Step-wise Reduction of Hematite Pellets with CO-CO₂ Gas Mixtures*

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Synopsis

A series of reduction experiments was made in which hematite pellets were reduced step-wise from Fe₂O₃ to Fe₃O₄, Fe₃O₄ to Fe_xO, and finally Fe_xO to Fe by CO-CO₂ mixtures of appropriate compositions in the temperature range from 800° to 1 050°C. The hematite pellets were made from pyrite cinder, and the porosity was approximately 13%. Experimental data for each reduction step were analyzed in terms of the mixed-control kinetics based on the isothermal unreacted-core model. Reduction curves calculated for each reduction step by using the rate parameters based on the unreacted-core model are in satisfactory agreement with experimental results.

I. Introduction

Many investigators¹⁾ have studied the reduction of hematite to iron with pure reducing gas like as H₂ or CO, and have applied the one-interface unreacted-core model, assuming only one gas-solid reaction at the iron/wustite interface, to analyze the kinetics of the reduction of hematite to iron. However, when iron ore is reduced either in a fixed bed or in a countercurrent moving bed, there is a region of the bed where the partially spent gas is no longer capable of reducing wustite to iron. Nevertheless, the intermediate reaction products like as wustite or magnetite may be formed in this region. This phenomenon can not be explained satisfactorily by the one-interface unreacted-core model. Taking this aspect into account, R. H. Spitzer *et al.*²⁾ proposed a multi-interface model assuming gas-solid reaction at three interfaces, iron/wustite, wustite/magnetite, and magnetite/hematite. Since this model contains many parameters, it is difficult to determine the values of the parameters. Therefore, attempts²⁻⁴⁾ to determine the parameters have thus scarcely been carried out. R. H. Spitzer *et al.*²⁾ determined the parameters metallographically from the rates of movement of the reaction interfaces, assuming three effective diffusion coefficients and using McKewan's data²⁾ on the rate constants of chemical reaction. In their method, there are some weak points that the measurement of interface movement is subject to even greater experimental error than weight-loss measurements, because the movement of interfaces must be determined from many partially reduced samples, and the values of three effective diffusion coefficients must be assumed.

S. P. Trushenski *et al.*⁵⁾ carried out the step-wise reduction of hematite pellets with CO-CO₂ gas mixtures using the same sample consecutively. However,

it is difficult to apply their results to commercial pellets, for their pellets had extraordinary high porosity of 75%.

In this study, step-wise reduction experiments were carried out with commercial hematite pellets by CO-CO₂ mixtures of appropriate compositions. Experimental data were analyzed by a graphical method called mixed-control plot, from which parameters for the multi-interface model were determined.

II. Experimental Method

The experimental apparatus is shown schematically in Fig. 1. The weight-loss of a pellet due to reduction was measured by a thermo-balance made of a strain gauge (Shinko Tsūshin Co. Ltd., Type UL-10-120, sensibility 1 mg). The output of the strain gauge was about 0.8 mV for 1 g of weight-loss, and the maximum load was 10 g. The weight-loss was recorded automatically by a multi-range recorder (minimum full scale was 0.5 mV, chart width was

Fig. 1. Schematic representation of the apparatus

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25 cm). As the strain gauge was sensitive to the circumstances, it was kept in a water-cooled container through which a small amount of N_2 gas was flushed. The strain gauge was thus hardly affected by a change of the furnace atmosphere, because thermal conductivities of CO and CO_2 were almost identical to that of N_2 .

The reduction furnace was kept at a constant temperature by a SCR voltage regulator and a PID controller. The uniform temperature zone within $\pm 1^\circ C$ extended over about 3 cm. The inside diameter of the reaction tube made of transparent pyrex glass was 3.44 cm or 3.5 cm.

