Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 404 (2003) 265–270
thermochimica acta
www.elsevier.com/locate/tca

Short communication

Calorimetric study of the mechanochemically activated sphalerite

Zhongliang Xiao [a,b,*], Qiyuan Chen [a], Zhounan Yin [a], Pingmin Zhang [a]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China
[b] Chemistry Department, Changsha University of Electric Power, Changsha 410077, PR China

Received 27 September 2002; received in revised form 1 February 2003; accepted 3 February 2003

Abstract

The thermal behavior of mechanochemically activated sphalerite during aging was investigated by calorimetry. The results indicate that mechanochemically activated sphalerite releases the stored energy which may origin from a series of complex transformations. The amount of energy released increases with the grinding time but remains almost constant after grinding for 1 h. It is independent of the grinding atmosphere and is related to the ball-mill medium. The XRD results illustrate a difference of the microstructure between activated and non-activated sphalerite. The microstructure of the activated sphalerite remains the same when it is heated in a calorimeter for the measurement of the heat released. The particle size analyses show that the particle size of the activated sphalerite increases when it is heated in the calorimeter. Therefore, it can be concluded that the released energy is probably caused by the decrease of the specific surface energy.

Keywords: Mechanochemical activation; Sphalerite; Calorimetry; Surface energy

1. Introduction

The mechanical action on solid substances generates a series of complex transformations, breaking the order of the crystalline structure, producing cracks and new surfaces, therefore, changing its physical and chemical properties, such as increasing the specific surface energy and elastic strain energy [1,7,8]. Sometimes the changes can be utilized to increase surface reactivity, decrease reaction time and processing temperature, increase the rate of the leaching reaction, etc. [2]. Extraction of non-ferrous metals from sulfidic ores is economically important tasks. But, because of the drastic reaction conditions which is technically difficult, the mechanical activation is used widely in hydrometallurgy.

The most commonly used methods to study mechanical activation are IR and XRD techniques which normally allow the identification of the products [3–6]. Evidence of modification of surfaces through mechanochemical treatment can be provided by these method. Other techniques like HREM, EXFAM, XPS and X-ray cyclotron resonance, etc., have been used to study the chemical change of new surfaces of the milled products [2,10–12]. The differences of the energy releasing behaviors between non-activated and mechanochemically activated sulfide ores were seldom studied by calorimetry.

Sphalerite, as an important part of sulfidic ores, belongs to the group of substances exhibiting great sensitivity to mechanical stress [1]. Since the reactivity of the mechanochemically activated sphalerites has relations with its storage energy, the main purpose of our recent work was to research into the energy releasing behaviors of non-activated and

* Corresponding author. Tel.: +86-731-8877364.
E-mail address: xiaozhongliang@163.com (Z. Xiao).

0040-6031/$ – see front matter
doi:10.1016/S0040-6031(03)00143-6

mechanochemically activated sphalerites by calorimetry experiments.

2. Experimental

2.1. Sample preparation

Natural pure hand-sorted sphalerite ore was purchased from a domestic mine, and its chemical compositions are summarized in Table 1. It was found by X-ray diffraction analysis that the natural sphalerite contained cubic sphalerite as a predominant component. The non-activated sphalerite was prepared by crushing the natural sphalerite in a jaw crusher to a particle size of $\leq$1 mm, then stored for more than six months. The samples of the activate sphalerite were prepared as follows: the non-activated sphalerite (10 g) was poured into a stainless vessel with six balls of 18 mm in diameter and 12 balls of 8 mm in diameter and the balls were made of steel or agate. The vessel was encapsulated directly; or kept in higher vacuum, followed by bubbling high pure nitrogen into this vessel through an inlet of this vessel for half an hour, and then mechanochemically activated in a planetary mill (QM-ISP Planetary mill, PR China) under a rotation rate of 200 rpm, a powder:ball mass ratio of 1:25, and time of activation $t = 10$, 20, 40 and 120 min to get mechanochemically activated sphalerite.

2.2. Principle of measurement

The calorimetric measurement was performed in a HT-1000 heat conduction calorimeter (SETARAM, France). The detailed description of the calorimeter was given in our earlier publications [9]. The sensitivity of the calorimeter was calibrated by an electrical method.

