JOURNAL OF MATERIALS SCIENCE **39** (2004) 3025–3029

A study of mechanochemical reduction of lead sulphide by elemental iron on the surface by X-ray photoelectron spectroscopy

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The mechanochemical reduction of lead sulphide with elemental iron in a high-energy mill was studied. X-ray photoelectron spectroscopy was used for characterization of obtained products of reduction. Elemental lead as well as its divalent forms were identified in the surface layer of products of mechanochemical reduction. The mechanochemical reduction of lead sulphide with elemental iron on the surface is a complicated reaction and the identification of compounds formed in the surface layer is not unambiguous.

However, only 23% of elemental lead on the surface is produced. The degree of mechanochemical transformation in the surface layer is not very high under chosen conditions. Higher power input is needed for further progress of the reaction.

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1. Introduction

Mechanochemical processing belongs to novel synthesis routes which were introduced recently as a high-energy process to prepare nanocrystalline materials. The mechanochemical processing is generally defined as the high energy ball milling of powder materials [1].

Mechanochemical processing induces significant changes in behaviour of the activated solid materials which include increasing of leaching rate and leaching efficiency, decreasing of the treatment temperature and reaction time, growing of surface activity and achieving of better catalytic action, synthesis of new materials, improvement of sinterability and production of more rigid materials [2].

The utilization of mechanical effect for preparation of new advanced materials can be mentioned among the latest applications [3]. Here belong such sophisticated materials as amorphous alloys, superconducting materials, rare earth permanent magnets, superplastic alloys and intermetallic compounds with nanometer-sized dimension [4].

These approaches eliminate high-temperatures as well as wet processing of metals and their production is accomplished by the low-temperature dry process directly from the solid phase (so called "solid state" or "dry" technologies, as reactions in gas and liquid phases are excluded) [5].

Various interesting and advanced materials can be prepared by mechanochemical processing of different inorganic compounds [1, 6–11].

The mechanochemical reduction for preparation of the products with properties of advanced materials is an example of such processes.

The mechanochemical treatment of lead sulphide with elemental Fe has been studied [12]. X-ray diffraction has been applied to analysis of the products of mechanochemical reduction of lead sulphide which proceeds according to Equation 1.

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

The peaks of product phases elemental lead and pyrrhotite FeS as well as residual iron were observed in the XRD patterns. The reduction process is very fast and ambient temperature and atmospheric pressure are sufficient for its propagation. However, the

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surface products in this process have not been studied so far.

X-ray photoelectron spectroscopy (XPS), as a powerful surface analytical tool, can be used to obtain information about the elemental composition of the outermost atom layers of the milled mixture and the chemical binding state.

The aim of this work is to apply the method of XPS for identification of the products of mechanochemical reduction of lead sulphide which proceeds according to Equation 1.

2. Experimental

For the mechanochemical reduction of lead sulphide by reaction (1) the following starting materials were used: stoichiometric amounts of PbS (particle size under 200 μm) and elemental iron as the reducing element (particle size under 100 μm).

The starting mixture (5 g) was milled in a planetary mill Pulverisette 6 (Germany) under the following conditions: 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 rev$\cdot$min^{-1}; time of milling in argon atmosphere: 30 and 60 min.

The photoelectron spectra were recorded in a VG ESCA 3 Mk II electron spectrometer. The pressure of residual gases was in the $<10^{-6}$ Pa range. The XPS measurements were performed using Al K_α radiation (1486.6 eV) source at a power of 220 W. The spectrometer was operated in a fixed analyser transmission mode with a pass energy of 20 eV. The XPS spectra were collected and analysed using a PC/AT computer. The binding energies were measured relative to the C(1s) line of carbon ($E_B = 284.8$ eV) used as internal standard for spectral calibration and for the correction of charging effects.

The spectral intensities were converted to the surface elemental concentrations after subtracting the background according to Shirley [13]. The ratios of atomic concentrations were determined by correcting the photoelectron peak areas for their cross sections [14] and by taking into account the dependence of photoelectron mean free path and analyzer transmission on electron kinetic energy [15]. The overlapping spectral features were resolved into the individual components of Gaussian-Lorentzian shape using a modified version of the damped non-linear squares procedure published by Hughes and Sexton [16].

