Journal of Thermal Analysis, Vol. 35 (1989) 1751–1759

OXIDATION KINETICS OF IRON SULFIDE IN THE FORM OF DENSE PLATE, PELLET AND SINGLE PARTICLE

Z. Asaki and *Y. Kondo*

PROFESSOR AND PROFESSOR EMERITUS, RESPECTIVELY,
DEPARTMENT OF METALLURGY, KYOTO UNIVERSITY, SAKYO-KU,
KYOTO 606, JAPAN

(Received June 14, 1989)

The oxidation behaviours of pyrrhotite in the form of dense plate, pellet and single particle were compared. In the oxidation of dense plate of FeS, preferential oxidation of iron took place to form a dense oxide layer in the earlier stage of oxidation, and the subsequent oxidation accompanying the evolution of SO_2 gas proceeded after the composition of pyrrhotite attained $Fe_{0.9}S$. In the oxidation of FeS pellet, both the above reactions take place simultaneously because the pellet consists of fine particles. In the oxidation of single particle of small size, ignition of the particle occurred due to the heat of oxidation, and the particle melted in a very short time less than 1 second.

The oxidation of iron sulfide is of basic importance to understand the processes of non-ferrous metallurgy. Thornhill et al. studied the oxidation of FeS particles of 30 to 40 mesh size and reported that a dense layer of iron oxide was formed on the particle surface in the earlier stage of oxidation and that the oxidation preceeded irregularly into the interior of particles in the later stage [1]. They made microscopic observations to follow the progress of oxidation, but accurate measurement of the oxidation rate was difficult because of the small particle size. Kinetics of heterogeneous reaction like the oxidation of iron sulfide may be markedly affected by the size and porosity of the sample. The authors studied the oxidation kinetics of iron sulfide in the form of dense plate, pellet and particle. It is intended in this paper to elucidate the correlation between the oxidation behaviour and size and form of iron sulfide based on the oxidation mechanism reported in the previous papers [2–4].

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Dense plate of iron sulfide

The iron sulfide, FeS, was synthesized by heating the mixed powder of iron and sulfur of 99.99% purity in an evacuated quartz tube and the resulting dense lump was cut into rectangular plates of 10 mm length, 7 mm width and 3 mm thickness. It was oxidized in a mixed Ar–O_2 gas stream at the temperatures between 1023 and 1123 K and oxygen partial pressure of 1 to 20 kPa.

The time variation of the sample mass and the SO_2 concentration in the exit gas from the reaction tube measured by an automatic microbalance and an infrared gas analyser, respectively, are shown in Fig. 1. The sample mass increases rapidly during the first five minutes of oxidation without the evolution of SO_2 gas. The rate of mass increase was lowered, but the mass continued to increase for 15 to 80 ks depending on the experimental conditions. This mass increase was followed by a mass decrease which was accompanied by the evolution of SO_2 gas. In the following discussion, the initial stage of rapid mass increase, the subsequent stage of slow mass increase and the later stage of mass decrease accompanied by the SO_2 gas evolution are referred to as the first, second and third stages of oxidation, respectively.

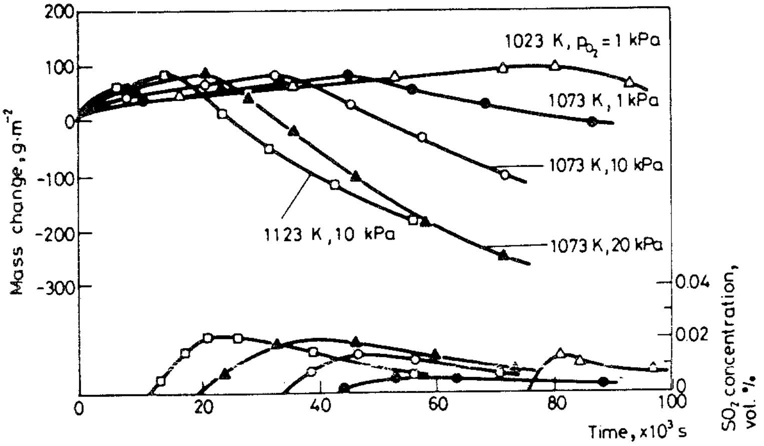

Fig. 1

It was found from the observations under a microscope that a dense magnetite layer of about 5 μm in thickness was formed on the sample surface at the end of the first stage of oxidation. It has grown to a thickness of about 25 μm at the end of the second stage. A thin layer of hematite was also observed outside the magnetite. In the third stage of oxidation, the oxidation proceeded irregularly to the interior of the sulfide core, and porous magnetite and hematite were formed.

