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FORMATION AND REACTIVITY OF COPPER SULPHIDE, Part II*, OXIDATION

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ABSTRACT

The oxidation behaviour of precipitated copper sulphide samples has been studied by thermogravimetry, and correlations have been made with the particulate properties. The particle size affects both the temperature of the oxidation and the composition of the products.

INTRODUCTION

The thermogravimetric behaviour of copper sulphide in flowing air has been previously investigated, particularly by Razouk et al (ref. 1) and by Shah and Khalafalla (refs. 2-4). The oxidation pattern of copper sulphide in flowing air is thus fairly well understood.

In this work, variations in thermogravimetric behaviour have been correlated with the particulate properties of the copper sulphide samples prepared under different precipitation conditions, as described previously (ref. 5).

MATERIALS

The TG curves obtained were compared with those of BDH technical grade copper(II) sulphide and Alfa Products 95% copper(I) sulphide.

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*Part I, Thermochimica Acta. This volume, previous paper.

EXPERIMENTAL

The oxidation of the copper sulphide samples was investigated using thermogravimetry, using a Stanton Redcroft TG-750 microbalance. Phase compositions of products were determined by x-ray powder diffraction. The oxidations were performed using 5-10 mg samples in a platinum crucible, in an atmosphere of flowing air (20 cm^3 min^{-1}). The temperature was increased at a rate of 10°C per minute, from ambient to 1000°C.

Oxidation of slightly larger samples (approx. 0.5g) for x-ray identification of intermediate products, was followed using the Stanton Redcroft TRI thermal balance.

When the phases present in the intermediate stages of the thermal oxidation of copper sulphide had been established, a computer program was devised to calculate the mole fractions of each phase present at the relevant stage, and to determine the stoichiometry of the precipitated material.

RESULTS

Generally, the oxidation behaviour of the copper sulphide samples in flowing air showed typical thermal analyses, as in earlier work (refs. 1-4), giving curves of the form shown in Figure 1.

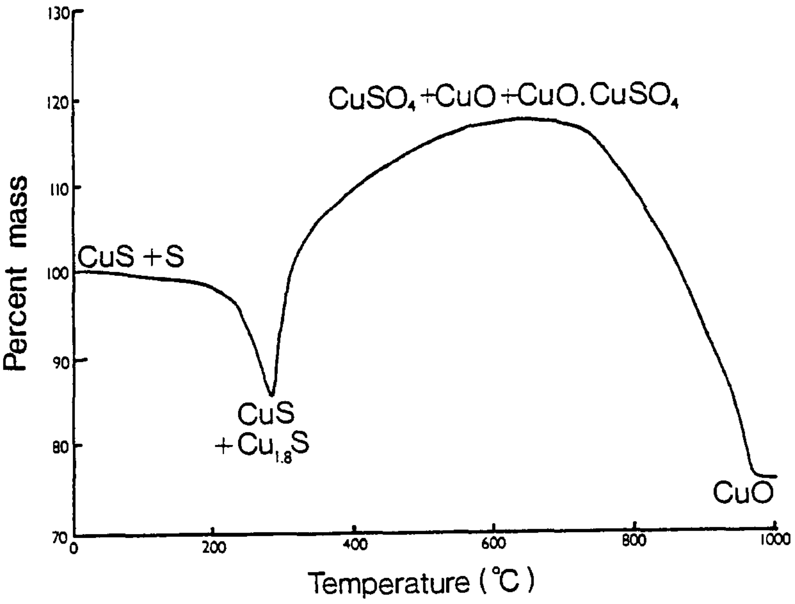

Fig. 1 Typical TG curve for copper sulphide precipitates

Traces of Cu_2O have been reported (ref. 6) at the minimum point in the curve at temperatures around 300°C. In this work, x-ray diffraction did not show such traces of Cu_2O.

X-ray diffraction did prove the presence of the double salt $CuO.CuSO_4$ at the maximum point on the curve. Similar behaviour occurs during the oxidation of lead sulphide (ref. 7), where three different basic sulphates have been identified.

Assuming the CuO at 1000°C in Figure 1 to be pure (verified by x-ray diffraction), the mole fractions of the phases present at the minimum and maximum points on the TG curve have been calculated and the stoichiometry of each precipitate determined.

Tables 1, 2 and 3 show the differences in the oxidation behaviour of each precipitate. The sample codes correspond to those used previously (ref. 5).

