# Sb/FeS nanocomposite prepared by mechanochemical reduction

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## Abstract

The mechanochemical reduction of antimony sulphide with elemental iron was studied using a laboratory planetary mill and an industrial eccentric vibratory mill. The composition and properties of the obtained Sb/FeS nanocomposites were analysed by XRD, VSM, $^{57}$Fe-Mössbauer spectroscopy, and SEM methods. The process kinetics shows that most of the reduction (about 90%) is complete after 60 min of milling in the planetary mill. The transformation kinetics is slower when the industrial vibratory mill is used, as it has lower specific energy input than the planetary laboratory mill. Mechanochemical reduction is a very straightforward, one-step, ambient temperature process that can be readily utilized to make Sb/FeS nanocomposites.

Key words: mechanochemistry, nanocomposite, antimony, iron sulphide

## 1. Introduction

The mechanically induced chemical reactions have attracted considerable scientific and technical interest in recent years due to the unique nanostructures and properties obtained by this process. It is usually carried out in high-energy ball mills that can be scaled-up to large quantities relatively easily [1–7]. Energetic milling results in mixing of the components on the nanometer scale. A high density of atomically pure interfaces forms, where reactions can take place at a considerable rate. The kinetics of the mechanochemical reduction of metal sulphides *Me*S (*Me* = Fe, Cu, Pb) with elemental iron and silicon has been studied earlier [8–11]. The structure and magnetic properties of the obtained products have also been reported.

Conventionally, antimony sulphide is reduced at high temperature using a reducing agent such as hydrogen or iron [12, 13]. Nanosized metal powders are expected to display better properties than a conventional antimony powder with coarse grains. The mechanochemically synthesized Sb/FeS nanocomposite powders can be applied in technology as produced, e.g. as supported metal catalysts in chemical engineering, or their components have to be separated in order to obtain pure nanometals with unique properties.

The aim of the present work is to study the mechanochemical reduction of antimony sulphide $Sb_2S_3$ with elemental iron at ambient temperature in a laboratory planetary mill as well as in an industrial eccentric vibratory mill.

## 2. Experimental

### 2.1. Synthesis

Mechanochemical reduction of antimony sulphide $Sb_2S_3$ with elemental iron Fe as reducing element was performed in a Pulverisette 6 laboratory planetary mill (Fritsch, Germany). A 250-ml tungsten carbide (WC) grinding chamber and 50 WC balls of 10 mm diameter (total weight 360 g) were used. The weight of the milled powder charge was 3 g. The speed of the planet carrier was set to 500 rpm. Milling times between 10 and 180 min were applied. The atmo-

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*Corresponding author: tel.: +421 557922606; fax: +421 557922604; e-mail address: godocik@saske.sk sphere inside the milling chamber was argon. The same process was also performed in an industrial eccentric vibratory mill ESM 654 (Siebtechnik, Germany). Milling was carried out in air for durations between 15 and 180 min. The milling chamber was filled with tungsten carbide balls and the weight of milled powder mixture was 50 g. The rotational speed of the eccenter was 960 rpm. This mill was developed and constructed by Gock et al. [14, 15] and it is currently implemented for the production of ultrafine particles in industry.

The mechanochemical reaction between antimony sulphide $Sb_2S_3$ and elemental iron Fe is described by the reaction

$$\mathrm{Sb_2S_3 + 3Fe \xrightarrow{milling} 2Sb + 3FeS.} \tag{1}$$

The reaction is thermodynamically possible, as the enthalpy change for reaction (1) is negative, $\Delta H^{\circ}_{298} = -116.7\ \mathrm{kJ\ mol^{-1}}$.

### 2.2. Characterization techniques

X-ray diffraction measurements were carried out using a Philips X'Pert diffractometer, working in the

