The High-Temperature Reaction of Iron with Sulfur Dioxide

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The reaction of Fe with SO_2 has been studied in the temperature range from 923 K to 1123 K and in the pressure range from 1.3 kPa to 101 kPa. The reaction obeyed the parabolic law except for the initial period, and the rate constant was equal to that in O_2. In the scale, Fe_3O_4, FeO, and FeS were found as the reaction products. Among them, FeS was formed only in the initial period of the reaction and stayed at the scale/metal interface. The constant amount of sulfide in the scale became larger at higher temperatures or at lower SO_2 pressures. The sulfide formation in the initial period of the reaction might cause the increase in the corrosion of Fe at low pressures of SO_2 and cause the difference from the corrosion by O_2.

The corrosion of metals by SO_2 gas causes severe problems in the combustion processes of fossil fuels containing sulfur and also in thermochemical hydrogen production, where high-concentration SO_2 is utilized at high temperatures.

Several reports on the high temperature corrosion of Fe in SO_2 have been published.[1–5] Baukloh and Valena[1] studied the corrosion of Fe in 101 kPa SO_2 and found that the reaction started at 473 K and obeyed the parabolic law between 673—1273 K. Chretien and Broglin,[2] however, observed a deviation from the parabolic law in the initial period between 773 and 1073 K. Flatley and Birks[3] studied the reaction in the temperature range of 773—1273 K and the SO_2 pressure range of 0.25—20 kPa. The reaction obeyed the linear law in the initial period and the parabolic law in the latter period. The same tendency was reported by Kurokawa[5] at 1073 K. According to Flatley and Birks,[3] the parabolic rate constant reached a maximum value at a SO_2 pressure of 2 kPa at 1073 K. When the SO_2 pressure was increased beyond 2 kPa, however, the parabolic rate constant decreased until it reached that in pure oxygen.

Three kinds of iron compounds, FeS, FeO, and Fe_3O_4, were found in the scale.[3–5] FeS always appeared at the metal/scale interface, and its existence promoted the falling of the scale during thermal cycles. Therefore, it is important to elucidate the mechanism of FeS formation in a scale. According to Rahmel,[6] FeS is formed as a result of the inward penetration of SO_2 through micropores in the scale as well as by the diffusion of sulfur from the gas/scale interface to the scale/metal interface. Ross et al.[7,8] studied the reaction between mild steel and sulfur and speculated that FeS is formed in the initial period of the reaction where the reaction rate is high. However, they presented no supporting experimental result. Gilewicz-Wolter[9] studied the corrosion of Fe in SO_2 of 101 kPa at 1073 K using a radio-isotope ^{35}S and found that FeS was formed along the cracks in the scale, mostly in the initial stage of the reaction.

These works carried out previously have thus not yielded a clear interpretation of the mechanism of FeS formation in SO_2. The present paper aims to evaluate the formation of FeS during the reaction between Fe and SO_2 by means of a chemical analysis in order to elucidate the mechanism of the formation of FeS around 1073 K.

Experimental

(1) Specimen. A pure iron sheet supplied by the Nippon Steel Corp. was used as the sample. Table 1 shows the result of the chemical analysis of the impurities. The sheet was cut into rectangular specimens 10×10×0.8 mm; they were polished with No. 1000 SiC polishing paper, washed with soap and water, rinsed in alcohol, and dried.

(2) Reaction-Rate Measurement. A finished and weighed specimen was suspended in the room-temperature region of a mulite reaction tube; then the entire system was evacuated, and SO_2 gas was introduced. The specimen was lowered to the reaction zone, the temperature of which was controlled to within 2 K. In order to react the iron specimen with SO_2, SO_2 gas was circulated by means of a magnetic piston pump. After the predetermined time of reaction, the specimen was taken out of the reaction tube and the weight change was determined.

(3) Analysis of Scale. The reaction products were examined by the X-ray diffraction methods. The cross-sections of the reacted specimens were studied by EPMA as well as with an optical microscope.

Table 1. Results of Chemical Analysis of Iron

Component	wt%	Component	wt%
C	0.003	Si	<0.01
Mn	<0.01	P	0.002
S	0.004	Ti	<0.001
N	0.0013	O	0.0020
Al	0.001		

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In order to know the sulfide growth, the total amount of sulfur in the scale was chemically analyzed by the following method. A reacted specimen was dissolved in a HCl (1 M[§])–Br_2 (0.01 M) solution in order to oxidize the sulfide ions to sulfate ions. After the filtation, the solution was passed through cation-exchange resin (Dow Chemical 50W-X8) and the Fe ions were removed. Then $BaSO_4$ was precipitated by adding a $BaCl_2$ solution to the solution. The amounts of sulfur were calculated from the weight of the $BaSO_4$ precipitate.

