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EFFECT OF SLAG COMPOSITION ON THE KINETICS OF THE REDUCTION OF IRON OXIDE IN MOLTEN SLAG BY GRAPHITE

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Synopsis

A kinetic study has been made on the reduction of iron oxide in molten slag with graphite, at 1300 ℃. Composition of the slag was changed so that SiO_2 mole fraction varied between 0.33 and 0.50, and slag basicity between 1 and 2. The initial concentration of FeO was kept at 10% and rotation speed of the graphite cylinder at 100 rpm. The reaction rate is greatly affected by the slag composition. From values of the mass transfer coefficient, calculated by using the penetration theory, it is presumed that for the slags with basicity of 2, the reaction rate is controlled by mass transfer in the slag phase, but chemical reaction resistance is predominant in slags with lower basicities. Applying a mixed-control model to the latter case, the apparent chemical reaction rate constant was calculated. The rate constant decreases largely with increasing the SiO_2 activity. The reaction rate also decreases with presence of phosphorus in the slag. These behaviors imply that the reaction rate is very sensitive to the interfacial chemisorption of the surface active agents.

Key words: smelting reduction; FeO reduction; molten slag; slag composition; solid graphite; reaction mechanism; reduction rate; chemisorption.

1. Introduction

Kinetics of the reactions involved in smelting reduction of iron oxide has been of particular interest to metallurgists and, therefore, extensively studied under several conditions. Nevertheless, still further study is necessary for the clarification of the reaction mechanism and recognition of the factors influencing the reaction rate.

2. Experimental

The apparatus was the same as that of a previous study[1)]. A 5.5 kW SiC resistance furnace was used to melt the slag. Experiments were carried out by using an alumina crucible which was held in a mullite reaction tube. Graphite was used in the form of cylinder, 1 cm in diameter and 4 cm in length. The composition of the primary (base) slag, before adding iron oxide, is given in Table 1. The mole fraction of SiO_2 and basicity, respectively, were varied between 0.33 to 0.50, and from 1 to 2. Synthetic Fe_tO, hereinafter referred to as iron oxide or FeO, was prepared in the same way as described earlier[1)].

Experimental procedure was almost the same as mentioned in the previous work[1)]. The weight of the primary slag was 75 g for each run. All experiments were performed at 1300 ℃, under the argon gas atmosphere (flow rate ~ 1000 cm^3/min). The initial concentration of iron oxide was kept at 10% and rotation speed of the graphite cylinder at 100 rpm.

3. Results and discussion

3.1. Rate of reduction

Figure 1 shows the decrease in iron oxide concentration with time. It is obviously seen that the reduction rate is strongly dependent on the slag composition.

Variation of the slag height with time is shown in Figure 2.

The plot of ln(%FeO) against time (Fig. 3) shows that for the first stage of reaction, up to about 6 min, apparent order of the reaction can be considered as unity, with respect to the iron oxide concentration.

Table 1: Composition of primary slag.

Base Slag	Composition (mole fraction)				B*
	SiO_2	CaO	Li_2O	Al_2O_3	
A	0.333	0.333	0.333	0.000	2.0
B	0.473	0.000	0.459	0.067	1.0
C	0.378	0.203	0.366	0.053	1.5
D	0.320	0.320	0.320	0.040	2.0
E	0.320	0.192	0.448	0.040	2.0
F	0.320	0.448	0.192	0.040	2.0
G	0.384	0.000	0.576	0.040	1.5
H	0.402	0.320	0.229	0.050	1.4
I	0.494	0.320	0.148	0.038	1.0
J	0.402	0.229	0.320	0.050	1.4

