Reduction of Iron Oxide Contained in Molten Slags with Solid Carbon*

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Synopsis

The reduction rate of iron oxide contained in molten slags by rotating carbon rod or coke rod was measured. The range of temperature was from 1350° to 1450°C and of iron oxide concentration is from 5 to 90%. At the higher revolution speed of a rod, it has no effect on the reduction rate. Thus, in this range, the rate-determining step can be best interpreted to be at the chemical reaction and the reduction rate is proportional to the first order of the estimated activity of iron oxide contained in slags. The obtained rate equation is;

$$-\frac{1}{A} \dot{m}_{\text{FeO}} = 17.3 \exp\left(-\frac{39700}{RT}\right) \times a_{\text{FeO}}$$

Since "FeO" activity is generally not known at every temperature, a practical rate equation is set up, in which the activity of "FeO" at 1600°C obtained by Samarin and Schwartsman was used.

The bubbles cover a part of the reaction surface and suppress the reaction in the case of its slow generating rate, but break the laminar film on the rod and accelerate the reaction rate in the case of its fast generating rate. Foaming of the slag vigorously occurs in a certain range of the slag composition with high viscosity and surface tension.

I. Introduction

A large number of studies have been carried out on the rate and mechanism of reduction of solid iron oxide with reducing gas. However a little studies on the reduction of iron oxide contained in molten slag have been made because of its experimental difficulty.

The reduction kinetics of iron oxide contained in molten slags has been reviewed by Mori.¹⁾ In addition to the reports reviewed, Krainer *et al.*²⁾ examined the rate of reduction of "FeO" in FeO-SiO₂, FeO-SiO₂-CaO and FeO-SiO₂-CaO-Al₂O₃ slags with graphite or coke crucible using thermobalance in the range of 1200° to 1500°C. It has been concluded from the investigation that the reduction of "FeO" in molten 2FeO-SiO₂ system at 1400°C was a first order reaction with respect to FeO concentration, and its reaction rate constant was 3.1 to 3.4 × 10⁻⁶ mol FeO/cm²·sec with graphite crucible and 3.2 to 3.6 × 10⁻⁶ mol FeO/cm²·sec with coke crucible. The value of activation energy is 27 kcal/mol.

Philbrook and Kirkbride³⁾ have been examined the reduction of molten slag (100 g) with 300 g of carbon saturated iron in graphite crucible of 48 mm inside diameter and 140 mm deep. They have estimated that the reaction rate was proportional to the square of FeO concentration and obtained that the value of the reaction rate constant between slag and graphite was 1.2 × 10⁻⁴ g-FeO/cm²·min and the activation energy was 10 kcal/mol. Shabrin⁴⁾ melted FeO-contained slag in an alumina crucible and put a 15 mmφ graphite ball into it, and obtained the rate of FeO reduction

by the generated gas. The experimental slag composition was 5.3 to 19.6%FeO, 31.3 to 38.8%CaO, 34.7 to 42.0%SiO₂, 8.8 to 14.0%Al₂O₃, and 0 to 5.0%MgO. They have calculated their experimental data as a second order reaction with respect to FeO concentration, and obtained the activation energy of 40 to 50 kcal/mol.

Tarby and Philbrook⁵⁾ have studied on FeO reduction with graphite crucible. They reported that the reaction order was second order at the initial stage and then pseudo-first order at the following stage. They concluded that the primary reaction was considerably affected by the stirring of slag caused by CO gas, and that the difference in the reaction rate might result from the activity of "FeO" in a slag.

Summarizing the above mentioned experiments, the reaction rate was generally discussed in the range of low FeO content, but not in the range of high FeO content. Therefore, the experiments in relatively high FeO content were planned, and their results are reported in this paper.

II. Experimental Method

1. Apparatus

The apparatus used for the present experiments is shown in Fig. 1. The crucible ⑩ was made of pure iron. Slag sample ④ was heated in the pure iron crucible with a high frequency induction coil. Temperature of slag was measured by a 6 to 30 Rh-Pt thermocouple ⑤ which was covered with pure iron cap ⑧, and controlled within the range of 10°C. The molten slag was reduced by a rotating carbon rod ⑬, whose diameter was 1.2 or 2.0 mm. From the experimental results, there was no difference of reduction rate per unit surface area between both rods under a revolutionary speed more than a certain value, therefore 2.0 mm diameter carbon rod was used in most of the experiments.