The oxidation in the first and second stages can be written as

$$3\mathrm{FeS}+2x\mathrm{O}_2 = 3\mathrm{Fe}_{1-x}S+x\mathrm{Fe}_3\mathrm{O}_4 \tag{1}$$

where $\mathrm{Fe}_{1-x}\mathrm{S}$ represents nonstoichiometric pyrrhotite. It is assumed that the rate of oxidation in the first stage is controlled by the diffusion of iron within the inner sulfide core toward the pyrrhotite/magnetite interface since the magnetite film formed on the sulfide surface is very thin. Assuming that the self-diffusivity of sulfur in pyrrhotite is several orders of magnitude lower than that of iron [5], the diffusion of iron in pyrrhotite is expressed by

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y}\left(cD^{*}_{\mathrm{Fe}}\frac{\partial \ln a_{\mathrm{Fe}}}{\partial y}\right) \tag{2}$$

where c and a_{Fe} are iron concentration in the units of mol $\mathrm{Fe}\cdot\mathrm{m}^{-3}$ and activity of iron in pyrrhotite, respectively, and D^{*}_{Fe} is self-diffusivity of iron. Initial and boundary conditions for Eq. (2) are c = 54,600 mol $\mathrm{Fe}\cdot\mathrm{m}^{-3}$ (FeS) at $t = 0$, $c = c_1$ at $y = 0$ ($\mathrm{Fe}_{1-x}\mathrm{S}/\mathrm{Fe}_3\mathrm{O}_4$ interface) and $\partial c/\partial y = 0$ at $y = d$ (center). The rate of mass increase of the sample is represented by

$$\frac{\mathrm{d}\Delta m}{\mathrm{d}t} = \frac{2}{3}M_{\mathrm{O}_2}cD^{*}_{\mathrm{Fe}}\left.\frac{\mathrm{d}\ln a_{\mathrm{Fe}}}{\mathrm{d}y}\right|_{y=0} \tag{3}$$

where Δm is mass increase per unit sample surface. The iron concentration at the pyrrhotite/magnetite interface, c_1, was determined by trial and error so that the mass increase calculated from Eqs (2) and (3) was in accordance with the measurement. The mass increase calculated under the presumption of c_1 = 52,900 mol $\mathrm{Fe}\cdot\mathrm{m}^{-3}$ is shown in Fig. 2. As seen in this figure, the calculated mass increase is in good agreement with the measurement during the initial one minute.

The mass increase of the sample in the second stage of oxidation is plotted in Fig. 3 against the square root of reaction time. The parabolic rate constant, K_p, in the

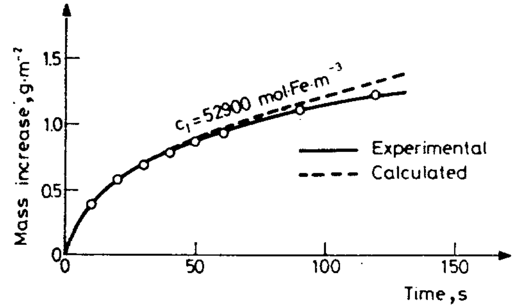

Fig. 2

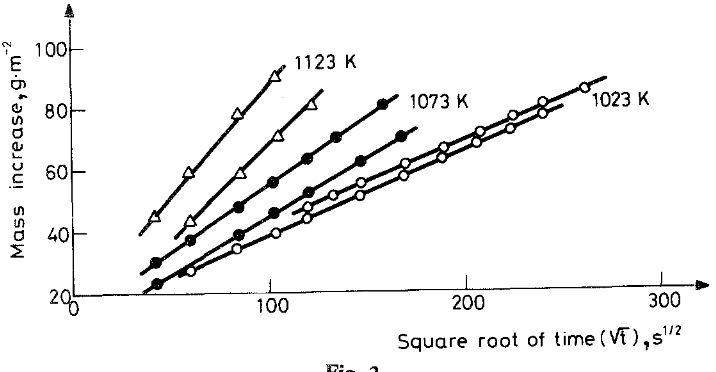

Fig. 3

form of

$$\Delta m = K_p\sqrt{t} + (\text{const.}) \tag{4}$$

was calculated from Fig. 3 as 2.6×10^3 to 7.3×10^3 $g \cdot m^{-2} \cdot s^{-1/2}$. The K_p-value was markedly affected by the reaction temperature and an activation energy of 105 $kJ \cdot mol^{-1}$ was obtained. Himmel et al. reported that the parabolic rate law held for the oxidation of wustite to magnetite and the activation energy was 100 $kJ \cdot mol^{-1}$. It can be said from these values of activation energy that the oxidation rate in the second stage is controlled by the diffusion of iron through the magnetite layer on the sulfide sample.

