Mechanochemical reduction of metal sulphides with magnesium in a planetary mill

E. Dutková[1]*, P. Baláž[1], J. Kováč[2], A. Šatka[2]

[1] *Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovak Republic*
[2] *Department of Microelectronics, Slovak University of Technology and International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovak Republic*

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Abstract

The mechanochemical reduction of copper sulphide (Cu_2S), zinc sulphide (ZnS), lead sulphide (PbS), and antimony sulphide (Sb_2S_3) with elemental magnesium Mg in a planetary mill has been studied. Metallic Cu, Zn, Pb, and Sb are obtained due to the reducing power of Mg. It is demonstrated that Mg can successfully be used to fully reduce Cu_2S, Sb_2S_3, and not fully reduce ZnS and PbS in only 60 minutes of milling. The Me/MgS nanocomposites have been characterized by XRD and SEM methods. Mechanochemical reduction is a very straightforward, one-step, ambient temperature process that can be readily utilized to make Me/MgS nanocomposites.

K e y w o r d s: metal sulphides, mechanochemical reduction, magnesium, nanocomposites

1. Introduction

Recently, mechanochemical processing via high-energy milling has been reviewed as a means of the synthesis of a wide variety of nanocrystalline materials [1–3]. The chemical reactions occur at the interfaces of the nanometersize grains that are continually regenerated during milling. High-energy milling with a reactive metal can initiate the transformation of metal sulphides via so-called mechanochemical reduction. The properties of produced powders with dimensions in nanorange are considerably different from those of polycrystalline powders prepared by conventional methods. High-energy milling has a potential for easy scale-up to large quantities [4–8]. The mechanochemical reduction of metal sulphides MeS (Me = Fe, Cu, Pb, Sb) with elemental iron and silicon has been studied recently [9–15]. Such as-formed Me/FeS nanocomposites are of interest as prospective materials for precursors of catalyst for heterogeneous chemical reactions [16]. The mechanochemical reduction of antimony sulphide with elemental magnesium under ambient temperature has already been studied [17].

The aim of the present work is to study the mechanochemical reduction of copper sulphide (Cu_2S), zinc sulphide (ZnS), lead sulphide (PbS), and antimony sulphide (Sb_2S_3) with elemental magnesium at ambient temperature in a laboratory planetary mill and to compare the kinetics process of these four different systems performed under the same conditions.

2. Experimental

2.1. S y n t h e s i s

Mechanochemical reduction of metal sulphides Cu_2S, ZnS, PbS, and Sb_2S_3 with elemental magnesium as reducing element in a ratio corresponding to Eqs. (1)–(4) was performed in a Pulverisette 6 laboratory planetary mill (Fritsch, Germany). A 250-ml tungsten carbide (WC) milling chamber and 50 WC balls of 10 mm diameter (total weight 360 g) were used. The speed of the planet carrier was set to 500 rpm. Milling time 60 minute was applied. The atmosphere inside the milling chamber was argon. The mechanochemical reduction of metal sulphides with elemental mag-

*Corresponding author: tel.: +421 55 7922606; fax: +421 55 7922604; e-mail address: dutkova@saske.sk

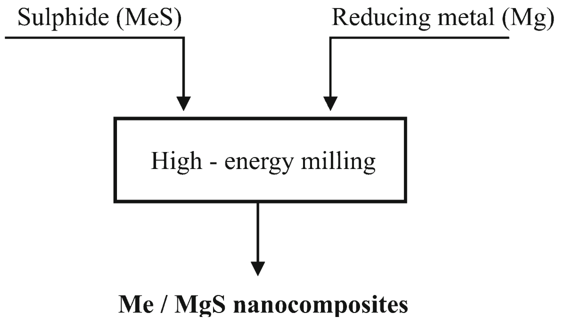

Fig. 1. Flowsheet of the Me/MgS nanocomposite preparation.

nesium has been performed according to the flowsheet given in Fig. 1.

2.2. Characterization techniques

X-ray diffraction measurements were carried out using a Philips X'Pert diffractometer (the Netherlands), working in Θ-Θ geometry with Cu Kα radiation. Comparing the measured patterns to the JCPDS data cards identified the XRD lines. The morphology of the samples was analysed 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

3.1. The copper/magnesium sulphide system

The mechanochemical reduction of copper sulphide with elemental magnesium can be described by the equation

$$Cu_2S + Mg \xrightarrow{\text{milling}} 2Cu + MgS. \qquad (1)$$

The reaction is thermodynamically feasible at the ambient temperature, as the enthalpy change for the reaction (1) is negative. The value $\Delta H^{\circ}_{298} = -266$ kJ mol^{-1} was calculated from the thermodynamic data published in [18].