2. Experimental Procedure

After the sample melted and reached to the required temperature, the carbon rod was dipped in the slag and its lower surface was placed at 10 mm from the bottom of the crucible. The amount of slag was about 300 g. Inside of the whole apparatus was filled with argon of 3 to 4 l/min. The sample could be observed through a prism at the top of the apparatus. The heating rate of sample was about 10°C/min.

After the carbon rod was inserted into the molten

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Fig. 1. Experimental apparatus

slag, the rotation was immediately started. The first sampling was made after the liquid was stirred uniformly. The sampling was made every 5 to 10 min with a steel rod and its amount was 2 to 3 g. The depth of liquid was measured by the adhered slag length on the steel rod. The experimental temperature was ranged from 1 350° to 1 450°C, because the crucible was made of pure iron.

3. Sample

The range of FeO concentration in slag was rather restricted, because the slag must be kept in liquid state during the whole period of reaction in the above mentioned temperature range.

Some examples of initial FeO concentration in slags used for experiments are shown in Fig. 2. The range of slag composition were as follows:

- (i) FeO-SiO₂; FeO 60 to 80%
- (ii) FeO-SiO₂-CaO; FeO 20 to 80%, SiO₂ 45 to 10%, CaO 35 to 5%
- (iii) FeO-SiO₂-Al₂O₃; FeO 40 to 80%, Al₂O₃ 15 to 5%, SiO₂ 45 to 15%
- (iv) FeO-SiO₂-MgO; FeO 65 to 80%, MgO 5%, SiO₂ 30 to 15%
- (v) FeO-SiO₂-Al₂O₃-CaO; FeO 5 to 30% (1 350°C)
- (vi) FeO-SiO₂-Al₂O₃-MgO; FeO 5 to 30% (1 350°C)

Fig. 2. Initial composition of samples about system FeO-SiO₂-CaO showing liquidus range at 1 400°C

III. Experimental Result and Discussion

1. State of Sample during Reduction

The slag temperature fell about 30°C just after the graphite rod was put into the slag, but recovered to the previous one after a few minutes. The molten slag depth was about 50 mm at first. At the just beginning of reduction, it increased owing to the CO gas generated by FeO reduction and decreased gradually as FeO concentration in slag decreased.

In case of the rapid reaction a phenomenon of "foaming" occurred and sample in a crucible sometimes overflowed (this is referred later).

Metallic iron reduced from FeO mostly deposited at the bottom of the crucible. According to spectroscopic analysis, silicon was hardly determined and carbon was less than 0.6% (Table 1). Therefore, it was assumed that the reduction of FeO with carbon contained in the reduced iron was little.

2. Experimental Results

During the experimental runs the diameter of carbon rod, and thus, the area of reaction surface decreased and the stirring condition might change. Therefore, the data for analysis are only those, in which the changes of temperature and the reaction surface were less than 10% and the decrease of FeO in charged slag was less than 20%. An example of slag composition change in an experiment is shown in Table 2.

The rate of surface reaction under an isothermal condition is generally defined by the following equation.

$$r = -\frac{1}{A} \left(\frac{dn}{dt} \right) \quad \dots\dots\dots (1)$$

where, r : reaction rate
 n : FeO mol number in slag
 A : surface area of reaction
 t : time.

If the reaction rate is linearly proportional to the FeO mol concentration, it can be expressed by the following equation.

$$r = -\frac{1}{A} \frac{dn}{dt} = K_1 C = K_1 \frac{n}{V} \quad \dots\dots\dots (2)$$

where, V : liquid volume

K_1 : the first-order reaction rate constant.

