

THE EFFECT OF MECHANICAL ACTIVATION ON THE THERMAL DECOMPOSITION OF CHALCOPYRITE*

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Experimental results on the influence of preliminary mechanical activation on the thermal decomposition of chalcopyrite are presented and discussed. The following experimental facts were found:

1. a decrease in the temperature of the endothermic DTA peak of β -CuFeS₂ from 821 K for a non-activated sample to 763 K for an optimally activated one;
2. a decrease in the apparent activation energy of the thermal decomposition of CuFeS₂ from 238 kJ mol⁻¹ for a non-activated sample to 72 kJ mol⁻¹ for an optimally activated sample.

The intensive grinding of chalcopyrite leads to a shift in temperature of the endothermic DTA peak and brings about a decrease in the activation energy of the thermal decomposition of CuFeS₂. These results can be attributed to the mechanically produced alterations in structure and surface properties of the mineral.

Chalcopyrite is a classic cupriferous mineral. Its relatively complicated structure and industrial importance explain why in recent decades it has become an attractive model and has stimulated the joint research efforts of metallurgists and chemists interested in problems of the solid phase.

This mineral occurs in several modifications. The low-temperature modification, the α -phase, is tetragonal. In an inert atmosphere the thermal decomposition of chalcopyrite starts at temperatures over 673 K. This process gives rise to the high-temperature β - and γ -phases with a sulphur deficit. At 823 K the tetragonal γ -phase is formed. This phase is unstable and turns into the cubic β -phase [1]. The γ -phase may also occur if the β -phase is heated to temperatures over 500 K. In some recent publications the formation of the γ -phase at 823 K is not mentioned, and only the transformation of the α -phase into the cubic β -phase is taken into consideration [2, 3].

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Many transformations in the solid phase exhibit a direct dependence on the character and concentration of the defects. Thus, we can intentionally influence the character of these transformations by convenient choice of the external factors modifying the arrangement and also the energetic state of a solid [4]. The effects of mechanical forces are included among the factors of this kind, together with heat, radiation and other influences.

A characteristic feature of the mechanical treatment of solids consists in the fact that this treatment may be either constant (continuous) or periodic. In the first case, the reactivity is changed by the constant field of stress that is applied to the solid. In the second case, the stress is applied periodically by subjecting the solid to a sequence of powerful mechanical impulses (comminution in industrial mills, ball or vibration mills, attritors, etc.) [5].

Numerous publications are concerned with the mechanical activation of chalcopyrite by grinding [6–11]. Experiments have shown that the intensive structure violation caused by grinding is accompanied by the formation of a new surface. It has also been revealed that the mechanically stimulated phase transitions take place under conditions of intense stresses. The influence of mechanical activation on the process of oxidative decomposition of chalcopyrite was evidenced in papers [12, 13]. The favourable influence of the mechanical activation of chalcopyrite on the rate of leaching of copper in an acid or oxidizing medium is reported in very many papers [6–10, 12, 14–17].

Experimental

The investigations were carried out with a sample of chalcopyrite from the locality of Slovinky (East Slovakia). The sample was withdrawn from the deposit, crushed in a press and separated under a binocular magnifier. The chemical analysis gave the following composition of the mineral: 28.07% Cu, 28.39% Fe, 31.62% S, 0.65% As, 7.47% SiO₂ and 3.80% insoluble residue.

The mechanical activation was performed in a four-chamber vibration mill (original construction of the Mining Institute, Slovak Academy of Sciences, Košice). The material was ground in the dry; the mill was 75% filled with grinding bodies. The experimentally determined frequencies and amplitudes of the vibratory motion and the known masses of the charge and grinding media were used to calculate the specific energy of grinding from the following formula [18]:

$$W = \frac{m_1}{2m_2} \cdot n \cdot t \cdot (4\pi a n)^2$$

where W , m_1 , m_2 , a , t and n are the specific energy of grinding, the mass of the grinding media, the mass of the charge, the amplitude, the grinding time, and the frequency of the vibratory motion, respectively.

The specific surface of the investigated samples S_A was determined via the adsorption of benzene vapour by the BET method [19]. The change in content of the crystalline phase of chalcopyrite X was estimated from the X-ray phase analysis by using the additional reference component method [20]. A 30% addition of CaF_2 was used as reference component. The X-ray measurements were carried out with a DRON 2.0 instrument (USSR) by using the following regime: Cu anode ($U = 30 \text{ kV}$, $I = 20 \text{ mA}$), shift of the counting tube 0.033 deg s^{-1} , chart drive 0.04 m s^{-1} , sensitivity $10^4 \text{ impulses s}^{-1}$.

The thermal decomposition was investigated with a Derivatograph Q-1580 D (Hungary) under the following conditions: quantity of sample 2 g, rate of heating 0.17 deg s^{-1} , inert substance Al_2O_3 , argon atmosphere $6.94 \text{ cm}^3 \text{ s}^{-1}$.

