Mechanism of mechanical activation for sulfide ores

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Abstract: Structural changes for mechanically activated pyrite, sphalerite, galena and molybdenite with or without the exposure to ambient air, were systematically investigated using X-ray diffraction analysis(XRD), particle size analysis, gravimetrical method, X-ray photo-electron spectroscopy(XPS) and scanning electron microscopy(SEM), respectively. Based on the above structural changes for mechanically activated sulfide ores and related reports by other researchers, several qualitative rules of the mechanisms and the effects of mechanical activation for sulfide ores are obtained. For brittle sulfide ores with thermal instability, and incomplete cleavage plane or extremely incomplete cleavage plane, the mechanism of mechanical activation is that a great amount of surface reactive sites are formed during their mechanical activation. The effects of mechanical activation are apparent. For brittle sulfide ores with thermal instability, and complete cleavage plane, the mechanism of mechanical activation is that a great amount of surface reactive sites are formed, and lattice deformation happens during their mechanical activation. The effects of mechanical activation are apparent. For brittle sulfide ores with excellent thermal stability, and complete cleavage plane, the mechanism of mechanical activation is that lattice deformation happens during their mechanical activation. The effects of mechanical activation are apparent. For sulfide ores with high toughness, good thermal stability and very excellent complete cleavage plane, the mechanism of mechanical activation is that lattice deformation happens during their mechanical activation, but the lattice deformation ratio is very small. The effects of mechanical activation are worst.

Key words: sulfide ore; mechanism; mechanical activation; structural change

1 Introduction

The use of mechanical activation as a means of accelerating leaching is not new. GERLACH and GOCK [1] granted a German patent in 1973, which included the application of mechanical activation to sulphide ores. BALAZ and EBERT[2] referenced five studies, dated from 1977 to 1987, which demonstrated this effect on the leaching of zinc from sphalerite. MAURICE and HAWK[3] investigated ferric chloride leaching of mechanically activated chalcopyrite. Ultrafine grinding of chalcopyrite increases its reactivity so that less severe leaching conditions are required to recover the copper[4−5]. In the past 10 years, much focused effort has been made to quantify the enhancement due to

mechanical activation[6−8]. Thus the term 'mechanical activation' refers to mechanically induced enhancement of the chemical reactivity of a system[9], which is attributed to increased specific surface area, enhanced surface reactivity, and changes in crystalline structure.

Whereas, according to our previous research work [10−11], mechanical activation can effectively intensify hydrometallurgical processes of predominant sulfide ores that are difficult to be leached, but can't apparently enhance hydrometallurgical processes for some sulfide ores, such as molybdenite. Nowadays, most research works just describe experimental phenomena to single mineral, and no suitable theory can forecast the effect of mechanical activation. Therefore, it is necessary to find the general rules in order to predict the mechanisms and the effects of mechanical activation for different sulfide

ores.

In this paper, structural changes for mechanically activated pyrite, sphalerite, galena and molybdenite were studied. Based on the structural changes for mechanically activated sulfide ores and related reports by other researchers, several qualitative rules of the mechanisms and the effects of mechanical activation for sulfide ores are obtained.

2 Experimental

2.1 Materials

Natural pyrite ore was purchased from a domestic geological museum. Naturally pure hand-sorted galena, sphalerite and molybdenite ores were purchased from a domestic mine, and their chemical compositions are presented in Tables 1−4. It was found by X-ray diffraction analysis that the natural pyrite, sphalerite and galena contained cubic pyrite, cubic sphalerite and cubic galena as a predominant component, respectively. And the natural molybdenite contained hexagonal molybdenite as a predominant component. The natural molybdenite was floated with about 5×10^{-5} xanthate as a floatation reagent. 40 g floated molybdenite and 200 mL CCl_4 were added into a 250 mL flask, refluxed for 72 h, and then filtrated to leave xanthate in the filtrate and obtain a filter residue. The filter residue was dried at 80 ℃ in vacuum to yield unactivated molybdenite. The unactivated pyrite or sphalerite or galena was prepared by crushing respective ores in a jaw crusher to a certain particle size, then stored in air for more than 1 year, sieved to obtain above 1 mm pyrite or sphalerite or galena.

