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# Mechano-chemical sulfidization of zinc oxide by grinding with sulfur and reductive additives

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**Abstract:** A novel process for sulfidation of ZnO by co-grinding with sulfur and reductive additives (P, Fe, Al, and Mg) was developed. The sulfidation extent of ZnO with the addition of P, Fe, Al or Mg can reach 85.2%, 81.6%, 96.7% and 92.6% after grinding for 4, 6, 1 and 1 h, respectively. Based on the chemical phase composition analysis and morphological characteristics of sulfidized products by XRD, SEM and TEM, a possible reaction mechanism, mechanically induced self-propagating reaction (MSR), was proposed to explain the sulfidization reaction. In addition, the floatability of sulfidized products was investigated for the recovery of metal sulfide and ZnS can be concentrated with a high concentration ratio and concentrate grade. By using the sulfidizing process, it is expected that the recovery of zinc from the wastes or purification of heavy-metal-containing hazardous residues is technically feasible.

Key words: mechano-chemical sulfidization; zinc oxide; reductive additives; self-propagating reaction; flotation

# **1** Introduction

Zinc, as well as other base metals, is mostly extracted from sulfide ores in the world. With the unceasing exploitation of resources in the world, the high-grade sulfide ores are exhausted day by day; and primary sources are insufficient to satisfy the demand. On the other hand, it is reported that 10%-30% of the annual output of nonferrous metals, such as Zn, Pb and Cu, have been abandoned in various types of wastes all over the world [1]. In China, millions tons of smelting slags discharged from Pb/Zn processing and refining industries have been identified as hazardous solid waste according to the national list of dangerous waste of China, which was proposed by the Ministry of Environmental Protection and National Development and Reform Commission of the People's Republic of China in 2008 [2]. The discharge of heavy-metal-containing wastes not only wastes natural resources, but also potentially imposes a negative impact on environment due to the possible release of toxic elements [3]. Therefore, the recycling of heavy metals and elimination of hazardous elements from the wastes are highly desirable from the viewpoints of environmental resource preservation and sustainable development.

Heavy metals in wastes are rarely in sulfide form but rather are oxides and oxidized compounds in addition to the metal itself [4,5]. In the past years, many processes have been tested for the treatment of heavy-metalcontaining wastes and oxidized ores, such as flotation [6–8], gravity separation combined with flotation [9], hydrometallurgy [10–12] and pyrometallurgy [13–15]. However, it is evident that these inherent treatments are characterized by low recovery of lead and zinc and other disadvantages that make the recovery of lead and zinc from the wastes and oxide ores generally uneconomical and unattractive. If a simple and reliable method was

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developed to sulfidize the wastes, the above-mentioned mineral processing methods and metallurgical processes could be applied to treating these synthetic sulfides. Thus, the valuable metal recycling system becomes technologically and economically feasible.

Methods have been reported in sulfidization of metals, such as high-temperature reaction, precipitation from solution using  $H_2S$  and other sulfides [16–18]. However, these methods are accompanied by secondary emission of wastes and the release of toxic gases as well as high energy consumption. Therefore, it is of significant importance to develop a sulfidization method with free pollution and low energy consumption.

Mechano-chemical processing has been widely applied in waste management and synthesis of functional materials including metal alloys and inorganic compounds [19-22]. Mechano-chemical reactions are characterized by the repeated welding and fracture of reacting particles during ball-powder collisions, which continually regenerate reacting interfaces. As a consequence, reactions which would normally require high temperatures to occur due to separation of the reacting phases by the product phases can occur at low temperatures in ball mill [23]. So, in this study, we present a novel method to sulfidize ZnO by co-grinding with sulfur and reductive additives. The solid-state reaction induced by mechanical force resulted in the formation of ZnS without emission of hazardous gases and wastes. The characteristics of products and the mechanism of mechano-chemical sulfidization were discussed. In addition, a conventional flotation test was performed to investigate the floatability of the treated samples.

