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THERMAL DECOMPOSITION OF MECHANICALLY ACTIVATED SPHALERITE

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ABSTRACT

The changes in surface, structural and spectroscopic properties of sphalerite produced by mechanical activation, as well as the influence of these changes on the rate of thermal decomposition of this mineral in a reducing atmosphere, have been investigated. The samples exhibited amorphization of the crystallographic structure of the mineral as well as of the hyperfine structure of the accessory manganese. The presence of a new phase was discovered in the samples activated for longer periods of time. The reactivity of sphalerite with respect to hydrogen is dependent on the specific surface and on crystallographic or hyperfine structures and demonstrates the structural sensitivity of the reaction investigated.

INTRODUCTION

Zinc sulphide, ZnS, is one of the minerals which are extensively exploited for zinc and its accessory metals, especially cadmium. In addition to the hydrometallurgical processes that have already been applied in industry [1–3], some innovations of classical thermal processes have also been investigated with the aim of eliminating the emissions of sulphur oxides. Among these innovations, the direct reduction of the sulphides of non-iron metals with hydrogen is interesting [4].

In nature, zinc sulphide occurs in two forms: cubic sphalerite and the less stable hexagonal wurtzite. The cubic and hexagonal modifications are terminal members of the series represented by the so-called polytypes, the structures of which differ from each other only by the different periodicity of the sequence of layers in the individual modifications [5]. The stoichiometry of zinc sulphide is disturbed not only by the occurrence of vacancies on account of deviations in the Zn/S ratio, but also by the substitution of other metals, e.g. iron and manganese, for zinc in the lattice. The vacancies influence the type of conductivity of the mineral, while the presence of iron and manganese affects its spectroscopic properties.

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The object of this study has been to quantify the extent of the changes in surface, structural and spectroscopic properties of sphalerite arising in the course of mechanical activation and to compare them with the rate of thermal decomposition of this mineral in a reducing atmosphere.

EXPERIMENTAL METHODS

The investigations were carried out on sphalerite from the Soviet Union with the following composition: 44.60% Zn, 33.58% S, 15.53% Fe, 2.48% insoluble residue.

The mechanical activation of samples was performed in a vibration mill (Mining Institute, Slovak Academy of Sciences Košice, Č.S.F.R.) under the following conditions: revolutions of the mill, 18.5 s^{-1}; amplitude, 6.6 mm; ball charge, 80 balls of diameter 15 mm; weighed amount of sample, 20 g; time of activation $t_G = 7.5$, 15, 60, 150 and 240 min.

The specific surface area S_A was determined from the adsorption isotherms of benzene vapour by the Brunauer–Emmett–Teller method [6].

The change in content of the crystalline phase X was estimated by diffraction phase analysis using the method of internal standard. The diffraction data were obtained on a DRON 2.0 diffractometer (U.S.S.R.) working with the following regime: radiation Cu $K\alpha$, 30 kV, 20 mA; time constant, 1 s; limit of measurement, 10^3 impulses s^{-1}; rate of detector 2° min^{-1}; paper drive, 2,400 mm h^{-1}.

EPR spectra of mechanically activated sphalerite were obtained on an ERS-XQ instrument (Jena, F.R.G.).

The particle morphology was monitored by an electron scanning microscope BS 300 (Tesla, Č.S.F.R.).

The reaction of sphalerite with hydrogen was investigated in a dynamic reactor in a static layer of the solid phase under following conditions: weighed amount, 100 mg; rate of volume flow of hydrogen, 3.3×10^{-4} dm^3 s^{-1}; temperature, 400–500 °C. Experimental results were processed using the Ginstling–Brounstein equation [7]:

$$1 - 2/3\alpha - (1-\alpha)^{2/3} = k_{GB}t \qquad (1)$$

where α is the degree of conversion, t the reaction time and k_{GB} the apparent rate constant.

RESULTS AND DISCUSSION

Changes in surface, structural and spectroscopic properties

Table 1 gives general information on the changes in specific surface S_A, in the content of crystalline phase X, and in the EPR properties of the

TABLE 1

Changes in specific surface area S_A, content of the crystalline phase X, amorphization A ($A = 1 - X$), and parameters of EPR spectra of sphalerite ($A_{Mn^{2+}}$ and $\Delta H_{Mn^{2+}}$, amplitude and width of the resonance line of manganese respectively a.u., arbitrary units)

Grinding time t_G (min)	Specific surface area S_A (10^3 m^2 kg^{-1})	Crystalline phase X (%)	Amorphization A (%)	EPR	
				$A_{Mn^{2+}}$ (a.u.)	$\Delta H_{Mn^{2+}}$ (a.u.)
–	0.12	100	0	140	7.5
7.5	2.81	64	36	22	15
15	3.82	60	40	13	16
60	3.95	55	45	12	17
150	4.02	53	47	10	18
240	4.18	52	48	6	21

mechanically activated samples of sphalerite. The results represented in Fig. 1 demonstrate the changes in surface and volume of the mineral caused by mechanical stress. These changes proceed rapidly up to $t_G = 0.25$ h and then slow down. From a macroscopic point of view, this retardation is accompanied by the formation of agglomerates starting at $t_G = 0.125$ h and becoming predominant at $t_G = 4$ h (Fig. 2).

