Reduction of Molten Iron Oxide in CO Gas Conveyed System*

By Fumitaka TSUKIHASHI,** Kimio KATO,*** Ken-ichi OTSUKA****

and Tanekazu SŌMA****

Synopsis

The kinetics of reduction of molten iron oxide with CO gas at high temperatures of 1 450 and 1 600 °C were investigated. In order to reduce the influence of mass transfer rate on overall reaction rate of reduction, fine powders of iron oxide were used as specimen and were reduced in a transport reactor. After the specimens of fine powder of reagent grade were melted during falling down in reaction zone, liquid oxide drops thus formed were reduced with CO gas. Mean diameter of liquid particles was 25 μm.

The oxide particles were melted and became spherical, and the reduced iron was surrounded by liquid iron oxide. It is assumed that liquid iron oxide always exists on whole spherical surface and the nucleation, growth and cohesion of iron in liquid drop did not influence the overall reaction. The results were analyzed by considering only the mass transfer in a gas film and the chemical reaction at the gas liquid interface.

The value of mass transfer coefficient in gas film k_g was estimated by using the Ranz–Marshall equation

$$\frac{k_g d}{D} = 2.0 + 0.6 Re^{1/2} Sc^{1/3}.$$

Considering the shrinkage of particles by production of metallic iron, the values of rate constant of chemical reaction k_c were obtained as 19.4 cm/sec at 1 600 °C and 9.3 cm/sec at 1 450 °C.

I. Introduction

The reduction reaction of iron oxide in molten state is an elementary and important reaction, since it contributes to understanding the reaction of softening and melting zone in a blast furnace and developing of the smelting processes. The iron oxide in molten state reacts with refractory so fast that the experiment of reduction at high temperature was very difficult and few reports have been provided on this study.

The reduction reaction of molten iron oxide is

or

A few studies of reduction of iron oxide in molten state with solid carbon have been reported.^{1–5)} Few studies on kinetics of reduction reaction of molten iron oxide with CO gas have been made.

P. Grievson and E. T. Turkdogan⁶⁾ have reported the reduction kinetics of molten iron oxide. After equilibrium was established between iron oxide and the mixture of CO and CO₂ gases of specified composition, the molten iron oxide in iridium crucible was oxidized and reduced at 1 550 °C. They con-

cluded that the rate controlling step is interdiffusion of iron and oxygen.

Some of the authors, Kato, Sasaki and Sōma,⁷⁾ have reduced the molten iron oxide with CO gas that was blown downward onto the oxide surface in recrystallized alumina crucible at 1 600 °C and investigated the reduction kinetics of molten iron oxide with CO gas. They reported that the reduction rate is proportional to square root of gas flow rate when the gas flow rate is in the range of 0.6 to 16 Nl/min and the rate controlling step is mass transfer in gas film and the rate constant of chemical reaction of Eq. (2) is extremely large.

But the chemical reaction rate of reduction of iron oxide in molten state with CO gas is not clarified. So the purpose of this report is to estimate the rate constant of chemical reaction of molten iron oxide with CO gas. In order to reduce the influence of mass transfer rate on the overall reaction rate of reduction, fine powders of iron oxide were used as specimen in this experiment. The specimen was transported in dilutely dispersed state and then melted during falling down in reaction zone and liquid oxide drops were reacted with CO gas. The present report discusses the rate controlling mechanism of reduction reaction of molten iron oxide with CO gas at high temperatures of 1 450 and 1 600 °C.

II. Experimental Method

1. Specimen

The specimen of fine iron oxide powder used in this study was iron oxide powder of reagent grade. To obtain fine particles having a narrow size distribu-

Photo. 1. External view of wustite specimen.

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** Graduate School, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

*** Formerly Graduate School, The University of Tokyo. Now at Yawata Works, Nippon Steel Corporation, Yawatahigashi-ku, Kitakyushu 805.

**** Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

tion under 325 mesh, iron oxide powders were classified by sedimentation method. Photograph 1 shows the external view of specimen of iron oxide. Their shapes are angular. The X-ray diffraction pattern of the specimens shows that they contained not only wustite but also magnetite. From the chemical analysis the content of T. Fe was 74.0 to 74.2 %.