Results and Discussion

Figure 1 shows a parabolic plot of the weight increase in Fe at the SO_2 pressure of 101 kPa. The temperature range was from 923 K to 1123 K. Clearly, the reaction obeys the parabolic rate law except for the very initial period. In order to compare with the oxidation reaction, the oxidation of Fe in 101 kPa O_2 was carried out at 1073 K. The oxidation reaction obeyed the parabolic rate law from the initial period. The parabolic rate constants for oxidations in SO_2 and in O_2 were the same (6.6×10^{-8} g^2 cm^{-4} s^{-1}); the only difference appeared in the initial period. These results agree well with those of Baukloh[1] and Flatley.[3]

By the observations of the cross-sections of specimens reacted with SO_2 in 101 kPa at 1073 K utilizing a optical microscope, the scale was found to be composed of a monolayer at the very initial period of the reaction and to become double layers after a 1-h reaction. The inner layer or the layer at the metal/scale interface showed a lamellar structure, as has been shown in previous papers.[3–5]

After Fe was oxidized in 101 kPa SO_2 at 1073 K for 16 h, the products were examined by the X-ray diffraction methods. X-Ray diffraction obtained by gradual sectioning from the surface revealed that the scale had a layer structure of Fe_3O_4/FeO/FeO–FeS. When the scale was peeled off from the base metal and ground to a powder, however, only FeO was detected. This result indicates that FeO is the major oxide for this sample and that Fe_3O_4 exists only on the surface of the scale.

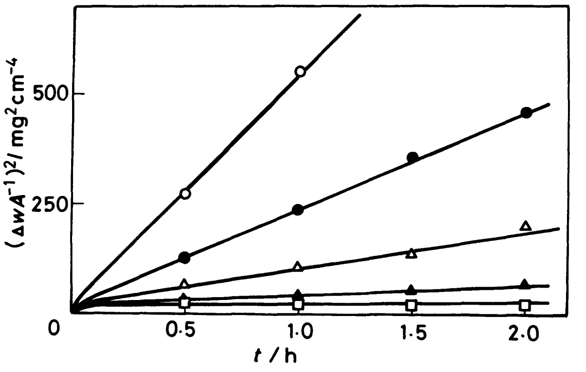

Fig. 1. Parabolic plot of reaction of Fe in SO_2 (101 kPa).
○: 1123 K, ●: 1073 K, △: 1023 K, ▲: 973 K, □: 923 K.

Figure 2 shows the Arrhenius plots of the parabolic rate constants for Fe in 101 kPa SO_2. The parabolic rate constants for oxidation in pure O_2[10,11] (B, C) and in S_2[12] (A) are also shown for the sake of comparison. A linear relation is observed for SO_2 reaction. The rates are very close to the oxidation rate in O_2.

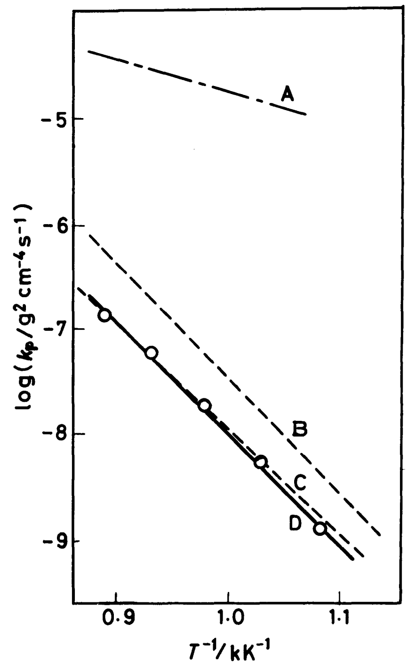

Fig. 2. Arrhenius plot of parabolic rate constant.
A: Sulfidation in S_2.[12] B: Oxidation in O_2.[10] C: Oxidation in O_2.[11] D: This work.