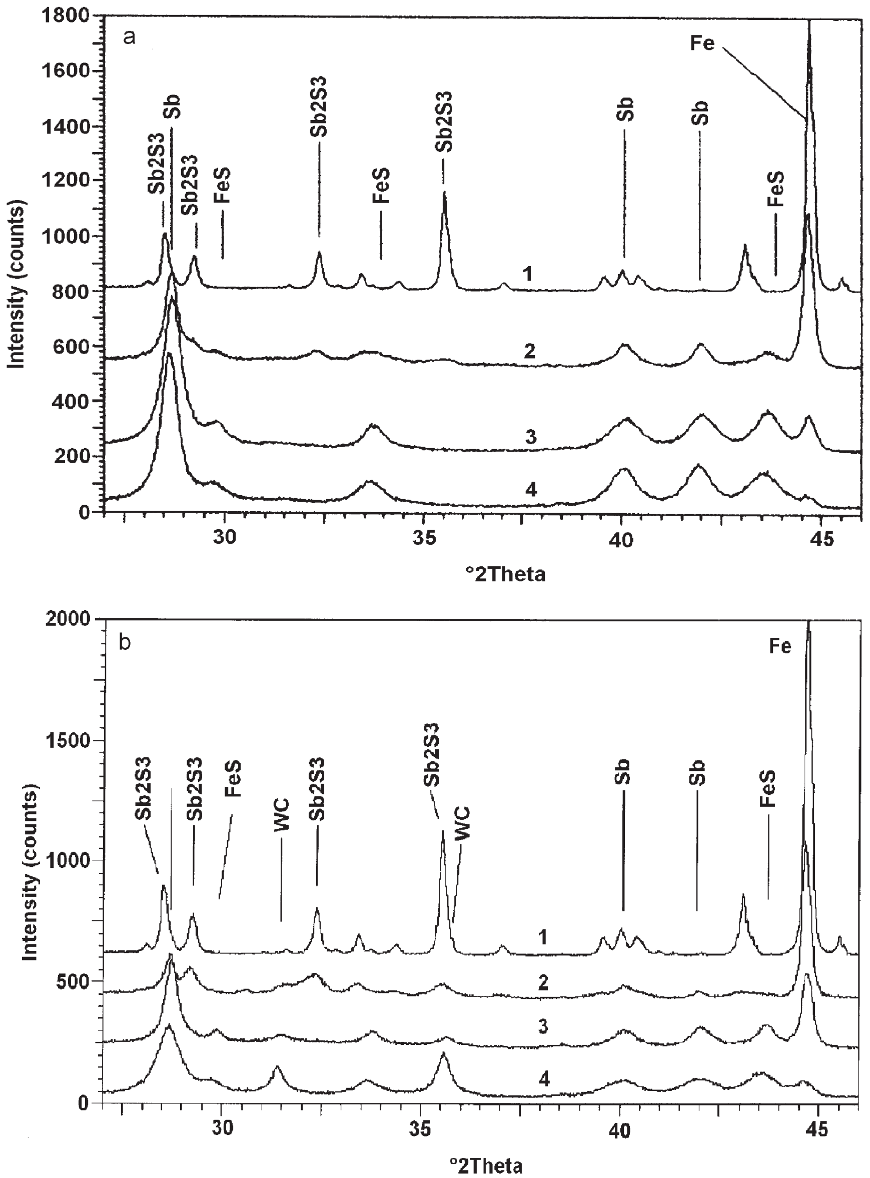

Fig. 1. XRD patterns as a function of milling time in the laboratory mill. 1 – stoichiometric mixture of $Sb_2S_3$ and Fe before milling. The milling times for patterns 2–4 are 20 min, 60 min, and 120 min, respectively (a). XRD patterns as a function of milling time in the industrial mill (b). 1 – stoichiometric mixture of $Sb_2S_3$ and Fe before milling. The milling times for patterns 2–4 are 15 min, 60 min, and 180 min, respectively.

Θ-Θ geometry with CuK$_\alpha$ radiation. The JCPDS database was utilized for phase identification. Magnetization data were obtained by employing a vibrating sample magnetometer (VSM) equipped with a superconducting coil. The magnetic field was increased up to 3 T in order to assure the magnetic saturation of the specimens at room temperature. The Mössbauer measurements were carried out at room temperature in transmission geometry using a conventional spectrometer in constant acceleration mode. A $^{57}$Co/Rh gamma-ray source was used. The velocity scale was calibrated relative to $^{57}$Fe in Rh. A proportional counter was used to detect the transmitted gamma-rays. The Mössbauer spectral analysis software "Recoil" [16] was employed for the quantitative evaluation of the spectra. The morphology of the samples was analysed using FE-SEM LEO 1550 scanning microscope. The samples were not covered with any conductive material in order to keep their original properties.