2. Apparatus and Method

If the reaction rate of fine liquid drop with reducing gas is measured in dispersed state, the effect of mass transfer rate on overall reaction rate may be small. Accordingly the reduction reaction was proceeded by using transport reactor. So as to reduce oxide drops to various reduction degrees, the residence time of liquid particles in the reaction zone was varied by changing the reducing gas flow rate. After passing through a reaction zone, the liquid particles were quenched in a cooling zone immediately to stop the reduction. Then reacted particles were submitted to the chemical analysis of T.Fe in order to determine the degree of reduction.

The schematic diagram of experimental apparatus is illustrated in Fig. 1. Figure 2 shows the schematic cross section of the chemical reactor and feeder of oxide particles used. Fluidized bed was used to supply the specimen to the stream of CO gas. The dis-

persed iron oxide particles were introduced into the chemical reactor with gas flow. The reduction was carried out in recrystallized mullite combustion tube (42 mm i.d., 50 mm o.d., 600 mm length) that was indirectly heated by a graphite tube inserted in a high frequency induction coil. An alumina crucible was set at the bottom of the reactor tube in cooling zone to collect the reduced particles of iron oxide.

Experimental temperature was measured by Pt6%Rh-Pt30%Rh thermocouple located at the center of the reactor tube, and was controlled by manual adjustment. All experiments were carried out at 1 450 and 1 600 °C. The isothermal zone, which was the region of experimental temperature ± 15 °C, was 10 cm long and this length of isothermal zone was used for calculation of the residence time of iron oxide particles in reaction zone.

Inlet system of CO gas from reservoir to reactor consisted of two paths, one of which was a pass through the fluidized bed and the other was a short cut pass directly to the reactor. Experiments started when the CO gas was introduced into the fluidized bed and fine iron oxide particles were fluidized. The maximum flow rate of CO gas to supply the specimen uniformly from fluidized bed to reactor is 1.8 Nl/min. In the case that the CO gas flow rate was less than 1.8 Nl/min, all of CO gas passed through the fluidized bed and flowed to the reaction zone, transporting fine iron oxide. In the case that the gas flow rate was more than 1.8 Nl/min, part of gas flowed directly to the reaction zone without passing through fluidized bed and the specimen of fine iron oxide was dispersed uniformly and supplied to reaction zone. After the gas in chemical reactor was replaced with the CO gas, the fluidization was started and iron oxide powder was carried to the reactor through glass tube. The iron oxide powder was melted and reduced with CO gas during falling down in reactor tube, then deposited in an alumina crucible set at the bottom of the tube. Each experimental time was 7 to 10 min and the total amount of oxide particles conveyed with CO gas was 1.0 to 3.0 g. After the experiment, the reactor was flushed with deoxidized N₂ gas to prevent the reoxidization of reduced particles. The reduced iron oxide was analyzed chemically to give the value of total iron percent (T.Fe%). From the value of

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Schematic cross section of chemical reactor.

Fig. 3. Typical size distribution of molten wustite particles.

T.Fe%, the degree of reduction (*R*%) was calculated by the following equation.

$$R\% = \frac{100(1 - T.Fe(1)/T.Fe(2))}{100 - T.Fe(1)} \cdot 100 \dots\dots\dots(3)$$

The mean diameter of oxide particles was determined by taking a microscopic photographs of them and measuring the diameters of 500 to 800 particles melted in N₂ gas conveyed system. The mean diameter was 25 μm. Figure 3 shows the typical distribution of particle diameters. The residence time of particles in the isothermal zone was calculated by the following equation (4):

$$\left. \begin{aligned} U_p &= U_g + U_s \\ U_s &= \frac{(\rho_p - \rho_g) \cdot g \cdot \bar{d}^2}{18\mu} \\ U_g &= Q/S \\ t &= L/U_p \end{aligned} \right\} \dots\dots\dots(4)$$

