© *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 53, 2271—2274 (1980)*

The Reaction Process between α-Iron(III) Oxide and Sulfur Dioxide in the Presence of Carbon

Hiromitsu Araki, Young Hong Ryoo,† Motonori Eguchi,
Ryoko Matsuzaki, and Yuzo Saeki*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227

(Received January 9, 1980)

The reaction products obtained by heating a mixture of α-Fe_2O_3 and carbon in a SO_2 stream at various temperatures were examined. The possible reactions during the above process were also examined. The solid products obtained by heating a mixture of α-Fe_2O_3 and carbon in a SO_2 stream were Fe_3O_4 at 500—700 °C, pyrrhotite and Fe_3O_4 at 750 °C, and pyrrhotite ($Fe_{0.88}S$) alone at 800 °C. Sulfur was obtained outside the heating zone throughout the temperature range. The process of the formation of pyrrhotite by the reaction between α-Fe_2O_3 and SO_2 in the presence of carbon can be represented as follows: The reaction between carbon and SO_2 occurs even at 350 °C to form sulfur, and the reaction proceeds markedly above *ca.* 700 °C. Above *ca.* 500 °C, the reductions of α-Fe_2O_3 with carbon and sulfur occur to form Fe_3O_4. Above *ca.* 750 °C, pyrrhotite is formed by the reaction between Fe_3O_4 and sulfur. These results were supported by the thermodynamical consideration based on the chemical potential diagram for the Fe–S–C–O system.

As sulfidizing agents for synthesizing the transition-metal sulfides, sulfur, hydrogen sulfide and carbon disulfide have been well known. It is not only interesting from the viewpoint of the synthesis of the transition-metal sulfide itself, but also important for the development of sulfur dioxide(SO_2) utilization, to obtain knowledge of the chemical process for synthesizing the sulfide from the oxide using SO_2 as a sulfidizing agent. In this work, the reaction process between α-iron(III) oxide(α-Fe_2O_3) and SO_2 in the presence of carbon was investigated in order to understand the above chemical process.

Pechkovskii[1)] has reported that iron sulfide is formed at 650—800 °C by heating a mixture of Fe_2O_3 and carbon in a SO_2 stream and that 99.7% of the charged Fe_2O_3 is sulfidized at 800 °C by using a 8 : 1 mixture of carbon and Fe_2O_3 (molar ratio). Pechkovskii and Mal'tseva[2)] have carried out a differential thermal analysis for the mixture of Fe_2O_3 and carbon (Fe_2O_3: C=1: 5 by molar ratio) in a SO_2 stream and have observed the formation of pyrrhotite($Fe_{1-x}S$) above 640 °C. Also, they have estimated that the pyrrhotite may be formed through the reaction between FeO and gaseous sulfur, both substances having been formed during the reaction between Fe_2O_3 and SO_2 in the presence of carbon. The composition of the pyrrhotite formed was not mentioned.

In this work, the reaction products between α-Fe_2O_3 and SO_2 in the presence of carbon were examined. The reactions between carbon and SO_2, α-Fe_2O_3 and carbon, α-Fe_2O_3 or Fe_3O_4 and sulfur in a SO_2 stream, and Fe_3O_4 and sulfur in the presence of carbon were examined in order to elucidate the reaction process between α-Fe_2O_3 and SO_2 in the presence of carbon. Some thermodynamical consideration were also made of the formation of pyrrhotite.

Experimental

Materials. The α-Fe_2O_3 used was prepared by the thermal decomposition of the guaranteed reagent, $Fe(NO_3)_3 \cdot 9H_2O$, and confirmed as α-Fe_2O_3[3)] by X-ray analysis. The chemical analysis gave Fe, 70.0$_0$% (Calcd for Fe_2O_3; Fe, 69.94%). The Fe_3O_4 was synthesized by Harber's method[4)] and confirmed as Fe_3O_4[5)] by X-ray analysis. The chemical analysis gave Fe, 72.2$_6$% (Calcd for Fe_3O_4; Fe, 72.36%). The carbon was prepared by the thermal decomposition of the guaranteed reagent glucose. The above materials were used as powders under 150 mesh. Gaseous SO_2 was dried by passing it through concd H_2SO_4 and over P_2O_5.

