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Liberation of valuable materials in waste printed circuit boards by high-voltage electrical pulses

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ABSTRACT

Printed circuit boards (PCBs) are found in every electrical and electronic equipment. In this study, epoxy resin was employed as the model material to conduct high-voltage (HV) electrical pulse experiments. A complete liberation of PCBs was achieved using SELFRAG Lab, and the surface morphology and chemical composition of suspended particles were analyzed by SEM. The results show that the liberation and crushing mechanism of PCBs mainly include the formation and expansion of discharge channels, transformation of shock wave, reflection and refraction effects, and physical and chemical reactions under the high-pressure environment; among all of them, the physical and chemical reactions between metal and organics are specific phenomena, which only exist when using HV electrical pulses for the crushing process of waste PCBs. Furthermore, the results also show that HV electrical pulses can achieve a narrow-fraction metal concentration; this feature is conducive for the separation of metals from epoxy resin in the future. In particular, the crushing performance reaches its best level when the electrical pulse reaches 400, during which 97.92% copper was accumulated in −2 mm products.

1. Introduction

Over the past several years, the electrical and electronics industry has been one of the fastest growing industries. This rapid development has caused an increase in waste electrical and electronic equipment (EEE). Printed circuit boards (PCBs) are an essential part of almost all EEE. Consequently, a large amount of waste PCB is generated (Lee et al., 2004; Pilone and Kelsall, 2003). Waste PCB has a high potential value because they contain up to twenty types of nonferrous and rare metals. Waste PCB also contains several toxic heavy metals including lead, cadmium, mercury, and nickel as well as brominated flame retardants, all of which pose a potential danger to the soil, environment, and biological organisms (Tan et al., 2011; Diao et al., 2013). The reutilization of waste PCB is an important topic in the field of environment protection and resource recycling. The crushing process is a crucial process for the reutilization of waste PCBs; however, for recycling waste PCBs by chemical or biometallurgy methods, the leaching process may contaminate the particle surface with lixiviants. In the physical/mechanical recycling methods, the crushing of metals from PCBs can decrease the efficiency of successive separation, recovery rate, and purity of metal (Zhao et al., 2004; Zuo et al., 2012; Hao et al., 2012). Extensive studies show that waste PCBs can be crushed to particles by a two-stage shredding operation to liberate metals from other components. Metals in the slots (ISA, PCI, AGP, etc.) of PCBs could be easily liberated from nonmetals, and an excellent liberation could be achieved in the −5 mm or −3 mm fraction (Duan et al., 2009; He et al., 2006). Metals in printed wiring boards and integrated cards were difficult to liberate from nonmetals. Commonly, in the −1 + 0.5 mm, −0.5 + 0.3 mm and −0.3 mm fractions, almost all the metals achieved complete liberation. The metal liberation degree of PCB increased with decreasing particle size; however, the capability of the separation to recover those fine particles usually decreased (Xue and Xu, 2013; Zhou and Xu, 2012). In China, shaking table and corona electrostatic separations are the main techniques used for fine particles of PCB in the size range 0.1–2 mm (Guo et al., 2009). However, for −0.074 mm superfine particles, over 70% metals are lost to tailings due to mismatch in the velocity settings in shaking table separation technology (Zhao et al., 2012). The corona electrostatic separation experimental results show that particles are easily repelled, attracted, or agglomerated together with the decrease in size; for the −0.074 mm particles, it was difficult to achieve effective separation. The inefficient liberation and overgrinding of PCBs can be attributed to the fact that mechanical comminution is not a specific process for

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liberating valuable minerals, but a technology for reducing the dimensions of the ore aggregates of valuable minerals, where the liberation occurs as a side effect (Andres, 1995; Andres et al. 2001a). Therefore, the current breakage methods cannot completely liberate metals from wiring boards; moreover, these methods may lead to high energy consumption, soaring financial cost, and environmental problems (Li et al., 2004; Groot and Pistorius, 2008).

Recent years have witnessed an increasing interest in the application of high-voltage (HV) electrical pulses to dissociate diamond, emerald, gold, silver and several other rare metals (Anders, 2010; Ito et al., 2009; Dal Martello et al., 2012) similar to PGM as well as to recycle rebar (Narahara et al., 2007; Inoue et al., 2009; Yao et al., 2011; Maeda et al., 2009; Aoki et al., 2009), cobblestone, sand, and many other building materials. The quoted studies often showed better mineral recovery or higher concentrate grade as a result of better liberation. One concern has been the amount of energy consumption in the electrical breakage process itself. If the performance improves at the expense of energy, the technology can become economical. Experiments have also been conducted on sulphide, platinum, copper, copper/gold, and lead zinc ores. The results show that compared to traditional mechanical crushing process, HV electrical pulse crushing can better liberate metal-bearing minerals than mechanical comminution technologies. Moreover, the product usually contains less fine particles because of the pre-weakening effect the overall consumption of energy is reduced, saving 24% (Wang et al., 2011; Wang et al., 2012a; Wang et al., 2012b; Wang et al., 2012c; Shi et al., 2012, 2013).

