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DIRECT REDUCTION OF MECHANICALLY ACTIVATED GALENA AND SPHALERITE WITH HYDROGEN

P. Balá [1] and J. Briančin[2]

[1]Institute of Geotechnics, Slovak Academy of Sciences, 043 53 Košice, Slovakia
[2]Institute of Material Research, Slovak Academy of Sciences, 043 57 Košice, Slovakia

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Abstract

In this paper the reduction of lead and zinc sulphide by hydrogen is described. It has been found that the rate of formation of elemental lead or zinc is favourably affected by mechanical activation of PbS and ZnS produced by intensive grinding. This effect was observed in the region 678–1048 K for galena and in the region 851–1023 K for sphalerite. It has appeared that disordering in the structure of both minerals results in the decrease in experimental activation energy.

Keywords: galena, hydrogen, lead, mechanical activation, sphalerite, thermal reduction, zinc

Introduction

The classical pyrometallurgical reduction of non-ferrous metals is based on application of solid state reducing agents such as carbon and lime. As for gaseous reducing agents, methane, carbon monoxide and lately hydrogen have been used. A survey of application of different reducing agents is given in paper [1].

In contrast to utilization of SO_2 in the form of H_2SO_4 involving problematic sale of sulphuric acid, the utilization of reduction products in the form of H_2S (which can be further utilized in the form of elemental sulphur and hydrogen) is more prospective and ecologically less objectionable.

In this study the results of experiments aimed at intensification of the reduction of galena (PbS) and sphalerite (ZnS) with hydrogen provided these sulphides were subjected to mechanical activation before reduction are presented. Mechanical activation was proved to be successful in our previous works for intensification of other thermal processes of sulphides such as oxidation, decomposition in inert atmosphere (pyrolysis) as well as sublimation [2–10].

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Experimental

The investigations were carried out with galena and sphalerite.

Galena originated from Banská Štiavnica (Slovakia) was of the following composition: 78.41% Pb, 13.74% S, 0.20% Cu, 0.71% Fe, 2.31% Zn and 1.56% insoluble rest. It was found by X-ray diffraction phase analysis that this sample contained galena (JCPDS 5-592) and minor amount of quartz (JCPDS 5-490).

Sphalerite originated from Zabaykal (Russia) was of the following composition: 44.60% Zn, 15.53% Fe, 33.58% S, 3.81% SiO_2 and 2.48% insoluble rest. It was found by X-ray phase analysis that the sample contained sphalerite (JCPDS 5-0566) and minor amounts of quartz (JCPDS 5-490) and pyrite (JCPDS 6-0710).

The samples of both minerals (–200 μm granularity each) were separately mechanically activated in a Pulverisette 4 (Fritsch, Germany) planetary mill under the following conditions: volume of grinding chamber 350 ml; mass of sample, 20 g; grinding balls of tungsten carbide (25 pieces of 10 mm diameter and 5 pieces of 25 mm diameter); relative acceleration of mill b/g, 10.3; grinding time 5, 10 and 15 min.

The thermal decomposition of both minerals was investigated in a dynamic reactor with a static layer of the solid phase, under the following conditions: weighed amount, 100 mg; volume flow rate of hydrogen, $0.67\cdot10^{-3}$ dm^3 s^{-1}; temperature: 937–1049 K for PbS and 851–1023 K for ZnS. The experimental details of the apparatus are given in [9].

The following conversion functions were used for primary kinetic characterization

$$\alpha=1-6\pi e^{-k_1t} \tag{1}$$

for galena reduction and

$$\alpha=k_2t^{1/2} \tag{2}$$

for sphalerite reduction, where α is the conversion degree calculated from the mass difference of sulphide samples before and after reduction, k_1, k_2 are rate constants and t is the reaction time.