If V and A do not change during FeO reduction, the above differential equation can be solved with an initial condition $n=n_0$ at $t=0$

$$-\frac{V}{A}\ln\left(\frac{n}{n_0}\right)=K_1t$$

where, n_0 : initial FeO mol number

n : FeO mol number at time t .

n is determined taking into account that SiO_2 in slag does not decrease during reduction. That is, n_0 and n are given by

$$n_0=W_i(\text{Fe}^{++}-M.\text{Fe})_i/55.85\cdots\cdots\cdots(3)$$

$$n=W_i(\text{Fe}^{++}-M.\text{Fe})_t/55.85\cdots\cdots\cdots(4)$$

where, W : slag weight

Fe^{++} : weight fraction of ferrous oxide

$M.\text{Fe}$: weight fraction of metallic iron

$$W_t=W_i\times(\text{SiO}_2)_i/(\text{SiO}_2)_t$$

SiO_2 : weight fraction of silica.

The subscripts i and t refer to initial time ($t=0$) and $t=t$, respectively and initial time was decided the first sampling time. The reaction rate constant, K_1 , can be calculated by use of these values. The several experimental results are plotted in Fig. 3. Because the linearity of $(V/A)\ln(n/n_0)$ vs. time in each experiment is fairly well, the assumption of the first order reaction with respect to the iron oxide concentration may be accepted within a small range of the concentration change.

1. Effect of Revolutinal Speed of Rod

In the range of small revolutinal speed of carbon rod, the reaction rate increased with the revolutinal speed. However, it became constant at the revolutinal speed above 400 rpm. The effect of rotation of carbon rod upon reaction curve and rate constant

Table 1. Silicon and carbon percent in the reduced iron

Exp. No.	Initial composition of sample	Reduction temp. (°C)	Si (wt%)		C % in red. iron
			Crucible	Red. iron	
7	2FeO·SiO ₂	1 350	<0.05	<0.05	0.6
20	FeO 80 : SiO ₂ 20	1 400	<0.05	<0.05	0.4
28	FeO 90 : SiO ₂ 10	1 400	<0.05	0.07	0.5
29	2FeO·SiO ₂ 96 TiO ₂ 4	1 450	<0.05	0.06	0.2

Table 2. An example of experimental data (slag composition: 2FeO-SiO₂, reduction temp.: 1 350°C, rotation speed: 840 rpm)

Sampling No.	Time (min)	T. Fe (%)	M. Fe (%)	FeO (%)	SiO ₂ (%)
1	0	53.48	0.98	63.51	29.40
2	15	53.56	1.12	63.94	30.45
3	30	51.80	0.98	61.96	32.35
4	45	50.82	1.14	61.06	33.55
5	60	49.15	1.12	58.84	33.70
6	75	48.31	1.17	58.77	36.00

is shown in Figs. 3 and 4. In these figures, d is diameter of the carbon rod, N is revolution per second and hence d^2N is the value proportional to Reynolds number of a rotating speed. The reaction rate did not increase under the condition that d^2N is more than 50 cm²/sec ($d=2.0$ cm, $N=750$ rpm) and this relationship was confined to be valid for other multi-component slag systems. Therefore, the experimental data with d^2N value over 50 cm²/sec were used for the analysis of the chemical reaction rate.

2. Chemical Reaction Rate Analysis by Differential Method

Results of calculation of reaction rate with d^2N value over 50 cm²/sec are given in Table 3. In this

Fig. 3. Relationship between revolution of carbon rod and change of FeO concentration with 2FeO·SiO₂ system at 1 400°C (V : slag volume, A : reaction surface, n : FeO concentration, n_0 : initial FeO concentration)

Fig. 4. Effect of rotation of carbon and coke rod on the FeO reduction rate concerning the system FeO-SiO₂ (d : diameter of rod, N : revolutions per sec)

table, A is the reaction surface area of rod excluding the bottom surface because of latter treatment (error for neglect of bottom surface is within 10%) and V is the slag volume. These values were calculated from the length of slag adhered to the sampling rod. Analysed values of metallic iron at $t=0$ denote the reduced iron in the period until slag temperature settles to an appointed value before the first sampling. Metallic iron was almost suspended in slag because of

its small size. Each value of $(1/A)(dn/dt)$ and $(W/A) \cdot (dC_1/dt)$ are obtained from the slope of the FeO concentration against time and are expressed the value of reaction rate with mol and weight percent as FeO concentration. K_1 express the first order reaction rate constants calculated on the above-mentioned assumption that reaction order is first with respect to mol concentration of FeO (mol FeO/cm³). Either wt% or mol% of FeO can be used in the limited range of

