

## Mechanochemical Reduction of Sulphides for Nanocrystalline Metals Preparation

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### Abstract

The mechanochemical reduction of copper sulphide ( $\text{Cu}_2\text{S}$ ) and lead sulphide ( $\text{PbS}$ ) with elemental Fe as well as reduction of copper sulphide ( $\text{Cu}_2\text{S}$ ) with silicon are studied. Metallic Cu and Pb are obtained due to the reducing power of iron and silicon, respectively. The obtained particles are characterized by XRD, VSM, SEM and TEM methods. While for  $\text{Cu}_2\text{S}$  and  $\text{PbS}$  the reduction by iron is rather straightforward leading to Cu and Pb metals in 10–23 nm dimensions, the process of  $\text{Cu}_2\text{S}$  reduction by silicon is more intricate. In this case the overall process proceeds *via* complicated mechanism with several overlapping steps. Phase transformations in copper sulphide phases, the formation of elemental nanocopper with X-ray determined particle size of 23 nm and formation of ternary sulphide  $\text{Cu}_9\text{SiS}_6$  with anomalous surface area values are the main products of the mechanochemical reaction.

### INTRODUCTION

Nanocrystalline materials have been of interest of more than 20 years and this interest is still increasing. The main cause is in their unusual properties based on the high concentration of atoms in interfacial structures and the relatively simple ways of their preparation [1–6]. High-energy milling as a way for nanomaterials synthesis was originally developed in metallurgy as a means to prepare oxide dispersion strengthened solids [7, 8]. Later the application was directed to the preparation of amorphous alloys, superconducting materials, rare permanent magnets, superplastic alloys and intermetallic compounds. Additionally, it was recognized that this technique can be used to induce chemical reactions in powder mixtures at room temperature or at much lower temperatures than normally required to synthesize pure metals [9–16].

Metal nanocomposites as systems with high density of interface boundaries provide the large surface of initial components. The mixing of components during high-energy milling is performed at the nanometer level when the

contact between the components is performed by atomically pure planes.

It is the aim of the present paper based on three published works to illustrate the method of mechanochemical reduction of copper and lead sulphides by iron and silicon as reducing metals. In the following, the properties of nanocrystalline Cu and Pb metals will be described and discussed.

### EXPERIMENTAL

Milling experiments were performed in a Fritsch Pulverisette 6 planetary mill (Germany). For the mechanochemical reduction of  $\text{Cu}_2\text{S}$  and  $\text{PbS}$  with elemental Fe (Eqs. 1, 2) the following milling conditions were used: loading of the mill with 50 balls (mass 360 g) of 10 mm diameter; material of grinding chamber and balls: tungsten carbide; rotation speed of the planet carrier: 400–500 rpm; time of milling in an argon atmosphere: 1–60 min. Starting mixture of copper sulphide and silicon powders (after Eq. 3) was milled for 1–20 min. The planet carrier rotated at 400 rpm.

XRD measurements were carried out using a DRON-2.0 diffractometer (Russia) with a Gur 5 goniometer and using  $\text{FeK}_\alpha$  radiation. The data of the International Centre for Diffraction Data (ICDD, version 1998) were used for the identification of phases under study.

Magnetization data were obtained by employing a vibration sample magnetometer (VSM) equipped with a superconducting coil. A maximum magnetic field of 3 T was used in order to assure the magnetic saturation of the specimens at room temperature.

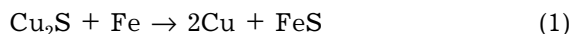
The synthesized nanoparticles were analysed using FE-SEM LEO 1550 scanning microscope in order to investigate the surface morphology. The samples were left uncovered by any conductive material as to keep their original properties.

Transmission electron microscopy was carried out using a Jeol-2000FX microscope (Jeol, Japan).

## RESULTS AND DISCUSSION

### Copper sulphide and iron system [17]

The mechanochemical reaction between copper sulphide,  $\text{Cu}_2\text{S}$ , and elemental iron is described by the equation



The reaction is thermodynamically possible at ambient temperature, as a small but negative enthalpy change ( $\Delta H_{298}^\circ = -13.4 \text{ kJ/mol}$ ) is obtained from thermodynamic data [18].