XRD analysis (Fig. 2) revealed that after 60 minutes of mechanochemical reduction of copper sulphide with magnesium are only present the reaction products – elemental copper Cu (JCPDS 04-0836) and magnesium sulphide MgS (niningerite, JCPDS 35-0730). It follows from that the conversion degree to elemental copper for 60 minutes is 100 %.

SEM image of the synthesized Cu/MgS nanocomposites is seen in Fig. 3. According to the observed sur-

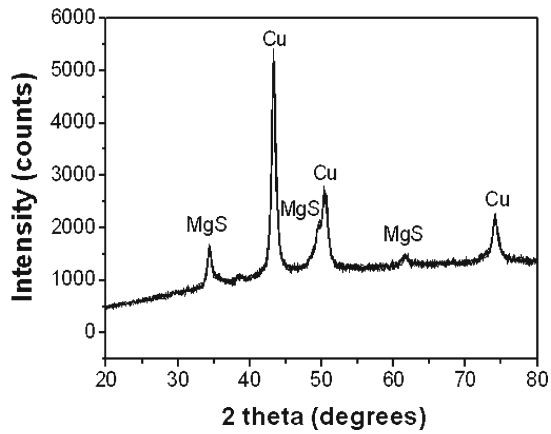

Fig. 2. XRD pattern of Cu/MgS nanoparticles; milling time 60 min.

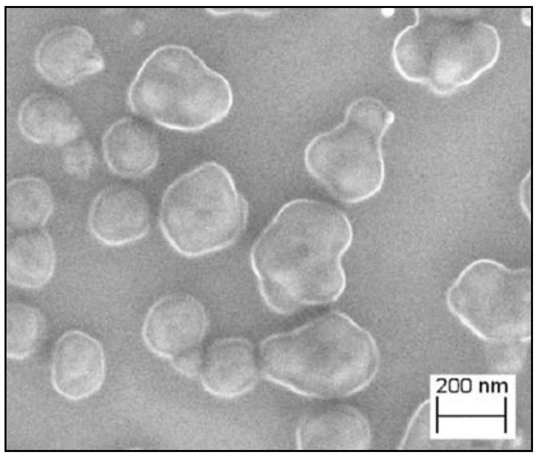

Fig. 3. SEM image of Cu/MgS nanoparticles; milling time 60 min.

face morphology individual nanoparticles have tendency to form nanoparticle agglomerates during milling process.

3.2. The zinc/magnesium sulphide system

The mechanochemical reduction of zinc sulphide with elemental magnesium can be described by the equation

$$ZnS + Mg \xrightarrow{\text{milling}} Zn + MgS. \qquad (2)$$

The reaction is thermodynamically feasible at the ambient temperature, as the enthalpy change for reaction (2) is negative. The value $\Delta H^{\circ}_{298} = -141$ kJ mol^{-1} was calculated from the thermodynamic data published in [18]. The mechanochemical

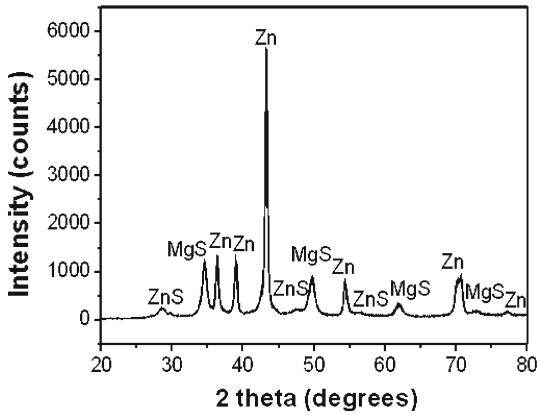

Fig. 4. XRD pattern of Zn/MgS nanoparticles; milling time 60 min.

reaction (2) for 60 minutes of milling studied by XRD analysis is depicted by the XRD pattern in Fig. 4.

The primary process – the reduction of zinc sulphide ZnS by elemental magnesium while zinc metal Zn (JCPDS 04-1831) and magnesium sulphide MgS (niningerite, JCPDS 35-0730) are formed – is clearly seen as well as a very small amount of ZnS (JCPDS 05-0566) is present after 60 min of milling. The conversion degree defined as the ratio $I_{Zn}/(I_{Zn} + I_{ZnS})$ was calculated on the basis of XRD data. 96 % conversion to zinc metal was achieved during the 60 min of milling.