TABLE 1

Oxidation behaviour of CuS (H_2S precipitant)

Sample code	Stoichiometry CuS_x x=	Mole fraction $Cu_{1.8}S$ at minimum	Temp of minimum /°C	Mole fraction $CuSO_4$ at maximum
H1	1.40	0.02	312	0.61
H2	1.44	0.17	289	0.56
H3	1.97	0.03	311	0.34
H4	1.89	0.19	343	0.35
H5	2.13	0.57	300	0.37
H6	1.96	0.40	304	0.40
H7	1.27	0.40	268	0.55
H8	Impure product. EDTA complex stable			
H9	Impure product. EDTA complex stable			
H10	1.05	0.20	290	0.51
H11	1.27	0.32	294	0.53

TABLE 2

Oxidation behaviour of CuS (CH_3CSNH_2 precipitant)

Sample code	Stoichiometry CuS_x x=	Mole fraction $Cu_{1.8}S$ at minimum	Temp of minimum /°C	Mole fraction $CuSO_4$ at maximum
T1	1.34	0.29	280	0.56
T2	1.03	0.62	309	0.39
T3	1.31	0.55	338	0.44
T4	0.89	1.00	294	0.41
T5	1.09	0.71	359	0.51
T6	1.08	0.72	314	0.41
T7	1.31	0.67	270	0.50
T8	1.20	0.55	383	0.40
T9	1.35	0.20	283	0.53
T10	1.05	1.00	226	0.39
T11	1.14	0.42	256	0.53
T12	1.34	0.43	295	0.54
T13	1.18	0.57	279	0.51
T14	1.71	0.78	270	0.37
T15	1.54	0.32	296	0.45
T16	No reaction			
T17	Impure product, EDTA complex stable			

TABLE 3

Oxidation behaviour of CuS (Na_2S precipitant)

Sample code	Stoichiometry CuS_x x=	Mole fraction $Cu_{1.8}S$ at minimum	Temp of minimum /°C	Mole fraction $CuSO_4$ at maximum
S1	0.77	0.68	(215)	0.45
S2	Impure product			
S3	1.04	0.05	243	0.41
S4	0.65	0.60	(253)	0.44
S5	1.11	0.07	246	0.54
S6	0.96	0.36	344	0.47
S7	Impure product			
BDH CuS	2.34	0.86	322	0.45
BDH CuS*	1.33	0.63	307	0.49

* = after extraction with CS_2

DISCUSSION

The evidence obtained suggests that the stoichiometry of the precipitates produced using Na_2S reagent is nearer to 1:1 sulphur to copper ratio (for CuS precipitates) than those produced using thioacetamide as precipitant. In turn, the precipitates produced by thioacetamide have a stoichiometry nearer to unity than those produced by H_2S. The explanation for this seems to be that sulphur is soluble in excess Na_2S, forming polysulphide anions (ref. 8). Thus any sulphur produced in the preparations from Na_2S tends to remain in solution so that a near-stoichiometric precipitate is produced. Thioacetamide undergoes slow hydrolysis in solution, releasing H_2S very slowly. This produces a low degree of supersaturation of the solution, resulting in a fairly stoichiometric precipitate. H_2S, when bubbled through solution, gives highly supersaturated conditions. This results in a state far from that of equilibrium, and thus it is possible for excess sulphur to be present in the precipitate mixture.

Evidence generally suggests that the temperature of the minimum mass on the TG curve, at approximate $300^{\circ}C$, decreases with decreasing particle size of the precipitate. This is not surprising because there is then more surface area available for reaction, and so the oxidation reaction with weight gain can occur at lower temperatures (ref. 9).

The mole fraction of $Cu_{1.8}S$ present at these minima varies considerably throughout the range of CuS samples, but the samples produced by thioacetamide generally contain more $Cu_{1.8}S$ at this point than those produced by other precipitates. This can be explained by the small, regular-shaped particles produced by thioacetamide having a high surface area available for reaction. Hence, more reduction to $Cu_{1.8}S$ has taken place before the oxidation reaction to $CuSO_4$ and CuO.

Other trends evident from the results are that a low temperature of the minimum mass correlates with a high mole fraction of $CuSO_4$ at the maximum, and also that a low mole fraction of $Cu_{1.8}S$ at the minimum correlates with a high mole fraction of $CuSO_4$ at the maximum. The reason for these correlations seems to be that the partial pressure of SO_2 produced during the oxidation of compositions rich in CuS is higher than that produced during the oxidation of compositions rich in $Cu_{1.8}S$. There is hence more SO_2 available for reaction to produce $CuSO_4$.

CONCLUSIONS

Regarding the oxidation behaviour (refer to Figure 1) more $CuSO_4$ is found at the maxima of the TG curves which have low temperatures and/or low mole fractions of $Cu_{1.8}S$ at the minima. Low minimum temperatures are promoted by small particle sizes. Copper sulphide samples precipitated by thioacetamide produce TG curves having a higher $Cu_{1.8}S$ content at the curve minima.

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