The binding energy data were estimated with an error limit to be ± 0.2 eV. The estimated accurancy of the calculated ratios of atomic concentrations amounts $\pm 10\%$.

3. Results and discussion

The presence of elements in the surface layers of lead sulphide and products of its mechanochemical reduction milled for 30 and 60 min in the form of XPS survey spectrum is presented in Fig. 1.

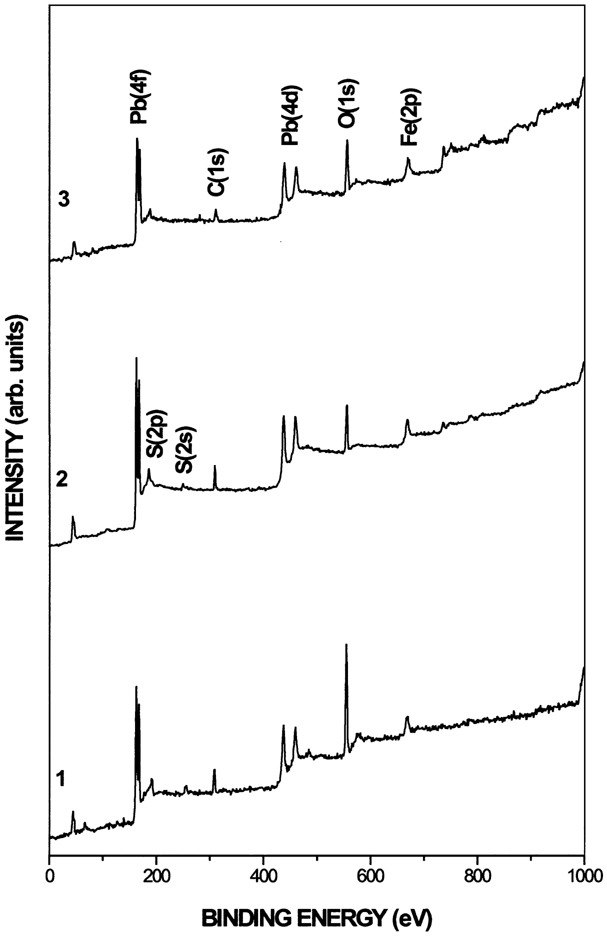

Figure 1 XPS survey spectrum of lead sulphide (1) and products of its mechanochemical reduction milled for 30 (2) and 60 (3) min.

Besides Pb, S and Fe, other elements such as C and O can be identified as well. The occurrence of C and O is a consequence of CO_2 and O_2 adsorption from the air.

The spectra of Pb(4f), S(2s) and Fe(2p) electrons were measured in the high-resolution regime and were analyzed in more detail.

The spectra of Pb(4f) electrons of lead sulphide (1) and products of mechanochemical reduction of lead sulphide with elemental iron milled for 30 (2) and 60 (3) min are shown in Fig. 2.

The results of the curve fitting of the spectra of Pb(4f) electrons are summarized in Table I.

The spectra of S(2s) photoelectrons of lead sulphide and products of its mechanochemical reduction are displayed in Fig. 3.

The results of the XPS quantitative analysis of S(2s) spectra are listed in Table II.

TABLE I Values of binding energies (E_B) and atomic concentration of lead compounds (c) in the lead sulphide surface and in the products of its mechanochemical reduction surface

	Pb(4f)		
Sample	E_B (eV)	c (at.%)	Form of lead in sample
PbS (0 min) (1)	139.2	83	Pb^{2+} ($PbSO_4$)
	137.4	17	Pb^{2+} (PbS)
PbS + Fe (30 min) (2)	138.4	100	Pb^{2+} (PbS or PbO)
PbS + Fe (60 min) (3)	138.4	77	Pb^{2+} (PbS or PbO)
	136.6	23	Pb^0

TABLE II Values of binding energies (E_B) and atomic concentration of lead compounds (c) in the lead sulphide surface and in the products of its mechanochemical reduction surface

S(2s)			
Sample	E_B (eV)	c (at.%)	Form of sulphur in sample
PbS (0 min) (1)	231.6 225.2	82 18	S^{6+} (PbSO$_4$) S^{2-} (PbS)
PbS + Fe (30 min) (2)	225.4	44	S^{2-}(PbS or FeS)
PbS + Fe (60 min) (3)	–	–	–

The spectra of Fe(2p) photoelectrons measured are displayed in Fig. 4.

