

Stoichiometric Study of Iron Sulfide Prepared by Mechanochemical Reaction

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Abstract. In the present study, pure elemental powders of Fe and S were mixed to give the desired compositions of Fe₅₀S₅₀. A SPEX 8000D high-energy ball mill was used to synthesize iron sulfide powders under an Ar-filled atmosphere. The prepared powders were examined by conventional X-ray diffractometry and synchrotron X-ray absorption spectroscopy. The experimental results revealed that mechanochemical reactions occurred during the ball milling process for all the compositions. The Fe₅₀S₅₀ phase was obtained after ball milling for 20 h. Extended X-ray absorption fine structure (EXAFS) results revealed that the nearest neighbor bond lengths of the radial distribution function (RDF) for iron decreased when iron sulfides formed. X-ray absorption near edge structure (XANES) of S *K*-edges distinguished better the structural evolution of these iron sulfides.

Introduction

Mechanical alloying (MA) involving mechanochemical reactions and solid-state reactions, therefore, has been widely used to synthesize equilibrium and/or non-equilibrium phase in many alloy systems including amorphous materials, metastable crystals, nanocrystalline materials, and intermetallics due to its high-energy of ball-milling process [1,2]. Though the relatively simple technique has been developed before more than 30 years ago [3], it has attracted considerable interests to investigate material limitations and manufacture alloys that are difficult or impossible to produce by conventional melting and casting techniques.

Synchrotron radiation with two main techniques, XANES and EXAFS, were used to study the product materials by means of X-ray absorption spectroscopy. XANES can be used to investigate the electronic structure of specific elements, while EXAFS is used to investigate the local atomic structure of detected atoms. Type and number of elements, and nearest neighbor bond length, can be obtained. The results from X-ray absorption spectroscopy (electronic structure and local atomic environment) can be combined with those obtained from conventional X-ray diffraction (long range order) and transmission electron microscopy to understand better the structure of materials. For instance, the EXAFS technique has been applied successfully to investigate phase transformation behavior during MA [4].

In the present study, the preparation and characteristics of iron sulfide powders from elemental Fe and S mixture by mechanical alloying were investigated. During the milling process, the induced mechanical energy may lead to mechanochemical reactions of Fe and S [2,5]. The structural evolution during the mechanochemical reaction process will be investigated in detail.

Experimental

Pure elemental powders of Fe (99.98%, <325 mesh) and S (99.98%, <325 mesh) were mixed to give the desired composition of $\text{Fe}_{50}\text{S}_{50}$, and then loaded into a high speed steel vial (40 mm in diameter and 50 mm in height) together with Cr steel balls (7 mm in diameter with ball-to-powder weight ratio = 5:1) in an argon-filled glove box. Subsequently, a SPEX 8000D shaker ball mill was carried out for the mechanochemical reaction. The overall mechanochemical process lasted 20 hours but was interrupted every 15 minutes for the first one hour and every 30 min thereafter. Each interruption was followed by an equal length of time (30 min) to cool down the vial.

The techniques included X-ray diffractometry (XRD) and X-ray absorption spectroscopy (XAS) were used to examine the amorphization status of the powder mixtures. The X-ray analysis was performed using a Philips X'pert PW3040 diffractometer with monochromatic Cu $K\alpha$ radiation (40 kV and 30 mA). X-ray absorption measurements were performed at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, using the Wiggler C and B15B double crystal monochromator beamlines. XANES spectra were measured $\sim 50\text{eV}$ before and after the absorption edge of detected element. While EXAFS spectra were measured between energies $\sim 100\text{eV}$ before the edge and 800–1,000 eV above the edge.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of the as-milled $\text{Fe}_{50}\text{S}_{50}$ powder mixture as a function of milling time. With increasing the milling time, as revealed in this figure, most Bragg diffraction peaks from pure Fe and S decreased gradually and disappeared after 5h of milling. When milling was proceeded after 3h, however, it was found that the milling vial generated an dramatic increase in temperature and needed an excess time to cool down. A new phase, identified as Fe_{1-x}S (x ranged from 0 to 0.2) [6], formed after 3h of milling. After the disappearance of the diffraction peaks of Fe and S, only Fe_{1-x}S phase was noticed till the end of 20h milling. Moreover, the broadened diffraction peaks of the Fe_{1-x}S product powders also indicated their strain, significantly fine crystallite, and amorphous structure induced by the process of mechanochemical reaction [7].