The velocity of particle *U_p* was the sum of the gas velocity *U_g* and the Stokes' terminal velocity *U_s*, and the residence time was the time that the particle was required to pass through the isothermal zone of 10 cm length with velocity *U_p*. Viscosity of gas was determined from Eq. (5)⁸⁾:

$$\mu = 2.6693 \cdot 10^{-5} \cdot \frac{\sqrt{MT}}{\sigma^2 \Omega \mu} \dots\dots\dots(5)$$

III. Experimental Results

1. Experimental Results of Reduction at 1 600 °C

Table 1 shows the results of reduction of molten iron oxide with CO gas at 1 600 °C. In each experiment, the size distribution of specimen after reduction was measured by the microscopic photograph of the specimen. And the value of mean diameter was used to calculate the terminal velocity. So in each exper-

Table 1. Experimental results of reduction of wustite with CO gas at 1 600 °C.

No.	<i>Q</i> (Nl/min)	<i>U_g</i> (cm/sec)	<i>U_s</i> (cm/sec)	<i>U_p</i> (cm/sec)	<i>t</i> (sec)	<i>R</i> (%)
1	0.91	7.51	2.15	9.66	1.035	44.2
2	1.20	9.90	2.46	12.36	0.809	43.5
3	1.27	10.48	2.19	12.67	0.789	54.7
4	1.02	8.42	2.40	10.82	0.924	62.3
5	1.60	13.21	2.36	15.57	0.642	52.4
6	1.99	16.42	2.18	18.60	0.538	38.2
7	1.62	13.37	2.54	15.91	0.629	43.7
8	0.93	7.68	2.02	9.70	1.031	60.8
9	2.42	19.97	3.79	23.76	0.420	37.1
10	3.10	25.59	4.51	30.10	0.332	24.7
11	0.67	5.53	2.39	7.92	1.263	71.1
12	3.72	30.70	4.14	34.84	0.287	21.9
13	1.78	14.69	2.11	16.80	0.595	26.0
14	2.66	21.96	2.63	24.59	0.407	23.6
15	1.80	14.86	1.48	16.34	0.612	35.0
16	2.40	19.81	1.79	21.60	0.463	29.2

iment, the terminal velocities were different. The relation between the degree of reduction and the residence time at 1 600 °C is shown in Fig. 4. It becomes clear that the liquid iron oxide was reduced about 60 % during first 1 sec. Photograph 2 is the external view of reduced particles and it shows that the oxide particles become melted and spherical. The microstructure of cross section of particles, reduction degrees of which were 23.9 and 60.8 %, are shown in Photo. 3. The white round part is the reduced iron and is surrounded by the dark part of wustite. The reduced iron was surrounded by wustite, so the reduction reaction occurred on all surface of wustite particles. From the observation of microstructure of the reduced specimen etched with nital, it is found that the reduced iron was not carburized.

2. Experimental Results of Reduction at 1 450 °C

Table 2 shows the experimental results at 1 450 °C. Figure 5 is the relation between the degree of reduction and the residence time in the reaction zone at 1 450 °C. In this case the length of isothermal zone was also 10 cm and the mean diameter of particles reduced at 1 450 °C was the same as that at 1 600 °C. From the comparison of Figs. 4 and 5, it is found that the reduction rate at 1 450 °C is smaller than that at 1 600 °C. Photograph 4 shows the microstructure of cross section of reduced particles at 1 450 °C. The degrees of reduction were 26.1 and 35.1 %. In most experiments, several iron particles were dispersed inside a wustite particle as shown in Photo. 4. As a result of etching of reduced specimens with nital, the carburization of spherical iron also was not observed. At this experimental temperature of 1 450 °C, wustite

Fig. 4. Time change of reduction degree of wustite at 1 600 °C.

Photo. 2. External view of reduced wustite particles at 1 600 °C.

Reduction degree: (a) 23.9 % (b) 60.8 %

Photo. 3. Cross section of reduced wustite particles at 1 600 °C.

Reduction degree: (a) 26.1 % (b) 35.1 %

Photo. 4. Cross section of reduced wustite particles at 1 450 °C.

Table 2. Experimental results of reduction of wustite with CO gas at 1 450 °C.

