Note

Thermal decomposition of mechanically activated tetrahedrite

P. Baláž [a,*], J. Briančin [b], L'. Turčániová [a]

[a] *Institute of Geotechnics of the Slovak Academy of Sciences, 043 53 Košice, Slovak Republic*
[b] *Institute of Material Research of the Slovak Academy of Sciences, 043 57 Košice, Slovak Republic*

Abstract

A comparative study of the thermal non-oxidative decomposition of tetrahedrite $Cu_{12}Sb_4S_{13}$ ground in a planetary mill has shown that the mechanical activation does not change the mechanism of this decomposition but has positive influence on its rate. The formation of agglomerates from finely ground particles of tetrahedrite restricts the extent of this influence. Bornite Cu_5FeS_4 and digenite $Cu_{1.765}S$ were identified in the decomposition products obtained at 773, 893 and 1113 K. The values of activation energy found for the decomposition in the temperature region 765–972 K indicate that diffusion is the rate-determining process.
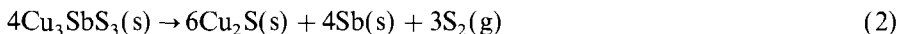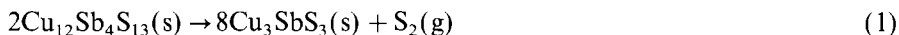
Keywords: Activation energy; Decomposition; Diffusion; Mechanical activation; Tetrahedrite

1. Introduction

The thermal decomposition of tetrahedrite $Cu_{12}Sb_4S_{13}$ has been investigated by Imriš et al. [1–3] and by Ibragimov and Isakova [4,5]. Because a great number of other elmements occur in the mineral, e.g. Hg, Fe, Zn, Ag, Cd, Co, Cr, Mo, Ni, Pb,

---

* Corresponding author.

Sn and Bi in the Slovak tetrahedrites, a description of the decomposition is rather complicated. In an inert medium at temperatures 823–1153 K, it may be expressed by the equations

$$2Cu_{12}Sb_4S_{13}(s) \rightarrow 8Cu_3SbS_3(s) + S_2(g) \qquad (1)$$

$$4Cu_3SbS_3(s) \rightarrow 6Cu_2S(s) + 4Sb(s) + 3S_2(g) \qquad (2)$$

The heating of tetrahedrite in an inert medium may also involve the escape of SbS and Hg and the disintegration of the mineral in two phases. Chalcopyrite $CuFeS_2$ and fematinite Cu_3SbS_4 has been identified in the decomposition at 773 K and a melt of sulphides, as well as fematinite, has been identified at 903 K.

The influence of the mechanical activation of tetrahedrite on the course of its thermal non-oxidative decomposition has not yet been investigated.

2. Experimental

The investigations were carried out with tetrahedrite originating from Rudňany (Slovakia) of composition: 33.40% Cu, 20.24% Sb, 30.74% S, 4.4% Fe, 0.80% Zn, 2.10% As, and 5.02% Hg. In addition to the major phase containing tetrahedrite,
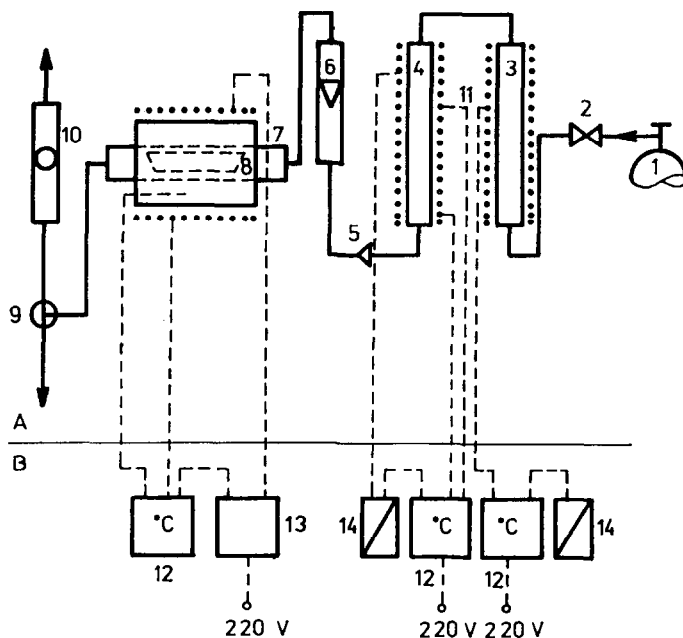