CO was generated by CO_2 flowing through the packed bed of charcoal (particle size was less than 5 mm) at about $1000^\circ C$. The generated gas was purified by passing through 33% KOH aqueous solution, soda lime, and silica gel, respectively. Hydrogen content of the generated gas was less than 1%, and CO_2 was not found by the gas chromatography.

CO- CO_2 mixture of a desired composition was prepared by flow meters set in the gas path before the reaction tube. The gas was analyzed by an Orsat analyzer or gas chromatograph. Gas sample was taken from a rubber tube, (16) in Fig. 1, by a micro syringe (2.5 ml).

The step-wise reduction was carried out as follows: In the first, a hematite pellet was reduced to magnetite with CO- CO_2 gas mixture of the composition range where magnetite is stable (10~15% CO at the temperature of 900° to $1050^\circ C$ and 15~20% CO at the temperature of 800° to $900^\circ C$). The reduction was continued until it was confirmed from the weight-loss that hematite was converted fully to magnetite. Next, the magnetite sample thus obtained was reduced to wustite by changing the gas composition to 50% CO-50% CO_2 . After it was confirmed that the magnetite changed completely to wustite, the wustite sample was finally reduced to iron with pure CO gas.

The weight-loss measured in each reduction step agreed well with a theoretical value calculated from the initial weight of the pellet.

The temperature range of experiments was from 800° to $1050^\circ C$.

The hematite pellets were made from pyrite cinder (T. Fe: 62wt%, SiO_2 : 6.29wt%, CaO: 2.79wt%), and their porosity was $13 \pm 3\%$.

The pellets of relatively low porosity were used in the present study, because the reaction interfaces become blurred in the reduction of a more porous pellets. In such condition, unreacted-core model is not applicable, and an analysis of their reduction behavior becomes difficult.

III. Method of Analysis

Kinetics of gaseous reduction of iron oxide pellets is described by the unreacted-core model for a pellet, in which the reduction proceeds topochemically, or by the porous pellet model^{6,7)} for a pellet, in which

reducing gas penetrates into inner parts of the porous pellet and the reduction proceeds nontopochemically.

There were some problems for the application of the unreacted-core model to the reduction behavior of the pellets used in the present work, since Thiele's modulus was less than 20 as shown later, and reaction interfaces observed on the section of a partially reduced pellet were not always sharp. But the application of the porous pellet model is not always practicable, because there are many problems to be solved as follows: It takes a long time to calculate with this model, and becomes difficult to determine the parameters included in the model. Moreover, it is not known how to estimate the effective diffusion coefficient in the reaction zone and how to determine the relation between the reaction surface and fractional reduction, etc. Therefore, the unreacted-core model was used here to analyze the experimental data.

The reaction rate is generally affected by the change of temperature of the pellet due to the heat of reaction. But the heat of reaction is small in the CO reduction of a hematite pellet, so it was assumed that the reaction proceeded isothermally.

According to the unreacted-core model in which mass transfer in the gas film, intraparticle diffusion, and chemical reaction at the interface are assumed to proceed in series, the relation between reaction time θ and the relative thickness of product layer f ($=1 - r/r_0 = 1 - (1 - F)^{1/3}$) is given by:

$$\frac{C_b - C_e}{r_0 d_o} \cdot \theta = \frac{1}{3k_f} (3f - 3f^2 + f^3) + \frac{r_0}{6Ds} (3f^2 - 2f^3) + \frac{f}{kc(1 + 1/Ke)} \dots (1)$$

Using *LHS* and *X* given by Eqs. (2) and (3),

$$LHS = \frac{C_b - C_e}{r_0 d_o} \cdot \frac{\theta}{f} - \frac{1}{k_f} \cdot \frac{(3 - 3f + f^2)}{3} \dots \dots (2)$$

$$X = 3f - 2f^2 \dots \dots \dots (3)$$

Eq. (1) is rewritten as follows:

$$LHS = \frac{r_0}{6Ds} X + \frac{1}{kc(1 + 1/Ke)} \dots \dots \dots (4)$$

For a reaction which is described by the isothermal unreacted-core model, the plot of *LHS* against *X* will yield a straight line. Then, the chemical reaction rate constant, *kc*, and the intraparticle effective diffusion coefficient, *Ds*, will be determined from the intercept and the slope of the straight line.⁸⁾ The authors will henceforth refer to the plot of *LHS* vs. *X* as the mixed-control plot.