No.	Q (Nl/min)	U_g (cm/sec)	U_s (cm/sec)	U_p (cm/sec)	t (sec)	R (%)
1	1.04	7.90	5.77	13.67	0.732	26.6
2	1.95	14.80	2.10	16.90	0.591	35.1
3	2.35	17.84	2.81	20.65	0.484	28.3
4	0.96	7.29	1.85	9.14	1.094	40.3
5	3.15	23.91	1.98	25.89	0.386	27.0
6	1.44	10.93	2.42	13.35	0.749	29.9
7	3.29	24.98	1.70	26.68	0.375	35.0
8	1.38	10.48	2.87	13.35	0.749	34.3
9	0.74	5.62	2.05	7.67	1.304	62.4
10	2.36	17.92	3.12	20.94	0.478	26.1

Fig. 5. Time change of reduction degree of wustite at 1 450 °C.

was in molten state but reduced iron did not melt. So in this case, at the temperature of 1 450 °C, the wustite in molten state surrounded the reduced iron, and wustite reacted with CO gas on all surface of spherical wustite.

3. Effect of Particle Diameter on Reduction Rate

To estimate the effect of diameter on reduction rate, smaller specimens were made by crushing and sieving in water. The mean diameter of them was 16 μm. Figure 6 shows the effect of particle diameter on the reduction rate at 1 600 °C. When the diameter became smaller, the reduction rate was smaller.

4. Effect of Prereduction Degree on Reduction Rate

It is known that Fe³⁺/Fe²⁺ ratio influences the interdiffusion coefficient. Then, if the diffusion in liquid drop is a factor controlling the reaction rate, the Fe³⁺/Fe²⁺ ratio will be found to affect the reaction rate. So the prereduced specimen of fine iron oxide was reduced in transport reactor. Figure 7 shows the relation between the degree of reduction of prereduced iron oxide in molten state and the time. The ratio of Fe³⁺/Fe²⁺ hardly influenced the reduction rate.

IV. Discussion

According to the observation of cross section of reduced particles, the reduced spherical iron (solid or liquid) is wrapped with wustite. It is considered that liquid wustite always exists at the gas liquid interface, and the nucleation of iron proceeded on the whole surface of liquid drop. It means that diffusion inside the liquid drop need not be considered. It is supposed that the nucleation, growth and cohesion of iron in liquid drop did not influence the overall reaction rate, and the reduction reaction was analyzed by considering only the mass transfer in gas film and the chemical reaction at the gas liquid interface. Besides,

the amount of CO₂ gas generated with reduction was little and the bulk concentration of CO gas hardly varied with the progress of the reduction, because only a very few fine iron oxides were conveyed in transport reactor. The reduction reaction was presented by Eq. (2),

The rate of mass transfer in gas film from bulk gas to gas liquid interface $\dot{n}_g$ is given by

$$\dot{n}_g = 4\pi r_p^2 k_g (C_{\text{CO}}^b - C_{\text{CO}}^i) \quad \dots\dots\dots(6)$$

The rate of chemical reaction at the gas liquid interface $\dot{n}_c$ is given by

$$\dot{n}_c = 4\pi r_p^2 k_c (C_{\text{CO}}^i - C_{\text{CO}}^*) \cdot a_{\text{FeO}} \quad \dots\dots\dots(7)$$

As assumed that the reaction is steady, hence

$$\dot{n}_g = \dot{n}_c = \dot{n}_{\text{overall}} \quad \dots\dots\dots(8)$$

From Eqs. (6) to (8), as the activity of FeO, a_{FeO} , is unity, the overall reaction rate $\dot{n}_{\text{overall}}$ is given by

$$\dot{n}_{\text{overall}} = 4\pi r_p^2 \frac{C_{\text{CO}}^b - C_{\text{CO}}^*}{\frac{1}{k_g} + \frac{1}{k_c}} \quad \dots\dots\dots(9)$$

Here, as the iron, the density of which is ρ_2 , is produced from the wustite, having the density of ρ_1 , considering the shrinkage of particles by production of metallic iron, the radius of particles is presented as

$$r_p = \sqrt[3]{(1-R) + \frac{\rho_1}{\rho_2} R} \cdot r_0 \quad \dots\dots\dots(10)$$

Fig. 6. Effect of wustite particle diameter on reduction rate at 1 600 °C.