Waste PCB is typically made up of glass fiber cloth, epoxy resin, and many other metals (mostly copper), and the electrical properties of the compositions are different (Huang et al., 2009; Li et al., 2007; Andres et al., 2001b). Thus, waste PCB is most suitable for HV electrical pulse crushing.

In this study, waste PCB was crushed by HV electrical pulses using SELFRAG Lab. The surface morphology and chemical composition of the crushed waste PCB particles were analyzed, and the liberation mechanism of waste PCB by HV electrical pulse crushing was elucidated. Moreover, further experiments were conducted to determine the optimum electrical pulse for future applications.

2. Experimental

2.1. Sample preparation and characterization

Liberation of components from PCB is relatively easy, so it was decided to focus on metal recovery from the circuit board itself. The waste PCB without electronic elements was obtained from a local PCB factory. The total content of copper in the waste PCBs is ~5.5%. Waste PCBs were cut into 100 cm^2 pieces so that they can fit into the reaction tank and ensure sample uniformity. This is a FR-4-type epoxy glass-cloth copper clad laminate. The two sides of the PCB were called "Green Side" and "Yellow Side" according to the color difference, as shown in Fig. 1.

The epoxy glass laminated sheet in PCB consisted of glass fiber cloth and cured epoxy resin, made by bonding and pressing; the internal organizational structure is asymmetric. The surface morphology of the PCB was analyzed by SEM; some fine particles adhered to the yellow surface of PCB during the manufacturing process, contributing to the surface roughness as shown in Fig. 2(a). Moreover, tiny cracks were present, as shown in Fig. 2(b). The green surface of copper foil in the PCB had regular vertical scratches on the surface of copper foil, as shown in Fig. 2(c). After stripping the copper foil and epoxy glass laminated sheet in the PCB manually, the joint surface of epoxy glass laminated sheet was analyzed by SEM. The copper foil had a rough surface, similar to sands of different sizes on the surface, as shown in Fig. 2(d), arising from the processing technology of copper foil. To enlarge the contact area with epoxy glass laminated sheet attaching them tightly, during the processing, a layer of tuberculate copper particle was electroplated on the side where the copper foil and epoxy glass laminated sheet contact each other, i.e., the rough surface. Then, a layer of compact copper was deposited within the gap of those tuberculate copper, increasing the contact area of copper and epoxy glass laminated sheet as well as decreasing the roughness of the rough surface of copper foil, thus enhancing the bond strength within copper and epoxy glass laminated sheet.

2.2. High-voltage (HV) pulse breakage equipment

The HV pulse breakage equipment in this trial experiment, which was manufactured by SELFRAG AG, was setup in the Institute of Geology Chinese Academy of Geological Sciences, Beijing, China. A schematic diagram of the HV pulse equipment is shown in Fig. 3.

The equipment consists of a HV power supply, a HV pulse generator, and a reaction tank. The HV pulse generator is continuously charged by the HV power supply. The HV pulse technology stores energy from the HV power supply in capacitors over time, and this energy is released in a single pulse with an extremely short duration (Chernet and Marmo, 2003). The high energy density obtained by slow energy storage is rapidly released to the sample as HV pulse causing complex mechanical and electrical effects. The waste PCB was immersed in deionized water in a reaction tank. The deionized water, as the dielectric liquid, has a high dielectric strength when voltage rise time is maintained below 500 ns. Therefore, discharges are most likely to travel through the immersed waste PCB rather than the water because of a large contrast in the two dielectric's electrical properties. The main parameters of the equipment are listed in Table 1.

In HV pulse technology for crushing waste PCB, energy is apt to be applied to the interface of metals and nonmetals, which are located between the copper foil and epoxy glass laminated sheet of waste PCB, successfully liberating and selectively crushing the metals in the presence of nonmetals based on the difference in their electrical properties, thus concentrating the metals to a narrow size range for ease of subsequent separation. The HV pulse breakage occurs in water, producing less secondary pollution, and it is easy to control the limited range harmful to people, thus decreasing the damage towards human health and environment.

3. Results and discussion

3.1. HV breakage performance

In the experiment, the electrode gap was set at 30 mm, the pulse frequency was set at 5 Hz and the voltage was set at 190 kV. The waste PCBs were crushed using 100 and 400 electric pulses. Next, the products were dried, weighed, screened and the copper contents were analyzed using an X-ray fluorescence spectrometer, as shown in Table 2a and b

As shown in Table 2, the copper purity exceeds 13% in all the −2 mm products, showing significant improvement on the metal purity compared to the copper content of original PCB (~5.5%). However, for the products that were crushed with a total amount of 100 electric pulses, the +2 mm product still contained 51.72% copper, indicating over half of the copper were still attached to epoxy resin and fiberglass and they are not liberated in HV breakage process. Clearly, more electric pulses were needed.