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OXIDATION OF METAL SULPHIDES AND DETERMINATION OF CHARACTERISTIC TEMPERATURES BY DTA AND TG

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Abstract

The oxidation of metal sulphides and sulphide concentrates was studied by means of DTA, TG and DTG curves. The behaviour of ZnS, CdS, GaS, Tl_2S, Sb_2S_3 and Sb_2S_5 during thermal treatment in an oxidizing medium was investigated. The properties of these sulphides were compared and conclusions were drawn about their probable oxidation reactions and the kind of end-products obtained. The characteristic temperatures of the studied sulphides were determined on the basis of curves (DTA). The values obtained were used to compare the behaviour of the sulphides during the oxidation process in a fluid bed. The results can be used to improve the technological and economic indices in the industrial production of zinc.

Keywords: characteristic temperatures, concentrates, DTA, DTG, oxidation, sulphides, TG

Introduction

The oxidation of metal sulphides is a typical complex, multistage, exothermic process. A number of studies have been dedicated to this topic [1–4]. Its thermodynamics, kinetics and mechanism have been investigated, but it still is one of the most important issues to be clarified in the theory of metallurgical processes [5, 6].

The main component in zinc concentrates is the β-ZnS phase. The concentrates additionally contain sulphides of Fe, Cu, Pb, Cd, Ni, Ag, Sb, Ga, ln, Tl, etc. Quite important among them is cadmium sulphide, which is a source for obtaining cadmium [1, 7].

The study of the oxidation of metal sulphides and sulphide concentrates is a complicated problem, the solution of which requires systematic investigations using different methods and equipment [1, 8–13]. Important information in this connection is gathered through differential-thermal analysis and thermogravimetry [14, 15].

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The studies in this field have proved the necessity to determine the characteristic temperatures of the individual sulphides and sulphide concentrates [14].

The references show that no unified widely accepted methodology has been used for their determination. The values of the determined temperatures depend on the method of investigation, the nature and concentration of the sulphide, the chemical, phase and granulometric contents, the medium (pure oxygen, air or air enriched with oxygen), etc. The use of DTA and TG gives comparable results for determining the characteristic temperatures of sulphides and sulphide concentrates [5, 11, 14].

The aims of the present study are to investigate the oxidation of different metal sulphides which are present together with β-ZnS in zinc concentrates, to determine the characteristic temperatures and to suggest the probable mechanism of the oxidizing processes taking place.

Experimental

DTA, TG and DTG (Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 0.5 mV; DTG, 0.5 mV; TG, 100 mg; heating rate, 10 K min^{-1}; sample mass 100 mg. A platinum crucible was used. All the studies were performed in an air medium

X-ray diffraction analysis was carried out with a TUR-M62 apparatus (Dresden, Germany), using CoK_α radiation and an iron target.

All the studied sulphides were obtained by using various chemical methods; they were polycrystalline or monocrystalline substances. The particle size was –0.075 mm.

Results and discussion

The characteristic temperatures obtained are presented in Table 1.

In order to examine the probable mechanism of the oxidation processes taking place, Table 2 presents the probable reactions during the oxidation of the studied sulphides (based on data from the references and our own investigations).

Zinc sulphide – ZnS

Two kinds of zinc sulphide were studies: one from Fluka and the second (a monocrystalline one) from Russia. Their TG, DTG and DTA curves are presented in Fig. 1. Both types of zinc sulphide follow the oxidizing pattern of reaction 2 (Table 2). This is quite obvious from the TG curve, which is almost horizontal until the beginning of the oxidation process. The final mass loss at 1000°C (Table 1) confirms that the product of oxidation is zinc oxide. The theoretical mass loss is 16.4%, while the experiments show a loss between 13.5 and 15.0%. These values are very close to the theoretical ones and confirm that zinc sulphide oxidation follows the oxide theory, i.e. zinc oxide is obtained directly. The presence of impurities in zinc sulphide can change the curves obtained [16].