Table 1
The chemical analyses of the natural sphalerite

Elements	Content (wt.%)
Zn	61.39
S	32.11
Fe	2.38
Pb	1.92
Cd	0.28
Sb	0.05
Bi	0.01
In	0.03

The calorimeter's temperature was maintained at 323.35 K throughout the experiment. After the baseline of the calorimeter reached a stable state, an aluminum crucible containing sphalerite sample at a constant temperature of 289.75 K was dropped quickly into the isothermal zone of the calorimeter cell. The heat flow data were recorded by a datum acquisition computer until the system reached the thermal steady state. Then the absorbed heat for 1 g sphalerite absorbed was obtained by datum treatment. The absorbed heat of the mechanochemically activated sphalerite during measurement consists of two parts. The first part is the absorbed heat when the temperature of the non-activated sphalerite increases from 289.75 to 323.35 K. The second part is the heat released for the activated sphalerite. Therefore, the storage energy of the activated sphalerite can be given as:

$$E = E_1 - E_2$$

where E is the storage energy of mechanochemically activated sphalerite caused by mechanically action; E_1 the absorbed energy of 1-g non-activated sphalerite from 289.75 to 323.35 K. $E_1 = 1.436\,\mathrm{J\,g^{-1}}$ (average value of four test results). E_2 is the absorbed energy of 1 g mechanochemically activated sphalerite from 289.75 to 323.35 K.

2.3. Surface structural characteristics

The structural disorder of mechanochemically activated sphalerite was characterized by X-ray diffraction analysis on a diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.54$ Å; voltage, 40 kV; current, 20 mA) with time constant, 0.5 s; limit of measurement, 10 impulses $\mathrm{s^{-1}}$; step size, 0.03; and collection time, 3 s $\mathrm{step^{-1}}$ (no internal standard).

The average particle size was measured using Mastersizer 2000 Laser Diffraction Particle Size Analyzer (Malvern, GB), and distilled water was used as a dispersing agent.

3. Results and discussions

The effect of the grinding time on energy released for the activated sphalerite was investigated. The

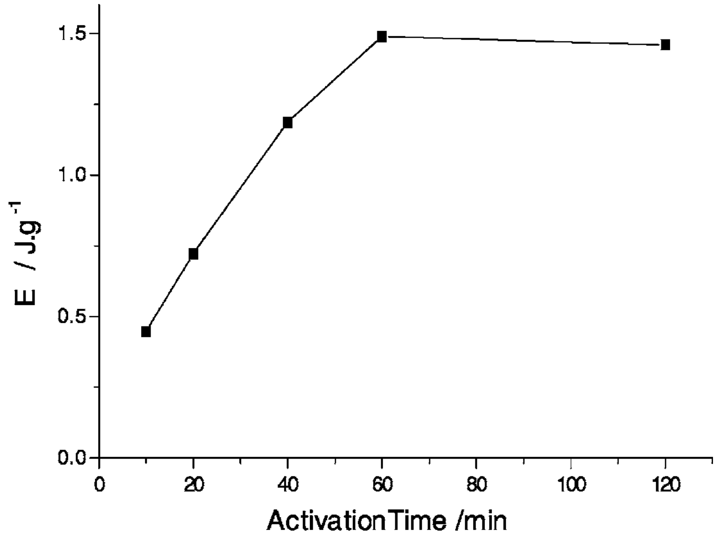

Fig. 1. Energy release of sphalerites after grinding for different times.

results, which is shown in Fig. 1, indicate that the energy release increases with the grinding time of the mechanochemically activated sphalerite and remains almost constant after grinding for 1 h.

Sphalerite is a non-conductive solid and superficial oxidation reactions will be strongly limited in the absence of surface activation [13].The difference of the energy released for the sphalerite mechanically activated in oxidative atmosphere (such as air) or inert atmosphere (such as N_2) is shown in Table 2. The results indicate that the grinding atmosphere does not affect, obviously, the energy released for the activated sphalerite.

