Recovery of Lead in Lead Zirconate Titanate Ceramics by Wet Ball Mill with Acidic Solution

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酸性溶媒を用いたボールミルによる PZT セラミックスからの鉛の回収

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The possibility of preferential recovery of lead from lead zirconate titanate (PZT) ceramics by wet ball milling with aqueous H_2SO_4 solution was investigated. The wet ball milling was performed using a pot mill apparatus in air for 0–96 h at room temperature with the rotational speed fixed at 300 rpm. Untreated PZT was dipped in aqueous H_2SO_4 solution for comparison with the wet-ball-milled specimen. The diffraction lines of the PZT crystallites disappeared completely from the XRD results, and only the diffraction lines of PbSO_4 were confirmed by the wet ball milling for more than 48 h. For all the dipped specimens, the diffraction lines of PZT were identified even when the specimens were treated in 4.5 mol/dm^3 H_2SO_4 solution for 96 h. According to ICP analysis of the dissolved components into the H_2SO_4 filtrate, the amounts of zirconium and titanium dissolved in the solution were found to increase with increasing treatment time, and the leaching behavior of both ions conformed closely to the collapsing behavior of the PZT crystal structure. As for lead ion in the solution, the dissolution amount was below 0.1% compared with the initial lead content in PZT ceramics under all the ball milling conditions. These results indicated that more than 99.9 mass% of lead in PZT can be recovered as PbSO_4 by wet ball milling for more than 48 h. The purity of the recovered PbSO_4 calculated from the ICP results was approximately 98 mass%.

[Received March 28, 2003; Accepted August 29, 2003]

Key-words: Ball mill, PZT, Lead recovery, PbSO_4

1. Introduction

Lead is a heavy metal whose discharge into the environment has been strictly regulated because it is hazardous when contained in the human body. However, a large amount of lead-containing products, such as lead accumulator, lead glass and lead-based dielectric devices, still continue to be produced and consumed. Some of the wastes containing lead from industries and households have been disposed by land filling without any effort exerted to recovering lead in the products and/or recycling it as resources. Lead-based piezoelectric materials such as lead zirconate titanate (PZT) and lead-free piezoelectric materials, which are expected to replace lead-based piezoelectric materials, have been extensively investigated by many researchers.^{1)–5)} However, it is anticipated that a large amount of lead-based dielectric materials will still be produced and discharged even in the future because lead-based materials have superior properties.^{6)–8)}

The mechanochemical (MC) process is available not only for the fabrication of engineering materials^{9)–14)} but also for extracting precious and rare metals from wastes.^{15), 16)} Moreover, detoxification and decomposition processes of hazardous organic compounds, such as dioxins, have been recently developed using the MC process.^{17), 18)} However, the recovery of heavy metals in electronic materials has not been reported. In the present study, PZT ceramics were treated by wet ball milling at room temperature with aqueous H_2SO_4 solution, and the possibility of preferential recovery of lead in its sulfate form by reacting PZT ceramics with H_2SO_4 solution during milling was investigated.

2. Experimental procedure

2.1 Specimen and wet ball mill

Commercially available PZT sintered compact (Kojundo Chemical Lab. Co., Ltd., composition: $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$,

crystal system: tetragonal) having a morphotropic phase boundary neighborhood composition was used as a specimen. A PZT sintered compact was roughly precrushed in agate mortar by hand. The wet ball milling of the precrushed PZT was performed using a pot mill apparatus in air for 0–96 h at room temperature, and the rotational speed was fixed at 300 rpm. About 2.5 g of precrushed PZT (7.7 mmol) was placed in a polypropylene container of inner volume 50 ml together with ZrO_2 balls (diameter: 5 mm, weight ratio of PZT/ $\text{ZrO}_2 = 1/50$), and then 4 ml of aqueous H_2SO_4 solution (4.5 mol/dm^3) was added into the container. On the other hand, a dipped specimen was prepared by exposing the precrushed PZT into 4 ml of aqueous H_2SO_4 solution (4.5 mol/dm^3) for 0–96 h at room temperature to compare it with the milled specimens. The wet-ball-milled and dipped specimens were sonicated in 100 ml of aqueous H_2SO_4 solution (0.5 mol/dm^3) for 15 min, after which solid constituents in the solution were separated by filtration, and they were washed by the filtrate again. Finally, solid constituents on the filter were dried at 323 K in an oven for 24 h.

