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Study on the surface sulfidization behavior of smithsonite at high temperature

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ABSTRACT

Surface sulfidization behavior of smithsonite at high temperature was investigated by X-ray powder diffractometer (XRD) along with thermodynamic calculation, X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA). The XRD and thermodynamic analyses indicated that the smithsonite was decomposed into zincite at high temperatures. After introducing a small amount of pyrite, artificial sulfides were formed at surface of the obtained zincite. The XPS analyses revealed that the sulfide species including zinc sulfide and zinc disulfide were generated at the zincite surface. The EPMA analyses demonstrated that the film of sulfides was unevenly distributed at the zincite surface. The average concentration of elemental sulfur at the sample surface increased with increasing of pyrite dosage. A suitable mole ratio of FeS_2 to $ZnCO_3$ for the surface thermal modification was determined to be about 0.3. These findings can provide theoretical support for improving the process during which the zinc recovery from refractory zinc oxide ores is achieved by xanthate flotation.

1. Introduction

Smithsonite containing nearly 52% Zn is a typical zinc oxide mineral. With continuous exploitation of resources, the existing sulfide resources are soon going to be insufficient to supply the demand. The low-grade zinc oxide ores have been developed to offer the above metals and this needs to process the ores to obtain a marketable product [1,2]. In the past years, many technologies such as flotation, hydrometallurgy and pyrometallurgy have been tested for treating the refractory ores, among which flotation is the most commonly used method for pretreatment of zinc oxide minerals.

Flotation of zinc oxide mineral is more difficult than that of the corresponding sulfide minerals due to its higher solubility and more extensive surface hydration [3,4]. In the literature available, it was found that the flotation with amine as collectors and Na_2S as modifier is of wide use for zinc recovery. However, its effectiveness is always unsatisfactory especially when large quantities of slimes exist [5,6]. By contrast, sulfidization-xanthate flotation method is less sensitive to the slime. After treating with Na_2S at a moderate dosage, the hydrophilicity of the mineral surface decreases because of the presence of the chemisorbed sulfide ion. In the present case, the zinc oxide minerals should be effectively collected by xanthate [7,8]. Factually, their sulfidization are extremely difficult to be achieved, often resulting in ineffective mineral processing [9,10].

In order to improve the sulfidization of zinc oxide mineral, significant amounts of studies have been reported. Wu et al. [11] investigated the solubility and flotation performance of smithsonite under different conditions. It was found that the surface solubility of smithsonite significantly decreases in the presence of ammonium ions, corresponding to its flotation recovery increased by 25%. However, this was only carried out for a pure smithsonite and its effectiveness for the zinc oxide ore with a complex composition was not illustrated. Chai et al. [12] and Wang et al. [13] proposed mechanical-chemical method to transform the zinc oxides to zinc sulfides, but the flotation concentrate exhibited a poor recovery due to fine crystallization nature of the artificial sulfides. Additionally, hydrothermal sulfidization was also proposed to treat the zinc oxide material [14]. However, its further application in practice seems to be difficult.

Recently, sulfidization roasting has received considerable attentions to transform the zinc oxide minerals to sulfides. There are usually two kinds of vulcanizing agents including elemental sulfur and pyrite. Li et al. [15] and Zheng et al. [16] investigated the sulfidization roasting of zinc oxide mineral with elemental sulfur

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as vulcanizing agent. The results indicated that the sulfidization extent of Zn could reach above 90% and a flotation concentrate containing 38.9% Zn was obtained with a recovery of 88.2% [15]. Han et al. [17] found that addition of iron oxides could not only improve the sulfidization reaction between ZnO and elemental sulfur, but also promote the formation and growth of ZnS crystals. Compared with the elemental sulfur, pyrite seems to be potential in practical operation attributed to a low cost and the slow release of sulfur from the crystal lattice, which make the process easier to be controlled. After sulfidization, the zinc recovery can reach 70–75% by conventional flotation technology [18,19].

Generally speaking, the zinc oxide minerals after sulfidization roasting can be easily collected by xanthate. However, the previous studies about sulfidization at high temperatures have been mainly restricted to improvement of sulfidization extent, and information involving surface changes for zinc oxide mineral before and after sulfidization treatment is of severe lack. Factually, the flotation performance of zinc oxide minerals depends on whether a stable sulfide film can be formed at the mineral surface to the greatest extent. Therefore, it is very necessary to comprehensively and specifically investigate their surface sulfidization behavior at high temperatures.

In this study, phase transformation at surface of the smithsonite before and after sulfidization roasting with pyrite was firstly identified by XRD along with thermodynamic calculation. Then, surface composition changes were detected by XPS to interrupt the sulfidization mechanisms at an atomic level. Finally, EPMA was carried out to compare the surface differences of natural sphalerite and smithsonite after surface thermal modification. The objective of this study is to clarify the surface sulfidization behavior of smithsonite at high temperatures and to provide an excellent theory reference for the processing of refractory zinc oxide resources.

