Mechanochemical Reduction of Chalcopyrite CuFeS$_2$: Changes in Composition and Magnetic Properties

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High-energy milling of sulphides with a reactive metal in so-called mechanochemical reduction mode can lead to products in nanorange and to composition which simplifies the following metallurgical processing. Chalcopyrite CuFeS$_2$, a ternary semiconductor with antiferromagnetic properties represents promising candidate as an advanced material for use in inexpensive nanoelectronics (solar cells, magnetic area), as well as copper ore source in metallurgical operations. In this work, the process of mechanochemical reduction of chalcopyrite with elemental iron is studied. The composition and properties of nanopowder prepared by high-energy milling were analyzed by X-ray diffraction and magnetic measurements. Most of the reaction takes place during 30 min with chalcocite Cu$_2$S and troilite FeS as the only reaction products. The magnetic investigations reveal significant increase of saturation magnetization as a result of milling. Unlike the conventional high-temperature reduction of chalcopyrite, the mechanochemical reduction is fast and ambient temperature and atmospheric pressure are sufficient for its propagation.

1. Introduction

The chalcopyrite CuFeS$_2$ is a ternary semiconductor belonging to I–III–VI group with antiferromagnetic structure. The properties of CuFeS$_2$ nanocrystals strongly influence its electrical, magnetic and electrochemical behavior [1, 2]. The ternary compound has many potential applications in inexpensive nanoelectronics such as solar cells and in magnetic area [3]. Chalcopyrite is the Earth most abundant Cu-bearing mineral and accounts for approximately 70% of the world's copper reserves. The extraction of Cu may be conducted using a pyrometallurgical or hydrometallurgical treatment [4, 5]. When copper can be produced in nanosize, the product value is even multiplied [6]. Mechanochemical pretreatment of CuFeS$_2$ is an innovative procedure that improves the efficiency of subsequent technological processes via several facts, most importantly due to formation of new surface area. This process is accompanied by fine and hyperfine structure changes [7]. These changes can influence the physical and chemical properties of solids.

As a consequence, further processing can be performed in simpler and less expensive reactors during shorter reaction times.

The aim of the present work is to study the kinetics of CuFeS$_2$ mechanochemical reduction with the application of elemental iron as the reducing element in redox reaction

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$$2CuFeS_2 + Fe \rightarrow Cu_2S + 2FeS. \qquad (1)$$
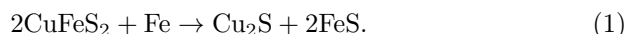
Reaction (1) is interesting from the theoretical point of view (changes in magnetic properties of Fe-bearing species), as well as practical application (transformation of refractory CuFeS$_2$ to better treatable Cu$_2$S).

2. Experimental

Samples of chalcopyrite mineral CuFeS$_2$ from Slovakia (deposit Slovinky) and Kazakhstan (deposit Zhezkazgan) were used for all experiments. Small traces of quartz SiO$_2$ in sample from Slovinky have been identified. As a reducing agent, the elemental Fe was applied.

For milling experiments a planetary mill Pulverisette 6 (Fritsch, Germany) was applied. The following conditions were used:

- Number of milling balls ($d = 10$ mm) from tungsten carbide (WC) — 50,

- Volume of milling pot from WC — 250 ml,

- Milling speed — 500 min^{-1},

- Milling time — till 60 min,

- Milling atmosphere — argon.

The structure changes upon milling were characterized using a D8 Advance X-ray diffractometer (Bruker, Germany) in the Bragg–Brentano geometry working with a Cu K_α ($\lambda = 0.15406$ nm) radiation and a scintillation detector. The data were collected over the angular range $10° < 2\Theta < 100°$ with scanning steps of $0.02°$ and the measurement step time interval of 6 s. For the

data processing, the commercial Bruker tools have been used. Namely, for the phase identification, the Diffrac^{plus} Eva and ICDD PDF2 database were used. A nitrogen-adsorption apparatus NOVA 1200e Surface Area and Pore Size Analyzer (Quantachrome Instruments, Great Britain) was employed to obtain the specific surface area (S_{BET}) values. SQUID magnetometer Quantum Design MPMS XL5 (USA) was used for characterization of magnetic properties of samples at temperature 300 K and in external magnetic fields up to 5 T.