The energy released for the mechanochemically activated sphalerite under different grinding media is shown in Fig. 2. It indicates that the energy released

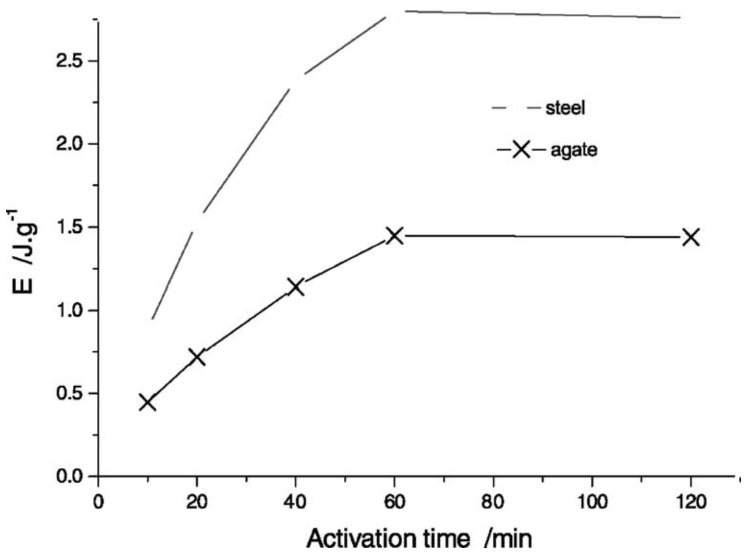

Fig. 2. Energy release of sphalerites under different grinding media.

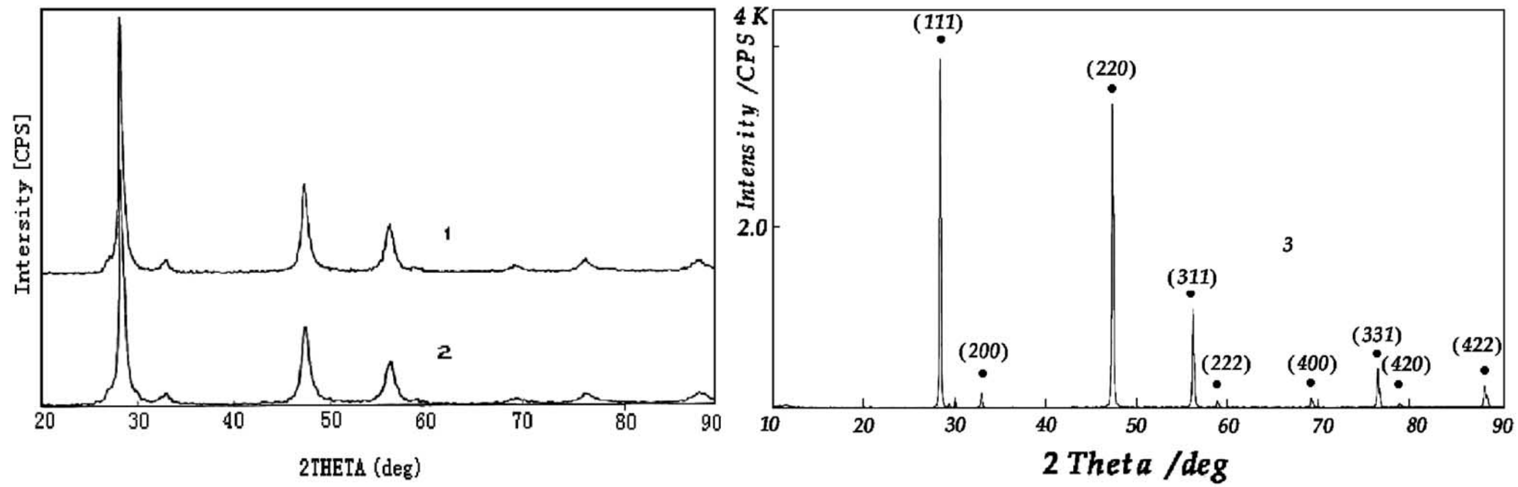

Fig. 3. The XRD patterns of the non-activated and activated sphalerites: (1) grinding for 2 h before energy release; (2) grinding for 2 h after energy release; and (3) the non-activated sphalerite.

