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THE OXIDATION OF IRON (II) SULPHIDE

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The oxidation in air and oxygen of iron (II) sulphide $Fe_{1-x}S$ was studied using TG, DTA, X-Ray powder photography and chemical analysis. A reaction sequence was deduced, in which in the temperature range 425—520° partial oxidation occurred forming $FeSO_4$, FeS_2, Fe_3O_4. Rapid oxidation to Fe_2O_3 was usually observed in the range 520—575° but under certain conditions this reaction did not occur. In the temperature range 575—625° oxidation of $FeSO_4$ to $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$ took place. Decomposition of this material gave Fe_2O_3 as the final product at 725°.

The iron-sulphur system has been extensively studied because of its importance in mineralogy and metallurgy, and the phase diagram of the system has been published [1]. The principal compounds are FeS_2 (pyrite), FeS (troilite), $Fe_{1-x}S$ (hexagonal pyrrhotite) and Fe_7S_8 (monoclinic pyrrhotite) [1, 2]. No attempt is made in this paper to distinguish between the two forms of pyrrhotite. The formula $Fe_{1-x}S$ is used, unless a published work using the formula Fe_7S_8 is being quoted.

The study of the oxidation of these and other sulphides by thermal analysis methods has been discussed by a number of workers, who have pointed out the importance of good air circulation, constant experimental conditions and small sample size [3—6]. Interpretations of the reactions of iron (II) sulphide on roasting in air have differed, and several intermediate compounds have been described [8—13].

The roasting of FeS in air, investigated by thermal analysis methods, is reported to lead to the formation of $FeSO_4$, $Fe_2(SO_4)_3$ and Fe_2O_3, with Fe_2O_3 the only product formed above 477° [7].

In a study of sulphide oxidation using micrographic, X-ray and chemical methods the oxidation of closely sized particles of $Fe_{1-x}S$ and FeS is reported. The $Fe_{1-x}S$ is said to oxidize by the formation of a thin layer of Fe_2O_3 on the surface of each particle. When oxidation occurs at 650°, a layer of Fe_3O_4 is found between the Fe_2O_3 and the $Fe_{1-x}S$. The oxidation of FeS is reported to occur in two stages, involving an initial formation of $Fe_{1-x}S$:

$$FeS + 0.075\ O_2 \rightarrow Fe_{0.9}S + 0.05\ Fe_2O_3$$

$$Fe_{0.9}S + 0.625\ O_2 \rightarrow 0.45\ Fe_2O_3 + SO_2 \qquad (8)$$

The kinetics of the oxidation of several iron sulphides including FeS has been reported [9]. The same workers have studied the mechanism of the oxidation by examining the structure of the scale formed on the surface of oxidized sulphides. They found no accumulation of intermediate species (sulphates) and proposed a mechanism involving the formation and decomposition of "labile complexes" [10].

An extensive survey of the thermal analysis of sulphides and arsenides under oxidative conditions reports the formation of Fe_2O_3 and SO_2 from $Fe_{1-x}S$ at 600° [11].

A recent investigation has suggested that FeS oxidation can be explained by the formation of $FeSO_4$ or FeO depending on the temperature conditions. In the region of thermal stability of $FeSO_4$ the primary reaction is said to be:

$$FeS + 2O_2 \rightarrow FeSO_4$$

At higher temperatures the primary reaction becomes:

$$FeS + 1.5O_2 \rightarrow FeO + SO_2$$

It was further reported that the sulphate formed as a primary product may undergo reaction with unoxidized FeS such as:

$$FeS + 3FeSO_4 \rightarrow 4FeO + 4SO_2 \qquad (12)$$

During a study of complex sulphides, we examined the oxidation of $Fe_{1-x}S$ and consistently found the formation of FeS_2, which had hitherto not been reported as being involved in this reaction.

To clarify the reactions, a detailed study of the oxidation of iron (II) sulphide and the species involved was carried out. The results of this study are reported in this paper, and a mechanism by which oxidation of Fe_{1-x} S occurs is proposed.

Experimental

Oxidation runs were followed on a Stanton TR-1 thermobalance modified to receive upflowing gas. Temperature control was achieved using a Stanton Redcroft Linear Temperature Variable Rate Programmer, model LVP CT 10/R. Heating rates of 2–10 degrees per minute were used, with a gas flow rate of 150 ml per minute. Sample sizes of 200 or 500 mg were used for TG; all weight changes were expressed as percentage starting weight. Samples were contained in shallow silica pans and were distributed in thin layers to ensure maximum exposure to the oxidizing atmosphere.