Fig. 7. Effect of prereduction degree on reduction rate at 1 600 °C.

Substituting Eq. (10) into Eq. (9), then

$$\dot{n}_{\text{overall}} = 4\pi \left[1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right]^{2/3} r_0^2 \frac{C_{\text{CO}}^b - C_{\text{CO}}^*}{\frac{1}{k_g} + \frac{1}{k_c}} \quad \dots\dots(11)$$

Equation (11) is rewritten using the relation

$$\dot{n}_{\text{overall}} = O_i \frac{dR}{dt} \quad \dots\dots\dots(12)$$

$$O_i = \frac{4}{3} \pi r_0^3 \rho_1 \quad \dots\dots\dots(13)$$

thus

$$O_i \frac{dR}{dt} = 4\pi \left[1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right]^{2/3} r_0^2 \frac{C_{\text{CO}}^b - C_{\text{CO}}^*}{\frac{1}{k_g} + \frac{1}{k_c}} \quad \dots\dots(14)$$

By integrating Eq. (14) from 0 to t , then

$$r_0 \frac{\rho_1 \rho_2}{\rho_1 - \rho_2} \left[1 - \left\{ 1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right\}^{1/3} \right] = \frac{C_{\text{CO}}^b - C_{\text{CO}}^*}{\frac{1}{k_g} + \frac{1}{k_c}} t \quad (15)$$

The densities of iron at 1 450 and 1 600 °C are 7.12 and 7.00 g/cm³, respectively.⁹⁾ The density of wustite at the temperature of 1 450 °C is 4.35 g/cm³.¹⁰⁾ It seems to be quite all right to consider that the density of wustite at 1 600 °C is not so different from that at 1 450 °C, and that the value of density at 1 600 °C is assumed to be the same as that of 1 450 °C. The densities of wustite and molten iron at 1 600 °C represented in the unit of mol/cm³ are 4.35/71.8 and 7.00/55.8 mol/cm³, respectively.

Substituting these values at 1 600 °C into Eq. (15), the relation between $1 - (1 - 0.517R)^{1/3}$ and t is derived. Figure 8 shows this relation of observed data. As the gradient of the line in Fig. 8 represents the value of

$$\frac{\rho_1 - \rho_2}{r_0 \rho_1 \rho_2} \cdot (C_{\text{CO}}^b - C_{\text{CO}}^*) / (1/k_g + 1/k_c)$$

the overall resistance $1/K$ was obtained from the gradient of this line. Equilibrium pressures of CO gas of the reaction (2) at 1 450 and 1 600 °C are calcu-

Fig. 8. Relation between time and $1 - (1 - 0.517R)^{1/3}$.

lated from the following free energy data¹¹⁾:

$$\Delta G^\circ = -26\,700 - 20.95T \quad (298 \sim 2\,000 \text{ K})$$

$$\Delta G^\circ = -94\,200 - 0.20T \quad (298 \sim 2\,000 \text{ K})$$

$$\Delta G^\circ = 51\,975 - 8.855T \quad (1\,642 \sim 1\,808 \text{ K})$$

$$\Delta G^\circ = 55\,620 - 10.83T \quad (1\,808 \sim 2\,000 \text{ K})$$

Since equilibrium pressure of CO of the reaction (2) is 0.858 atm when the total pressure is 1 atm, the reduction potential is 0.142 atm at 1 600 °C. This value is translated to the concentration of CO gas in the unit of mol/cm³ by using the equation of state of ideal gas. $C_{CO}^b - C_{CO}^*$ is 9.23×10^{-7} mol/cm³ at 1 600 °C, then from the gradient of the line in Fig. 8, the value

$$\left[1 - \left\{ 1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right\}^{1/3} \right] / t$$

is 0.123. Substituting these values into Eq. (15), the value of overall resistance is

$$\frac{1}{K} = \frac{1}{k_g} + \frac{1}{k_c} = 5.2 \times 10^{-2} \text{ sec/cm} \quad \dots\dots\dots(16)$$