# 2 Experimental

## 2.1 Materials

All the chemical reagents were of analytical grade and used as-received. Zinc oxide (ZnO), sulfur (S), carbon powder (C), amorphous phosphorus (P), iron powder (Fe), aluminum powder (Al, 40–75  $\mu$ m) and magnesium powder (Mg) were used in mechanochemical sulfidization. Element sulfur was used as the sulfidizer; and C, P, Fe, Al and Mg were employed as reductive additives. Glacial acetic acid (CH<sub>3</sub>COOH), ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) and saturated bromine water (3% Br<sub>2</sub>) were used in measurement of sulfidation extent. Carboxyl methyl cellulose (CMC), copper sulfate (CuSO<sub>4</sub>), butyl xanthate and pine camphor oil were used in flotation test.

#### 2.2 Procedure and apparatus

Zinc oxide was mixed with sulfur and additives at

stoichiometric ratio corresponding to Eqs. (1)–(5), respectively.

 $2ZnO+2S+C=2ZnS+CO_2(g) \tag{1}$ 

$$5ZnO+5S+2P=5ZnS+P_2O_5$$
(2)

$$4ZnO+4S+3Fe=4ZnS+Fe_{3}O_{4}$$
(3)

$$3ZnO+3S+2Al=2ZnS+Al_2O_3 \tag{4}$$

$$ZnO+S+Mg=ZnS+MgO$$
(5)

A planetary ball mill (QM–3SP4, Nanjing, China) was used for grinding of the mixtures. 10 g starting compounds were placed into a stainless steel pot (500 cm<sup>3</sup> inner volume) with 500 g stainless steel balls (9 balls with 20 mm in diameter and the others with 10 mm in diameter) and were subjected to grind in air at 541 r/min for different time. After grinding, the products were solid powders, and the ground samples were collected from the pot.

Then a flotation test was performed through a conventional rougher flotation process (Fig. 1) to investigate the floatability of the as-prepared samples. The mixture of 10 g as-ground samples and 20 g calcium sulfate which were used as a simulation of gangue composition was employed in flotation experiment. Flotation tests were made with laboratory scale flotation machines (XFD-0.25 L). The pulp density was 20% and the pulp temperature was adjusted to 60 °C. The procedures are shown in Fig. 1. After flotation test, the flotation sample (mixtures of as-ground sample and calcium), concentrate and tailing were digested by a mixture of concentrated hydrofluoric acid, perchloric acid and nitric acid at 200 °C, and the digested solution was collected to calculate Zn content of the flotation samples, concentrate and tailing. The flotation efficiency was evaluated on the basis of recovery of Zn, zinc grade of concentrate, zinc grade of tailing and concentration ratio (the grade of concentrate divided by grade of flotation sample).





Fig. 1 Process flow sheet of flotation

#### 2.3 Analysis

The crystallographic composition of the sulfidation products was characterized by X-ray diffraction (XRD, D/max2550 VB+18 kW). The XRD lines were identified by comparing the measure patterns to the JCPDS data cards. Morphological change of the samples during ball milling was observed by a scanning electron microscope (SEM, Nova NanoSEM 230, Chech). Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were performed using JEM2100F microscope operated at optimum defocus with accelerating voltages of 200 kV.

The reaction was also evaluated quantitatively by measuring sulfidation extent based on the chemical phase analysis of the sulfide ore [24,25]. The extent of sulfidation is determined by Eq. (6), where X is the sulfuration extent (%),  $m_{ZnS}$  (%) is the Zn content existing as ZnS in sulfidized products, and  $m_{Zn}$  (%) is the total Zn content in sulfidized products.