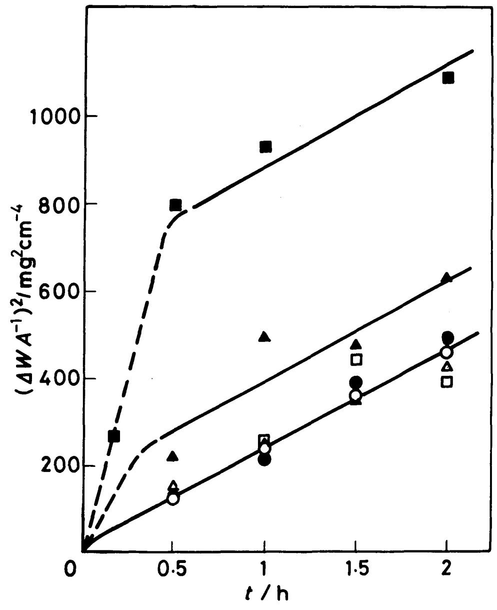

Fig. 3. Parabolic plot of reaction of Fe in SO_2 at 1073 K.
■: 1.3 kPa, ▲: 2.1 kPa, △: 13 kPa, □: 25 kPa, ●: 51 kPa, ○: 101 kPa.

[§] 1 M=1 mol dm^{-3}.

Compared to the sulfidation rate (A), the absolute value and the slope of line are both different. This shows that the reaction of Fe in 101 kPa SO_2 might be fundamentally the same as that in pure O_2, including the rate determining step.

Figure 3 shows the parabolic plot of the weight increase in Fe in SO_2 gas at 1073 K. The SO_2 pressures are 1.3, 2.1, 13, 25, 51, and 101 kPa respectively. The low SO_2 pressure was controlled by the temperature of the cold spot in the reaction system utilizing a Dry Ice–ethanol mixture. The reacted amounts are almost the same when the SO_2 pressure is between 13 and 101 kPa. At lower SO_2 pressures, the reacted amounts increase. However, the difference appears only at the initial period (less than 0.5 h). After a 1-h reaction the parabolic rate constants do not depend on the SO_2 pressure; that is, the rate is equal to that in O_2. The corrosion reaction that is characteristic of SO_2 gas might take place only in the initial period of the reaction.

Figure 4 shows the results of EPMA analysis for the cross-sections of specimens reacted in 101 kPa SO_2 at 1073 K for 10 min, 1.5 h, and 8 h respectively. In this figure, l denotes the scale thickness, and 0, the metal/scale interface. The scale/gas interface is the point where the oxygen concentration diminishes to zero. The sulfide is formed near the metal/scale interface. It appears from these results that the oxide thickness increased during the reaction, while sulfide did not grow.

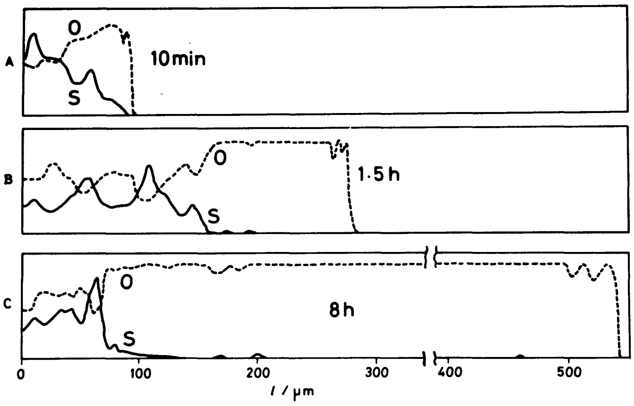

Fig. 4. Distribution of sulfur and oxygen in the scales reacted 10 min, 1.5 h and 8 h in SO_2 (101 kPa) at 1073 K.

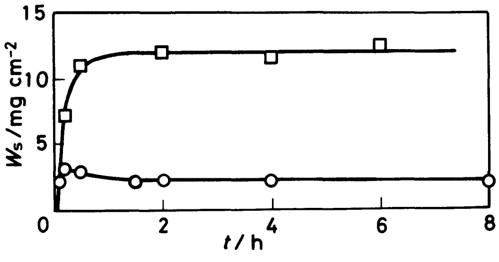

Fig. 5. Change of the total sulfur weight in the scale during the reaction of Fe in SO_2 at 1073 K.
□: 1.3 kPa, ○: 101 kPa.

Figure 5 shows the amounts of sulfur (W_s) in a scale, as obtained by chemical analysis. The total amounts of sulfur are constant after the reaction times of 5 min and 1 h under SO_2 pressures of 101 and 1.3 kPa respectively. These results indicate that the sulfide is formed only in the initial period of the reaction. The constant amount of sulfur in 101 kPa SO_2 was smaller than that in 1.3 kPa SO_2. The difference in the reactions in the initial period shown in Fig. 3 might be explained by the sulfide formation. At low SO_2 pressures a large amount of sulfide formation takes place during the initial period, thus leading to the increase in the total amount reacted. However, once the formation of sulfide ceases, only the oxidation reaction proceeds. At this stage there is no significant difference in the reaction rates (parabolic rate constants).