B*(Basicity) $=(N_{CaO}+N_{Li2O})/N_{SiO2}$
N_i= mole fraction of component i

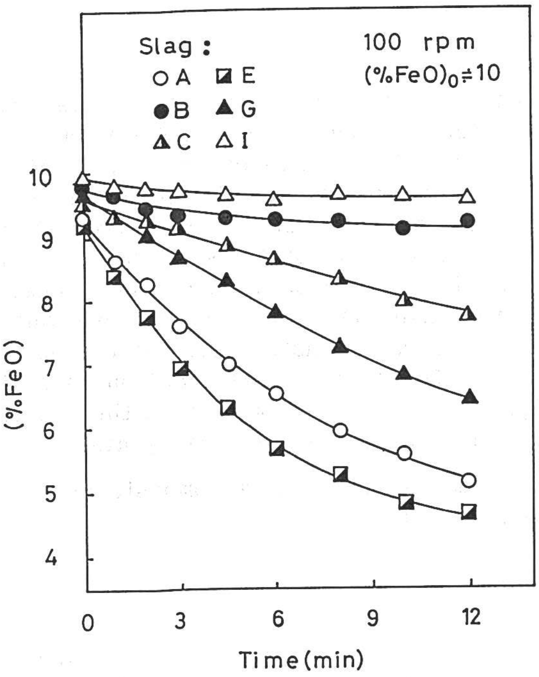

Fig. 1. Change in FeO concentration with time.

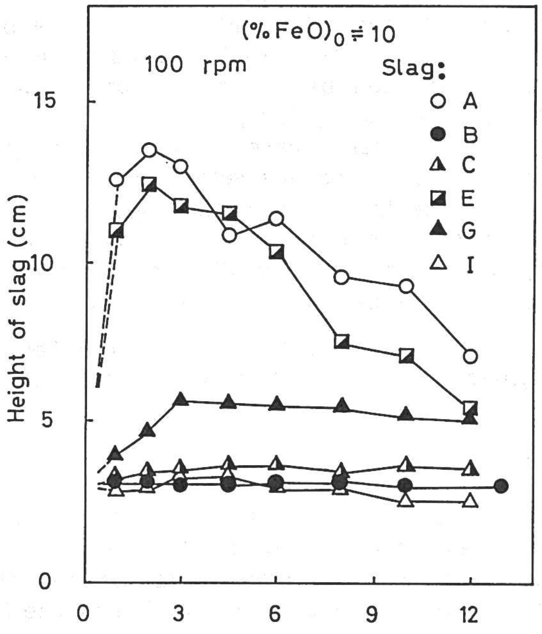

Fig. 2. Variation of slag height with time.

Hence, assuming FeO concentration at the interface to be zero, kinetic equation will be

$$-d\ln(\%FeO)/dt=k(A/V_s) \qquad (1)$$

where k, A and V_s, respectively, are the apparent rate constant, interfacial area and volume of the slag.

As mentioned in the previous paper$^{1)}$, in kinetic analysis of a foamed system, due corrections must be made for the effect of foaming and Eq. (2) was adopted.

$$-d\ln(\%FeO)/dt=k_B(A/A_o h_{av}) \qquad (2)$$

where k_B, h_{av}, and A_o, respectively, are the apparent rate constant in the foamed system, average height of the foamed slag and cross sectional area of the crucible.

It was also concluded that the relation between k_B, the apparent rate constant in a foamed system, and k_A, the apparent rate constant in the same system neglecting the effect of foaming, is given by

$$k_B=k_A/(1-\varepsilon) \qquad (3)$$

where ε is the gas holdup factor.

Gas holdup factor, ε, is the ratio of volume of the gas contained in slag ($V_g=V_s-V_D$) to the total volume of the foamed slag (V_s),

$$\varepsilon=(V_s-V_D)/V_s=1-W_s/(\rho_s A_D h_{av}) \qquad (4)$$

Where W_s and ρ_s are the slag weight and density, respectively.

3.2. Reaction mechanism

Figure 4 shows the relation between the apparent first order rate constant and the activity of iron oxide for various base slag compositions. Activity coefficients have been calculated by using regular solution model. Interaction energy parameters (α_{ij}) for the cation couples including Li^+ were taken from Pan Wei[2], and for the other cation couples from Ban-ya[3]. It was assumed that the effect of Al_2O_3, in concentrations below 0.1 mole fraction, on the activity coefficient of iron oxide is negligible . The activity coefficient of iron oxide in some of the slags was measured experimentally. A fairly good agreement was observed between the experimental and calculated values. Since the apparent rate constant decreases with increasing iron oxide activity, as seen in Fig. 4, it can be concluded that an absolutely chemical control model is not applicable and some retarding phenomena are interfering in the reaction mechanism.