The values of binding energies (E_B) and content of iron (c) in the milled mixture surface are described in Table III.

In the galena surface two chemical states of lead (Table I, Fig. 2) and sulphur (Table II, Fig. 3) can be seen. The observed binding energies of Pb(4f) peaks, 139.2 and 137.4 eV agree with values reported [17] for divalent lead in sulphate and sulphide, respectively. A similar situation can be observed in the case of S(2s) peaks, the binding energies 231.6 and 225.2 eV correspond to the values reported for hexavalent sulphur and divalent sulphur, respectively [17].

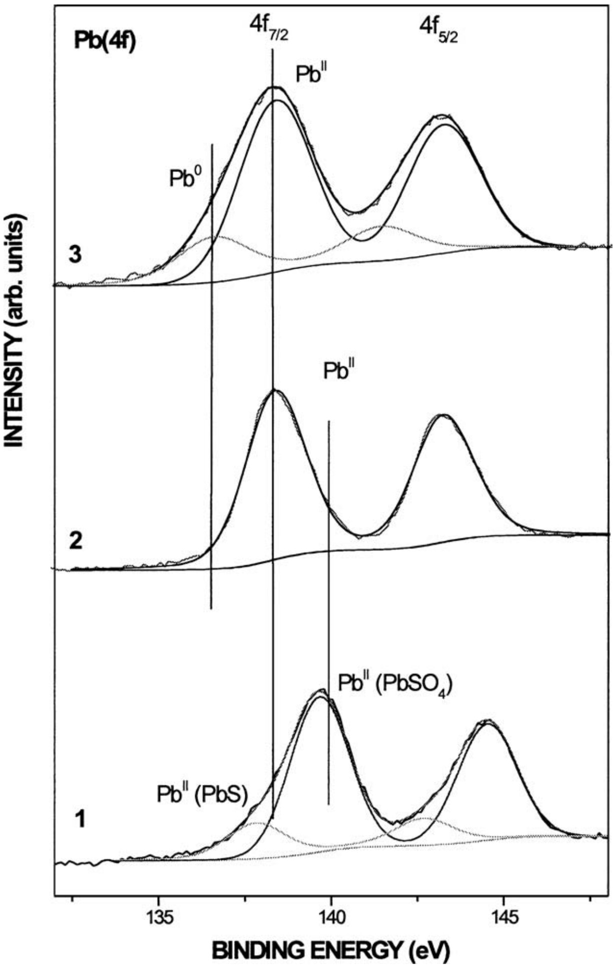

Figure 2 Fitted Pb(4f) core level spectra taken from lead sulphide (1) and products of its mechanochemical reduction milled for 30 (2) and 60 (3) min.

TABLE III Values of binding energies (E_B) and atomic concentration of lead compounds (c) in the lead sulphide surface and in the products of its mechanochemical reduction surface

Fe(2p)			
Sample	E_B (eV)	c (at.%)	Form of iron in sample
PbS + Fe (30 min) (2)	710.6	8	Fe^{2+}or Fe^{3+}(FeS, FeO or Fe$_2$O$_3$)
PbS + Fe (60 min) (3)	709.8	38	Fe^{2+}or Fe^{3+}(FeS, FeO or Fe$_2$O$_3$)

In Table I we can see that rather large amount of divalent lead (83%) in the form PbSO$_4$ and 17% of divalent lead in the form PbS are in accordance with the amounts of hexavalent sulphur (82%) and divalent sulphur (18%) (Table II). It follows from this finding that the lead sulphide surface is strongly oxidised in the sample used for mechanochemical reduction.