3. Results and discussion

In Fig.1, the dependence of the specific surface area S_{BET} on milling time t_M is given for the mixture ($CuFeS_2$ + Fe) milled up to 30 min. The linear increase of S_{BET} values from 2.61 to 9.01 m^{2}g^{-1} is observable till 15 min of milling. However, at $t > 15$ min, S_{BET} values are decreasing and later on, their stagnation can be observed. The course of $S_{BET}(t_M)$ curve resembles general phenomena accompanying mechanical activation of sulphides [7]. After creation of small particles at the beginning of milling, they have tendency to form agglomerates to compensate high surface energy. However, in our case the course of curve is also influenced by formation of dense product nanocomposite Cu_2S/FeS. Therefore we speculate that the process according to reaction (1), can be divided into two stages.
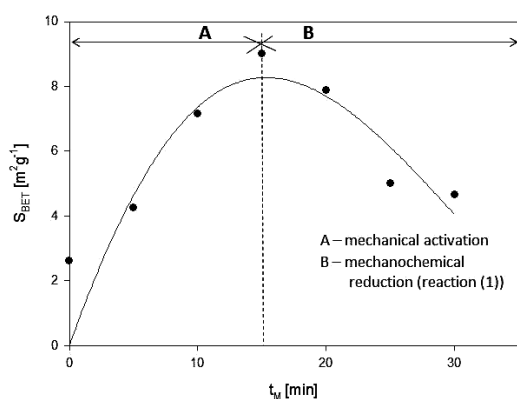

Fig. 1. Specific surface area S_{BET} vs. time of milling t_M for the mixture $CuFeS_2$ (Slovinky) + Fe.

In the first stage (A), the system is mechanically activated and the particles of $CuFeS_2$ and Fe are getting smaller. As a result, diffraction peaks of $CuFeS_2$ are getting lower and broader as a consequence of crystalline phase decrease and increase in lattice strain (the X-ray diffraction (XRD) patterns are given in Fig. 2). Fe peaks are still observable. In the second stage (B), Fe starts to be no more observable and at $t_M = 30$ min, only small traces of $CuFeS_2$ can be still seen. In this stage, the mechanochemical reduction of $CuFeS_2$ to troilite FeS is confirmed. The second product, chalcocite, Cu_2S was not detected, as a consequence of its strong amorphization and/or the possible overlapping of its main diffraction lines with those of troilite.
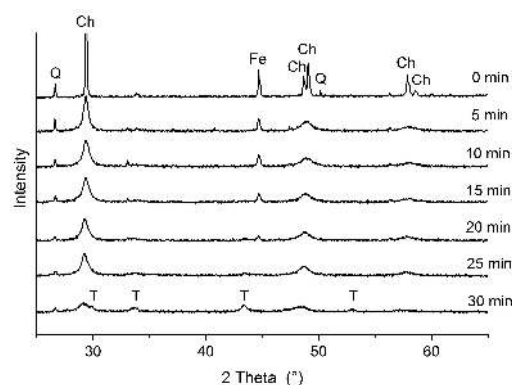

Fig. 2. X-ray diffraction patterns for mixture of $CuFeS_2$ (Slovinky) with Fe milled for different times: 0, 5, 10, 15, 20, 25, and 30 min; Q — SiO_2, Ch — $CuFeS_2$, T — FeS.
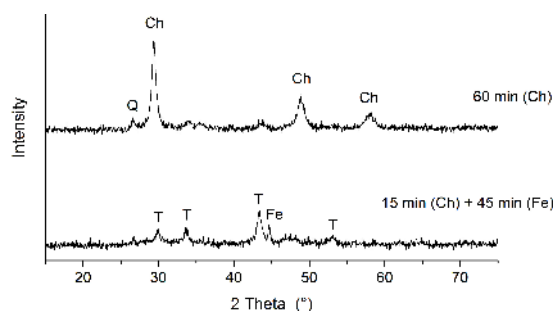

Fig. 3. X-ray diffraction patterns for $CuFeS_2$ (Slovinky) milled for 60 min (top) and mixture of the $CuFeS_2$ with Fe milled for 60 min (bottom): for 15 min, pure chalcopyrite was milled and then Fe was added and the mixture was then milled for further 45 min; Ch — $CuFeS_2$, T — FeS.

The propagation of the reaction (1) can also take place in the combined two-step mode where after activation of $CuFeS_2$, its reaction with Fe is realized (Figs. 3 and 4). Both chalcopyrite minerals (deposit Slovinky — Fig. 3, as well as deposit Zhezkazgan — Fig. 4) are suitable for such type of chalcopyrite processing.

In Fig. 5, the dependence of magnetization on magnetic field for various samples of $CuFeS_2$ (deposit Zhezkazgan) is given. In comparison with the non-milled sample (0 min), the magnetization for the milled sample (30 min) is lower. This phenomenon can be ascribed to the magnetic order-disorder transformation of $CuFeS_2$ as a result of milling described earlier [8]. However, the highest values of magnetization have been obtained for the mixture ($CuFeS_2$+ Fe) milled for 30 min. From the possible "magnetic" components — antiferromagnetic $CuFeS_2$, ferromagnetic Fe, and antiferromagnetic troilite FeS — only the last one can be detected in the products of reaction (1) — Fig. 4 (bottom). Troilite is antiferromagnetic between room temperature and Néel's temperature of 588 K [9].

