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Thermoanalytical study of mechanically activated cinnabar

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Abstract

The investigation of the properties of mechanically activated cinnabar has shown that the surface area of this mineral and the amorphization of its structure increase. In the course of activation the mechanochemical transformation $\alpha \rightarrow \beta$ sets in while the metastable β-phase containing accumulated excess energy can re-transform into the more stable and less-strained α-phase during DSC experiments. The process is overlapped by dissociative sublimation of the mineral. A linear relationship has been found between the maximum temperatures of DSC effects and the empirical coefficient of disorder of mechanically activated samples.

INTRODUCTION

One of the methods producing disordered structures in inorganic substances is mechanical activation of these materials in equipment used for intensive grinding. A characteristic feature of the substances thus activated is the occurrence of defects in non-equilibrium density. The state of the so-created solids can be characterized as metastable [1]. The excess energy produced by grinding is accumulated in the solid and can be detected by different methods, among which differential scanning calorimetry (DSC) has been successfully used [2–6].

In this study the changes produced in cinnabar by its mechanical activation in a planetary mill were investigated by XPS, BET, XRD, and DSC.

EXPERIMENTAL

The investigations were carried out with cinnabar originating from Almaden (Spain) and of the following composition: 51.87% Hg, 14.08% Fe

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and 8.93% SiO_2. It was found by X-ray diffraction phase analysis that this sample contained hexagonal cinnabar α-HgS (ASTM 6-256) as a major component and pyrite FeS_2 (ASTM 6-710), haematite α-Fe_2O_3 (ASTM 4-755) and quartz SiO_2 (ASTM 5-490) as minor constituents.

The samples (20 g) were mechanically activated in a planetary mill, Pulverisette 4 (Fritsch, Germany), under the following conditions: ball charge, 25 balls 15 mm in diameter plus 5 balls 25 mm in diameter; ball material, WC; time of grinding, 5–30 min in air; relative acceleration of the mill, $b/g = 10.3$; initial particle size of the sample, -200 μm.

The specific surface area S_A was determined from the adsorption isotherms of benzene vapour by the BET method [7].

The morphology of cinnabar was monitored on a BS 300 electron scanning microscope (Tesla, Czechoslovakia).

The XPS analysis was carried out on an ESCA 3 MK II instrument (VG Scientific, Gt. Britain) in 10^{-6} Pa vacuum. The electrons were excited by the Al Kα emission of $h\nu = 1486$ eV. The transmission energy of the electron analyser was 20 eV and the width of the entrance slit of the analyser was 4 mm.

The structural disorder of mechanically activated samples was determined by X-ray diffraction phase analysis on the diffractometer DRON 2.0 (Russia) by using the following regime: radiation Cu Kα; 30 kV; 20 mA; time constant, 1 s; limit of measurement, 10 impulses s^{-1}; rate of detector, 2° min^{-1}; paper drive, 2.4 m h^{-1}. The degree of structural disorder was evaluated from the change in amorphization A (expressed as a percentage) of the cinnabar structure defined by the following equation:

$$A = (1 - I^*/I_0)100 \tag{1}$$

where I^* and I_0 are integral intensities of the peaks of the activated sample and non-activated standard (40 μm) respectively. The calculation according to eqn. (1) was performed for the diffraction peak of cinnabar (101) corresponding to the value $d = 0.335$ nm.

The measurements pertaining to DSC and thermogravimetry were simultaneously performed by using a simultaneous thermal analyser STA 409 (Netzch, Germany) under the following conditions: sample weight, 100 mg: temperature program, 25–600°C; heating rate, 10 K min^{-1}, atmosphere, argon; reference material, Al_2O_3.

RESULTS AND DISCUSSION

Study of changes in surface structure of mechanically activated cinnabar

The samples of cinnabar were activated by intensive grinding in a planetary mill. The characteristics of their surface structure are represented in Fig. 1 and summarized in Tables 1 and 2. The XPS survey