$$X = \frac{m_{\rm ZnS}}{m_{\rm Zn}} \times 100\% \tag{6}$$

### **3** Results and discussion

#### 3.1 Mechanochemical sulfidization of zinc oxide

The main reason that this study focused only on zinc oxide was that lead oxide (PbO), cadmium oxide (CdO) and metals themselves could be sulfidized by the mechanochemical process after grinding some time. WANG et al [1] proved that when Zn, Pb and Cd were mixed with sulfur at an equimolar ratio and ground for 60 min, ZnS, PbS and CdS were found in the product [1]. In fact, the mechano-chemical reaction offers an easy method to synthesize sulfide materials [26–28]. This suggests that it is quite possible to transform such metals in wastes into sulfides. Moreover, our preliminary experiments confirmed that reaction (7) occurred during grinding (see Fig. 2).

$$4MeO+4S=3MeS+MeSO_4(Me=Pb, Cd)$$
(7)

When PbO and CdO were mixed with sulfur at the stoichiometric ratio according to Eq. (7) and ground for 5 h and 60 h, respectively, PbS and CdS were detected in products (Fig. 2). However, when the ZnO was ground with sulfur for 60 h, sulfidizing reaction was not observed yet. Thermodynamic calculations reveal that the Gibbs free energy change of reaction between ZnO and S is  $\Delta G$ =-186.559 kJ/mol at 25 °C [29], which shows that the reaction is favorable thermodynamically. So it is the dynamical condition that restricts the occurrence of this reaction. However, method of transforming oxides into sulfide is of vital importance in the sulfidizing-flotation treatment of residues containing



Fig. 2 XRD patterns of ZnO (PbO, CdO) ground with sulfur

heavy metals. Our further research shows that it requires additives, functioning as a reductant to the ZnO. So, the reductants such as C, P, Fe, Al and Mg, were considered in this study.

3.1.1 System of ZnO-S-C

Figure 3 shows the XRD patterns and the sulfidation extent of a ZnO–S–C mixture ground for different time. As shown in Fig. 3(a), only the peaks of S and ZnO were observed throughout the process and the peaks decreased



**Fig. 3** XRD patterns (a) and sulfidation extent (b) of ZnO–S–C mixture ground for different time

in intensity and broadened somewhat with the increase of milling time. It can also be found that there was no significant increase in the sulfidation extent of the ZnO–S–C mixture after 1–16 h grinding (see Fig. 3(b)). The sulfidation extent was only 12.3% after 16 h. There was no observable appearance of ZnS phases in the XRD patterns because the minor ZnS phase might exist as amorphous state after 16 h ball-milling. Therefore, it can be concluded that it is difficult to enforce the sulfidization of ZnO with C as additive.

#### 3.1.2 System of ZnO–S–P

Figure 4 shows the XRD patterns and the sulfidation extent of a ZnO–S–P mixture at different time. Figure 4(a) shows only the starting materials were observed in the sample after grinding for 0.5 h. When the grinding time increased to 1 h, the peaks corresponding to ZnS were detected and the peaks associated with ZnO almost disappeared, indicating that amorphization of ZnO might occur or most of the ZnO was transformed into ZnS. With the increase of grinding time, the peaks corresponding to ZnS decreased in intensity and broadened somewhat, suggesting that ZnS crystal might take place with grain size reduction and crystal dislocation or defects. Phosphorus and its compounds



**Fig. 4** XRD patterns (a) and sulfidation extent (b) of ZnO–S–P mixture ground for different time

were not detected through XRD because amorphous phosphorus was used in original material and the generated phosphorus oxide might exist as amorphous state.

Figure 4(b) shows that the sulfidation extent of the ZnO–S–P mixture increased dramatically when milling time increased from 0.5 h to 1 h; thereafter, the sulfidation extent then increased slowly and did not reach 91.8% until 8 h grinding. The results imply that sulfidization reaction occurred rapidly and propagated to most areas of the system; and with the increase of milling time the reaction proceeded in unreacted area. 3.1.3 System of ZnO–S–Fe

