Studies on the Oxidation of Ferrous Sulfide

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Recent investigations on the reduction of metallic oxides or oxidation of metallic sulfides have shown that the mechanism of these reactions should be discussed on the basis of the defect theory of crystal lattice. Along this line Anderson[1] and Wagner[2] have discussed the mechanisms for many cases of reactions which involve the reduction of metallic oxides with hydrogen or carbon monoxide, oxidation of metallic sulfides with oxygen, and reduction of metallic sulfides with hydrogen or other metals. Successful applications have also been carried out by Parravano[3] and Hauffe[4] on the reduction of nickel oxide with hydrogen.

When a metallic oxide is reduced with hydrogen, first the chemisorption of hydrogen on the surface of oxide takes place, being accompanied by the decrease of positive holes or the increase of free electrons. Then the reaction proceeds by filling cation vacancies or increasing excess cations until metallic nuclei appear, resulting in an appreciable change of metal/oxygen ratio. The analogous non-stoichiometric departure has been found for some cases of oxidation of metallic sulfide[1], although the change of the metal/anion ratio is opposite to that in the case of reduction of oxide. For the oxidation of sulfide, however, experimental data are very scarce up to date.

Most compounds have so small a range of deviation from the stoichiometric composition that it is difficult to observe it by means of

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[1] J.S. Anderson, *Discussions Faraday Soc.*, No. 4, 163 (1948).

[2] C. Wagner, *J. Metals*, **4**, 214 (1952).

[3] G. Parravano, *J. Am. Chem. Soc.*, **74**, 1194 (1952).

[4] K. Hauffe and A. Rahmel, *Z. phys. Chem.* [N.F.], **1**, 104 (1954).

the ordinary X-ray diffraction method. But fortunately ferrous sulfide has a relatively wide range of non-stoichiometric composition[5,6], so the X-ray diffraction method may be useful for the present purpose.

Although studies on the roasting of ferrous sulfide have been carried out by several investigators, some disagreements still remain as to those results: Schwab and Philinis[7] have measured the rate of oxidation with a precise thermobalance and have concluded that the rate is controlled by diffusion of gas, similarly to the case of pyrite. Chufarov and Averbukh[8] have found that the oxidation of ferrous sulfide proceeds as follows: Up to 250°C the oxidation takes place without evolution of gas, showing that the product is $FeSO_4$. At 350–450°C the product is a mixture of $FeSO_4$ and iron oxides, and above 450°C it is a mixture of ferric oxide and magnetite. Kameda, Yazawa, and Kurosawa[9] have investigated the kinetics of the oxidation of artificial ferrous sulfide, and have shown that the initial stage of the reaction is autocatalytic, an induction period being observed. According to Kushima and Kondo[10] who have studied the oxidation products with thermobalance, the sulfate which is produced during oxidation is presumed to be $Fe_2(SO_4)_3$, also, complete formation of oxides is observed above 600°C.

Experimental

(a) Material.—Ferrous sulfide used was prepered as follows: Two boats which had been filled with electrolytic iron and sulfur respectively were put in a quartz tube, and after evacuation up to about 10^{-4} mmHg the tube was heated to 800–900°C. After the sulfurization had been finished, which took about two days, the product was powdered and was then evacuated again at 900°C to remove excess sulfur. The final product was powdered again and its fraction between 170 and 200 mesh was collected by sieving. One-tenth grams of this fraction were used in every run.

The analysis of sample resulted as,

Fe; 61.98%, S; 38.11%.

No other line except that of ferrous sulfide was observed by X-ray powder photograph.

(b) Spring Balance.—The spring balance used is the same as that described in the writers' previous paper[11]. The rate of flow of air was fixed at 200 cc./min., because no effect on the rate of reaction was observed when the rate of flow was increased above this.

(c) X-ray Diffraction Method.—X-ray diffraction patterns were obtained by means of an ordinary powder camera with diameter of 90 mm and CoK_α radiation. Since an X-ray tube of rotating-anode-type was used, the exposure was only about ten minutes. To prepare the specimen for X-ray study, samples were quenched in nitrogen gas in a way similar to that adopted in the previous work[11].

Results

(1) Rate of Oxidation Measured with Spring Balance.—The rates of oxidation measured with spring balance over the temperature range from 504° to 700°C are shown in Fig. 1, in which the decrease of weight (%) is plotted against reaction time (min.).