Its progress is illustrated by XRD patterns in Fig. 1. The primary process – the reduction of copper sulphide by iron while copper metal and iron sulphide are formed – is clearly seen, particularly by inspecting the relative intensities of the diffraction lines of Cu and Fe metal.

The process is significantly complicated by the existence of several copper sulphide and iron sulphide phases. Already 1 min of milling decreases the relative amount of djurleite  $\text{Cu}_{1.94}\text{S}$  and increased the fraction of chalcocite  $\text{Cu}_2\text{S}$ . After 10 min of milling, only the reflections from Cu, cubic FeS and Fe can be observed. With increasing time of milling cubic FeS changes to its hexagonal modification troilite FeS. This phase is considered the stable modification of stoichiometric FeS.

Figure 2 shows the room temperature magnetization data for investigated samples as a function of external magnetic field. It is evident that the resulting magnetization curves are well saturated after an application of magnetic field higher than 2 T. The difference in

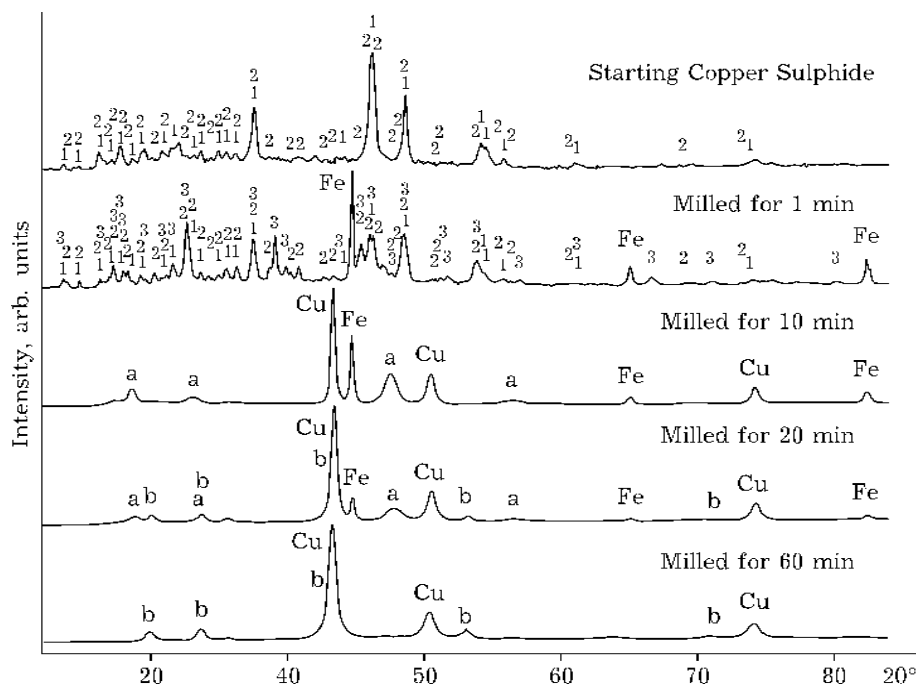


Fig. 1. XRD patterns as a function of milling time. The lines of copper sulphides djurleite,  $\text{Cu}_{1.94}\text{S}$  (1), chalcocite,  $\text{Cu}_2\text{S}$  (2) and tetragonal  $\text{Cu}_{1.81}\text{S}$  (3); cubic (a) and hexagonal (b) FeS; and the metals copper (Cu) and iron (Fe) are marked.

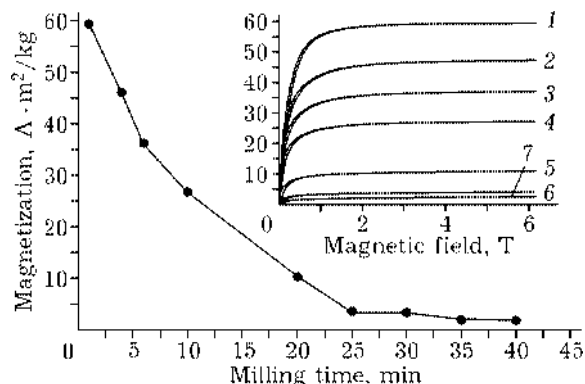


Fig. 2. Magnetization as a function of external magnetic field and/or of milling time for reaction (1). Milling time, min: 1 (1), 4 (2), 6 (3), 10 (4), 20 (5), 25–30 (6), 35–40 (7).

the saturation magnetization of the samples milled for different times, as displayed in the inset of this Figure, is mainly caused by the varied amount of the ferromagnetic component in these samples. The inset shows that the amount of metallic iron, which is the only ferromagnetic component in samples, decreases continuously for milling times up to 40 min. At this time the saturation magnetization is negligible indicating that the constituent phases are almost entirely paramagnetic and/or antiferromagnetic, *i.e.* the reaction (1) tends to be finished.

