

INFLUENCE OF MECHANICAL ACTIVATION ON DECOMPOSITION OF A CHALCOPYRITE-PYRITE MIXTURE IN AN OXIDIZING ATMOSPHERE

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The influence of the addition of pyrite and mechanical activation on an oxidative decomposition of chalcopyrite was studied. The course of the thermoanalytical curves and X-ray identification of the products showed that addition of pyrite affects mainly the endothermic processes taking place in region of low temperatures but does not significantly influence the temperature of CuSO_4 formation and its content in the products of decomposition. Changes in fine and superfine structure of chalcopyrite brought about by mechanical activation at grinding cause the complex of exothermic oxidative reactions to proceed at temperatures as much as 180 deg lower than for a non activated sample. The endothermic effect of these oxidation reactions become more marked and the proportion of CuSO_4 in the products of the oxidative decomposition increases significantly.

The decomposition of chalcopyrite in an oxidizing atmosphere is widely used as a preparatory operation in hydro- and pyrometallurgy. The complicated chemism and technological importance of this process attracted attention beginning from the early 1920-s [1].

Thermoanalytical study of the oxidative decomposition of chalcopyrite and X-ray identification of the intermediates and products have provided much information about the sequence of reactions occurring in this process. It has been revealed that the exothermic oxidation reactions prevail in the region of low temperatures [2, 3]. One of the intermediates is copper(II) sulphate, the desulphatization of which is an endothermic process. It has also been found that the final product is a mixture of copper ferrites.

Contemporary opinions concerning the nature of the exothermic reactions taking place in the region of low temperatures may be classified into two main groups. According to the first group the precursor of copper(II) sulphate is

copper(II) oxide, formed by oxidation of Cu_2S [4] or Cu_2O [5] while the second view is that copper(II) sulphate originates in the oxidation of bornite [2, 3].

The lack of consistence in the papers dealing with the oxidative decomposition of chalcopyrite suggests that the nature of the products formed at a given temperature depends on internal factors related with the chemical character and structure of the reacting substance. Natural minerals differ from each other in the quantity and kind of foreign substances. Their influence may be modelled by experiments involving the oxidative decomposition of chalcopyrite in the presence of additives. It is reported in [6, 7] that the addition of Fe_2O_3 and NaCl brings about a decrease in the temperature at which copper is oxidized to sulphate and the overall proportion of CuSO_4 in the products of thermal decomposition increases. In our study, we have used pyrite as an additive, the paragenesis of which with chalcopyrite frequently occurs in nature.

The actual structure of chalcopyrite may vary as a consequence of a great many external factors. The grinding used to prepare a powdered sample is a factor which increases the reaction surface and the concentration of irreversible defects in the bulk of the comminuted grains.

A change in the initial state of a solid substance due to mechanical stress may affect the course of its chemical reactions in different ways. If a chemical reaction is accelerated its energetic requirements are favourably influenced, or the sorptive or catalytic activity is improved, we speak about mechanical activation of the solid phase [8–9].

The results of a thermoanalytical study of mechanically activated chalcopyrite are presented in [10]. For mechanically activated samples of pure chalcopyrite a distinct structuralization of the exothermic effect in the DTA records and a shift in the characteristic maxima towards lower temperatures were observed. The proportion of CuSO_4 in the products of low-temperature decomposition increased, as in firing with additives. A satisfactory explanation of these facts has not yet been presented.

Starting from above analysis, we have investigated the changes in the fine and hyperfine structures of chalcopyrite and pyrite in the course of grinding with the aim of elucidating their influence on the thermal decompositions of the individual components of the mineral mixture in oxidizing atmosphere.

Experimental

The investigations were carried out with natural chalcopyrite and its mixture with pyrite (80% chalcopyrite, particle size 1000–100 μm , mixed with 20% pyrite, particle size finer than 200 μm). The chemical compositions of the investigated minerals are given in Table 1.

Table 1 Chemical analysis of minerals

Mineral	%					
	Cu	Fe	S	As	SiO ₂	Insoluble rest
CuFeS ₂	27.22	28.39	31.62	0.65	7.47	4.65
FeS ₂	—	42.81	49.66	—	7.53	—

The mechanical activation was accomplished in a vibration mill designed in the Mining Institute, Slovak Academy of Sciences, Košice. Amounts of 50 g were dry-ground at 75% packing of the mill, with steel balls 15 mm in diameter. The time of grinding t_m was varied from 0.125 to 8 hours, at a relative acceleration of the mill $b/g = 8.1$.