## 3. Results and discussion

The progress of the mechanochemical reduction of antimony sulphide by elemental iron is illustrated by the selected XRD patterns in Fig. 1. Spectra of the samples prepared in the laboratory mill are shown on the left and those prepared in the industrial mill on the right. The process is rather straightforward with elemental antimony Sb (JCPDS 05-0562) and FeS (pyrrhotite-4H, JCPDS 22-1120) being the only solid products. The intensity of the (110) line of iron metal decreases upon continued milling and only a very small amount of iron is detectable after 120 min of milling with the planetary mill (pattern 4) while in the case of the industrial mill, 25% of the metallic iron is still present after the same milling time. There is a small hump in the spectra at about 2Θ = 31–32° which originates from tungsten carbide abraded from the milling balls. In the starting material (pattern 1) several additional small peaks are seen which also belong to stibnite, $Sb_2S_3$ (JCPDS 42-1393).

The conversion degree to antimony is shown as a function of milling time in Fig. 2a; the remaining iron fraction is illustrated in Fig. 2b. The data were obtained by normalizing the intensities of appropriate XRD lines. It is clear that most of the reduction is complete after 60 min with the intensity of $Sb_2S_3$ decreasing faster than that of Fe. There is no reason to expect different phase ratios here, as the content of Fe and $Sb_2S_3$ should change parallel according to Eq. (1). A possible explanation is the partial amorphization of stibnite, which is indeed manifested in an increased background of the XRD patterns. The higher energy input of the laboratory planetary mill explains the faster kinetics obtained with that instrument.

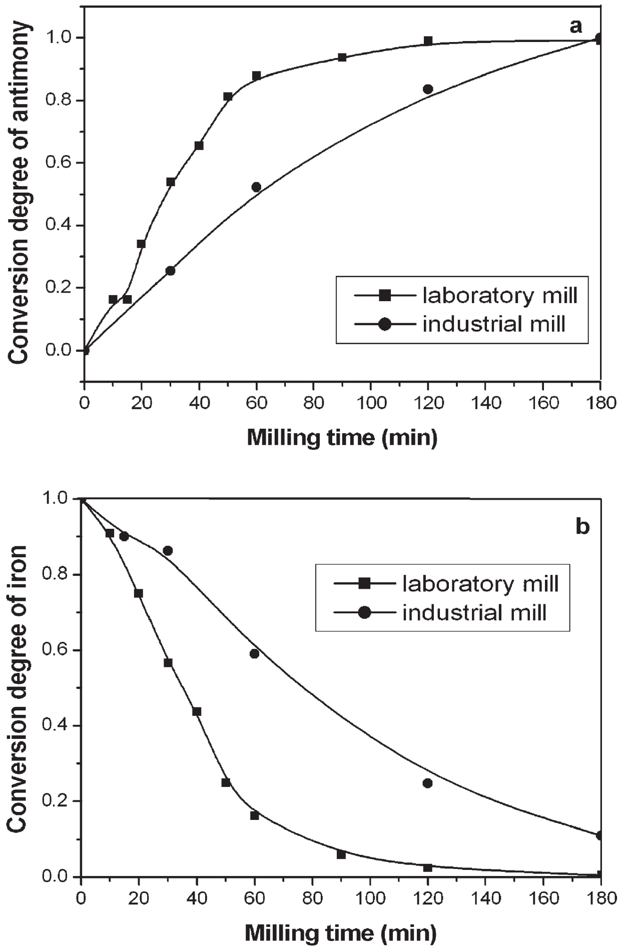

Fig. 2. Conversion degree of reaction (1) for antimony (a) and iron (b) calculated from normalized XRD line intensities as a function of milling time.

The XRD line widths of the sample milled in the laboratory mill for 180 min have been analysed in order to confirm the presence of nanometric particles. The grain size of Sb was found to be 19 nm with 0.35% residual strain and the particle size of FeS is about 10 nm. It is consistent with the TEM image, that also shows the strongly agglomerated nature of the powder [17]. The agglomeration of nanoparticles is a general phenomenon originating from the tendency to reduce the surface area.

Figure 3 shows the room-temperature magnetization data for the investigated samples as a function of external magnetic field. It is evident that the resulting magnetization curves are well saturated after the application of a magnetic field higher than 2 T. The variation of the saturation magnetization as a function of milling time, as displayed in Fig. 4, reflects the amount of metallic iron, the only ferromagnetic component in the samples. In good agreement with the XRD results shown in Fig. 2, the Fe fraction decreases continuously for milling times up to 180 min,