DTA runs were carried out using a Stanton STA attachment. For all DTA runs under oxidizing conditions 25 mg samples were used to obtain a thin layer of material in the sample crucible. An equal weight of calcined alumina was used in the reference crucible.

A sample of iron (II) sulphide was obtained commercially and analysed as $Fe_{0.97}S$. Other samples were prepared by reaction between the elements in vacuo in silica tubes [13, 14]. Samples were ground under nitrogen in a glove box to – 125 microns before use. Species were identified by X-ray powder photography using a Philips PW/1008 X-ray diffractometer with Co K_α radiation filtered through iron.

Analysis of residues for sulphate was carried out be extraction with dilute hydrochloric acid, removal of iron by ion exchange and gravimetric determination of sulphate as $BaSO_4$ [15].

Results and discussion

The oxidation of $Fe_{0.97}S$ under oxygen is shown in Figure 1 and Table 1.

Table 1

TG of 200 mg. $Fe_{0.97}S$ in oxygen at 10°min^{-1}

Temperature range, °	Weight change, mg
425–520	4.0 (2.0%)
520–575	−10.0 (−5.0%)
575–625	3.0 (1.5%)
625–725	−17.0 (−8.5%)

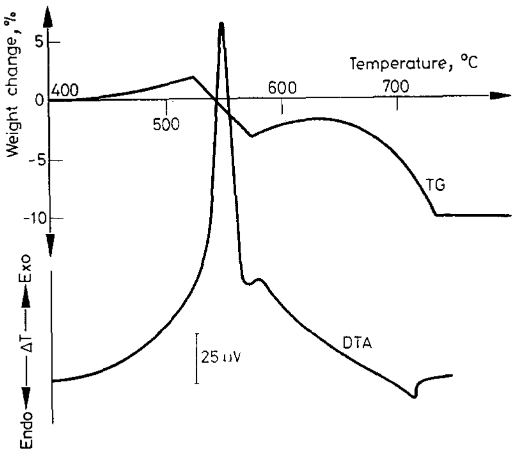

Fig. 1. TG and DTA of $Fe_{0.97}S$ heated in oxygen at 10° min^{-1}

The curve profiles were found to vary significantly depending on the particular sample and heating rate used, but the final product of the reaction was always Fe_2O_3.

Since it appeared that the initial weight gain was not allowed to reach completion in these runs, isothermal runs were carried out at 460–480° with the results

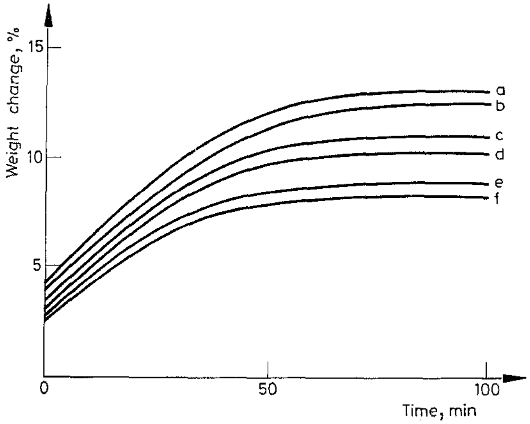

Fig. 2. Isothermal TG runs on 500 mg $Fe_{0.97}S$. (a) in oxygen, initial heating rate 10° min^{-1}; (b) in oxygen, initial heating rate 10° min^{-1}; (c) in oxygen, initial heating rate 10° min^{-1}; (d) in air, initial heating rate 10° min^{-1}; (e) in air, initial heating rate 10° min^{-1}; (f) in air, initial heating rate 10° min^{-1}

Table 2

Weight gained by 500 mg, $Fe_{0.97}S$ under isothermal conditions

Run No.	Atmosphere	Heating rate to constant T, °min^{-1}	Weight gain, mg
16	Oxygen	10	66 (13.2%)
15	Oxygen	10	63 (12.6%)
10	Oxygen	4	55 (11.0%)
14	Air	10	52 (10.4%)
11	Air	10	45 (9.0%)
12	Air	4	42 (8.4%)

indicated in Table 2 and Fig. 2. In Fig. 2 the plots do not commence at 0 on the ΔW axis because of the weight gained as the samples were heated to the isothermal temperature. Time 0 in Fig. 2 corresponds to the commencement of the isothermal temperature. The material at the constant weight plateau of the TG curve was isolated; $FeSO_4$ was found in the aqueous extract of the material, $Fe_2(SO_4)_3$ being absent. X-ray examination of the residue showed the presence of FeS_2 (pyrite), Fe_3O_4, Fe_2O_3 and $Fe_{1-x}S$.