The sample mass decreased with the evolution of SO_2 gas in the third stage. The reaction may be written as

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

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \tag{6}$$

It is supposed that the gaseous oxygen diffuses through the cracks in the oxide layer into the interior of sulfide core where the reactions (5) and (6) take place. The progress of oxidation was in an irregular fashion. Furthermore, porous oxide was produced due to the evolution of SO_2 gas.

As described above, the reaction mechanism is quite different between the second and third stages of oxidation. Transition from the second to the third stage can be explained as follows. The average composition of the inner sulfide core at the end of second stage can be calculated from the amount of mass increase and Eq. (1). The calculated results were between $Fe_{0.90}S$ and $Fe_{0.92}S$ irrespective of the experimental conditions. The eqilibrium partial pressure of SO_2 at the pyrrhotite/magnetite interface increases with the increase in cation deficit of pyrrhotite and the temperature [5, 7]. It reaches 80 kPa at the composition of $Fe_{0.9}S$

and the experimental temperatures, and the reaction (5) accompanying the evolution of SO_2 gas is feasible.

Iron sulfide pellet

Iron sulfide pellet, about 9 mm in diameter, was prepared from synthesized iron sulfide powder. The composition of iron sulfide was chosen at $Fe_{0.9}S$ and $Fe_{1.0}S$. The size distribution of the powder was between 5 and 40 μm and the mean particle diameter was 17.4 μm.

The pellet was oxidized at the temperature of 773 to 973 K and the oxygen partial pressure of 20 kPa. It is known that the overall rate of oxidation is controlled by the diffusion of gaseous oxygen through the oxide layer formed on the pellet surface at higher temperature, and the experimental temperature lower than that in the oxidation of dense plate of iron sulfide was chosen. It was observed that the reaction took place in a topochemical fashion and the oxidation product was Fe_2O_3 with a very small amount of Fe_3O_4. The mass change of the pellet and the SO_2 concentration in the exit gas during the oxidation are shown in Figs 4 and 5. The mass change is shown by the value per unit surface area of the pellet.

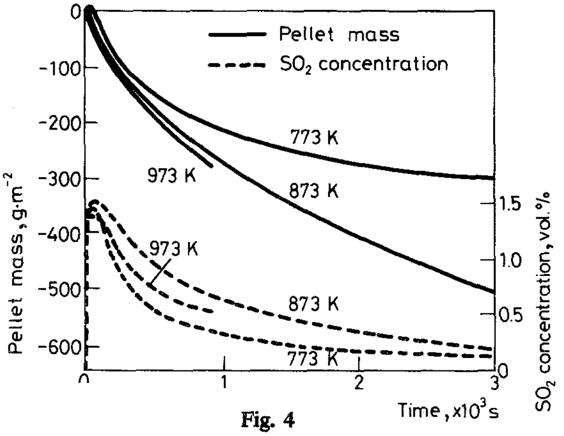

Fig. 4

In the oxidation of $Fe_{0.9}S$ pellet at 773 K, as seen in Fig. 4, a very slight increase of pellet mass was observed at the start of oxidation, which was followed by a decrease. At the temperatures of 873 and 973 K, on the other hand, the pellet mass decreased and an appreciable amount of SO_2 gas was evolved from the start of oxidation. These observations indicate that the reactions (5) and (6) take place from

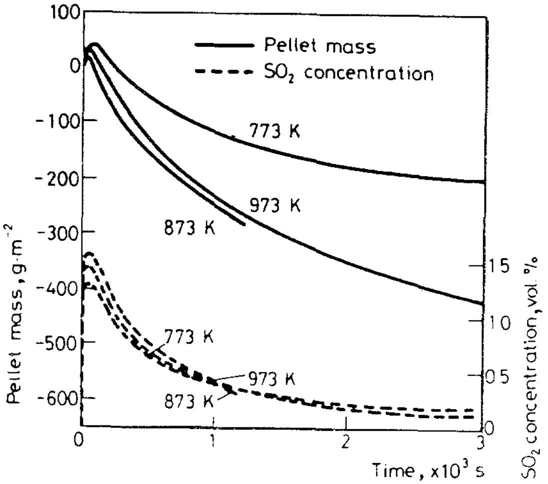

Fig. 5

the start of oxidation in the oxidation of $Fe_{0.9}S$ pellet at higher temperatures. This is because of higher SO_2 partial pressure at the pyrrhotite/oxide interface.

