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Mechanochemical reduction of lead sulphide by elemental iron

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Metallic lead as well as cubic pyrrhotite were produced by the mechanochemical reduction of lead sulphide with elemental iron during milling in a planetary mill Pulverisette 6 (Fritsch, Germany) as a result of the reducing power of iron. The reaction kinetics has been examined by X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). The surface properties have been characterized by transmission electron microscopy (TEM). The process of mechanochemical reduction of lead sulphide is quite more straightforward due to the monophase nature of the lead sulphide precursor. Both products are present in the form of Pb/FeS nanoparticles and the average grain size of the freshly formed lead is between 13–21 nm depending on the milling conditions. Unlike the conventional high-temperature reduction of lead sulphide, the mechanochemical reduction is very fast and ambient temperature and atmospheric pressure are sufficient for its propagation.
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1. Introduction
Mechanochemical processing belongs to a group of novel synthesis routes which were applied as high-energy processes to prepare nanocrystalline materials [1, 2]. The mechanochemical reduction for the preparation of products with advanced materials properties is an example of such processes. The mechanochemical reduction of metal oxides and metal chlorides with a more reactive metal has already been studied [3–6], but relatively a few studies of the sulphide mechanochemical reduction have been presented [7, 8].

The conventional high-temperature lead recovery process from lead sulphide is based on reduction with iron scrap [9]. Recently, Szczygiel *et al.* [10] have obtained 92–94% lead recovery by the direct reduction of lead sulphide with elemental iron in the temperature interval 1000–1150 °C for 180 min.

However, the mechanochemical reduction of lead sulphide with elemental iron under ambient temperature has not been studied so far. The reaction can be described by the equation

$$PbS + Fe \rightarrow Pb + FeS \qquad (1)$$

The aim of this work is to study the kinetics of reaction (1) and the properties of the obtained products.

2. Experimental
Mechanochemical reduction of the lead sulphide (particle size $<200 \mu m$) with elemental iron as reducing element (particle size $<100\ \mu m$) was performed in a planetary mill Pulverisette 6 (Fritsch, Germany). The following milling conditions were used: loading of the mill with 50 balls (weight 360 g) of 10 mm diameter; material of grinding chamber and balls: tungsten carbide; rotation speed of the planet carrier: 500 rpm; time of milling in an argon atmosphere: 10–180 min. The X-ray diffraction (XRD) measurements were carried out using a diffractometer DRON 2.0 (Russia) with goniometer GUR 5 and Fe K_α radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. The conversion degree, β was defined as $\beta = [I_{Pb}/(I_{Pb} + I_{PbS})] \cdot 100$ (%), where I_{Pb} and I_{PbS} are the intensities of the Pb[111] and PbS[200] diffraction lines. Magnetization data were obtained by employing a vibrating 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. Transmission electron microscopy (TEM) was performed using a Jeol-2000FX TEM microscope.