The specific surface S_A was determined via the adsorption of benzene vapour by the BET method [11]. The changes in structure were investigated through X-ray diffraction and ESR spectra.

The content of crystalline chalcopyrite X was determined by the method of an additional reference component [12]. A 50% addition of quartz served as reference component. The measurements were performed with a DRON 2,0 X-ray instrument (USSR) under the following conditions: Cu anode ($U = 30$ kV, $I = 20$ mA), displacement of counting tube 0.033 °/s, displacement of paper 0.04 m/s, sensitivity 10^7 impulses/s. Qualitative information about changes in the hyperfine structures of the investigated minerals in the course of grinding were obtained from the ESR spectra taken on an ERS-XQ instrument developed in the Central Institute of Physical Chemistry, Academy of Sciences, Berlin (GDR). The magnetic susceptibility was measured with a KAPPABRIDGE KLY-1 instrument (Institute of Applied Geophysics, Brno).

The thermal analysis was performed in the Institute of Geology and Geophysics, Academy of Sciences, Novosibirsk, USSR. The derivatograph (MOM, Hungary) was used under the following conditions: 50 mg amounts of pure sample, range of measurements 573–1273 K, oxidizing atmosphere, heating rate 10 deg/min. The results of DTA measurements were qualitatively evaluated and compared with the results of X-ray phase analysis, which was performed with samples calcined at the temperatures corresponding to the extremes in the DTA curves. The method of TG analysis was used to determine the mass increase due to the gradual oxidation of CuFeS₂ to CuSO₄.

Results

The low-temperature decomposition of chalcopyrite in an oxidizing atmosphere is characterized by exothermic effects in the DTA curves (Fig. 1), with maxima at 693, 733, 773 and 843 K. These maxima correspond to the minima at 613, 653, 713, 763 and 823 K in the DTG curves, and to a gradual mass decrease in the TG curves (Fig. 2). X-ray phase analysis of the products of decomposition at 673 K revealed the presence of hematite besides chalcopyrite (Table 2). Bornite was identified together with chalcopyrite and hematite at 743 K. The diffraction lines of chalcopyrite are impaired at 813 K, and the presence of CuSO_4 is indicated. In the temperature interval 843–953 K, the TG record indicates a mass increase due to the oxidation of bornite to CuSO_4 . In the temperature interval 933–1073 K, two endothermic effects are observed in the DTA curve, with a mass increase in the TG curve. According to X-ray diffraction analysis, a gradual desulphatization of CuSO_4 to oxysulphate, CuO and SO_2 proceeds in this temperature region. The presence of oxysulphate, which is a product of partial desulphatization, was ascertained at 1043 K. The desulphatization is completed at 1273 K, and only iron and copper oxides and copper ferrite are present in the product.

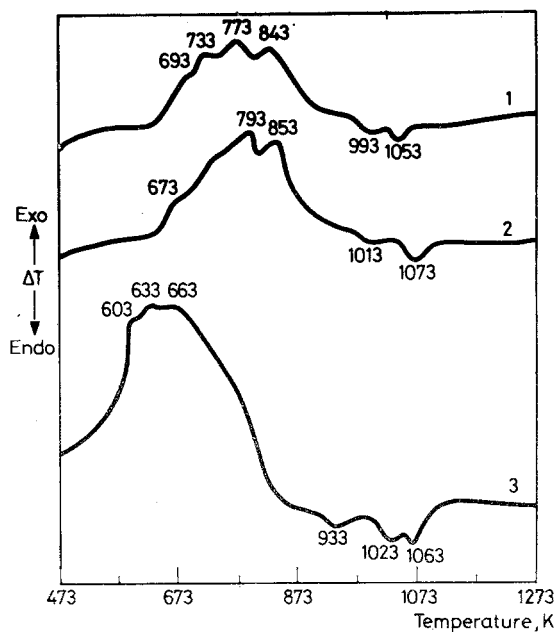


Fig. 1 DTA curves of non-activated CuFeS_2 (1), a CuFeS_2 - FeS_2 mixture (2), and a CuFeS_2 - FeS_2 mixture ground for one hour (3), in the temperature range 473–1273 K

