

Oxidation behavior of mechanically activated galena in thermogravimetry (TG)

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Abstract

The oxidation behaviors of non-activated and mechanically activated galenas were investigated by thermogravimetry method (TG) in flowing highly pure oxygen atmosphere at the heating rate of 10 K min^{-1} . It is found that the mass increase between 400 and 850 K in the TG curves rises with the increase of grinding time of galena. The difference in oxidation reactivity of non-activated and mechanically activated galenas was also discussed. The specific granulometric surface area (S_G) and the structural disorder of mechanically activated galenas were analyzed by X-ray diffraction laser particle size analyzer and X-ray powder diffraction analysis (XRD), respectively. The results show that the specific granulometric surface area (S_G) of mechanically activated galenas almost remains constant after grinding for a certain period, and lattice distortions (\hat{a}) increase, but the crystallite sizes (D) decrease with the increase of the grinding time. All the results imply that the mass increase between 400 and 850 K in the TG curves for mechanically activated galenas is mainly caused by the increase of lattice distortions (\hat{a}) and the decrease of the crystallite sizes (D) with increasing the grinding time.

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1. Introduction

Extraction of non-ferrous metals from sulphidic ores belongs to the technically difficult and economically important tasks. The more chemically stable the sulfide, the more difficult the extraction is. Thus, either drastic reaction conditions have to be applied or the chemical stability of sulphides has to be modified by a suitable chosen pre-leaching treatment. The mechanical activation of the ore by intensive grinding is a typical representant of the second way [1]. The best way to study mechanochemical transformation of the mechanical activation for ores is to analyze in situ

the milled mixture using appropriate spectroscopic methods, since chemical handling can obscure the true nature of the initial products. But nowadays, most common tools are IR and XRD techniques which normally allow the identification of the products [2,3]. Other techniques like HREM, EXFAM, XPS and X-ray cyclotron resonance, etc. have been used to study the new surfaces of the milled products [4]. For example, P. Baláž et al [5] investigated the changes produced in cinnabar by its mechanical activation in a planetary ball mill through XPS, BET, XRD and DSC. And the DSC curves of non-activated and mechanically activated cinnabars represent an association of endothermic effects which differs from each other in shapes and values of the extreme temperatures. Whereas the differences of the oxidation behaviors

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between non-activated and mechanically activated sulfide ores were seldom studied by using thermogravimetry analysis (TG). Galena belongs to the group of substances exhibiting great sensitivity to mechanical activation through intensive grinding in a specially designed equipment, such as a planetary ball mill [6].

In the present paper, the oxidation behaviors of non-activated and mechanically activated galenas were studied with TG measurement for the first time. The difference in oxidation reactivity of non-activated and mechanically activated galenas was discussed. The changes of the specific granulometric surface area (S_G) and the structural disorder of different galenas were also studied.

2. Experimental

Natural pure hand-sorted galena 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 galena contained cubic galena as a predominant component, and cubic sphalerite as a main impurity (as shown in Fig. 1). The non-activated galena was prepared by crushing the natural galena in a jaw crusher to a particle size of ≤ 1 mm, then stored for >6 months. The non-activated galena (10 g) was added into a stainless vessel with six

Table 1
The chemical analyses of the natural galena

Elements	Contents (wt.%)
Pb	60.10
Zn	14.17
S	18.08
Fe	2.56
Cd	0.28
Sb	0.05
Bi	0.01
In	0.03

stainless steel balls of 18 mm in diameter and 12 balls of 8 mm in diameter, then kept in higher vacuum (the residue pressure ≤ 1 Pa), followed by bubbling highly pure nitrogen into this vessel through an inlet for 0.5 h, and these operations were performed once again (i.e. non-activated galena was kept under an inert atmosphere), and then mechanically activated in a planetary ball mill (QM-ISP Planetary mill, PR China) rate of 200 rpm, a powder-to-ball mass ratio of 1:25 was employed, and mechanically activated galenas were obtained after grinding for $t_G = 10, 40, 120, 180$ and 260 min, respectively.