In order to draw the mixed-control plot, a coefficient *k_f* in Eq. (2) must be known. *k_f* is the modified mass transfer coefficient through gaseous film surrounding the pellet, in which the dilution effect of the product gas was taken into account. *k_f* may be estimated from Eq. (6), where *k_g* is calculated by Eq. (5) which is known as the Ranz-Marshall's equation.⁹⁾

$$\frac{k_g(2r_0)}{D_{\text{CO-CO}_2}} = 2 + 0.6 \left(\frac{2r_0 \cdot u \cdot \rho}{\mu} \right)^{1/2} \left(\frac{\mu}{\rho \cdot D_{\text{CO-CO}_2}} \right)^{1/3} \dots (5)$$
$$k_f = 1 / (1/k_g + 4\pi r_0^2/V_T) \dots \dots \dots (6)$$

In Eq. (5), the diffusion coefficient of reducing gas, $D_{\text{CO-CO}_2}$, was estimated from the Fujita's equation,¹¹⁾ while the viscosity of gaseous mixture, μ , was predicted from Wilke's equation¹³⁾ using the values for each gas component calculated from the Licht-Stechert's equation.¹²⁾

The average gas velocity over the cross section of the reaction tube, $\bar{u}$, was used as the gas velocity toward the pellet, u , in Eq. (5). M. Ohmi and T. Usui¹⁴⁾ proposed to use the twice of $\bar{u}$ ($u = u_{\text{max}} = 2\bar{u}$) for u , because the velocity distribution of gas in the tube was Poiseuille's one and a pellet was in the central part of gas velocity distribution. But, when the diameter of a reaction tube is not so large as compared with that of a pellet, the cross-sectional area of a pellet extends to the region of low gas velocity. Moreover, it is meaningless to take the velocity distribution strictly into consideration, because it is assumed in deriving Eq. (6) that the bulk gas is uniformly diluted by product gas over the cross section of a reaction tube. Since the difference of values of k_f was small even if either $\bar{u}$ or $2\bar{u}$ was used as shown by M. Ohmi and T. Usui,¹⁴⁾ the average gas velocity, $\bar{u}$, was used in the present calculation.

For the equilibrium constants, Ke , following equations were used for the each reaction step:

IV. Results of Experiments and Their Analyses

1. Determination of the Rate Constant of Chemical Reaction and Intraparticle Effective Diffusion Coefficient

Experimental results (reduction curves) were analyzed by applying the unreacted-core model. Examples of the mixed-control plots are shown in Figs. 2 to 4 for $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step, $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step, and $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step, respectively. The lines in the diagrams were drawn by fitting the straight lines to data. The linearity of the plot in each reduction step and at each temperature is fairly good. But some points on the low fractional reduction side tend to deviate upward from the straight lines. This is mainly due to the diffused interface,⁷⁾ but partly to the sigmoid type¹⁷⁾ of the reduction curve, one of the reasons of which is the delay of nucleation of reduction products.