Table 3. Summary of experimental results for the calculation of reduction rate

Exp. No.	W_i (g)	A (cm ²)	V (cm ³)	Analyzed value at $t=0$ (wt%)							$\left(\frac{1}{A} \cdot \frac{dn}{dt}\right)$ (mol/ cm ² min) ($\times 10^{-3}$)	$\left(\frac{W}{A} \cdot \frac{dC_1}{dt}\right)$ (g/ cm ² min) ($\times 10^{-2}$)	K_1 (cm/ min) ($\times 10^{-1}$)
				T. Fe	M. Fe	Fe ₂ O	SiO ₂	CaO	Al ₂ O ₃	MgO			
1 350°C													
99	280	31.4	97.4	53.48	0.98	67.99	29.40	—	—	—	0.30	0.81	0.12
100	280	31.4	97.4	54.51	0.84	73.04	27.50	—	—	—	0.35	0.75	0.14
101	280	31.4	97.4	54.48	1.78	67.91	28.20	—	—	—	0.38	0.98	0.15
102	280	31.4	97.4	54.54	0.79	69.38	28.10	—	—	—	0.33	1.03	0.13
55	280	38.1	114.2	30.90	2.01	38.13	32.20	22.73	—	—	0.70	2.13	0.59
112	280	37.0	111.5	48.27	1.45	60.66	24.85	10.27	—	—	0.69	2.72	0.36
115	280	31.9	98.6	49.20	0.59	63.22	26.85	—	9.68	—	0.53	1.91	0.23
52	280	25.8	83.4	60.26	0.92	77.04	13.95	—	5.77	—	1.16	2.72	0.38
29	280	27.6	88.0	52.02	0.87	66.25	26.85	—	—	4.26	0.66	2.04	0.25
27	280	27.0	86.5	48.78	0.78	62.27	25.45	5.11	5.22	—	0.56	2.01	0.22
32	200	18.2	64.5	5.72	0.75	6.61	45.95	30.83	9.78	5.56	0.01	0.09	0.05
119	230	25.1	81.7	12.49	0.0	16.37	33.70	32.90	9.29	5.89	0.16	0.46	0.26
1 400°C													
103	280	31.4	97.4	54.17	1.90	67.57	30.35	—	—	—	0.46	1.17	0.20
104	280	31.4	97.4	54.17	0.84	69.17	29.75	—	—	—	0.48	1.34	0.20
105	280	31.4	97.4	54.23	0.78	69.20	30.60	—	—	—	0.47	1.28	0.20
106	250	15.0	89.7	53.90	0.81	68.63	28.10	—	—	—	0.43	1.14	0.18
109	350	40.8	121.0	59.93	0.70	76.77	20.85	—	—	—	0.61	1.66	0.26
110	350	40.8	121.0	60.60	0.92	77.29	20.35	—	—	—	0.69	1.57	0.25
13	280	28.5	90.3	61.07	1.14	77.80	20.10	—	—	—	0.84	1.39	0.28
111	350	32.6	100.5	68.50	0.84	88.50	9.48	—	—	—	1.86	1.62	0.50
43	200	22.4	74.9	17.13	0.11	22.24	43.35	33.62	—	—	0.10	0.51	0.13
41	200	31.5	97.7	30.05	1.82	37.41	33.35	23.85	—	—	0.51	1.97	0.56
39	200	36.0	108.9	38.15	2.49	46.69	29.70	20.34	—	—	0.76	3.32	0.93
25	280	28.2	89.5	46.48	0.95	58.74	28.40	4.70	—	—	0.74	2.60	0.34
113	280	34.9	106.2	48.39	1.68	60.60	25.45	10.30	—	—	0.83	3.43	0.41
30	280	27.6	88.0	51.19	0.89	65.01	27.00	—	—	5.10	0.87	2.39	0.32
40	200	18.4	64.9	61.60	1.42	78.54	14.70	—	—	4.40	1.29	2.60	0.46
51	280	41.9	123.8	33.23	0.56	42.15	43.70	—	14.38	—	0.45	3.01	0.35
24	280	28.7	90.8	47.78	1.62	59.44	31.00	—	5.09	—	0.50	1.58	0.21
116	280	33.3	102.1	48.89	0.56	63.13	23.95	—	9.10	—	0.65	1.92	0.33
117	280	29.1	91.7	48.48	0.89	61.72	25.35	—	13.30	—	0.74	2.24	0.33
23	280	29.0	91.6	46.89	0.89	60.21	22.95	—	15.79	—	1.00	3.13	0.43
50	280	29.5	92.7	60.54	0.95	77.59	14.45	—	5.86	—	0.92	2.03	0.33
22	200	12.0	49.0	5.53	0.0	7.28	31.10	31.35	9.50	6.65	0.08	0.58	0.30
26	280	29.5	92.8	48.78	0.72	62.36	25.60	5.05	5.13	—	0.80	0.28	0.36
1 450°C													
107	280	31.4	97.4	54.43	1.06	69.06	28.40	—	—	—	0.79	2.49	0.37
108	280	31.4	97.4	54.73	0.92	69.42	27.90	—	—	—	0.84	2.61	0.37
114	280	31.2	97.1	48.08	1.23	60.98	25.00	8.10	—	—	1.10	4.30	0.54
118	280	29.1	91.7	48.32	0.89	61.88	25.80	—	10.20	—	1.01	5.95	0.46
38	200	22.0	74.0	5.61	0.89	6.10	42.30	29.77	9.19	5.48	0.02	1.51	0.11

