Powder Technology 230 (2012) 63–66

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Mechanochemical sulfidization of lead oxides by grinding with sulfur

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ARTICLE INFO

Article history:
Received 25 January 2012
Received in revised form 8 June 2012
Accepted 29 June 2012
Available online 4 July 2012

Keywords:
Grinding
Mechanochemical sulfidization
Lead oxide
Lead sulfide

ABSTRACT

Lead oxide was co-ground with sulfur to investigate the possibility of stimulating a solid-state reaction to form lead sulfide. The formation of both lead sulfide and lead sulfate was confirmed, even without any other additive such as iron powder. The necessary conditions for sulfidizing the oxides can be explained based on thermodynamic considerations, namely a negative change in Gibbs free energy. This method can be applied to treat leaded glass by co-grinding it with sulfur to form sulfide as well as sulfate, so that current mineral processing techniques, such as flotation separation, might be used to recover lead from various kinds of leaded glass wastes.

1. Introduction

Non-ferrous metals such as Cu, Pb, and Zn have been widely used for many decades, and they generate a vast amount of toxic waste. For example, funnel glass, widely used in cathode ray tubes (CRTs), contains approximately 20 wt.% PbO [1,2]. Reclaiming and recycling these metals from the wastes is highly desirable, for resource preservation, sustainable development, and environmental protection. These metals can be extracted relatively easily by processing sulfide minerals such as sphalerite (ZnS), galena (PbS) and charcopyrite ($CuFeS_2$); technology is already available for processing these sulfides. However, the metals in toxic wastes are rarely in sulfide form, but instead are oxides and oxidized compounds, or simply the pure metal itself. If a simple and reliable method to sulfidize the waste could be developed, existing mineral processing methods and metallurgical processes could be applied to treat the synthetic sulfides. This approach could make the metal recycling system feasible, both technologically and economically, without the difficulty of developing a recycling process for each specific type of waste [3–7].

Metal sulfides can be created with mechanochemical reactions between metals and sulfur [8–12]. One mechanochemical method has been reported to be able to convert oxides of non-ferrous metals into sulfides by co-grinding the metal with both sulfur and iron powders. The iron sample works as a reducer to combine with oxygen from these oxides to form iron oxides, making possible the sulfidization of non-ferrous metals [13]. Recently it has been found that, unlike zinc oxide, lead oxide as well as leaded glass could be sulfidized by simply grinding it with sulfur, without the need of additional iron [13,14].

We have studied the reaction mechanism between lead oxide and sulfur during a grinding operation. Our results are reported in this paper, and can serve as the basis of further research for leaded glass recycling.

2. Material and methods

2.1. Grinding operation

All of the samples used, including oxides (PbO, PbO_2) and sulfur, were chemical reagents supplied by Wako Pure Chemical Industries, Ltd. Osaka, Japan. Oxide was mixed with sulfur at molar ratio of 1:1. A planetary ball mill (Pulverizette-7, Fritsch, Germany) was used for grinding the mixture. Seven zirconia balls of 15 mm diameter and 2 g of mixed powder were introduced to a zirconia vessel of 45 cm^3 inner volume. The grinding was operated in a nitrogen atmosphere at 500 rpm for varying periods of time.

2.2. Characterizations

The morphology of the ground samples was observed by a scanning electron microscope (SEM HATACHI 6600, Japan). The samples before and after grinding were examined by X-ray diffraction (XRD, Rigaku, Japan), using Cu Kα radiation within a recorded range of 2θ from 5° to 60°. A Fourier transformation infrared spectrometer (FTIR, Digilab Excalibur Series, FTS-3000) was used to analyze the ground samples with a conventional KBr method. For each sample, 20 scans were recorded, averaging from 2000 to 400 cm^{-1} with a resolution of 2 cm^{-1}. Thermal gravimetric (TG, Rigaku TAS-200, Tokyo, Japan) analysis was carried out in an N_2 atmosphere from room temperature

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doi:10.1016/j.powtec.2012.06.053

to 400 °C, at the rate of 10 °C/min, to assess the amount of sulfur remaining after each increase.

3. Results and discussion

3.1. SEM images of the ground samples

Fig. 1 shows the SEM photographs of the ground samples for lead oxide (A) with sulfur and lead dioxide (B) with sulfur. Both samples have quite similar morphology with a heavy agglomeration of small primary particles in the nano-range size. This is typically observed with products prepared by mechanochemical reaction.

3.2. XRD analysis of the ground samples

Fig. 2 shows the XRD patterns of the sample of lead oxide and sulfur ground for different periods of time. Compared to the sample mixed by hand (designated as 0 min) with initial samples of lead oxide and sulfur as marked, lead sulfide (PbS) was clearly observed in the patterns of the ground samples, and its peak intensity increased with an increase in grinding time from 15 min to 30 min. The peaks correspond to the crystal planes of 111, 200, 220, 311 and 222 of crystalline PbS [15,16]. It is also interesting to note that, in addition to lead sulfide, peaks of lead sulfate appeared in the pattern of the 30-min ground sample.