The value of the mass transfer coefficient in gas film, k_g , can be estimated by Ranz–Marshall equation (17).¹²⁾

$$\frac{k_g d}{D} = 2.0 + 0.6 Re^{1/2} Sc^{1/3} \quad \dots\dots\dots(17)$$

The value of viscosity of CO gas, μ_{CO} , is calculated from Eq. (5) and the value of diffusivity of CO–CO₂ is calculated from Eq. (18).

$$D_{CO-CO_2} = 0.0018583 \cdot \frac{\sqrt{T^3 \left(\frac{1}{M_{CO}} + \frac{1}{M_{CO_2}} \right)}}{P \cdot \sigma^2 Q_{D_{CO-CO_2}}} \quad \dots(18)$$

At 1 600 °C, the value of diffusivity, D , is 3.6 cm²/sec and viscosity is 6.2×10^{-4} g/cm·sec, then the calculated value of mass transfer coefficient k_g from Eq. (17) is a very large value of 2 900 cm/sec. Substituting these values into Eq. (16), the value of chemical reaction rate constant, k_c , is 19.4 cm/sec.

In the same manner as the case of 1 600 °C, Fig. 9 shows the relation between

$$1 - \left[1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right]^{1/3}$$

and t at 1 450 °C. From the value of gradient of the line in Fig. 9, the value of

$$\left[1 - \left\{ 1 - \left(1 - \frac{\rho_1}{\rho_2} \right) R \right\}^{1/3} \right] / t$$

is 0.086. At 1 450 °C, interdiffusivity of CO–CO₂,

Fig. 9. Relation between time and $1 - (1 - 0.524R)^{1/3}$.

D_{CO-CO_2} , is 3.10 cm²/sec, the viscosity of CO gas is 5.9×10^{-4} g/cm·sec and the density of CO gas is 1.98×10^{-4} g/cm³. Since the equilibrium pressure of CO at 1 450 °C is 0.810 atm when the total pressure is 1 atm, the reduction potential of CO gas is 0.190 atm. This value corresponds to $C_{CO}^b - C_{CO}^*$ = 1.34×10^{-6} mol/cm³ in the unit of mol/cm³ using the equation of state of ideal gas. Substituting these values into Eq. (15), the overall resistance was obtained.

$$\frac{1}{k_g} + \frac{1}{k_c} = \frac{1}{K} = 1.08 \times 10^{-1} \text{ sec/cm} \quad \dots\dots\dots(19)$$

The value of rate constant of chemical reaction k_c at 1 450 °C is calculated as 9.3 cm/sec.

The value of activation energy of chemical reaction calculated from the data of the temperatures of 1 450 and 1 600 °C is 31.4 kcal/mol.

As described in the introduction, in the experiment of reduction of molten iron oxide with CO gas blowing system, the molten iron oxide in alumina crucible was reduced with CO gas blown onto the surface of molten iron oxide. The CO gas was blown from the alumina tube of 5 mm inner diameter set 10 mm above the molten surface. The flow rate of CO gas was changed from 0.6 to 16 Nl/min and because the reaction rate is proportional to the square root of flow rate of CO gas, it is considered that the rate controlling step is the mass transfer in gas film in the reduction of molten iron oxide with CO gas blowing system. From the fact that the rate controlling step is the mass transfer in gas film, the chemical reaction rate was estimated indirectly and the estimated value was a very large value that was greater than 1 300 cm/sec.

In this experiment, as the fine oxide specimen was reduced in transport reactor, the mass transfer coefficient in gas film, k_g , was estimated from the Ranz–Marshall equation. Usually the Ranz–Marshall equation is applied to estimate the mass transfer coefficient in gas film for pellet the diameter of which is relatively large. But Ranz and Marshall proposed this equation based on the experiment of vaporization of liquid drop the diameter of which is about 1 mm, and

in any other experiments, this equation was applied to the case of smaller particle.¹³⁾ So it is reasonable to apply this equation to our specimen of experiment. Because the mass transfer coefficient in gas film, k_g , estimated from the Ranz–Marshall equation was a very large value in this experiment, it is considered that the resistance of gas film was negligible in this experiment. Consequently the chemical reaction rate constant, k_c , at 1 600 °C is 19.4 cm/sec and the value of 1 300 cm/sec obtained from the gas blowing experiment could not be verified.

