

## **THERMAL REDUCTION OF MECHANICALLY ACTIVATED CINNABAR (HgS) AND STIBNITE (Sb<sub>2</sub>S<sub>3</sub>)**

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### **Abstract**

The reduction of cinnabar (HgS) and stibnite (Sb<sub>2</sub>S<sub>3</sub>) by hydrogen was investigated. These investigations were performed in the temperature region 636–765 K for cinnabar and in the region 825–954 K for stibnite. It has appeared that the mechanical activation positively affects the thermal reduction of the sulphides. The thermal decomposition of HgS is accompanied by a change in mechanism taking place at 744 K. As to Sb<sub>2</sub>S<sub>3</sub>, the change in mechanism in the investigated temperature region was not observed.

**Keywords:** cinnabar, decomposition, hydrogen, mechanical activation, reduction, stibnite

### **Introduction**

The need to introduce waste-free and ecologically irreproachable technologies in extraction metallurgy stimulates the search for the methods of direct reduction of sulphides of non-ferrous metals for obtaining pure metals. The use of different reducing agents, e.g. hydrogen, carbon monoxide, methane and carbon has been investigated [1–5]. The application of hydrogen to reduction of simple sulphides gives rise not only to elemental metal but also to hydrogen sulphide, the decomposition of which yields sulphur and the arisen hydrogen may be recycled into the primary process.

In this study the results of experiments aimed at intensification of the reduction of cinnabar and stibnite with hydrogen provided these sulphides were subjected to mechanical activation before reduction are presented. Mechanical activation was proved to be successful also for intensification of other thermal processes of sulphides such as oxidation, decomposition in inert atmosphere as well as sublimation [6–14].

### **Experimental**

The investigations were carried out with cinnabar and stibnite.

Cinnabar originated from Almaden (Spain) was of the following composition: 51.87% Hg, 14.08% S, 9.31% Fe and 8.93% SiO<sub>2</sub>. It was found by X-ray diffraction

phase analysis that this sample contained hexagonal cinnabar ( $\alpha$ -HgS) (JCPDS 6-256), as the major component and pyrite FeS<sub>2</sub> (JCPDS 6-710), hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS 4-755) and quartz SiO<sub>2</sub> (JCPDS 5-490) as minor parts.

Stibnite originated from Rudňany (Slovakia) was of the following composition: 65.19% Sb, 23.45% S, 0.04% Fe, 0.33% Mg, 10.12% SiO<sub>2</sub> and 0.86% insoluble rest. The X-ray examinations showed the presence of stibnite Sb<sub>2</sub>S<sub>3</sub> (JCPDS 6-474) and quartz SiO<sub>2</sub> (JCPDS 5-490).

The sample of both minerals were separated and crushed for granularity minus 200  $\mu$ m. The prepared samples were used for the preparation of mechanically activated specimens by high-energy milling. The milling was performed in a Pulverisette 4 (Fritsch, Germany) planetary mill under the following conditions: volume of grinding chamber 350 ml; weighed amount 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 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,  $0.67 \cdot 10^{-3}$  dm<sup>3</sup> s<sup>-1</sup>; temperature: 636–835 K (for HgS), 851–929 K (for Sb<sub>2</sub>S<sub>3</sub>). The details of the apparatus are given in [13].

The experimental results were best fitted to Dünvald–Wagner equation

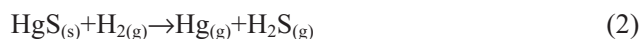
$$\alpha = 1 - \frac{6}{\pi} e^{-kt} \quad (1)$$

where the symbols  $\alpha$ ,  $k$ ,  $t$  stand for the conversion degree, apparent rate constant (s<sup>-1</sup>) and reaction time (s), respectively.