Fig. 1. Diagram of the apparatus: 1, pressure gas vessel with argon; 2, reducing valve; 3,4, purifiers; 5, needle valve; 6, rotameter; 7, dynamic reactor; 8, sample; 9, distributor; 10, rotameter; 11, thermocouples; 12, temperature controller; 13, regulating transformer; 14, contactor.

the presence of small amounts of pyrite and quartz were detected by X-ray diffraction phase analysis.

The samples of tetrahedrite of -200 μm granularity were ground 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, 5–30 min.

The thermal decomposition of tetrahedrite 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 argon, 0.67×10^{-3} dm³ s⁻¹; temperature, 765–972 K. A diagram of the apparatus is given in Fig. 1.

The experimental data were best fitted to the kinetic equation

$$\alpha = k t_T^{1/2} \tag{3}$$

where α is the conversion degree calculated from the mass difference of tetrahedrite samples before and after reaction, k is an apparent rate constant, and t_T is the reaction time.
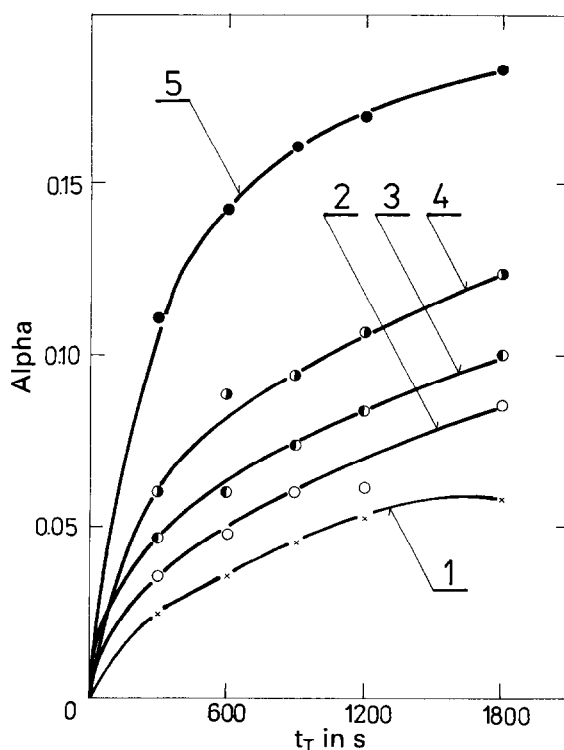

Fig. 2. The influence of the reaction time t_T on the conversion degree α of non-activated $Cu_{12}Sb_4S_{13}$ for different temperatures: 1, 765 K; 2, 808 K; 3, 868 K; 4, 920 K; 5, 972 K.