The highest values of magnetization spotted in our samples ($CuFeS_2$+ Fe) milled for 30 min can be caused
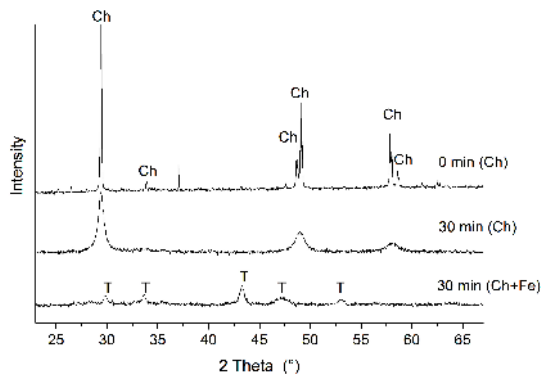
Fig. 4. X-ray diffraction patterns of CuFeS$_2$ (Zhezkazgan), non-milled (top), milled for 30 min (middle), and the mixture of CuFeS$_2$ with Fe milled for 30 min (bottom); Ch — CuFeS$_2$, T — FeS.
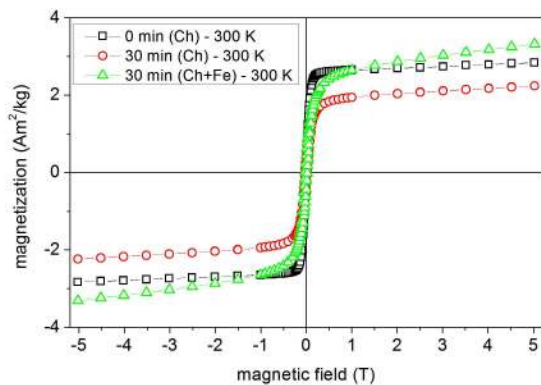

Fig. 5. Magnetization vs. magnetic field for CuFeS$_2$ (Zhezkazgan) for non-milled (black — squares), milled (red — circles), and mixture of CuFeS$_2$ with Fe milled for 30 min (green — triangles).

by imperfections in crystal symmetry and presence of vacancies incipient during milling process. This fact is confirmed also by widened appearance of XRD patterns [6]. The increase of the magnetization value with increased external magnetic field in higher region of fields implies the presence of multiphase system composed of antiferro- and ferrimagnetic components. It suggests the presence of non-stoichiometric compounds in the milled samples.

4. Conclusion

Kinetics of mechanochemical reduction of chalcopyrite CuFeS$_2$ with the application of elemental iron as the reducing element was studied in this article. Mechanochemical reduction is divided into the two partial stages, where in the first stage, the mechanical activation is accomplished and then in the second one, mechanochemical reduction takes place. Therefore, there is a possibility to perform chemical reduction without the requirement of high-energy consuming processes, on the contrary to pyrometallurgy. This fact makes mechanochemical processing more environmental and energetically effective way for the treatment of minerals in partial production steps.

References

[1] Y. Li, N. Kawashima, J. Li, A.P. Chandra, A.R. Gerson, *Adv. Coll. Interface Sci.* **197-198**, 1 (2004).

[2] X. Wu, Y. Zhao, Ch. Young, G. He, *J. Mater. Sci.* **50**, 4250 (2015).

[3] B. Li, L. Huang, M. Zhong, Z. Wei, J. Li, *RSC Adv.* **5**, 91103 (2015).

[4] F. Habashi, *Chalcopyrite: Its Chemistry and Metallurgy*, Mc Graw-Hill, New York 1978.

[5] T.Ch. Almeida, E.M. Garcia, H.W.A. Silva, T. Matenzio, V.F.C. Lins, *Int. J. Min. Proc.* **149**, 25 (2015).

[6] P. Baláž, *Mechanochemistry in Nanoscience and Minerals Engineering*, Springer, Berlin 2008.

[7] P. Baláž, *Extractive Metallurgy of Activated Minerals*, Elsevier, Amsterdam 2000.

[8] V.V. Boldyrev, K. Tkáčová, J.T. Pavlyuchin, E.G. Avvakumov, R.S. Sadykov, P. Baláž, *Dokl. Akad. Nauk.* **273**, 643 (1983).

[9] L.J. Horwood, M.G. Townsend, A.H. Welster, *J. Solid State Chem.* **17**, 35 (1976).