Surface morphology of the synthesized Zn/MgS nanoparticles is depicted in Fig. 5. Individual nanoparticles have tendency to form nanoparticle agglomerates during milling process and both entities can be clearly seen.

3.3. The lead/magnesium sulphide system

The mechanochemical reduction of lead sulphide with elemental magnesium can be described by the equation

$$PbS + Mg \xrightarrow{\text{milling}} Pb + MgS. \tag{3}$$

The reaction is thermodynamically feasible at the ambient temperature, as the enthalpy change for reaction (3) is negative. The value $\Delta H^{\circ}_{298} = -248\,\text{kJ}\,\text{mol}^{-1}$ was calculated from the thermodynamic data published in [18].

The course of the mechanochemical reduction between lead sulphide PbS and magnesium Mg is illustrated by the XRD pattern in Fig. 6. The lines of the elemental lead Pb (JCPDS 04-0686) and a small amount of the magnesium sulphide MgS (niningerite, JCPDS 35-0730) were observed. A possible explanation is the partial amorphization of MgS that is indeed manifested in an increased background of the XRD pattern. However, after 60 min of milling, the relative amount of lead sulphide PbS (galena, JCPDS 05-0592) is also present. It is clear that most of the reduction is complete after 60 min with the intensity of PbS decreasing slower than the Mg. In XRD pattern are also present PbO (massicot, JCPDS 38-1477) as a product of partial oxidation and SiO_2 (JCPDS 33--1161) as a consequence of ball cleaning after previous milling operations.

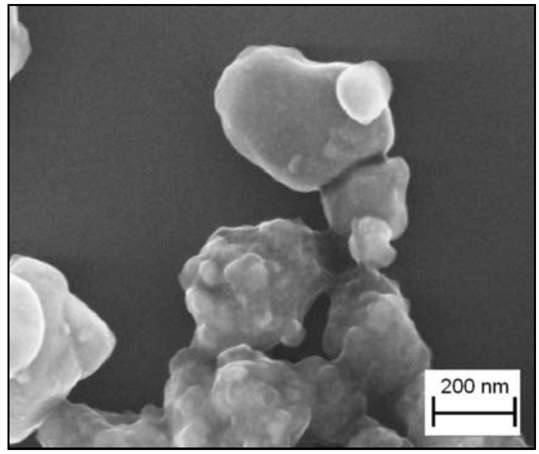

Fig. 5. SEM image of Zn/MgS nanoparticles; milling time 60 min.

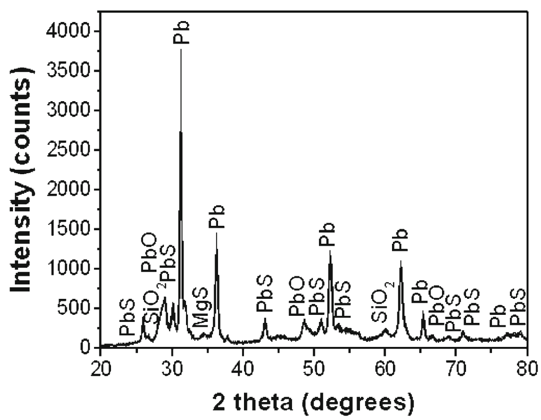

Fig. 6. XRD pattern of Pb/MgS nanoparticles; milling time 60 min.

Evaluation of the reaction kinetics was based on XRD data. The conversion degree, β, was defined as the ratio $I_{Pb}/(I_{Pb} + I_{PbS})$, where I_{Pb} and I_{PbS} are the intensities of the Pb (111) and PbS (200) diffraction lines. After 60 min of milling, the 88 % conversion to lead was achieved.

SEM of the mechanochemical products Pb/MgS is given in Fig. 7. SEM analysis reveals a non--homogeneous distribution of nanoparticles that have irregular shape and a strong tendency to agglomeration.

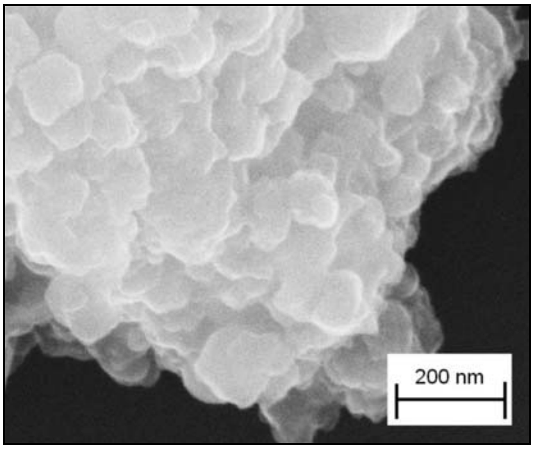

Fig. 7. SEM image of Pb/MgS nanoparticles; milling time 60 min.