The total sulphate content of the plateau material was determined and found to correspond to a 20–22% conversion of the initial sulphide to $FeSO_4$. Calculation of the expected weight gain for this conversion shows that additional reactions involving weight loss are necessary to account for the TG curves, as shown in Table 3.

Table 3

Sulphate formation in products of oxidation of 500 mg. $Fe_{0.97}S$ under isothermal conditions

Run No.	Wt. $FeSO_4$ mg	Wt. Gain (calcd.) mg	Wt. Gain (obsvd.) mg	Nett. Wt. Loss mg
10	185	77	55	22
12	175	73	42	31
13	187	78	46	32
15	172	71	63	8
16	182	75	66	9

These reactions could include:

$$3Fe_{(1-x)}S + (5 - 2x)O_2 \rightarrow (1 - x)Fe_3O_4 + 3SO_2$$

and

$$4Fe_{(1-x)}S + (7 - 3x)O_2 \rightarrow (2 - 2x)Fe_2O_3 + 4SO_2$$

Acid digestion of the plateau material yielded FeS_2 as an insoluble, black magnetic material. Chemical analysis showed the composition to be 45.3% Fe and 54.7% S. (Required for FeS_2: 46.67% Fe, 53.33% S) X-ray examination showed the presence of pyrite, pyrrhotite and sulphur. The presence of the latter species is explained by the reaction

$$(1 - x)FeS_2 \rightleftarrows Fe_{1-x}S + (1 - 2x)S$$

being frozen in the material on cooling. The presence of $Fe_{1-x}S$ accounts for the magnetism of the product, and the removal of some of the $Fe_{1-x}S$ in the acid digestion could explain the high sulphur content of the material.

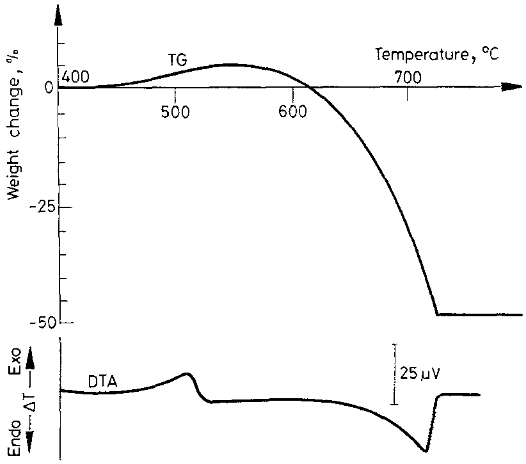

Fig. 3. TG and DTA of $FeSO_4$ heated in oxygen at 10° min^{-1}

Formation of FeS_2 was favoured by fast heating rates. Under oxygen, the percentage $Fe_{1-x}S$ converted to FeS_2 was 6.6% (2° min^{-1}), 8.1% (5° min^{-1}) and 17.9% (10° min^{-1}).

The formation of FeS_2 by reaction of $Fe_{1-x}S$ with SO_2 has been reported [16]. This process could account for the formation of FeS_2 during the oxidation of $Fe_{1-x}S$.

