Oxidation of Fe_{1-x}S Pellet

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The oxidation of iron sulfide pellet was studied at 773 to 973 K in a mixed $\text{O}_2\text{-N}_2$ gas stream. The composition of iron sulfide was $\text{Fe}_{0.90}\text{S}$ to $\text{Fe}_{1.00}\text{S}$. The oxygen partial pressure in the gas stream was between 5.05×10^3 and 2.02×10^4 Pa. The results were compared with those in the oxidation of dense plates of iron sulfide reported in a previous paper. In the oxidation of the pellet of higher sulfur activity, the pellet mass was decreased from the start of oxidation accompanied by the evolution of SO_2 gas. The rate of oxidation was controlled by gas film mass transfer in the initial stage of oxidation and by gas diffusion through the outer oxide layer of the pellet in the subsequent stage. In the oxidation of the pellet of lower sulfur activity, on the other hand, the pellet mass was increased in the initial stage of oxidation, which was followed by a decrease of the mass. The evolution of SO_2 gas was observed from the start of oxidation. This observation is different from that in the oxidation of dense plates of iron sulfide: no SO_2 gas was evolved during the period of mass increase. It was found that the preferential oxidation of iron which resulted in a mass increase took place in the inner core of the pellet simultaneously with the oxidation of sulfide of higher sulfur activity in the outer layer of the pellet which was accompanied by the evolution of SO_2 gas. It was also found that the preferential oxidation of iron in the sulfide particles of which the pellet consisted took place in a very short time. The overall rate of oxidation of the pellet was analysed by a simplified model.

(Received August 8, 1985)

Keywords: oxidation kinetics of iron sulfide, non-stoichiometric iron sulfide, oxidation of pellet, preferential oxidation, unreacted-core model, gas diffusion

I. Introduction

The oxidation of iron sulfide is of basic importance to understand the processes of non-ferrous extractive metallurgy. It is well known, for example, that iron is preferentially oxidized in the oxidation of copper concentrate. In a previous paper⁽¹⁾, dense plates of FeS 10 mm long, 7 mm wide and 3 mm thick were oxidized, and it was reported that iron diffused from the interior of the sulfide to the surface and it was preferentially oxidized in the earlier stage of oxidation without the evolution of SO_2 gas. After the sulfur was concentrated in the inner sulfide and the sulfur activity was raised, the oxidation proceeded accompanied by the evolution of SO_2 gas. It is clear from the above that the progress of oxidation of iron sulfide depends on the composition.

Cylindrical briquets of iron sulfide 12 mm in diameter and about 15 mm high were oxidized in an air stream at 573 to 1173 K by Henderson⁽²⁾. It was found from the experiments using the briquets of different voids from 24.5 to 31.2% that the overall rate of oxidation was controlled by the gas diffusion through the porous oxide layer. However, the sulfur content of the iron sulfide used in his experiments was 28.1 mass% which was considerably lower than the stoichiometric composition of 36.5 mass%S, and the sample contained metallic iron. It is supposed for this reason that the detailed mechanism of oxidation may be more complicated.

Pellet consists of fine particles and the gas diffusion through pores between particles plays an important role in the overall rate of oxidation. It was intended in the present work to study the oxidation of iron sulfide pellet and to compare the results with those in the oxidation of dense plates of iron sulfide reported in the previous paper⁽¹⁾. The composition of iron sulfide was varied from $\text{Fe}_{0.90}\text{S}$ to $\text{Fe}_{1.00}\text{S}$. In order to facilitate to estimate the rate of gas

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diffusion in the pellet, measurements of particle size distribution of iron sulfide with which the pellet was prepared and of pore size distribution of the pellet were also carried out.

II. Experimental

Iron sulfide was prepared from iron powder of 99.99% purity and sulfur powder of 99.999% purity. The weighed amount of the powder mixture was heated in an evacuated quartz tube at 523 K for 3 days and subsequently at 1173 K for 18 ks. The composition of iron sulfide was chosen at $\text{Fe}_{0.90}\text{S}$, $\text{Fe}_{0.94}\text{S}$ and $\text{Fe}_{1.00}\text{S}$. The resulting iron sulfide was ground to minus 150 mesh size, and the size distribution was measured by an Andreason pipette. The measured particle size distribution was between 5 and $40\text{ }\mu\text{m}$, and the mean particle diameter was $17.4\text{ }\mu\text{m}$.

