



Mechanochemical Reduction of Synthetic Sulphidic Copper-Bearing Minerals in an Industrial Scale

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Abstract

In this paper the mechanochemical reduction of binary sulphides chalcocite (Cu₂S) and covellite (CuS) by elemental iron were investigated. The composition and properties of nano-powders prepared by high-energy milling were analyzed by X-ray diffraction, X-ray photoelectron spectroscopy and magnetic measurements. The XRD results showed that in case of chalcocite Cu₂S the reaction takes place until 360 minutes, as no elemental iron, could be identified afterwards. In case of covellite CuS, after 480 minutes of mechanochemical reduction, a significant amount of non-reacted elemental iron could still be observed. The investigation of magnetic properties reveals significant decrease of saturation magnetization as a result of milling. XPS results showed a significant surface oxidation in both systems. Unlike the conventional high-temperature reduction of chalcocite and covellite, the mechanochemical reduction is fast and ambient temperature and atmospheric pressure are sufficient for its propagation.

Keywords: mechanochemistry, mechanochemical reduction, high-energy milling, sulphides

Introduction

Mechanochemical processing by high-energy milling is an innovative procedure that improves the efficiency of mineral processing via several factors, most importantly due to the formation of new surfaces and the creation of lattice defects (Tkáčová 1989, Baláž 2000a,b). In a typical technological process, the solid raw materials are transformed by liquid and/or gas phase reactions at high temperatures and pressures. The final products are then separated from the by-products, from the remaining starting materials and/or from the solvent. Very often, the final product is solid again (Boldyrev, 1998; Boldyrev and Tkáčová, 2000). Mechanochemical processing offers the possibility to simplify the entire technological process by avoiding operations in the gaseous and liquid states and to design the process according to the flowchart (Boldyrev, 1996a,b):

raw materials → solid state reaction → desired product

Among copper sulphides, covellite, CuS and chalcocite, Cu₂S are the most common. They are binary compounds of copper which contain the highest amount of copper from sulphide copper bearing minerals (Howard 1979, Goel 2014). Covellite (CuS) has wide range applications in photocatalysis, solar cells, sensors and as a cathode material in lithium chargeable batteries, etc. while, chalcocite (Cu₂S) is a p-type semiconductor having a band gap of 1.21 eV which is compatible for solar energy conversion, it can be used in solar cells, photocatalysts, biosensors and optoelectronic devices (Salavati-Niasari 2013, Yang 2014, Farhadi 2016, Sabah 2016, Cuevas 2016, Wu 2008, Zheng 2017). In addition to their unique properties, traditionally they are sources of copper in ores for metallurgical operations (Baláž 2002).

In this work, the processes of mechanochemical reduction of chalcocite and covellite with elemental iron at industrial scale conditions according to reactions (1, 2) were studied



The aim of this paper is to illustrate effectiveness of so-called process of mechanochemical reduction in an industrial scale using industrial eccentric vibration mill (Fig.1) on example of two binary sulphides with elemental iron which led to production of nanocomposite Cu/FeS as an only product. Big advantage of using an industrial eccentric vibration milling in comparison to laboratory high energy milling is in the possibility of scaling-up the reduction and synthesis.

Materials and methods

Materials

For mechanochemical synthesis of covellite and chalcocite copper (99% Merck, Germany) and sulfur (99% CG-Chemikalien, Germany) powders were used as elemental precursors. For mechanochemical reduction, mechanochemically synthesized copper sulphide covellite CuS (JCPDS 00-006-0464) or chalcocite Cu₂S (JCPDS 72-1071) and elemental iron Fe (99% Winlab, Germany) were used as precursors. Iron was used as a reduction reagent.