2.2 Mechanical activation

The unactivated sulfide ore (weighed charge in mill 10 g) was added into a stainless steel vessel with 6 stainless steel balls of 18 mm in diameter and 12 balls of 8 mm in diameter. A vacuum with residue pressure $\leqslant 1$ Pa was then pulled on the vessel followed by gassing highly pure nitrogen (99.999%, volume fraction) (abbreviated as nitrogen) through an inlet of this vessel for 1.5 h (the ore was considered being kept under inert atmosphere). Or this vessel was filled with laboratory air, then two inlets of this vessel were sealed (the ore was kept under less air). Or two inlets of this vessel were open (the ore was exposed to air). And then the sulphide ores were mechanically activated in a planetary ball mill (QM-ISP Planetary mill, China) under a rotation speed of 200 r/min. A powder-to-ball mass ratio of 1:25 was employed. Mechanically activated sulfide ores were obtained after grinding for t_G=20, 40, 120, 180, 260, 480 min, respectively.

2.3 Aging experiments

Pyrite, sphalerite and galena mechanically activated in nitrogen for 20 or 120 min were exposed to air for 3 months or 6 months, to obtain mechanically activated pyrite, sphalerite and galena aged in air, respectively.

2.4 Physico-chemical characteristics

X-ray powder diffraction analysis(XRD) for the milled powders was recorded on a 3014 diffractometer (Rigaku, Japan) using Cu K$_\alpha$ radiation (λ=1.54 Å, voltage 40 kV, current 20 mA) with step size of 0.03˚. The recorded XRD spectra were used for calculation of the degree of structural disorder. The lattice deformation ratio(ε) (presented as a percentage) and the crystallite size(D) were determined from the changes in profile of the diffraction peaks, such as (220) and (551) planes of pyrite, (111) and (331) planes of sphalerite, (200) and (400) planes of galena, (002) and (008) planes of molybdenite. The lattice deformation ratio(ε) and the crystallite size(D) can be calculated using Gaussian

Table 1 Chemical composition of natural pyrite (mass fraction, %)

Fe	S	Si	Ca	Sn	Sb	As	Zn	Co	Ni
45.63	53.28	0.1	0.01	0.01	0.01	0.03	0.05	0.005	0.001

Table 2 Chemical composition of natural sphalerite (mass fraction, %)

Zn	S	Fe	Pb	Cd	Sb	Bi	In
61.39	32.11	2.38	1.92	0.28	0.05	0.01	0.03

Table 3 Chemical composition of natural galena (mass fraction, %)

Pb	Zn	S	Fe	Cd	Sb	Bi	In
61.10	14.17	18.08	2.56	0.28	0.05	0.01	0.03

Table 4 Chemical composition of natural molybdenite (mass fraction, %)

Mo	S	Al	Mn	Si	Mg	Pb	Sn	Cr	Fe	W
41.92	31.88	0.035	0.003	3.1	0.003	0.003	0.005	0.05	0.15	0.015

function[12].

X-ray photoelectron spectra were obtained with a KRATOS XSAM800 X-ray photoelectron spectrometer, with a monochromatized Mg K$_\alpha$ X-ray source. The operating pressure in the analyzer chamber was $\leqslant 2 \times 10^{-7}$ Pa. The surface charge was measured relative to uncharged graphite C 1s at 284.6 eV.

The specific granulometric surface areas(S_G) of mechanically activated sulfide ores were calculated statistically from the corresponding particle size distribution data measured on a Mastersizer 2000 Laser Diffraction Particle Size Analyzer (Malvern, Great Britain). For pyrite, sphalerite and galena, distilled water was used as a dispersing agent. For molybdenite, ethyl alcohol (95%, volume fraction) was used as a dispersing agent.

The elemental sulphur contents of unactivated and mechanically activated sulfide ores were determined by using gravimetric method. And a typical operation was performed as follows. 2.0 g mechanically activated pyrite and 20 mL CCl$_4$ were added into a 50 mL flask, refluxed for 72 h, and finally filtered. CCl$_4$ was then evaporated at ambient temperature to yield elemental sulphur, which was then weighed to determine the elemental sulphur content.

The morphology analysis of unactivated or mechanically activated sulfide ores was performed using JSM-5600LV Scanning Electron Microscopy (JEOL, Japan).

3 Results and discussion

3.1 Structural changes of sulfide ores mechanically activated under different grinding atmospheres

The specific surface areas (S_G) of pyrite, sphalerite and galena mechanically activated under nitrogen increase with increasing grinding time, and remain constant after a certain grinding period[13−14]. This shows that the increase of S_G isn't a major factor for the enhancement of the hydrometallurgical process of mechanically activated sulphide ores. However, the specific surface areas (S_G) of molybdenite mechanically activated under nitrogen increase with increasing grinding time(Fig.1), which indicates that the mechanism of mechanical activation of molybdenite is quite different from that of other sulfide ores.

XRD patterns of pyrites, galena and sphalerite mechanically activated under different atmospheres for 120 min show that new phases can't be found[13−14].