Figure 5 shows the XRD patterns and sulfidation extent of a ZnO–S–Fe mixture ground for different reaction time. As indicated in Fig. 5(a), no ZnS peak was observed in the initial 2 h, implying that the sulfidation reaction barely occurred during that period. When the grinding time increased to 4 h, new peaks corresponding to ZnS and Fe<sub>3</sub>O<sub>4</sub> were found, although the peaks concerning ZnO and Fe were still observed. Comparing the peaks corresponding to ZnS after grinding for 4, 6 and 8 h, it is found that with the increase of milling time, significant line broadening of the peaks occurred, which suggested dramatic grain size reduction. According to the



**Fig. 5** XRD patterns (a) and sulfidation extent (b) of ZnO–S–Fe mixture ground for different time

XRD patterns, it is supposed that the reaction of Eq. (3) had been carried out mechano-chemically.

Figure 5(b) shows that the sulfidation extent of the ZnO–S–Fe mixture gradually increased with the increase of milling time. When the sample was ground for less than 2 h, the sulfidation extent maintained at a lower level of about 36%. Subsequently, the sulfidation extent increased to above 80% when the milling time was longer than 6 h. The results indicate that sulfidization reaction of this system took place in some parts initially and then gradually diffused to other parts.

#### 3.1.4 System of ZnO–S–Al

Figure 6 shows the XRD patterns and sulfidation extent of a ZnO–S–Al mixture ground for different time. It is clearly evident from Fig. 6(a) that ZnS and  $Al_2O_3$ were generated after 1 h of milling and the peaks associated with ZnO, S and Al disappeared, indicating that sulfidization reaction was induced by mechanical force in a short time. With the increase of grinding time, the peaks corresponding to ZnS and  $Al_2O_3$  decreased in intensity and broadened significantly, owing to the continuous reduction in the particle size and accumulation of lattice strain with increasing milling time. After 8 h of milling, the peaks of  $Al_2O_3$  disappeared, indicating that it was converted into amorphous structure.



**Fig. 6** XRD patterns (a) and sulfidation extent (b) of ZnO–S–Al mixture ground for different time

The appearance of FeS and Fe reflection in the XRD patterns might be attributed to the following reasons: 1) the tremendous reaction heat from reaction of Eq. (4) enhanced the reaction between irons (from external layer of the steel balls) and sulfur, leading to the formation of FeS; 2) the steel balls were weaned down and Fe entered into the products.

Figure 6(b) shows that the sulfidation extent of ZnO–S–Al system increased dramatically to 97.0% when milling time increased from 0.5 h to 1 h, and then it maintained stable with the increase of milling time. The results indicate that sulfidization reaction took place at a certain moment between 0.5 h and 1 h, almost instantaneously, and then rapidly propagated to the whole system, which was also illustrated by the XRD patterns.

#### 3.1.5 System of ZnO–S–Mg

Figure 7 shows the XRD patterns and sulfidation extent of a ZnO–S–Mg mixture at different grinding time. It can be seen from Fig. 7(a) that the peaks corresponding to ZnS and MgO were predominant when the milling time surpassed 1 h and no other phases were detected in sample ground for 1 h and 2 h, implying that the sulfidization reaction induced by mechanical force took place in a short time. After milling for 4 h, new



**Fig.** 7 XRD patterns (a) and sulfidation extent (b) of ZnO–S–Mg mixture ground for different time

peaks corresponding to Fe were observed, which could ascribe to the attrition of steel ball. With the increase of grinding time, the peaks corresponding to ZnS and MgO decreased in intensity and broadened significantly because of the continuous reduction in the particle size and accumulation of lattice strain.

Figure 7(b) shows that the sulfidation extent of ZnO–S–Mg system possessed the similar trend with the ZnO–S–Al system and sulfidation extent can reach over 90%. With the increase of milling time, the slight decrease in sulfidation extent of ZnO–S–Al and ZnO–S–Mg systems is mainly attributed to the adhesion and agglomeration of ZnS on the surface of pot and balls.