The EPR properties of sphalerite show the intricacy of its ultrafine structure [8]. For investigating these properties, the manganese which is always present in natural samples is used as a paramagnetic marker. On the basis of the form of the EPR spectrum of manganese of a non-activated sample ($t_G = 0$ h) we can assume that the Mn^{2+} ions occupy positions corresponding to cations in the sphalerite lattice. During mechanical activa-

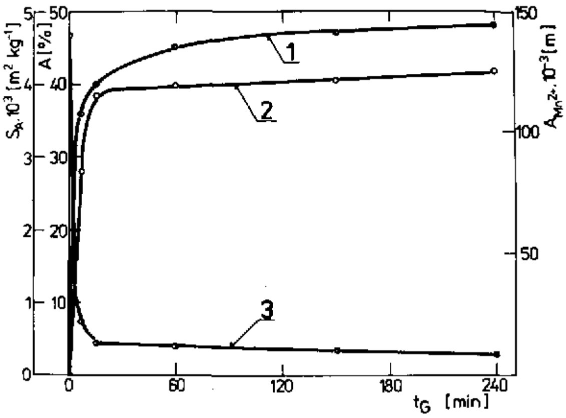

Fig. 1. The influence of grinding time t_G of sphalerite on the following: curve 1, the amorphization A; curve 2, the specific surface area S_A; and curve 3, the amplitude of the resonance line of manganese, $A_{Mn^{2+}}$.

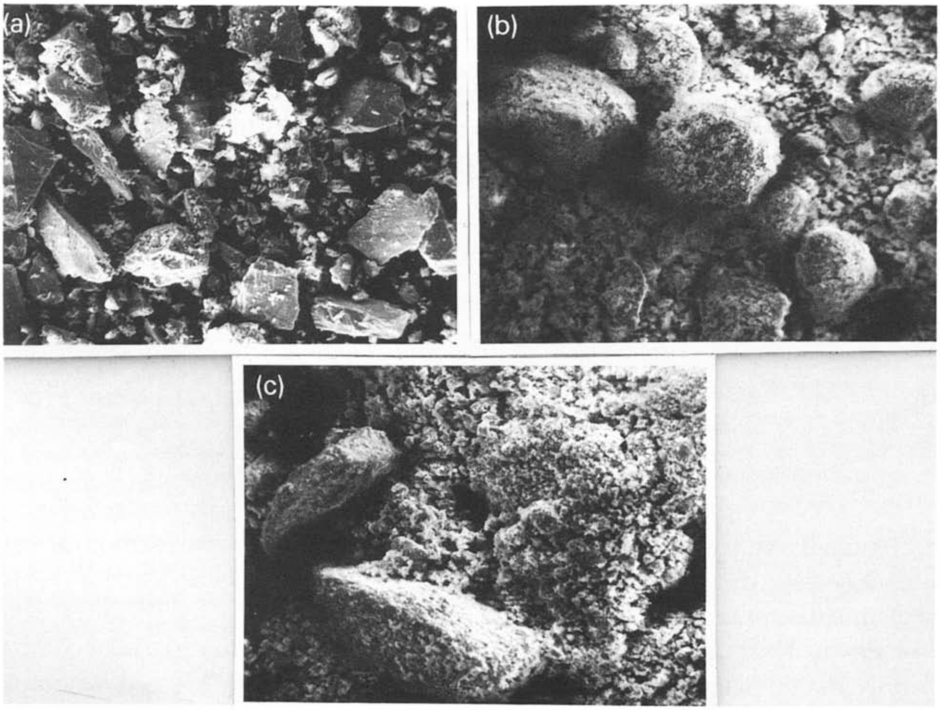

Fig. 2. Scanning electron micrographs of sphalerite: (a) as-received sample (-74 μm); (b) mechanical activation $t_G = 7.5$ min; (c) mechanical activation $t_G = 60$ min. Magnification, ×200.

tion, the amplitudes of the lines of manganese fall rapidly and their widths simultaneously increase (Table 1). For a sample activated for $t_G = 2.5$ h, a new spectrum of manganese appears, indicating the presence of a new phase. This phase, which is probably amorphous, is characterized by the Mn^{2+} ions being in interstitial positions in the sphalerite lattice [9].