Results and discussion

Galena (PbS)

In the eighties some papers dealing with the kinetics of reduction of galena with hydrogen appeared [11–14]. It was found on the basis of thermogravimetric investigations that a loss of mass of galena heated in hydrogen flow emerges already at temperatures over 773 K [11, 14]. The isothermal study [12] in the region 948–1098 K showed that the maximum rate of reduction took place at the commencement and was constant. At higher reaction times the rate decreased. The stoichiometry of the process in this region can be expressed by the following equations

$$PbS(s)+H_2(g) \rightarrow Pb(l)+H_2S(g) \qquad (3)$$

$$Pb(s) \rightarrow PbS(g) \qquad (4)$$

At temperature over 1023 K the reduced lead vaporizes. Reaction starts at 1058 K.

The degree of conversion of galena due to the reaction with hydrogen in our case is represented for a non-activated sample and a sample mechanically activated for 15 min in Figs 1 and 2. The reduction was investigated in the temperature interval 937–1048 K. Some differences between the above samples appeared only in the temperature range between 937 and 980 K. In agreement with Eq. (3), the surface of reacting particles was subjected to fusion at higher temperatures, as it is documented by the attached photomicrographs. In all cases, however, we can observe the maximum rate in the initial stage of reaction and the retardation at higher reaction time.

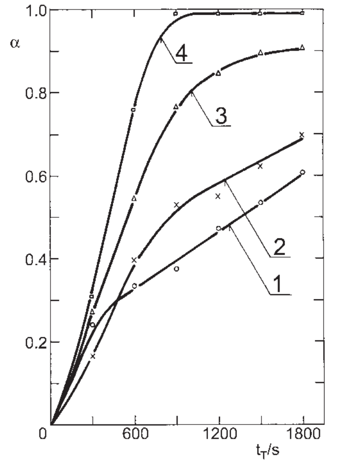

Fig. 1 The influence of the reaction time t_T on the conversion degree α of non-activated PbS. Reaction temperatures: 1 – 679 K; 2 – 980 K; 3 – 1023 K; 4 – 1048 K

The photomicrographs in Fig. 3 were taken for the samples of mechanically activated galena which were reduced at the temperatures of 937 K (B), 1048 K (C,E) and 1109 K (D,F). The photomicrograph of the sample before reduction is represented for comparison in Fig. 3A. If we apply the lowest temperature (B), we can observe that the porosity has remained preserved, but in comparison with non-ignited sample the proportion of smaller grains significantly decreased because of preferential reaction and consumption of these grains. We can observe that the pores are gradually closed at 1048 K (C) and this process continues at higher temperatures (D). If we apply smaller magnification (E, F) we can observe that the whole surface of particles is subjected to fusion. Owing to this fact, the reduction is retarded which is consistent with Eq. (1) and character of the kinetic curves in Figs 1 and 2. On the basis of X-ray phase analysis we identified lead (JCPDS 4-686) and monoclinic sulphur (JCPDS 13-141) in the products of decomposition.

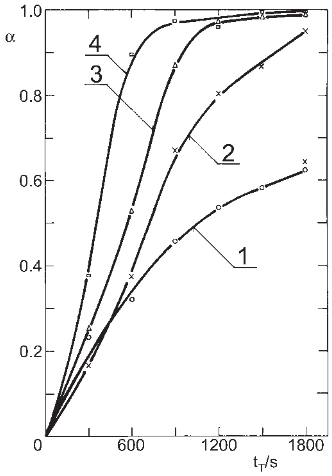

Fig. 2 The influence of the reaction time t_T on the conversion degree α of mechanically activated PbS for 15 min. Reaction temperatures: 1 – 679 K; 2 – 980 K; 3 – 1023 K; 4 – 1048 K