S 2p XPS and Zn 2p XPS spectra of mechanically activated sphalerites, S 2p XPS and Fe 2p XPS spectra of mechanically activated pyrites, Pb 4f XPS and S 2p XPS

spectra of mechanically activated galena are shown in Figs.2−7.

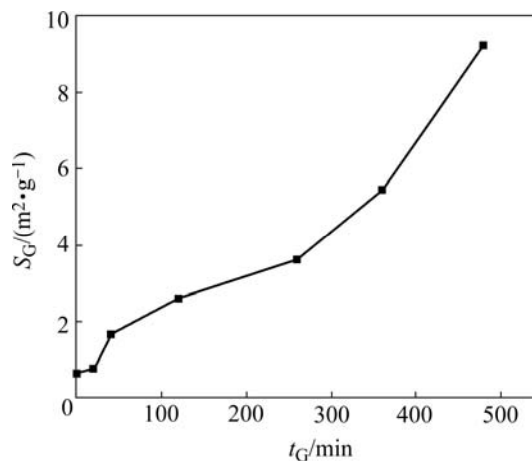Figs.2−7 show that S 2p and Zn 2p XPS spectra of mechanically activated sphalerite, Fe 2p XPS spectra of

Fig.1 Specific granulometric surface area S_G of mechanically activated molybdenites vs grinding time
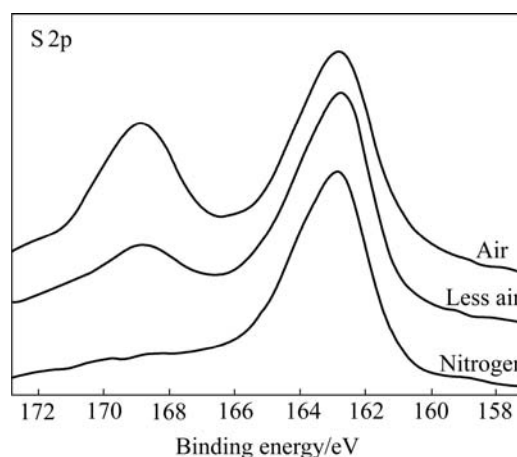

Fig.2 S 2p XPS spectra of pyrite mechanically activated under different grinding atmospheres for 120 min
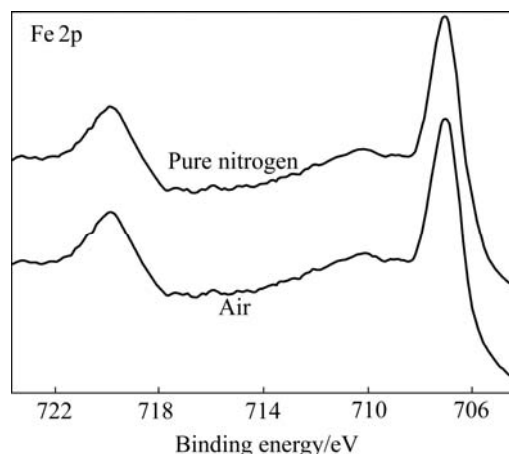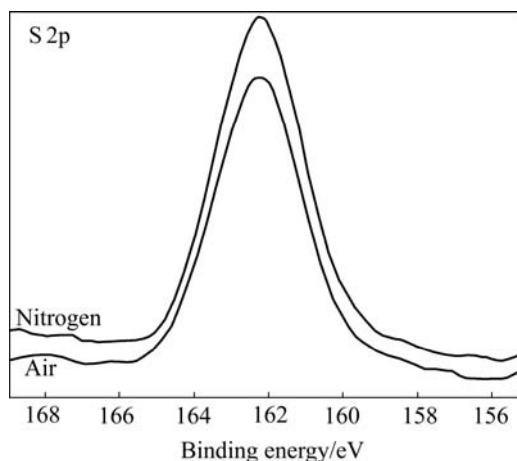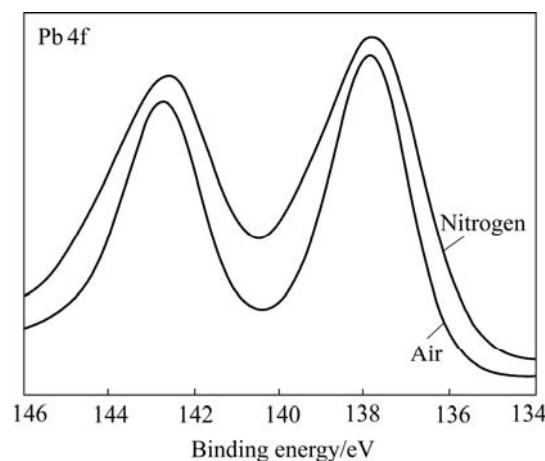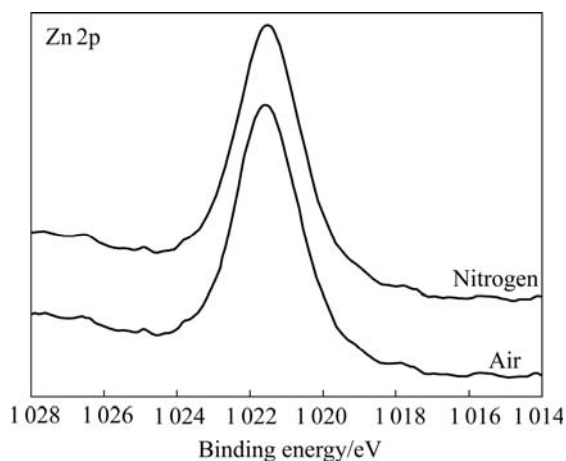