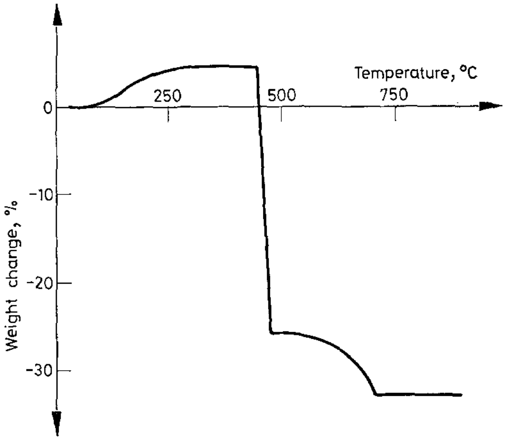

Fig. 4. TG of FeS_2 heated in oxygen at 10° min^{-1}

The TG curve in Fig. 1 shows a weight loss occurring between 520° and 575°. This step was very variable and was not observed at all with some samples. A sample of the material at the plateau at 625° following the weight loss was isolated and analysed; Fe_2O_3, FeS_2, $FeSO_4$ and $Fe_2(SO_4)_3$ were found to be present. A separate sample isolated at 520° at the maximum weight gain before the loss occurred was found to contain $Fe_{1-x}S$, FeS_2, Fe_3O_4 and $FeSO_4$. This material isolated at 520° still possessed its initial powdered form, in contrast to the material isolated at 625° which had clearly undergone sintering. These results suggest that the weight loss between 520° and 575° results from the oxidation of $Fe_{1-x}S$ directly to Fe_2O_3. The weight gain which persists after this reaction would appear to be due to further oxidation of products formed in the early stages of the oxidation, i.e. $FeSO_4$, Fe_3O_4 and FeS_2. To clarify this stage, samples of anhydrous iron (II) sulphate were heated in oxygen at 10°min^{-1}. The TG and DTA curves obtained are shown in Fig. 3.

The initial weight gain corresponds to the reaction

$$12FeSO_4 + 3O_2 \rightarrow 2[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$$

which is followed by decomposition of the oxidized material to Fe_2O_3.

$$[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3 \rightarrow 3Fe_2O_3 + 6SO_3.$$

These reactions are reported in the literature for $FeSO_4$ heated in air [17].

The DTA curve shows an endotherm peak at 714°. The shape of this endotherm is very similar to that of the endotherm found at the same temperature in the oxidation of $Fe_{1-x}S$ (Fig. 1). This suggests that the final reaction in $Fe_{1-x}S$ oxidation is the decomposition of $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$ to Fe_2O_3.

The conversion of FeS_2 to Fe_2O_3 in the temperature range 625–725° (Fig. 1) appears to take place via sulphate formation as no weight losses or exotherms were found that could be associated with direct oxidations such as:

$$4FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$$

A separate TG run on FeS_2 is shown in Fig. 4.

The curve shows close similarity to the $Fe_{1-x}S$ oxidation profile (Fig. 1) indicating that FeS_2 can be oxidized initially to sulphates as well as undergoing direct oxidation to Fe_2O_3.

The oxidation of FeS_2 occurred at a significantly lower temperature than that proposed for FeS_2 during the oxidation of $Fe_{1-x}S$. This could be a consequence of FeS_2 in the latter case being protected from the oxidizing atmosphere by the other reaction products.

The results of this investigation enable a reaction scheme to be defined for the oxidation of iron (II) sulphide:

1. Between 425–520° $Fe_{1-x}S$ is converted to $FeSO_4$ with accompanying formation of Fe_3O_4, Fe_2O_3 and FeS_2, formally represented by

$$Fe_{1-x}S + (2 - x)O_2 \rightarrow (1 - x)FeSO_4 + xSO_2 \qquad (I)$$

$$3Fe_{1-x}S + (5 - 2x)O_2 \rightarrow (1 - x)Fe_3O_4 + 3SO_2 \qquad (II)$$

$$4Fe_{1-x}S + (7 - 3x)O_2 \rightarrow (2 - 2x)Fe_2O_3 + 4SO_2 \qquad (III)$$

$$8Fe_{1-x}S + (2 - 4x)SO_2 \rightarrow (1 - 2x)Fe_3O_4 + (5 - 2x)FeS_2 \qquad (IV)$$

2. Between 520–572° $Fe_{1-x}S$ remaining after reactions (*I*), (*II*) and (*IV*) may undergo rapid oxidation to Fe_2O_3, as in reaction (*III*) above.
3. Between 575–625° FeS_2, Fe_3O_4 and $FeSO_4$ are oxidized:

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2 \qquad (V)$$

$$2FeSO_4 + 3O_2 \rightarrow 2[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3 \qquad (VI)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \qquad (VII)$$

4. Between 625–725° $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$ decomposes:

$$[Fe_2(SO_4)_3]_2Fe_2O_3 \rightarrow 3Fe_2O_3 + 6SO_3 \qquad (VIII)$$

The representation of some of these reactions by specific equations is at best formal since there is no means of determining whether for example Fe_3O_4 is formed by direct oxidation of sulphide, as shown in equation (*II*) above, or by sulphate – sulphide interactions such as

$$(5 - 2x)FeSO_4 + Fe_{1-x}S \rightarrow (2 - x)Fe_3O_4 + (6 - 2x)SO_2. \qquad (IX)$$

It was found that reactions such as (*IX*) did take place when mixtures of $FeSO_4$ and $Fe_{1-x}S$ were heated under nitrogen.

