure. E-mail: koyanaka@nire.go.jp

Hitoshi Ohya
Hitoshi Ohya received his BE and ME degrees in Chemical Engineering from Kyoto University. He has been at NIRE since 1986. He earned his doctor of engineering (DE) in 1997 from Kyushu University for a thesis entitled "Study on shape separation of particulate materials". He works presently for environmental impact assessment of resource recycling process. E-mail: ohya@nire.go.jp

Jae-chun Lee
Jae-chun Lee, Ph.D. is a senior researcher at Korea Institute of Geology, Mining & Materials. He stayed at NIRE as a research fellow in 1996. His main area of interest is refining of metallic and non-metallic materials by hydrometallurgical process.

Hiroyuki Iwata
Hiroyuki Iwata earned his DE degree in Mining Engineering in 1976 from Waseda University. He was the former leader of the Materials Handling and Characterization Division in NIRE. His major research interests are size reduction, characterization and separation of particulate solids. He works presently for international research cooperation program with eastern European countries.

Shigehisa Endoh
Shigehisa Endoh has been the leader of the Materials Handling and Characterization Division in NIRE since 1995. He received his BE and ME degrees in Chemical Engineering from Kanazawa University. He earned his DE degree in Chemical Engineering in 1984 from Osaka Prefecture University. His major research interest are characterization of particular materials and resource recycling of solid waste. E-mail: endoh@nire.go.jp