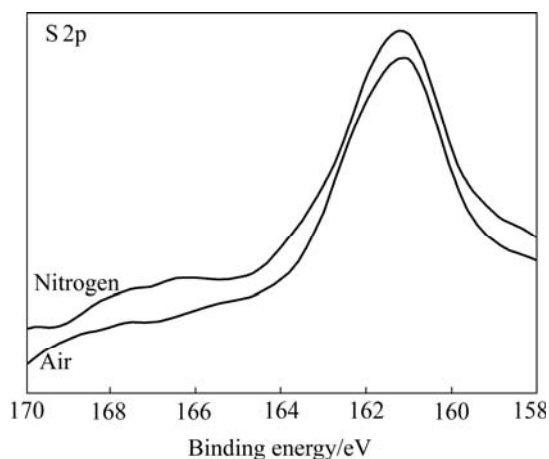**Fig.3** Fe 2p XPS spectra of pyrite mechanically activated under different grinding atmospheres for 120 min

Fig.4 S 2p XPS spectra of sphalerite mechanically activated under different grinding atmospheres for 120 min

Fig.5 Zn 2p XPS spectra of sphalerite mechanically activated under different grinding atmospheres for 120 min

Fig.6 S 2p XPS spectra of galena mechanically activated under different grinding atmospheres for 120 min

mechanically activated pyrite, Pb 4f XPS and S 2p XPS spectra of mechanically activated galena don't change, while the S 2p XPS spectra of mechanically activated pyrites are changed with grinding atmosphere. The significant differences in both shape and binding energy

Fig.7 Pb 4f XPS spectra of galena mechanically activated under different grinding atmospheres for 120min

of the S 2p XPS spectra of pyrite (Fig.2) show that one new S 2p peak occurs in the range from 168 eV to 170 eV for pyrite mechanically activated under air or less air. The corresponding S 2p binding energies at 163.2 eV and 169.3 eV are for pyrite S_2^{2-} species[15] and S^{6+} species of SO_4^{2-} [16], respectively, which shows that the relative content of the newly formed $FeSO_4$ for mechanically activated pyrite increases in a sequence of grinding atmosphere of pure nitrogen, less air and air. EYMERY and YLLI[17] investigated a structural transformation in pyrite mechanically activated under air for 3 h and 60 h using X-ray diffraction analysis(XRD) and ^{57}Fe Mössbauer spectroscopy and a newly formed $FeSO_4$ was also found. TAKAJI et al[18] studied the excellent complete cleavage plane (0001) of molybdenite using scanning Auger microscope, and the result showed that the excellent complete cleavage plane (0001) of molybdenite cannot absorb oxygen, which is the reason why molybdenite can be a lubricant for high vacuum pump[19].

The lattice deformation ratio(ε) and the crystallite size(D) of mechanically activated sulfide ores are listed in Table 5. Table 5 shows that lattice deformation ratio increases with increasing grinding time, and the lattice deformation ratios(ε) of mechanically activated pyrite, sphalerite, galena and molybdenite are 0.07%, 1.15%, 0.47% and 0.04% at t_G=260 min, respectively.