Surface morphology of the synthesized Cu/FeS nanoparticles with estimated size from 20–30 nm is depicted in Fig. 3. Individual nanoparticles have tendency to form nanoparticle agglomerates during milling process and both entities can be clearly seen.

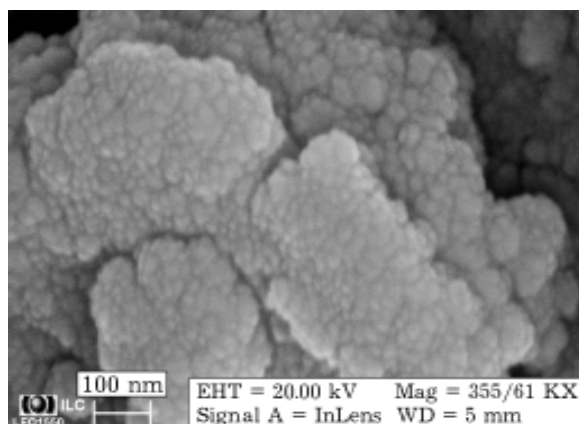


Fig. 3. SEM image of the Cu/FeS nanocomposite prepared by milling for 40 min.

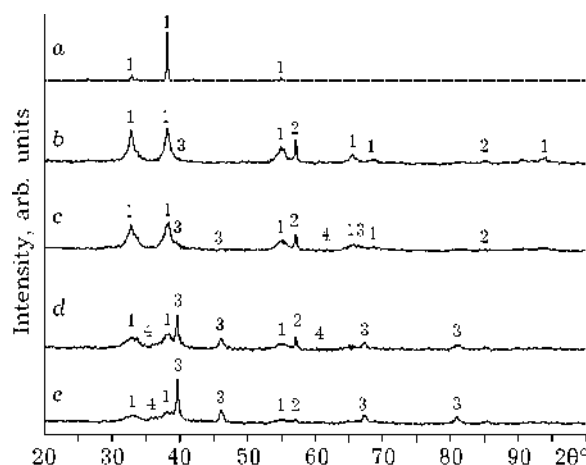


Fig. 4. XRD patterns at different stages of reaction (1) as a function of milling time: a – PbS; b–e – PbS + Fe milled for, min: 20 (b), 30 (c), 40 (d), 60 (e); 1 – lead sulphide, 2 – iron, 3 – lead, 4 – FeS (cubic).

#### Lead sulphide and iron system [19]

The mechanochemical reaction between lead sulphide PbS and elemental iron can be described by the equation



The reaction is thermodynamically possible at ambient temperature, as the enthalpy change is negative. The value  $\Delta H_{298}^{\circ} = -1.3$  kJ/mol was calculated from the thermodynamic data published in [18].

The course of the mechanochemical reaction between lead sulphide and iron is illustrated by the XRD patterns in Fig. 4. The XRD pattern is still dominated by the lines characteristic of PbS which illustrates incomplete recovery. The significant line broadening suggests dramatic grain size reduction. The lines of the product phases of elemental Pb and pyrrhotite, FeS, as well as residual Fe were also observed.

It is evident in magnetic measurements (Fig. 5) that the magnetization curves are well saturated after the application of a magnetic field higher than 2 T. The difference in the saturation magnetization of the samples, as displayed in the inset of this Figure, is mainly caused by different amount of the ferromagnetic component in the milled samples which is bcc Fe. For longer milling times the saturation magnetization is negligible indicating that the constituent phases are almost entirely paramag-

