

# MECHANOCHEMICAL REDUCTION OF ANTIMONY SULPHIDE $Sb_2S_3$ WITH MAGNESIUM IN A PLANETARY MILL

E. Godočiková<sup>1</sup>, L. Takacs<sup>2</sup>, P. Baláž<sup>1</sup>, J. Kováč<sup>3</sup>, A. Šatka<sup>3</sup> and J. Briančin<sup>1</sup>

<sup>1</sup>Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia

<sup>2</sup>University of Maryland Baltimore County, Department of Physics, Baltimore, MD 21250, USA

<sup>3</sup>Department of Microelectronics, Slovak University of Technology and International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovakia

Received: March 29, 2008

**Abstract.** Nanosized antimony was prepared by mechanochemical reduction of antimony sulphide ( $Sb_2S_3$ ) with elemental Mg. High-energy milling was performed in a planetary ball mill for 10-120 min. The composition and properties of the obtained powders were analyzed by XRD, specific surface area measurements and SEM. Most of the reaction took place as a self-sustaining reaction between 20 and 30 min, with only microstructural changes occurring during additional milling. Mechanochemical reduction is a very straightforward, one-step, ambient temperature process that can be readily utilized to make Sb nanoparticles.

## 1. INTRODUCTION

Mechanically induced chemical reactions attracted considerable scientific and technical interest in recent years due to the unique nanostructures and properties obtainable by this process. It is usually carried out in high-energy ball mills that can be scaled-up to large quantities relatively easily [1-3]. High-energy milling of a metal sulphide with a more reactive metal can result in the reduction of the sulfide. The mechanochemical reduction of metal sulphides MeS (Me = Fe, Cu, Pb, Sb) with elemental iron and silicon has been studied recently [4-7].

Ultrafine Mo particles can be produced as a result of the slow burning transition into detonation in the  $MoS_2$ -Mg mixture [3]. However, the mechanochemical reduction of antimony sulphide with elemental magnesium under ambient temperature has not been studied before.

The conventional method of preparing antimony involves the reduction of antimony sulphide at high

temperature, using a reducing agent such as hydrogen or iron [8,9]. Antimony nanoparticles have been prepared recently, using electrodeposition, solvothermal, and gas-evaporation method,  $\gamma$ -ray radiation as well as a self-assembly technique [10-12]. Nanosized metal powders are expected to display better properties than powders with coarser grains in applications like catalysis and recording.

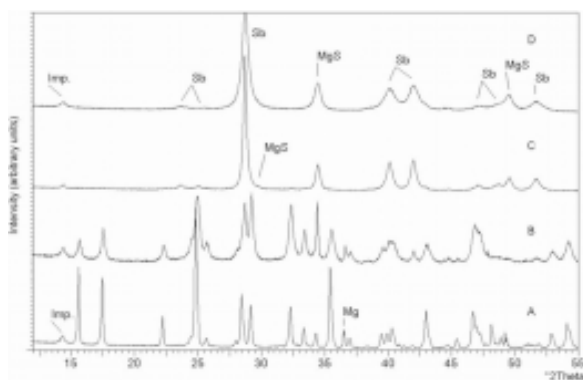
The aim of the present work is to study the mechanochemical reduction of antimony sulphide ( $Sb_2S_3$ ) with elemental magnesium at ambient temperature in a laboratory planetary mill.

## 2. EXPERIMENTAL

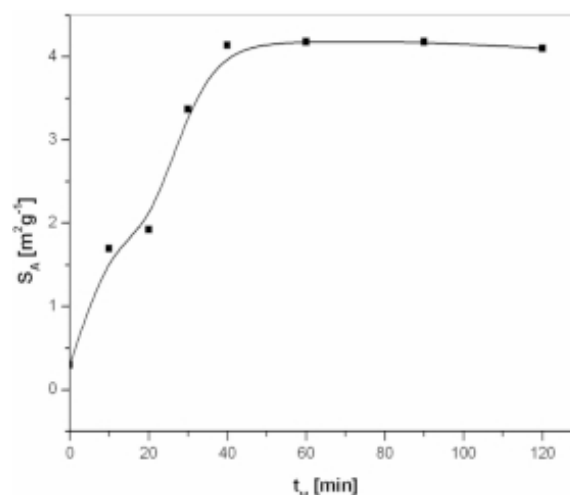
### 2.1. Synthesis

Mechanochemical reduction of antimony sulphide  $Sb_2S_3$  (98%) with elemental magnesium (s.p.) as reducing element in a ratio corresponding to equation (1) was performed in a Pulverisette 6 labora-

Corresponding author: E. Godočiková, e-mail: godocik@saske.sk

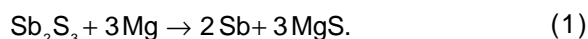


**Fig. 1.** XRD patterns as the function of the milling time. A-stoichiometric mixture of  $Sb_2S_3$  and Mg before milling. The milling times for patterns B-D are 20 min, 30 min and 120 min, respectively.