In the oxidation of $Fe_{1.0}S$ pellet, as shown in Fig. 5, the pellet mass increased significantly at the start of oxidation due to the reaction (1). However, an appreciable amount of SO_2 gas was evolved from the start of oxidation. This observation is different from that in the oxidation of dense plate of iron sulfide where no SO_2 gas is evolved during the mass increase. The reason for this difference is considered as follows. The pellet consisted of fine particles whose mean diameter was 17.4 μm. The time required for the conversion of a single $Fe_{1.0}S$ particle to $Fe_{0.9}S$ due to the reaction (1) can be calculated. Approximating that the particle is regarded as a sphere of radius r_0, the diffusion of iron in the sulfide particle is represented by

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial r}\left(cD^*_{\mathrm{Fe}}\frac{\partial \ln a_{\mathrm{Fe}}}{\partial r}\right) + \frac{2}{r}cD^*_{\mathrm{Fe}}\frac{\partial \ln a_{\mathrm{Fe}}}{\partial r} \tag{7}$$

Initial and boundary conditions are $c = 5.5 \times 10^4$ mol·m^{-3} ($Fe_{1.0}S$) at $t = 0$, $c = 4.9 \times 10^4$ mol·m^{-3} ($Fe_{0.9}S$) at $r = r_0$ and $\partial c/\partial r = 0$ at $r = 0$.

When an $Fe_{1.0}S$ particle of $r_0 = 8.7$ μm is converted to $Fe_{0.9}S$, a mass increase of 3.6×10^{-9} g is expected. The rate of mass increase of a single particle is given by

$$\frac{\mathrm{d}\Delta m}{\mathrm{d}t} = -0.75\mathrm{M}_{\mathrm{O}_2}\cdot 4\pi r_0^2\, cD^*_{\mathrm{Fe}}\frac{\partial \ln a_{\mathrm{Fe}}}{\partial r}\bigg|_{r=r_0} \tag{8}$$

Time required for a 90% mass increase of the above value is calculated from Eq. (8) to be 0.07 s at 873 K.

It can be said from the above that the sulfide particles on the pellet surface are converted from $Fe_{1.0}S$ to $Fe_{0.9}S$ due to the reaction (1) in an instant and that the reactions (5) and (6) take place on the pellet surface at the subsequent stage while the reaction (1) continues to take place in the inner sulfide particles. This may be the reason for the evolution of SO_2 gas during the mass increase in the initial stage of oxidation.

Single particle of iron sulfide

Pyrrhotite particles of mean diameter of 51 and 88 μm were fed from a rotating disc feeder to a vertical reaction tube, 20 mmID and 1.8 m high, which was made of plain carbon steel and heated with electric furnace at 825 to 1015 K. The composition of pyrrhotite particles was $Fe_{0.97}S$. Feeding rate of pyrrhotite particles was 0.04 $g \cdot s^{-1}$. Mixed O_2–N_2 gas was sent to the reaction tube from the upper end at a flow rate of 5×10^{-5} $m^3 \cdot s^{-1}$ at 298 K. The oxidized particles were sampled at the bottom of the reaction tube and the sulfur content was analysed by the conventional gravimetric method from which the fractional reaction, x, was calculated. In this experiment, the particle concentration in the vertical reaction tube is very low because of small feeding rate of pyrrhotite particles, and the oxidation of pyrrhotite particles can be regarded as that of single particle.

When the temperature of reaction tube, T_w, was higher than 923 K, the x-value increased in proportion to oxygen partial pressure and no variation of x with the wall temperature and particle size was observed, indicating that x was virtually determined by the amount of oxygen supplied to the reaction tube.