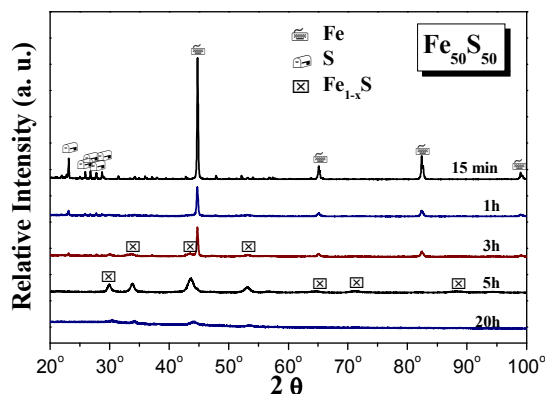


Figure 1: XRD patterns of as-milled $\text{Fe}_{50}\text{S}_{50}$ powder mixtures as a function of milling time.

XAS technique was carried out to further reveal the structural evolution of the milled $\text{Fe}_{50}\text{S}_{50}$ mixture powder during mechanical alloying. Figure 2(a) shows the EXAFS spectra of the as-milled $\text{Fe}_{50}\text{S}_{50}$ powders at Fe K -edge as a function of milling time. It can be found in this figure that a slight difference at the photon energy of $\sim 7160\text{eV}$ after 1h of milling, implying the formation of Fe_{1-x}S phase might start as early as 1h of milling. Furthermore, after Fourier transformation of the EXAFS spectra, the RDF for surrounding the Fe atom in as-milled $\text{Fe}_{50}\text{S}_{50}$ powders as a function of milling time were obtained, as shown in Fig. 2(b). A slight difference can also be noticed in the local atomic environments of Fe after 1h of milling. Figure 3 shows the differentiated curves from the spectra in Fig. 2(a). A small shift of the differential curve toward lower energy shown in Fig. 3 at the energy of $\sim 7120\text{eV}$ also indicates the formation of the Fe_{1-x}S after 1h of milling. Obvious differences where the peak at $\sim 7112\text{eV}$ decreased while that at $\sim 7120\text{eV}$ increased can be noticed

at the powder mixture after 5h of milling. At the same milling time of 5h, a significant change shown in Fig. 3 suggests the formation of Fe_{1-x}S phase, showing good agreement with that in Figs. 2. With prolonging the milling time, the EXAFS spectra (Fig. 2(a)) and their differential curves (Fig. 3) reveal almost no change. In both the Figs. 2 and Fig. 3, similar trends can be observed.

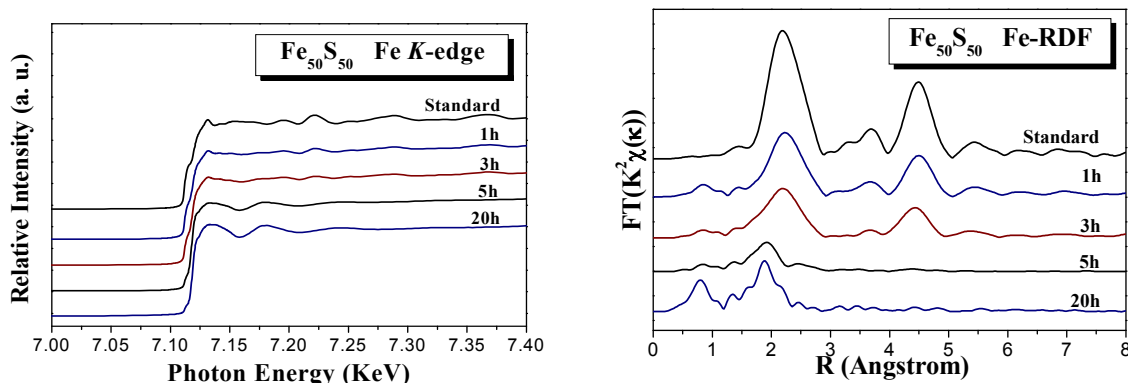


Figure 2(a): EXAFS spectra of as-milled $\text{Fe}_{50}\text{S}_{50}$ powder mixtures at iron K -edge as a function of milling time. (b): RDF of Fe atom for $\text{Fe}_{50}\text{S}_{50}$ powder mixtures as a function of milling time.