The obtained iron sulfide particles were pressed into a briquet 11 mm in diameter and *ca.* 10 mm high at a pressure of 196 MPa, and it was cut into a spherical pellet. The diameter of the pellet was measured in three different directions at right angles with one another. The mean diameter of the pellet, d , was listed in Table 1 together with the experimental conditions. The porosity of the pellets, ε , was calculated from the mass and the diameter of pellet and is also listed in Table 1. The density of iron sulfide was taken as $4.79 \times 10^6\text{ g}\cdot\text{m}^{-3}$ ⁽⁵⁾.

The experimental apparatus and the procedure were described in a previous paper⁽⁴⁾; an iron sulfide pellet was placed on a platinum net and heated in a quartz reaction tube of 30 mm ID in which nitrogen gas was sent at a flow rate of $1.5 \times 10^{-5}\text{ m}^3\cdot\text{s}^{-1}$. The nitrogen gas flow was switched to the mixed $\text{O}_2\text{-N}_2$ gas flow of the same flow rate, and the oxidation was started. The oxygen partial pressure in the mixed $\text{O}_2\text{-N}_2$ gas was varied between 5.05×10^3 and 2.02×10^4 Pa. The mass change of the sulfide pellet was continuously measured during the oxidation by a Shimadzu automatic microbalance RMB-50, and the SO_2 concentration in the exit gas from the reaction tube was measured by a Shimadzu infrared gas analyser URA-2S.

III. Results

The time variations of the sample mass and the SO_2 concentration in the exit gas are shown in Figs. 1 to 4. The sample mass shown in these figures is the value per unit surface area of the pellet, because the pellet diameter was of some variety, as shown in Table 1.

As seen in Figs. 1 and 2, a good agreement was obtained between the repeated measurements of sample mass in the same experimental conditions. It is seen in Fig. 1 that in the oxidation of $\text{Fe}_{0.90}\text{S}$ pellet at 773 K, a very slight increase of sample mass was observ-

Table 1 Experimental conditions.

Run	$(1-x)$	$p_{\text{O}_2} \times 10^{-4}$ (Pa)	Temperature (K)	w_0 (g)	$d \times 10^3$ (m)	ε (—)
1	0.90	2.02	873	0.9826	8.25	0.304
2	"	"	973	0.7899	7.80	0.338
3	"	"	773	1.0051	8.43	0.332
4	0.94	"	873	0.7665	7.78	0.352
5	"	"	973	1.5912	9.45	0.250
6	"	"	873	0.4627	6.32	0.270
7	0.90	"	873	1.5270	9.62	0.317
8	1.00	"	873	0.9093	8.02	0.298
9	"	"	973	1.5528	9.57	0.295
10	0.94	"	773	1.1583	8.62	0.280
11	1.00	"	773	1.2909	9.07	0.311
12	"	"	973	1.1950	8.78	0.297
13	0.90	"	773	1.0758	8.25	0.237
14	1.00	1.01	773	1.2382	8.93	0.308
15	"	0.51	773	1.2393	8.67	0.243

Fig. 1 Mass change of sample and SO_2 concentration in exit gas ($\text{Fe}_{0.90}\text{S}$ and $p_{\text{O}_2} = 2.02 \times 10^4$ Pa).

Fig. 3 Mass change of sample and SO_2 concentration in exit gas ($\text{Fe}_{1.00}\text{S}$ and $p_{\text{O}_2} = 2.02 \times 10^4$ Pa).

Fig. 2 Mass change of sample and SO_2 concentration in exit gas ($\text{Fe}_{0.94}\text{S}$ and $p_{\text{O}_2} = 2.02 \times 10^4$ Pa).

ed at the start of oxidation, which was followed by the decrease. At the temperatures of 873 and 973 K, on the other hand, the sample mass was decreased from the start of oxidation. A relatively large amount of SO_2 gas was evolved in the initial stage of oxidation, and the SO_2 concentration was decreased with the reaction time. The effect of temperature on the SO_2 concentration was not evident.

It is seen in Fig. 2 that a slight increase of the sample mass was observed at the start of oxidation at each experimental temperature of 773, 873 and 973 K in the oxidation of $\text{Fe}_{0.94}\text{S}$ pellet. Further marked mass increase was observed at the start of oxidation of $\text{Fe}_{1.00}\text{S}$ pellets, as shown in Fig. 3.

