Thermochimica Acta, 93 (1985) 709-712
Elsevier Science Publishers B.V., Amsterdam

THERMOANALYTICAL INVESTIGATION OF THE OXIDATIVE DECOMPOSITION OF MECHANICALLY ACTIVATED CHALCOPYRITE

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ABSTRACT

Depending on the kind and intensity of mechanical stress, intense fine grinding of chalcopyrite will lead to changed solids properties. In this contribution, we will report especially on the thermoanalytical results of the oxidative decomposition of wet and dry ground chalcopyrite.

INTRODUCTION

It has been already noted elsewhere that in addition to an enlargement of surface area also changes of fine structure and reactivity in dissolving reactions and thermical processes are caused by intense comminution of chalcopyrites /1, 2/. The results discussed in the following refer to a comparison between wet and dry grinding. The investigated thermical decomposition of chalcopyrite in air and subsequent leaching in sulfuric acid are also of a certain technological interest. The results show that with partially decomposed prodncts nearly selective copper leaching is possible. As test material a pyritiferous and quartz-bearing chalcopyrite of the Slovinky deposit (Czechoslovakia) was used. For fine grinding tests a laboratory vibration mill as well as a tube vibration mill (dry grinding under N_2 inert gas) and an attrition mill (wet grinding with H_2O) were used at varied grinding times. Further details concerning grinding conditions and the physical-chemical characterization of ground products are given in /2/.

MEASURING METHODS

Thermoanalytical studies were carried out in the Mettler thermoanalyzer TA 1 within a temperature range of 25 to 1000°C under atmosphere at a heating rate of 6 K/min. Having a weighed sample amount of 5 mg and Al_2O_3 as reference sample the following

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Proceedings of ICTA 85, Bratislava

measuring ranges were chosen: TG = 1 mg, DTG = 2 mg/min, DTA = 100 μV (Pt/PtRh thermoelements).

In addition to unnealed samples, partially decomposed reaction products (1 h annealing at 300-600°C in the muffle furnace under air exit) were leached under the following conditions: H_2SO_4 concentration = 17,5 %, solid-liquid ratio = 1:60 leaching time - 2 h at intense mixing and in presence of air and at a temperature of 25°C. The dissolved amounts of iron and copper were analyzed by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

In agreement with literature /3/, chalcopyrite is decomposed by thermical treatment in presence of air at first under liberation of sulfur. Above 250°C sulfide oxidation proceeds in rather a complex way being associated with an incease of mass and several exothermal DTA effects. Above 600°C sulfate decomposition occurs to a higher degree being associated with a decrease of mass and endothermal DTA effects. From the thermoanalytical results - discussed in the following - it can be seen that the kind and intensity of mechanical stress cause partially a remarkable decrease of reaction temperature and a change of the decomposition mechanism. Selected thermogravimetric results covering the interesting temperature range from 300 to 700°C are represented in Fig. 1.

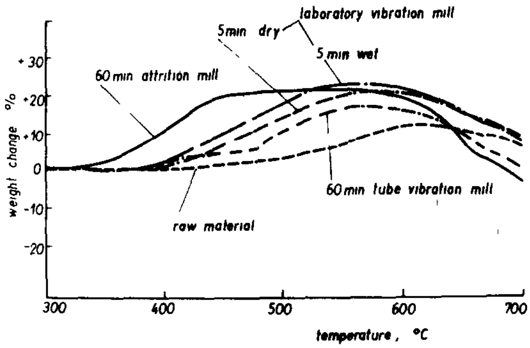

Figure 1:
Change of mass during the oxidative decomposition of chalcopyrite as a function of temperature for the raw material and the products ground for 5 min by wet or dry grinding in the laboratory vibration mill, for 60 min in the attrition mill or for 60 min in the tube vibration mill

Although the changes of fine structure are proven to be greater in dry grinding (see /2/), a higher reactivity occurs in wet grinding, as mechano-chemical reactions are already proceeding between H_2O and $CuFeS_2$. It is typical that especially on the reactive wet ground samples (laboratory vibration mill or attrition mill) a marked distinction between sulfide oxidation and sulfate decomposition is observed. On the initial sample and at dry vibration grinding this plateau of the DTA curve is not detectable. There are also typical differences in the thermoanalytically detectable DTA effects. As shown in the DTA curves of Fig. 2 grinding causes stronger structurization of exothermal effects, a distinct shifting to lower temperatures being observed with increasing intensity of stress.

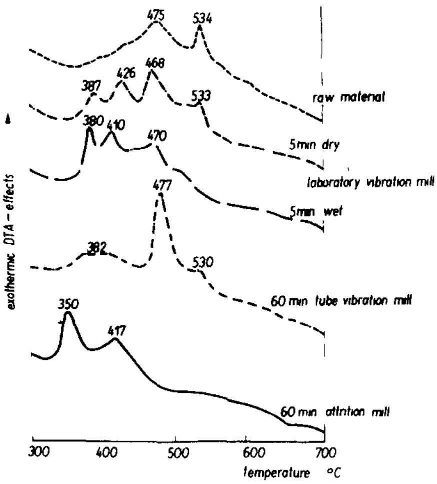

Figure 2:
Shape of DTA curves for selected chalcopyrite samples

The outlined differences in reactivity become still more instructive by the use of quasi-isothermal thermoanalysis. More details about this are given in the poster and in another publication /3/. As shown by the selected leaching results given in the following table, also in H_2SO_4 leaching without pressure a certain increase of dissolving reactivity is achieved by intense fine grinding.

Table: Dissolving behaviour of chalcopyrite in 17,5 % sulfuric acid after mechanical activation and subsequent annealing under air atmosphere.

Absolute content in the initial sample: copper=23 %, iron=31 %

Temperature of decomposition °C	Raw material Cu	Fe	60 min tube vibration mill Cu	Fe	60 min attrition mill Cu	Fe
	rel.%		rel.%		rel.%	
25	2	7	16	23	16	30
300	2	9	53	55	55	59
400	52	53	57	50	67	45
500	76	25	69	26	79	30
600	87	8	86	8	86	8

The sulfates formed by oxidative decomposition lead to a marked increase of the soluble copper and iron amounts. With increasing temperature of decomposition the amount of copper continues to increase, whereas the iron amount clearly decreases due to the formation of α-Fe_2O_3. With samples tempered at 600°C nearly selective copper leaching is achieved. As expected the effect of grinding progressively diminishes during annealing.

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