The Arrhenius plots of the rate constant of chemical reaction, kc_i , for each reduction step obtained from the intercept of the lines are shown in Figs. 5 to 7. The method of least squares was applied to the rela-

	No.	T (°C)	Q (Nl/min)	r ₀ (cm)	P _{CO} (atm)	k _f (cm/sec)
○	52	900	2.5	0.553	0.2	6.98
△	66	950	3.35	0.613	0.149	7.55
●	98	1000	3.35	0.625	0.149	7.89

Fig. 2. Determination of D_s and kc for the reduction of hematite to magnetite

	No.	T (°C)	Q (Nl/min)	r ₀ (cm)	P _{CO} (atm)	k _f (cm/sec)
○	280	900	1	0.557	0.5	4.86
△	229	950	1	0.540	0.5	5.38
●	48	1000	1	0.604	0.5	5.01

Fig. 3. Determination of D_s and kc for the reduction of magnetite to wustite

	No.	T (°C)	Q (Nl/min)	r ₀ (cm)	P _{CO} (atm)	k _f (cm/sec)
○	270	800	2	0.521	0.98	5.84
△	90	900	1	0.633	1	4.16
●	63	1000	1	0.624	1	4.78

Fig. 4. Determination of D_s and k_c for the reduction of wustite to iron

Fig. 5. Arrhenius plot of rate constant for the reduction of hematite to magnetite

tion between $\ln(kc_i)$ and $1/T$, and the following equations were obtained for each reduction step:

$$kc_m = \exp(7.768 - 18.92 \times 10^3/RT) \quad \text{.....(10)}$$

$$kc_w = \exp(12.18 - 28.80 \times 10^3/RT) \quad \text{.....(11)}$$

$$kc_{Fe} = \exp(12.70 - 29.91 \times 10^3/RT) \quad \text{.....(12)}$$

The activation energies were about 19 kcal/mol for the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step, about 29 kcal/mol for the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step, and about 30 kcal/mol for the $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step. S. P. Trushenski *et al.*⁵⁾ obtained the activation energies of 16.5~23.9 kcal/mol for the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step, 15.4~18.7 kcal/mol for the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step, and 27.7 kcal/mol for the $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step from the results of the step-wise reduction of pellets of very high porosity by the simulation based on the porous pellet model. These values of activation energy are in fairly good agreement with those obtained by the present authors except for the value for the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step. The rate constants of

Fig. 6. Arrhenius plot of rate constant for the reduction of magnetite to wustite

Fig. 7. Arrhenius plot of rate constant for the reduction of wustite to iron

chemical reaction, kc_m , kc_w , and kc_{Fe} , obtained in this work are nearly the same with one another within the experimental error of the data as shown in Eqs. (10) to (12) and Figs. 5 to 7.

It was assumed that the intraparticle effective diffusion coefficient D_s was expressed by Eq. (13).

$$D_s = D_{\text{CO-CO}_2} \varepsilon_i \xi_i \quad \text{.....(13)}$$

Substituting for D_s obtained from the slope of straight lines in Figs. 2 to 4 into Eq. (13), the labyrinth factor ξ_i for each product layer was determined. The results are shown in Figs. 8 to 10. Here, the porosity of the product layer, ε_i , was estimated by Eqs. (14) to (16). The equations for estimating the porosity of each product layer in the reduction of pure hematite have already been proposed.^{1,2)} But in this study, it was necessary to correct the equations, since pyrite cinder pellets used here contained gangue. For simplicity, it was assumed that the hematite in the pellet did not combine chemically with gangue minerals and that the diameter of the pellet did not change during reduction. Under these assumptions, the equations^{1,2)} of porosity were modified for each product layer as follows:

Fig. 8. Labyrinth factor of magnetite layer *vs.* reduction temperature

Fig. 10. Labyrinth factor of iron layer *vs.* reduction temperature

Fig. 9. Labyrinth factor of wustite layer *vs.* reduction temperature

$$\varepsilon_m = 0.008 + 0.992\varepsilon_h \quad \dots\dots\dots(14)$$

$$\varepsilon_w = 0.122 + 0.878\varepsilon_h \quad \dots\dots\dots(15)$$

$$\varepsilon_{Fe} = 0.435 + 0.565\varepsilon_h \quad \dots\dots\dots(16)$$

The ξ_i values, though scattering considerably as shown in Figs. 8 to 10, were expressed by the following equations for each product layer:

$$\log_{10} \xi_m = 0.382 \times 10^{-2} T - 5.352 \quad \dots\dots\dots(17)$$

$$\log_{10} \xi_w = 0.159 \times 10^{-2} T - 2.467 \quad \dots\dots\dots(18)$$

$$\log_{10} \xi_{Fe} = 0.124 \times 10^{-2} T - 1.734 \quad \dots\dots\dots(19)$$

$$\log_{10} \xi_{Fe} = 0.102 \times 10^{-1} T - 12.25 \quad \dots\dots\dots(20)$$