Thermal decomposition in a reducing atmosphere

The reaction of sphalerite with hydrogen obeys the following equation:

$$ZnS + H_2 \rightarrow Zn + H_2S \qquad (2)$$

The analysis of kinetic curves of the transformation $\alpha(t)$ has shown that the rate of reaction is greatest at the start of the reaction and gradually decreases as the reaction proceeds. The $\alpha(t)$ relationships were processed using the set of equations commonly used to describe the kinetics of reactions in the solid phase [10]. The statistical evaluation of these equations by the method of linear regression has shown that the Ginstling–Brounstein equation, eqn. (1), derived for reactions controlled by diffusion through the solid product, is the most convenient for the formal description of the

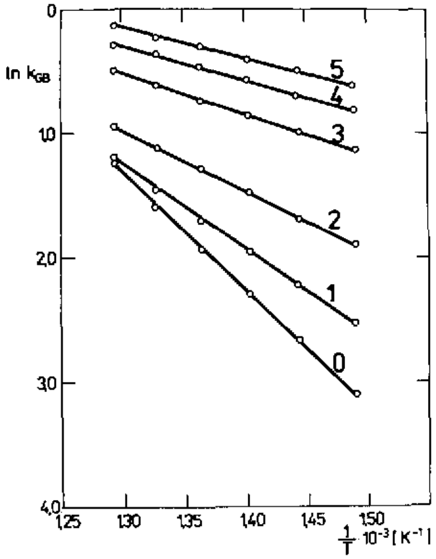

Fig. 3. Arrhenius plot for reaction (2): k_{GB}, apparent rate constant; T, temperature (line 0, non-activated sample; lines 1–5, mechanically activated samples of time $t_G = 7.5$, 15, 60, 150 and 240 min).

reaction macrokinetics in eqn. (2). For this reason, we assumed that because of its properties, the solid reaction product hinders the transport of H_2S from the reaction interphase and that the rate of overall reaction is determined by diffusion through this product.

An investigation into the temperature sensitivity in the 400–500 °C region enabled the influence of mechanical activation on the kinetics parameters of reaction (2) to be quantified. The mechanical activation resulted in the decrease in the apparent activation energy, as can be deduced from the slopes of the Arrhenius plots in Fig. 3. The relationship between apparent activation energy E_A and the logarithm of the pre-exponential factor Z (Fig. 4) indicates a statistically significant occurrence of a compensation effect ($r = 0.998$).

Structure–reactivity relationship

The results given in Table 1 and Fig. 1 show that the changes in specific surface (S_A), in amorphization of crystallographic structure (A) and in hyperfine structure of manganese ($A_{Mn^{2+}}$, $\Delta H_{Mn^{2+}}$) are significant at the beginning of mechanical activation, while their intensity decreases with grinding time. The limiting time value is $t_G = 0.25$ h.

The relationship between the reactivity of mechanically activated sphalerite expressed by the apparent rate constant of thermal decomposition (k_{GB}) and the changes in surface structural properties S_A/X (Fig. 5B) or in

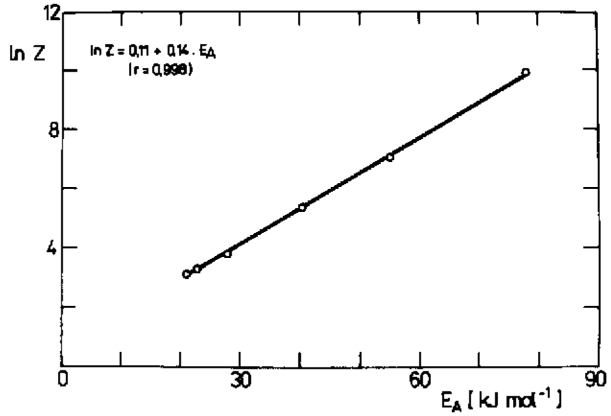

Fig. 4. The logarithm of the pre-exponential factor Z vs. apparent activation energy E_A for the reaction of sphalerite with hydrogen.

hyperfine structure $S_A/A_{Mn^{2+}}$ (Fig. 5A) are represented in Fig. 5. A small response of reactivity to significant changes in the properties of sphalerite is characteristic of the initial region limited by the value $t_G < 0.25$ h. At $t_G > 0.25$ h, the structure of sphalerite is so altered that further rather small

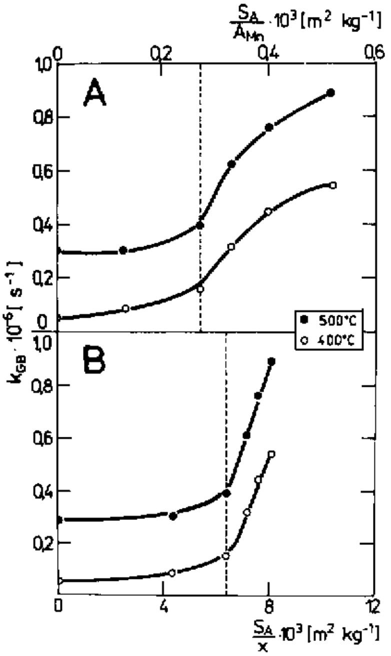

Fig. 5. Reactivity of mechanically activated sphalerite: A, k_{GB} vs. S_A/A_{Mn}; B, k_{GB} vs. S_A/X (k_{GB}, apparent rate constant; S_A, specific surface area; A_{Mn}, amplitude of the resonance line of Mn^{2+}; X, content of crystalline phase.

changes in structure bring about a rapid increase in reactivity. It is probable that the new phase identified by the EPR method contributes to this enhanced reactivity.

This information demonstrates the structural sensitivity of reaction (2). A similar relationship was also found for heterogeneous reactions of the s-l type [11]. The results obtained are consistent with literature data concerning the influence of the level of the defects on the course of heterogeneous reactions of the s-l or s-g type [12].

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