X-ray diffraction (XRD) profiles from the milled powders were recorded on a 3014 diffractometer (Rigaku, Japan) using Cu $K\alpha$ radiation ($\lambda = 1.54$ Å, voltage 40 kV, current 20 mA) with time constant 0.5 s, limit of measurement 10 impulses per second,

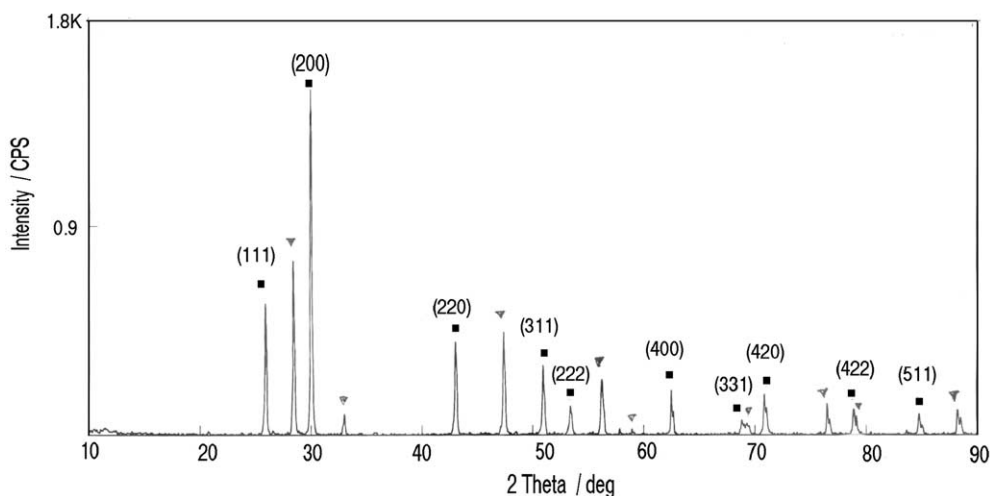


Fig. 1. XRD phase analysis for natural galena, (■) cubic galena; (▼) cubic sphalerite.

step size 0.03° . The recorded XRD spectra were used for calculation of the degree of structural disorder—the distortion (\hat{a}) of crystal lattice (presented as a percentage) and the crystallite size (D) was also observed, which was determined from the changes in profile of the diffraction peaks [7], such as (2 0 0) and (4 0 0) planes of different galenas. As the increase of the profile breadths mainly results from the increase of the lattice distortion (\hat{a}) and the decrease of the crystallite size (D), \hat{a} and D can be calculated using the model of Gaussian function [8].

The measurements pertaining to thermogravimetry analysis were performed by using a thermal analyzer TGA/SDTA 851^c (Mettler Toledo, USA and Switzerland) with temperature program from 298 to 1273 K at the heating rate of 10 K min^{-1} under highly pure oxygen with flowing rate of 70 ml min^{-1} . The sample mass is about 31 mg. The maximum mass increase rate (α_{\max}) between 400 and 850 K in the TG curves for different galenas were calculated according to the following equation:

$$\alpha_{\max}(\%) = \frac{w_2 - w_1}{w_1} \times 100$$

where w_1 and w_2 is the remaining weight of the sample at 400 K and 850 K, respectively.

The specific granulometric surface area (S_G) of mechanically activated galenas was calculated from the corresponding average particle size measured using Mastersizer 2000 Laser Diffraction Particle Size Analyzer (Malvern, Great Britain), and distilled water was used as a dispersing agent.

Non-activated and mechanically activated galenas (the latter was milled for 3 h in inert atmosphere) were treated for 1 h in an oven at 850 K under flowing pure oxygen (70 ml min^{-1}), oxidation products were obtained and characterized by X-ray diffraction phase analysis, respectively.