The labyrinth factors ξ_i of each product layer are nearly the same with one another within the experimental error of data as seen in Figs. 8 to 10. But the value of ξ_{Fe} at 800°C is extremely small and temperature dependency of ξ_{Fe} under 900°C is different from that over 900°C. The abnormal temperature dependency of ξ_{Fe} seems to be related to the swelling of the pellet during reduction. The pellet swelled a little in the reduction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$, but shrunk in the reduction step $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ at 800°C

probably because of longer time required for reduction. At temperatures above 900°C, however, the pellet swelled also in the reduction step $\text{Fe}_y\text{O} \rightarrow \text{Fe}$, following the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step, which may be one of the reasons for high values of ξ_{Fe} . Although the value of ξ_i must be less than unity theoretically, some of the experimental values of ξ_{Fe} was greater than unity, which was attributed to the swelling of pellets. As the actual porosities are not exactly the same as the values calculated by Eqs. (14) to (16) owing to the swelling, it seems that diffusibilities should be used instead of labyrinth factors ξ_i . The diffusibility δ_i defined by $\delta_i = D_s/D_{\text{CO-CO}_2}$ represents the combined effect of ε_i and ξ_i . But it is not adequate to analyze the intraparticle diffusion data in terms of the diffusibility, because the porosity of a product layer is different from pellet to pellet. Although labyrinth factor may vary with porosity, the labyrinth factor was used for the purpose of eliminating the effect of the porosity. (The ξ_i obtained here is somewhat different from the true labyrinth factor.)

As the diameter of a pellet changed during reduction, the result would be better if this change was taken into account in the analysis. But this effect was neglected because of the difficulty of the analysis. The error due to the neglect in the analysis is small in the case of volume expansion less than 30%.¹⁸⁾

The ratio of swelling was 0~8% for $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step, 5~8% for $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step, and 3~11% for $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O} \rightarrow \text{Fe}$ step on a basis of initial hematite pellet diameter. The tendency of swelling became larger at higher temperature.

2. Comparison of Calculated Results with Experimental Ones

The reduction curves calculated by Eq. (1) based on the isothermal unreacted-core model, in which the parameters obtained by the above-mentioned method were used, are shown in Figs. 11 to 13. In the calculation the mean values of parameters were used.

In Fig. 11, the reduction curves for the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step are shown. The calculated results agreed

Fig. 11. Reduction curves of hematite to magnetite

	No.	T (°C)	Q (Nl/min)	r_0 (cm)	ε_h
●	52	900	2.5	0.553	0.099
○	96	850	2.5	0.625	0.114
△	18	800	2.5	0.581	0.117

	No.	k_f (cm/sec)	D_s (cm ² /sec)	k_c (cm/sec)	P_{CO} (atm)
●	52	6.98	0.032	0.701	0.2
○	96	5.82	0.0216	0.488	0.2
△	18	5.81	0.0131	0.329	0.2

	No.	T (°C)	Q (Nl/min)	r_0 (cm)	ε_h
●	86	1 050	1	0.643	0.0957
○	63	1 000	1	0.624	0.169
△	62	950	1	0.634	0.145
□	52	900	1	0.553	0.0993
▲	96	850	1	0.625	0.114
■	92	800	1	0.615	0.134

