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An environmentally friendly ball milling process for recovery of valuable metals from e-waste scraps

Zhi-Yuan Zhang [a,b,*], Fu-Shen Zhang [a,b], TianQi Yao [c]

[a] Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China
[c] Nankai University, No. 94 Weijin Road, Tianjin 300191, China

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ABSTRACT

The present study reports a mechanochemical (MC) process for effective recovery of copper (Cu) and precious metals (i.e. Pd and Ag) from e-waste scraps. Results indicated that the mixture of $K_2S_2O_8$ and NaCl (abbreviated as $K_2S_2O_8$/NaCl hereafter) was the most effective co-milling reagents in terms of high recovery rate. After co-milling with $K_2S_2O_8$/NaCl, soluble metallic compounds were produced and consequently benefit the subsequent leaching process. 99.9% of Cu and 95.5% of Pd in the e-waste particles could be recovered in 0.5 mol/L diluted HCl in 15 min. Ag was concentrated in the leaching residue as AgCl and then recovered in 1 mol/L NH_3 solution. XRD and XPS analysis indicated that elemental metals in the raw materials were transformed into their corresponding oxidation state during ball milling process at low temperature, implying that solid–solid phase reactions is the reaction mechanism. Based on the results and thermodynamic parameters of the probable reactions, possible reaction pathways during ball milling were proposed. Suggestion on category of e-waste for ball milling process was put forward according to the experiment results. The designed metal recovery process of this study has the advantages of highly recovery rate and quick leaching speed. Thus, this study offers a promising and environmentally friendly method for recovering valuable metals from e-waste.

1. Introduction

Recycling of e-waste is an important subject not only from the point of waste treatment but also from the recovery aspect of valuable materials (Cui and Zhang, 2008; Oguchi et al., 2011). Among the resources in e-waste, metals contribute to more than 95% of the materials' market value (Chancerel et al., 2009). Hence, the recovery of valuable metals is the inherent motive in e-waste disposal.

In the past decades, many techniques for recovering valuable metals from e-waste have been developed such as gravity separation, magnetic separation and electrostatic separation, (Kaya, 2016; Veit et al., 2005), synthesis of CuCl with e-waste(Zhang and Zhang, 2013), separation of PCBs with organic solvent method (Zhu et al., 2013), cyanide and non-cyanide lixiviants leaching (Akcil et al., 2015) methods, ammonium persulfate leaching (Alzate et al., 2016), bioeaching methods (Işıldar et al., 2016; Karwowska et al., 2014) or a combination of these approaches (Kim et al., 2011; Xiu et al., 2013). Among those methods, hydrometallurgical methods are more accurate, predictable and controllable than others. Therefore, hydrometallurgical techniquesare most active in the research of valuable metals recovery from electronic scraps in the past two decades. However, traditional hydrometallurgical methods are acid dependent, time-consuming and inefficient for simultaneously recovery of precious metals. Remarkably, large amount of corrosive or toxic reagents, such as aqua regia, nitric acid, cyanide and halide, are consumed, producing large quantities of toxic and corrosive fumes or solution (Chagnes et al., 2016; Cui and Zhang, 2008). Therefore, it is necessary to seek more environmentally friendly method for the recovery of valuable metals from e-wastes.

Recently, mechanochemical (MC) technology has been widely applied in extractive metallurgy, waste treatment, crystal engineering and material engineering (Chai et al., 2013; Guo et al., 2010; Plescia et al., 2003). In MC treatment, repeated fracturing and cold welding occurred to the reacting particles during collisions when the respective wastes or materials are milled with reactive chemicals in a ball mill (Zhang et al., 2013). Thus, MC solid phase reactions that cannot occur normally due to separation of

* Corresponding author at: Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China.
E-mail address: zhangzy@rcees.ac.cn (Z.-Y. Zhang).

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the reacting phases may occur across the welded interfaces when several ingredients are milled together. Recently, many researches have applied MC technology to metal recovery from e-waste, such as waste fluorescent lamps (Tan et al., 2015), liquid–crystal display panels (Hasegawa et al., 2013), waste printed circuit boards (Ou and Li, 2014), cathode ray tube funnel glass (Yuan et al., 2012; Yuan et al., 2013), phosphors (Mio et al., 2001), spent lithium-ion batteries (Wang et al., 2016), and gold-containing waste (Ficeriová and Baláž, 2010) etc. The foregoing processes are mainly MC leaching, MC sulfidization, and mechanical activation. MC leaching produces aqueous slurry or solution of activated materials and requires milling pots and balls made of special materials (Tan and Li, 2015). MC sulfidization converts non-ferrous metals oxides into metal sulfides, followed by pyrometallurgy, a necessary post-treatment process (Guo et al., 2010). Mechanical activation involves an increase in the reactivity of target substances, which could promote the subsequent leaching process (Nasser and Mingelgrin, 2012). These techniques indicated that MC technology exhibited potential benefits for base metal recovery from e-waste. However, little attention has been paid to the recovery of precious metals. The influence of MC technology on precious metal recovery from e-waste with multiple metals is unknown.