Almost no elemental sulfur is produced when sphalerite and molybdenite are mechanically activated under nitrogen. The contents of the elemental sulphur for pyrite and galena mechanically activated under nitrogen are listed in Tables 6 and 7, respectively. The contents of the elemental sulphur for mechanically activated pyrite are larger than those for mechanically activated galena. The formation of elemental sulfur during mechanical activation results in the formation of reactive sites on the surface of mechanically activated sulfide ores. Therefore, it's easier for pyrite to form reactive sites than galena

Table 5 Relationship between D, ε of different sulphide ores and grinding time t_G

t_G/min	Molybdenite		Pyrite[14]		Sphalerite[15]		Galena[16]	
	D/Å	ε/%	D/Å	ε/%	D/Å	ε/%	D/Å	ε/%
0	935	0	4 032	0	964	0	4 040	0.01
40			675	0.05	472	0.45	670	0.11
120			564	0.06	339	0.92	197	0.25
260	661	0.04	544	0.07	163	1.15	110	0.47
480	268	0.32						

Table 6 Elemental sulphur content of pyrite versus grinding time

t_G/min	0	20	40	120	260
Element sulphur content/mg	0	4.1	8.3	11.1	16.1

Table 7 Elemental sulphur content of galena versus grinding time

t_G/min	0	20	40	120	180	260
Element sulphur content/mg	0	3.4	4.3	6.1	7.3	12.6

during mechanical activation, but it's quite difficult for sphalerite and molybdenite to form reactive sites during mechanical activation.

The morphologies of non-activated and mechanically activated molybdenite, pyrite, sphalerite and galena are shown in Figs.8−11. As shown in Figs.8−11, pyrite, sphalerite and galena are broken into rough particles or rods by grinding for 120 min, but the layered structure of molybdenite is kept after grinding for 120 min. Because pyrite has a plane of incomplete cleavage, sphalerite and galena have planes of complete cleavage[20], it is easier for these sulphide ores to break into small particles or rods. Whereas, molybdenite belongs to a family of layered transition metal dichalcogenides with closedly packed planes of transition metal atoms(M) sandwiched between two similar planes of chalcogen atoms(X) and has very excellent complete cleavage. These X-M-X slabs are weakly bonded by van der Waals forces, while bonding within the X-M-X slabs is mainly covalent and fairly

Fig.8 SEM images for non-activated pyrite (a) and pyrite mechanically activated for 120 min under nitrogen (b)

Fig.9 SEM images for non-activated galena (a) and galena mechanically activated for 120 min under nitrogen (b)
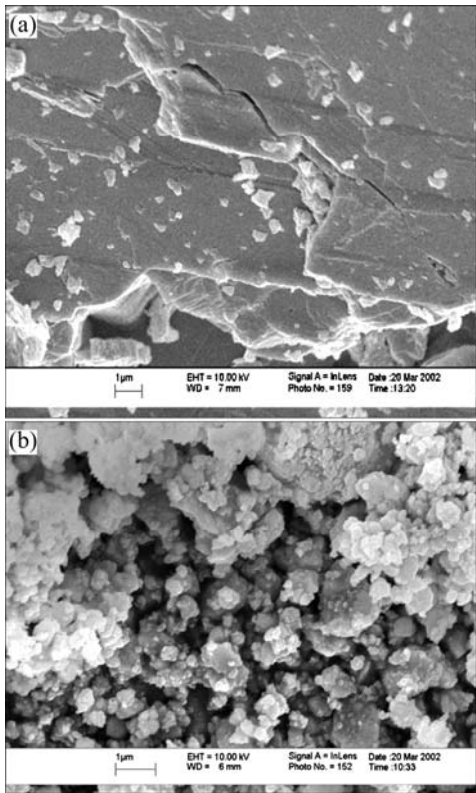
Fig.10 SEM images for non-activated sphalerite (a) and sphalerite mechanically activated for 120 min under nitrogen (b)
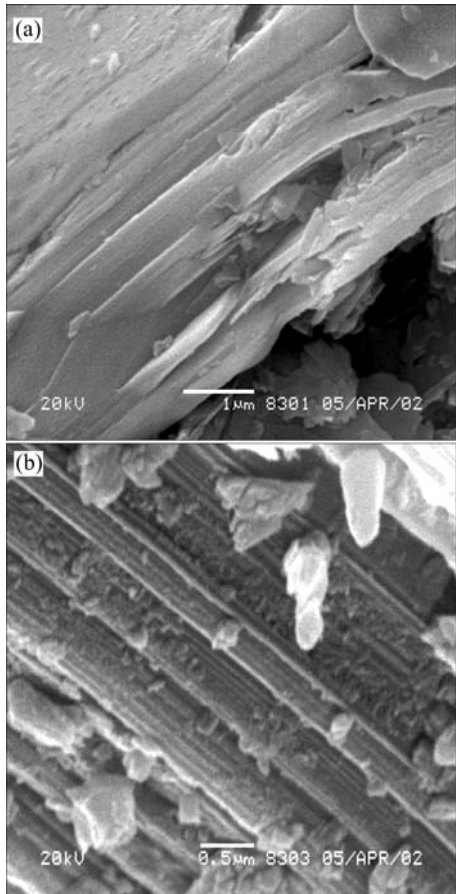

Fig.11 SEM images for non-activated molybdenite (a) and molybdenite mechanically activated for 120 min under nitrogen (b)

strong[21]. When molybdenite is intensively ground, it is easy for molybdenite to slip along the plane of very excellent cleavage.