the FeO concentration. However FeO activity must be generally used for the wide range of the FeO concentration. In order to analyse the reduction rate on the basis of the activity of iron oxide “FeO,” its value in the present experimental conditions must be known.

The “FeO” activity in the present experimental temperatures has been investigated on FeO–SiO₂ and FeO–SiO₂–CaO systems. Bodsworth *et al.*^{6,7)} have determined FeO activity in FeO–SiO₂–CaO slag at temperatures between 1 265° and 1 365°C. But the value of FeO activity at 1 400°C, which are necessary for the present calculation, has not been determined experimentally. However, they extrapolated FeO activities at 1 600°C from their data obtained in the range between 1 265° and 1 365°C and found that these values agreed well with those measured by Elliott.⁹⁾ Therefore, FeO activity in FeO–SiO₂–CaO slag at 1 400° and 1 450°C can be estimated by means of interpolating from Elliott’s data at 1 600°C and Bodsworth’s ones between 1 265° and 1 365°C. Activity diagrams thus obtained are shown in Fig. 5. Furthermore, assuming that the effect of MgO on the FeO activity is nearly equal to that of CaO,⁸⁾ FeO activity in FeO–SiO₂–MgO slag can also be estimated.

The reaction rates (1/*A*) (dn/dt) for FeO–SiO₂, FeO–SiO₂–CaO, and FeO–SiO–MgO slags at 1 350°, 1 400°, and 1 450°C are plotted in Fig. 6 against FeO activity which is obtained from Fig. 5. The slopes of lines for each slag system are almost the same as shown in Fig. 6(b) except two points in high FeO activity range. Especially in spite of the wide composition range concerning with FeO–SiO₂–CaO slag, it is interesting that data are on the same line. The average of slopes

of these lines reaction order is about 1.15 within the error of 0.2 concerning with two and three component slag as shown in Table 4. The lines considered that the reaction rate is proportional to the first order of FeO activity, are drawn with bold lines in Fig. 6 in relation to each temperature. All reaction rate can be expressed by these lines within errors of 30%. Therefore, the reduction rate of FeO in slag can be considered to be proportional to FeO activity. The activation energy of the reaction calculated from these results is 39.7 kcal/mol. The obtained reaction rate equation is as follows:

$$\dot{n}_{FeO} = -1.73 \times 10^2 \times A \times \exp(-39\,700/RT) \times a_{FeO}$$

- where, $\dot{n}_{FeO}$: rate of reduction in mol number of FeO in slag per minute
A: surface area of reaction (cm²)
 a_{FeO} : activity of FeO based on mol fraction.