	No.	k_f (cm/sec)	D_S (cm ² /sec)	k_c (cm/sec)	P_{CO} (atm)
●	86	4.93	0.246	3.387	0.5
○	63	4.82	0.251	2.202	0.5
△	62	4.46	0.176	1.383	0.5
□	52	4.90	0.116	0.834	0.5
▲	96	4.00	0.095	0.481	0.5
■	92	3.80	0.0785	0.264	0.5

Fig. 12. Reduction curves of magnetite to wustite

	No.	T (°C)	Q (Nl/min)	r_0 (cm)	ε_h
●	63	1 000	1	0.624	0.169
○	90	900	1	0.633	0.149
△	270	800	2	0.521	0.155

	No.	k_f (cm/sec)	D_s (cm ² /sec)	k_c (cm/sec)	P_{CO} (atm)
●	63	4.78	0.966	2.386	1
○	90	4.16	0.611	0.870	1
△	270	5.84	0.0455	0.263	0.981

Fig. 13. Reduction curves of wustite to iron

well for the most part with experimental data.

In Fig. 12, the reduction curves for the $Fe_3O_4 \rightarrow Fe_xO$ step are shown. The calculated results agreed well with experimental data except for the cases of 900° and 950°C.

In Fig. 13, the reduction curves for the $Fe_xO \rightarrow Fe$ step are shown. The calculated results agreed well with experimental data.

Here, the Thiele's modulus which is one of the measures of the applicability of unreacted-core model will be examined. The Thiele's modulus ϕ is defined by

$$\phi = r_0 \sqrt{\frac{kv}{D_s'}} \dots \dots \dots (21)$$

where kv is the chemical reaction rate constant per unit volume of a pellet, and D_s' is the effective diffusion coefficient in the unreacted-core. When ϕ is large, the reaction interface becomes sharp, for the rate of the gas diffusion into unreacted-core is smaller than the rate of consumption of reducing gas by the chemical reaction. On the other hand, when ϕ is small, the reaction zone expands, and the reaction interface becomes blurred, because the reducing gas diffuses into inner part of the pellet. Y. Hara⁷⁾ reported that the unreacted-core model may be applied to the reduction of a pellet when ϕ was greater than 20. In the present work, ϕ was a little less than 20, for example $\phi=19.6 \sim 57.8$ for the $Fe_2O_3 \rightarrow Fe_3O_4$ step, $\phi=13.8 \sim 15.4$ for the $Fe_3O_4 \rightarrow Fe_xO$ step, and $\phi=5.3 \sim 22.2$ for the $Fe_xO \rightarrow Fe$ step. It was observed on the cross section of a partially reduced pellet that the interface became blurred. Nevertheless, the reduction curves were interpreted well by the unreacted-core model. Therefore, for practical purpose, the unreacted-core model can be satisfactorily applied

to the analysis of the individual reduction step of the pellet.

3. Resistance Ratio

The variations of the contributions of the resistances of three processes in each reduction step to the overall resistance during the reduction are shown in Figs. 14 to 16. The overall resistance, R_M , is given by:

$$R_M = \frac{1}{k_f} + \frac{r_0(r_0-r)}{rD_s} + \frac{(r_0/r)^2}{kc(1+1/Ke)} \dots\dots\dots(22)$$

The contributions of each resistance to the overall resistance may be determined by dividing the each term of the right hand side of Eq. (22) by R_M .

In Fig. 14, the contributions of the three resistances to overall resistance of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step are shown at three different temperatures. In the range of lower fractional reduction, the chemical reaction resistance is predominant and in the range of higher fractional reduction, the intraparticle diffusion resistance is important. As temperature rises, the intraparticle diffusion resistance decreases relatively, whereas the chemical reaction resistance increases. This tendency is against the general behavior¹⁾ that the chemical reaction resistance gets smaller relatively with rising temperature. But this is explained by the fact that the rate constant of chemical reaction, kc_m , increases at a smaller rate with temperature than the labyrinth factor, ξ_m . In other words, although the molecular gas diffusion coefficient, $D_{\text{CO}-\text{CO}_2}$, does not vary with temperature very much, the pore structure of the pellet changes with temperature remarkably, which results in a corresponding change of the labyrinth factor, consequently, increase of the intraparticle effective diffusion coefficient.