3.2 Structural changes of mechanically activated sulfide ores after exposure to ambient air

The specific granulometric surface areas(S_G) of pyrite, sphalerite and galena mechanically activated in nitrogen for 120 min, followed by exposure to ambient air, are listed in Table 8.

XRD patterns of pyrites, sphalerite and galena mechanically activated in nitrogen for 20 min or 120 min, followed by exposure to ambient air are shown in Figs.12−14.

Table 8 Relationship of S_G of sulfide ores mechanically activated under nitrogen for 120 min with aging conditions

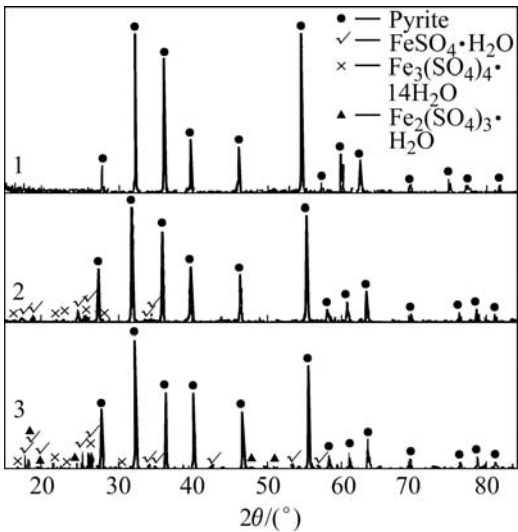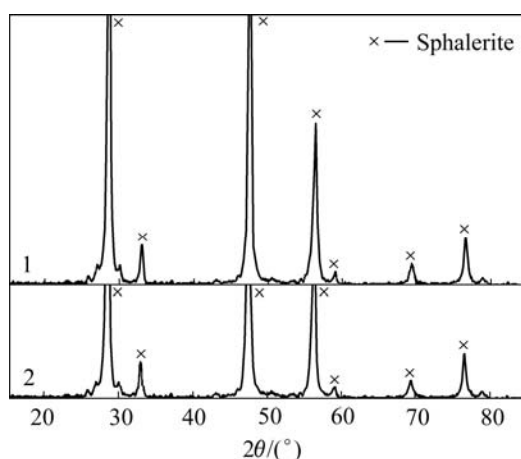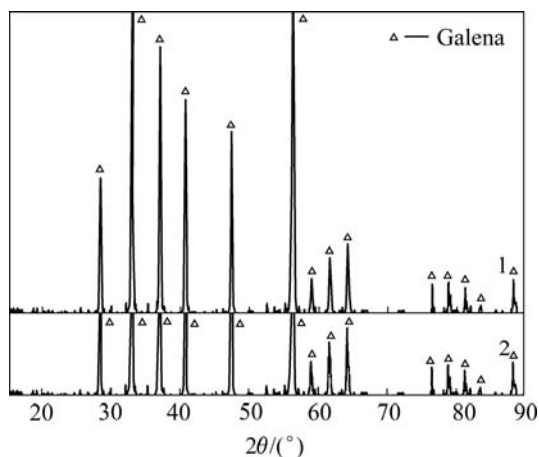| Aging condition	S_G/(m^2·g^{-1})		
	Pyrite	Sphalerite	Galena
Without aging	24.31	7.56	3.26
Exposed to ambient air for 3 months	10.22	6.95	3.09
Exposed to ambient air for 6 months	9.95	6.76	2.95

Fig.12 XRD patterns of pyrite mechanically activated in nitrogen for 20 min, followed by exposure to air at ambient temperature for a certain period: 1 Without aging; 2 Exposed to air for 3 months; 3 Exposed to air for 6 months

