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INVESTIGATION OF THE OXIDATION OF METAL SULPHIDES AND SULPHIDE CONCENTRATES

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ABSTRACT

In this systematic investigation of the oxidation of metal sulphides and sulphide concentrates by various methods, including chemical, mineralogical and sieve analysis, together with combined DTA, DTG and gas phase analysis, it was found that the system could be defined by the use of the following characteristic temperatures:

T_1, the temperature at the onset of the process of oxidation;

T_2, the temperature at the onset of the intensive carrying out of the process of sulphide oxidation;

T_2', the temperature at the onset of the intensive oxidation of the most easily oxidized sulphide of the concentrate;

T_2'', The temperature at the onset of the intensive oxidation of the main sulphide of the concentrate;

T_3, the temperature of the intensive carrying out of the process of oxidation;

T_4, the minimum temperature above which the processes are carried out at high speed up to the degree of desulphurization necessary for the practice;

T_5, the maximum acceptable temperature of roasting the concentrates in a fluid bed;

T_6, the minimum temperature at which the material is sintered and falls on the grid (in fluid-bed roasting).

The suggested temperatures have a comparative character, due to the complexity of the processes of oxidation and the influence of many factors.

INTRODUCTION

The preliminary characteristics of natural sulphides and sulphide concentrates is of great importance for their processing [1–3]. The temperatures at which the processes of oxidation are carried out during the processing of the metal sulphides and sulphide concentrates depend on many conditions: (a) chemical, mineralogical and granulometric content of the raw material; (b) the purpose of the thermal processing; (c) additional steps of the

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technological process; (d) the apparatus used; (e) the possibility of extracting the heat released from the process; (f) economical considerations, etc. [4–7].

In literature, the concentrates are usually characterized by their chemical and granulometric content [8,17,18] and very rarely by their temperature of ignition. The temperature of ignition (T_{ign}) represents the lowest temperature up to which the sulphide has to be heated for the burning to begin and spread further through its mass without additional external heat. At this temperature and above, the process of oxidation takes place at such a speed that the released heat is sufficient to maintain the reaction [5–11]. The temperature of ignition is not constant. It is a conditional kinetic characteristic of sulphide reactivity and depends on its physical and chemical properties as well as on the conditions of oxidation [6,9].

Due to the inadequate degree of development of the theory of solid substances burning in cases where solid products are generated, and the lack of systematic data about the character of the heat- and mass-transport in such systems [6,8,11], it is not possible to calculate the temperature of ignition; usually it has been determined experimentally by DTA. Some authors [7,12–14] determine T_{ign} from the differential curve.

Previous investigations show that such a determination is not correct [15]. The process begins at the onset temperature of the DTA peak but after some time the reaction slows down, not reaching the whole mass of the substance. From a technological point of view, of greater interest is the minimum temperature at which the process, once begun, will be completed to the necessary degree of transformation (desulphurizing) without outside interference.

EXPERIMENTAL

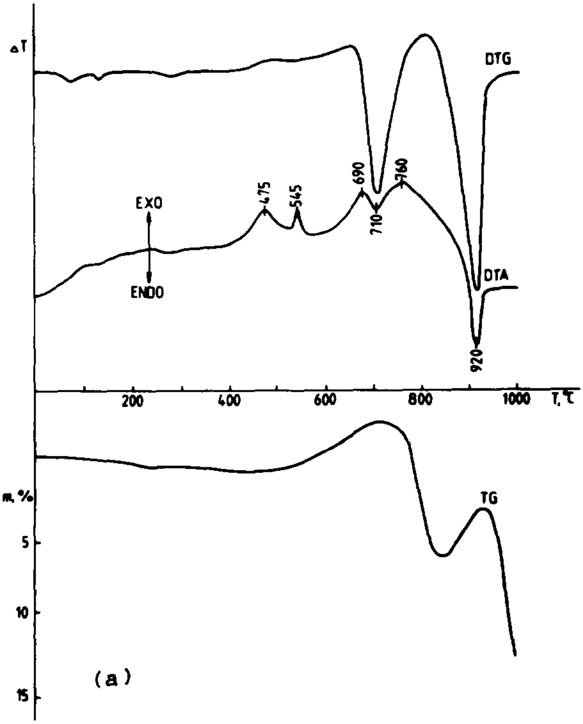
Bearing in mind the complexity of the heterogenic process taking place during the oxidation of metal sulphides of the type solid + gas, it is suggested that for technological purposes a more complete and exact characterization of the natural metal sulphides and sulphide concentrates is necessary. The thermogravimetric, X-ray, chemical and gas analyses, γ-resonance spectroscopy and electronic microscopy methods of investigation have been used for the purpose of the present work. Experiments were conducted using the electroresistivity method [16,17] and the sieve, mineralogical and X-ray analyses of the products of roasting, aimed at examining the possibility of intensifying the roasting of the sulphides by increasing the temperature.