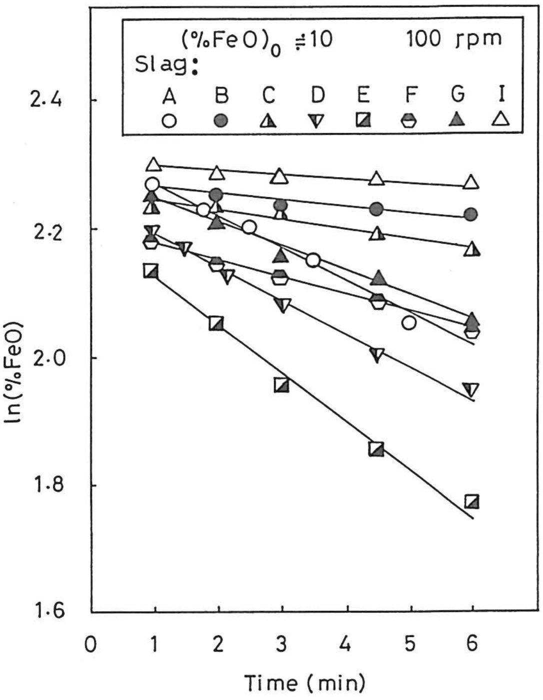

Fig. 3. Relation between ln(%FeO) and time.

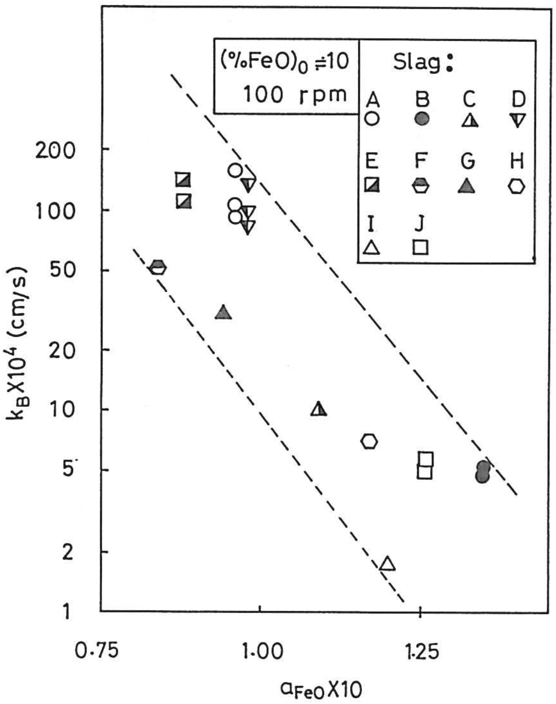

Fig. 4. Relation between apparent rate constant (k_B) and FeO activity.

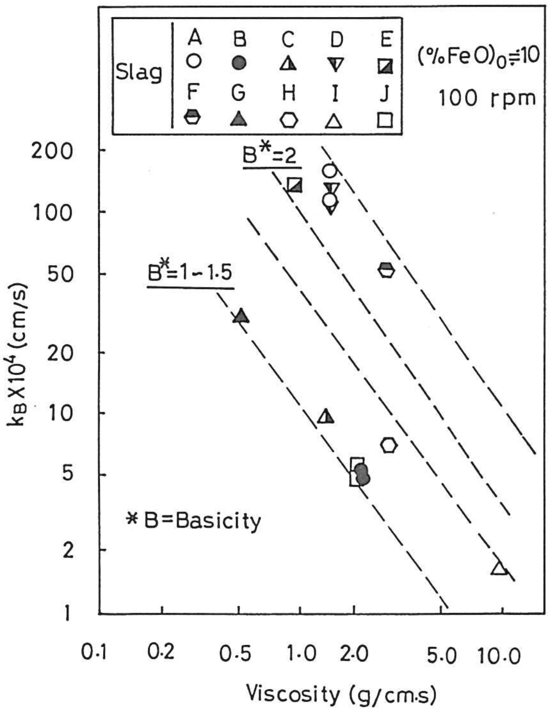

Fig. 5. Relation between apparent rate constant (k_B) and slag viscosity.