3. Results and discussion

3.1. TG curves for different galenas

The TG curves for different galenas were obtained (Fig. 2). And the maximum mass increase rate (α_{\max}) between 400 and 850 K in the TG curves for different galenas were also presented in Table 2.

Table 2 shows that the maximum mass increase rate (α_{\max}) between 400 and 850 K in the TG curves rises gradually with increasing the grinding time. The minus α_{\max} value of non-activated galena indicates

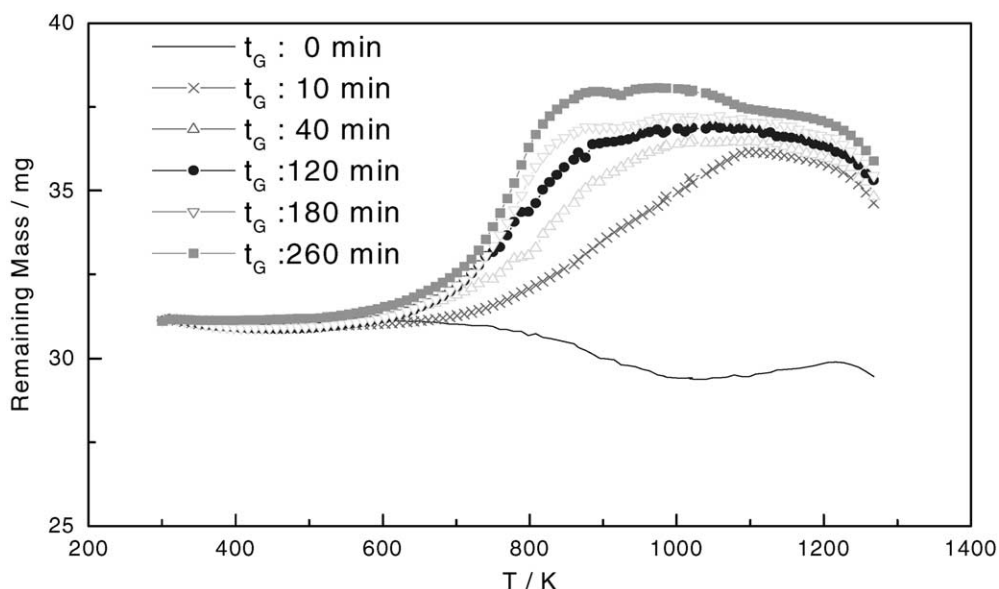


Fig. 2. TG curves of different galenas after grinding for different time.

Table 2
The relationship between the maximum mass increase rate (α_{\max}) and grinding time (t_G)

t_G (min)	α_{\max} (wt.%)
0	-2.08
10	5.10
40	10.64
120	14.95
180	17.61
260	21.31

that non-activated galena may be subjected to less oxidation and the impurity—cubic sphalerite may undergo intensive oxidation to get zinc oxide, which results in the overall mass loss of non-activated galena. Whereas, mechanically activated galenas were reacted with pure oxygen to obtain orthorhombic lead sulfate (PbSO_4), which leads to the mass increase in TG curves. Therefore, mechanically activated galena is more easily subjected to oxidation than non-activated

galena. The next experiment will also support this opinion.

Oxidation products were obtained from the 1 h treatment of non-activated and mechanically activated galenas (the latter was milled for 3 h in an inert atmosphere) in an oven at 850 K under flowing pure oxygen, followed by being characterized by X-ray diffraction phase analysis, respectively, (shown in Fig. 3).

Fig. 3 shows that non-activated galena is almost stable in pure oxygen at 850 K only with a very small amount of orthorhombic lead sulfate (PbSO_4) formed, and impurity cubic sphalerite is oxidized into hexagonal zinc oxide (ZnO) with gaseous sulphur dioxide giving off, which leads to the overall mass loss of non-activated galena during oxidation, but oxidation products for mechanically activated galena contain predominant orthorhombic lead sulfate (PbSO_4). This is an additional support for the above opinion.