The thermograms of the sulphides and the sulphide concentrates were made on a Mettler type thermograph in air at a heating rate of 8°C min^{-1} and using 0.02–0.05 g of the samples. The X-ray phase analysis was performed on a TUR-M-62 diffractometer. The γ-resonance spectra were obtained on a standard Mössbauer spectrometer, operating in conditions of constant acceleration regime and using a multichannel analyzer. The measurements were performed at room temperature with powder samples. The surfaces of the sulphide minerals were examined on a "JEOL"-IXA 50A scanning electronic microscope. The same apparatus was used for the X-ray microanalysis of the individual mineral grains of the high temperature sintered material from the bottom of a fluid-bed furnace.

The change of the electric resistivity of the fluidized material of the sulphide charge, at a temperature raised to 1200°C at a heating rate of 10°C min^{-1}, was measured using apparatus described previously [16].

RESULTS

A thermogravimetric investigation of sulphide minerals and concentrates was conducted. The size of the metal sulphide particles was $-0.25+0.10$ mm, and that of the concentrates -0.50 mm. A part of the obtained results is shown in Fig. 1 and Tables 1 and 2. T_1 is the temperature at the onset of the process of oxidation (Fig. 2), and is established by the use of DTA (the first change in the direction of the curve) and analysis of the gas phase (SO_2 liberation was established).



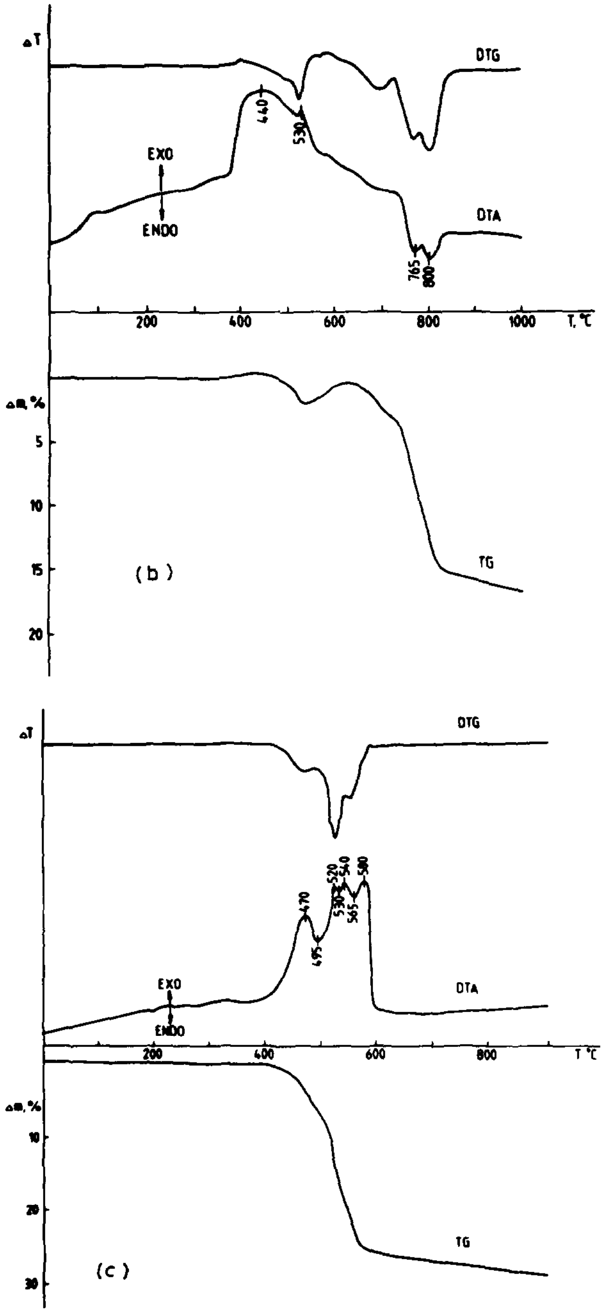


Fig. 1. DTA and DTG thermograms of sulphide concentrates. (a) Zinc; (b) copper; (c) pyrite.