XPS spectra of mechanically activated pyrite and galena after exposure to ambient air for different periods are shown in Figs.15 and 16.
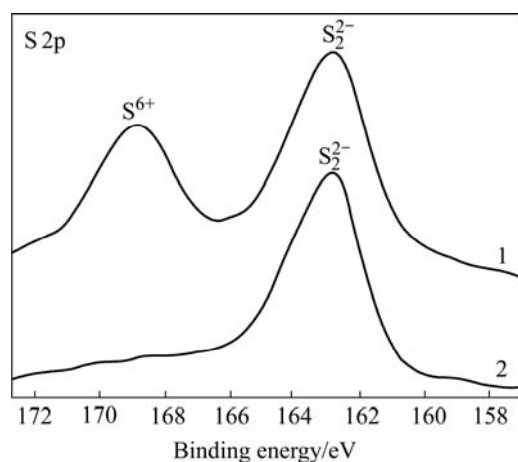
Although no oxidation phenomena are observed during mechanical activation of galena in air and after being aged of mechanically activated sphalerite for 6 months in ambient air, mechanically activated pyrite and galena were partially oxidized after being aged in ambient air for 6 months. The sensitivity to ambient
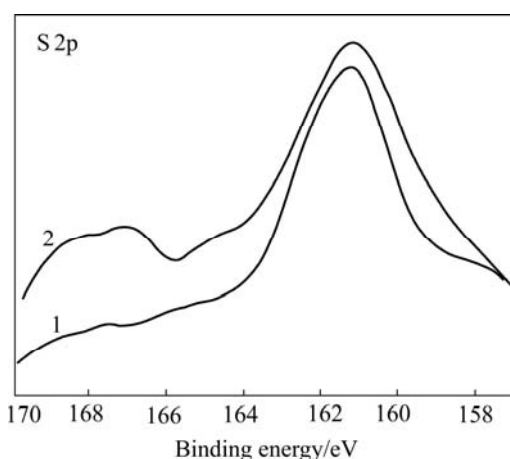
Fig.13 XRD patterns of sphalerite mechanically activated in nitrogen for 120 min, followed by aging under different conditions: 1 Without aging; 2 Exposed to ambient air for 6 months

Fig.14 XRD patterns of galena mechanically activated in nitrogen for 120 min, followed by aging under different conditions: 1 Without aging; 2 Exposed to ambient air for 6 months

Fig.15 S 2p XPS spectra of pyrite mechanically activated in nitrogen for 20 min, followed by aging under different conditions: 1 Exposed to ambient air for 6 months; 2 Without aging

Fig.16 S 2p XPS spectra of galena mechanically activated in nitrogen for 20 min, followed by aging under different conditions: 1 Without aging; 2 Exposed to ambient air for 6 months

aging air increases in the order of sphalerite, galena and pyrite. Therefore, the sensitivity to grinding atmosphere during mechanical activation of sulfide ores increases in the order of sphalerite (and molybdenite), galena and pyrite.

Why is it easier for galena and pyrite to produce elemental sulfur or to absorb oxygen than other sulfide ores during mechanical activation? Why are there differences of lattice deformation ratio among different sulfide ores during mechanical activation? Why are the lattice deformation ratio of mechanically activated pyrite and molybdenite too small? According to our previous research work [10−11], mechanical activation can apparently reinforce the hydrometallurgical process of pyrite, galena and sphalerite, but cannot apparently reinforce the hydrometallurgical process of molybdenite. In order to answer these questions, some explanations will be given below.

Physico-chemical properties of some common sulfide ores[20] are listed in Table 9. Table 9 shows that pyrite has extremely incomplete (100) and (111) cleavages, sphalerite has a complete (110) cleavage, and galena has a complete (100) cleavage. Pyrite has much more bond linkages between two cleavage planes than sphalerite or galena. For molybdenite, no chemical bond linkages exist between two very excellent complete cleavage planes. When these sulfide ores are intensively ground, the amount of reactive sites produced under the same mechanical activation condition decreases in the order of mechanically activated pyrite, mechanically activated sphalerite (and mechanically activated galena), and mechanically activated molybdenite. On the other hand, the elemental sulfur is produced during mechanical activation of pyrite and galena. No elemental sulfur is produced during mechanical activation of sphalerite and

Table 9 Physico-chemical properties of some common sulfide ores[20]

Sulfide ore	Hardness	Thermal stability under inner atmosphere	Cleavage plane
Pyrite	6−6.5 (brittle)	Unstable	Extremely incomplete cleavage planes along (100) and (111) planes
Galena	2−3 (brittle)	Unstable	Complete cleavage plane along (100) plane
Sphalerite	3−4.5 (brittle)	Stable	Complete cleavage plane along (110) plane
Arsenopyrite	5.5−6 (brittle)	Unstable	Incomplete cleavage plane along (101) plane
Chalcopyrite	3−4 (brittle)	Unstable	Incomplete cleavage plane along (112) and (101) planes
Molybdenite	Slice with good flexibility	Stable below 1 350 ℃	Very excellent complete cleavage plane along (0001) plane

molybdenite. Therefore, the overall amount of reactive sites produced under the same mechanical activation condition decreases in the order of mechanically activated pyrite, mechanically activated galena, mechanically activated sphalerite and mechanically activated molybdenite. The more the reactive sites there exist on the surface of mechanically activated sulfide ores, the more sensitive to oxidative grinding atmosphere or ambient aging air the mechanically activated sulfide ores are. That's why it is easier for galena and pyrite to absorb oxygen than other sulfide ores during mechanical activation or exposure to ambient air.