**Fig. 2.** Specific surface area as the function of the milling time.

tory 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 120 min were applied. The atmosphere inside the milling chamber was argon. The mechanochemical reaction between antimony sulphide  $Sb_2S_3$  and elemental magnesium Mg is described by the equation



The reaction is thermodynamically possible, as the enthalpy change for reaction (1) is negative,  $\Delta H_{298}^\circ = -872.4 \text{ kJ mol}^{-1}$  [13].

## 2.2. Characterization techniques

X-ray diffraction measurements were carried out using a Philips X'Pert diffractometer (the Netherlands), working in  $\theta$ - $\theta$  geometry with  $CuK_\alpha$  radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. The grain sizes of the particles were calculated using the Williamson-Hall method [14]. The specific surface area was determined by the low temperature nitrogen adsorption method in a sorption apparatus Gemini 2360 (Micromeritics, USA). The morphology of the samples was analyzed using FE-SEM LEO 1550 scanning microscope (Germany). The samples were not covered with any conductive material in order to avoid artefacts.

## 3. RESULTS AND DISCUSSION

The progress of the mechanochemical reduction of antimony sulphide ( $Sb_2S_3$ ) by elemental magnesium is illustrated by XRD patterns of the starting powder (A) and taken after 20 (B), 30 (C), and 120 (D) min of milling (Fig. 1). Pattern A is dominated by stibnite,  $Sb_2S_3$  (JCPDS 75-1310); all the unmarked lines correspond to this phase. The (101) peak of magnesium (JCPDS 35-0821) and an unidentified peak at about  $14.3^\circ$  are also visible. This latter line probably originates from an inert impurity that does not participate in the reaction. There is very little chemical change during the first 20 min of milling, although the presence of some rhombohedral Sb metal (JCPDS 35-0732) is indicated by the (012) peak at  $28.7^\circ$  and the (110) peak at about  $42^\circ$ . The most obvious change is the broadening of the diffraction peaks.

There is a qualitative difference between patterns B and C, indicating a fast chemical change between 20 and 30 min. It seems that most of the reaction takes place as a self-sustaining reaction some time between 20 and 30 min; the transformation is practically complete at 30 min. This is not surprising. The ratio of the reaction heat to the room temperature heat capacity is about 4660K and values above 2000K indicate the possibility of a self-sustaining reaction [2]. Elemental antimony and magnesium sulphide, MgS (niningerite, JCPDS 35-0730) are the only solid state products. The lines are relatively narrow after 30 min of milling, sug-

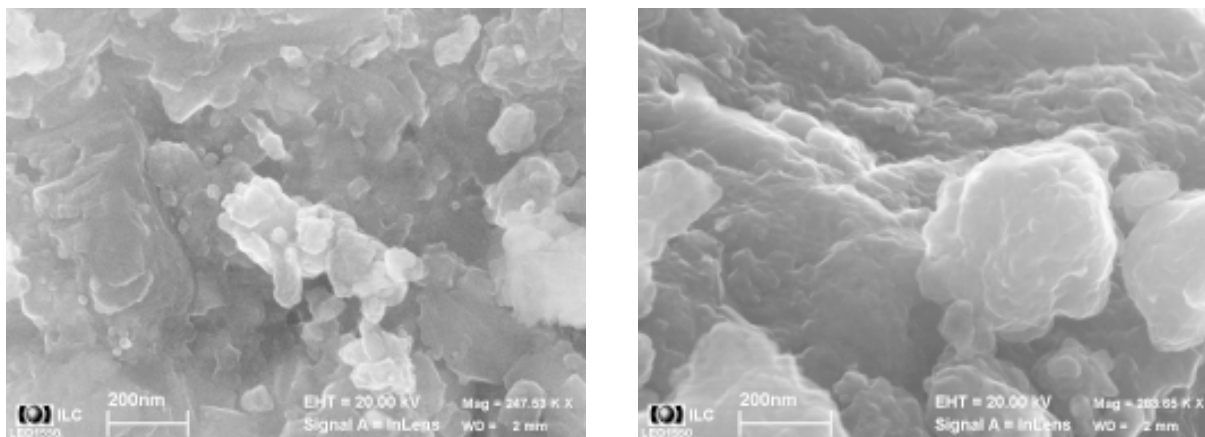


Fig. 3. SEM image of Sb/MgS nanoparticles; milling time 30 (A) and 120 (B) min.

gesting that a high temperature process resulted in larger particles. Only the line broadening changes between 30 min and 120 min.

The reaction proceeds according to Eq. (1) without intermediate phases and it is completed in 30 min. Due to the small degree of transformation before 20 min, a small amount of  $\text{Sb}_2\text{S}_3$  remains after at least 30 min of milling. A small peak at  $43.2^\circ$  is the only sign that a minor amount of  $\text{Sb}_2\text{S}_3$  is present after 30 min. Probably a small fraction of Mg was oxidized and therefore not available as reducing agent. The X-ray patterns were measured up to  $120^\circ$ , but we opted for showing a narrower range of angles with better resolution.