Overall reaction rate in this experiment is 2.8×10^{-4} g-Oxygen/cm² sec and that value in gas blowing experiment is 1.6 to 5.0×10^{-4} g-Oxygen/cm² sec, both of these values are of the same order.

According to the Ranz–Marshall equation (17), when the diameter of particle is small, the value of mass transfer coefficient in gas film, k_g , becomes large, and the resistance in gas film which controlled the reaction rate in gas blowing system may be ignored. So the overall reaction rate was expected to increase. But the value of overall reaction rate of this investigation is nearly the same as that of gas blowing system.

Therefore it is necessary to reestimate the reaction rate constant measured by the gas blowing system. In the gas blowing system, the reaction rate was analyzed assuming that the blowing CO gas exists over the whole reaction surface of molten iron oxide. But in the case that much CO₂ gas is generated with the reduction, the reduction potential of reducing gas becomes small. Partial pressure of CO gas after reaction caused by the generation of CO₂ is 0.90 to 0.97 atm, while the pressure before reduction is 1 atm. As the equilibrium pressure of the reaction (2) is 0.86 atm, the decrease of reduction potential caused by the generation of CO₂ gas could not be ignored.

Figure 10 shows the overall reaction rate divided by the driving force of reduction plotted against the flow rate of CO gas. As the flow rate increased, the value of overall reaction rate divided by the mean reduction potential of inlet and outlet increased. If the chemical reaction is the rate controlling step and the chemical reaction rate is proportional to the reduction potential, the value of overall reaction rate

Fig. 10. Overall reaction rate divided by the driving force of reduction plotted against the flow rate of CO gas.

divided by the mean reduction potential of inlet and outlet remains constant. From the fact that this value changes when the CO gas flow rate increases and the reduction potential becomes nearly constant, the flow rate affects the value of mass transfer coefficient in gas film, k_g . It is considered that the mass transfer in gas film contributes to the overall reaction rate when the CO gas flow rate is up to 16 NL/min.

Taniguchi *et al.*, who investigated the mass transfer in gas blowing system, proposed the following experimental equation based on the experiment of oxidation of graphite in a crucible type of reactor.¹⁴⁾

$$\frac{k_g d}{D} = n \left(\frac{r_s}{d} \right)^{-1.5} Re^{0.66} Sc^{0.5} \dots\dots\dots (20)$$

$$n = 0.32 \pm 0.06$$

where, d is the inner diameter of blowing nozzle and r_s is the radius of crucible.

As the experiment of Taniguchi *et al.*¹⁴⁾ is similar to the CO gas blowing system, the experimental results of CO gas blowing system were analyzed with Eq. (20). Substituting each value of physical properties into Eq. (20), the value of mass transfer coefficient in gas film, k_g , is about 50 cm/sec when the flow rate of CO gas is 16 NL/min. This value of mass transfer coefficient in gas film, k_g , is same as the value of overall reaction rate constant in the case of 16 NL/min of gas blowing system, and the mass transfer in gas film is the rate controlling in the CO gas blowing system.

Because the reaction rate in this experiment decreased when the particle diameter decreased, the dispersion of particles in the reactor becomes important. It is considered that the particle diameter did not increase by cohesion from the measurement of diameter of particles after reduction. If the diameter was small, the particle did not disperse in the reactor and the CO₂ concentration becomes greater, but the dispersion phenomenon in transport reactor is not clear.

As shown in Photo. 3 of the cross section of reduced particles, the reduced iron particles were surrounded by the iron oxide particles. At the surface of molten iron oxide, the reduced iron particles were surrounded by iron oxide as soon as the iron particles were generated on the iron oxide–CO gas interface and iron oxide always exists at the surface of iron oxide. As the iron nuclei generated on the surface were surrounded by iron oxide in molten state reduction, it is considered that the rate of nucleation of iron on the iron oxide surface affected the reaction rate.