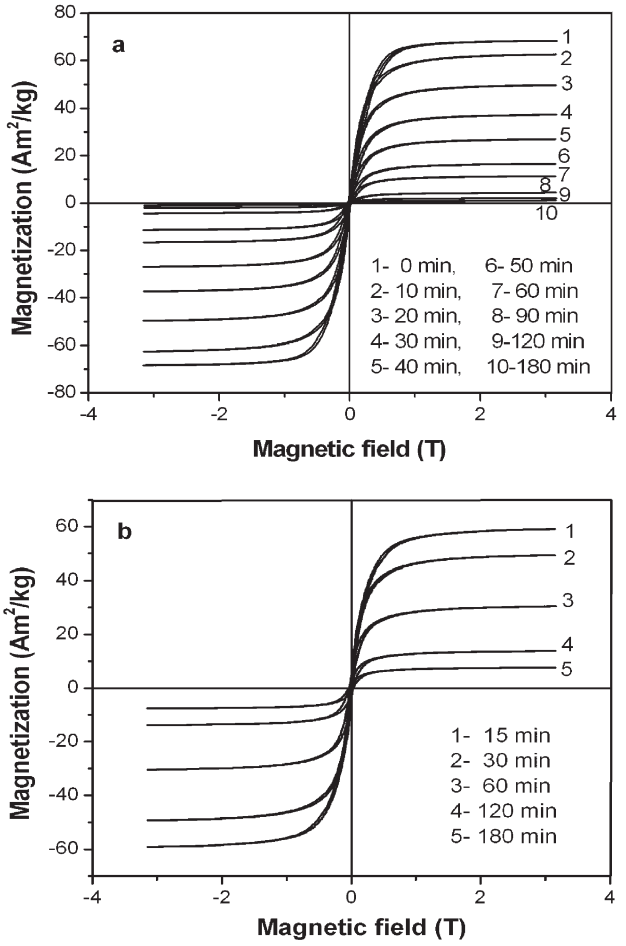

Fig. 3. Magnetization as a function of external magnetic field for several milling times in the laboratory mill (a) and in the industrial mill (b).

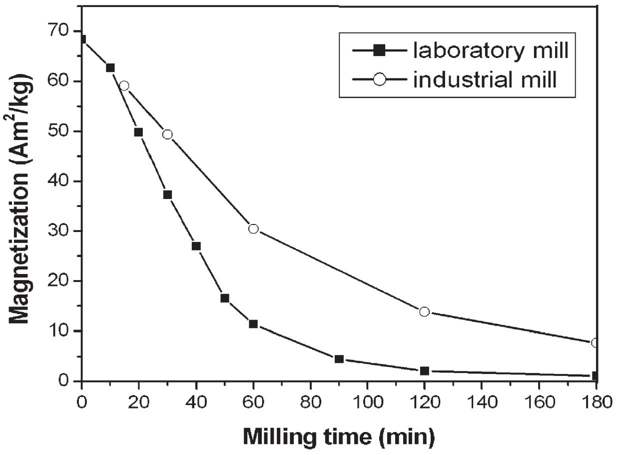

Fig. 4. Saturation magnetization as a function of milling time.