Table 1 Characteristic temperatures [14] of the studied metal sulphides

N	Sulphide	Temperature/°C				Δm at 1000°C/%
		T_1	T_2	T_3	T_4	
1	ZnS-Fluka	520	530	660	685	–13.5
2	ZnS-R (monocr.)	590	625	745	835	–15.0
3	CdS-Merck 1	505		635, 770	790	+1.0
4	CdS-Merck 2	505	535	630, 755	820	–6.0
5	CdS-BG	450	495	595, 680	725	0.0
6	CdS-R (monocr.)	660	725	790	830	–11.6
7	GaS	490	595	620, 660	720	–7.5
8	Tl_2S			450, 620		–80.0
9	Sb_2S_3			420, 585		–11.5
10	Sb_2S_5			190, 360, 565		–17.5

Note: R=Russian, BG=Bulgarian, monocr.=ground monocrystalline sample, T_1=temperature of the beginning of the oxidation process, T_2=temperature of the beginning of intense oxidation of the sulphide, T_3=temperature at which intense oxidation takes place, T_4=minimum temperature above which processes take place at a high rate up to the stage of desulphurization required

Comparison of the characteristic temperatures of the two sulphides (Table 1) reveals that the monocrystalline ZnS is oxidized at higher temperature. Its oxidation begins and ends at higher values of T_1 and T_4. The intense stage (T_3) also differs by 85°C. This may be explained through the different origins of the two sulphides: the ZnS of Fluka is obtained through a method which results in the formation of very thin particles. This in turn decreases the ignition temperature of the sulphide and its oxidation. The monocrystalline ZnS is ground to a particle size of less than 0.075 mm, which is larger than the one obtained through precipitation. The type of the crystal lattice and the way it is formed probably also affect the oxidation.

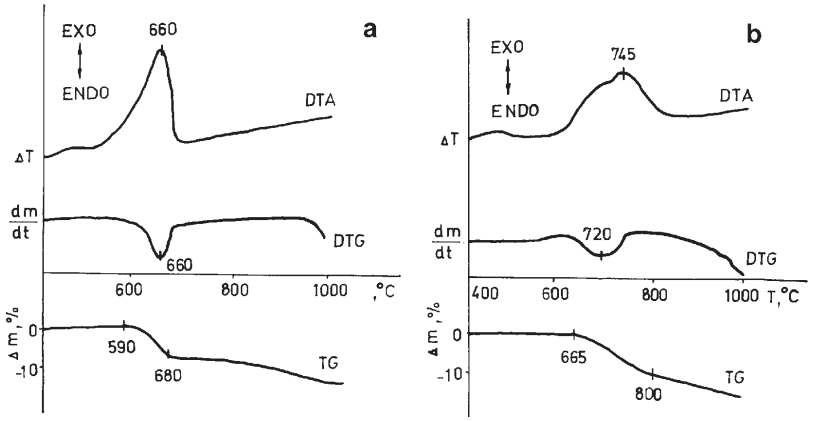

Fig. 1 TG, DTG and DTA curves of ZnS; a – Fluka; b – Russian (monocrystalline)

Cadmium sulphide – CdS

Four kinds of CdS were studied: two from Merck, a Bulgarian product and a Russian one. Both the German and the Bulgarian CdS samples are polycrystalline. The monocrystalline Russian CdS was ground to a particle size <0.075 mm. The TG, DTG and DTA curves of the tested samples are presented in Fig. 2.

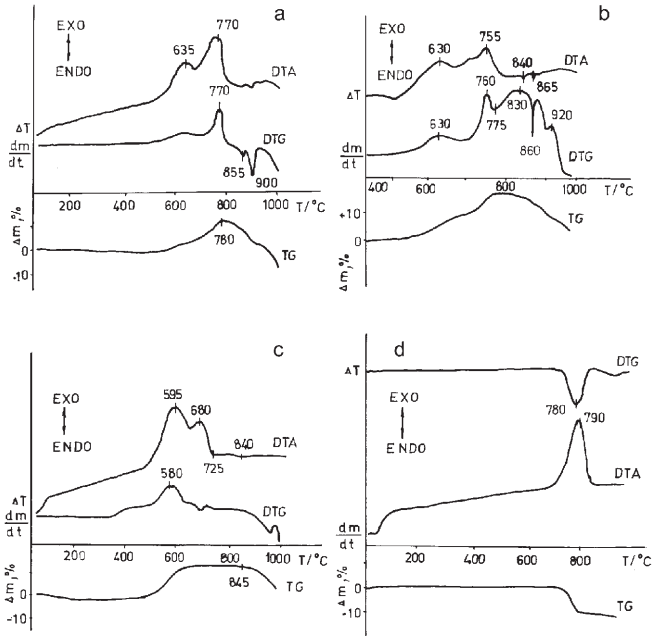

Fig. 2 TG, DTG and DTA curves of CdS: a – Merck 1; b – Merck 2; c – Bulgarian; d – Russian (monocrystalline)

Both Merck CdS samples gave quite similar types of DTA, DTG and TG curves, characterized by two-stage oxidation, the DTA curve maxima being at about 630 and 755°C. A similar picture was obtained in the oxidation of the Bulgarian CdS, but there was a shift in the temperatures T_1–T_4 towards lower values (Table 1).