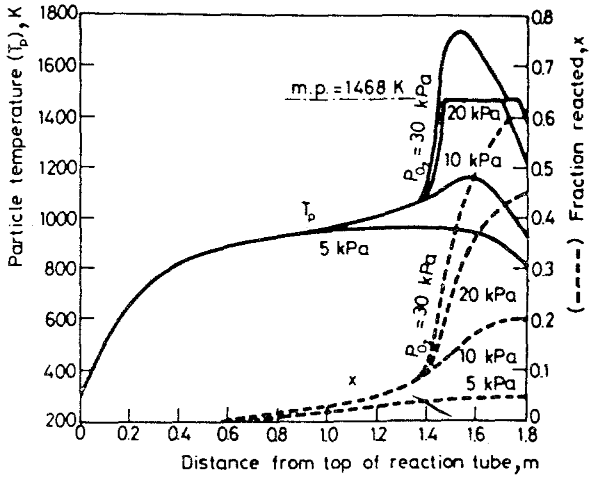

Fig. 6

Micrographic observation revealed that the oxidized particles were melted and became spherical when T_w was higher than 896 K and oxygen partial pressure was higher than 20 kPa. The oxidation product was found to be magnetite with a very small amount of hematite by the X-ray diffraction analysis. A mathematical model for the progress of oxidation of pyrrhotite particles was proposed. The heat and mass balances on gas and particles were taken into consideration, and the reaction (5) was assumed to take place during the descent of particles in the vertical reaction tube, to which unreacted core model was applied. The calculated results of particle temperature, T_p, and fraction reacted, x, are shown in Fig. 6. In this calculation, the rate constant of reaction (5) was determined so that the calculated fractional reaction coincided with the measurement at the bottom of the reaction tube. The residence time of the particles in the reaction tube was calculated from the falling velocity as about 1 second. As seen in Fig. 6, the particle temperature rises in the upper portion of the reaction tube due to the heat transfer from the reaction tube. When the particle temperature attained about 1150 K, it was further increased rapidly due to the heat of oxidation and exceeded the melting point, 1468 K, provided that the oxygen partial pressure was higher than 20 kPa. These results of calculation were in good agreement with the micrographic observation of the oxidized particles.

Conclusion

When the composition of pyrrhotite was stoichiometric FeS, preferential oxidation of iron took place and no SO_2 gas was evolved, which was followed by the oxidation accompanying the evolution of SO_2 gas after the composition attained $Fe_{0.9}S$. In the preferential oxidation of iron, diffusion of iron in the inner sulfide core and produced dense oxide layer determines the overall rate of oxidation. Porous oxide was formed in the subsequent oxidation with the evolution of SO_2 gas. Pellet consists of fine particles and both the above oxidations take place simultaneously in the oxidation of FeS pellet. In the oxidation of single particle of pyrrhotite whose mean particle diameter was 51 and 88 μm, the particle temperature increases rapidly due to the heat of oxidation and the particles melted in a very short time less than 1 second.

References

1 P. G. Thornhill and L. M. Pidgeon, J. Metals, 9 (1957) 989.

2 Z. Asaki, K. Matsumoto, T. Tanabe and Y. Kondo, Metall. Trans. B, 14B (1983) 109.

3 Z. Asaki, T. Atsumi and Y. Kondo, Trans. Japan Inst. Met., 27 (1986) 351.

4 Z. Asaki, S. Mori, M. Ikeda and Y. Kondo, Metall. Trans. B, 16B (1985) 627.

5 E. T. Turkdogan, Trans. TMS–AIME, 242 (1968) 1665.

6 L. Himmel, R. F. Mehl and C. E. Birchenall, Trans. AIME, 197 (1953) 827.

Zusammenfassung – Es wird das Oxydationsverhalten von dichten Plättchen, Pelletts und einzelnen Partikeln aus Magnetkies verglichen. Bei der Oxydation von dichten FeS-Plättchen geschieht in erster Linie eine Oxydation von Eisen unter Bildung einer dichten Oxidschicht während des frühen Stadiums der Oxydation, anschließend daran erfolgt die Oxydation begleitet durch die Entstehung von SO_2–Gas, insofern die Zusammensetzung von Magnetkies $Fe_{0.9}S$ erreicht. Da Pellets aus feinen Partikeln bestehen, laufen bei der Oxydation von FeS–Pellets beide obengenannten Oxydationsvorgänge gleichzeitig ab. Bei der Oxydation von einzelnen Partikeln geringer Größe entzünden sich diese wegen der Oxydationswärme, die Partikel schmelzen in einer Zeit von weniger als 1 Sekunde.

Резюме — Сопоставлен процесс окисления пирротита в форме плотных пластинок, таблеток и его отдельных частиц. При окислении плотных пластинок FeS на ранней стадии окисления имеет место предпочтительное окисление железа с образованием плотного оксидного слоя, а последующее окисление сопровождается выделением двуокиси серы, после чего состав пирротита становится $Fe_{0.9}S$. При окислении таблеток FeS обе вышеуказанные реакции протекают одновременно, поскольку таблетки состоят из очень мелких частиц. При окислении отдельных частиц малого размера происходит их воспламенение, что обусловлено теплотой окисления, вследствии чего частицы плавятся в течении времени меньше одной секунды.