Mechanochemical synthesis and reduction

Mechanochemical solid state reductions were performed in an industrial eccentric vibratory ball mill ESM 656-0.5 ks (Siebtechnik, Germany) working under the following conditions: 5 L steel satellite milling chamber attached to the main corpus of the mill, tungsten carbide balls with a diameter of 35



Fig. 1. Eccentric vibratory mill with attached closed satellite (left), open satellite filled with balls (right) (Baláž 2018)

Rys. 1. Mimośrodowy młyn wibracyjny z dołączonym zamkniętym satelitą (po lewej), otwarty satelita wypełniony kulkami (po prawej) (Baláž 2018)

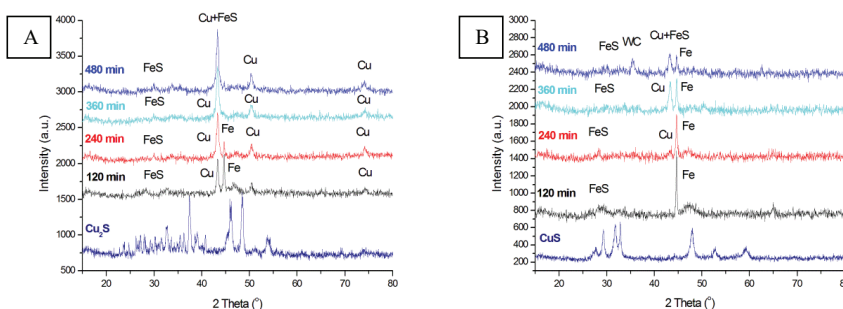


Fig. 2. XRD patterns recorded during mechanochemical reaction of covellite (Cu_2S) (A) and chalcocite (CuS) (B) with iron powder. The XRD patterns of starting Cu_2S and CuS are also provided.

Rys. 2. Widma XRD zarejestrowane podczas reakcji mechano-chemicznej kowelinu (Cu_2S) (A) i chalkozynu (CuS) (B) z proszkiem żelaza. Przedstawiono również widma XRD stanu początkowego Cu_2S i CuS .

mm with a total mass of 30 kg, 80% ball filling, amplitude of the mill = 20 mm, rotational speed of the eccentric = 960 min^{-1} , argon atmosphere, 100 g of feed. The milling was performed for various times (t_M). In the case of mechanochemical synthesis of CuS and Cu_2S precursors, milling for 40 and 60 min, respectively, has been applied. In case of mechanochemical reduction of chalcocite Cu_2S and covellite CuS according to reactions (1) and (2), respectively, t_M 480 min has been applied. The amounts of corresponding sulphide and iron were calculated with respect to the stoichiometries of equations (1) and (2).

Characterization techniques

X-ray diffractometry (XRD)

The identification of phase composition was performed by XRD method with an X'Pert PW 3040 MPD diffractometer (Phillips, Germany) and D8 Advance diffractometer (Bruker Germany), both working in the 2θ geometry with Cu K_α (40kV, 40 mA) radiation.

Mass magnetization measurement

In order to obtain information on magnetic properties of the studied samples, mass magnetization was measured. The measurements were performed by using vibrating sample magnetometer (VSM) installed on a cryogen free superconducting magnet (Cryogenic Limited). The samples were measured in powder form packed in a specialized capsule. After the measurements, the magnetic moment values were divided by the sample mass, yielding the mass magnetization.

Photoelectron spectroscopy (XPS)

XPS measurements of samples were performed using XPS

instrument SPECS equipped with PHOIBOS 100 SCD and non-monochromatic X-ray source. The survey surface spectrum was measured at 70 eV transition energy and core spectra at 20 eV at room temperature. All spectra were acquired at a basic pressure of 1×10^{-8} mbar with $\text{AlK}\alpha$ excitation at 10 kV (200 W). The data were analyzed by SpecsLab2 CasaXPS software (Casa Software Ltd). The spectrometer was calibrated against silver (Ag 3d). All samples showed variable degrees of charging due to their insulating nature. The problem was resolved by the calibration on carbon.

Results and discussion

In Fig. 2 A and B, XRD patterns of two systems ($\text{Cu}_2\text{S}+\text{Fe}$) and ($\text{CuS}+\text{Fe}$) are shown, respectively. In both cases the main peak corresponding to copper is overlapping with the troilite one. Therefore, the progress of the reaction can be traced mainly by observing the decrease of the intensity of main iron peak located at $2\theta \sim 44^\circ$. For $\text{Cu}_2\text{S}+\text{Fe}$ system, iron peak is no longer visible after t_M 360 min, suggesting the completion of the reaction. However, for the $\text{CuS}+\text{Fe}$ system, there is still a significant amount of iron visible after 480 min of milling, therefore we can conclude that reaction is still not completed.

