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Original Research Paper

Mechano-chemical processing and characterization of nano-structured FeS powder

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ABSTRACT

In this paper, preparation of FeS nano-powder by high energy mechanical milling of Fe–S and FeS_2–Fe powder mixtures was studied. Effect of NaCl as a process control agent on the progress of reactions, morphology of particles and magnetic properties was investigated. The structural evolution, morphology and magnetic properties of powders were evaluated using X-ray diffraction, field emission electron microscope and vibrating sample magnetometer. It was found that FeS formed after 15 h and 9 h milling of Fe–S and FeS_2–Fe as starting materials, respectively. Addition of NaCl prolonged the process and changed the combustion reaction mechanism to gradual one in Fe–S mixture. It also reduced the mean particle size to 56 nm. Hysteresis parameter indicated the presence of different magnetic phases where antiferromagnetic phase was the dominant phase.

1. Introduction

Sulfides are currently recognized as inorganic materials with interesting applications. For example, iron sulfide (FeS) are used as advanced inorganic materials with non-conventional applications. Applications of iron sulfide include, high-energy density batteries, precursors for the synthesis of superconductors, solar energy materials, and materials for photoelectrolysis and chalcogenide glasses [1]. In addition, iron sulfide has been suggested as an efficient adsorbent for treating heavy metal contaminated waters [2,3]. Iron sulfides have been synthesized recently by different chemical routes, such as hydrothermal and solvothermal methods [4–7]. Some difficulties associated with these processes such as autoclave technique and expensive starting materials. Mechano-chemical processing via high-energy ball milling is a novel technique for preparation of nano-sized materials. In this method, powder particles are subjected to severe mechanical deformation during collisions with balls and vial and are repeatedly deformed, cold welded, and fractured. This may accompanied by a solid-state reaction in powder blends [1]. The advantage of mechano-chemical synthesis of iron sulfides in comparison with chemical routes [4–7], is relatively inexpensive and abundant starting materials. Relatively few studies have been directed toward synthesis of iron sulfides by high energy mechanical milling [1,8,9]. However, further development requires better understanding of the process. Use of different starting materials, characterization of product and evaluation of properties like surface and magnetic properties regarding to different applications has not been thoroughly investigated. In the present work, the synthesis of nano-structured FeS powder through mechano-chemical reactions of different starting materials was described according to the reactions (1) and (2).

$$FeS_2 + Fe \rightarrow 2FeS, \quad \Delta H = -14.7\ \text{kJ/mol} \tag{1}$$

$$Fe + S \rightarrow FeS, \quad \Delta H = -107.6\ \text{kJ/mol} \tag{2}$$

Particular attention has been paid to the mechanism of reactions and effect of NaCl as a process control agent (PCA) on the reactions progress. Structural and morphological variations during the mechanical milling together with surface and magnetic properties were compared in details.

2. Experimental procedure

The FeS_2 mineral used in this study was hand selected from the Shahr-e-Babak mine (Kerman, Iran), which was ground into particles finer than 15 μm. Chemical analysis of FeS_2 mineral by X-ray fluorescence (XRF) (ARL8410) showed that Fe and S contents are 46 and 53 wt.%, respectively. Also, iron powder with 99.99% purity (particle size about 20–70 μm, Sigma-Aldrich Co), sulfur powder

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Table 1
Milling conditions of the samples.

Sample	Powder mixture	NaCl addition (wt.%)
S1	FeS_2–Fe	0
S2	FeS_2–Fe	5
S3	Fe–S	0
S4	Fe–S	5

with 99% purity (10–15 μm, Sigma-Aldrich Co) and NaCl powder with 99% purity (<75 μm, Sigma-Aldrich) were used as the starting materials for mechanical milling. The amounts of reactants were determined according to the stoichiometry of the reactions (1) and (2). The powder mixtures of FeS_2–Fe and Fe–S were milled in a high energy planetary ball mill (PM2400) under a high purity argon gas. About 10 g of starting mixture was charged into a stainless steel vial with stainless steel balls. The ball-to-powder weight ratio (BPR) and milling speed were 30:1 and 300 rpm, respectively. In order to study the effect of PCA on reaction progress, the milling process of some samples was carried out with 5 wt.% NaCl. The quantity of the PCA has been chosen based on the literature [10], to reach a maximum influence in mechanical milling process. Table 1 summarizes the milling conditions of different samples.

The phase identification of the products was evaluated using X-ray diffraction (XRD) (Philips PW 3040/60) with a radiation of Cu K_α. The line broadening due to the instrument was calculated from Warren's method [11]. The mean crystallite size was obtained using Williamson–Hall plot [12]. The particles morphology was evaluated by a field emission scanning electron microscope (FESEM) (Hitachi S4160) equipped with an energy dispersive spectrometer (EDS) (Samx). A vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Iran) was used for the room temperature magnetic measurements. The average specific surface area (S_a) of the powders was determined by nitrogen adsorption at 77 K (BEL-Belsorp II instrument) employing the Brunauer–Emmet t–Teller (BET) isotherm equation. To ensure proper degassing under secondary vacuum, the temperature and duration of degassing were 250 °C and 8 h, respectively.