3. Results and discussion

The dependence of the tetrahedrite conversion degree α is represented in Figs. 2 and 3 for different experiments. We can observe that the conversion degree increases with temperature and the graphs describing this process exhibit a parabolic character. The α values for mechanically activated samples are greater. The plot of α versus t_T for 765 K and all activated samples is represented in Fig. 4. Provided it is valid that the grinding time $t_G \leq 10$ min, considerable differences in the values of α appear between individual samples, while these differences for samples activated for higher values of t_G are small because of the effect of
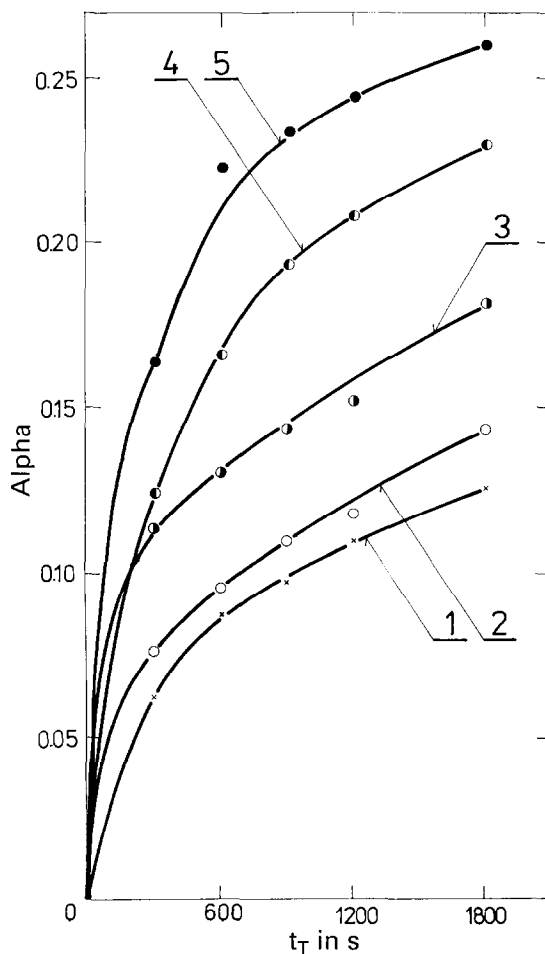
Fig. 3. The influence of the reaction time t_T on the conversion degree α of non-activated $Cu_{14}Sb_4S_{13}$ for different temperatures: 1, 765 K; 2, 808 K; 3, 868 K; 4, 920 K; 5, 972 K.

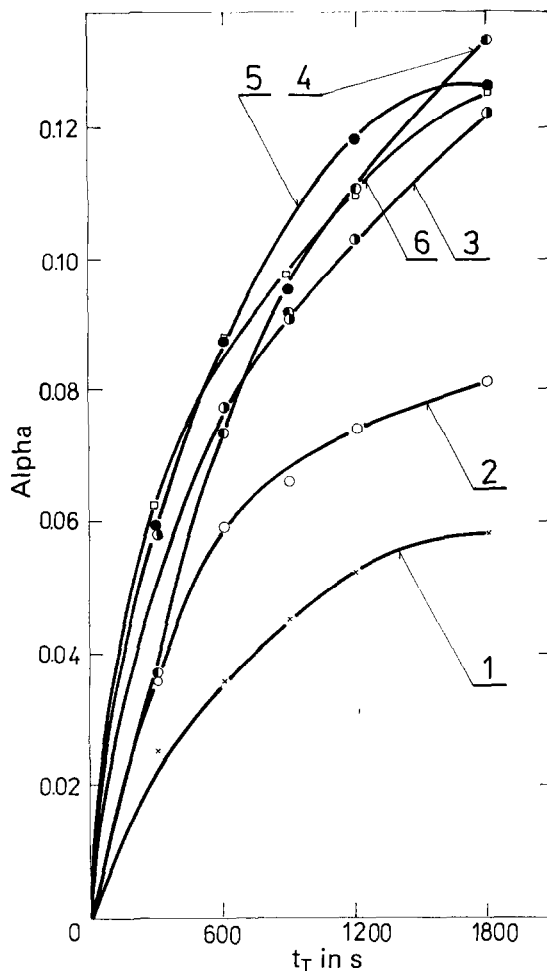Fig. 4. The influence of the reaction time t_T on the degree of conversion α of $Cu_{14}Sb_4S_{13}$ for different grinding times: 1, 0 min; 2, 5 min; 3, 10 min; 4, 15 min; 5, 20 min; 6, 30 min.

agglomeration. The formation of agglomerates from finely ground particles of tetrahedrite is illustrated in Fig. 5. We have also observed this retardation effect in other sulphide reactions [6].

The X-ray phase analysis was performed with a non-activated sample as well as with a sample mchanically activated for 30 min. Bornite Cu_5FeS_4 (ASTM 14-323) and digenite $Cu_{1.765}S$ (ASTM 23-960) were identified in the decomposition products obtained at 773, 893 and 1113 K. Only differences in the quantitative proportions of these decomposition products were observed for both samples. These results are consistent with the investigations of Ibragimov and Isakova [4,5].