#### 3.2 Mechano-chemical sulfidization mechanism

On the basis of XRD patterns and results of sulfidation extent measurement, a possible reaction mechanism, mechanically induced self-propagating reaction (MSR), is proposed to explain the sulfidization reaction. Ball milling induced chemical reactions and alloving have been the subjects of numerous investigations. In particular, displacement reaction between a metal compound (oxide, halid and/or chalcogenide) and a reducing metal (most frequently aluminum) has attracted significant interest for synthesis of sulfide materials [19,23,30]. Generally, MSR is observed in highly exothermic reactions [31]. It is commonly accepted that an exothermic reaction would not become self-sustaining unless  $\Delta H/C > 2000$  K ( $\Delta H/C$ is the enthalpy of reaction divided by the room temperature heat capacity for reaction). However, if  $\Delta H/C > 1300$  K in some metal-oxides systems, MSR can also be ignited [21,32].

Table 1 shows the thermodynamic calculations results of sulfidization reaction [29]. Thermodynamic calculations reveal that the Gibbs free energy changes  $(\Delta G_{298})$  of all the reactions are negative, which shows that the reactions are favorable and ZnS can be produced in theory. However, the thermodynamic condition, the negative changes in  $\Delta G_{298}$ , was found to be necessary but not sufficient, which can be also demonstrated by the experiment results of ZnO-S system and ZnO-S-C system. As for the MSR,  $\Delta H/C$  is a more effective thermodynamic criterion over  $\Delta G_{298}$ . And  $\Delta H/C>1300$  K can be used as a necessary criterion. It can be seen that  $\Delta H/C$  of the reactions, except for ZnO-S and ZnO-S-C systems, is higher than the critical value of 1300 K. Therefore, the initiation of MSR is anticipated when ball milling process is carried out on a stoichiometric mixture of ZnO, S and additives such as P, Fe, Al and Mg, which is consistent with the experimental results. The sulfidization reaction of ZnO-S and ZnO-S-C systems cannot take place and the corresponding  $\Delta H/C$  value is lower than 1300 K, indicating it is reasonable to use

MSR to explain the mechanochemical sulfidization mechanism.

 
 Table 1
 Thermodynamic calculations results of mechanochemical sulfidization reaction

No.	Reaction	$\Delta G_{298}^{\Theta} / (\text{kJ} \cdot \text{mol}^{-1})$	$(\Delta H/C)/K$
1	2ZnO+2S+C==2ZnS+CO <sub>2</sub> (g)	-150.622	765
2	5ZnO+5S+2P==5ZnS+P <sub>2</sub> O <sub>5</sub>	-752.787	2280
3	4ZnO+4S+3Fe=4ZnS+Fe <sub>3</sub> O <sub>4</sub>	-527.796	1585
4	3ZnO+3S+2Al=3ZnS+Al <sub>2</sub> O <sub>3</sub>	-1216.709	5749
5	ZnO+S+Mg=ZnS+MgO	-447.498	5473
6	4ZnO+4S==3ZnS+ZnSO <sub>4</sub>	-186.559	737
7	4PbO+4S=3PbS+PbSO <sub>4</sub>	-354.953	1382
8	4CdO+4S=3CdS+CdSO <sub>4</sub>	-343.315	1426
9	Zn+S=ZnS	-198.516	4436
10	Pb+S=PbS	-97.774	2009
11	Cd+S=CdS	-145.915	3155

Figure 8 shows the morphology changes of ZnO-S-Al mixture under different milling time. It can be seen from the SEM images that the ZnO-S-Al mixture underwent pulverization, amorphization, and agglomeration and grain refinement under the mechanical force in the process of sulfidation reaction. Combined the SEM images with XRD patterns, it is easily found that each of the reactions had an activation period, during which size reduction and mixing took place, but very little product was formed. And this corresponds with the models of MSR which was proposed by Schaffer and McCormick [31]. The model shows that MSR consists of three steps. The first stage is the activation period, which is characterized by the occurrence of size reduction and mixing as well as the formation of chemically active sites. Generally, very little product is formed in this period. By the end of the activation period, the powder reaches a critical state. The second stage is ignition, which takes place when the particle size decreases, reactants mix on an increasing fine scale, chemically active defect sites form, newly created dislocations and interfaces provide fast diffusion pathway, etc. After the activation period, ignition occurs rapidly, almost instantaneously, and propagates, which is observed in ZnO-S-P, ZnO-S-Al and ZnO-S-Mg systems. The release of heat results in an abrupt increase of the temperature. The reaction is often incomplete immediately after the self-sustaining process; and continued milling is needed to obtain fully reacted product with uniform structure and properties, which is also displayed by the results of sulfidation extent in the systems of ZnO-S-Fe and ZnO-S-P. The characteristics of these mechano-chemical sulfidization