Fig. 4 Mass change of sample and SO_2 concentration in exit gas ($\text{Fe}_{1.00}\text{S}$ and 773 K).

Figure 4 shows the variations of the sample mass and the SO_2 concentration with the oxygen partial pressure at 773 K. The composition of iron sulfide was $\text{Fe}_{1.00}\text{S}$. When p_{O_2} was 2.02×10^4 Pa, the sample mass was increased in the initial 100 s, which was followed by a decrease. At lower p_{O_2} of 1.01×10^4 and 5.05×10^3 Pa, the sample mass continued to increase for 200 s and 1 ks, respectively. The SO_2 concentration was decreased at lower p_{O_2} . It was also noted that an appreciable amount of SO_2 gas was evolved during the period of mass increase.

The cross section of the pellet oxidized at 873 K for 1.26 ks (run 8) is shown in Fig. 5. As seen in this photograph, the oxidation proceed-

Fig. 5 Micrograph of a cross section of oxidized pellet ($\text{Fe}_{1.00}\text{S}$, 873 K and $p_{\text{O}_2}=2.02 \times 10^4$ Pa).

Fig. 6 Scanning electron micrograph of particles near reaction interface ($\text{Fe}_{1.00}\text{S}$, 873 K and $p_{\text{O}_2}=2.02 \times 10^4$ Pa).

ed inward from the pellet surface. From a scanning microscopic observation of the particles near the reaction interface shown in Fig. 6, it was revealed that the sulfide particles adjacent to the interface were scarcely oxidized, in-

dicating that the unreacted-core model can be applied to the analysis of the progress of oxidation.

Powder X-ray diffraction patterns of $\text{Fe}_{1.00}\text{S}$ pellets oxidized at 773 and 973 K showed that the oxidized product was Fe_2O_3 with a very small amount of Fe_3O_4 . It was also found that the composition of the inner sulfide core was shifted to $\text{Fe}_{0.90}\text{S}$ to $\text{Fe}_{0.88}\text{S}$ due to the oxidation.

IV. Discussion

1. Progress of the oxidation

It was mentioned above that the sample mass was increased at the start of oxidation and subsequently decreased. The reaction of mass increase may be written as follows:

The reaction mechanism was considered in the previous paper⁽¹⁾; iron diffuses from the inner sulfide core outward to the surface, and it is oxidized to form oxide. No SO_2 gas is evolved in these reactions. The reaction of mass decrease may be written as follows:

In order to examine the feasibilities of the reactions (1) and (2) and of the reaction (4), SO_2 partial pressure in equilibrium with Fe_{1-x}S and Fe_3O_4 is calculated⁽¹⁾⁽⁴⁾. The equilibrium S_2 pressure of Fe_{1-x}S needed for this calculation was taken from the data summarized by Burgmann *et al.*⁽³⁾ The calculated results are shown in Fig. 7. The experimental conditions in which the sample mass was decreased from the start of oxidation are shown by open circles, and those of mass increase at the initial stage of oxidation are shown by closed circles.

Fig. 7 Partial pressure of SO₂ gas in equilibrium with Fe_{1-x}S and Fe₃O₄.

As seen in this figure, the progress of reaction (4) is feasible, when p_{SO_2} is higher than about 40 Pa. This is because successive removal of SO₂ gas from the reaction interface is necessary for the successive progress of reaction (4). When the p_{SO_2} is higher, the rate of mass transfer of SO₂ from the reaction interface to the surrounding becomes higher, resulting in the progress of reaction (4). At lower p_{SO_2} , iron is preferentially oxidized according to the reactions (1) and (2), and sulfur is concentrated in the inner sulfide.

As seen in Fig. 4, an appreciable amount of SO₂ gas was evolved from the start of oxidation while the sample mass was increased, indicating that the reactions (1) to (3) and the reactions (4) and (5) took place simultaneously in the pellet. This observation is different from that in the previous work⁽¹⁾: no SO₂ gas was evolved during the period of mass increase in the oxidation of dense plates of iron sulfide. The reason for this difference is considered as follows. The pellet consisted of fine particles whose mean diameter was 17.4 μm , as mentioned above. It is intended to calculate the time required for the conversion of a single Fe_{1.00}S particle to an Fe_{0.90}S particle due to the reactions (1) to (3) at 873 K on the assumption

that the reaction rate is controlled by the iron diffusion in the sulfide⁽¹⁾.