In the milled mixture during 30 min the divalent lead in the sulphide or oxide form is only present on the surface. The measured value of binding energy of the Pb(4f) peak ($E_B = 138.4$ eV) is characteristic of PbS and/or PbO [17]. The values of binding energies for PbS and PbO are almost equal (138 ± 0.2 eV) and therefore it is possible to assume that PbS as well as PbO can be formed on the surface.

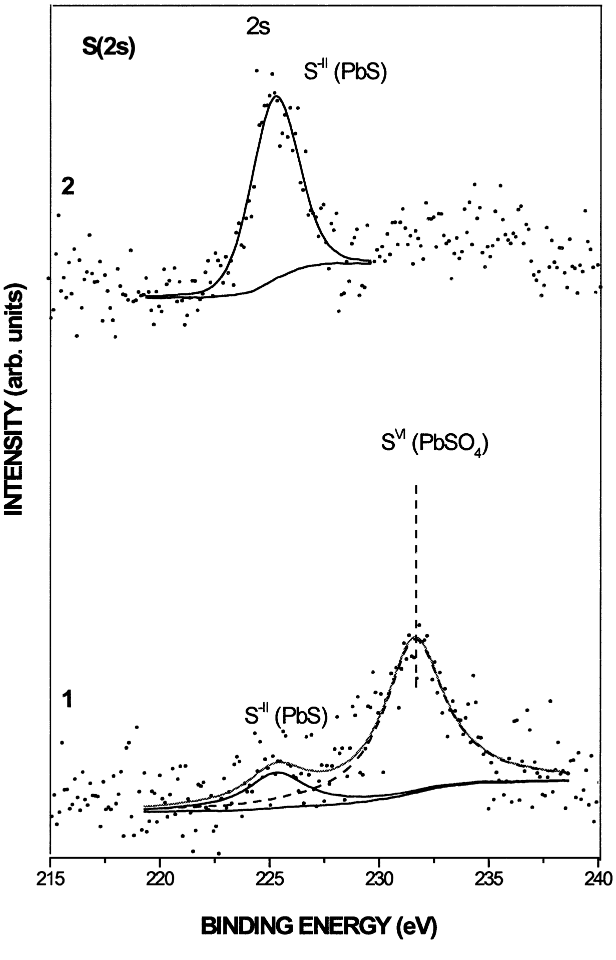

Figure 3 Fitted S(2s) core level spectra taken from lead sulphide (1) and products of its mechanochemical reduction milled for 30 min (2).