Procedures. A mixture of α-Fe_2O_3 and carbon in a quartz boat (length: 72 mm, width: 16 mm, depth: 9 mm) was placed in a transparent quartz reaction tube (inner diameter: 28 mm, length: 1000 mm). Gaseous SO_2 was then introduced into the reaction tube. The sample part was positioned in the middle of a tubular electric furnace (heating length: 300 mm) maintained at a specified temperature for 1 h. The temperature of the sample part was controlled within ±2 °C. After heating, the sample was held at 100 °C for 1 h in an argon stream in order to release the adsorbed SO_2 on unreacted carbon. The reactions between carbon and SO_2, α-Fe_2O_3 and carbon in an argon stream, α-Fe_2O_3 or Fe_3O_4 and sulfur in a SO_2 stream, and Fe_3O_4 and sulfur in the presence of carbon in an argon stream were examined in a similar manner.

Analytical. The X-ray analysis of the sample was performed with an X-ray powder diffractometer equipped with a proportional counter using Mn filtered Fe radiation.

Concerning the chemical analysis of pyrrhotite, the sample was oxidatively decomposed in HNO_3 with $KClO_3$. The iron and sulfur contents were determined by the volumetric method with $KMnO_4$ and the gravimetric method as $BaSO_4$, respectively. In the case of a mixture of pyrrhotite, unreacted carbon, and sulfur adsorbed on the carbon, the sample was oxidatively decomposed and the contents of iron and total sulfur in the filtrate were determined by the above techniques. Then, after dissolving pyrrhotite in the sample selectively with dilute HCl, the undissolved residue, which consisted of unreacted carbon and sulfur adsorbed on it, was oxidatively decomposed in HNO_3 with $KClO_3$, and the amount of sulfur adsorbed on the carbon was gravimetrically determined. The

---

† Present address: College of Engineering, Korea University, 1, Anam-Dong, Sungbuk-ku, Seoul 132, Korea.

amount of sulfur due to pyrrhotite was calculated as the difference between the above total sulfur and the sulfur adsorbed on the carbon. From this value and the foregoing iron content, the composition of pyrrhotite was determined.

Results and Discussion

Reaction Products between α-Fe_2O_3 and SO_2 in the Presence of Carbon. The products obtained by heating the mixture of α-Fe_2O_3 (2.00 g) and carbon (1.20 g) (Fe_2O_3: C=1:8 by molar ratio) at various temperatures for 1 h in a SO_2 stream at a flow-rate of 100 cm^3/min were examined. The results are shown in Table 1, together with the weight changes in the samples. The solid products were identified by X-ray analysis.[3,5,6]

Table 1. Products obtained by heating a mixture of α-Fe_2O_3 and carbon in a SO_2 stream at various temperatures

Temp/°C	Weight change/%	Sample in the boat	Amount of sulfur obtained outside the heating zone/g
350	+0.2	α-Fe_2O_3	Trace
400	+0.1	α-Fe_2O_3	Trace
450	+0.1	α-Fe_2O_3	Trace
500	+0.1	α-$Fe_2O_3 \gg Fe_3O_4$	Trace
550	−0.1	α-$Fe_2O_3 \gg Fe_3O_4$	0.01
600	−0.2	α-$Fe_2O_3 \approx Fe_3O_4$	0.01
650	−1.1	$Fe_3O_4 \gg$ α-Fe_2O_3	0.06
700	−2.2	Fe_3O_4	0.14
750	−12.3	$Fe_{1-x}S > Fe_3O_4$	0.39
800	−25.5	$Fe_{1-x}S$	1.11

The formation of Fe_3O_4 was observed above 500 °C, while the formation of pyrrhotite($Fe_{1-x}S$) in addition to Fe_3O_4 was observed above 750 °C. The only solid product obtained at 800 °C was pyrrhotite. Sulfur was obtained outside the heating zone throughout the temperature range in this experiment, and the amount of sulfur markedly increased above *ca.* 700 °C. Also, the sample weight markedly decreased above *ca.* 700 °C. The slight increase in the sample weight at 350—500 °C was due to the adsorption of the sulfur formed by the reaction on the unreacted carbon, as will be described later.

The composition of the pyrrhotite obtained at 800 °C was determined by chemical analysis. The analysis gave Fe, 59.1_4%; S, 38.6%. From the results, the composition of the pyrrhotite formed was determined to be $Fe_{0.88}S$.

Possible Reactions during the Reaction between α-Fe_2O_3 and SO_2 in the Presence of Carbon. To elucidate the reaction process between α-Fe_2O_3 and SO_2 in the presence of carbon, the following experiments were carried out under conditions similar to those described above.