With an approximation that the sulfide particle is regarded as a sphere of radius r_0 , the diffusion of iron is represented by

$$\frac{\partial c_{\text{Fe}}}{\partial t} = \frac{\partial}{\partial r} \left(c_{\text{Fe}} D_{\text{Fe}}^* \frac{\partial \ln a_{\text{Fe}}}{\partial r} \right) + \frac{2}{r} c_{\text{Fe}} D_{\text{Fe}}^* \frac{\partial \ln a_{\text{Fe}}}{\partial r} \quad (6)$$

Initial and boundary conditions are

$$c_{\text{Fe}} = 5.46 \times 10^4 \text{ mol} \cdot \text{m}^{-3} (\text{Fe}_{1.00}\text{S}) \quad \text{at } t=0,$$

$$c_{\text{Fe}} = 4.91 \times 10^4 \text{ mol} \cdot \text{m}^{-3} (\text{Fe}_{0.90}\text{S}) \quad \text{at } r=r_0$$

and

$$\frac{\partial c_{\text{Fe}}}{\partial r} = 0 \quad \text{at } r=0.$$

The iron concentration, c_{Fe} , in Fe_{1.00}S was calculated from the density of $4.79 \times 10^6 \text{ g} \cdot \text{m}^{-3}$ obtained by Haraldsen⁽⁵⁾. The c_{Fe} in Fe_{0.90}S was estimated from the above density neglecting the variation of molar volume with the composition. The iron activity, a_{Fe} , was calculated from the p_{S_2} -values obtained by Burgmann *et al.*⁽³⁾ and Turkdogan⁽⁶⁾ using Gibbs-Duhem equation. The self-diffusivity of iron in iron sulfide, D_{Fe}^* , was estimated from the data obtained by Turkdogan⁽⁶⁾ and Condit⁽⁷⁾, and it was approximated by the following expression.

$$D_{\text{Fe}}^* = 5.95 \times 10^{-11} \left(1 - \frac{N_{\text{Fe}}}{N_{\text{S}}} \right) \quad \text{at } 873 \text{ K.} \quad (7)$$

Equation (6) was numerically solved using the above values of parameters.

Taking x and x' in eqs. (1) to (3) as 0 and 0.1, respectively, the overall reaction is written as

When an Fe_{1.00}S particle of $r_0 = 8.7 \mu\text{m}$ is converted to Fe_{0.90}S obeying the reaction (8), a mass increase of $3.61 \times 10^{-9} \text{ g}$ accompanies. The rate of mass increase of a sulfide particle is given by

$$\frac{d\Delta w}{dt} = -0.75 M_{\text{O}_2} \cdot 4\pi r_0^2 c_{\text{Fe}} D_{\text{Fe}}^* \frac{\partial \ln a_{\text{Fe}}}{\partial r} \bigg|_{r=r_0} \quad (9)$$

Time required for a 90% mass increase of the above value of a particle is calculated from eq. (9) to be 0.07 s at 873 K. Similar calculations under other experimental conditions including the oxidation of $\text{Fe}_{1.00}\text{S}$ and $\text{Fe}_{0.94}\text{S}$ pellets at 873 and 973 K showed that the particle composition converted to $\text{Fe}_{0.90}\text{S}$, at which composition the preferential oxidation of iron was not observed at these temperatures, in a very short time.

It can be said from the above that the sulfide particles on the pellet surface are converted from $\text{Fe}_{1.00}\text{S}$ or $\text{Fe}_{0.94}\text{S}$ to $\text{Fe}_{0.90}\text{S}$ due to the preferential oxidation of iron in an instant and that the reactions (4) and (5) take place on the pellet surface at the subsequent stage while the reactions (1) to (3) continue to take place in the inner sulfide cores. This may be a reason why SO_2 gas is evolved from the start of oxidation which is accompanied by the mass increase.

2. Rate of mass increase of pellet

In the oxidation of $\text{Fe}_{1.00}\text{S}$ pellet, the pellet mass was evidently increased at the initial stage of oxidation, as shown in Figs. 3 and 4. The mass increase and SO_2 concentration in the exit gas in the initial 60 s are again illustrated in Fig. 8. As seen in this figure, the temperature

Fig. 8 Mass increase and SO_2 concentration in exit gas at initial stage of oxidation of $\text{Fe}_{1.00}\text{S}$ pellets.