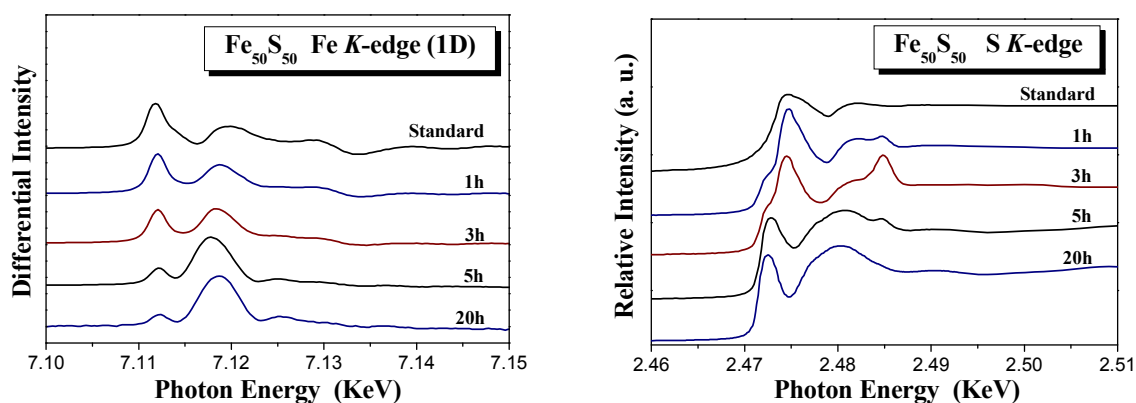


Figure 3: Differential curves of XANES spectra of as-milled $\text{Fe}_{50}\text{S}_{50}$ powder mixtures at Fe K -edge as a function of milling time.

Figure 4: XANES spectra of as-milled $\text{Fe}_{50}\text{S}_{50}$ powder mixtures at sulfur K -edge as a function of milling time.

Additionally, the XANES of S K -edge can better examine the structure of this phase. Figs. 4 shows the XANES spectra of $\text{Fe}_{50}\text{S}_{50}$ powder mixtures at S K -edge as a function of milling time. It can be seen that an extra peak at ~ 2485 eV was detected as early as after 1h milling, indicating the primary formation of Fe_{1-x}S phase [8]. Obvious differences can be found in this figure at those of 5h as-milled powders, where the peak at ~ 2472 eV increased while those at ~ 2474 and 2485 eV decreased. The XANES on the S K -edge confirmed the XRD and EXAFS results. It is interesting to note the extra peak at ~ 2485 eV in this figure. The peak started from 1h of milling, exhibited highest intensity at 3h, decreased with increasing the milling time, and finally disappeared after 20h of milling. It reveals that the formation of nonstoichiometric Fe_{1-x}S phase occurred in the powder mixture milled for 1h. The amount of Fe_{1-x}S phase first increased with the increase of milling time from 1h to 3h. Subsequently, it decreased with increasing the milling time, and finally disappeared until 20h. Meanwhile, the results also implied that the stoichiometric FeS phase was finally reacted by prolonging the milling time to 20h.

In thermodynamics, Fe and S would rather react to form FeS_2 than FeS due to the lower free energy of FeS_2 formation [7]. Therefore, the primary formation of Fe_{1-x}S may be attributed to the formation of FeS_2 in the early mechanochemical process. It can be noted in Fig. 4 that the peak of the 3h as-milled powder mixture at ~ 2474 eV and ~ 2485 eV were identified as the formation of FeS_2 [9]. With increasing the milling time, the shift of the peak from 2474 eV to 2472 eV and the decrease of the peak at 2485 eV were attributed to the formation of stoichiometric FeS phase. Prolonged milling induced no observable differences in the XANES spectra and their differential curves.

Conclusions

The mechanochemical reactions of iron sulfide occurred during the process using a SPEX 8000D ball mill. Due to the formation of FeS and FeS₂ from the starting composition of Fe₅₀S₅₀, the Fe_{1-x}S phase tended to be formed at the early milling stage. The results of S K-edge spectra identification, the sensitive technique to reveal these reactions, showed that the Fe_{1-x}S phase was disappeared to form stoichiometric FeS phase after 20h of milling.

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