The detailed analysis of XRD patterns has been performed in order to determine grain sizes and strains using the Williamson-Hall method [14]. During the first 20 min the particle size of stibnite decreases, down to 65 nm after 10 min and 35 nm after 20 min of milling. The random strain is less than 0.1% as expected of a brittle substance. Right after the reaction at 30 min, the particle size is 130 nm with 0.3% strain. The strain remains the same until 90 min, the particle size drops to 25 nm and remains about the same from 40 min to 90 min. There is a little extra broadening after 120 min of milling, providing 18 nm particle size and 0.35% strain.

The dependence of the specific surface area on milling time is shown in Fig. 2. Two stages of the formation of new specific surface area can be identified. In the first period of up to 30 min, the specific surface area increases; the effect of the reaction is not obvious.

After 40 min the surface area is approximately constant, suggesting a dynamic equilibrium between particle fracturing and agglomeration [15]. In these examples of polydisperse systems the presence of very fine particles along with relatively coarse particles greatly facilitates the formation of aggregates, due to the enhanced role of the van der Waals forces. Particles in the nanometer size range have a strong tendency to agglomerate due to their relatively large specific surface area.

The surface morphology of the mechanochemically prepared Sb/MgS nanoparticles is depicted in Fig. 3, where the agglomeration of nanoparticles can be clearly seen. The agglomeration increases with the increasing milling time. The solid state combination of nanoparticles into agglomerates is a general phenomenon; one of the ways a nanocrystal system is able to compensate for its unsaturated surface forces via surface reconstruction.

#### 4. CONCLUSIONS

1. Nanocrystalline antimony was prepared from antimony sulphide  $\text{Sb}_2\text{S}_3$  and elemental magnesium by mechanochemical reduction.
2. The process is rather straightforward with elemental antimony (JCPDS 35-0732) and magnesium sulphide (ningerite, JCPDS 35-0730) as the only solid state products.
3. Mostly self-sustaining reaction took place between 20 and 30 minutes; the transformation was almost complete at 30 min.

4. Unlike the conventional high-temperature reduction of antimony sulphide the mechanochemical reduction is fast and it takes place at ambient temperature and atmospheric pressure.

## ACKNOWLEDGEMENTS

The support through projects VEGA 2/5151/5, Center of Excellence NANOSMART and Slovak State programme (SP-26) is gratefully acknowledged.

## REFERENCES

- [1] C. Suryanarayana // *Progr. Mater. Sci.* **46** (2001) 1.
- [2] L. Takacs // *Progr. Mater. Sci.* **47** (2002) 355.
- [3] E. Gaffet and G. Le Caër, In: *Mechanical processing for nanomaterials, Encyclopedia of Nanoscience and Nanotechnology*, ed. by H.S. Nalwa (American Scientific Publishers, 5, 2004), p. 91.
- [4] P. Baláž, L. Takacs, J.Z. Jiang, V. Soika and M. Luxová // *Mater. Sci. Forum* **386-388** (2002) 257.
- [5] E. Godočiková, P. Baláž, E. Boldížárová, I. Škorvánek, J. Kováč and W.S. Choi // *Journal of Materials Science* **39** (2004) 5353.
- [6] P. Baláž, E. Boldížárová and E. Godočiková // *Mater. Science Forum* **480-481** (2005) 453.
- [7] P. Baláž, L. Takacs, E. Godočiková, I. Škorvánek, J. Kováč and W.S. Choi // *J. Alloys Comp.* **434-435** (2007) 773.
- [8] A.E. Torma and O.T. Onal // *J. Less- Common Metals* **64** (1979) 107.
- [9] F. Habashi, *Extractive Metallurgy, Vol. 3 – Pyrrrometallurgy* (Gordon and Breach, New York, 1986).
- [10] L. Li, G.H. Li, Y. Zhang, Y.W. Yang and L.D. Zhang // *J. Phys. Chem. B* **108** (2004) 19380.
- [11] W.Q. Zhang, L.Q. Xu, G.C. Xi, W.C. Yu and Y.T. Qian // *Chem. Lett.* **33** (2004) 1476.
- [12] Y.W. Wang, B.H. Hong, J.Y. Lee, J.S. Kim, G.H. Kim and K.S. Kim // *J. Phys. Chem. B* **108** (2004) 16723.
- [13] O. Kubaschewski and L.L. Evans, *Metallurgical Thermochemistry* (London, Pergamon Press, 1955).
- [14] G.K. Williamson and W.H. Hall // *Acta Metall.* **1** (1953) 22.
- [15] P. Baláž, *Extractive Metallurgy of Activated Minerals* (Elsevier, Amsterdam, 2000).