From a theoretical point of view, the TG curves of the studied samples are of greater interest. The three kinds of sulphides have one feature in common: with the beginning of their oxidation, an increase in sample mass begins. This is due to reaction 4 (Table 2), i.e. the process of CdS oxidation (of the above-mentioned nature) confirms the sulphate theory. The process of $CdSO_4$ formation takes place up to a certain temperature (for the Merck samples 1 and 2, up to about 770 and for the Bulgarian CdS, up to about 845°C). Above the mentioned temperatures, decomposition begins.

The calculated theoretical increase in sample mass for the complete oxidation of CdS to $CdSO_4$ is 44.3%, while the experimentally determined value $+\Delta m$ was 13–18%.

This might mean that CdS is not completely oxidized to $CdSO_4$. Before the sulphate formation ends, its decomposition begins. Another probable explanation of the obtained results is the formation of $2CdO{\cdot}CdSO_4$ as an intermediate product [6]. Evidence that $CdSO_4$ is obtained in the course of oxidation is the presence of two endothermic effects at 825–840 and 840–865°C. These are related to the phase transformations α–$CdSO_4 \rightarrow \beta$-$CdSO_4 \rightarrow \gamma$–$CdSO_4$, which take place at the above-mentioned temperatures [17]. At a temperature of 1000°C, the process of $CdSO_4$ decomposition is still incomplete. From a theoretical point of view, in order to obtain pure CdO, the sample mass should decrease by 11.1%. The experimental data show that Δm varies within the limits of –6.0 and +1.0%, which is an indication that at 1000°C a blend of CdO and $CdSO_4$ is obtained.

Table 2 Possible reactions during oxidation of metal sulphides

N	Reactions	Δm/%
1	$ZnS+2O_2 \rightarrow ZnSO_4$	+65.7
2	$ZnS+3/2O_2 \rightarrow ZnO+SO_2$	–16.4
3	$ZnSO_4 \rightarrow ZnO+SO_2+1/2O_2$	–49.6
4	$CdS+2O_2 \rightarrow CdSO_4$	+44.3
5	$CdS+3/2O_2 \rightarrow CdO+SO_2$	–11.1
6	$CdSO_4 \rightarrow CdO+SO_2+1/2O_2$	–38.4
7	$3CdS+5O_2 \rightarrow 2CdO{\cdot}CdSO_4+2SO_2$	+7.3
8	$GaS+2O_2 \rightarrow GaSO_4$	+62.9
9	$2GaS+7/2O_2 \rightarrow Ga_2O_3+2S_2$	–7.9
10	$4GaS+17/2O_2 \rightarrow Ga_2(SO_4)_3+Ga_2O_3+SO_2$	+51.1
11	$Tl_2S+2O_2 \rightarrow Tl_2SO_4$	+15.7
12	$Tl_2S+3/2O_2 \rightarrow Tl_2O+SO_2$	–3.6
13	$Tl_2SO_4 \rightarrow Tl_2O+SO_2+1/2O_2$	–15.8
14	$Tl_2O+O_2 \rightarrow Tl_2O_3$	+7.5
15	$Tl_2O_3 \rightarrow Tl_2O+O_2$	–7.0
16	$Sb_2S_3+6O_2 \rightarrow Sb_2(SO_4)_3$	+56.6
17	$Sb_2S_3+9/2O_2 \rightarrow Sb_2O_3+3SO_2$	–14.1
18	$Sb_2(SO_4)_3 \rightarrow Sb_2O_3+3SO_2+3/2O_2$	–45.2
19	$Sb_2O_3+O_2 \rightarrow Sb_2O_5$	+11.0
20	$Sb_2O_5 \rightarrow Sb_2O_3+O_2$	–9.9
21	$Sb_2S_5+10O_2 \rightarrow Sb_2(SO_4)_5$	+79.3
22	$Sb_2S_5+15/2O_2 \rightarrow Sb_2O_5+5SO_2$	–19.8
23	$Sb_2(SO_4)_5 \rightarrow Sb_2O_5+5SO_2+5/2O_2$	–15.3
24	$Sb_2S_5 \rightarrow Sb_2S_3+S_2$	–15.9

The behaviour of CdS, obtained as a monocrystal, is very different (Fig. 2d). In this case, the oxidation takes place in one stage, T_3 having a value of 790°C. The TG

curve does not change until about 660°C, after which the mass begins to decrease. The change in Δm obtained at 1000°C (–11.6%) is quite close to the theoretical value (–11.1%) when reaction 5 is complete.