T_2 indicates the onset of the process of intensive oxidation of the metal sulphide (the sharp bend of the DTA curve). Many authors take [7,12–14] this temperature for T_{ign}. With the concentrates the onset of the intensive

TABLE 1

Results from the investigations with natural sulphide materials

Mineral and content	Characteristic temps. (°C)						Δm	
	T_1	T_2	T_3	T_4	T_m		T (°C)	(–), %
					Exo	Endo		
Sphalerite								
Zn, 65.9%; S, 32.4%	650	680	800	980	800*		900 1000	12.13 15.21
Marmatite								
Zn, 55.1% Fe, 11.7%; S, 33.01%	640	665	760	695	750*	890	900 1000	12.77 15.04
Galena								
Pb, 85.4%; S, 12.9%	750	780	800	970	830* 950*	910	900	2.0
Chalcopyrite								
Cu, 32.8%; Fe, 30.2%; S, 34.65%	370	420	500	840	450* 510 565* 600	770 820	800 850	1.06 12.01
Chalcocite								
Cu, 79.7%; S, 20.2%	300	415	480	1100	470* 560* 620	835 1080*	1000	11.28
Pyrite								
Fe, 46.3%; S, 52.5%	370	440	480	730	505* 550*	510 570* 620*	700	31.94

* The highest peaks on the thermograms.

TABLE 2

Results from the investigations with sulphide concentrates

Concentrate and content	Characteristic temps. (°C)							Δm		Phases
	T_1	T_2'	T_2''	T_4	T_5	T_m		T(°C)	(−), %	
						Exo	Endo			
Zinc Zn, 48.76%; Pb, 2.75%; Cu, 1.10%; Fe, 9.37%; SiO_2, 4.4%; S, 31.96%	410	450	650	970	1100	475 545 690 760*	710 920*	1000	12.23	β-ZnS, mZnS, nFeS, PbS, α-SiO_2
Copper Cu, 13.65%; Fe, 30.18%; S, 34.21%; SiO_2, 12.95%; Al_2O_3, 2.75%	370	380	380	825		440* 530	765 800	900	10.3	$CuFeS_2$, FeS_2, α-SiO_2
Copper–zinc Zn, 26.00%; Cu, 11.00%; Fe, 17.92%; Pb, 2.25%; S, 32.16%; SiO_2, 0.75%	280		350	880	920	460* 550 770 700 950	520 660* 880*	1000	11.00	β-ZnS, $CuFeS_2$, FeS_2, PbS
Pyrite Fe, 41.26%; S, 41.00%; Zn, 1.00% SiO_2, 11.00%; Al_2O_3, 2.35%	380		420	600		470* 520 540 580	495* 565	700	26.33	FeS_2, α-SiO_2

* The highest peaks on the thermograms.

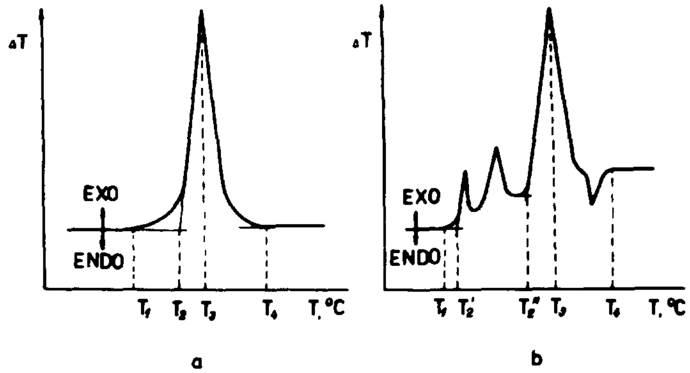


Fig. 2. Thermograms with the characteristic temperature for the oxidation of (a) metal sulphides; and (b) sulphide concentrates.

oxidation of the most easily oxidized sulphide is given as T'_2. The temperature at the onset of oxidation of the main sulphide is as T''_2, and is determined by DTA.

T_3 is the temperature of the thermogram peak, and is close to the temperature of completion of the process of oxidation with time [15]. It is established from photographs of the isothermal thermograms, measuring the area of the peaks and analyzing the quantity of the released SO_2.

The minimum temperature above which the processes are carried out at a high rate up to the degree of desulphurizing, necessary in practice, is T_4, and is determined by DTA, gas phase analysis and measuring the change in the sample weight.

T_5 is the maximum acceptable temperature of roasting the material in a fluid bed, and is determined by measuring the electroresistivity of the fluid bed at increased temperature and sieve analysis of the product.