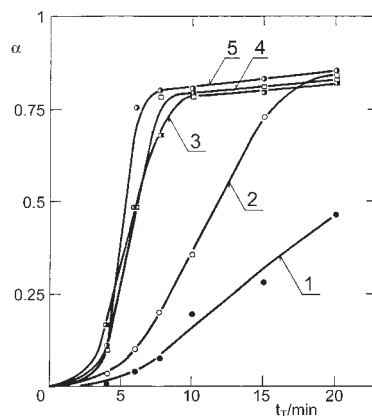
## Results and discussion

### *Cinnabar*

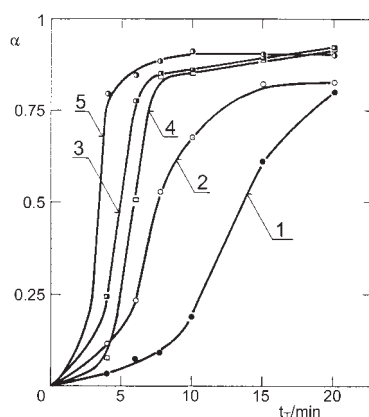
At temperature exceeding 613 K the reaction between cinnabar and hydrogen [14] takes place according to the following equation



We investigated this decomposition in the temperature range 636–835 K for a non-activated sample as well as for a sample mechanically activated for 15 min. The dependence of the degree of conversion  $\alpha$  on the time of thermal reduction  $t_T$  for different experiments is given in Figs 1 and 2. While we can observe that the rate of decomposition increases in the whole interval of the values of reaction time  $t_T$ , a gradual retardation of the decomposition appears at higher temperatures and the decomposition is limited by the degree of conversion  $\alpha=0.8$ – $0.9$ . If we compare the above figures with each other, we can see that the mechanical activation does not probably change the mechanism of decomposition and accelerates the decomposition rate only slightly. The influence of mechanical activation decreases with increasing temperature.



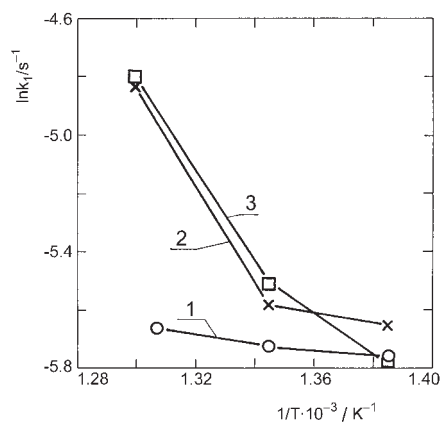
**Fig. 1** The influence of the reaction time  $t_T$  on the conversion degree  $\alpha$  of non-activated HgS. Reaction temperatures: 1 – 636 K; 2 – 679 K; 3 – 743 K; 4 – 722 K; 5 – 835 K



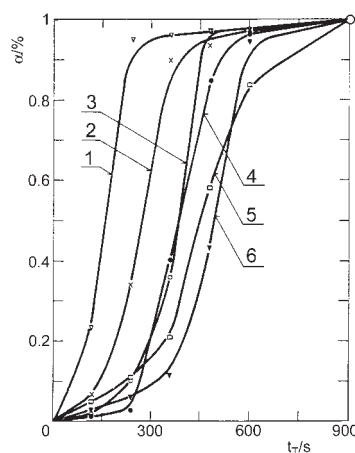
**Fig. 2** The influence of the reaction time  $t_T$  on the conversion degree  $\alpha$  of mechanically activated HgS for 15 min. Reaction temperatures: 1 – 636 K; 2 – 679 K; 3 – 743 K; 4 – 722 K; 5 – 835 K

The results of X-ray phase analysis of a sample mechanically activated for 15 min and thermally treated for 10 min revealed the presence of mercury in the products of decomposition.

The Arrhenius plots in Fig. 3 give evidence of a change in reaction mechanism at  $T=744$  K ( $1/T=1.345 \cdot 10^{-3}$  K). This change manifests itself by the break at this temperature in the case of non-activated sample as well as of samples mechanically activated for 5 and 15 min. The change in mechanism can be related with the process of dissociative sublimation which begins just at this temperature [11]. At temperatures above 744 K the process involving simultaneous dissociative sublimation and reduction of cinnabar proceeds. The elemental sulphur formed in this first process immedi-



**Fig. 3** The influence of mechanical activation of HgS on Arrhenius plot,  $T=722\text{--}765\text{ K}$ . Time of mechanical activation: 1 – 0, 2 – 5, 3 – 15 min