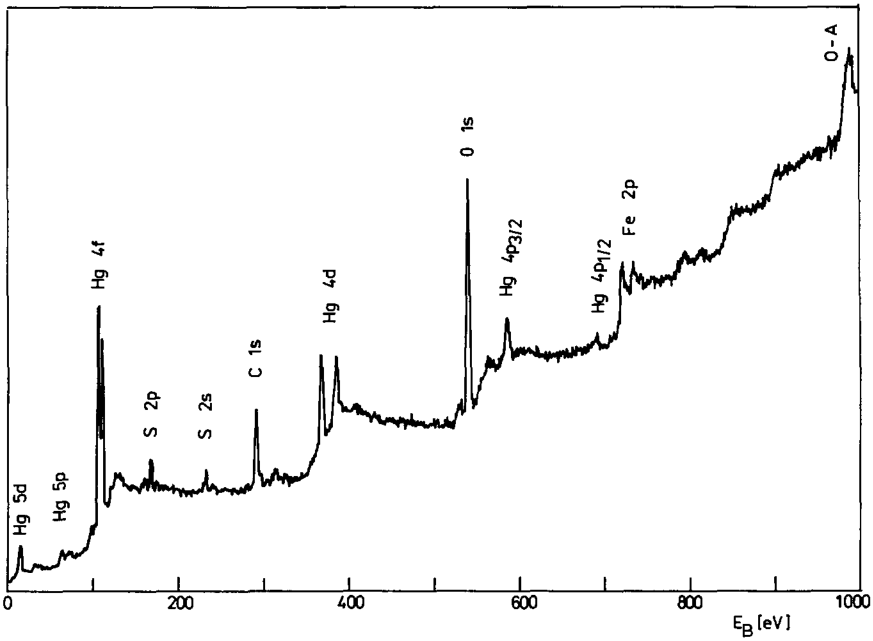

Fig. 1. The XPS spectrum of non-activated cinnabar.

TABLE 1

Atomic concentrations of S^{2-}, S^{6+}, C and O in the surface layer of cinnabar

Grinding time t_G (min)	Relative atomic concentration (referred to Hg)				
	S^{2-}	S^{6+}	C	O	S^{2-}/S^{6+}
0	0.9	0.2	5.1	5.3	4.7
30	0.9	0.1	1.6	2.4	6.6

TABLE 2

Change in specific surface area S_A and amorphization A of the structure of the cinnabar mechanically activated for grinding time t_G

t_G (min)	S_A ($m^2\ kg^{-1}$)	A (%)	$\delta = S_A/(100-A)$
0	1600	0	16
5	3800	10.5	42
10	6300	11.6	71
15	7500	18.2	92
20	8100	18.7	99
30	8800	19.4	109

spectrum indicates the presence of mercury, sulphur, iron, carbon and oxygen in the surface layer of the mineral. The presence of iron and oxygen may be due to the occurrence of slight quantities of FeS_2, α-Fe_2O_3 and SiO_2, which were identified by X-ray diffractometry. The occurrence of carbon in mineral surfaces is usual.

The intensive grinding of sulphides results not only in desorption of adsorbed components from the surface but also in its mechanochemical oxidation. By investigating the surface of mechanically activated chalcopyrite and sphalerite by XPS we observed intensive oxidation of the sulphidic sulphur to sulphate sulphur [8,9]. On the basis of the values of atomic concentrations of oxygen and of the ratio S^{2-}/S^{6+} in Table 1 we can, however, come to the conclusion that the grinding of cinnabar is not accompanied by mechanochemical oxidation. A similar conclusion was also drawn by Kulebakin who observed only considerable amorphization produced by mechanical activation [10].

The values of the specific surface and of the amorphization of the structure of the mechanically activated cinnabar are given in Table 2. This table also contains values of the empirical coefficient of disorder, $\delta = S_A/(100 - A)$, which expresses the overall effect of the change in surface and bulk properties by means of the integral quantities S_A and A [11].

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The DSC curves (Fig. 2) represent an association of endothermic effects, which differ from each other in shape and values of the extreme temperatures. We can observe subpeaks in temperature region I (320–560°C) and strongly structured peaks at temperatures over 560°C (region II).

For a non-activated sample (Fig. 2, curve 0) we observe a small endo effect at 356°C, a suggestion of which also appears in the case of a sample activated for 5 min. The occurrence of this endo effect cannot be excluded even for more-disordered samples. In this case, it can, however, be blurred with the subsequent dominant endo effect. According to the literature [10,12,13] this temperature can be attributed to the polymorphous transformation

$$\underset{\text{cinnabar}}{\alpha\text{-HgS(s)}} \rightleftarrows \underset{\text{metacinnabar}}{\beta\text{-HgS(s)}} \qquad (2)$$

which is not, in accordance with expectation, accompanied by a change in the weight of the sample (Fig. 3).

Provided that $T > 360°C$, we observe a large exo effect with a maximum at 554°C for a non-activated sample. Its existence is due to the process of dissociative sublimation of β-HgS [14,15] ($n = 3$–8):

$$\beta\text{-HgS(s)} \rightarrow \text{Hg(g)} + (1/n)\text{S}_n\text{(g)} \qquad (3)$$

which leads to a considerable decrease in the weight of the sample.