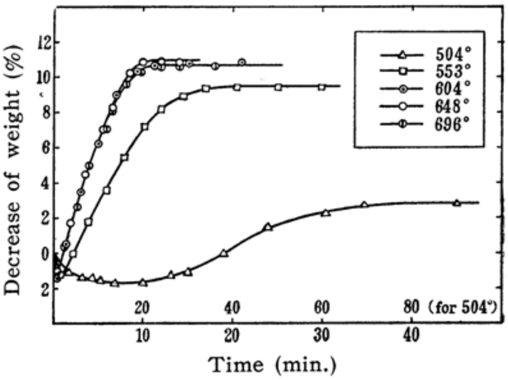

Fig. 1. Change of weight during oxidation of ferrous sulfide.

At reaction temperature of 504°C, some increase of weight appears first, and continues for about fifteen minutes until the weight begins to decrease gradually. (For this run the scale of abscissa in Fig. 1 is reduced to one half that of others.) The decrease of weight, however, is only 2.8% even after ninety minutes, which is far less than that of oxides, viz. 9.1% for ferric oxide and 12.2% for magnetite. Thus sulfate may exist. At 553°C small amounts of sulfate may also be formed; above 604°C, the product undoubtedly comprises oxides only.

Two striking phenomena are observed from Fig. 1: First, for every temperature there is an increase of weight of about 1.0–1.8% at the initial stage of reaction, and secondly above 604°C the rate of oxidation does not change with temperature. The latter fact means that the energy of activation for reaction is very small, so the rate-determining factor may be diffusion of gas.

(2) Dependence of Reaction Rate on the Amount of Sample.—Two cases of rate-controlling by diffusion can be considered: One is the diffusion of gas through the pores of the product layer formed on the surface of each particle as Schwab and Philinis have reported[7], and the

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5) R. Juza, W. Biltz and K. Meisel, *Z. anorg. allgem. Chem.*, **205**, 273 (1932).

6) H.S. Roberts, *J. Am. Chem. Soc.*, **57**, 1034 (1935).

7) G-M. Schwab and J. Philinis, *J. Am. Chem. Soc.*, **69**, 2588 (1947).

8) G.I. Chufarov and B.D. Averbukh, *Zhur. Obshei. Khim.* (*J. Gen. Chem.*), **19**, 857 (1949).

9) M. Kameda, A. Yazawa and T. Kurosawa, *J. Mining Inst. Japan*, **68**, 71 (1952).

10) I. Kushima and Y. Kondo, ibid., **68**, 319 (1952).

11) K. Niwa and T. Wada, *J. Japan Inst. Metals*, **18**, 1 (1954).

other is that in the bed of the whole sample[12]. To decide whether or not the diffusion in a particle is the only factor in rate-determination, an experiment, namely the measurement of the rate of oxidation using various amounts of the sample, was carried out. If the diffusion in a particle is the rate-determining factor, the rate should be independent of the amount of sample. If, on the other hand, the rate is controlled by diffusion in the bed of the sample, it may vary with the amount of sample. The results are shown in Fig. 2. They indicate that the rate depends on the amount of sample. Thus the observation supports the latter of the two considerations mentioned just above.

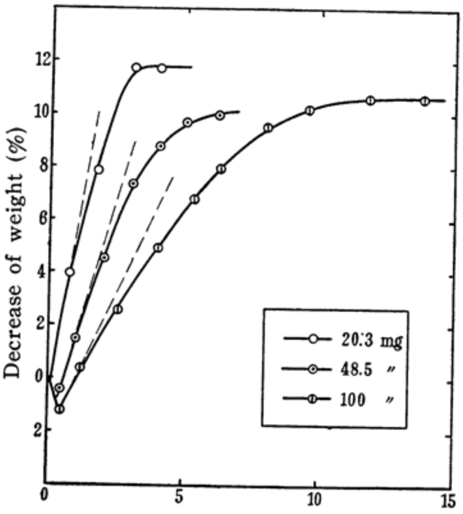

Fig. 2. Dependence of the rate of oxidation upon the amount of sample.
The broken lines indicate the relative rate of oxidation cited in Table III.

(3) X-ray Diffraction Study of Initial Stage.—Identification of oxidation products and measurements on the change of lattice parameter of ferrous sulfide in initial stage were carried out by X-ray analysis.

Since the whole data of X-ray diffraction can not be represented on account of limitation of space, only one example is shown in Table I. In this case magnetite and hematite were identified, while the existence of wüstite is not certain because the assigned line is only a very weak one. Data on identified substances are summarized in Table II.

An appreciable change of lattice parameter of ferrous sulfide was observed in this stage of reaction. This is as shown in Fig. 3b where the change of interplanar spacings of (102), (103), (004), and (202) lines may be seen in connection with change of weight which is shown in 3a. The rate of oxidation is somewhat lower than that of Fig. 1 because 200 mg. of sample was taken in this case.