The summary mass change of the sample is Δm and the highest peak of the thermograms is indicated by *.

Copper and iron sulphides oxidize at lower temperatures, while those of zinc and lead oxidize at considerably higher temperatures (Table 1). FeS decreases the characteristic temperatures of marmatite compared with those of sphalerite. The results obtained show that the different samples of one and the same material may differ in their characteristic temperatures, due to the difference in the impurities in the lattice, the different types, size and concentration of the surface defects (Fig. 3), structural defects, and different degrees of crystallization. For example, the alloying of CdS with donor impurities (Ga) reduces the onset temperature of the process of oxidation, while alloying with acceptor impurities (Ag) increases the temperature, compared with pure sulphide. The alloying with impurities reduces the other characteristic temperatures compared with pure CdS [15].

The chemical and phase contents of the sulphide concentrates are shown

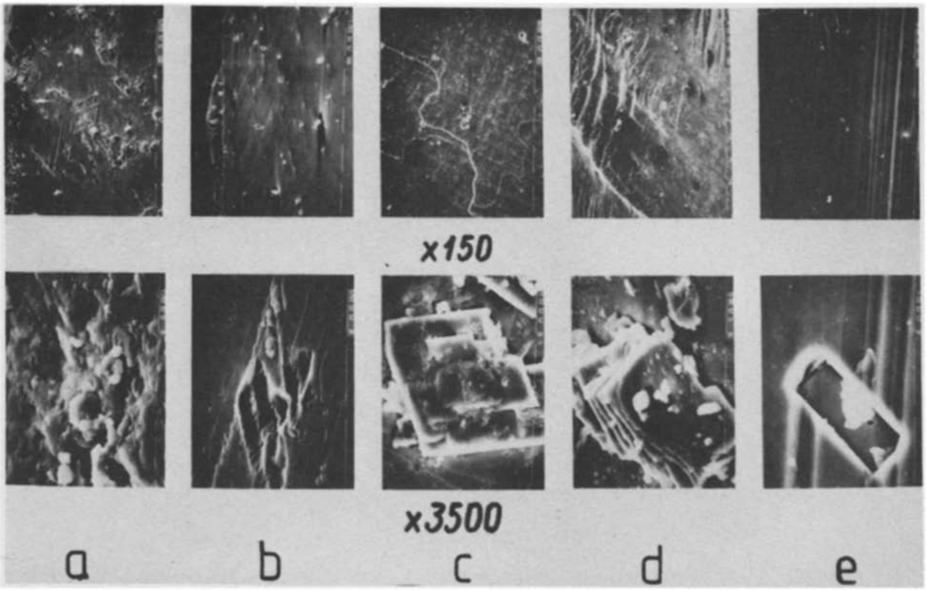


Fig. 3. Electron microscope photographs of the surfaces of sulphide minerals (×150 and ×3500). (a) Sphalerite; (b) marmatite; (c) galena; (d) chalcopyrite; (e) pyrite.

in Table 2, along with the characteristic temperatures. The phase content was established with the help of X-ray phase analysis. Mössbauer spectroscopy was used for the more exact identification of the iron containing phases.

It is interesting to compare some of the characteristic temperatures from Tables 1 and 2; for example, T_m of the sphalerite, marmatite and zinc concentrates. Through the DTA and DTG curves (Fig. 1) for marmatite and the concentrate it was possible to establish the endo effects, as well as the change in the sample weight, characteristic for $ZnSO_4$ decomposition to $ZnO \cdot 2\ ZnSO_4$ and ZnO [19]. With the sphalerite this is shown only on the DTA curve and to a rather small degree. This may be explained by the formation of secondary sulphates in the process of roasting due to the catalytic oxidation of SO_2 to SO_3 in the presence of iron oxides.

The behaviour of the mixture of sulphides and complex metal concentrates differs from that of the separate component parts [4]. It is possible for the reaction of one component to mask the reaction of another and this makes it more difficult to decode the data obtained from DTA.

With the sulphide concentrates a reduction of the onset temperature of the intensive oxidation is observed (Table 2) compared with the respective metal sulphides. This may be explained by the presence of some other minerals in the concentrates (except the main one), the presence of smaller size particles, and the greater amount of defects in the sulphide structure contained in the concentrates.