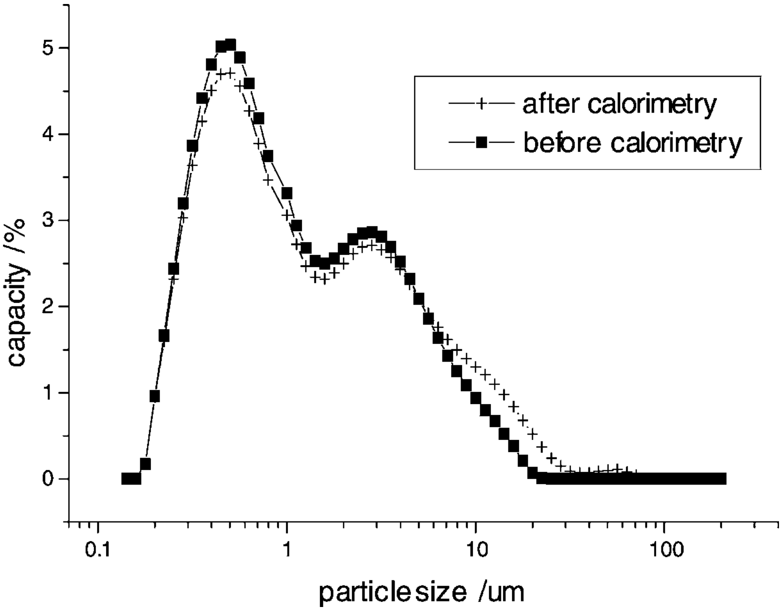

Fig. 4. Particle size analysis of the mechanochemically activated sphalerite (grinding time: 2 h).

for the mechanochemically activated sphalerite using agate ball is, obviously, less than that of the mechanochemically activated sphalerite using steel ball.

The XRD results in Fig. 3 show that the decrease in intensity and broadening of the diffraction line of mechanical activated sphalerite illustrate a decrease in crystallite size with the mechanochemical treatment, but the XRD pattern remains the same after the mechanochemically activated sphalerite is heated in a calorimeter for the measurement of the energy released. The particle size analyses, in Fig. 4, show that the mean particle size of the activated sphalerite increases from 2.09 to 3.13 μm when it is heated in a calorimeter. Therefore, it can be concluded that the energy released comes from the decrease of the specific surface energy.

Table 2
The energy release for the sphalerite activated under different atmospheric conditions

Activation time (min)	E (J g^{-1}; grinding in air)	E (J g^{-1}; grinding in N_2)
10	0.449	0.454
20	0.705	0.732
40	1.106	1.163
60	1.435	1.424
120	1.424	1.433

4. Conclusions

1. The energy of the mechanochemically activated sphalerite released increases with the grinding time.
2. The grinding atmosphere does not effect, obviously, the energy release from the activated sphalerite.
3. The energy released comes from the decrease in the specific surface energy.

Acknowledgements

The work has been supported by the Key Project 59934080 of the National Natural Science Foundation of PR China (No. 59934080) and the Doctorate Program Fund of National Ministry of Education in PR China (No. 2000053321).

References

[1] P. Baláz, Z. Bastl, J. Briancin, I. Ebert, J. Lipka, J. Mater. Sci. 27 (1992) 653.

[2] J.F. Fernández-Bertran, Pure Appl. Chem. 71 (1999) 581.

[3] I. Persson, P. Persson, M. Valli, S. Fózó, B. Malmensten, Atomic absorption spectrophotometry and calorimetry, Int. J. Process. 33 (1991) 67.

[4] K. Sasaki, H. Konno, M. Inagaki, J. Mater. Sci. 29 (1994) 1666.

[5] R.L. Frost, É. Makó, J. Kristóf, E. Horváth, J. Theo Kloprogge, J. Colloid Interface Sci. 239 (2001) 458.

[6] É. Makó, R.L. Frost, J. Kristóf, E. Horváth, J. Colloid Interface Sci. 244 (2001) 359.

[7] P. Baláz, E. Post, Z. Bastl, Thermochim. Acta 200 (1992) 371.

[8] M. Asomoza, M.P. Dominguez, S. Solis, et al., Mater. Lett. 33 (1997) 153.

[9] Q. Chen, W. Zeng, X. Chen, S. Gu, G. Yang, Z. Zhou, Thermochim. Acta 253 (1995) 33.

[10] H.A. Skinner, Experimental Thermochemistry, vol. II, Interscience, New York, 1986.

[11] J.C. de Lima, T.A. Grandi, R.S. de Biasi, J. Non-Cryst. Solids 286 (2001) 93.

[12] Y. Chen, T. Hwang, M. Marsh, J.S. Williams, Mater. Sci. Eng. A226–A228 (1997) 95.

[13] Ph. de Donato, M. Kongolo, O. Barres, Powder Technol. 105 (1999) 141.