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Preparation of nanosized antimony by mechanochemical reduction of antimony sulphide Sb_2S_3

P. Baláž [a,*], L. Takacs [b], E. Godočíková [a], I. Škorvánek [c], J. Kováč [c], W.S. Choi [d]

[a] *Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia*
[b] *University of Maryland Baltimore County, Department of Physics, Baltimore, MD 21250, USA*
[c] *Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 043 53 Košice, Slovakia*
[d] *Pusan National University of Korea, Pusan 609 735, South Korea*

Abstract

The preparation of nanosized antimony (grain size 19 nm) by high-energy milling of antimony sulphide Sb_2S_3 with elemental Fe as reducing element is reported. The mechanochemical reduction was performed in a planetary ball mill for 10–180 min. The process is rather straightforward with elemental antimony and iron sulphide (pyrrhotite-4H) being the only solid-state products. The process kinetics as described by X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) magnetometry shows that most of the reduction is complete after 60 min of milling.

Keywords: Metals; Nanostructures; High-energy ball milling; Mechanochemical synthesis

1. Introduction

A wide variety of techniques are being used to synthesize nanocrystalline materials. One of them is high-energy milling that has a potential for easy scale-up to large quantities [1–7]. Matteazzi and Le Caër [8] were the first to study high-energy ball milling in mixtures of a sulphide and a reducing metal in order to obtain nanostructures. They demonstrated that the mechanochemical reduction of metal sulphides MeS (Me = Fe, Cu, Co, Pb, Zn) with suitable reducing metal was feasible using room temperature vibratory milling. The reduction of CuS with Ti, Zr and Hf was studied by Takacs [6]. It was shown that these reactions take place as mechanically induced self propagating reactions [6], as indicated by a characteristic sudden temperature increase as a function of milling time.

The kinetics of the mechanochemical reduction of MeS (Me = Fe, Cu, Pb) with elemental iron and silicon as well as the magnetic properties of the obtained systems have been studied by Baláž et al. [9–12].

The direct reduction of antimony sulphide by milling has not been studied before. Conventionally, antimony sulphide is reduced via high temperature annealing in the presence of reducing agents such as hydrogen or iron. Torma and Inal [13] have investigated the reduction with hydrogen at atmospheric pressure and at temperatures between 473 and 873 K. Only 60% of Sb_2S_3 was converted to metallic antimony. The reduction with elemental iron is possible at temperatures 773–823 K but the process is inefficient because the antimony sulphide dissolves in the already formed iron sulphide [14]. The yield of both processes is low, they need high temperatures and the products have large grain size.

The aim of the present work is to study the mechanochemical reduction of antimony sulphide Sb_2S_3 with elemental iron at ambient temperature, according to the equation

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS \qquad (1)$$

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

2. Experimental

2.1. Synthesis

Mechanochemical reduction of antimony sulphide Sb_2S_3 with elemental iron as reducing element (1) was performed in a planetary mill Pulverisette 6 (Fritsch, Germany). Tungsten carbide (WC) grinding chamber of 250 ml volume and 50

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[*] Corresponding author. Tel.: +421 55 79 22603; fax: +421 55 79 22604.
E-mail address: balaz@saske.sk (P. Baláž).

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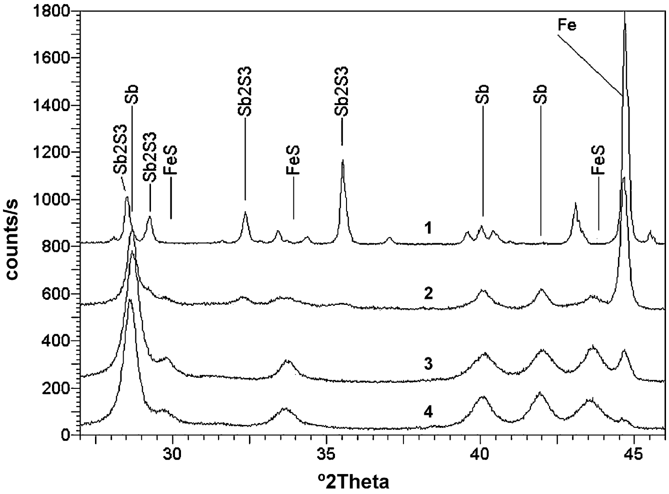

Fig. 1. XRD patterns as a function of milling time. 1-Stoichiometric mixture of Sb_2S_3 and Fe before milling. The milling times for patterns 2–4 are 20, 60 and 120 min, respectively.