2.2 Characterization

The precrushed PZT and the specimens treated by ball milling and dipping were identified by XRD (Rigaku; RINT2500H). The surface morphology and texture of the specimens were observed by scanning electron microscopy (SEM; JEOL, JSM-6330F). The distribution of elements included in the recovered powder was analyzed by energy dispersive X-ray spectroscopy (EDS; JEOL, JFC-2140). Quantitative and qualitative analyses of lead, zirconium and titanium ions dissolved in the H_2SO_4 filtrate were performed by inductively-coupled-plasma atomic-emission spectroscopy (ICP-AES; Perkin Elmer Japan, 3300DV).

3. Results and discussions

3.1 Dipped specimen

Figure 1 shows the XRD profiles of (a) the precrushed PZT powder and the specimens obtained after dipping in aqueous H_2SO_4 solution for (b) 4, (c) 12, (d) 48 and (e) 96 h. In all the XRD profiles of the dipped specimens, new peaks corresponding to PbSO_4 appeared. The intensities of the PZT peaks decreased gradually with increasing treatment time. In contrast, the intensities of the peaks of PbSO_4 increased with increasing treatment time. However, the peaks of PZT were still confirmed even after dipping for 96 h. This is because the reaction of PZT with H_2SO_4 solution occurs only on the coarse particle surface of the precrushed PZT.

Figure 2 shows the SEM images of (a) the precrushed PZT powder, and the specimen obtained after dipping for (b) 4 and (c) 12 h. The particle sizes of precrushed PZT ceramics were approximately 2–10 μm , as seen in Fig. 2(a). The recovered powder after dipping in H_2SO_4 solution mainly consisted of fine particles with diameters less than 500 nm which adhered on particles as large as those of the precrushed PZT, as seen in Figs. 2(b) and (c). Moreover,

the number of formed fine particles was found to increase with treatment time, and the large particles were fully covered with fine particles. This SEM observation leads to the conclusion that the contact areas of PZT particles with H_2SO_4 solution decrease with increasing treatment time, because the PbSO_4 fine particles precipitated on the surface of the larger PZT particles. Therefore, it takes a very long time to transform PZT into PbSO_4 under the present conditions.

Figure 3 shows the EDS images of (a) the secondary-electron image (SEI) and the element maps for (b) Pb, (c) Zr and (d) Ti in the recovered powder after dipping for 48 h. The gray part in the element map indicates the existing area of each element. EDS images show that the particles with a relatively large grain size (3–4 μm) are basically composed of Pb, Zr and Ti atoms. In contrast, fine particles are seen in the SEI (Fig. 3(a)) which overlaps only with the Pb image. This result also indicates that the large particles are PZT particles and fine particles correspond to the precipitated PbSO_4 . This conclusion is supported by the results of the XRD analysis shown in Fig. 1.

Fig. 1. XRD profiles of (a) the precrushed PZT powder and the specimens obtained after dipping in aqueous H_2SO_4 solutions for (b) 4, (c) 12, (d) 48 and (e) 96 h. Symbols show PZT (▼) and PbSO_4 (●).

Fig. 3. EDS images of (a) the secondary-electron image and the element maps for (b) Pb, (c) Zr and (d) Ti in the recovered powder after dipping for 48 h.

Fig. 2. SEM images of (a) the precrushed PZT powder and the specimens obtained after wet ball milling for (b) 4 and (c) 12 h.