From a technological point of view the temperature T_4, above which the intensive oxidation takes place to the necessary degree of desulphurizing in the whole of the concentrate, is of great interest. It allows a suggestion about the temperature of roasting the respective concentrates to be made. At the same time the kinetics of the process and the possibilities of agglomeration of the particles as a result of the appearance of some quantity of a liquid phase should be considered. The character of further technological operations and the production economy have also to be considered.

In industry the individual concentrates are roasted in fluid beds at different temperatures: zinc, 950°C, copper, 750°C, copper–zinc, 800–900°C and pyrite, 700–750°C. In the roasting of copper and copper–zinc concentrates one is not attempting the full sulphur elimination, which explains why temperatures lower than T_4 are used in industry.

Our previous investigations of the kinetics and mechanism of the oxidation of metal sulphides have shown that the principal factor in the investigation of these processes is the increase in temperature. The results of the investigations using electric resistivity and sieve analysis of the products of roasting show the following characteristic temperatures: T_5, the temperature above which the fluid-bed roasting is difficult and there is the danger of the bed falling on the floor of the furnace, and T_6, the lowest temperature at which the material is sintered and falls on the grid.

The results of the investigations, carried out with different zinc concentrates [17] (1, Bulgarian, 2, Peruvian, 3, Australian, 4 and 5, Turkish, 6, Irish, 7, Yugoslavian and 8, copper–zinc) are presented in Table 3. The results obtained show that zinc concentrates of standard and higher (in certain limits) Pb, SiO_2, Fe, Cu, etc., contents may be roasted in a fluid bed up to 1000°C. Concentrates 6 and 8 should be roasted at temperatures not higher than 960°C and 900°C, respectively (eventual local superheating leads to coarsening of particles).

The investigations aim at the determination of the character of the metal sulphides and sulphide concentrates. This necessitated experiments to study the kinetics and the mechanism of oxidation of the sulphides and the roasting of the sulphide concentrates. On the grounds of laboratory investi-

TABLE 3

Characteristic temperatures for the roasting of zinc concentrates in a fluid bed

	Concentrate							
	1	2	3	4	5	6	7	8
T_5	1100	1030	1060	1050	1070	990	1080	920
T_6	1180	1100	1140	1160	1160	1130	1180	1020

gations and available literature, industrial investigations have been carried out with the purpose of intensifying the roasting of zinc concentrates in a fluid bed [18,20] and establishing a proper technological regime of roasting of copper–zinc concentrates.

CONCLUSIONS

On the grounds of the systematic investigations of the oxidation of the metal sulphides and the roasting of the sulphide concentrates, as well as the data from the literature, with the purpose of obtaining preliminary information about the possibilities of applying some chemicotechnological processes, the following suggestions are made.

(1) In characterizing the metal sulphides the following temperatures have to be considered, as well as chemical, mineralogical and sieve analyses:

T_1, the temperature at the onset of the process of oxidation—determined by DTA and gas phase analysis;

T_2, the temperature at the onset of the process of intensive oxidation—determined by DTA;

T_3, the temperature of the process of intensive oxidation determined by the peak of the thermogram;

T_4, the minimum temperature above which the processes are carried out at high speed to the degree of desulphurizing necessary for the practice—determined by DTA, gas phase analysis and measuring the change of the sample weight.

(2) In characterizing the metal sulphide concentrates, as well as the chemical, mineralogical and sieve contents, the following temperatures have to be considered:

T_1, the temperature at the onset of the process of oxidation—determined by DTA and gas phase analysis;

T_2', the temperature at the beginning of the intensive oxidation of the most easily oxidized sulphide—determined by DTA;

T_2'', the temperature at the onset of the intensive oxidation of the main sulphide of the concentrate—determined by DTA;

T_3, the temperature of the intensive carrying out of the process of oxidation—determined by the DTA peak of the thermal effect of the main sulphide;

T_4, the minimum temperature above which the processes are carried out at high speed to the degree of desulphurizing necessary for the practice—determined by DTA, gas phase analysis and measuring the change of the sample weight;

T_5, the maximum acceptable temperature of roasting the material in a fluid bed—determined by measuring the change in electric resistivity of the fluidized material and sieve analysis;

T_6, the lowest temperature at which the material has sintered and falls on the grid.

Due to the complexity of the processes carried out, and the influence of both the very material and the experimental conditions, the suggested temperatures are of a comparative character. They help the study of the sulphide oxidation and at the same time are of interest in the practice of the processing of the sulphide concentrates. The reactivity of the sulphides and concentrates in their high temperature oxidation can be determined by a combination of DTA, DTG and gas phase analyses.

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