TABLE I

AN EXAMPLE OF X-RAY POWDER PHOTOGRAPHS

Sample: No. 7, 600°C, 100 sec.

d(kX)	*I*	Substance
5.72	w	FeS (001) (?)*
2.97	m	FeS (100)
2.70	vw	Fe_2O_3
2.64	st	FeS (101)
2.52	w	Fe_3O_4, Fe_2O_3
2.21	vw	Fe_2O_3
2.16	vw	FeO
2.10	vw	Fe_3O_4
2.06	st	FeS (102)
1.840	vw	Fe_2O_3
1.717	st	FeS (110)
1.680	vw	Fe_2O_3
1.612	vw	Fe_3O_4
1.602	w	FeS (103)
1.483	w	FeS (200)
1.440	w	FeS (201)
1.426	w	FeS (004)
1.317	m	FeS (202)

TABLE II

PRODUCTS OF INITIAL STAGE DETECTED BY X-RAY DIFFRACTION

Reaction temperature (°C)	Time (sec.)	Detected substances (except FeS)
500	30	—
〃	75	Fe_3O_4
〃	120	Fe_3O_4
〃	180	Fe_3O_4
〃	240	Fe_3O_4, (Fe_2O_3)**
600	20	—
〃	40	Fe_3O_4
〃	60	Fe_3O_4, Fe_2O_3, (FeO)
〃	100	Fe_3O_4, Fe_2O_3, (FeO)
〃	150	Fe_3O_4, Fe_2O_3, (FeO)
700	20	Fe_3O_4, (FeO)
〃	36	Fe_3O_4, (Fe_2O_3), (FeO)
〃	60	Fe_3O_4, Fe_2O_3, (FeO)
〃	90	Fe_3O_4, Fe_2O_3, (FeO)
〃	120	Fe_2O_3, Fe_3O_4, (FeO)
〃	180	Fe_2O_3, (Fe_3O_4), (FeO)

** The existence of parenthesized substance is not certain.

It is obvious that this contraction of lattice parameter is due to the change of molar ratio of iron/sulfur. The change of lattice parameter is so rapid, that the material has become almost saturated when the increase of weight is maximum. The velocity of the change, however, depends very much on reaction temperature, which suggests a relatively high energy of activation.

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[12] S. E. Woods, *Discussions Faraday Soc.*, No. 4, 184 (1948).

* It may be open to question whether or not this weak line of 5.72 kX is assigned to (100) of ferrous sulfide, which should disappear in NiAs structure. But it is also impossible to assign it to oxide or sulfate. Thus a doubt arises as to ideal NiAs structure of pyrrhotite. Details will be discussed elsewhere. cf. F. Bertaut, *Compt. rend.*, 234, 1295 (1952).

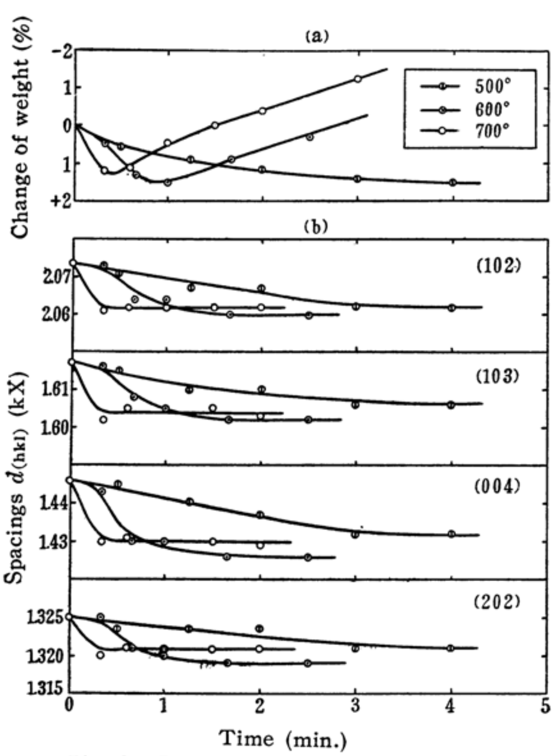

Fig. 3. Reaction of initial stage.
(a): Change of weight.
(b): Change of interplanar spacings of FeS.

The relation between lattice parameter and molar ratio of iron/sulfur has already been determined by some investigators[13,14]. According to the results of Ueda et al[14], whose measurements seem to be most reliable, these changes of lattice parameter correspond to changes of composition amounting to about 1.5–1.8, 2.1–2.4, and 1.6–1.8 atomic % of sulfur for 500°, 600°, and 700° respectively.