Fig. 4. XRD profiles of the specimens obtained after wet ball milling for (a) 4, (b) 12, (c) 48 and (d) 96 h. Symbols show PZT (▼) and PbSO₄ (●).

Fig. 5. Treatment time dependence of the XRD intensity ratio $[PbSO_4 / (PZT + PbSO_4)]$ for wet ball-milled specimens (■) and dipped specimens (□).

3.2 Wet-ball-milled specimen

Figure 4 shows the XRD profiles of the wet-ball-milled specimens for (a) 4, (b) 12, (c) 48 and (d) 96 h. The peaks of PbSO₄ were confirmed in all the wet-ball-milled specimens as in the case of the dipped ones. The same trend of the intensity change in PZT and PbSO₄ peaks in both milled and dipped specimens was observed, i.e., with an increase in milling time, the intensity of the PZT peaks gradually decreased while the intensity of the PbSO₄ peaks gradually increased. In the case of a milling time of more than 48 h, the PZT peaks completely disappeared, as seen in Figs. 4 (c) and (d). Figure 5 shows the dependence of XRD intensity ratio $[I_{PbSO_4} / (I_{PZT} + I_{PbSO_4})]$ on the treatment time for wet-ball-milled (■) and dipped specimens (□). Peak intensities of PZT and PbSO₄ species were measured from the diffraction lines at 30.9° and 29.7°, respectively. The XRD intensity ratio for the milled specimen increased markedly compared with that for the dipped specimen. This is not

Fig. 6. SEM images of the specimens obtained after wet ball milling for (a) 12 and (b) 48 h.

only because the PZT particles are finely ground, but also because PbSO₄ particles precipitated on the PZT surface are detached and well dispersed during the milling process. Preliminary experiments revealed that the perfect conversion of lead in the PZT sintered compact to PbSO₄ was not attained by hydrothermal treatment with aqueous H₂SO₄ solution. Thus, milling of the PZT plays a significant role in accelerating the reaction rate by enlarging the fresh surface area of the PZT particles. A few milligrams (1–3 mg) of weight loss of ZrO₂ balls were observed after wet ball milling with aqueous H₂SO₄ solution.

Figure 6 shows the SEM images of the specimens obtained after wet ball milling for (a) 12 and (b) 48 h. In the case of a ball-milling time of 12 h, it is apparent that the particle size is reduced by comparing it with that of an unmilled specimen (Fig. 2(a)) and that of the dipped specimen for 12 h (Fig. 2(c)). The grinding effect and the reaction with H₂SO₄ solution cause this particle size reduction. Furthermore, when the ball-milling time became 48 h, PZT particles that were also observed in the dipped specimen for 48 h (Fig. 3) disappeared, and only fine particles with a diameter of approximately 300 nm were observed. This result is also supported by the results of the XRD analysis in Fig. 5.

3.3 Leaching behavior of PZT

Figure 7 shows the dependence of the dissolution percentages of lead, zirconium and titanium ions in the H₂SO₄ filtrate on treatment time. In all cases of ball milling and dipping, the dissolution percentage of zirconium and titanium in the filtrate was found to increase with treatment time. No difference in dissolution percentage between zirconium and titanium can be observed in all the specimens. Zirconium and titanium are elements of the same group, so that both elements seem to exhibit a similar dissolution behavior under this condition. It is considered by comparing Fig. 5 with Fig. 7 that the leaching behavior of both components

(Fig. 7) is closely related to the collapsing behavior of the PZT crystal structure (Fig. 5). These results, therefore, indicate that the dissolution of zirconium and titanium in the PZT crystal structure and the collapsing of the PZT crystal structure took place simultaneously.