3. Results and discussion

3.1. XRD results

Fig. 1(a) shows the XRD patterns of S1 sample milled for various times, revealing the structural evolution of the powder as milling progressed. The increment of milling time produce a decrement in the intensity of the peaks associated to FeS_2. Finally, after 9 h of milling those peaks disappeared. The FeS peaks appeared after 3 h of milling. It seems that single phase FeS with hexagonal structure (Troilite) was obtained after milling for 9 h. It can be found that, the reaction (1) was progressed gradually during milling of FeS_2 and Fe. Actually, the increase of FeS peaks intensities are related to the formation of it by the reaction (1). On the other hand, the decrease of Fe and FeS_2 peaks intensities are related to the consumption of them by this reaction.

The adiabatic temperature that is a measure of the local heat generated by the reaction is used to characterize the mechanism of reactions. Based on thermodynamic estimations [9,13], it requires that the adiabatic temperature be at least 1800 K for a reaction to become combustion process. This is usually an accepted criterion. The adiabatic temperature calculated from thermodynamic data for reaction between FeS_2 and Fe is 300 K, far smaller than the usual limit of 1800 K. Indeed, the mechano-synthesis of FeS proceeds gradually. This is consistent with gradual FeS formation which was found by XRD results.

Fig. 1(b) shows the XRD patterns of S2 sample milled for various times. It should be noted that, the diffraction peak corresponding to NaCl was not observed in the XRD patterns, due to its small quantity [11,14]. It seems that single phase FeS was obtained after 12 h of milling. It is obvious that use of NaCl delayed FeS formation compared to S1 sample. The suppression of reaction by NaCl is primarily due to the decrease in contact area between reactants [10]. Similar to S1 sample, the reaction mechanism is gradual and hence, NaCl has no effect on the mechanism of reaction (1).

The XRD patterns for the S3 sample after different milling times are shown in Fig. 2(a). It can be seen that after milling for 10 h, the diffraction peaks for S can hardly be detected and after 14.5 h of milling, S peaks disappeared completely. Meanwhile, the expected reaction product, i.e., FeS peaks could not be observed in XRD patterns up to 14.5 h of milling. The possible reason is that small S particles transformed to amorphous structure could not be detected by XRD. Another reason may be that, S phase with smaller crystalline domains than 7 nm could not be detected by XRD [14]. However, the XRD pattern changed dramatically after 15 h of milling. It can be seen that the FeS phase became the major one at this time. This suggests a combustion reaction occurrence between 14.5 and 15 h of milling. Another approval of the combustion reaction mechanism is adiabatic temperature. The adiabatic temperature calculated for reaction (2) is 2136 K which is greater than 1800 K. This value confirms the occurrence of a combustive reaction that is in agreement with high enthalpy of reaction (2).

Fig. 2(b) shows XRD patterns of the S4 sample. Again, the diffraction peak corresponding to NaCl was not observed in the XRD patterns, due to its small quantity [11,14]. After 23 h of milling and in the presence of NaCl as the PCA, a few peaks of FeS_2 were observed. Nevertheless, these peaks disappeared with

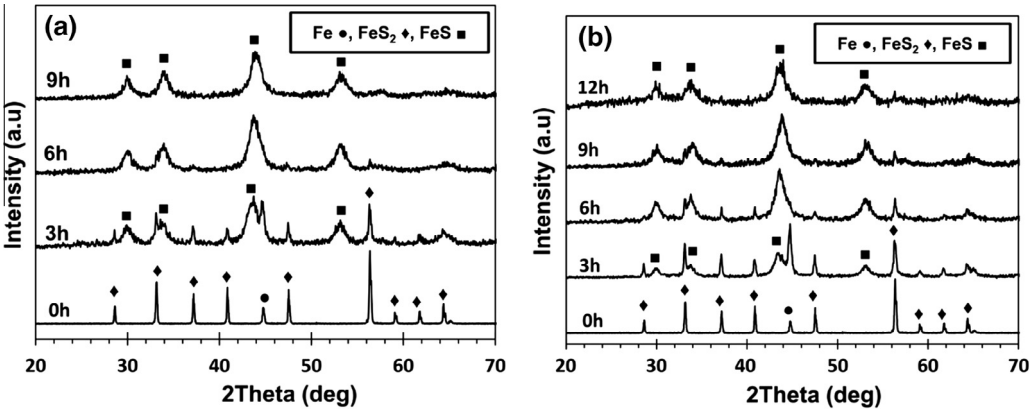

Fig. 1. XRD pattern of (a) S1 and (b) S2 samples after different milling times.