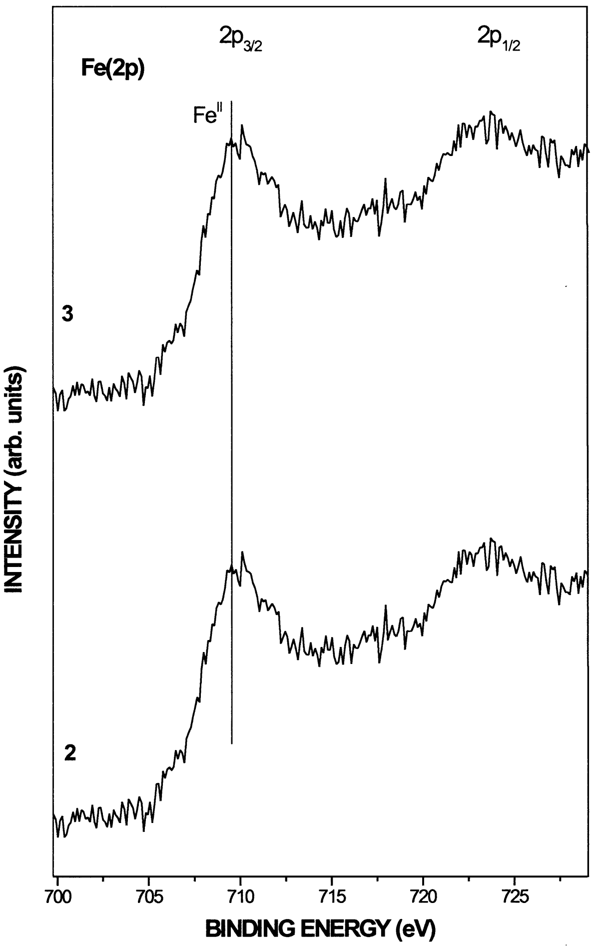

Figure 4 Spectra of Fe(2p) electrons of the products of mechanochemical reduction of lead sulphide milled for 30 (2) and 60 (3) min.

In accordance with Equation 1, elemental lead was not identified in this milled mixture on the surface. In the surface layer of the mechanochemical reduction products milled for 30 min oxidized iron with binding energy of Fe(2p$_{3/2}$) electrons at $E_B = 710.6$ eV (8%) (divalent or trivalent iron) is present, while elemental iron (as reducing element) was not identified. The value of $E_B = 710.6$ eV is in a good agreement with the values reported [17] for FeS in the products of reduction (Equation 1).

In the case of the surface composition of lead sulphide milled for 60 min we can observe two peaks of lead (Fig. 2, Table I). While the peak located at 138.4 eV corresponds to divalent lead (77%), the peak centered at 136.6 eV is typical of elemental lead (23%).

The spectrum (Fig. 1, (3)) showed no evidence of sulphur on the galena surface milled for 60 min. Its absence on the surface of milled mixture may be due to the sulphur occurring deeper in the bulk of milled mixture. This is in accordance with works of Balaz *et al.* [18, 19] who studied similar system and did not identify sulphur in the surface layer of products milled for a longer time. It follows from this that the amount of sulphur present in the surface decreases with increasing time of milling [18]. On the other hand sulphur in the surface was observed by EDX elemental microanalysis the sampling depth of which is much higher than that of XPS.

In the case of iron (Fig. 4, Table III) we can see the Fe(2p) peak at $E_B = 709.8$ eV, which corresponds to divalent or trivalent iron in the oxide or sulphide form. It is difficult to distinguish between divalent and trivalent iron because the values of binding energies of Fe(2p$_{3/2}$) electrons for FeS, FeO or Fe_2O_3 are very close. It is also difficult to distinguish PbS from FeS [20]. By comparison of the iron content (c) in the milled mixtures for 30 and 60 min we can see that the effective iron content on the surface increases from 8 to 38% (iron concentrations were calculated assuming homogeneous sample).

Mechanochemical reduction of lead sulphide with elemental iron on the surface is a complicated reaction and the identification of compounds formed in the surface layer is not unambiguous.

The surface of nanocrystalline products prepared by mechanochemical reduction of lead sulphide is probably very reactive and quickly undergoes surface oxidation leading to the formation of PbO, $PbSO_4$, FeO and Fe_2O_3.

While elemental lead and pyrhotite were identified among the products of reaction formed after 20 min of milling by XRD method [12], elemental lead was identified in the products of reaction formed until 60 min by XPS method which analyzes the samples to the depth of approx. 5 nm.

4. Conclusions

The mechanochemical reduction of lead sulphide by elemental iron on the surface was proven. Elemental lead as a result of reducing power of iron was proven by XPS method in the surface layer of products of mechanochemical reduction milled even after 60 min. However, only 23% of elemental lead on the surface is produced. The divalent lead as well as the divalent iron were also identified in the surface of PbS. Clear identification was not possible due to the similarities of their binding energies.

It follows from results that mechanochemical reduction of galena is not so pronounced on the surface as in the bulk. The degree of mechanochemical transformation is not very high under chosen conditions. Higher power input is needed for further progress of the reaction.

Acknowledgement

We would like to thank Mrs. Mária Galdová for technical assistance. The authors thank the Slovak Grant Agency VEGA (grant no. 2/2103/22), APVT-20-018402 and NANOSMART for financial support of this paper.

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Received 8 July 2003
and accepted 20 January 2004