The state of the activated solids can be characterized as metastable [9]. So non-activated galena transforms

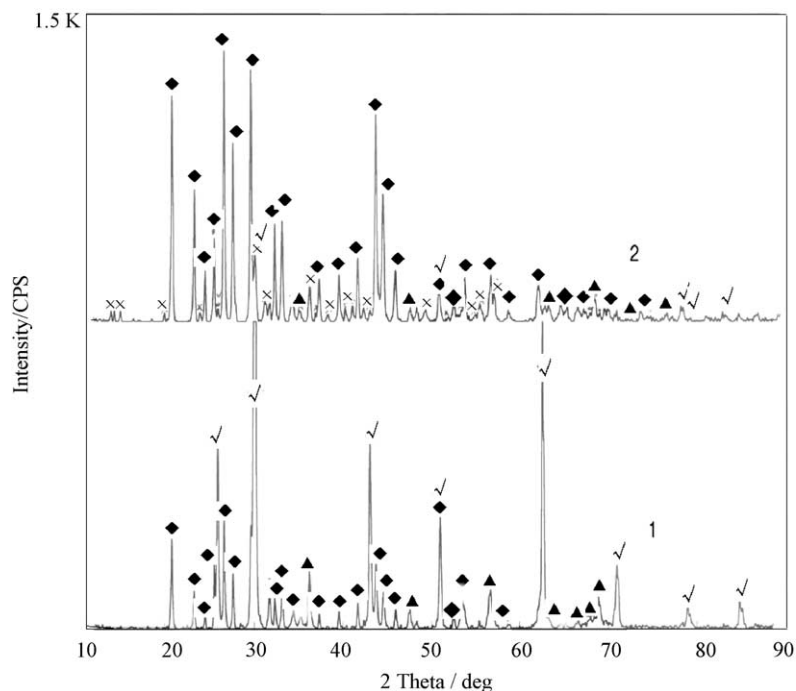


Fig. 3. XRD patterns for oxidation products of non-activated and activated galenas. (1): oxidation products of non-activated galena; (2): oxidation products of mechanically activated galena; (◆): orthorhombic lead sulfate (PbSO_4); (×): monoclinic lead oxide sulfate (Pb_2OSO_4); (▲): hexagonal zinc oxide (ZnO); (✓): cubic galena (PbS).

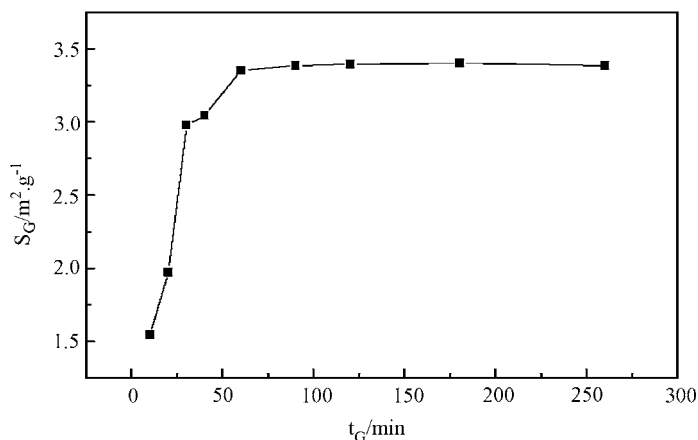


Fig. 4. The specific granulometric surface area (S_G) of mechanically activated galenas vs. the grinding time.

into metastable galena after mechanical activation. It is more liable for metastable galenas to react with highly pure oxygen than for non-activated galena, which is in agreement with thermoanalytical study of mechanically activated cinnabar by Baláž [5].