Fig. 9 A model for mass increase in oxidation of $\text{Fe}_{1.00}\text{S}$ pellets.

variation of mass increase is minor in the initial 20 s, and it is markedly affected by the oxygen partial pressure. The SO_2 concentration is also decreased at lower p_{O_2} . Then it is supposed that the rate of reaction of mass increase is affected by the diffusional process of oxygen.

It was already mentioned that the reaction (8) took place in sulfide particles within a very short time of about 0.07 s. Then a simplified model schematically illustrated in Fig. 9 was proposed to investigate the rate of mass increase. The reaction (8) takes place at an interface of radius z_i , and the rate of this reaction is determined by the rate of oxygen diffusion to the interface. Subsequently, the reaction,

takes place in the shell from z_i to z_0 .

It is thought, however, that a dense Fe_2O_3 film is formed on the particle surface due to the reaction (8) and the oxygen diffuses through cracks of the dense Fe_2O_3 film, which causes the reaction (10) to occur at the subsequent state⁽¹⁾. Consequently the analysis of the rate of reaction (10) is relatively complicated, and the progress of reaction (10) was estimated from the observed SO_2 concentration in the

following calculation.

Assuming a quasi-steady state, diffusion of oxygen in the pellet is represented by

$$\frac{D_e}{RT} \left(\frac{d^2 p_{O_2}}{dz^2} + \frac{2}{z} \frac{dp_{O_2}}{dz} \right) - n_{O_2} = 0, \quad (11)$$

where n_{O_2} is the number of moles of oxygen consumed due to the reaction (10) per unit time and unit volume of the pellet, and n_{O_2} was assumed to be uniform throughout the shell between z_i and z_0 . Boundary conditions for eq. (11) are

$$D_e \frac{dp_{O_2}}{dz} = k_g (p_{O_2}^b - p_{O_2}^s) \quad \text{at } z = z_0 \quad (12)$$

and

$$p_{O_2} = 0 \quad \text{at } z = z_i. \quad (13)$$

In the above boundary condition (13), p_{O_2} was approximated to zero, because the reaction (8) was assumed to be of diffusion control of oxygen and the equilibrium p_{O_2} of this reaction was also assumed to be low enough. Solution of eq. (11) is given by

$$p_{O_2} = \frac{n_{O_2} RT}{6D_e} (z^2 - z_i^2) - z_0^2 \left(\frac{1}{z_i} - \frac{1}{z} \right) A, \quad (14)$$

where

$$A = \frac{n_{O_2} RT z_0}{3D_e} - \frac{k_g}{D_e} \left\{ p_{O_2}^b - \frac{\frac{n_{O_2} RT}{6} (z_0^2 - z_i^2) - z_0 \left(\frac{z_0}{z_i} - 1 \right) \left(\frac{n_{O_2} RT z_0}{3} - k_g p_{O_2}^b \right)}{D_e + k_g z_0 \left(\frac{z_0}{z_i} - 1 \right)} \right\}. \quad (15)$$

The n_{O_2} was estimated by

$$n_{O_2} = \frac{0.01675 v c_{SO_2}}{(4/3)\pi(z_0^3 - z_i^3)RT}, \quad (16)$$

where c_{SO_2} was the observed SO_2 concentration.

The rate of oxygen diffusion to the interface is given by

$$\begin{aligned} J_{O_2(z=z_i)} &= 4\pi z_i^2 \frac{D_e}{RT} \frac{dp_{O_2}}{dz} \bigg|_{z=z_i} \\ &= 4\pi z_i^2 \frac{D_e}{RT} \left(\frac{n_{O_2} RT z_i}{3D_e} - \frac{z_0^2}{z_i^2} A \right). \end{aligned} \quad (17)$$

The rate of mass increase due to the reaction (8) is

$$\left(\frac{d\Delta w}{dt} \right)_I = \frac{M_{O_2}}{4\pi z_0^2} J_{O_2(z=z_i)}, \quad (18)$$

and the rate of mass decrease due to the reaction (10) is

$$\left(\frac{d\Delta w}{dt} \right)_{II} = -\frac{10.46}{4\pi z_0^2} \frac{v c_{SO_2}}{100RT}. \quad (19)$$