The study of CdS oxidation reveals that it cannot be assumed that this complicated heterogeneous process takes place in accordance with either the oxide or the sulphate theory alone. In this particular case, CdS of different origins and with different crystal structures confirms both theories.

Gallium sulphide – GaS

In the hydrometallurgical production of zinc, the removal of impurities (Ga, In, Tl, As, Sb and Ge) from the zinc sulphate solution is of considerable importance. This is achieved through co-precipitation with the $Fe(OH)_3$ obtained in the neutral cycle of zinc calcine leaching.

Because of the low concentration of the admixed elements, it is difficult to carry out a particular study of their sulphides under the conditions of industrial oxidation. Therefore DTA and TG were used under laboratory conditions in an attempt to draw conclusions about the probable behaviour of Ga, Tl and Sb sulphides during oxidation.

The probable reactions of GaS oxidation are presented in Table 2, and the obtained TG, DTG and DTA curves in Fig. 3. The DTA curve points to the fact that GaS oxidation takes place in two stages, with a maximum at 620–660°C. The first process is connected with a small increase in sample mass, which means that reaction 8 partially takes place. At above 620°C, the mass begins to decrease, but this process is only very weakly manifested until about 900°C. Beyond this temperature, the mass decreases much more rapidly and at 1000°C $-\Delta m$ is 7.5%. This is very close to the theoretical value for quantitative reaction 9. This means that the final product of GaS oxidation will be an oxide which remains in the solid phase.

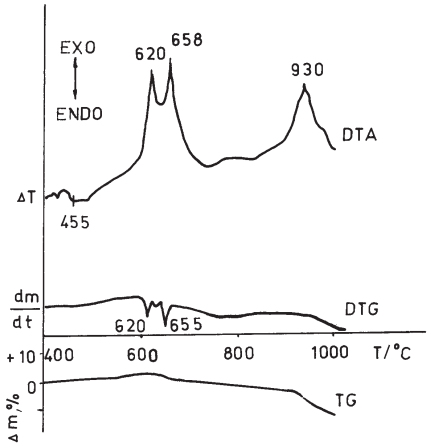

Fig. 3 TG, DTG and DTA curves of GaS

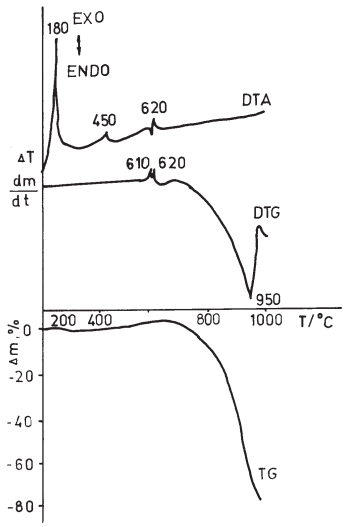

Fig. 4 TG, DTG and DTA curves of Tl_2S

The results obtained point to the conclusion that the oxidation of GaS present in zinc concentrates will result in the formation of an oxide that remains in the calcine and later passes into the zinc sulphate solution.

Thallium sulphide –Tl_2S

Thallium is among those elements whose concentrations in zinc concentrates are always controlled. Its quantity is merely several grams per ton, but it is nevertheless very harmful for the electrolysis of zinc sulphate solution if not eliminated in advance.

The TG, DTG and DTA curves of Tl_2S (Fig. 4) show the presence of thermal effects at about 450–600°C. After the exothermic effect at 450°C, a small increase in sample mass is noted, which is evidence that thallium sulphate is partially formed (reaction 11). This process continues slowly up to 630°C, after which a decrease in sample mass begins, this being particularly intense at 800°C. The oxidation of Tl_2S to Tl_2O_3 is associated with an increase in sample mass of 7.5%, while the oxidation to Tl_2O involves a decrease in sample mass by 3.6%. In this case, it is quite obvious that the loss of more than 80% of the mass is due to evaporation of the oxidation product.