Discussion

The increase of weight at the initial stage of reaction is rather too great to regard its cause as merely chemisorption of oxygen. If the specific surface of the sample is of the order of 10^3 or 10^4 cm^2 per gram, about 10^2 molecular layers of adsorbed oxygen correspond to the 1–2% of weight increase. Furthermore, magnetite is found as an oxidation product at a very early stage of reaction as shown in Table II. Therefore the cause of increase of weight may be the formation of oxide on the surface rather than chemisorption.

Thus the mechanism of initial reaction can be interpreted as follows: First, oxygen is chemisorbed on the sulface, being accompanied by the formation of cation vacancies and positive holes near the surface. Then these cation vacancies diffuse into the interior of the crystal, or in other words, cations diffuse to the surface. This stage is continued until the deficiency of cation reaches the saturation where the oxide phase may already exist on the surface because the amount of chemisorbed oxygen becomes so great.

If a reaction occurs as follows,

$$FeS+\frac{2}{3}xO_2=Fe_{1-x}S+\frac{x}{3}Fe_3O_4$$

the increase of weight is expected to be 1.4–1.7%, 2.0–2.3%, and 1.5–1.7% for 500°, 600°, and 700° respectively from the values of iron/sulfur ratio. These are comparable to the experimental values which are 1.5% for 500° and 600° and 1.2% for 700°.

The rapid change of lattice parameter of ferrous sulfide indicates that the diffusion of cation vacancies or opposite diffusion of cations is relatively easy.

After this induction period, the oxidation proceeds with evolution of sulfur dioxide, and the rate is controlled by diffusion of gas at least at temperature above 600°C. Schwab and Philinis[7] have considered that the observed rate is controlled by diffusion of oxygen through the pores of the product layer formed on the surface of each particle. The diffusion coefficient thus determined from their observation, however, was of the order of 10^{-5} cm^2 sec^{-1}, which was far less than that of ordinary gas, viz., about 10^{-1} cm^2 sec^{-1}, indicating, according to their opinion, that the porosity of the product was very low.

In the present case, however, the reaction rate of oxidation depends on the amount of sample as described above. So the diffusion in the bed of the whole sample must be considered.

In Table III the relative and molar rate

TABLE III

RELATIVE AND MOLAR RATE OF OXIDATION FOR VARIOUS AMOUNTS OF SAMPLES AT 700°C

Amount of sample (mg.)	dx/dt (sec^{-1})	dm/dt (mol. sec^{-1})	A(cm^2)	$\frac{1}{A}\frac{dm}{dt}$ (mol. sec^{-1} cm^{-2})
20.3	0.76×10^{-2}	1.8×10^{-6}	0.35	0.51×10^{-7}
48.5	0.49×10^{-2}	2.7×10^{-6}	0.50	0.54×10^{-7}
100	0.30×10^{-2}	3.4×10^{-6}	0.70	0.49×10^{-7}

x: Fraction of oxidized ferrous sulfide.
m: Moles of oxidized ferrous sulfide.
A: Area of extent of sample bed in the bucket.

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[13] J. Hägg and I. Sucksdorff, *Z. phys. Chem.*, (B) **22**, 444 (1933).

[14] R. Ueda, T. Ichinokawa and T. Mitsui, *Busseiron Kenkyu* (Rescarches on Chem. Phys.), **33**, 55 (1950).

of oxidation which are determined from the slopes of curves in Fig. 3, and area of extent of sample bed in bucket are recorded. As shown in the fifth column of this table, the molar rate of oxidation per unit area is almost constant. This fact offers valid evidence for the view that the diffusion in the bed contributed predominantly to the rate of oxidation.

Summary

The rate and mechanism of oxidation of ferrous sulfide was studied by means of a spring balance and X-ray diffraction analysis over the temperature range from 500°C to 700°C. The conclusion reached is as follows:

(1) Complete oxidation, in which only the formation of oxides proceeds, begins at 600°C.

(2) At the initial stage of oxidation, a slight increase of weight is found. It was observed by X-ray that the deficiency of cation in ferrous sulfide occurs in this stage. This may be due to the formation of oxide on the surface rather than to chemisorption, which is accompanied by creation of cation vacancies in ferrous sulfide crystal.

(3) Above 600°C, the rate of oxidation does not change with temperature, so the rate-determining factor is diffusion of gas. Since the observed rate of oxidation depends upon the quantity of the sample, the diffusion in the bed of sample may determine the rate.

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