Figure 5 shows that the apparent rate constant decreases as slag viscosity increases. The viscosity has been calculated by applying Bottinga and Weill's model[4]. From Fig. 5, one can conclude that mass transfer resistance may have a contribution to the overall one.

In the previous paper[1], it was argued that if the reaction rate is controlled by mass transfer in the slag phase, it would be controlled by the transfer of oxygen ions towards the interface. Also, on the basis of the penetration theory, the following equation was derived for the calculation of the mass transfer coefficient under the conditions of the present study,

$$k_m \fallingdotseq 6.61[(W_s/d_c^3)(-\Delta\%FeO/\Delta t)D]^{1/2} \qquad (5)$$

where D is the diffusivity of oxygen.

Diffusivity of oxygen is calculated in the same way as described in the previous paper. Here, again, bubble diameter is assumed to be about 5 mm. The calculated mass transfer coefficient, k_m, is plotted against the overall rate constant, k_B, in Fig. 6. This figure shows that for the slags with basicity of 2, values of the apparent rate constant measured experimentally, are close to the calculated values of the mass transfer coefficient. Therefore, in this case, the reaction seems to be controlled by mass transfer in the slag phase. But, for the slags with basicities between 1 and 1.5, k_m is much larger than k_B. Hence, chemical reaction at the interface and possibly mass transfer in the slag phase may jointly control the rate of the reaction.

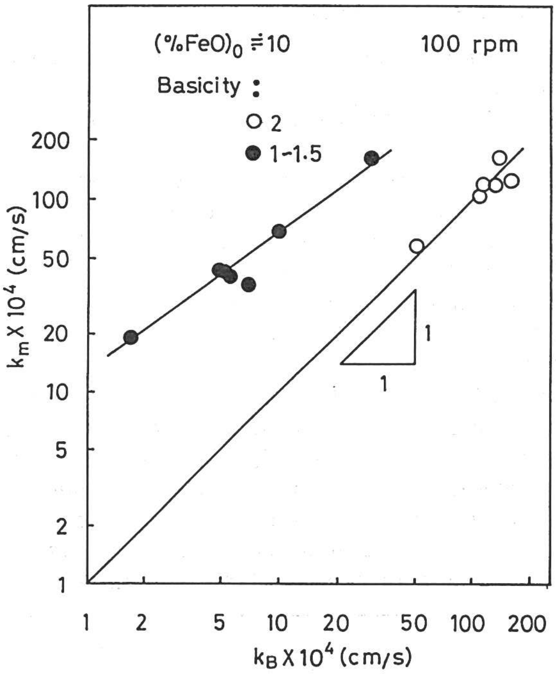

Fig. 6. Comparison between the calculated mass transfer coefficient (k_m) and apparent rate constant (k_B).

3.3. Kinetic model

If the reaction rate is mix-controlled, then the following relation is maintained.

$$r_c=r_m=r_{ov} \qquad (6)$$

where, r_c, r_m, and r_{ov} are the rates of chemical reaction, mass transfer, and overall reaction, respectively.

Then,

$$r_c=k_cA(a_{FeO})^i \qquad (7)$$

$$r_m=k_mA[(\%FeO)-(\%FeO)^i] \qquad (8)$$

$$r_{ov}=k_BA(\%FeO) \qquad (9)$$

where k_c, k_m and k_B, respectively, are the chemical reaction rate constant, mass transfer coefficient and apparent rate constant (considering the effect of foaming).