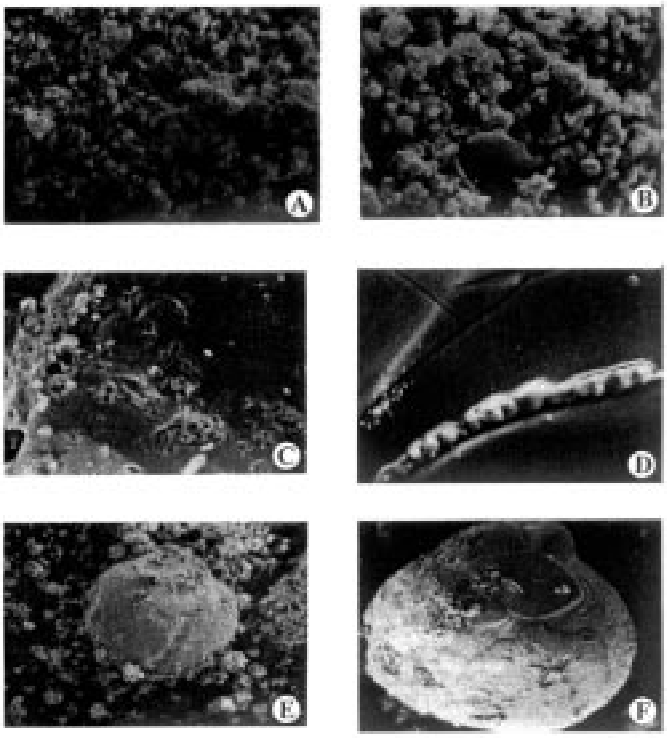

Fig. 3 Scanning electron micrographs of PbS (mechanical activation 15 min). Temperature: A – laboratory, B – 937 K, C and E – 1048 K, D and F – 1109 K. Magnification: A–D 6000×, E 950×, F 450×

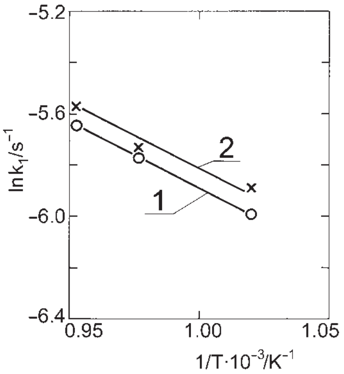

Fig. 4 The influence of mechanical activation of PbS on Arrhenius plot T=980–1048 K.
Time of mechanical activation: 1 – 0 min, 2 – 15 min

The Arrhenius plots for the reduction of galena represented in Fig. 4 were used for calculation of experimental activation energy which amounts to 42 kJ mol^{-1} for non-activated sample and 38 kJ mol^{-1} for the sample activated for 15 min (Table 1). The character of plots indicates that no change in mechanism due to temperature and/or structure disordering by mechanical activation takes place in the investigated temperature interval.

Table 1 Numerical processing of temperature-conversion data for PbS reduction

Mechanical activation/ min	$1/T\cdot10^3$/K^{-1}	$\ln k_1$/s^{-1}	Calculated parameters
	1.0203	–5.9932	E=42 kJ mol^{-1}
–	0.9774	–5.7733	A= –5.086 s^{-1}
	0.9533	–5.6531	r=0.99997
	1.0203	–5.8872	E=38 kJ mol^{-1}
15	0.9774	–5.7396	A= –4.587 s^{-1}
	0.9533	–5.5697	r=0.97899

E – activation energy, A – pre-exponential factor, r – regression coefficient

Sphalerite (ZnS)

In comparison with galena the reducibility of sphalerite is worse [15]. Jovanovič *et al.* has alleged that the degree of reduction of ZnS reaches the value α=0.35 for the temperature of 1070 K [14]. The process is complicated by the fact that zinc is evaporated in the hydrogen flow at high temperatures. At the same time hydrogen sulphide originating in the reaction of hydrogen with the sulphur atoms of sphalerite leaves the surface. At the temperatures between 1173 and 1223 K hydrogen sulphide can react with zinc vapour to form secondary ZnS [15–16].