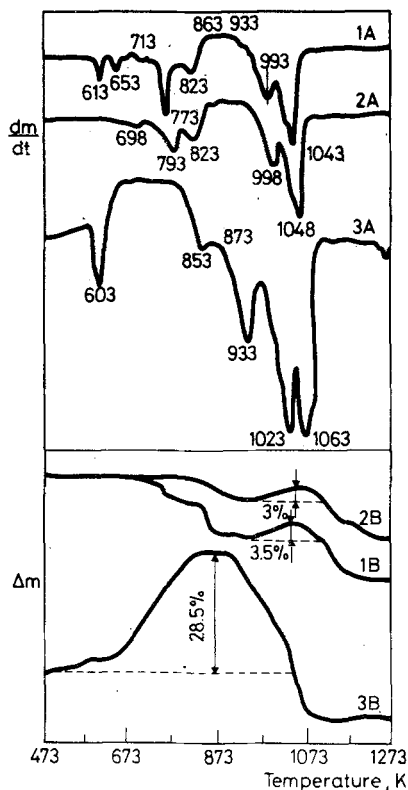


Fig. 2 TG and DTG curves of non-activated CuFeS_2 (1A, 1B), a CuFeS_2 - FeS_2 mixture (2A, 2B), and a CuFeS_2 - FeS_2 mixture ground for one hour (3A, 3B), in the temperature range 473–1273 K

The addition of pyrite affects the character of the endothermic processes taking place in the region of low temperatures. It suppresses the structuralization of the thermoanalytical curves and brings about slight shifts to higher temperatures in the characteristic maxima in the DTA and DTG curves. The presence of bornite in the products of oxidative decomposition was not proved. The first solid products of oxidation are CuSO_4 and $\alpha\text{-Fe}_2\text{O}_3$. The endothermic processes of desulphatization and the composition of the products of decomposition in the region of higher temperatures are not affected by the addition of pyrite. Similarly, the mass increase in the region of CuSO_4 formation is approximately equal to that observed for pure chalcopyrite.

Mechanical activation of the chalcopyrite-pyrite mixture has a significant influence on the course of the thermoanalytical curves and the composition of the reaction products at different temperatures. According to the DTA record, the

Table 2 X-ray diffraction analysis (ASTM data (13)) of chalcopyrite, pyrite and products of their oxidative decomposition in the temperature range between the extremes on DTA curves

Sample	Temperature, K	Grinding time, h	CuFeS ₂	FeS ₂	Cu ₃ FeS ₄	CuSO ₄	α-Fe ₂ O ₃	CuO, CuSO ₄	CuO	Fe ₂ CuO ₄	Cu ₂ O·Fe ₂ O ₃
CuFeS ₂	673		+				+				
	743		+		+		+				
	813	—	(+)			+	+				
	1043						+	+	+	+	
	1273						+		+	+	+
CuFeS ₂ + FeS ₂	583		+	+		(+)	+				
	673		+	+							
	793										
	853					+	+				
	1013						+	+			
CuFeS ₂ + FeS ₂	1143						+		+	+	
	1273						+		+	+	
	673		+	+		+	(+)				
	833–843					+	+				
	973	1				+	+				
FeS ₂	1043					+	+				
	1143								+	+	
	1273								+	+	+

endothermic oxidation reactions begin at temperatures as much as 180 deg lower than for non-activated samples. Two indistinct peaks are recorded, at approximately 633 and 663 K. The oxidative decomposition of chalcopyrite is accompanied in a wide temperature range by a mass increase, which proceeds in two steps. The maximum mass increase is almost 10 times greater than that observed with non-activated samples and is $\Delta m = 28.5\%$. Only CuSO₄ and α-Fe₂O₃ are present in the solid residue, as products of the oxidative decomposition in the temperature region 583–973 K. The gradual desulphatization of a large quantity of CuSO₄ is manifested in a mass decrease in the TG curve, and by three endothermic peaks, at 933, 1023 and 1063 K, in the DTA record. The presence of oxysulphate, which is a product of partial desulphatization, was observed as for the non-activated sample at 1043 K. The desulphatization is completed at 1143 K. CuO and the ferrites Fe₂CuO₄ or Cu₂O·Fe₂O₃ are present in the products. Hematite in the non-bound form is no longer present. These facts indicate that the decrease in the temperature