**Fig. 4** The influence of the reaction time  $t_r$  on the conversion degree  $\alpha$  of non-activated Sb<sub>2</sub>S<sub>3</sub>. Reaction temperatures: 1 – 954 K; 2 – 929 K; 3 – 903 K; 4 – 877 K; 5 – 851 K; 6 – 825 K

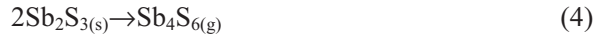
ately reacts with the flowing dynamic atmosphere of hydrogen to give hydrogen sulphide owing to which the reaction surface is set free and the overall process is accelerated. For the activated samples the values of experimental activation energy in the temperature region 744–765 K are equal to 155–162 kJ mol<sup>-1</sup> which points out that the chemical reaction is the rate determining step of the whole process.

#### *Stibnite*

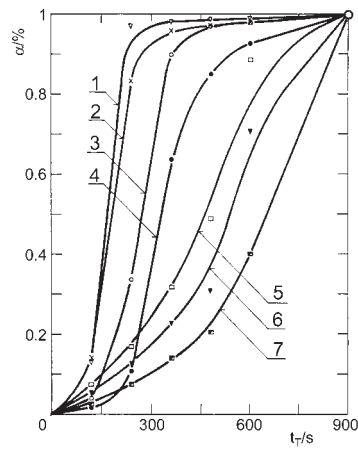
The reaction of Sb<sub>2</sub>S<sub>3</sub> with hydrogen [15] obeys the following equation



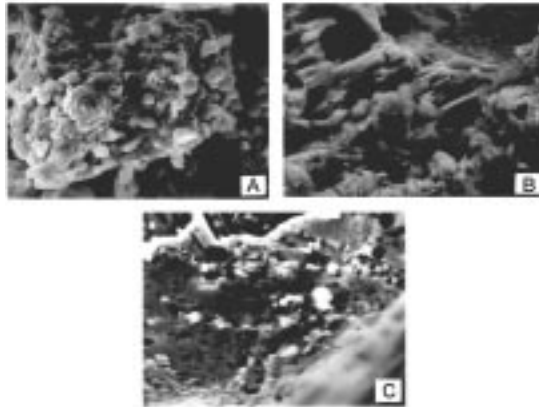
According to the temperature [15] stibnite can turn into volatile and partially decomposed forms:



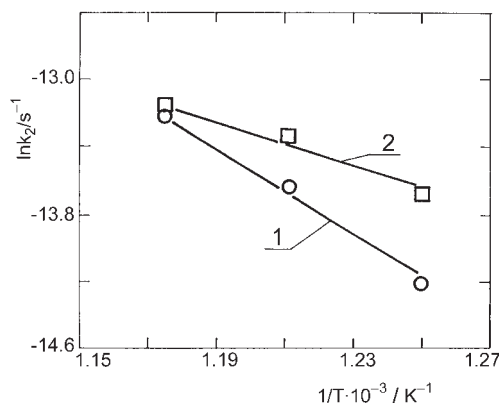
The investigation of the decomposition products of Sb<sub>2</sub>S<sub>3</sub> [15] has shown gaseous SbS, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>2</sub>, S<sub>2</sub>, Sb<sub>3</sub>S<sub>3</sub>, Sb<sub>3</sub>S<sub>4</sub>, Sb<sub>4</sub>S<sub>4</sub> and Sb<sub>4</sub>S<sub>5</sub> occur among the products of reactions (4) and (5).



**Fig. 5** The influence of the reaction time  $t_r$  on the conversion degree  $\alpha$  of mechanically activated Sb<sub>2</sub>S<sub>3</sub> for 15 min. Reaction temperatures: 1 – 954 K; 2 – 929 K; 3 – 903 K; 4 – 877 K; 5 – 851 K; 6 – 825 K; 7 – 800 K



**Fig. 6** Scanning electron micrographs of Sb<sub>2</sub>S<sub>3</sub> (mechanical activation 15 min). Temperature: A – 800 K, B – 825 K; C – 929 K. Magnification: 6000×



**Fig. 7** The influence of mechanical activation of Sb<sub>2</sub>S<sub>3</sub> on Arrhenius plot,  $T=800\text{--}851\text{ K}$ . Time of mechanical activation 1 – 0 min, 2 – 15 min

The results of our study of the decomposition of Sb<sub>2</sub>S<sub>3</sub> in hydrogen atmosphere are illustrated by the kinetic relationships conversion reaches the value  $\alpha=1$  under given experimental conditions and the temporal course is dependent on temperature.