Fig. 8 SEM images of ZnO-S-Al powders milled for different time: (a) 0.5 h; (b) 1 h; (c) 2 h; (d) 4 h

provide further evidence that the mechanism of sulfidization reaction is mechanically induced self-propagating reaction.

In addition, the heat of vaporization of sulfur is about 1.717 kJ/mol, which is much smaller than that released from the reaction. So sulfur powder volatilized easily during MSR, and sulfur was observed to be adhered to the internal surface of the pot's lid. This is the possible reason why the sulfidation extent cannot approach to 100%. Therefore, additional S powder is needed to obtain the highest sulfidation extent.

#### **3.3 Floatability**

Recently, sulfidizing-flotation treatment has received attention as a possible means of heavy metal recovery [6,18,24]. Therefore, the floatability of sulfidized products should be discussed. The floatability of mineral is influenced by many physical and chemical factors such as surface roughness, heterogeneity, particle shape and size [33-35]. In order to investigate the effect of morphology on the floatability of as-ground samples, typical bright-field TEM image, selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) image of the ZnO-S-Al ground for 1 h are shown in Fig. 9. Figure 9(a) reveals the irregular shape of ZnS crystal with the diameter ranging from 200 to 300 nm. The amorphous ZnS crystal consists of hundreds of



**Fig. 9** TEM image and SAED pattern (a) and HRTEM image (b) of ZnO–S–Al ground for 1 h

nanometer particles. The SAED pattern in Fig. 10(a) shows the distinct electron diffraction ring of ZnS crystal with diffraction spot, which identified that the sulfidation

product was polycrystalline ZnS phase. The HRTEM image in Fig. 10(b) confirmed that ZnS crystals were surrounded by amorphous phase film with thickness of 2–3 nm. The irregular curved lattice plane fringes observed revealed that the ZnS particles contained some ZnS crystal with a lower crystallinity.



**Fig. 10** Results of flotation test for different samples: (a) Grade or zinc recovery; (b) Concentration ratio

The flotation test was preformed by using ZnO-S-P mixture ground for 6 h, ZnO-S-Fe mixture ground for 6 h, ZnO-S-Al mixture ground for 1 h and ZnO-S-Mg mixture ground for 1 h, respectively. The zinc grade of concentrate, zinc grade of tailing, recovery of zinc and concentration ratio were investigated and the results are shown in Fig. 10. It can be seen that concentration ratio of ZnO-S-Fe, ZnO-S-Al and ZnO-S-Mg systems were above 2.5 and the concentrate grade was obtained with 36.4%, 39.2% and 34.6% of Zn for ZnO-S-Fe, ZnO-S-Al and ZnO-S-Mg systems, respectively, indicating that zinc could be concentrated effectively. The grade and concentration ratio of the ZnO-S-P system were lower than other systems. It is because that the as-ground ZnO-S-P mixture contains P<sub>2</sub>O<sub>5</sub>, which would lead to acidic pulp environment. Generally, the flotation of sulfide ores is preformed at alkaline conditions [36,37]. So, it is unfit for the flotation of ZnS under this acidic condition. The zinc recovery of each sample was lower than 25%, which was attributed to the particular structure and surface properties of ZnS crystal such as irregular shape, polycrystalline phase, amorphous phase film and low crystallinity.