Then the mass change of the pellet is given by

$$\frac{d\Delta w}{dt} = \left(\frac{d\Delta w}{dt} \right)_I + \left(\frac{d\Delta w}{dt} \right)_{II}. \quad (20)$$

The time variation of z_i is represented as

$$\frac{dz_i}{dt} = -\frac{13.3 M_{FeS}}{4\pi z_i^2 (1-\varepsilon) \rho_{FeS}} J_{O_2(z=z_i)}. \quad (21)$$

The time variation of the pellet mass was calculated numerically from the above equations, changing the z_i -value due to eq. (21). The mass transfer coefficient, k_g , was estimated from the Ranz-Marshall equation⁽⁸⁾,

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}. \quad (22)$$

The effective diffusivity, D_e , was calculated by the following expressions⁽⁹⁾⁽¹⁰⁾.

$$D_e = \varepsilon^2 D. \quad (23)$$

$$\frac{1}{D} = \frac{1 - (1 - \sqrt{M_{O_2}/M_{N_2}}) y_{O_2}}{D_{O_2}} + \frac{1}{D_k}. \quad (24)$$

$$D_k = 97 r_e \sqrt{\frac{T}{M_{O_2}}}. \quad (25)$$

The porosity of the pellet, ε , listed in Table 1 was used in eq. (23). The mean pore radius, r_e , in eq. (25) was measured by an AMINCO mercury porosimeter to be 8.0×10^{-7} m. The molecular diffusivity of oxygen in nitrogen, D_{O_2} , was estimated by Chapman-Enskog equa-

Table 2 Effective diffusivity and mass transfer coefficient for the calculation of eq. (27).

Run	$D_e \times 10^6 \text{ (m}^2 \cdot \text{s}^{-1}\text{)}$	$k_g \times 10^2 \text{ (m} \cdot \text{s}^{-1}\text{)}$
8	8.22	5.12
11	7.56	3.83
12	9.46	5.61
14	7.36	3.88
15	4.51	3.98

Fig. 10 Mass decrease in oxidation of $\text{Fe}_{0.90}\text{S}$ pellets and fractional resistance. ($p_{\text{O}_2} = 2.02 \times 10^4 \text{ Pa}$).

tion⁽¹¹⁾ neglecting the effect of SO_2 gas. In the calculation of k_g and D_e , the density and the viscosity of gas at the reaction temperatures were used. The values of k_g and D_e thus estimated are listed in Table 2. The calculated results of the time variation of pellet mass are shown in Fig. 8 by dotted lines. Though the calculated results were somewhat deviated from the observations, the mass increase was markedly affected by the oxygen partial pressure at the initial stage of oxidation. On the other hand, it was not evidently affected by the temperature.

3. Rate of mass decrease of pellet

In the oxidation of $\text{Fe}_{0.90}\text{S}$ pellet, the pellet mass was decreased from the start of oxidation at 873 and 973 K, as shown in Fig. 1. It is again illustrated in Fig. 10 by solid lines. The overall reaction is represented by eq. (10).

The initial rate of oxidation is determined by the gas film mass transfer and the chemical reaction on the pellet surface, since the oxide is

not yet formed. On the assumption that the initial rate is controlled by the gas film mass transfer, the rate of mass decrease per unit surface area of the pellet is represented as

$$\left. \frac{d\Delta W}{dt} \right|_{t=0} = -6.245 \frac{k_g}{RT} p_{\text{O}_2}. \quad (26)$$

The mass transfer coefficient, k_g , was estimated from the Ranz-Marshall equation⁽⁸⁾ of eq. (22) at 6.18×10^{-2} and $4.42 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$ for runs 2 and 7, respectively. The result of calculation of mass decrease are shown in Fig. 10 by dotted and dashed lines. As seen in this figure, a good agreement was obtained between the calculated and the observed initial rate of mass decrease, indicating that the resistance to the chemical reaction was negligible.