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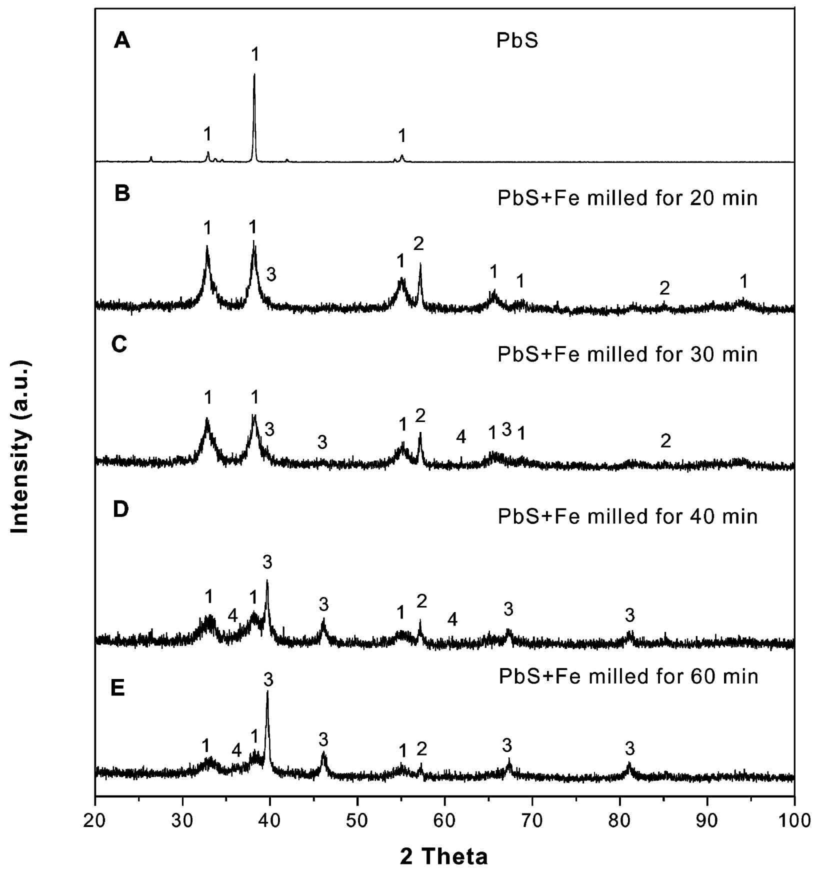

Figure 1 XRD patterns at different stages of reaction (1) as a function of milling time, A: PbS, B–E: PbS + Fe milled for 20–60 min (1—lead sulphide, 2—iron, 3—lead, 4—FeS (cubic)).

3. Results and discussion

The mechanochemical reaction between lead sulphide and iron is illustrated by the XRD patterns in Fig. 1. The primary process—the reduction of lead sulphide by iron while lead metal and iron sulphide are formed- is clearly seen. After 20 min of milling, the relative amount of lead sulphide decreased and the lead is formed as indicated by the diffraction peak at 39.9° (JCPDS-04-0686). The process kinetics as described by the conversion degree, β is shown in Fig. 2.

Only 19% conversion to lead metal was achieved during the initial 20 min of milling. The intensity of the iron (JCPDS-06-0696) and lead sulphide (JCPDS-78-1897) reflections decreases upon continued milling, but these phases are detectable even after 60 min of milling. After 60 min of mechanical treatment, the reflections from lead metal and cubic FeS (JCPDS-23-1123) can be observed and 75% conversion to lead was achieved.

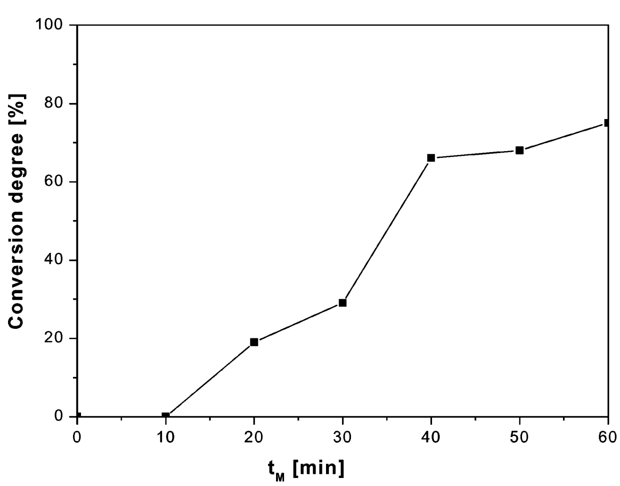

Figure 2 Conversion degree, β, as a function of milling time.

It is evident that the magnetization curves are well saturated after the application of a magnetic field higher than 2 T (Fig. 3). The difference in the saturation magnetization of the samples milled for different times, as displayed in the inset of this figure, is mainly caused by the different amount of the ferromagnetic component in these samples. As indicated by the X-ray diffraction data, the only ferromagnetic components is bcc-Fe. The inset in Fig. 3 shows that the amount of metallic iron in our specimens decreases continuously for milling times up to 180 min. For longer milling times the saturation magnetization is negligible indicating that the constituent phases are almost entirely paramagnetic and the mechanochemical reduction is complete.