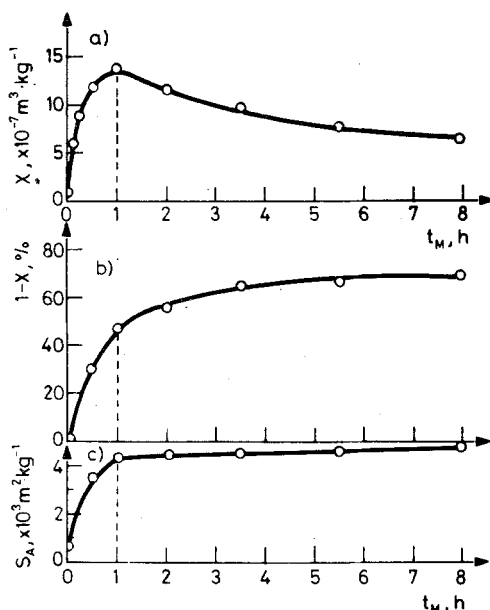


Fig. 3 Variations of specific surface S_A (plot 1A), content of crystalline phase X (plot 1B), and volume magnetic susceptibility χ (plot 1C) with the time of mechanical activation t_M

at which the primary oxidation processes take place is associated with a decrease in the temperature at which ferrites are formed in the region of higher temperatures.

In order to elucidate the influence of mechanical activation on the oxidative decomposition of chalcopyrite, we subjected the mineral chalcopyrite-pyrite mixture to mechanical activation during different times of grinding. Figure 3 provides information on the changes in physical properties of the chalcopyrite-pyrite mixture in the course of grinding. The specific surface increases up to 1 hour and subsequently stabilizes owing to the aggregation of the particles. During grinding, a quasi-generation of amorphous chalcopyrite takes place, while the structure of pyrite does not change. The transformations of the surface and the structure are accompanied by changes in the volume magnetic susceptibility of the mineral mixture. The 5 or even 15-fold increase in magnetic susceptibility suggests that the magnetically arranged phase is transformed into a non-arranged phase, and the substance passes from an antiferromagnetic into a paramagnetic state. This interpretation is confirmed by the changes in the ESR spectra presented in Fig. 4.

We have used the maximum mass increase Δm , corresponding to the amount of CuSO_4 in the products of thermal decomposition (Fig. 5), to estimate the effect of mechanical preactivation on the process of oxidative decomposition. A comparison of Figs 2, 3, 4 and 5 shows that the investigated quantities exhibit characteristic



Fig. 4 ESR spectra of chalcopyrite-pyrite mixtures. 1: non-activated sample; 2: mechanically activated sample, $t_M = 1$ hour

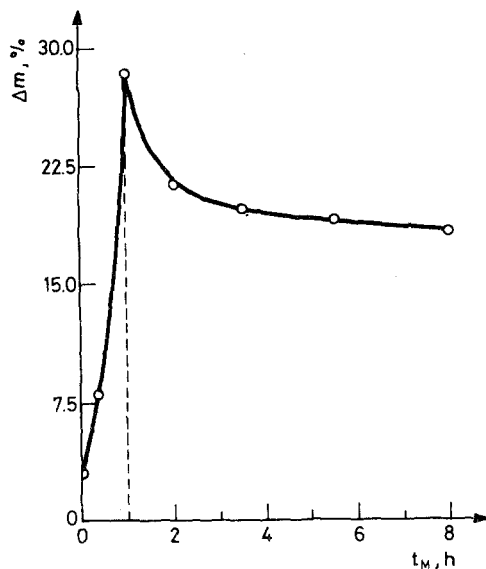


Fig. 5 Variation of maximum mass increase Δm in TG curves with time of mechanical activation t_M

extremes for the time of grinding at which the volume magnetic susceptibility attains its maximum and the highest concentration of paramagnetic centres is to be observed.

Discussion and conclusion

A comparison of the presented results with literature data [1-7] demonstrates that the chemism of the oxidative decomposition of chalcopyrite is perceptibly changed by the addition of pyrite and also by the alterations in the structure in the course of grinding.

In conformity with [2, 3], the oxidative decomposition of pure chalcopyrite proceeds through bornite as intermediate. The addition of pyrite results in the dissociation of chalcopyrite and its oxidation to CuSO_4 occurring in immediate succession, owing to which the presence of bornite in the products of the low-temperature decomposition has not been proved.