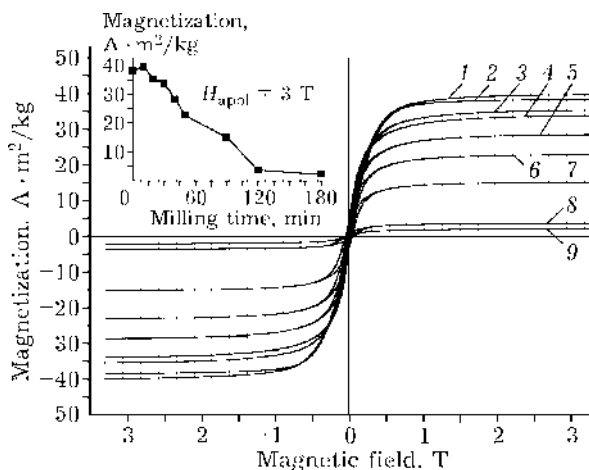


Fig. 5. Magnetization as a function of external magnetic field and/or of milling time for reaction (2). Milling time, min: 0 (1), 10 (2), 20 (3), 30 (4), 40 (5), 50 (6), 90 (7), 120 (8), 180 (9).

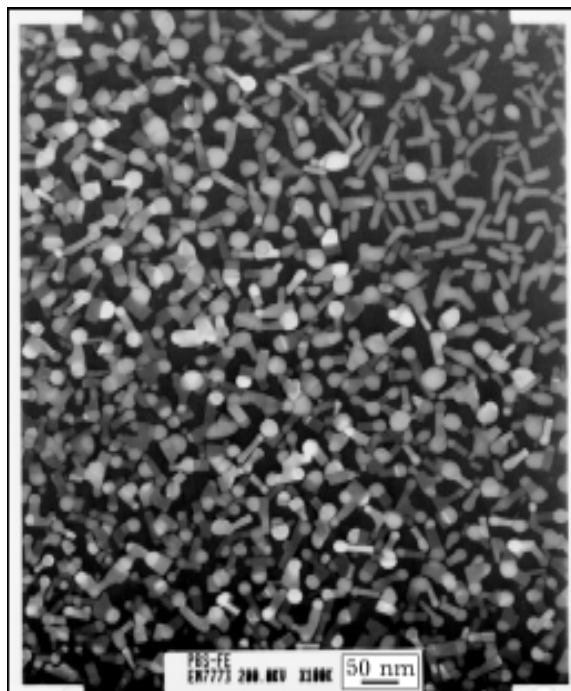


Fig. 6. TEM image of the Pb/FeS nanocomposite prepared by milling for 120 min.

netic and the mechanochemical reduction is complete.

The reaction product consists of nano-crystalline particles with diameters of 13–21 nm for lead as calculated from XRD line widths. Figure 6 shows a typical TEM image of the mechanochemical product. Examination of TEM shows that the as-milled powder is composed of spherical and rod-like particles. Dimensions of spherical particles are close to the nanometer particle size determined by XRD.

### Copper sulphide and silicon system [20]

The set of starting copper sulphide and silicon mixtures was milled for different time and the products were identified by X-ray diffractometry (Fig. 7). Djurleite Cu<sub>1.94</sub>S and chalcocite Cu<sub>2</sub>S together with unreacted silicon were identified in powders milled till 3 min (see Fig. 7, a, b). Cu<sub>1.96</sub>S phase formed at milling time 6 min (see Fig. 7, c) seemed to be the most stable phase even in case when ternary sulphide is formed during prolonged milling. For longer milling (see Fig. 7, d–f) elemental copper (1) and the ternary copper silicon sulphide Cu<sub>8</sub>SiS<sub>6</sub> are the main reaction products together with the described Cu<sub>1.96</sub>S phase.

The dependence of specific surface area on milling time for starting copper sulphides, starting silicon and reaction mixture of copper sulphides with silicon is given in Fig. 8. There are small changes in values of S<sub>A</sub> for copper sul-