The X-ray phase analysis applied to a sample mechanically activated for 15 min and thermally processed at 851, 877 and 929 K for 5 min indicated the presence of monoclinic sulphur (JCPDS 13-141) and metallic antimony (JCPDS 5-562). The photomicrographs of the same sample processed at 799, 825 and 928 K are given in Figs 6A–C. For the temperature of 799 K we can observe a particle of stibnite covered with metallic antimony which volatilizes at higher temperatures [17].

The microstructure of the mineral comprises a considerable number of micropores (Figs 6B–C) while the reaction surface is not blocked.

The character of the Arrhenius plots in Fig. 7 indicates that no change in reaction mechanism takes place in the investigated temperature region. The mechanical activation brings about a decrease in experimental activation energy from  $130\text{ kJ mol}^{-1}$  for non-activated sample to the value of  $58\text{ kJ mol}^{-1}$  for a sample activated for 15 min. Both values point out that the reaction at the surface of Sb<sub>2</sub>S<sub>3</sub> is the rate determining step. The value of  $130\text{ kJ mol}^{-1}$  is in very good agreement with the value of  $121\text{ kJ mol}^{-1}$  found by Liu [17] for equal reaction of non-activated Sb<sub>2</sub>S<sub>3</sub> in the temperature region 723–793 K.

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## References

- 1 F. Habashi and R. Dugdale, *Metall. Trans. B*, 4B (1973) 1865.
- 2 D. M. Či ikov, J. V. Rumjancev and T. B. Goldštejn, *DAN SSSR*, 215 (1974) 406.

- 3 T. C. Tan and J. D. Ford, *Metall. Trans. B*, 15B (1984) 719.
- 4 M. Moinpour and Y. K. Yao, *Canad. Metall. Quart.*, 24 (1985) 69.
- 5 I. A. Onajev and V. S. Spitčenko, *Reduction of Sulphides*, Nauka, Alma-Ata 1988 (in Russian).
- 6 P. Balá , K. Tkáčová and E. G. Avvakumov, *J. Thermal Anal.*, 35 (1989) 1325.
- 7 K. Tkáčová, P. Balá and Z. Bastl, *Thermochim. Acta*, 170 (1990) 277.
- 8 P. Balá and I. Ebert, *Thermochim. Acta*, 180 (1991) 117.
- 9 P. Balá , H.-J. Huhn and H. Heegn, *Thermochim. Acta*, 194 (1992) 189.
- 10 P. Balá , J. Briančin, V. Šepelák and I. Hocmanová, *Thermochim. Acta*, 196 (1992) 349.
- 11 P. Balá , E. Post and Z. Bastl, *Thermochim. Acta*, 200 (1992) 371.
- 12 P. Balá and M. Balassaová, *J. Thermal Anal.*, 41 (1994) 1101.
- 13 P. Balá , J. Briančin and L', Turčániová, *Thermochim. Acta*, 249 (1995) 375.
- 14 P. Balá , *Extrative Metallurgy of Activated Minerals*, Elsevier, Amsterdam 2000.
- 15 K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworth, London 1974.
- 16 C. L. Sullivan, J. E. Prusaczyk and K. D. Carlson, *J. Chem. Phys.*, 53 (1970) 1289.
- 17 Liu Chumpeng, Liu Zhonghua and Zhu Zuze, Reduction kinetics of stibnite with hydrogen and recovery of metallic antimony/lead by evaporation, in *Proc. of the First Int. Conf. on the Metallurgy and Materials Science of Tungsten, Titanium Rare Earths and Antimony 'W-Ti-RE-Sb'88'* (Fu Chongyue, Ed. in Chief), Vol. 1, Pergamon Press, Oxford 1988, p. 539.