Mechanical activation of the chalcopyrite-pyrite mixture results in the exothermic oxidation reactions taking place at lower temperatures than for the non-activated mixture, the exothermic effect increases and the content of CuSO_4 in the products of thermal decomposition increases significantly.

Study of the structural transformations in the grinding products enables us to interpret the influence of mechanical activation on the process of oxidative decomposition on the basis of the following reasoning. The resulting enthalpic effect of the processes involved in the oxidation of sulphides may be simply expressed as an additive quantity:

$$\Delta H = \Delta H_R + \Delta H_K \quad (1)$$

where $\Delta H_R < 0$ is the reaction heat and $\Delta H_K > 0$ is the heat consumed for the work against cohesion forces when sulphur passes from the solid to the gaseous state in the form of SO_2 .

The increases in the reaction surface and the lability of the bonds in the disturbed structure result in a decrease in the cohesion work accompanying the liberation of SO_2 , and thus produce an increase in the resulting exothermic effect in the region of primary oxidation processes.

The mechanical activation also influences the mechanism of the oxidative decomposition. The formation of active paramagnetic centres on the fresh surface produced by alterations in the hyperfine structure of chalcopyrite significantly affects the temperature of CuSO_4 formation. The temperature at which chalcopyrite is oxidized to CuSO_4 decreases with increasing content of the paramagnetic phase in the products of grinding. The temperature of desulphatization does not appreciably change as a consequence of mechanical activation. The temperature interval in which CuSO_4 is formed is considerably extended, and the amount of CuSO_4 in the products of thermal decomposition rises. This fact may be put to practical use in the oxidative decomposition of chalcopyrite ore in hydrometal-

lurgy, because it may result in a useful saving of the heat needed for decomposition and elevate the content of the fraction soluble in water and dilute acids.

The chemism of the oxidative decomposition of chalcopyrite is perceptibly changed by the addition of pyrite and by the structural alterations during mechanical activation. The oxidative decomposition of chalcopyrite proceeds through bornite as intermediate. However, bornite does not occur in the presence of pyrite in the decomposition products. The impairment of the bonds and the generation of active paramagnetic centres on the fresh surface due to the alterations in the fine and hyperfine structures of chalcopyrite during grinding cause the exothermic oxidative reactions to proceed at temperatures as much as 180 deg lower than those for the non-activated mineral mixture. The exothermic effect is increased and the content of CuSO_4 in the products of decomposition is also significantly higher.

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Zusammenfassung — Am oxidativen Zerfall von Chalkopyrit wurde der Einfluss der Zugabe von Pyrit sowie der mechanischen Aktivierung untersucht. Der Verlauf der thermoanalytischen Kurven und Röntgendiffraktionsanalyse der Produkte zeigten, dass die Zugabe von Pyrit hauptsächlich die sich bei niedrigeren Temperaturen abspielenden endothermen Prozesse beeinflusst, nicht aber die Bildungstemperatur von CuSO_4 sowie dessen Gehalt in den Zersetzungsprodukten. Durch mechanisches Aktivieren mittels Feinmahlen hervorgerufene Veränderungen in der Fein- und Superfeinstruktur lassen die Gesamtheit der exothermen oxidativen Reaktionen bei Temperaturen ablaufen, die etwa 180 Grad

unterhalb derer für unaktivierte Proben liegen. Die endotherme Färbung dieser Oxidation wird eindeutiger und der Anteil von CuSO_4 in den Produkten des oxidativen Zerfalles nimmt eindeutig zu.

Резюме — Изучено влияние добавок пирита и механического активирования на окислительно-восстановительное разложение халькопирита. Ход термоаналитических кривых и рентгенофазовый анализ образующихся продуктов показал, что добавка пирита затрагивает в основном эндотермические процессы в области низких температур и оказывает незначительное влияние на температуру образования сульфата меди и содержания ее в продуктах разложения. Изменения тонкой и сверхтонкой структуры халькопирита, вызванные механическим активированием путем размола, вызывают сложные экзотермические окислительно-восстановительные реакции, протекающие при температурах на 180° ниже, чем для неактивированного образца. Эндотермический эффект этих реакций становится более заметным и значительно увеличивается доля сульфата меди в продуктах окислительно-восстановительного разложения.