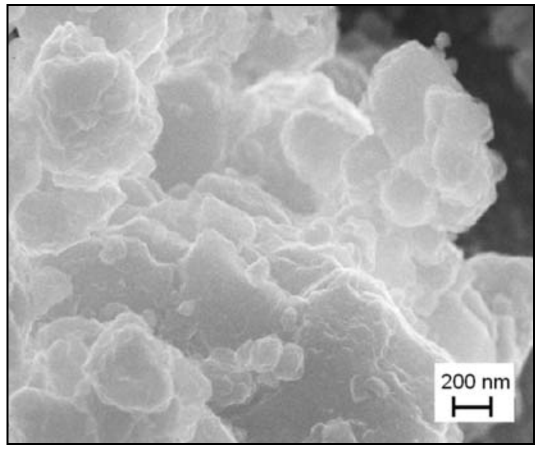

Fig. 9. SEM image of Sb/MgS nanoparticles; milling time 60 min.

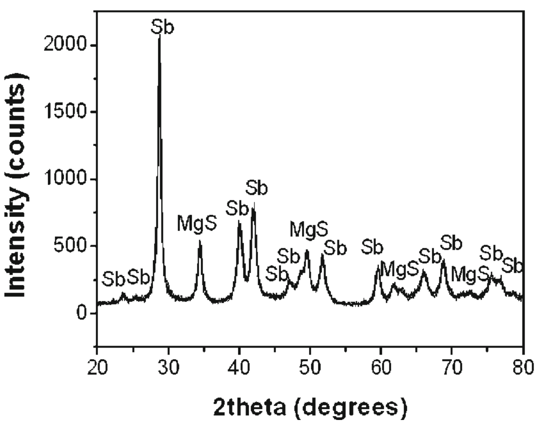

Fig. 8. XRD pattern of Sb/MgS system milled for 60 min.

3.4. The antimony/magnesium sulphide system

The mechanochemical reduction of antimony sulphide with elemental magnesium can be described by the equation

$$Sb_2S_3 + 3Mg \xrightarrow{\text{milling}} 2Sb + 3MgS. \qquad (4)$$

The reaction is thermodynamically feasible at the ambient temperature, as the enthalpy change for reaction (4) is negative. The value $\Delta H^{\circ}_{298} = -872\,\mathrm{kJ\,mol^{-1}}$ was calculated from the thermodynamic data published in [18].

The products of the mechanochemical reduction of antimony sulphide (Sb_2S_3) with elemental magnesium are illustrated by XRD pattern taken after 60 min of milling (Fig. 8). Elemental antimony Sb (JCPDS 35-0732) and magnesium sulphide MgS (niningerite, JCPDS 35-0730) are the only solid-state products. The process kinetics of this system and reaction mechanism has been studied in paper [16]. Most of the reaction took place by a self-sustaining reaction. The reaction kinetics based on XRD data shows that milling of this system for 60 min resulted in 100 % conversion to elemental antimony.

The surface morphology of the mechanochemically prepared Sb/MgS nanoparticles is depicted in Fig. 9, where the agglomeration of nanoparticles can be clearly seen. The solid-state combination of nanoparticles into agglomerates is a general phenomenon and represents a way that nanocrystal system compensates its unsaturated surface forces via surface reconstruction.

4. Conclusions

Cu/MgS, Zn/MgS, Pb/MgS, and Sb/MgS nanocomposites were prepared from corresponding metal sulphides and elemental magnesium by mechanochemical reduction. The mechanochemical process is rather straightforward with elemental copper, zinc, lead, and antimony, respectively, and magnesium sulphide being the only solid-state products. The process kinetics described by XRD shows that 100 % of the reduction is complete after 60 min of milling in the case of Cu/MgS and Sb/MgS system. 96 % conversion to Zn and 88 % conversion to Pb resulted after 60 min in the case of Zn/MgS and Pb/MgS, respectively. In these systems Mg content is consumed faster than ZnS and PbS content, respectively. 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. Unlike the conventional high-temperature reduction of metal sulphides the mechanochemical reduction is fast and ambient temperature and atmospheric pressure are sufficient for its propagation. The mechanochemical reduction of MeS with Mg is a suitable system for a large-scale mechanochemical preparation.

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