Previously, when the formation of sulfide only was expected (as represented by Eq. (1)), it was difficult to obtain sulfate by grinding, and the positive changes in the reactions given by Eq. (1) were understood to be attributable to the standard Gibbs free energy change ΔG_{298}: 120.1 (Zn), 91.7 (Pb), 85.6 (Cd) and 74.8 kJ/mol (Cu).

$$MO + S = MS + 1/2O_2 (M = Zn, Pb, Cd, Cu). \tag{1}$$

When iron is added, as represented by Eq. (2), the sulfidization reaction is successfully realized, and the negative changes in ΔG_{298} of Eq. (2) explain the thermodynamics.

$$4MO + 4S + 3Fe = 4MS + Fe_3O_4 (M = Zn, Pb, Cd). \tag{2}$$

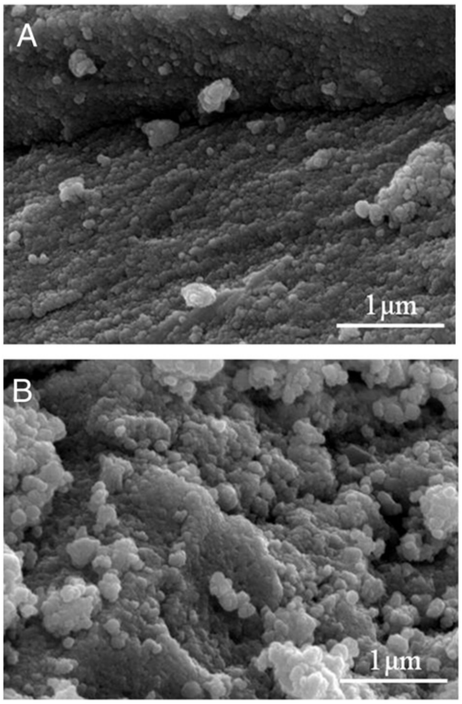

Fig. 1. SEM images of ground samples at 500 rpm for 2 h. (A) lead oxide + sulfur and (B) lead dioxide + sulfur.

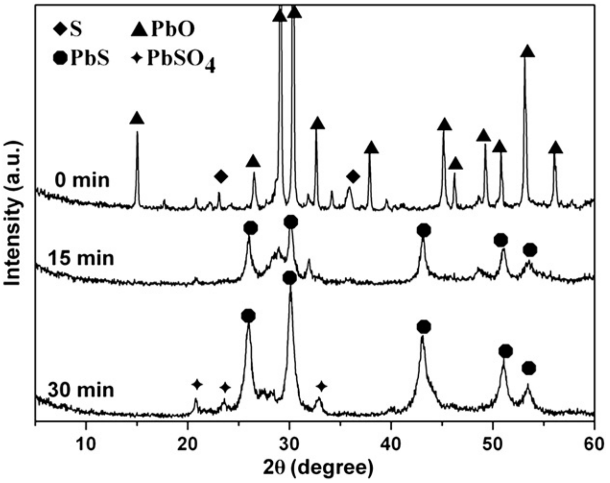

Fig. 2. XRD patterns of lead oxide and sulfur mixture ground for varying durations.

In this study, however, using lead oxide only, even without adding iron, a mechanochemical reaction was observed between lead oxide and sulfur. Another reaction mechanism is needed, to explain this result. Eq. (3) provides this explanation: a negative change in ΔG_{298} of −352.6 kJ/mol confirms that this result is thermodynamically possible.

$$4PbO + 4S = 3PbS + PbSO_4. \tag{3}$$

Unlike the reaction mechanism represented by Eq. (2), where all the sulfur has been reduced into sulfide with the addition of reducer iron, the reaction mechanism represented by Eq. (3) involves both oxidation and reduction of sulfur: three fourths of the sulfur is reduced and one fourth is oxidized. Such simultaneous occurrence of oxidation and reduction within the same composition is seldom reported [17,18], although other mechanochemical reductions and oxidations have been widely reported, suggesting that this mechanochemical reaction may exhibit special characteristics worth further investigation for other possible applications.

Since lead sulfate formation is the key factor for facilitating the mechanochemical reaction, additional oxygen might speed up the reaction. Lead dioxide was used to test this theory. Fig. 3 shows the XRD patterns of the ground sample with lead dioxide as the initial sample. Similar to the results shown in Fig. 2, lead sulfide is obtained from the ground sample and the peak intensity increased with an increase in

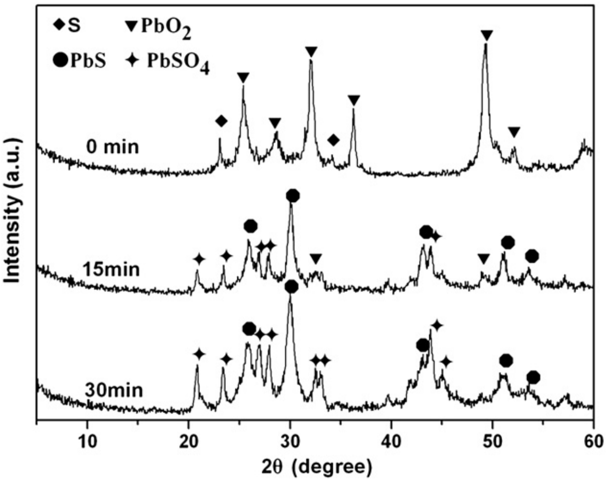

Fig. 3. XRD patterns of lead dioxide and sulfur mixture ground for varying durations.