In Fig.3, the dependence of mass magnetization on milling time t_M for both studied systems is given. Regarding the starting mixtures, the highest magnetization value was evidenced for ($\text{CuS}+\text{Fe}$) system and the lowest for ($\text{Cu}_2\text{S}+\text{Fe}$) system. In both cases, magnetization decrease with t_M , which correlates with the consumption of Fe in reactions. In the case of ($\text{Cu}_2\text{S}+\text{Fe}$) system reaction (1), the magnetization value after t_M 360 min and 480 min is around $10 \text{ Am}^2/\text{kg}$, which con-

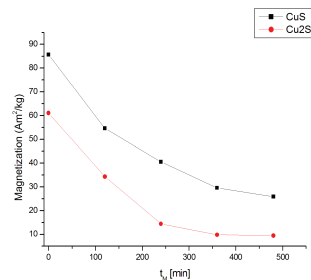


Fig. 3. Magnetization vs. t_M for the reduction of chalcocite Cu₂S according to reaction (1) (red – circles), and that of covellite CuS according to reaction (2) (black – squares)

Ryc. 3. Namagnesowanie vs t_M dla redukcji chalkozynu Cu₂S zgodnie z reakcją (1) (czerwone – kółka), a kowalinowej CuS według reakcji (2) (czarne – kwadraty)

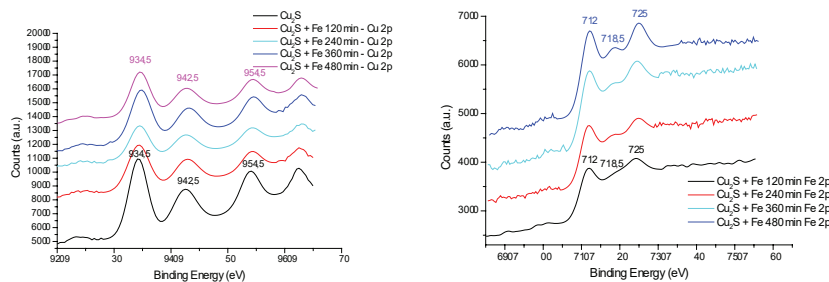


Fig. 4. High resolution XPS spectra of the mechanochemical reduction of chalcocite Cu₂S with elemental iron: A – copper 2p, B – iron 2p

Rys. 4. Widma XPS o wysokiej rozdzielczości mechano-chemicznej redukcji chalkozynu Cu₂S za pomocą żelaza pierwiastkowego: A – miedź 2p, B – żelazo 2p

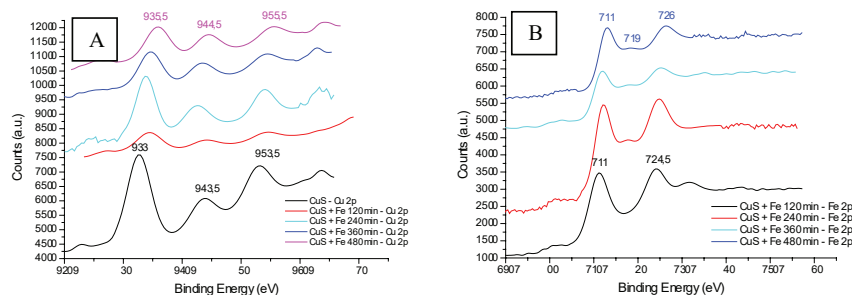


Fig. 5. High resolution XPS spectra of the mechanochemical reduction of covellite CuS with elemental iron: A – copper 2p, B – iron 2p

Rys. 5. Widma XPS o wysokiej rozdzielczości mechano-chemicznej redukcji CuS kowelinu z żelazem pierwiastkowym: A – miedź 2p, B – żelazo 2p

firmes the observation from XRD that the reaction is almost completed already after t_M 360 min.

To compare of (Cu₂S+Fe) and (CuS+Fe) systems, the lowest value of saturation magnetization is observed in the first case for t_M=480 min, which correlates with Fig.2 (A). Regarding to the reaction (2) (covellite CuS reduction), the final value of saturation magnetization is higher, as the reaction did not proceed totally. This fact correlates with Fig.2 (B) where after t_M=480 min, elemental iron (Fe) is still observed.