It is then assumed that the progress of reaction (10) at the subsequent stage is controlled by both the gas film mass transfer and the gas diffusion through the outer oxide layer. The inner $\text{Fe}_{0.90}\text{S}$ is oxidized through Fe_3O_4 to form Fe_2O_3 . However, the amount of Fe_3O_4 in the oxidized pellet is negligibly small as mentioned before, and the interface between $\text{Fe}_{0.90}\text{S}$ and Fe_2O_3 is taken into account in the analysis of the rate of mass decrease. Denoting the pellet radius by z_0 , the rate of mass decrease under the above assumptions is represented by

$$\frac{d\Delta w}{dt} = -6.245 \frac{p_{\text{O}_2}}{RT \left\{ \frac{1}{k_g} + \frac{z_0(z_0 - z_i)}{z_i D_e} \right\}}. \quad (27)$$

The mass decrease can be correlated with the radius of interface, z_i , as

$$\Delta w = -a(z_0^3 - z_i^3), \quad (28)$$

where

$$a = 10.46 \frac{(1 - \varepsilon_h) \rho_{\text{Fe}_{0.90}\text{S}}}{3z_0^2 M_{\text{Fe}_{0.90}\text{S}}}. \quad (29)$$

After substituting z_i in eq. (28) for eq. (27), integration of eq. (27) with the initial condition of $\Delta w = 0$ at $t = 0$ yields

$$\left(\frac{1}{k_g} - \frac{z_0}{D_e} \right) \Delta w + \frac{3az_0^2}{2D_e} \left(\frac{\Delta w}{a} + z_0^3 \right)^{2/3} - \frac{3az_0^4}{2D_e} = -\frac{6.245 p_{\text{O}_2}}{RT} t. \quad (30)$$

In the calculation of eq. (30), the density of Fe_{0.90}S, $\rho_{\text{Fe}_{0.90}\text{S}}$, was estimated at $4.49 \times 10^6 \text{ g} \cdot \text{m}^{-3}$ from the density of Fe_{1.00}S, $4.79 \times 10^6 \text{ g} \cdot \text{m}^{-3}$, neglecting the variation of molar volume of pyrrhotite with the composition. In order to estimate the effective diffusivity of oxygen, D_e , in eq. (30), the pore size distribution of the Fe₂O₃ layer was measured by an AMINCO mercury porosimeter, and the porosity, ε_h , of 0.41 and the mean pore radius, r_e , of $2.4 \times 10^{-7} \text{ m}$ were obtained. These values were substituted for eqs. (23) and (25), and the mole fraction of oxygen, y_{O_2} , was taken as 0.2 in eq. (24). The calculated effective diffusivity was 1.18×10^{-5} and $1.06 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ for runs 2 and 7, respectively. In this calculation, the effect of SO₂ gas was neglected.

The mass decrease calculated from eq. (30) was shown in Fig. 10 by dotted lines. As seen in this figure, the values of calculated mass decrease were in good agreement with the observed values.

From eq. (27), the fractional resistances to the gas film mass transfer, η_1 , and the oxygen diffusion through the oxide layer, η_2 , are represented as follows.

$$\eta_1 = \frac{\frac{1}{k_g}}{\frac{1}{k_g} + \frac{z_0(z_0 - z_i)}{z_i D_e}} \quad (31)$$

$$\eta_2 = \frac{\frac{z_0(z_0 - z_i)}{z_i D_e}}{\frac{1}{k_g} + \frac{z_0(z_0 - z_i)}{z_i D_e}} \quad (32)$$

The calculated η_1 and η_2 are also shown in Fig. 10. As seen in this figure, though the resistance to the gas film mass transfer is predominant at the initial stage of oxidation, the overall rate of oxidation is virtually controlled by gas diffusion through the oxide layer at the subsequent stage.

V. Summary

Iron sulfide of the composition of Fe_{0.90}S, Fe_{0.94}S and Fe_{1.00}S were synthesized, and spherical pellets were made from the obtained iron sulfide particles. Mass change of the pellet

and the SO₂ concentration in the exit gas were continuously measured during the oxidation. The temperature was chosen between 773 and 973 K, and the oxygen partial pressure in the mixed O₂-N₂ gas stream was varied between 5.05×10^3 and $2.02 \times 10^4 \text{ Pa}$. The experimental results were compared with those in the previous work⁽¹⁾, in which dense plates of Fe_{1.00}S were oxidized.