Owing to the complicated mechanism, we chose the temperatures between 673 and 1023 K to study the influence of mechanical activation on the rate of reduction of sphalerite. In this temperature interval zinc does not vaporize because and the reaction can be described by the overal equation

$$ZnS(s)+H_2(g) \rightarrow Zn(s)+H_2S(g) \tag{5}$$

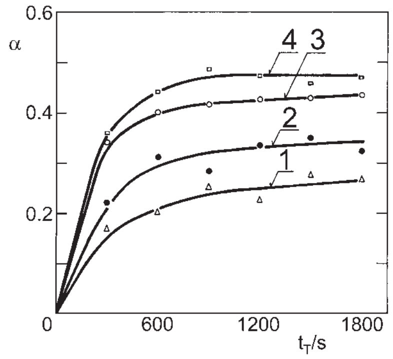

Fig. 5 The influence of the reaction time t_T on the conversion degree α of mechanically activated ZnS. Time of mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10 min,

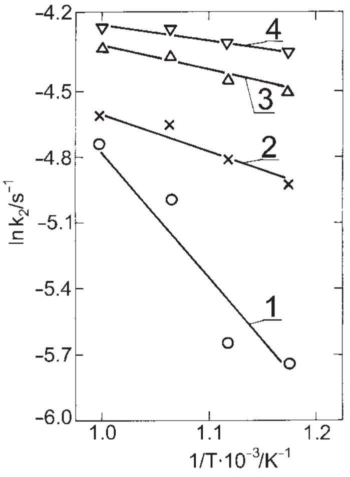

Fig. 6 The influence of mechanical activation of ZnS on Arrhenius plot, T=851–1023 K. Time of mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10

In Fig. 5 the dependence of the degree of conversion α on reaction time t_T is given for the sphalerite samples mechanically activated for 5–30 min in a planetary mill. In the case of all samples we can observe the parabolic course of reduction with the maximum rate at the commencement. The presence of zinc (JCPDS 4-831) and elemental sulphur (JCPDS 8-247) was detected by X-ray phase analysis of the sample mechanically activated for 15 min and subsequently reduced by hydrogen for 20 min at the temperatures of 937 and 1023 K.

The presence of elemental sulphur in reaction products may be a result of hydrogen sulphide decomposition. In paper [15] it is alleged that reverse reaction of zinc with hydrogen sulphide takes place in the cooler part of the reaction tube which could lead to the explanation of the retardation of the process.

The values of experimental activation energy calculated from the plots in Fig. 6 are 49, 12, 7 and 4 kJ mol^{-1} for non-activated sample and samples activated for 5, 10 and 30 min, respectively (Table 2).

Table 2 Numerical processing of temperature-conversion data for ZnS reduction

Mechanical activation/ min	$1/T\cdot10^3$/K^{-1}	$\ln k_1$/s^{-1}	Calculated parameters
–	1.1749	–5.5363	E=49 kJ mol^{-1}
	1.1184	–4.9630	A= –5.861 s^{-1}
	1.0671	–4.9124	r=0.89313
	0.9774	–4.7063	
5	1.1749	–4.8505	E=12 kJ mol^{-1}
	1.1184	–4.7659	A= –1.452 s^{-1}
	1.0671	–4.6303	r=0.86303
	0.9774	–4.6000	
10	1.1749	–4.5086	E=7 kJ mol^{-1}
	1.1184	–4.4566	A= –0.854 s^{-1}
	1.0671	–4.3742	r=0.95222
	0.9774	–4.3457	
30	1.1749	–4.3645	E=4 kJ mol^{-1}
	1.1184	–4.3228	A= –0.438 s^{-1}
	1.0671	–4.2776	r=0.85504
	0.9774	–4.4279	

E – activation energy, A – pre-exponential factor, r – regression coefficient

The disordering of sphalerite by mechanical activation brings about reductions in the values of activation energy. These values give evidence that the diffusion regime [17] likely involving the secondary ZnS originating from the above-mentioned recombination of Zn and H_2S determines the rate of reaction (5).

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