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Dissociative sublimation of mechanically activated cinnabar

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Abstract

The dissociative sublimation of mechanically activated cinnabar has been studied in the range 589–658 K. The mechanical activation weakens the Hg–S bonds between chains owing to which the apparent activation energy decreases from 54 to 34 kJ mol^{-1} and the rate of decomposition of the mineral increases. The morphology of the particles subjected to mechanical pretreatment and thermal treatment has been thoroughly investigated.

INTRODUCTION

In studying the kinetics of heterogeneous reactions we frequently meet complications in connection with formation of the solid reaction product which hinders the temporal development of reaction. One of the possibilities of accelerating the kinetics of these reactions is mechanical pretreatment in equipment for intensive grinding [1]. In spite of a favourable effect on the rate of reaction, a lower sensitivity to the disordering of structure appears in the region of formation of the solid-phase product. The overall rate can be enhanced only by changing the nature of the reaction product or its porosity [2]. From this view point the reactions of the s–g type affording a gaseous product are appropriate for theoretical study. These reactions are widely used in pyrometallurgy, e.g. in volatilizing roasting of ores of non-ferrous metals such as mercury, antimony and zinc [3]. If these reactions are investigated in dynamic regime under continuous removal of reaction products, their kinetics are determined by temperature and strength of chemical bonds in structural units of the solid phase.

EXPERIMENTAL

The investigations were carried out with cinnabar originating from Almaden (Spain) of the following composition: 51.87% Hg, 14.08% S, 9.31% Fe 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 the major component and pyrite FeS_2 (ASTM 6-710), hematite α-Fe_2O_3 (ASTM 4-755) and quartz SiO_2 (ASTM 5-490) as minor parts.

The samples (20 g each) were mechanically activated in a planetary mill Pulverisette 4 (Fritsch, Germany) under the following conditions: ball charge 25 balls of diameter 15 mm plus 5 balls of diameter 25 mm, 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 adsorption specific surface area S_A of the samples was determined from the adsorption isotherms of benzene vapour by the BET method [4].

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

The "granulometric" specific surface area S_G was calculated statistically from particle size distribution data measured on a sedimentation balance (Sartorius, Germany).

ESR spectroscopy of mechanically activated samples was carried out on an ESR-XQ instrument (Jena, Germany).

The structural disorder of mechanically activated samples was determined by X-ray diffraction phase analysis on a diffractometer DRON 2.0 (USSR) 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 amorphisation (A in %) of cinnabar structure defined by the equation

$$A = \left(1 - \frac{I^*}{I_0}\right) \times 100 \qquad (1)$$

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

The dissociative sublimation of cinnabar was investigated in a dynamic reactor with a static layer of the solid phase under the following conditions: weighed amount of the sample 100 mg, flow rate of argon 3.3×10^{-1} m^3 s^{-1}, temperature interval 589–658 K. The experimental results were processed by means of the equation

$$\alpha = k t_T^2 \qquad (2)$$

where k is the apparent rate constant (s^{-1}), α is the conversion degree and t_T stands for the reaction time (s).

RESULTS AND DISCUSSION

At temperatures exceeding 613 K mercuric sulphide is liable to dissociative sublimation according to the equation

$$\mathrm{HgS(s)} \rightarrow \mathrm{Hg(g)} + \frac{1}{n}\mathrm{S}_n\mathrm{(g)} \qquad (3)$$

where $n = 3$–8. The decomposing HgS can occur either in the α form or in the β form. The polymorphous transformation of these modifications was investigated by the methods of thermal analyses [5,6].

The mechanical activation influences the physico chemical properties of cinnabar. The course of halfwidth of the ESR resonance line of admixed manganese $\Delta H_{\mathrm{Mn}^{2+}}$ (A), extension of the diffraction (101) line (B) and enlargement of the specific adsorption surface S_{A} (C) and specific granulometric surface S_{G} (D) as functions of the time of mechanical activation of cinnabar are represented in Fig. 1. The values A and B characterise the