In the oxidation of Fe_{0.90}S pellet at 873 and 973 K, the pellet mass was decreased from the start of oxidation. The oxidation proceeded from the pellet surface to the interior, and the product of oxidation was Fe₂O₃ with a very small amount of Fe₃O₄. From the analysis of the reaction rate based on the unreacted-core model, it was found that the overall rate of oxidation was controlled by the gas film mass transfer at the initial stage of oxidation and by the gas diffusion through the oxide layer at the subsequent stage.

In the oxidation of Fe_{0.94}S pellet, the pellet mass was slightly increased at the initial stage of oxidation, and it was decreased at the subsequent stage. In the oxidation of Fe_{1.00}S pellet, on the other hand, a marked mass increase was observed in the initial stage. In both cases of Fe_{0.94}S and Fe_{1.00}S pellets, an appreciable amount of SO₂ gas was evolved from the start of oxidation. This observation is different from that in the previous work⁽¹⁾: no SO₂ gas was evolved during the mass increase in the oxidation of dense plates of iron sulfide.

It was reported in the previous paper⁽¹⁾ that the reaction of mass increase was a preferential oxidation of iron without the evolution of SO₂ gas. This is due to a lower sulfur activity of iron sulfide. It was supposed from theoretical considerations that this reaction proceeded within the sulfide particles on the pellet surface in a very short time of about 0.07 s at the initial stage of oxidation of iron sulfide pellets, and that the reaction of mass decrease accompanied by the evolution of SO₂ gas took place on the pellet surface at the subsequent stage, while the reaction of mass increase simultaneously proceeded in the inner part of the pellet. The rate of oxidation was controlled by the diffusional processes of oxygen in the pellet.

Nomenclature

a_{Fe} : iron activity in sulfide, [—]
 c_{Fe} : iron concentration, $[\text{mol} \cdot \text{m}^{-3}]$
 c_{SO_2} : SO_2 concentration, [vol %]
 d : pellet diameter, [m]
 D_e : effective diffusivity, $[\text{m}^2 \cdot \text{s}^{-1}]$
 D_{Fe}^* : self-diffusivity of iron, $[\text{m}^2 \cdot \text{s}^{-1}]$
 D_K : Knudsen diffusivity, $[\text{m}^2 \cdot \text{s}^{-1}]$
 D_{O_2} : molecular diffusivity of oxygen, $[\text{m}^2 \cdot \text{s}^{-1}]$
 $J_{\text{O}_2}(z=z_i)$: rate of oxygen supply to interface, $[\text{mol} \cdot \text{s}^{-1}]$
 k_g : mass transfer coefficient, $[\text{m} \cdot \text{s}^{-1}]$
 M_i : molecular mass of species i ($i = \text{O}_2, \text{N}_2, \text{FeS}$ and $\text{Fe}_{0.90}\text{S}$), $[\text{kg} \cdot \text{mol}^{-1}]$
 n_{O_2} : oxygen consumption due to reaction (12), $[\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
 N_i : atomic fraction of i ($i = \text{Fe}$ and S), [—]
 p_{O_2} : oxygen partial pressure, [Pa]
 $p_{\text{O}_2}^b$: p_{O_2} in bulk gas stream, [Pa]
 $p_{\text{O}_2}^s$: p_{O_2} at pellet surface, [Pa]
 r : radial distance in a particle, [m]
 r_e : mean pore radius, [m]
 r_0 : radius of particle, [m]
 R : gas constant ($= 8.314$), $[\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
 Re : Reynolds number, [—]
 Sc : Schmidt number, [—]
 Sh : Sherwood number, [—]
 t : time, [s]
 T : temperature, [K]
 v : gas flow rate, $[\text{m}^3 \cdot \text{s}^{-1}]$
 Δw : mass change of a particle, [kg]

ΔW : mass change of pellet per unit surface area, $[\text{kg} \cdot \text{m}^{-2}]$
 y_{O_2} : mole fraction of oxygen, [—]
 z : radial distance in pellet, [m]
 z_i : radius of interface, [m]
 z_0 : radius of pellet, [m]
 ε : porosity of pellet, [—]
 ε_h : porosity of Fe_2O_3 layer, [—]
 ρ_i : density of species i ($i = \text{Fe}_{1.00}\text{S}$ and $\text{Fe}_{0.90}\text{S}$), $[\text{kg} \cdot \text{m}^{-3}]$
 η_i : fractional resistance, [—]
 $i = 1$: gas film mass transfer
 $i = 2$: gas diffusion through oxide layer

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