The reaction products are present in the form of nanocrystalline particles. Particle size of 13–21 nm for lead (estimated from XRD linewidth using the Scherrer formula) have been obtained. Fig. 4 shows a typical TEM image of the polydisperse Pb/FeS nanoparticles formed by mechanochemical reduction of lead sulphide with iron during 60 min. Examination of TEM shows that the as-milled powder is composed of spherical and rod-like particles. Dimension of spherical particles are close to that determined by XRD.

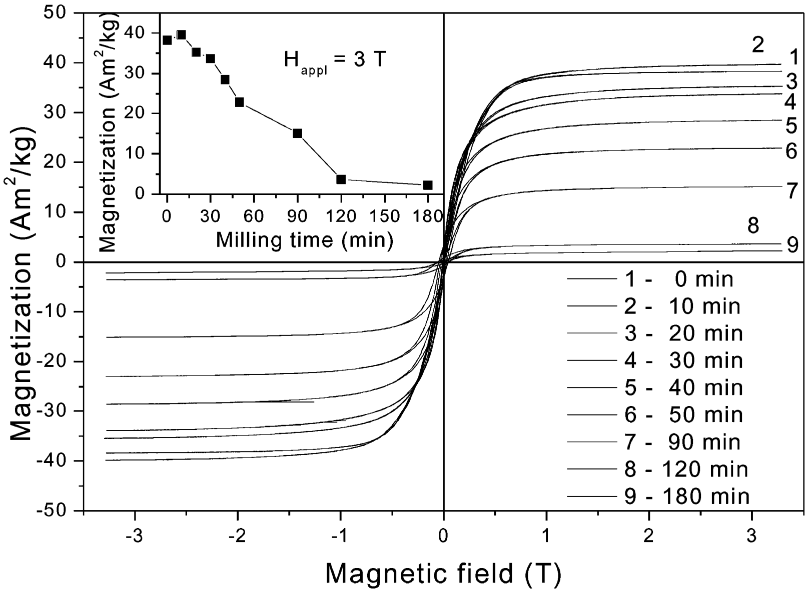

Figure 3 Magnetization as a function of external magnetic field and kinetics of the mechanochemical reduction (inset in Fig. 3).

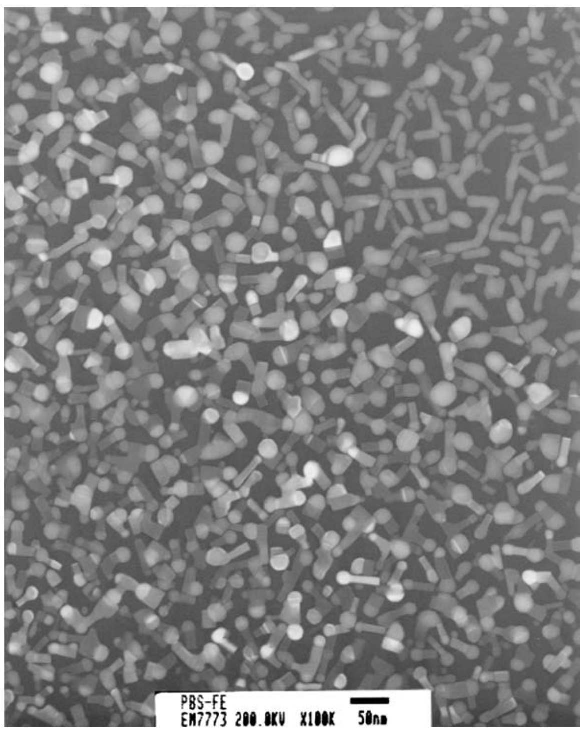

Figure 4 TEM image of the Pb/FeS nanoparticles formed by mechanochemical reduction of lead sulphide with iron during 60 min.

Acknowledgments
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