Figure 15 shows the resistance ratios for $\text{Fe}_3\text{O}_4 \rightarrow$

Fe_xO step. In this reaction step, the chemical reaction resistance decreases with temperature and the intraparticle diffusion resistance becomes large relatively, which conforms to the general tendency.

In Fig. 16, the contributions of resistances to overall resistance of $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step are shown. In this figure, the gas film mass transfer resistance is found to increase with temperature. In this case, the temperature dependence of both the chemical reaction resistance and intraparticle diffusion resistance is irregular, which is probably attributable to the change of pore structure of the pellet.

	T (°C)	k_f (cm/sec)	D_s (cm ² /sec)	kc (cm/sec)
—	1 000	6.22	0.203	2.202
---	900	5.49	0.121	0.834
- - -	800	4.79	0.0716	0.264

GR: Diffusion resistance in gas film
DR: Diffusion resistance in wustite layer
CR: Chemical reaction resistance
 $r_0=0.5$ cm $\varepsilon_h=0.11$ $Q=1$ Nl/min

Fig. 15. Contributions of resistances to the overall resistance (Reduction step of magnetite to wustite)

	T (°C)	k_f (cm/sec)	D_s (cm ² /sec)	kc (cm/sec)
—	1 000	6.16	0.905	2.386
---	900	5.45	0.585	0.870
- - -	800	4.76	0.0433	0.263

GR: Diffusion resistance in gas film
DR: Diffusion resistance in iron layer
CR: Chemical reaction resistance
 $r_0=0.5$ cm $\varepsilon_h=0.11$ $Q=1$ Nl/min

Fig. 16. Contributions of resistances to the overall resistance (Reduction step of wustite to iron)

	T (°C)	k_f (cm/sec)	D_s (cm ² /sec)	kc (cm/sec)
—	1 000	6.23	0.0982	1.326
---	900	5.50	0.0350	0.701
- - -	800	4.80	0.0124	0.329

GR: Diffusion resistance in gas film
DR: Diffusion resistance in magnetite layer
CR: Chemical reaction resistance
 $r_0=0.5$ cm $\varepsilon_h=0.11$ $Q=1$ Nl/min

Fig. 14. Contributions of resistances to the overall resistance (Reduction step of hematite to magnetite)

Comparing the effect of resistances with one another in the three reaction steps, the effect of the gas film mass transfer resistance is remarkable in the $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step and is not important in the other steps. The contributions of the chemical reaction resistance to the overall resistance is large in the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ step except for the region of higher fractional reduction. In the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step, the contributions of the chemical reaction resistance and the intraparticle diffusion resistance are nearly equal. In the $\text{Fe}_x\text{O} \rightarrow \text{Fe}$ step, the chemical reaction resistance is greater than the intraparticle diffusion resistance at 900° and 1 000°C, but is nearly the same at 800°C.

V. Conclusion

A series of reduction experiments was made in which hematite pellets were reduced step-wise from Fe_2O_3 to Fe_3O_4 , Fe_3O_4 to Fe_xO , and finally Fe_xO to Fe by CO-CO₂ mixtures of appropriate compositions in the temperature range from 800° to 1 050°C. The hematite pellets were made from pyrite cinder, and the porosity was approximately 13%. Experimental data for each reduction step were analyzed in terms of the mixed control kinetics based on the isothermal unreacted-core model.