Figure 6 shows the dependence of the constant

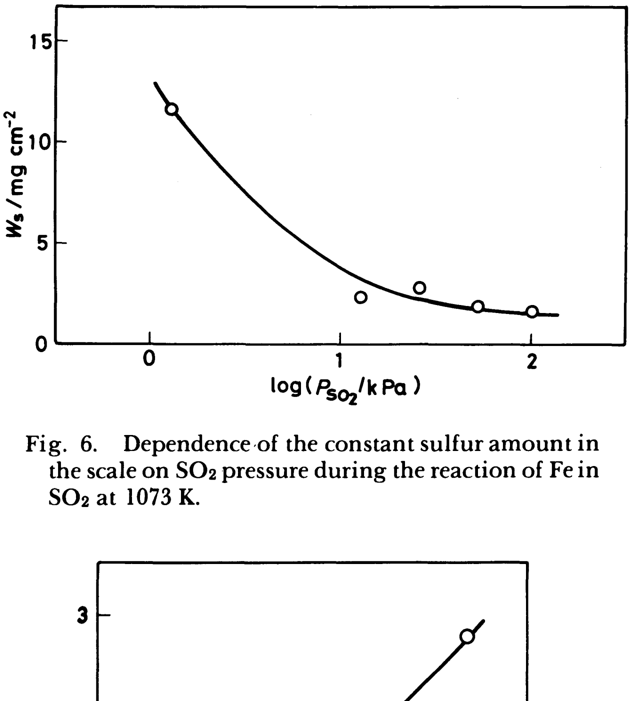

Fig. 6. Dependence of the constant sulfur amount in the scale on SO_2 pressure during the reaction of Fe in SO_2 at 1073 K.

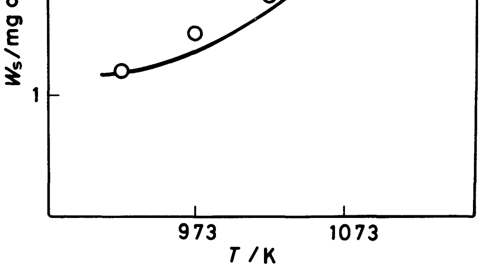

Fig. 7. Dependence of the constant sulfur amount in the scale on temperature during the reaction of Fe in SO_2 (101 kPa).

sulfur amount in the scale on the SO_2 pressure. The amount of sulfur increases at lower SO_2 pressures. Figure 7 shows the dependence of the constant sulfur amount in the scale on the temperature. The sulfur amount increases with the rise in the reaction temperature.

FeS is thermochemically unstable in a SO_2 atmosphere.[5] In order to study the reaction of FeS on Fe with SO_2 and confirm a stable phase, Fe was sulfided for 20 min in pure H_2S at 1073 K and then reacted with SO_2 of 101 kPa for 20 h at 1073 K. It was found that, after the reaction, the sulfide scale was covered with the oxides, FeO and Fe_3O_4. Another experiment was carried out using a single crystal of FeS. It was reacted with SO_2 of 101 kPa at 1073 K. By means of an X-ray diffraction study, only Fe_3O_4 was found as the reaction product. From this result, Fe_3O_4 was found to be a stable compound in 101 kPa SO_2 at 1073 K.

In order to know whether sulfur diffuses inward through the oxide scale, Fe was oxidized for 10 and 30 min in pure O_2 at 1073 K and then reacted with SO_2 of 101 kPa for 20 h. In both cases, no sulfide was detected by the chemical analysis. The sulfide formed after oxidation might be less than 1/20 of that without preoxidation, considering the limits of the analysis. According to Gilewicz-Wolter,[9] sulfur does not diffuse through the scale after Fe is reacted with SO_2 for 3 h at 1073 K. Watanabe and Ohira[13] reported that sulfide was not formed at 1023 K during the reaction of SO_2 and Fe, which was covered with a thick oxide film formed by the preoxidation for 4 h in pure O_2 at 1023 K. The present study has shown that a thin oxide film formed by only a 10-min preoxidation is able to suppress the sulfur diffusion throughout the scale. From these results it is concluded that sulfur cannot diffuse easily through a dense oxide scale. Thus, the FeS at the scale/metal interface is not formed as a result of the penetration of sulfur through the oxide layer. FeS might, however, be formed by the direct reaction between Fe and sulfur in the initial period of the reaction, as has been proposed by Chattergie[4] and Kurokawa.[5]

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