3.2. Study on the changes of the surface structure of non-activated and mechanically activated galenas

It is well known that mechanical activation, which results in the formation of metastable solids [9], is a means of accelerating the leaching process for sulfidic ores, contributing to the success of this technique are [4,10,11]: (1) increased surface area; (2) the microstructural modifications stemming from the deformation; (3) chemical reaction. As mechanical activation of the samples in this experiment was performed under inert atmosphere, we can overlook oxidation reaction of galena with air during mechanical activation.

The specific granulometric surface area (S_G) of mechanically activated galenas are shown in Fig. 4.

Fig. 4 shows that the specific granulometric surface area (S_G) of mechanically activated galenas remain constant after $t_G > 60$ min, which implies that the increase of the structural disorder may result in the mass increase between 400 and 850 K in the TG curves for mechanically activated galenas after a certain activation period.

By analyzing X-ray diffraction peaks (2 0 0) and (4 0 0) of non-activated and mechanically activated

Table 3
The relationship between D , \bar{a} and grinding time t_G

	t_G (min)			
	0	40	120	260
D (\AA)	4040	670	197	110
\bar{a} (%)	0.01	0.11	0.25	0.47

galenas, the values of D and \bar{a} are obtained (Table 3) and X-ray diffraction peaks (2 0 0) and (4 0 0) for different galenas are also listed in Figs. 5 and 6, accordingly.

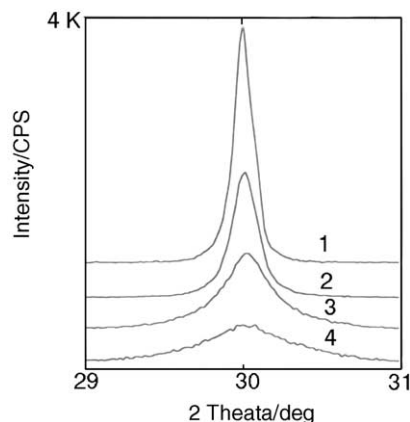


Fig. 5. Peaks (2 0 0) of X-ray diffraction patterns for different galenas after different grinding time (t_G): (1) 0; (2) 40; (3) 120; (4) 260 min.

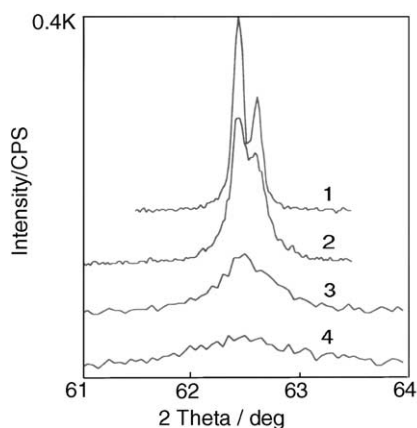


Fig. 6. Peaks (4 0 0) of X-ray diffraction patterns for different galenas after different grinding time (t_G): (1) 0; (2) 40; (3) 120; (4) 260 min.

Table 3 shows that the crystallite sizes (D) decrease and the deformations of the crystal (\hat{a}) increase gradually with increasing the grinding time, which is similar with the study of mechanically activated chalcopyrite and pyrite [12,13].

Therefore, non-activated galena undergoes the structural distortion during grinding in inert atmosphere, which leads to the formation of metastable galenas. The metastable galenas containing accumulated excess energy can react more easily with highly pure oxygen than non-activated galena, and this structural sensitivity of oxidation behavior of these galenas confirms the structural sensitivity of thermal decomposition of mechanically activated chalcopyrite, sphalerite and pyrite [9,13,14].

4. Conclusions

The mass increase between 400 and 850 K in the TG curves rises gradually with increasing the grinding time of mechanically activated galenas, which mainly

results from the increase of the structural disorder during the mechanical activation of galenas under inert atmosphere. Mechanically activated galena is more easily subjected to oxidation than non-activated galena. It can also be concluded that TG is a useful indirect method for the characterization of mechanically activated galenas.

Acknowledgements

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