The results obtained are summarized as follows:

(1) Rate constants for the reduction steps of Fe_2O_3 to Fe_3O_4 , Fe_3O_4 to Fe_xO , and Fe_xO to Fe are expressed, respectively, by following equations:

$$kc_m = \exp(7.768 - 18.92 \times 10^3/RT) \quad (\text{cm/sec})$$

$$kc_w = \exp(12.18 - 28.80 \times 10^3/RT) \quad (\text{cm/sec})$$

$$kc_{Fe} = \exp(12.70 - 29.91 \times 10^3/RT) \quad (\text{cm/sec})$$

(2) Labyrinth factors of the reduction product layers of Fe_3O_4 , Fe_xO , and Fe are expressed, respectively, by following equations:

$$\log_{10} \xi_m = 0.382 \times 10^{-2}T - 5.352 \quad (—)$$

$$\log_{10} \xi_w = 0.159 \times 10^{-2}T - 2.467 \quad (—)$$

$$\log_{10} \xi_{Fe} = 0.124 \times 10^{-2}T - 1.734 \quad (T \geq 1\,173\text{K}) \quad (—)$$

$$\log_{10} \xi_{Fe} = 0.102 \times 10^{-1}T - 12.25 \quad (T < 1\,173\text{K}) \quad (—)$$

(3) Reduction curves calculated for each reduction step by using the rate parameters based on the unreacted-core model are in satisfactory agreement with experiments.

(4) The contribution of the intraparticle diffusion resistance was not always larger than that of the chemical reaction resistance at higher temperatures because of the effect of the pore structure of the pellets.

Nomenclature

C_b : bulk concentration of CO gas (mol/cm³)

C_e : equilibrium concentration of CO gas (mol/cm³)

$D_{\text{CO-CO}_2}$: molecular diffusivity of CO-CO₂ gas mixture (cm²/sec)

D_s, D_i : intraparticle effective diffusion coefficient in the product layer (cm²/sec)

D'_s : effective diffusion coefficient in the unreacted-

core (cm²/sec)

d_o : concentration of reducible oxygen in the oxide (g-atom/cm³)

F : fractional reduction (—)

$f = (r_0 - r)/r_0$: the relative thickness of the reduced shell (—)

Ke : chemical equilibrium constant (—)

kc, kc_i : chemical reaction rate constant (cm/sec)

k_f : modified mass transfer coefficient in the gas film which takes account of the resistance due to the rate of gas flow $4\pi r_0^2/V_T$ (cm/sec)

k_g : mass transfer coefficient in the gas film estimated from the equation of W. E. Ranz and W. R. Marshall (cm/sec)

kv : chemical reaction rate constant per unit volume of the pellet (sec⁻¹)

LHS : function defined by Eq. (2) (sec/cm)

Q : gas flow rate (Nl/min)

R : gas constant (1.987 cal/mol·K or 82.05 cm³·atm/mol·K)

R_M : overall resistance (sec/cm)

r : radius of unreacted core in a pellet (cm)

r_0 : radius of a pellet (cm)

T : temperature (K or °C)

u : gas velocity toward the pellet (cm/sec)

$\bar{u}$: average gas velocity over the cross section of the reaction tube (cm/sec)

u_{max} : maximum gas velocity in the tube (cm/sec)

V_T : gas flow rate (cm³/sec)

X : $3f - 2f^2$ (—)

δ_i : diffusibility of layer i (—)

θ : reducing time (sec or min)

μ : viscosity of gas (g/cm sec)

ρ : density of gas (g/cm³)

ε_i : porosity of layer i (—)

ξ_i : labyrinth factor of layer i (—)

ϕ : Thiele's modulus (—)

Subscripts

$i = Fe, w, m, h$

Fe associates principal symbol with iron phase or $\text{Fe}/\text{Fe}_x\text{O}$ interface.

w associates principal symbol with wustite phase or $\text{Fe}_x\text{O}/\text{Fe}_3\text{O}_4$ interface.

m associates principal symbol with magnetite phase or $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ interface.

h associates principal symbol with hematite phase.

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