The temperature dependence of the decomposition of tetrahedrite in the region 765–972 K is represented in the Arrhenius coordinates for individual mechanically
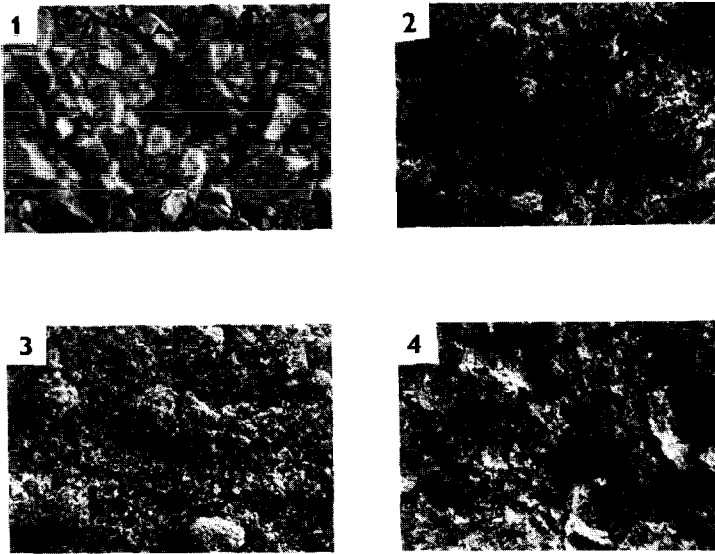
Fig. 5. Scanning electron micrographs of $Cu_{12}Sb_4S_{13}$. Grinding time: 1, 0 min; 2, 10 min; 3, 20 min; 4, 30 min. Magnification 190 × .
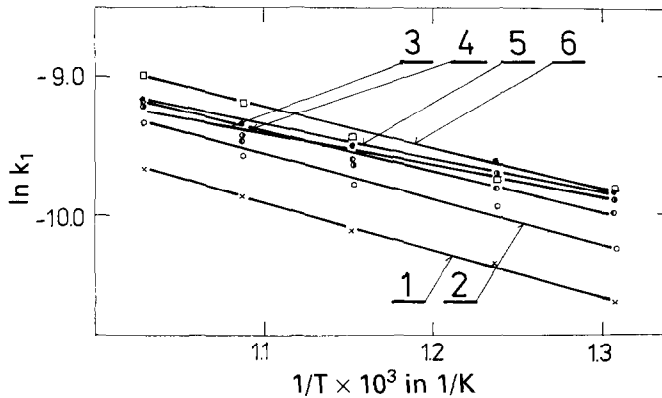

Fig. 6. The influence of grinding time t_G of $Cu_{12}Sb_4S_{13}$ on the Arrhenius plot, $T = 765–972$ K: 1, 0 min; 2, 5 min; 3, 10 min; 4, 15 min; 5, 20 min; 6, 30 min.

activated samples in Fig. 6. These plots do not show any break which would indicate a change in reaction mechanism. The corresponding apparent activated energies are listed in Table 1. Their low values and small sensitivity to mechanical disordering of the mineral structure indicate that diffusion is the rate-determining step in the decomposition of tetrahedrite in the region 765–972 K in argon atmosphere.

Table 1
The apparent activation energy E of mechanically activated samples of $Cu_{12}Sb_4S_{13}$

Grinding time t_G/min	Temperature T/K	E/kJ mol^{-1}
0	765–972	30
5		26
10		19
15		22
20		18

Acknowledgements

References

[1] I. Imriš and L'. Komorová, Production of Metallic Antimony, Alfa, Bratislava, 1983.
[2] I. Imriš, L'. Komorová and F. Sehnálek, Complex tetrahedrite concentrates from Slovakia, in Proc. Complex Sulphide Ores, The Inst. Min. Metall., Rome, 1980, p. 63.
[3] I. Imriš, L'. Komorová and A. Holmstrom, Behaviour of antimony during the roasting of tetrahedrite concentrates, in Proc. Extraction Metallurgy. 85 symposium, The Inst. Min. Metall., London, 1985, p. 1015.
[4] T.A. Ibragimov and R.A. Isakova, Kompleksn. Ispol'z. Miner. Syr., 1 (1989) 25.
[5] T.A. Ibragimov and R.A. Isakova, Kompleksn. Ispol'z. Miner. Syr., 2 (1989) 45.
[6] P. Baláž, J. Briančin, V. Šepelák, T. Havlík and M. Škrobian, Hydrometal., 31 (1992) 201.