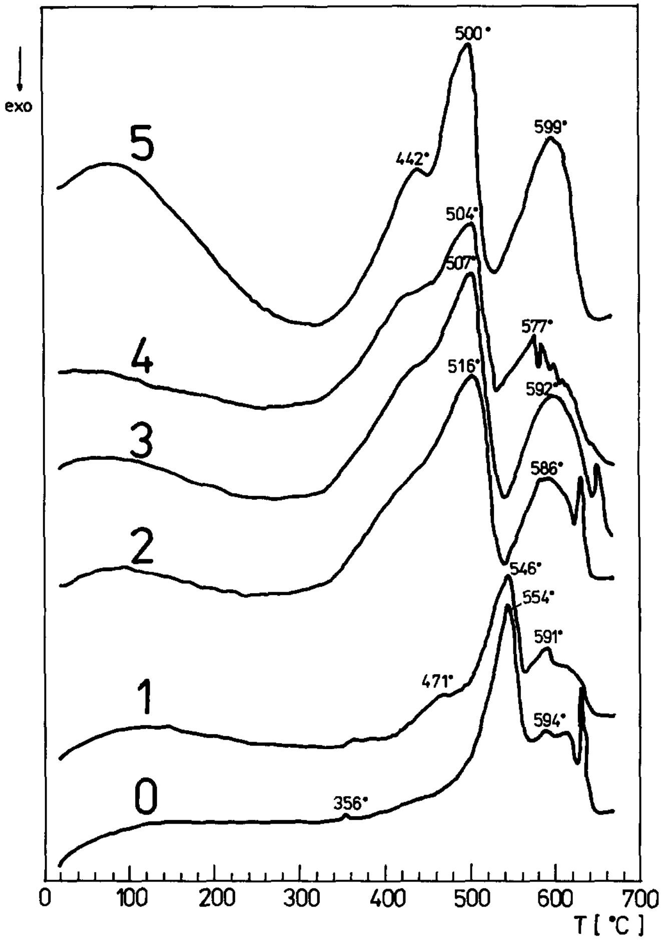

Fig. 2. DSC curve of a non-activated sample of cinnabar (curve 0) and curves of cinnabar samples activated for various grinding times, t_G: curve 1, 1–5 min: curve 2, 2–10 min: curve 3, 3–15 min: curve 4, 4–20 min: curve 5, 5–30 min.

Provided that $T > 500°C$, pyrite undergoes dissociation [16]:

$$FeS_2(s) \rightarrow FeS_{2-x} + xS(g) \qquad (4)$$

The temperature of the polymorphous transformation α-$SiO_2 \rightarrow \beta$-SiO_2 (573°C) is also situated in this temperature region. Both processes overlap and their unambiguous interpretation from the course of curve 0 in Fig. 2 for a non-activated sample is not possible.

The mechanical activation brings about a shift in temperatures of the above-mentioned endo effects to lower values and also manifests itself in their form (Fig. 2).

The maximum temperature of the dominant endo effect T_{max} decreases with increasing time of mechanical activation from the value of 554°C valid

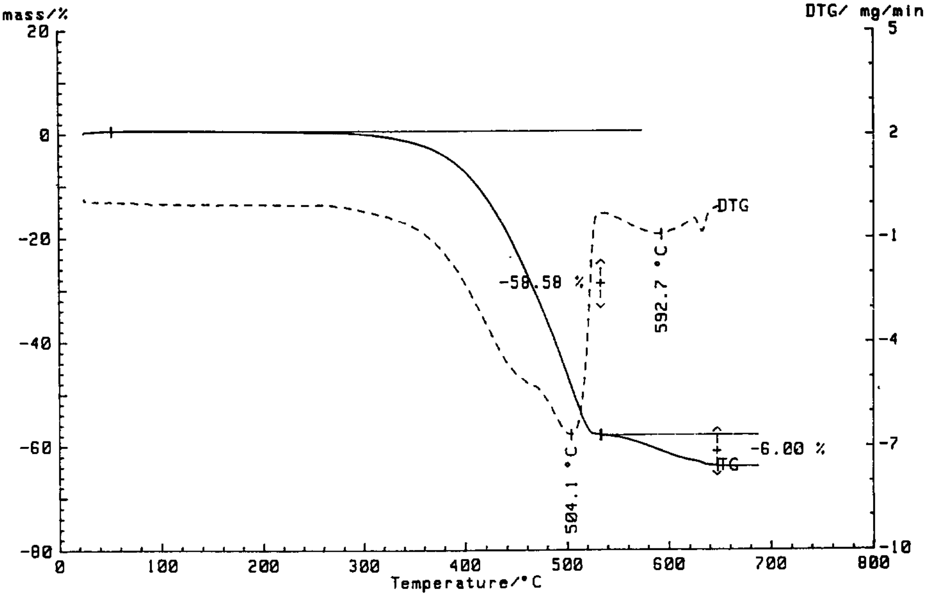

Fig. 3. TG–DTG curves of cinnabar activated for $t_G = 15$ min.