Reaction between Carbon and SO_2: Carbon (1.20 g) was heated in a SO_2 stream (100 cm^3/min) for 1 h. Under such conditions as in this experiment, sulfur is formed at temperatures below *ca.* 1000 °C.[7] Hence, the amounts of sulfur formed at various reaction temperatures were determined. A part of the sulfur was deposited outside the heating zone, while the other part was adsorbed on the unreacted carbon in the boat. The amount of adsorbed sulfur was determined by chemical analysis. The amount of sulfur formed is shown in Fig. 1, together with the weight change in the sample.

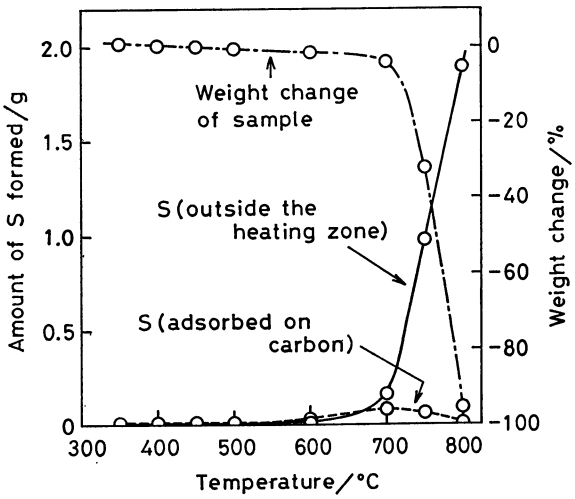

Fig. 1. Experimental results for the reaction between carbon and SO_2.

A slight amount of sulfur was formed even at *ca.* 350 °C, and the amount was markedly increased above *ca.* 700 °C. Also, the sample weight markedly decreased above *ca.* 700 °C. These facts indicate that the reaction between carbon and SO_2;

$$C(s) + SO_2(g) \longrightarrow S_n{}^{\dagger\dagger}(g) + CO_2(CO)(g) \qquad (1)$$

occurs even at 350 °C and proceeds markedly above *ca.* 700 °C.

Reaction between α-Fe_2O_3 and Carbon: The products formed by heating a mixture of α-Fe_2O_3 (2.00 g) and carbon (1.20 g) in an argon stream (100 cm^3/min) for 1 h were examined by X-ray analysis. The results are shown in Table 2.

The results indicate that the following known reactions;

$$Fe_2O_3(s) + C(s) \longrightarrow Fe_3O_4(s) + CO(CO_2)(g) \qquad (2)$$

Table 2. Reaction products between α-Fe_2O_3 and carbon at various temperatures

Temp/°C	Sample in the boat
350	α-Fe_2O_3
400	α-$Fe_2O_3 \gg Fe_3O_4$
450	α-$Fe_2O_3 \gg Fe_3O_4$
500	α-$Fe_2O_3 \gg Fe_3O_4$
550	α-$Fe_2O_3 \gg Fe_3O_4$
600	α-$Fe_2O_3 \approx Fe_3O_4$
650	$Fe_3O_4 >$ α-Fe_2O_3
700	Fe_3O_4
750	Fe_3O_4
800	$Fe_3O_4 \gg FeO$

[††] Above 650 °C, the S_2 is dominant in all species. At lower temperatures the S_6, S_7, and S_8 species become important constituents.[8]

$$Fe_3O_4(s) + C(s) \longrightarrow FeO(s) + CO(CO_2)(g) \qquad (3)$$

proceed above *ca.* 400 and *ca.* 800 °C respectively.

Reaction between α-Fe_2O_3 *and Sulfur*: The reaction between α-Fe_2O_3 and sulfur formed by the reaction of carbon with SO_2 was examined.

α-Fe_2O_3 (2.00 g) was heated in a stream of SO_2 containing a specified amount of gaseous sulfur at various temperatures for 1 h. The gaseous sulfur was formed by heating liquid sulfur and was carried by a stream of SO_2 (100 cm^3/min). The heating temperature of the sulfur was controlled so as to give the same amounts of gaseous sulfur as those obtained by the reaction between carbon and SO_2, described in the previous paragraph. The amounts of sulfur introduced were 0.01 g for the experiments at 400 and 500 °C and 0.03 g for the experiment at 600 °C.

X-Ray analyses of the samples in the boat showed them to be unreacted α-Fe_2O_3 alone at 400 °C, α-$Fe_2O_3 > Fe_3O_4$ at 500 °C, and α-$Fe_2O_3 \approx Fe_3O_4$ at 600 °C.