But, strictly speaking there are two problems in this result. These are, (1) the chemical reaction rate is affected not only by “FeO” activity but also by the variation of slag component, and (2) the very fast reaction rate in case of high FeO content at 1 400°C. Probably these problems can be thought to originate from the facts that the activities itself include certain magnitude of error, that Fe⁺⁺ and Fe⁺⁺⁺ might not be in equilibrium enough at the beginning of reaction, and that the state of reaction surface depending on generation and separation of CO bubbles are different with slag systems. Exact interpretation of these problems still remain unsolved.

In order to compare with the conclusion based on FeO acitivity, the reaction rate calculated from same data using weight percent FeO is shown in Fig. 7. The reaction rate differs considerably with slag composition in spite of the same FeO percent. Gradients of these lines reaction orders are in the range from

Fig. 5. Activity of FeO in the system FeO–SiO₂–CaO calculated from the results of Bodsworth⁷⁾ and Elliott⁹⁾

Fig. 6. Differential plot of FeO reduction concerning with FeO activity

Table 4. Apparent order of reaction determined by the differential method (at 1 400°C)

FeO–SiO ₂	FeO–SiO ₂ –CaO	FeO–SiO ₂ –MgO
1.26	0.89	1.31

1.0 to 4.0 as shown in the following equation. From this fact, it is difficult to express the reaction rate consistently as a function of FeO weight percent regardless of difference of slag component. In case of mol fraction of FeO, the same conclusion was derived.

Rate equations using weight percent at 1400°C are expressed for each slag system as follows.

FeO-SiO₂:

$$(1/A) \times \dot{n}_{\text{FeO}} = -1.31 \times 10^{-2} \times (\% \text{FeO} \times 10^{-2})^{3.79}$$

FeO-SiO₂-CaO (CaO/SiO₂ = 11/9):

$$(1/A) \times \dot{n}_{\text{FeO}} = -7.16 \times 10^{-2} \times (\% \text{FeO} \times 10^{-2})^{2.70}$$

FeO-SiO₂-MgO (SiO₂/MgO = 17/9):

$$(1/A) \times \dot{n}_{\text{FeO}} = -2.06 \times 10^{-2} \times (\% \text{FeO} \times 10^{-2})^{2.14}$$

FeO-SiO₂-Al₂O₃ (SiO₂/Al₂O₃ = 8/2):

$$(1/A) \times \dot{n}_{\text{FeO}} = -1.15 \times 10^{-2} \times (\% \text{FeO} \times 10^{-2})^{1.07}$$

After all it is most reasonable that chemical reaction rate is considered to be proportional to the first order of "FeO" activity.

IV. Reaction Mechanism

1. At Higher Rotating Speed (above 50 cm²/sec as d^2N)

In relation to the FeO reduction in molten slag, the following elementary processes are considered.¹⁾

- (1) Transfer of FeO to the reaction surface
- (2) Interface reaction

- (a) $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$
- (b) $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$
- (c) $\text{C} + \text{CO}_2 = 2\text{CO}$

- (3) Separation of the reaction products from the reaction surface.

In order to investigate the rate-determining step, CO gas was blown into molten slag with a flow rate of 50 to 360 cc/min. This amount is about 15 times CO gas produced during a run of experiment with the carbon rod. The amount of reduction by blown CO gas was 5 to 10% by the graphite rod. This fact shows that the reaction (b) is not so important. It may be thus improbable that (c) is an important side

reaction. There was no difference in the reduction rate between a graphite rod and a coke rod as shown in Fig. 4 regardless of the difference of surface condition. There are notable differences in the reduction rate constant and the reaction order due to the differences in slag components. So it is reasonable to consider that (a) is the rate determining reaction under high rotating speed of rod, because data in the wide range of temperature and slag composition can be well summarized and the reaction order is close to 1.0 with respect to the activity of FeO. If the inter-diffusion of FeO is the rate determining step, the reaction rate must increase as rotational speed of the graphite rod increases. But the reaction rate becomes constant as shown in Fig. 4. In order to explain this phenomenon tentatively, bubbles produced by reduction need to act just so as to cancel the effect of rotational speed. It is very difficult to consider that bubble has effect on reaction just like this interpretation. As a consequence, it is the most reasonable to consider that the chemical reaction (a) is the rate determining step because experimental results can be well explained with use of FeO activity in molten slag.