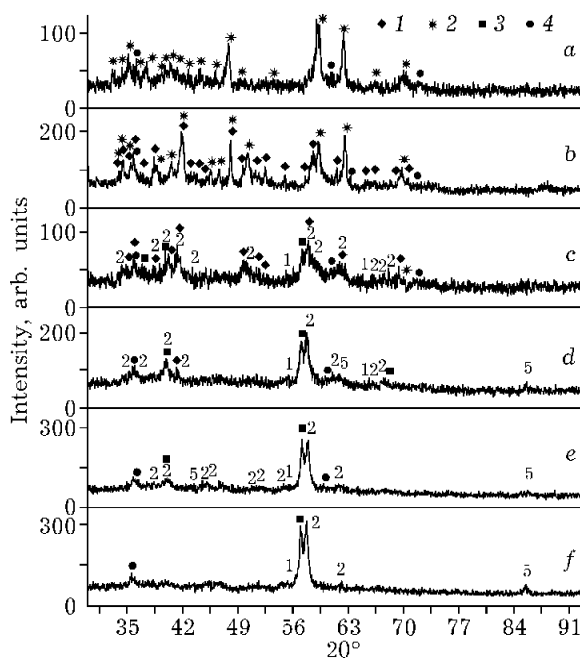


Fig. 7. XRD patterns of mixture of starting copper sulphides with silicon milled for different times, min: 1 (a), 3 (b), 6 (c), 10 (d), 15 (e), 20 (f) (silicon has been pre-milled for 10 min for all samples); 1 – chalcocite Cu<sub>2</sub>S (JCPDS – cards 46-1195, 84-1770, 72-1071); 2 – djurleite Cu<sub>1.9375</sub>S (JCPDS – card 34-0660); 3 – Cu<sub>1.96</sub>S – (card 12-0174); 4 – silicon (syn) Si (JCPDS – card 27-1402); 1 – copper (syn) Cu (JCPDS – card 04-0836); 2 – copper silicon sulphide Cu<sub>8</sub>SiS<sub>6</sub> (JCPDS – card 21-0305); 5 – tungsten carbide WC (card 25-1047).

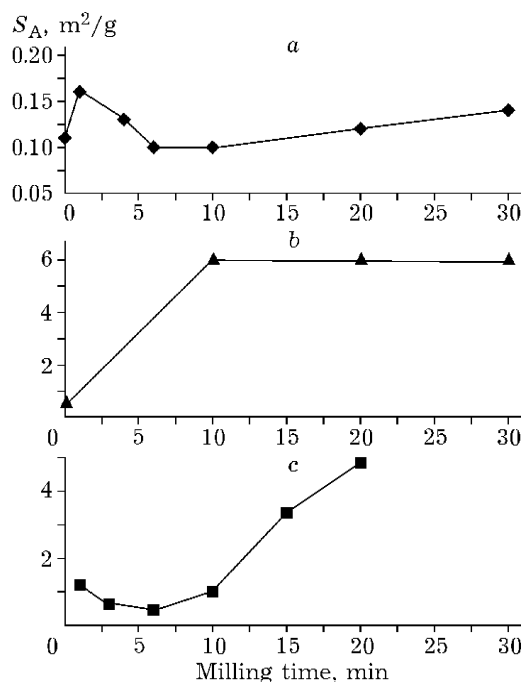
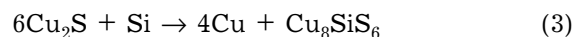


Fig. 8. Specific surface area ( $S_A$ ) vs. milling time: a – copper sulphides; b – silicon; c – mixture of copper sulphides with silicon.

phide milling in contrast to silicon, which seemed to be strongly agglomerated after 10 min of milling. Anomalous behaviour of surface area increase for starting mixture milled for 6–20 min ( $S_A = 0.43\text{--}4.86\text{ m}^2/\text{g}$ ) can be related to the formation of ternary copper silicon sulphide  $\text{Cu}_8\text{SiS}_6$  because the specific surface area of any milled copper sulphide is not higher than  $0.2\text{ m}^2/\text{g}$ .

The overall process of mechanochemical transformations in copper sulphide–silicon system proceeds *via* complicated mechanism with several overlapping steps. Phase transformations in copper sulphide phases, the formation of elemental nanocopper with X-ray determined particle size of 23 nm and formation of ternary sulphide  $\text{Cu}_8\text{SiS}_6$  with anomalous surface area values are the main products of the hypothetical reaction



## CONCLUSION

The mechanochemical synthesis of Cu/FeS, Pb/FeS and Cu/ $\text{Cu}_8\text{SiS}_6$  nanoparticles was performed by high-energy milling. This process has considerable potential for easily scaling up the production of nanocrystalline materials under ambient conditions in reasonable time. Mechanochemical synthesis of the selected systems was verified also in an industrial mill.

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