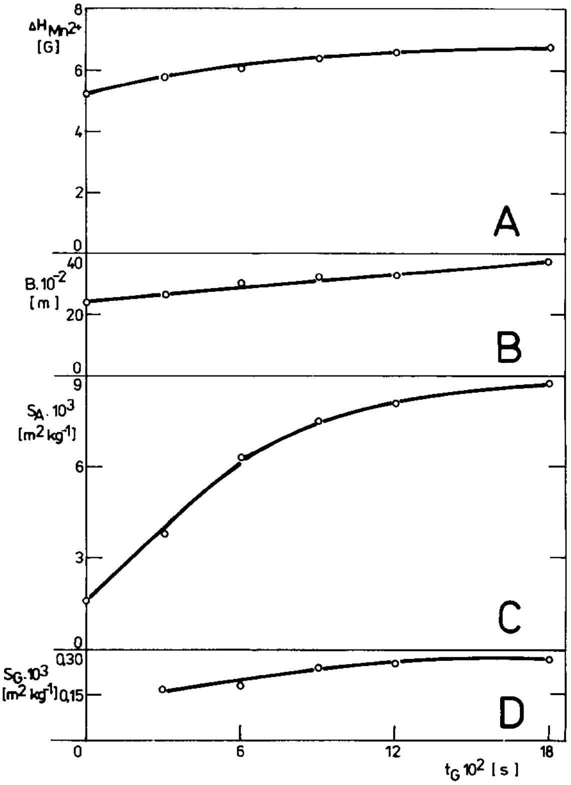

Fig. 1. Halfwidth of the resonance line of admixed manganese $\Delta H_{\mathrm{Mn}^{2+}}$ (A), broadening of the diffraction (101) line (B), specific adsorption surface S_{A} (C) and specific granulometric surface S_{G} as functions of the time of mechanical activation t_{G}.

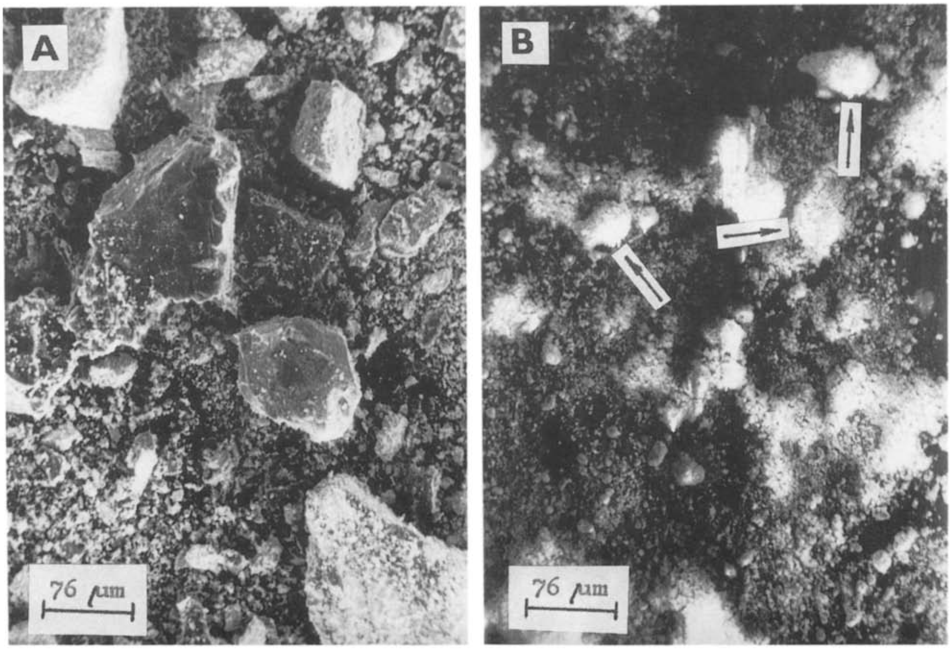

Fig. 2. Scanning electron micrographs of cinnabar: A, non-activated sample; B, sample activated for 30 min.