These results show that, even in a SO_2 stream, the reaction between α-Fe_2O_3 and gaseous sulfur proceeds above *ca.* 500 °C to form Fe_3O_4, according to the reaction,

$$Fe_2O_3(s) + S_n(g) \longrightarrow Fe_3O_4(s) + SO_2(g). \qquad (4)$$

From the above results, it could be explained that the sulfur and Fe_3O_4, formed by heating a mixture of α-Fe_2O_3 and carbon in a SO_2 stream (Table 1), were formed by Reaction 1 and by Reactions 2 and 4 respectively.

Formation Reaction of Pyrrhotite from Fe_3O_4: As has been mentioned before, when a mixture of α-Fe_2O_3 and carbon was heated in a SO_2 stream, pyrrhotite was formed above *ca.* 750 °C. Above this temperature, the amount of sulfur formed increased markedly and α-Fe_2O_3 was reduced to Fe_3O_4. Considering these results, the possible reactions giving the pyrrhotite were considered to be;

$$Fe_3O_4(s) + S_n(g) \longrightarrow Fe_{1-x}S(s) + SO_2(g), \qquad (5)$$

and;

$$Fe_3O_4(s) + C(s) + S_n(g) \longrightarrow Fe_{1-x}S(s) + CO(CO_2)(g). \qquad (6)$$

Therefore, Reaction 5 was examined in a SO_2 stream. Fe_3O_4 (2.00 g) was heated in a stream of SO_2 containing a specified amount of gaseous sulfur at 700—800 °C for 1 h. The amounts of sulfur introduced were controlled so as to be the same as those obtained by the reaction between carbon and SO_2, being 0.25 g for the experiment at 700 °C, 1.12 g at 750 °C, and 1.90 g at 800 °C.

X-Ray analyses of the samples in the boat showed them to be unreacted Fe_3O_4 alone at 700 °C, $Fe_3O_4 > Fe_{1-x}S$ at 750 °C, and $Fe_{1-x}S > Fe_3O_4$ at 800 °C. From these results, it is revealed that Reaction 5 proceeds above *ca.* 750 °C, even in a SO_2 stream.

The chemical analysis of the pyrrhotite free from unreacted Fe_3O_4, obtained at 800 °C for 2 h, gave Fe, 60.4_5%; S, 39.5%. From this result, the composition of the pyrrhotite formed by the reaction between Fe_3O_4 and sulfur was evaluated to be $Fe_{0.88}S$. This composition agreed with that of the pyrrhotite formed by heating a mixture of α-Fe_2O_3 and carbon in a SO_2 stream.

In order to examine Reaction 6, a mixture of Fe_3O_4 (2.00 g) and carbon (1.20 g) was heated in a stream of argon containing a specified amount of gaseous sulfur at 700—800 °C for 1 h. The amount of sulfur introduced was controlled so as to be the same (1.90 g) as that obtained by the reaction between carbon and SO_2 at 800 °C. The experimental results are shown in Table 3.

TABLE 3. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN Fe_3O_4 AND SULFUR IN THE PRESENCE OF CARBON

Temp/°C	Sample in the boat	Amount of SO_2 formed/g
700	$Fe_{1-x}S \gg Fe_3O_4$	0.80
750	$Fe_{1-x}S \gg Fe_3O_4$	0.77
800	$Fe_{1-x}S$	0.34

Pyrrhotite and SO_2 were formed at all experimental temperatures.

From the results, it is found that the formation of pyrrhotite is due to Reaction 5, in which SO_2 is also formed. When 2.00 g of the Fe_3O_4 used is converted to $Fe_{0.88}S$ by Reaction 5, the formation of 1.11 g of SO_2 must be expected. However, the values of SO_2 formed, shown in Table 3, were less than the calculated value. This suggests that the SO_2 formed by Reaction 5 tends to react with carbon according to Reaction 1. For this reason, it is considered that carbon does not directly take part in the sulfidizing reaction, but contributes to sulfur formation by reacting with SO_2.

From the above-mentioned experimental results, the formation process of pyrrhotite by the reaction between α-Fe_2O_3 and SO_2 in the presence of carbon can be represented as follows: (i) Reaction 1 occurs even at 350 °C to form sulfur, and the reaction markedly proceeds above *ca.* 700 °C. (ii) Above *ca.* 500 °C, α-Fe_2O_3 is reduced to Fe_3O_4 by Reactions 2 and 4. (iii) Above *ca.* 750 °C, Reaction 5 occurs between Fe_3O_4 and sulfur, which are formed by the reactions mentioned above, to form $Fe_{0.88}S$.