Tl_2O_3 is unstable and at above 1000°C it begins to dissociate into Tl_2O and O_2. Above 800°C, the Tl_2O obtained evaporates intensely, and at 1000°C it is transformed almost completely into the gas phase [17].

The results obtained show that in zinc concentrate roasting Tl_2O will pass completely into the furnace gases. After condensation, a minor proportion of it will be caught in the uptake and the cyclone, and a greater part in the electrostatic precipitator. The properties of Tl_2O determine the passage of some thallium into the gases used in sulphuric acid production.

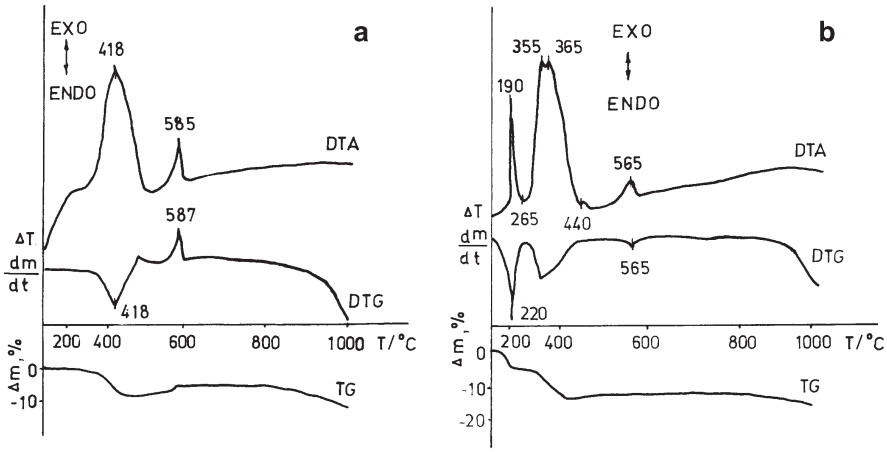

Fig. 5 TG, DTG and DTA curves of a – Sb_2S_3 and b – Sb_2S_5

Antimony sulphides – Sb_2S_3, Sb_2S_5

Antimony is one of the most harmful elements for zinc electrolysis. Its elimination by hydrolysis is therefore of utmost importance. In this connection, the oxidation of its sulphides could give an answer to the question of the products of roasting in which antimony is concentrated.

The TG, DTG and DTA curves of Sb_2S_3 and Sb_2S_5 (Fig. 5) demonstrate their very similar behaviour during oxidation. The presence of an exothermic effect for Sb_2S_5 at 190°C is due to its dissociation (reaction 24) and burning of the obtained sulphur. The oxidation process leads to the emission of more energy than that used for the dissociation, which results in an overall exothermic effect. Sb_2S_3 is oxidized at 360–420°C, most probably following reaction 17, which is associated with a theoretical decrease in sample mass by 14.1%. At 560–585°C, another exothermic effect is observed, but it is much weaker. This might be due to reaction 19, which results in the formation of a certain quantity of Sb_2O_5. When the temperature exceeds 845°C, the samples decrease in mass, most probably because of the volatility of Sb_2O_5. The final value of Δm is negative and very close to the theoretical one for the formation of Sb_2O_3. It might be possible for a certain quantity of Sb_2O_5 to be present in the end-product at 1000°C.

The results obtained allow the conclusion that antimony does not accumulate in any particular products of zinc concentrate roasting. A comparatively uniform distribution among the calcine, the dust from the uptake and the cyclone and the dust from the electrostatic precipitator is to be expected.

Conclusions

1. The characteristic temperatures in the oxidation of ZnS, CdS, GaS, Tl_2S, Sb_2S_3 and Sb_2S_5 have been determined. Suggestions are made about the behaviour of these sulphides in zinc sulphide concentrate roasting.
2. The results obtained show that, during oxidation, the metal sulphides follow either the oxide or the sulphate theory, which depends on the method of their production and the type of the crystal lattice.
3. At the temperature of zinc concentrate roasting (930–950°C), as a result of the oxidation of sulphides, the following compounds can be expected to be present in the calcine obtained: ZnO, CdO, $2CdO \cdot CdSO_4$, Ga_2O_3, Sb_2O_3 and Tl_2O, concentrated in the dusts.

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