Eq. (10) relates the activity of FeO in the slag to the weight percent of the component.

$$a_{FeO}=[(W_s\%FeO)/(100M_{FeO}n_{tot})]\gamma_{FeO} \qquad (10)$$

where γ_{FeO}, M_{FeO} and n_{tot}, respectively, are the activity coefficient of iron oxide, molecular weight of iron oxide and sum of the number of moles of all slag constituents.

Assuming that $\gamma_{FeO}W_s/n_{tot}$ for each slag composition is approximately constant, then,

$$(a_{FeO})^i=\alpha(\%FeO)^i. \qquad (11)$$

Here, α is nearly constant and dependent on the base slag composition.

Combining Eqs. (7) and (11) and taking $\alpha k_c=k'_c$, one obtains

$$r_c=k'_cA(\%FeO)^i \qquad (12)$$

where k'_C is defined as the apparent chemical rate constant.

In fact, k'_C is a chemical reaction rate constant which includes the effect of iron oxide activity coefficient.

Combination of Eqs. (6), (8), (9) and (12), leads to

$$k'_C = k_m k_B/(k_m - k_B). \qquad (13)$$

The chemical reaction and mass transfer resistances (R and M, respectively) can be calculated from Eqs. (14) and (15),

$$R = [k_m/(k_m + k'_C)] \times 100 \qquad (14)$$

$$M = [k'_C/(k_m + k'_C)] \times 100\ . \qquad (15)$$

3.4. Discussion

There are shown in Table 2 the values of k_B, ε, k_m, k'_C, M and R for different base slag compositions containing almost the same initial concentration of iron oxide (~ 10%). Silica activity (a_{SiO_2}), calculated from regular solution model, is also included in the table. The table shows that, in contrast to the slags with basicity of 2.0, the rate of reduction in slags with lower basicities (1 ~ 1.5) is predominantly controlled by the chemical reaction at the interface. Table 2 also shows that the apparent chemical reaction rate constant, k'_C, decreases as silica activity increases. Since for the slags of the present study, activity of iron oxide in slags with higher silica activity is higher or at least equal to that in the slags with lower silica activity, it may be reasonably assumed that chemisorption of silica to the interface is responsible for the higher chemical reaction resistances.

In the presence of surface active agents the apparent rate constant ,k_a, is given by

$$k_a = k/(1 + K_i a_i). \qquad (17)$$

where k, K_i and a_i, respectively, are the rate constant for the reaction at a completely bare surface, adsorption equilibrium constant, and activity of the surface active component.

Table 2: Kinetic characteristics of different primary slags containing about 10% iron oxide.

Base slag	Silica Activity	$(\%FeO)_0$	ε	$k_B \times 10^4$ (cm/s)	$k_m \times 10^4$ (cm/s)	$k'_C \times 10^4$ (cm/s)	M (%)	R (%)
A	0.0052	9.17	0.76	160.0	123.0		**	
A	0.0052	9.11	0.77	115.0	119.8		**	
D	0.0094	9.30	0.75	132.2	119.0		**	
D	0.0094	9.14	0.76	112.4	106.3		**	
E	0.0036	9.24	0.75	137.9	165.8		**	
F	0.0175	8.75	0.73	51.7	58.0		**	
I	0.1521	9.95	~ 0	1.7	19.4	1.86	8.8	91.2
H	0.0427	9.90	0.12	7.1	36.0	8.84	19.7	80.3
B	0.0298	9.77	~ 0	4.8	40.9	5.44	11.7	88.3
B	0.0298	9.67	~ 0	5.2	41.5	5.94	12.5	87.5
J	0.0248	9.80	~ 0	4.9	42.3	5.54	11.6	88.4
J	0.0248	9.59	~ 0	5.7	39.7	6.65	14.4	85.6
C	0.0169	9.54	0.13	9.9	69.4	11.55	14.3	85.7
G	0.0051	9.60	0.43	30.3	158.3	37.47	19.1	80.9

** = Mass transfer-controlled
Standard state for silica activity = Cristobalite

The plot of k'_C against SiO_2 activity, shown in Fig. 7, indicates that in the case of slags with lower basicities, the assumption of silica chemisorption seems to be acceptable.