2. At Lower Rotating Speed of Rod (under 50 cm²/sec with d^2N)

In this range rate-determining step is considered to be mixed one with iron oxide diffusion and chemical reaction, because reaction rate increases with revolution speed of rod. Furthermore one of characteristics of this reaction is bubble generation. This has direct effects upon FeO diffusion in laminar film. In the following this is discussed.

Assuming that the reaction is the first order one with mol% to simplify the treatment, the total reaction rate constant is estimated in the following equation,

$$1/K = 1/K_c + 1/K_f$$

where, K : the overall reaction rate constant

K_c : chemical reaction rate constant

K_f : mass transfer coefficient.

K_f can be considered much larger than K_c ($K_f \gg K_c$) in the range where K does not change with rotational speed of the rod. Therefore, K can be supposed equal to K_c . K_f , in the range of which K is affected with rotational speed, can be easily obtained from K and K_c .

Bubbles generated by the reduction should have various effects on the mass transfer between slag and graphite rod. In case of no bubble formation, Eisenberg⁹⁾ has derived the equation concerning the mass transfer in a radial direction of rod between benzoic acid (solid) and water-glycerol solution.

The equation is

$$J = (K_L/V_1) \times S_e^{0.644} = 0.0791 \times (R_e)^{-0.3}$$

where, K_L : mass transfer coefficient,

V_1 : peripheral velocity,

S_e : Schmidt number ($=\mu/\rho D$),

R_e : rod Reynolds number, ($V_1 \cdot d/\nu$),

D : diffusion coefficient.

Fig. 7. Differential plot of FeO reduction concerning with wt% FeO

The effect of bubbles can be shown by the ratio of K_f to K_L calculated with the above equation. In this calculation, the diffusion coefficient of FeO is 3.784×10^{-4} cm²/sec, according to Mori *et al.*^{10,11}, and K_L is corrected as the mean mol fraction of slag components except FeO is same.

The obtained value of K_f/K_L is closely related to the generating rate of bubbles, *i.e.* K_e , and is not related to Reynolds number of rotation as shown in Fig. 8. Bubbles are considered to act to obstruct the diffusion of reactants to the reaction surface as they attach to the reaction surface in the range of $K_f/K_L < 1$, and in the range of $K_f/K_L > 1$ to disturb the laminar film and to accelerate FeO diffusion, when they separate from the reaction surface.

Behavior of bubble is very complex and important for reaction. So it should be studied more in details.

In addition to the above mentioned, Foaming phenomena were often observed in a certain experiments. Especially vigorous foaming occurred in some slag composition and the slag overflowed from the crucible. This phenomenon notably occurred in the slag with high Al₂O₃ and CaO concentration. Foaming is related to the amount and rate of CO gas generation by FeO reduction. Furthermore slag properties, especially the relationship between viscosity and surface tension, has effect on the slag foaming (Fig. 9).

V. Conclusion

Following conclusions are obtained as a result of investigation with the reduction of FeO in molten slag by carbon rod.

(1) At high rotation speed the rate is not affected by the notation speed and the reduction rates obtained from the experimental data can be best expressed, when they are assumed to be proportional to the first order of FeO activity in slags. The obtained chemical reaction rate equation is

$$(-1/A)\dot{n}_{\text{FeO}} = 1.73 \times 10^2 \cdot \exp(-39700/RT) \cdot a_{\text{FeO}}$$

(2) The chemical reaction rate equation at 1400°C expressed by wt%FeO instead of activity is

Fig. 8. Effect of bubbles on the laminar film

shown as follows for the slag compositions indicated in paranthesis:

$$\text{FeO-SiO}_2; r = 1.32 \times 10 \text{ } (\% \text{FeO} \times 10^{-2})^{3.79},$$

$$\text{FeO-SiO}_2\text{-CaO } (\text{SiO}_2/\text{CaO} = 11/9);$$

$$r = 7.77 \times 10^{-2} \text{ } (\% \text{FeO} \times 10^{-2})^{2.70},$$

$$\text{FeO-SiO}_2\text{-MgO } (\text{SiO}_2/\text{MgO} = 17/3);$$

$$r = 2.063 \times 10^{-2} \text{ } (\% \text{FeO} \times 10^{-2})^{2.14},$$

and

$$\text{FeO-SiO}_2\text{-Al}_2\text{O}_3 \text{ } (\text{SiO}_2/\text{Al}_2\text{O}_3 = 4/1);$$