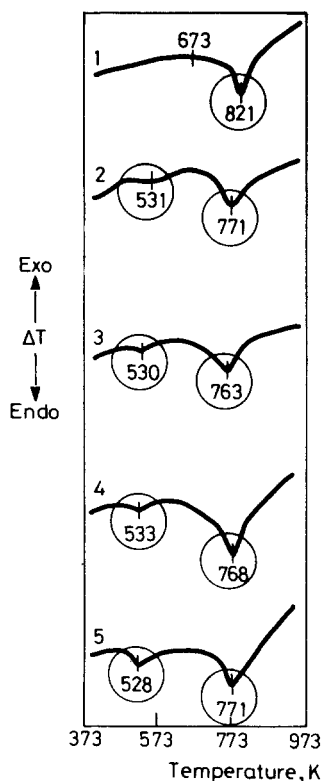


Fig. 1 DTA records of mechanically activated chalcopyrite (time of activation in minutes). 1 – 0 min, 2 – 15 min, 3 – 20 min, 4 – 25 min, 5 – 30 min

The activation energy of the thermal decomposition of chalcopyrite was calculated from the TG data by using the integral Coats–Redfern method [21].

Results and discussion

Figure 1 presents the DTA records of chalcopyrite either non-activated or activated for different grinding times.

In the DTA record of the non-activated chalcopyrite there is an endothermic peak at 821 K, which in line with [2, 3], corresponds to the β -phase. A new peak at 530 ± 3 K and a decrease in the temperature of the above-mentioned peak characterize the DTA records of the mechanically activated samples. The mechanical activation brings about a decrease in temperature of the β -phase from 821 K (non-activated sample) to 763 K (optimally activated sample).

The apparent activation energy of the thermal decomposition of chalcopyrite falls from 238 kJ mol^{-1} to 72 kJ mol^{-1} . The fall in both quantities takes place in

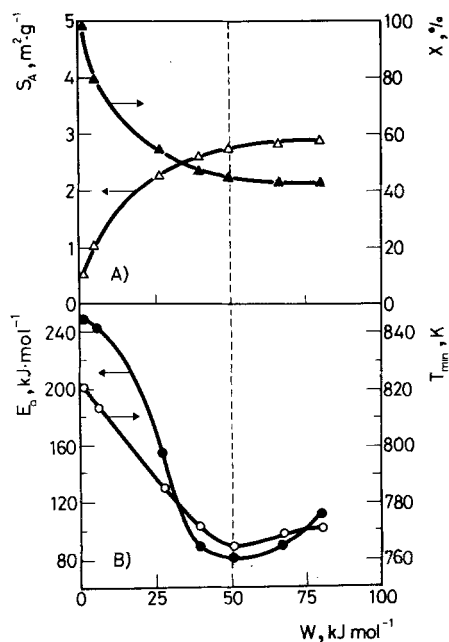


Fig. 2 A – Variations in specific surface S_A and crystalline phase content X of α - CuFeS_2 with specific energy of grinding W ; B – Variations in apparent activation energy E_a of thermal decomposition of CuFeS_2 and temperature T_{min} of endothermic DTA peak of β - CuFeS_2 with specific energy of grinding W

the interval of consumption of the specific energy of grinding $W \in \langle 0-50 \rangle$ kJ mol⁻¹ (Fig. 2). It is obvious that this region is characterized by the intensive formation of a new surface and by a decrease in content of the crystalline phase of chalcopyrite owing to transformation to the X-ray amorphous phase in the course of grinding. The aggregation of the particles during dry grinding and their sticking on the grinding media lead to constant specific surface and crystalline phase content values in the region $W > 50$ kJ mol⁻¹. The unfavourable influence of aggregation on the kinetics of thermal decomposition in this region manifests itself in slight increases in the values of E_a and T_{min} . Whereas the appearance of the β -phase is structure-sensitive, the temperature of the endothermic peak at 530 K does not change with varying surface and content of crystalline chalcopyrite in the course of grinding. In order to explain this fact, we rely on papers [7, 10], which report that β -chalcopyrite is produced by the intensive grinding of CuFeS₂, among other effects. The existence of the endothermic peak at 530 K for the mechanically activated samples may therefore be explained in agreement with the literature by the formation of the γ -phase from the β -phase.

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Zusammenfassung — Bei der experimentellen Untersuchung des Einflusses einer vorangehenden mechanischen Aktivierung auf die thermische Zersetzung von Kupferkies konnte folgendes ermittelt werden: 1. Absinken der Temperatur des endothermen DTA Peaks von β -CuFeS₂ von 821 K für unaktivierte Proben auf 763 K für optimal aktivierte Proben. 2. Absinken der scheinbaren Aktivierungsenergie der thermischen Zersetzung von CuFeS₂ von 238 kJ·mol⁻¹ für unaktivierte Proben auf 72 kJ·mol⁻¹ für optimal aktivierte Proben. Ein intensives Zermahlen von Kupferkies verändert die Temperatur für den endothermen DTA Peak und bringt ein Absinken der Aktivierungsenergie der Zersetzungsreaktion von CuFeS₂ mit sich. Beides kann den mechanisch hervorgerufenen Veränderungen in Struktur und Oberfläche des Minerals zugeschrieben werden.

Резюме — Представлены и обсуждены экспериментальные результаты о влиянии предварительной механической активации на термическое разложение халькопирита. Установлены следующие экспериментальные факты: а) Уменьшение температуры эндотермического ДТА пика от 821 К для неактивированного образца до 763 К для оптимально активированного, б) Уменьшение кажущейся энергии активации от 238 кдж·моль⁻¹ для неактивированного образца до 72 кдж·моль⁻¹ для оптимально активированного. Интенсивное измельчение халькопирита приводит к сдвигу температуры эндотермического пика ДТА и приводит к уменьшению энергии активации термического разложения халькопирита. Найденные результаты могут быть обусловлены механически наведенными отклонениями в структурных и поверхностных свойствах минерала.