This result disagrees with the above-mentioned estimation of Pechkovskii and Mal'tseva[2] that pyrrhotite is formed by the reaction between FeO and sulfur.

Thermodynamical Consideration. In order to discuss the present experimental results from the thermodynamical point of view, the chemical potential diagrams for the Fe–S–C–O system were constructed in a manner similar to that described by Yazawa[9] on the basis of the available thermodynamic data[10–13] and phase relations.[14] As an example, the diagram at 800 °C is shown in Fig. 2. N_S/N_{Fe} represents the atomic ratio of sulfur to iron in pyrrhotite. The broken line shows the oxygen and sulfur potentials in the gas phase formed by the reaction between carbon and SO_2, depending on the carbon content in the gas phase. The activity of carbon is unity at the dot mark. In these calculations, CO, CO_2, O_2, COS, CS_2, SO_2, SO_3, S_2, S_4, S_6, and S_8 were assumed to be gaseous products between carbon and SO_2.

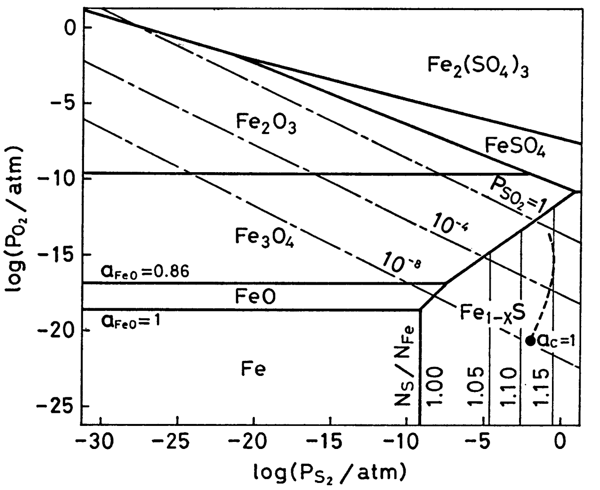

Fig. 2. Chemical potential diagram for the Fe–S–C–O system at 800 °C.

From the results shown in Fig. 2, it is clear that the reduction of Fe_2O_3 to Fe_3O_4 occurs at first when Fe_2O_3 is heated in the presence of carbon in a SO_2 stream. It is also shown that Fe_3O_4 is converted to pyrrhotite *via* FeO under a low pressure of SO_2 below *ca.* 10^{-7} atm, and that Fe_3O_4 is converted to pyrrhotite without FeO formation under a higher partial pressure of SO_2. Considering the experimental conditions in this work, the results in Fig. 2 support the above-mentioned estimation that pyrrhotite is formed through the $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_{1-x}S$ path without any FeO formation. $Fe_{0.88}S$ ($N_S/N_{Fe} \approx 1.14$) was obtained in this work. This composition of pyrrhotite is in the range of values shown by the broken line in Fig. 2. From this fact, it can be said that pyrrhotite with nearly an equilibrium composition is formed in this experiment.

References

1) V. V. Pechkovskii, *J. Appl. Chem. USSR*, **30**, 873 (1957).

2) V. V. Pechkovskii and T. G. Mal'tseva, *J. Appl. Chem. USSR*, **38**, 1190 (1965).

3) JCPDS, Powder Diffraction File, 13-534.

4) "Mukikagōbutsu No Gōsei [I], Shin-Zikkenkagaku-Kōza 8," ed by the Chemical Society of Japan, Maruzen, Tokyo (1976), p. 297.

5) JCPDS, Powder Diffraction File, 11-614.

6) JCPDS, Powder Diffraction File, 17-201, 20-534, 22-358, 22-1120, 25-410.

7) K. I. Ushakov, O. V. Nadinskaya, I. G. Dobrochiver, and S. P. Zharova, "Fiziko-Khimicheskie Osnovy Metallurgicheskikh Protsessov," Metallugia, Moskva (1967), p. 168.

8) M. Wakihara, J. Nii, T. Uchida, and M. Taniguchi, *Chem. Lett.*, **1977**, 621.

9) A. Yazawa, *Metall. Trans.*, **10B**, 307 (1979).

10) O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," 4th ed, Pergamon Press (1967).

11) F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.*, **171**, 165 (1952).

12) J. M. Skaeff and A. W. Espelund, *Can. Metall. Quart.*, **12**, 445 (1973).

13) L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945).

14) E. M. Levin and H. F. McMurdie, "Phase Diagram for Ceramists, 1975 Supplement," *Am. Ceram. Soc.*, (1975), p. 412.