X-ray photoelectron spectroscopy was used to elucidate the surface composition of the prepared powders after mechanochemical reduction of Cu₂S and CuS systems. High resolution spectra for Cu 2p and Fe 2p for both systems are shown in Figure 4 and 5 respectively.

In (Fig.4A) Cu 2p spectra at different t_M are shown for Cu₂S+Fe system. The detected signal for Cu in the spectrum for Cu₂S, are not in accordance with literature, concretely the observed peaks at 934.5 eV and 954.5 eV could hint to the

oxidation of Cu₂S to CuSO₄ and copper oxides at the surface, which is a common phenomenon (Todd 2003). The peak at 944.5 eV could be present because of CuO formation on the surface (Parmigiani 1992). The Fe 2p spectra for (Cu₂S+Fe) system are shown in (Fig.4B). The observed peaks at 712 and 725 eV, could hint to the slight surface oxidation to Fe (III) (Grosvenor 2004, Idczak 2016), as according to the literature the oxidation state of Fe in FeS is (II) (Skinner 2003). A satellite peak located at 718.5 eV also provides a proof for the presence of iron in oxidation state (III) (Idczak 2016).

Fig.5A,B spectra of Cu 2p and Fe 2p at different t_M are shown for (CuS+Fe) system. The detected signal for Cu in the spectrum for CuS, concretely the observed peaks at 935.5 and 955.5 eV are not in accordance with literature, due to presence of copper in oxidation state (II) (Ye 2015, Krylova 2009), which hints to the slight surface oxidation, as according to literature, the oxidation state of Cu in CuS, is (I) (Nduna 2014, Folmer 1980). A satellite peak located at 944.5 eV

also provides a proof for the presence of copper in oxidation state (II) (YE 2015, Krylova 2009). The detected signals for Fe are shown in (Fig.5B), concretely the observed peaks at 711 and 726 eV, could hint to the slight surface oxidation of Fe (III) (Grosvenor 2004, Idczak 2016), as according to the literature the oxidation state of Fe in FeS is (II) (Skinner 2003). A satellite peak located at 719 eV also provides a proof for the presence of iron in oxidation state (III) (Idczak 2016). As the XPS measurements were not performed using argon sputtering, the surface impurities can significantly affect the results for both samples.

Conclusion

The mechanochemical reduction of chalcocite Cu_2S and covellite CuS with elemental iron as the reducing element

was studied in this article. From the results we can conclude that mechanochemical reduction of both systems is possible. However, product is slightly oxidized on the surface due to high reactivity of produced nanoparticles. Our results suggest a possibility to perform chemical reduction without requirement of any high energy-consuming processes, e.g. in pyrometallurgy. This fact makes mechanochemical processing more environmental friendly and energy effective way for the treating of copper minerals in the partial production steps.

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Redukcja mechanochemiczna syntetycznych minerałów siarczkowo-miedziowych w skali przemysłowej

W artykule przedstawiono wyniki badań nad mechaniczno-chemiczną redukcją dwusiarczkowych chalkozynów (Cu₂S) i kowelinu (CuS) przez żelazo pierwiastkowe. Skład i właściwości nanoproszków wytworzonych przez mielenie wysokoenergetyczne analizowano metodą dyfrakcji rentgenowskiej, rentgenowskiej spektroskopii fotoelektronowej i pomiarów magnetycznych. Wyniki XRD wykazały, że w przypadku chalkozynu Cu₂S reakcja zachodzi do 360 minut, ponieważ później nie można zidentyfikować żelaza pierwiastkowego. W przypadku kowelinu CuS, po 480 minutach redukcji mechaniczno-chemicznej, można było zaobserwować znaczną ilość nieprzereagowanego żelaza pierwiastkowego. Badanie właściwości magnetycznych ujawnia znaczne zmniejszenie podatności magnetycznej w wyniku rozdrabniania. Wyniki XPS wykazały znaczne utlenienie powierzchni w obu przypadkach. W przeciwieństwie do konwencjonalnej wysokotemperaturowej redukcji chalkozynu i kowelinu, redukcja mechano-chemiczna jest szybka, a temperatura otoczenia i ciśnienie atmosferyczne są wystarczające do jej propagacji.

Słowa kluczowe: mechanochemia, redukcja mechaniczno-chemiczna, mielenie wysokoenergetyczne, siarczki