In this study, a new ball milling method was attempted for Cu and precious metal recovery from e-waste. The specialty of this study was aimed to produce soluble metallic compound after treatment with dry ball milling and consequently benefit the subsequent leaching process. The mechanism of the ball milling process used in our study is different from the existing MC leaching process. MC induced solid-state reaction is essential for the ball milling process. New co-milling reagents need to be selected and optimized. In this study, we used dry MC process to recover valuable metals from e-waste scraps by co-milling with different reagents. After milling, metal recovery with dilute HCl was studied. Separation of Pd from the leaching solution and selective recovery of Ag from the indissoluble solid residue were investigated. The characteristics of samples after milling were studied and the mechanism of MC induced solid-state reaction was proposed.

2. Materials and methods

2.1. Materials

E-waste scraps used in this work were supplied by XIAMEN OASIS Sources CO. Ltd., which were mainly composed of multilayer ceramic capacitors (MLCCs) and waste PCBsPCBs. Almost all of the components (relays, capacitors, etc.) were disassembled from the PCBs when we received these materials. The bare PCBs were pretreated with a thermal shock process and crushed in a hammer crusher. Then, a centrifugal air separator was used to obtain the metallic components (Zhang and Zhang, 2013). MLCCs, which contains high content of Ag and Pd, were used as the raw materials along with the metallic components from bare PCBs. The metallic components and MLCCs were mixed and sent to comminute in a cutting mill until the fraction reached particle size smaller than 0.25 mm (referred to as "e-waste particles"). Metal contents in the obtained e-waste particles were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA) after HNO_3-HF-$HClO_4$ digestion, as described in details in our precious study (Zhang and Zhang, 2013). The contents of major metallic elements are given in Table 1. As shown in Table.1, the highest content of element was Cu (57.11%), and followed by Zn (15.55%). Zn in the e-waste scraps has an uncommon high content, which is found to be from MLCCs (see Fig. S1). Pd and Ag were the main precious metals while Au was not detected in the e-waste scraps used in this study because of the dismantlement of electronic components. All of the chemical reagents used in the experiments were purchased from Chemical Reagent Company of Beijing in analytical grade.

Table 1
Metal contents in the e-waste scraps used for ball milling experiments (wt.%).

Elements	Content (wt.%)	Elements	Content (wt.%)
Ag	2.74	Ni	1.11
Pd	0.28	Co	0.21
Cu	57.11	Pb	0.25
Zn	15.55	Fe	0.20
Bi	2.27	Al	0.10
Sb	0.47		

2.2. Ball milling and leaching experiments

A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used in the experiments. During the ball milling process, co-milling reagents and e-waste particles were put together into a 250 mL-capacity corundum pot (100 mm in diameter) with 120 g zirconia balls (9 mm in diameter). After milling for the predetermined time, the samples were collected and preserved for further use. Totally six group of co-milling reagents were used to mill with e-waste particles for the selection of an appropriate co-milling system. They are NaCl, NH_4Cl, EDTA·2Na and the mixture of $K_2S_2O_8$ (a strong solid oxidant) and each of the above three reagents. Various ball milling parameters, including mass ratio of $K_2S_2O_8$ to NaCl, mass ratio of co-milling reagents to e-waste particles, rotation speed and milling time, were also test during the experiment.

After milling, the ground sample was mixed in 0.5 mol/L diluted hydrochloric acid (HCl) (phase ratios, V/w = 40) and the mixture was stirred by a magnetic stirrer in a flask for 15 min at room temperature. Then, the mixture was filtrated by a suction filter (0.22 μm) and the residue was collected and dried in an oven at 105 °C. The filtrate was measured by ICP-OES to determine the recovery efficiency of Cu, Ag, Pd and Zn. Pd in the leaching solution was recovered by diisoamyl sulfides olvent extraction, same with our previous study (Zhang and Zhang, 2014). Ag in the residue was then leached with 1 mol/L NH_3 solution for 15 min and reduced by hydrazine hydrate to precipitate Ag. The above process was shown in Fig. 1.

2.3. Characterization of the materials

The chemical composition changes and morphology information of the solid samples during the ball milling process were characterized. The crystalline phases of the samples before and after ball milling were characterized by X-ray diffraction spectroscopy (XRD, Rigaku D/max 2500) using Cu Kα radiation (γ = 1.5418 Å) with 30 kV voltage and 30 mA current. X-ray photoelectron spectroscopy (XPS) measurement was carried out with an ESCALAB 250 Xi spectrometer (Thermo Scientific) with Al Kα radiation ($h\nu$ = 1253.6 eV). Morphology of the samples before and after mechanochemical treatment was observed on a JSM-7001F field emission scanning electron microscopy (FESEM). Size distribution of the e-waste scraps before milling is measured with a Laser Particle Size Analyzers (Mastersize 2000, Malvern, UK)

3. Results and discussion

3.1. Comparison of different Co-milling reagents

It is known that Cu could not be leached with dilute HCl under room temperature without oxidant. As can be seen from

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