Figure 11 shows the XRD patterns of flotation sample and concentrates of the ZnO-S-Al mixture ground for 1 h. It clearly revealed that before flotation the major phase of flotation sample was CaSO<sub>4</sub> with minor ZnS. While after flotation the peak intensity of CaSO<sub>4</sub> decreased and the peak intensity of ZnS increased, which indicates that zinc is concentrated. This is consistent with the flotation results. Therefore, it can be concluded that in some ways ZnS can be concentrated by flotation from the as-ground samples and it is hopeful to improve the recovery by adopting the closed circuit flotation flowsheet of single-stage roughing, two-stage scavenging and three-stage cleaning. Moreover, after adding the additives, the ball milling time is immensely shortened and the damage of the surface structure of ZnS crystal from ball mill is greatly reduced, which would have a salutary effect on the flotation recovery.



Fig. 11 XRD patterns of original sample and concentrate after flotation

In general, a novel zinc recycling process has been developed: wastes containing heavy metal zinc (in oxide or metal form) can be treated by grinding with sulfur and reductive additives such as P, Fe, Al and Mg, and ZnS can be recycled by utilizing a flotation separation. The major concern focuses on the cost of the sulfidization technology. However, a large quantity of wastes containing high iron and aluminum content are discharged every year; thus, it is feasible to use these wastes as the reductive additives for practical application of this process. It is also potential and feasible to treat the neutralized sludge containing heavy metals such as Pb, Cu and Cd. Additionally, if the environmental benefit and ecological benefit are taken into consideration, this process would have a much brighter application prospect in the future for treatment of heavy metals containing hazardous residues. Consequently, based on the results in the present study, Fe and Al are effective and practical additives for the mechanical sulfidization of metallic oxide.

# **4** Conclusions

1) Sulfidization of zinc oxide can be achieved by milling ZnO with sulfur and reductive additives such as phosphorus, iron, aluminum and magnesium. Without the addition of additives, such sulfidizing reactions are not observed. After adding the additives, the ball milling time is immensely shortened and the damage of the surface structure of ZnS crystal from ball mill is greatly reduced.

2) The sulfidization extent of ZnO with the addition of P, Fe, Al or Mg can reach 85.2%, 81.6%, 96.7% and 92.6% after grinding for 4, 6, 1 and 1 h, respectively. Fe and Al are effective and practical additives for the mechanical sulfidization of metallic oxide.

3) The thermodynamic calculation results of  $\Delta H/C$  and the characteristics of the mechanochemical sulfidization indicate that the sulfidization reaction mechanism of ZnO–S–P, ZnO–S–Fe, ZnO–S–Al, and ZnO–S–Mg systems is mechanically induced self-propagating reaction.

4) The sulfidization products, ZnS, can be concentrated by a conventional rougher flotation process with high concentration ratio and concentrate grade.

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# 氧化锌-硫磺-还原性添加剂混合粉末的 机械化学硫化行为

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**摘 要:**采用高能球磨技术研究氧化锌-硫磺-还原性添加剂(P、Fe、Al、Mg)混合粉末的机械化学硫化行为。该 方法是氧化锌硫化的一种新方法。在添加 P、Fe、Al、Mg 的条件下,经过 4、6、1、1 h 的球磨,ZnO 的硫化率 分别达 85.2%、81.6%、96.7%、92.6%。利用 X 射线衍射(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM) 等分析了球磨样品的化学物相组成变化和形貌特征变化,提出了 ZnO 机械化学硫化的反应机制,即机械力诱发的 自蔓延反应(MSR)。另外,为了实现硫化产物的浮选回收,考察了硫化产物的可浮性。结果表明,机械硫化产物 中的 ZnS 能够通过浮选而高效富集。通过采用该硫化技术,有望实现废渣中锌的回收和重金属危险废物的净化解 毒。

关键词:机械化学硫化;氧化锌;还原性添加剂;自蔓延反应;浮选

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