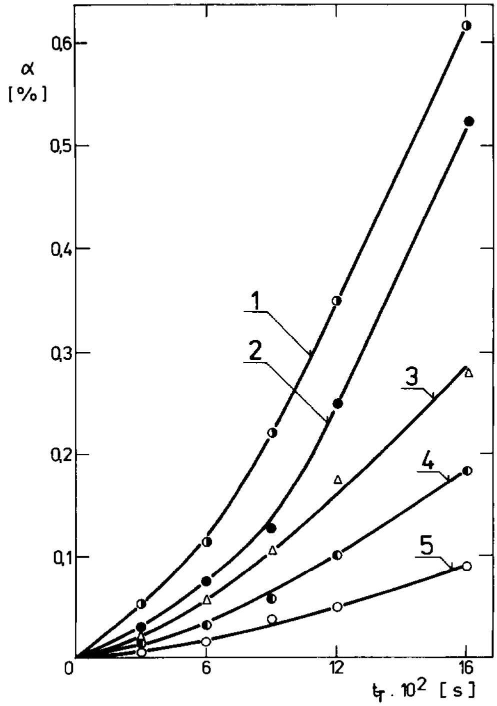

Fig. 3. Variation of the degree of conversion α with reaction time t_T for non-activated HgS. Temperatures of decomposition: 1, 650 K; 2, 641 K; 3, 624 K; 4, 606 K; 5, 589 K.

TABLE 1

Values of specific adsorption surface S_A, specific granulometric surface S_G, amorphisation of structure of cinnabar A, apparent rate constant k and apparent activation energy E_a of dissociative sublimation of cinnabar as functions of the time of mechanical pretreatment t_G

Property	Temp. (K)	t_G (min)			
		0	10	20	30
$S_A \times 10^3$ (m^2 kg^{-1})		1.6	6.3	8.1	8.8
$S_G \times 10^3$ (m^2 kg^{-1})		0.085	0.18	0.25	0.25
A (%)		0	11.6	18.7	19.4
$k \times 10^{-3}$ (s^{-1})	589	0.35370	0.57807	0.65776	0.60497
	606	0.50932	0.77440	0.82788	0.68762
	624	0.65552	0.89544	0.91998	0.95301
	641	0.94204	1.03693	1.12421	1.05362
	658	1.09281	1.22991	1.23083	1.18713
E_a (kJ mol^{-1})	589–658	54	34	29	33

changes in hyperfine structure and in crystal order, respectively. The relation between them was thoroughly investigated in our preceding work [7]. The quantities S_A and S_G are integral characteristics of the changes in surface of the mineral and characterise the overall value of surface (S_A) and indicate the formation of agglomerates (by a decrease in the value of S_G).

In Fig. 2 we can see the scanning electron micrographs of a reference (non-activated) sample (A) and of a sample mechanically activated for 30 min (B). The activation brings about a decrease in size of particles and we

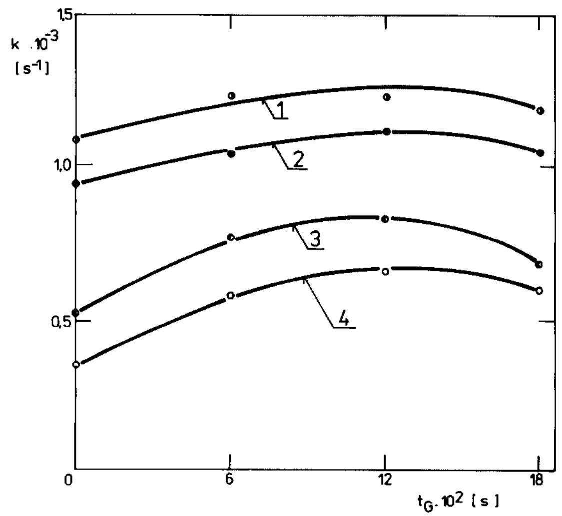

Fig. 4. Dependence of the apparent rate constant k on the time of mechanical activation t_G. Temperature of decomposition: 1, 658 K; 2, 641 K; 3, 606 K; 4, 589 K.