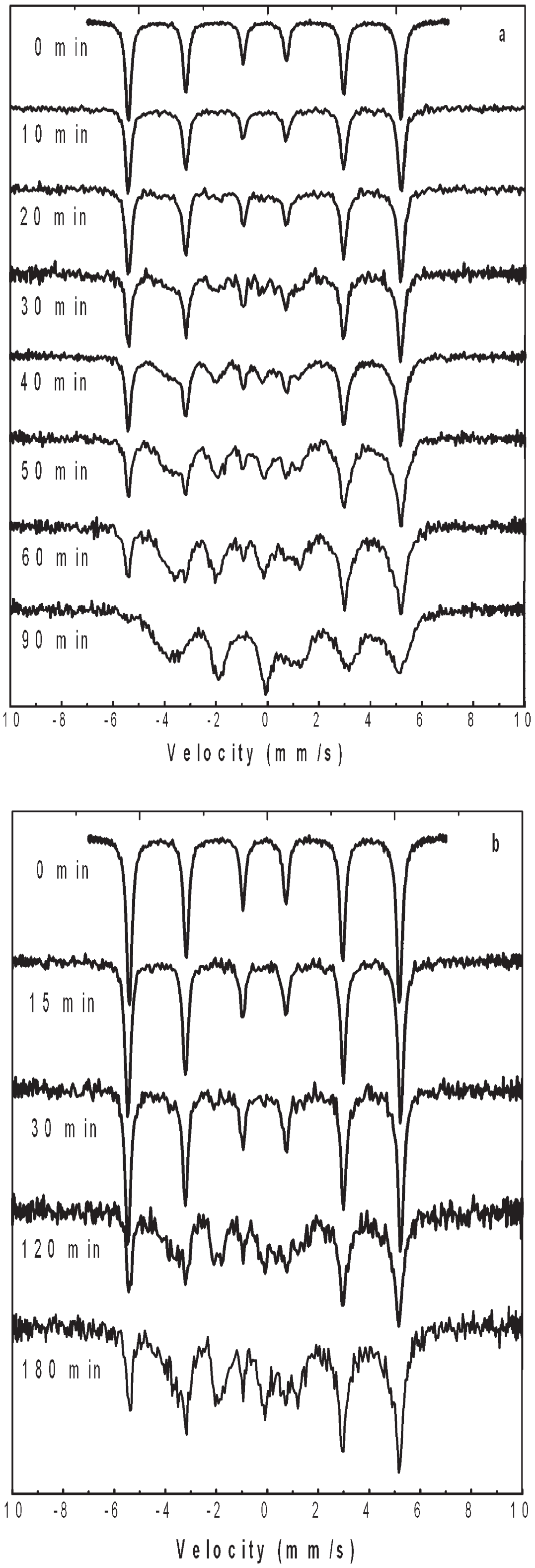

Fig. 5. Mössbauer spectra for reaction (1) performed in the laboratory mill (a) and in the industrial mill (b).

with more than 88% being transformed during the first 60 min. After 180 min of milling, the saturation magnetization is negligible, indicating that the constituent phases are almost entirely paramagnetic and/or anti-

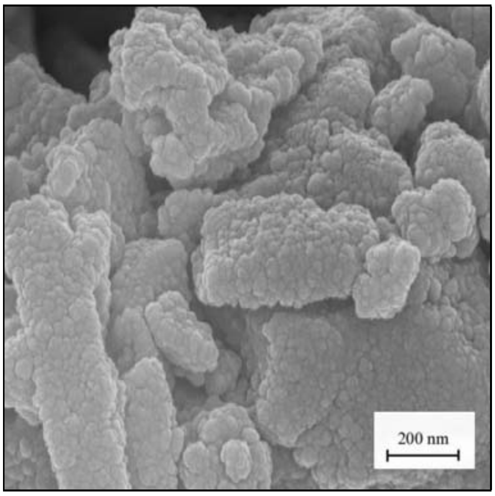

Fig. 6. SEM image of products of the reaction (1); milling time 180 min.

ferromagnetic, i.e. reaction (1) is practically complete. The efficiency of milling in the industrial mill is lower as compared to the laboratory mill.

The Mössbauer spectra of the samples are presented in Fig. 5. As can be seen, Mössbauer spectrum of the starting mixture shows one sextet with hyperfine field $B = 33.04$ T corresponding to metallic iron. With increasing milling time, the sextet becomes broader and disappears gradually. The Mössbauer spectra of the mixture milled for longer time than 30 min exhibit additional spectral components. This can be interpreted as the mechanochemical formation of a new iron-containing phase. The broad spectral lines of the product(s) of mechanochemical reaction indicate that the new phase is structurally disordered. It should be noted that the new phase is magnetically ordered at room temperature as demonstrated by the presence of the sextet structure in its Mössbauer spectrum.

The surface morphology of the mechanochemically prepared Sb/FeS nanoparticles is depicted in Fig. 6. Individual cauliflower-like nanoparticles with the sizes ranging from 30 to 60 nm have a tendency to form agglomerates, and both entities can be clearly seen.

## 4. Conclusions

1. The Sb/FeS nanocomposite was prepared from $Sb_2S_3$ and Fe by mechanochemical reduction. The mechanochemical process is rather straightforward with elemental antimony (JCPDS 05-0562) and iron sulphide (pyrrhotite-4H, JCPDS 22-1140) being the only solid state products.

2. The process kinetics, as described by XRD, VSM and Mössbauer spectroscopy, shows that about 90% of the reduction is over after 60 min of milling and the reaction is complete after milling for 180 min in the laboratory mill.

3. The studied reaction performed in the industrial mill for 60 min resulted in only 52% conversion to antimony and the iron content is consumed more slowly than in the case of reduction performed in the laboratory mill. The mechanochemical reduction after 180 min of milling is not yet finished in the industrial mill.

4. Unlike the conventional high-temperature reduction of antimony sulphide, the mechanochemical reduction is very fast and ambient temperature and atmospheric pressure are sufficient for its propagation.

5. The mechanochemical reduction of $Sb_2S_3$ with elemental iron is a suitable system for a large-scale mechanochemical preparation of nanocomposite even if the kinetics of mechanochemical reduction is slower.

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