WC balls of 10 mm diameter (total weight 360 g) were used. Weight of powder for milling was 3 g. The rotation speed of the planet carrier was 500 rev/min. Milling times between 10 and 180 min were applied. The atmosphere inside the milling chamber was argon.

2.2. Characterization techniques

X-ray diffraction (XRD) measurements were carried out using a Philips X'Pert diffractometer, working in the Θ–Θ geometry with Cu Kα radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. Magnetization data were obtained by employing a vibrating sample magnetometer (VSM) equipped with a superconducting coil. A maximum magnetic field of 3 T was applied in order to assure the magnetic saturation of specimens at room temperature. Transmission electron microscopy was carried out using a Jeol-2000FX instrument at an acceleration of 200 kV.

3. Results and discussion

The progress of the mechanochemical reduction of antimony sulphide Sb_2S_3 by elemental iron is illustrated by the selected XRD patterns in Fig. 1. The process is rather straightforward with elemental antimony Sb (JCPDS 05–0562) and FeS (pyrrhotite-4H, JCPDS 22–1120) being the only solid-state products. The intensity of the metal iron reflexion (1 1 0) decreases upon continued milling and only a very small amount of iron is detectable at 60 min (pattern 4). There is a small hump at $2\Theta = 31$–$32°$ which originates from tungsten carbide abraded from the balls during milling. In the starting material (pattern 1) more small peaks are seen which belong to stibnite Sb_2S_3 (JCPDS 42–1393).

The conversion degree for precursors (Sb_2S_3, Fe) and product (Sb) of reaction (1) as obtained by normalization of the XRD intensities is shown in Fig. 2. It is clear that most of the reduction is complete after 60 min with the intensity of Sb_2S_3 decreasing faster than 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.

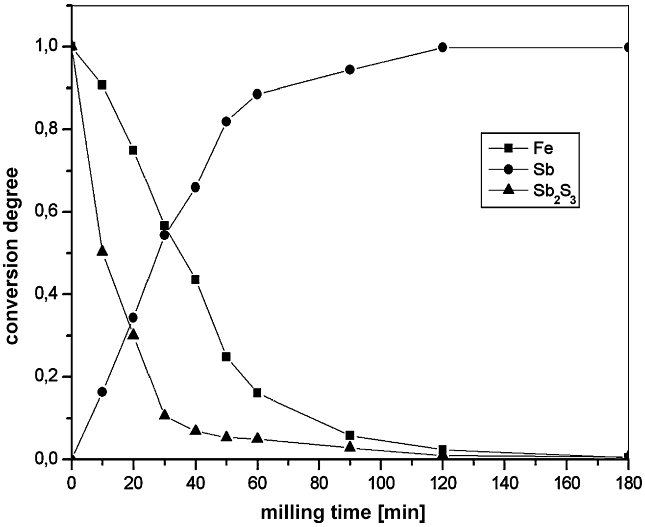

Fig. 2. The conversion degree for precursors (Sb_2S_3, Fe) and product (Sb) of reaction (1) calculated from normalized of XRD line intensities.

Fig. 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 the inset of Fig. 3, 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, with more than 80% 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 antiferromagnetic, i.e. reaction (1) is practically complete.

