THERMAL REDUCTION OF MECHANICALLY ACTIVATED CINNABAR (HgS) AND STIBNITE (Sb₂S₃)

P. Baláž and E. Godočíková

Institute of Geotechnics, Slovak Academy of Sciences, 043 53 Košice, Slovakia

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Abstract

The reduction of cinnabar (HgS) and stibnite (Sb₂S₃) 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 Sb₂S₃, 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% SiO₂. It was found by X-ray diffraction
phase analysis that this sample contained hexagonal cinnabar \((\alpha-\text{HgS})\) (JCPDS 6-256), as the major component and pyrite \(\text{FeS}_2\) (JCPDS 6-710), hematite \(\alpha-\text{Fe}_2\text{O}_3\) (JCPDS 4-755) and quartz \(\text{SiO}_2\) (JCPDS 5-490) as minor parts.

Stibnite originated from Rudhany (Slovakia) was of the following composition: 65.19\% Sb, 23.45\% S, 0.04\% Fe, 0.33\% Mg, 10.12\% \(\text{SiO}_2\) and 0.86\% insoluble rest. The X-ray examinations showed the presence of stibnite \(\text{Sb}_2\text{S}_3\) (JCPDS 6-474) and quartz \(\text{SiO}_2\) (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, \(0.67 \times 10^{-3} \text{dm}^3 \text{s}^{-1}\); temperature: 636–835 K (for \(\text{HgS}\)), 851–929 K (for \(\text{Sb}_2\text{S}_3\)). The details of the apparatus are given in [13].

The experimental results were best fitted to Dünvald–Wagner equation

\[
\alpha = 1 - \frac{6}{\pi} e^{-kt}
\]

where the symbols \(\alpha\), \(k\), \(t\) stand for the conversion degree, apparent rate constant \((\text{s}^{-1})\) and reaction time \((\text{s})\), respectively.

**Results and discussion**

**Cinnabar**

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

\[
\text{HgS}(s) + \text{H}_2(g) \rightarrow \text{Hg}(g) + \text{H}_2\text{S}(g)
\]

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 \(t_r\) 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 \(t_r\), 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.