In the experiment of reduction of molten iron oxide with CO gas in transport reactor, the chemical reaction constant of reduction of molten iron oxide drop is about 20 cm/sec, and it is considered that the rate constant of chemical reaction of CO gas blowing system is much greater than the value of rate constant obtained in transporting system.

V. Conclusion

To investigate the reaction mechanism and to estimate the chemical reaction rate of reduction of iron oxide in molten state with CO gas, fine molten iron

oxide was reduced in a transport reactor in which the effect of mass transfer in gas film was neglected at the temperatures of 1 450 and 1 600 °C. Following results were obtained:

(1) Reduction rates of molten iron oxide particles (mean diameter 25 μm) in CO gas conveyed system were 2.8×10^{-4} g-Oxygen/cm² sec at 1 600 °C and 2.0×10^{-4} g-Oxygen/cm² sec at 1 450 °C. The rate constants of chemical reaction were 19.4 cm/sec at 1 600 °C and 9.3 cm/sec at 1 450 °C. The value of activation energy of chemical reaction calculated from these values is 31.4 kcal/mol. The rate constant of chemical reaction of reduction of molten iron oxide reduced in a transport reactor is less than the value estimated from the result of experiment of CO gas blowing system.

(2) As the particle diameter becomes smaller from 25 to 16 μm , rate of reduction becomes lower and slight prereduction of the specimen did not affect the reaction rate.

(3) New phases generated from molten iron oxide were dispersed inside the oxide drop and cohesion of them gave a larger sphere at higher step of reduction. Molten iron oxide surrounded the reduced spherical iron, and the shape of particle is spherical.

Nomenclature

a_{FeO} : Activity of wustite (—)
 C_{CO}^b : Concentration of bulk CO gas (mol/cm³)
 C_{CO}^i : Concentration of CO gas at gas liquid interface (mol/cm³)
 C_{CO}^* : CO gas equilibrium concentration of reaction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ (mol/cm³)
 $\bar{d}$: Mean diameter of particles (cm)
 D : Diffusivity (cm²/sec)
 $D_{\text{CO}-\text{CO}_2}$: Coefficient of CO–CO₂ interdiffusivity (cm²/sec)
 g : Gravity (980 cm/sec²)
 k_c : Rate constant of chemical reaction (cm/sec)
 k_g : Mass transfer coefficient in gas film (cm/sec)
 K : Rate constant of overall reaction (cm/sec)
 L : Length of isothermal zone (cm)
 M : Molar weight (—)
 $M_{\text{CO}}, M_{\text{CO}_2}$: Molar weight of CO and CO₂ (—)
 $\dot{n}_c$: Chemical reaction rate (mol/sec)
 $\dot{n}_g$: Mass transfer rate in gas film (mol/sec)
 $\dot{n}_{\text{overall}}$: Overall reaction rate (mol/sec)
 O_i : Number of oxygen mole of specimen before reduction (mol)
 P : Pressure (atm)
 Q : Flow rate of gas (cm³/min)
 r_0 : Radius of molten particles before reduction

(cm)

r_p : Radius of molten particle (cm)

R : Degree of reduction (%)

Re : Reynolds number (—)

S : Area of cross section of reactor tube (cm²)

Sc : Schmidt number (—)

t : Residence time of particle (sec)

T : Temperature (K)

T. Fe (1): Content of total Fe of specimen before reduction (%)

T. Fe (2): Content of total Fe of specimen after reduction (%)

U_g : Velocity of gas (cm/sec)

U_p : Velocity of particle (cm/sec)

U_s : Terminal velocity of particle (cm/sec)

ΔG° : Standard Gibbs energies of reaction (cal/mol)

μ : Viscosity of gas (g/cm sec)

μ_{CO} : Viscosity of CO gas (g/cm sec)

ρ_g : Density of CO gas (g/cm³)

ρ_p : Density of particles (g/cm³)

ρ_1 : Density of wustite (mol/cm³)

ρ_2 : Density of iron (mol/cm³)

σ : Collision diameter (Å)

$\Omega_{D_{\text{CO}-\text{CO}_2}}$: Collision integral of diffusivity (—)

Ω_μ : Collision integral of viscosity (—)

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