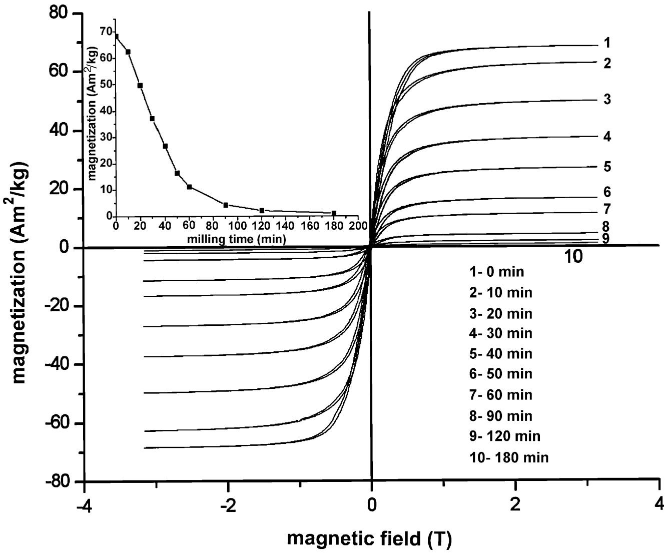

Fig. 3. Magnetization as a function of external magnetic field for several milling times. The inset shows the saturation magnetization as a function of milling time.

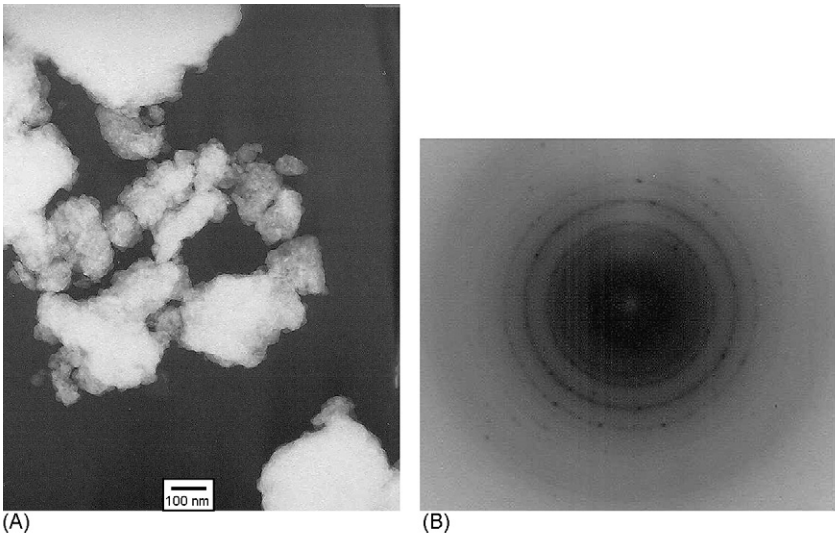

Fig. 4. (A) Dark field TEM image and (B) SAED pattern of (Sb + FeS) nanoparticles formed by mechanochemical reduction of Sb_2S_3 with Fe during 180 min of milling.

The XRD line widths of the sample milled for 180 min have been analyzed 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. Fig. 4A shows a typical dark field TEM image obtained using beams from the diffraction rings of the irregular shaped nanoparticles formed during 180 min of milling. Fig. 4B shows the SAED pattern of an area containing some nanoparticles. The SAED pattern shows a set of rings instead of spots due to the random orientation of the nanoparticles. The TEM image is consistent with the XRD grain size but also shows the strongly agglomerated nature of the powder. The agglomeration of nanoparticles is a general phenomenon originating from the tendency to reduce the surface area.

4. Conclusions

(1) Nanocrystalline antimony (grain size 19 nm) was prepared from antimony sulphide Sb_2S_3 and elemental iron by mechanochemical reduction.
(2) The process is rather straightforward with elemental antimony (JCPDS 05–0562) and iron sulphide (pyrrhotite-4H, JCPDS 22–1140) being the only solid-state products.
(3) The process kinetics as described by the XRD and VSM methods shows that more than 80% of the reduction is over after 60 min of milling and the reaction is complete after 180 min of milling.

Acknowledgements

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