Table 9 shows that pyrite and galena are thermally unstable under inert atmosphere. For molybdenite, it's thermally stable below 1 350℃ under inert atmosphere. For sphalerite, it's thermally stable under inert atmosphere. Our research group also determined the initial thermal decomposition temperatures of sulfide ores under highly pure nitrogen using thermogravimetric method, and the initial thermal decomposition temperature of pyrite (713 K)[22] is lower than that of galena (1 140 K) [14]. No thermal decomposition pheno-mena were observed when sphalerite and molybdenite were heated to 1 100 ℃ under highly pure nitrogen[11]. According to the physical model about mechanical energy transformation reported by other researchers[23], when mechanical energy is transformed into chemical energy during mechanical activation of substances, chemical reaction happens on these "micro-contacting" points where the temperature reaches about 1 300 K. This model can explain why no elemental sulfur is formed during mechanical activation of molybdenite and sphalerite, and more elemental sulfur is produced during mechanical activation of pyrite than that of galena.

There are experimental results reported by other researchers: 1) During mechanical activation of chalcopyrite under inert atmosphere, elemental sulfur was produced; sulfate was produced during grinding under air, which showed that chalcopyrite was sensitive to oxidative grinding atmosphere[24]. 2) During mechanical activation of arsenopyrite under inert atmosphere, a part of arsenopyrite was decomposed into ferrous sulfide and arsenic sulfide, and sulfate salts were produced during

grinding under air, which showed that arsenopyrite was sensitive to oxidative grinding atmosphere[25−26]. 3) Lattice deformation ratios during mechanical activation of these sulfide ores that are thermally unstable were very small[10,27]. And the effects of mechanical activation on the hydrometallurgical behaviors for chalcopyrite and arsenopyrite are apparent[10,27]. From Table 9, chalcopyrite and arsenopyrite have incomplete cleavage plane and thermal instability under inert atmosphere.

Therefore, for brittle sulfide ore with thermal instability and incomplete cleavage plane, the main factor to reinforce its hydrometallurgical process is newly formed reactive sites during mechanical activation. And the effect of mechanical activation on its hydrometallurgical behavior is apparent.

For brittle materials with good thermal stability and complete cleavage plane, such as sphalerite, the smaller the hardness of brittle materials, the bigger the plastic deformation is when these brittle materials are put under external force interaction[28], and the bigger the lattice deformation ratio is.

For brittle materials with thermal instability and complete or incomplete cleavage plane, such as galena and pyrite, when these brittle materials are put under external force interaction, one part of mechanical energy is transformed into chemical energy (for example, thermal decomposition happens during external force interaction), and one part of mechanical energy will lead to lattice deformation of materials. Therefore, for these materials, the more chemical energy the mechanical energy is transformed, the less the lattice deformation ratio is.

For tough materials with very excellent complete cleavage plane and high thermal decomposition temperature under inert atmosphere, such as molybdenite, the cleavage plane is also the slip plane[28]. When molybdenite is intensively ground, it is easy for molybdenite to slip along the plane of very complete cleavage plane, which results in its less lattice deformation and its increase of surface area, but the lattice deformation ratio is very small.

Therefore, if sulfide ores have good thermal

stability and very excellent complete or complete cleavage planes, the mechanism of mechanical activation for these ores is that lattice deformation happens during mechanical activation. And these sulfide ores are insensitive to oxidative grinding atmosphere. But the effect of mechanical activation on its hydrometallurgical behavior is not apparent.

4 Conclusions

1) For brittle sulfide ores with thermal instability, and incomplete cleavage plane or extremely incomplete cleavage plane, the mechanism of mechanical activation is that a great amount of surface reactive sites are formed during their mechanical activation. The effects of mechanical activation are apparent.

2) For brittle sulfide ores with thermal instability and complete cleavage plane, the mechanism of mechanical activation is that a great amount of surface reactive sites are formed, and lattice deformation happens during their mechanical activation. The effects of mechanical activation are apparent.

3) For brittle sulfide ores with excellent thermal stability and complete cleavage plane, the mechanism of mechanical activation is that lattice deformation happens during their mechanical activation. The effects of mechanical activation are apparent.

4) For sulfide ores with high toughness, good thermal stability and very excellent complete cleavage plane, the mechanism of mechanical activation is that lattice deformation happens during their mechanical activation, but the lattice deformation ratio is very small. The effects of mechanical activation are worst.

Acknowledgements

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