2. Materials and methods

2.1. Materials

The smithsonite, pyrite and sphalerite samples used in the experiments were obtained from Yunnan Province in China. All of the samples were crushed and dry ground in an agate torsion mortar. The ground products were sieved using a standard screen to achieve their particle range from −74 to +45 μm. Chemical analyses show that the smithsonite sample contained 49.52% Zn, the pyrite sample contained 44.5% Fe and 51.2% S and the natural sphalerite sample contained 65.3% Zn and 32.8% S, which indicated these samples with high purity. XRD patterns of theses samples are exhibited in Fig. 1 and only their respective crystals are observed. These results further confirmed the obtained samples with high purity.

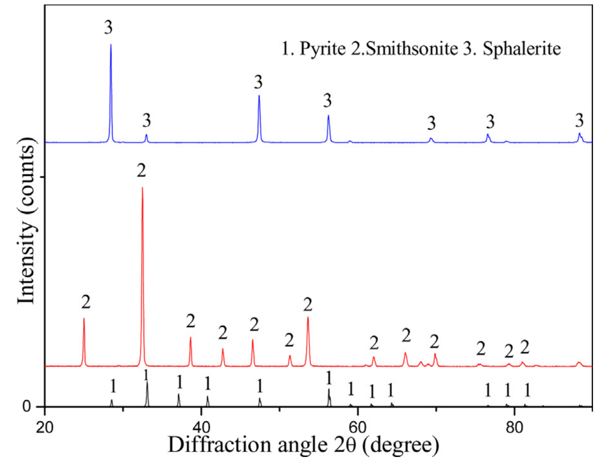

Fig. 1. XRD pattern of the prepared samples.

2.2. Experimental procedure

Roasting of smithsonite with pyrite was conducted under a tube furnace, as shown in Fig. 2, where some parameters such as temperature and time can be exactly preset. Firstly, smithsonite and pyrite were homogeneously mixed in an appropriate mole ratio. The mixture was loaded into a 100 mL quartz tube equipped with a cover. Then, the quartz tube was placed in the furnace while the nitrogen was introduced at a flow rate of 1.5 L/min. Finally, the heating procedure was started up until the desired temperature was obtained. After 60 min of residence time, the roasted sample was cooled under nitrogen, waiting for various analyses. In the literature available, most studies about sulfidization roasting were carried out in the temperature range of 650–750 °C [15,20,21]. Therefore, the medium temperature was determined to be 700 °C in this work.

2.3. Analytical techniques

The obtained samples from the roasting tests were examined on a Germany Bruker-axs D8 Advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). XPS (PHI5000, ULVAC-PHI, Japan) equipped with a monochromatic Al Ka X-ray source at 1486.6 eV were applied to identify the surface components. EPMA (JXA-8230) were used to determine the surface morphology and composition of the obtained sample at different pyrite dosage.

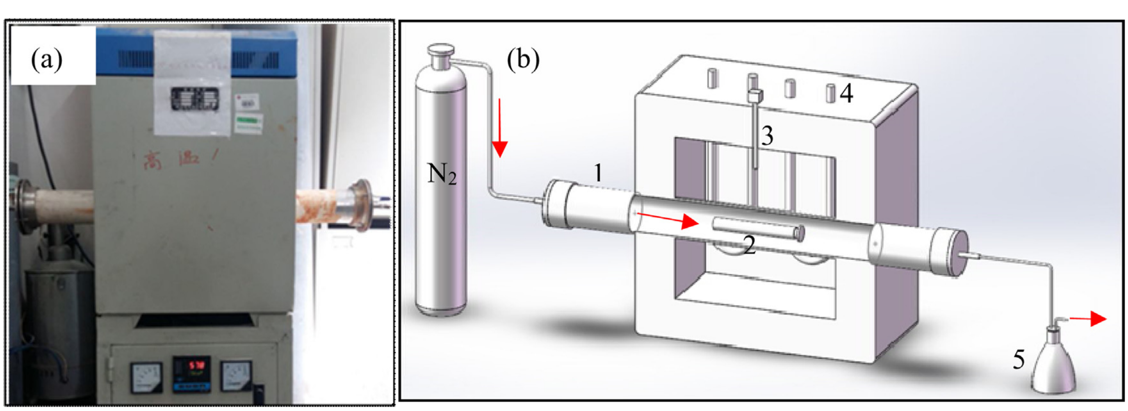

Fig. 2. Photograph (a) and schematic diagram (b) of the sulfidization roasting device (1: alundum tube; 2: quartz tube; 3: thermocouple; 4: rod of Si—C; 5: washing bottle of SO_2 gas).