$$r = 1.11 \times 10^{-2} \text{ } (\% \text{FeO} \times 10^{-2})^{1.07}.$$

(3) At lower rotation speed, the rate is considered to be controlled by both the diffusion in molten slags and the chemical reaction. Bubbles generated by reaction affect the diffusion in laminar film on a rod. According to the approximate calculation, the reaction surface seems covered by bubbles and the reaction rate decreases when the generation rate of bubbles is small. On the other hand in case of its fast generating rate, the bubbles break the laminar film on the rod and accelerate the reaction.

(4) Foaming in this experiment vigorously occurred in slags with high viscosity and surface tension, and their relationship was studied.

Notation

- A : surface area of reaction (cm²)
- a_{FeO} : activity of FeO (—)
- a'_{FeO} : value of activity of FeO at 1600°C obtained by Samarin and Shvartsman (—)
- C : mol concentration of FeO (mol/cm³)
- D : diffusion constant (cm²/sec)
- d : rod diameter (cm)
- h : length of rod in a molten slag (cm)
- K : total mass transfer coefficient (cm/min)
- K_1 : the first order reaction rate constant (cm/min)
- K_2 : the second order reaction rate constant (cm⁴/mol FeO·min)
- K_L : mass transfer coefficient of rotation rod (cm/min)

Fig. 9. Ranges of vigorous foaming and non-foaming under the FeO reduction experiment

Fig. 10. Differential plot of FeO reduction with FeO activity determined by Samarin *et al.*^{10,11)} at 1 600°C

* Obtained from Fig. 7

** The value is obtained from the conclusion of Section III.2.2. that reaction is proportional to FeO activity at its temperature 1 600°C. The value at 1 450°C is left out because of a few data.

Fig. 11. Relation between rate constant (a) and reaction order (b) of Fig. 8 and $1/T$

- K_c : ($=K_1$)
 K_r : mass transfer coefficient (cm/min)
 M_{Fe} : weight fraction of metallic iron (—)
 N : revolutional speed (r.p.m.)
 n_{FeO} : FeO mol number in liquid slag (mol)
 $\dot{n}_{FeO}$: reaction rate (mol FeO/min)
 R : gas constant (cal/mol·°K)
 Re : Reynolds number (—)
 r : reaction rate (mol FeO/cm²·min)
 Sc : Schmidt number (—)
 T : temperature (°K)
 $T.Fe$: weight percent of total Fe(—)
 t : time (min)
 V : volume of liquid slag (cm³)
 V_1 : peripheral velocity of graphite rod
 W, W_i : weight of sample charged (g)
 ρ : density of liquid (g/cm³)
 μ : viscosity of liquid (g/cm·sec)
 ν : dynamic viscosity (cm²/sec)

Appendix: Derivation of a Pactical Equation

From the result of the section III.2.2 the chemical reaction rate at various temperatures and slag systems can be obtained, if FeO activity is known. But it is difficult to make the rate equation at arbitrary temperature, because the activity diagrams are not easily available at the temperature. So FeO activity in a certain slag components is fixed regardless of the change of temperature. And such practical rate equation as its reaction constant and reaction order is changed with temperature, is made.

Some diagrams are published on FeO activity in multi-component slag.^{8,12-14)} In this report diagram at 1 600°C by Samarin and Shvartsman¹⁰⁾ and Matsushita¹¹⁾ was used, because it contained the most number

of slag components, especially alumina. Relationship between chemical reaction rate and FeO activity is shown in Fig. 10. Also rate constant and reaction order against the reciprocal of temperature are plotted in Fig. 11 (a) and (b). The practical equation obtained from Figs. 10 and 11 is as follows:

$$(-1/A) \times \dot{n}_{FeO} = 12.5 \times \exp(-13\,300/RT) \times (a'_{FeO})^m$$

where,

$$m = 4.76 \times 10^{(4350/T-3)}$$

a'_{FeO} : FeO activity derived from Samarin's diagram at 1 600°C.

Error of the reaction rate estimated from this equation, is within 50%.

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