for a non-activated sample to the value of 500°C valid for a sample subjected to the activation of 30 min.

The dependence of the values of the temperature of the individual endo effects on the empirical coefficient of disorder of mechanically activated samples is represented in Fig. 4. The sensitivity of thermal decomposition of cinnabar to violation of its structure documented by this relationship confirms the structural sensitivity of the decomposition of sulphides as

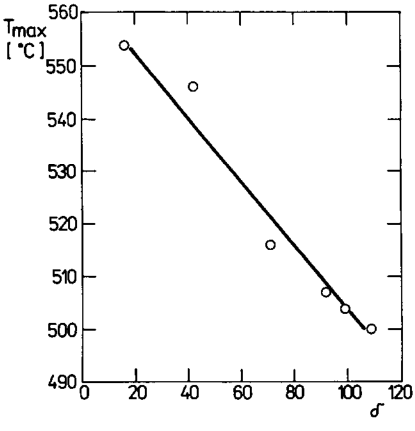

Fig. 4. Dependence of the maximum temperature of the dominant DSC effect T_{max} on the coefficient of disorder of mechanically activated samples, $\delta = S_A/(100 - A)$.

presented in our foregoing publications for chalcopyrite and sphalerite [8,17].

The TG records show the maximum increase in mass loss in the region of occurrence of the mentioned endo effects (Fig. 3). The discussed endo effect of mechanically activated samples is characterized by a larger area. Ohtani and Senna [3] investigated mechanically activated CdS and attributed the wide DSC traces to a sluggish energy release typical of the stored energy. In our case, we assume that the polymorphous transformation α-HgS → β-HgS sets in owing to intensive grinding. The increase in density as well as the change in colour confirms this assumption. The metastable β-phase containing accumulated excess energy can re-transform into the more stable and less strained α-phase which decomposes by the mechanism of dissociative sublimation. For a more detailed elucidation of both processes it will be necessary to combine DSC measurements with high temperature X-ray diffractometry.

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REFERENCES

1 V.V. Boldyrev, Proc. Indian Nat. Sci. Acad., Part A, 52 (1986) 400.
2 M. Senna, J. Appl. Phys., 49 (1978) 580.
3 G. Ohtani and M. Senna, Thermochim. Acta, 60 (1983) 125.
4 R. Blachnik and U. Walbrecht, Thermochim. Acta, 64 (1983) 377.
5 M. Senna, Cryst. Res. Technol., 20 (1985) 209.
6 C. Barriga, J. Morales and J.L. Tirado, J. Therm. Anal., 34 (1988) 421.
7 S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1939) 309.
8 K. Tkáčová, P. Baláž and Z. Bastl, Thermochim. Acta, 170 (1990) 277.
9 P. Baláž, Z. Bastl, J. Briančin, I. Ebert and J. Lipka, J. Mater. Sci., 1991, 27 (1992) 653.
10 V.G. Kulebakin, Prevrasceniya sulfidov pri aktivirovaniyi, Nauka, Novosibirsk, 1983, 208 pp. (in Russian).
11 K. Tkáčová, Mechanical Activation of Minerals, Elsevier, Amsterdam, 1989, 155 pp.
12 L.G. Berg and E.N. Shlyapkina, J. Therm. Anal., 8 (1975) 417.
13 M.M. Asadov, Izv. Akad. Nauk SSSR, Neorg. Mater., 11 (1975) 324.
14 K.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974, p. 366.
15 A.V. Vanyukov, R.A. Isakova and V.P. Bystrov, Termiceskaya Dissociaciya Sulfidov Metallov, Nauka, Alma-Ata, 1978, 271 pp. (in Russian).
16 F. Paulik, S. Gal and L. Erdey, Anal. Chim. Acta, 44 (1969) 153.
17 P. Baláž and I. Ebert, Thermochim. Acta, 180 (1991) 117.