The direct oxidation of $Fe_{1-x}S$ to Fe_2O_3 between 520° and 575° did not always occur. An example of the TG and DTA curves obtained when step 2 did not occur is shown in Fig. 5.

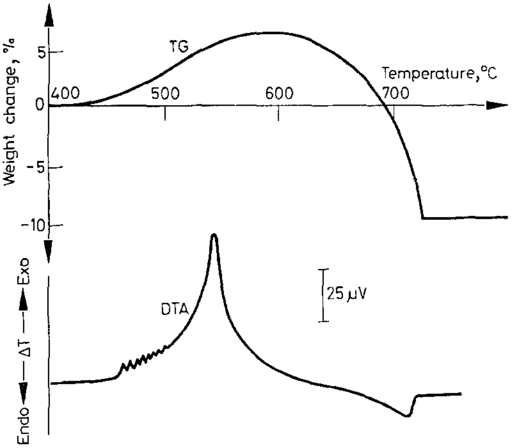

Fig. 5. TG and DTA of $Fe_{0.97}S$ heated in oxygen at 4° min^{-1}

The series of very sharp exotherms preceding the main oxidation can be interpreted as oxidation occurring at separate reactive sites without the oxidation of the bulk of the sample taking place. This effect has been reported for other sulphides [3].

The detection of previously unreported FeS_2 in the initial stage of the oxidation was the result of careful chemical and X-ray examination of the heated material at various stages of the reaction. This FeS_2 is believed to result from the reaction of $Fe_{1-x}S$ with SO_2 produced in reaction (*II*) and (*III*). It has been reported that with pure SO_2 and FeS the following reactions occur: (16)

$$38FeS + 2SO_2 \rightarrow 5Fe_7S_8 + Fe_3O_4 \quad (220-380°)$$

$$4Fe_7S_8 + 6SO_2 \rightarrow 19FeS_2 + 3Fe_3O_4 \quad (380-455°) \tag{16}$$

These may be combined to give:

$$8FeS + 2O_2 \rightarrow 5FeS_2 + Fe_3O_4$$

which is (*IV*) above, for the case when $x = 0$.

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RÉSUMÉ — On étudie l'oxydation du sulfure de fer(II), $Fe_{1-x}S$, dans l'air et dans l'oxygène par TG, ATD, enregistrement photographique des clichés de rayons X sur poudre et analyse chimique. Il se forme successivement $FeSO_4$, FeS_2 et Fe_3O_4 par oxydation partielle entre 425 et 520°. L'oxydation rapide en Fe_2O_3 se produit habituellement entre 520 et 570°, mais sous certaines conditions cette réaction peut ne pas se produire. L'oxydation de $FeSO_4$ entre 575 et 625° conduit à $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$ dont la décomposition donne Fe_2O_3 comme produit final à 725°.

ZUSAMMENFASSUNG — Die Oxydation des Eisen(II)sulfids $Fe_{1-x}S$ in Luft und Sauerstoff wurde durch TG, DTA, Röntgenpulver-Photographie und chemische Analyse untersucht. Eine Reaktionsfolge $FeSO_4$, FeS_2, Fe_3O_4 wurde zwischen 425 und 520° durch partielle Oxydation fesgestellt. Eine schnelle Oxydation zu Fe_2O_3 liess sich im Gebiet 520–575° beobachten, unter bestimmten Bedingungen trat jedoch diese Reaktion nicht auf. Zwischen 575 und 675° verlief die Oxydation von $FeSO_4$ zu $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$. Die Zersetzung dieses Verbindung ergab als Endprodukt bei 725° Fe_2O_3.

Резюме — Было изучено окисление сульфида железа (II) ($Fe_{1-x}S$) в атмосфере воздуха и кислорода с помощью TG, DTA рентгеновской порошковой фотографии и химического анализа. Была установлена последовательность реакций. В области температур 425—520° происхочастичное окисление с образованием $FeSO_4$, FeS_2 и Fe_3O_4. Быстрое окисление до Fe_2O_3 обычно наблюдалось в области 520—575°, но при определенных условиях эта реакция не происходит. В интервале температур 575—625° имеет место окисление $FeSO_4$ до $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$. Конечным продуктом разложения этого вещества при 725° является Fe_2O_3.