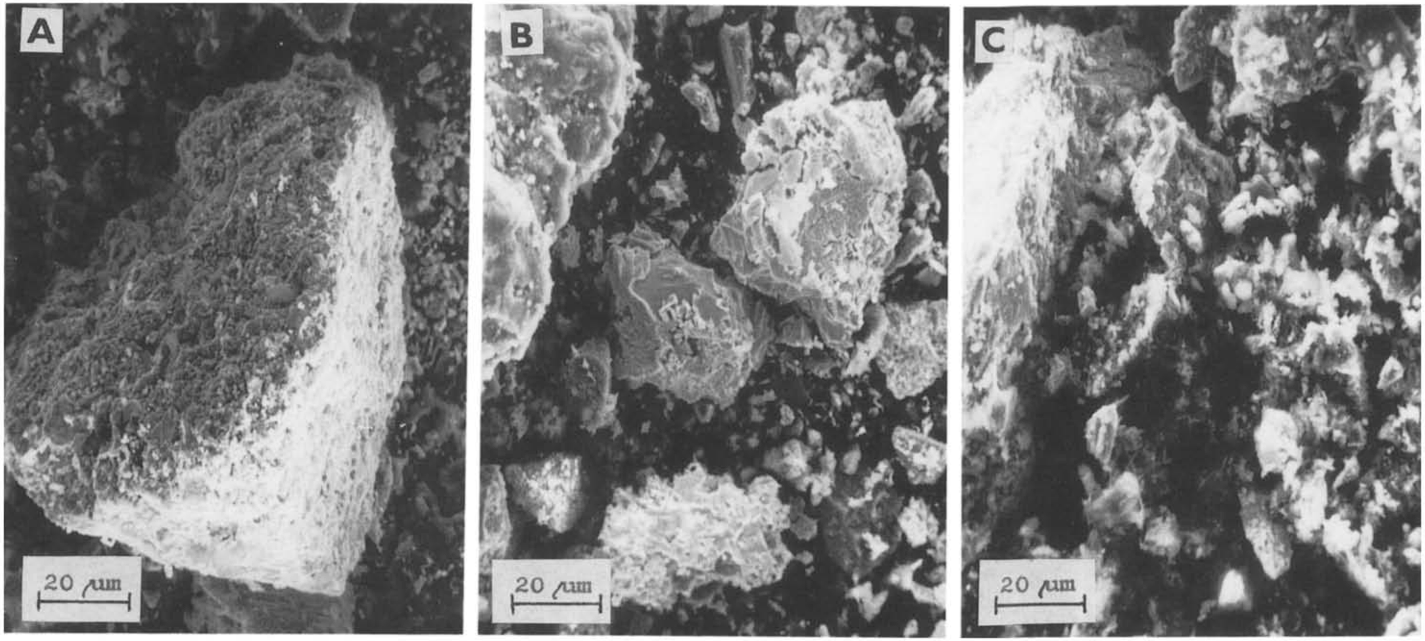

Fig. 5. Scanning electron micrographs of cinnabar (non-activated sample) after 30 min heating: A, without heating; B, after heating at 624 K; C, after heating at 658 K.

can observe the commencement of formation of agglomerates (arrow). Due to this fact a stagnation of the values of S_G sets in. For $t_G > 20$ min these values do not increase further.

The time dependence of the degree of thermal decomposition of non-activated sample in the region 586–658 K is represented in Fig. 3. The mathematical processing of the corresponding values by means of eqn. (2) is presented in Table 1 where the comparative values of the apparent rate constant of decomposition obtained for the samples mechanically activated for $t_G = 10$, 20, and 30 min are given as well. On the basis of the presented values we can conclude that the course of dissociative sublimation is positively affected not only by the temperature of reaction but also by the disordering of structure of cinnabar. However, as a result of the dependence of the values of k on the time of mechanical activation t_G (Fig. 4) the acceleration of decomposition appears only for $t_G \leqq 20$ min. Provided the grinding time is greater than 20 min, the value of the apparent rate constant decreases. These facts may be related to the beginning of agglomerate formation as mentioned earlier.

The surface change of the dissociated particles of cinnabar is documented by photomicrographs in Fig. 5. An original fine grained particle (A) disintegrates into smaller fragments (B, C) due to the effect of temperature. The structure of cinnabar consists of spiral chains S–Hg–S–Hg–S which are joined by weak Hg–S bonds [8]. These weak bonds preferentially relax owing to which the activation energy decreases and the rate of decomposition increases (Table 1) in the course of subsequent thermal treatment. An examination of the morphology of disintegrated particles (Fig. 5B) shows that the dissociative sublimation involves gradual peeling of compact areas.

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