In order to further clarify the effect of the surface active agents on the reaction rate, phosphorus was added to the primary slag A containing 10% iron oxide. Figure 8 shows that only small amount of phosphorus considerably lowers the rate of reduction. The effect of phosphorus on the apparent rate constant (k_B) is shown in Figure 9. It is presumed that the interfacial chemisorption is responsible for lowering the rate of the reaction.

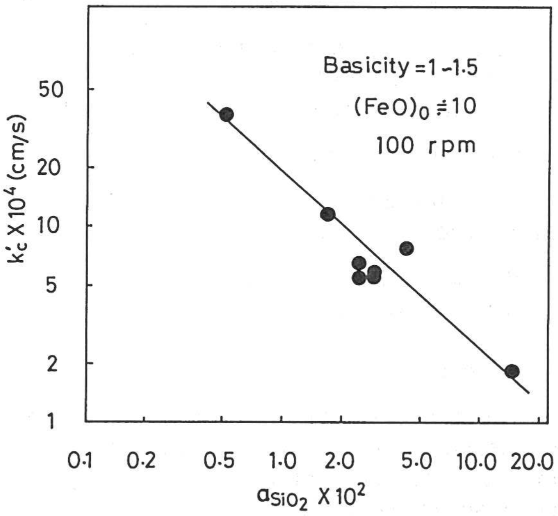

Fig. 7. Relation between apparent chemical rate constant (k'_C) and SiO_2 activity.

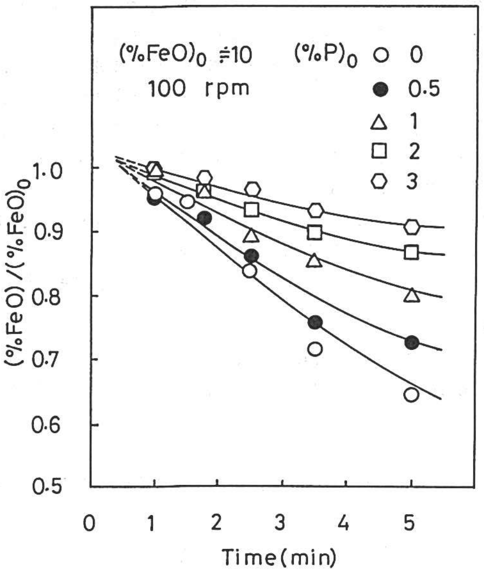

Fig. 8. Effect of phosphorus concentration on the change in (%FeO)/(%FeO)$_0$ with time.

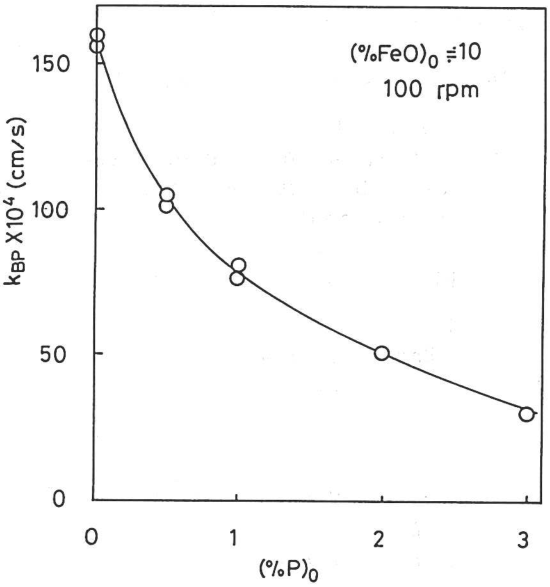

Fig. 9. Effect of phosphorus concentration on the apparent rate constant.

4. Conclusions

1). The reaction rate is significantly affected by the slag composition.

2). For the slags with basicity of 2 the reaction rate is controlled by mass transfer in the slag phase, but the chemical reaction resistance is predominant at lower basicities.

3). Chemisorption of surface active agents (silica and/or phosphorus) to the interface lowers the chemical reaction rate.

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