On the other hand, the dissolution percentage of lead in the H_2SO_4 filtrate was less than 0.1% compared with the initial lead content in PZT under all the ball milling conditions. This small amount of lead dissolved in the solution came from the dissociation of PbSO_4 according to

The amount of lead dissolved in the solution was less than that of lead calculated from the solubility product constant. The dissociation of PbSO_4 was significantly suppressed using H_2SO_4 solution in the milling and rinsing process, because the excess sulfate ions act by shifting the equilibrium to the left side of Eq. (1). These results lead to the conclusion that most of the lead exists either as PZT or as precipitated PbSO_4 , as supported by the previous XRD analysis. Therefore, it can be said that more than 99.9% of lead in PZT was transformed into solid PbSO_4 by ball milling for more than 48 h, when the diffraction line of the PZT completely disappeared.

3.4 Purity of the recovered PbSO_4

The remaining amount of lead, zirconium and titanium in the recovered powder obtained after wet ball milling for various milling times was calculated using the ICP results. Here, the remaining amount of each element was defined as

$$\begin{aligned} & \text{(Remaining amount)} \\ &= (\text{Initial content in PZT}) - (\text{Dissolved amount}). \end{aligned} \quad (2)$$

The purity of PbSO_4 in the recovered specimen was also calculated by converting the masses of the remaining lead, zirconium and titanium into those of PbSO_4 , ZrO_2 and TiO_2 . These results are summarized in Table 1. About 98 mass% of the powder recovered by the wet ball mill for more than 48 h was PbSO_4 . The rest of the 2 mass% of the recovered powder might consist of zirconium and titanium compounds.

The reaction of PZT with H_2SO_4 solution can be expressed by

Here, the dissolution form of zirconium and titanium was determined by the XRD analysis of the precipitates obtained after the concentration of the H_2SO_4 filtrate. Zirconium and titanium in PZT ceramics were extracted as an oxo-complex in the solution, while lead could be precipitated as PbSO_4 by ball milling.

4. Conclusions

Wet ball milling of PZT ceramics was performed at room temperature for 0–96 h with aqueous H_2SO_4 solution, and the possibility of the preferential recovery of lead in its sulfate form was investigated by reacting PZT ceramics with aqueous H_2SO_4 solution during milling. XRD measurements clarified that the diffraction lines of PZT completely disappeared and only the diffraction lines of PbSO_4 were confirmed by wet ball milling for more than 48 h. The amounts of lead, zirconium and titanium ions dissolved into the H_2SO_4 solution were analyzed by ICP measurement. The dissolution percentages of zirconium and titanium in the solution were found to increase with treatment time, and the leaching behavior of both ions is closely related to the collapsing behavior of the PZT crystal structure. In contrast, the dissolution percentage of lead was below 0.1% compared with the initial lead content of PZT ceramics under all the ball milling conditions. More than 99.9 mass% of lead in PZT can be recovered as PbSO_4 by wet ball milling for more than 48 h, and the purity of recovered PbSO_4 was approximately 98 mass%.

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Fig. 7. Treatment time dependence of the dissolution percentage of lead (■, □), zirconium (●, ○) and titanium (▲, △) ions in the H_2SO_4 filtrate. Filled symbols and open symbols indicate ball-milled specimens and dipped specimens, respectively.

Table 1. Remaining Amount of Pb, Zr and Ti, and the Purity of Recovered PbSO_4 Calculated from ICP Results

Milling time / h	Specimen / mg	Dissolved amount / mg			Remaining amount ^(*) / mg			Converted mass / mg				PbSO_4 / mass%
		Pb	Zr	Ti	Pb	Zr	Ti	PbSO_4	ZrO_2	TiO_2	Total	
48	2503.2	0.6	354.6	153.2	1592.5	10.0	23.5	2349.4	13.6	25.8	2388.8	98.4
72	2501.6	0.7	350.5	160.2	1591.4	14.0	16.4	2347.7	18.9	27.4	2394.0	98.1
96	2502.4	0.9	340.0	170.0	1591.5	24.6	6.6	2347.8	33.2	11.0	2392.1	98.2

(*): Remaining amount of each component was calculated as follows;

$$(\text{Remaining amount}) = (\text{initial content in PZT}) - (\text{dissolved amount})$$

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