

Rate of Reduction of Cr₂O₃ in Slag by Liquid Iron Containing Carbon

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ABSTRACT

The kinetics and the mechanism of the reduction of Cr₂O₃ in Cr₂O₃-CaO-SiO₂-Al₂O₃-CaF₂ slags by Fe-C-Cr-Si-S liquid alloys were investigated in the temperature range of 1500 to 1600 C under an argon atmosphere. The experimental results were well simulated by a kinetic model developed on the basis of the two-film theory. The present modeling study showed that the transfer rate of chromium from slag to metal was controlled by the chemical reaction at the slag-metal interface in the early stage of the reaction, but it was controlled by the mass transport in the slag phase in the later stage of the reaction.

1. INTRODUCTION

Chromium is one of the most important alloying elements in steel production. In the production of ferrochromium alloys and stainless steels, raw material costs dominate the total production cost. Therefore, a high chromium recovery is essential for overall process economy. Knowledge on the kinetics and the mechanism of the reduction of Cr₂O₃ in slag by carbon and silicon dissolved in iron melt is of great importance in developing technology to minimize chromium loss, i.e. improving process efficiency.

The reduction behavior of Cr₂O₃ under stainless steelmaking conditions has been the subject of several investigations^[1-3], but the reaction mechanism has not yet been established because of the difficulty of the experiments at high temperatures, and of the complexity of the reaction in which CO bubbles are formed at the slag-metal interface. Moreover, the chemical reaction at the slag-metal interface is considered to partially dominate the reduction rate of Cr₂O₃ in slag. Therefore, for the ferrochromium alloy production from chromite ore, and for the chromium recovery from the slag formed during the decarburization period of stainless steelmaking, it is desirable to theoretically clarify some kinetic features of the reduction of Cr₂O₃ from slag to metal.

In the present work, the rate of reduction of Cr₂O₃ in slag by liquid iron containing carbon at various conditions was measured for the purpose of determining the reduction mechanism of Cr₂O₃ formed in stainless steelmaking slags. The experimental results were analysed by a kinetic model developed on the basis of the two-film theory.

2. EXPERIMENTAL

An electric resistance furnace was employed for heating and melting Fe-C alloys in an alumina crucible. The reaction vessel was vertical alumina tube of 60-mm I.D. and 1000-mm

length. Both ends of the tube were closed with water-cooled brass caps to prevent the oxidation of liquid iron by air. The temperature was measured by a thermocouple placed just below the crucible.

About 120 g of Fe-C alloy was first melted in an alumina crucible (36-mm I.D.) under an argon atmosphere. After the experimental temperature was attained, an initial metal sample was taken by using a quartz tube. Then, about 20 g of liquid slag containing Cr_2O_3 was placed on the surface of Fe-C liquid alloy, the moment of which was taken as the starting point of the slag-metal reaction. Some metal samples were taken at certain time intervals during the reaction. The progress of the reaction was followed by chemical analysis of these metal samples. At the end of each experiment, the final slag sample for chemical analysis and X-ray diffraction analysis was taken by sticking slag to a fine iron wire. Temperatures were varied from 1500 to 1600 C and the reaction time for most of the experiments was 30 min.

Fe-C alloys were prepared by premelting an electrolytic iron, a graphite and other alloying elements in an induction furnace under an argon atmosphere. Cr_2O_3 -CaO-SiO₂-Al₂O₃-CaF₂ system was chosen for the experimental slags. Slags were prepared by mixing appropriate amounts of chemical reagent grade oxide powders. The mixtures were melted in a platinum crucible under an air atmosphere and then crushed to a powder. The initial slag compositions are as listed in Table 1.

The experiments were carried out to examine the effects of temperature, CaF₂ content in slag, Cr_2O_3 content in slag, CaO/SiO₂ ratio of slag, and additional elements, silicon and sulfur in liquid iron. The experimental conditions and compositions of the initial and the final iron of each experiment are summarized in Table 2. The alphabetical letter of "Run No." indicates the slag type shown in Table 1.

3. RESULTS

3-1. Explanation of the behavior of chromium and carbon in liquid iron

During the reduction reaction, the slag foaming due to the CO gas evolution was observed frequently, and it was confirmed that the higher initial carbon content in liquid iron was, the more intensively CO gas evolved. The reduction rate of Cr_2O_3 is relatively fast, so that almost all of Cr_2O_3 in slag is reduced within about 10 min, and thereafter, the chromium content in liquid iron remains constant. The carbon content in liquid iron decreases linearly with reaction time at first, but it gradually decreases even after the reduction of Cr_2O_3 ceased, because some of carbon is used for the reduction of SiO₂ in slag as seen from the increase in the silicon content in liquid iron at the later stage of a run. The nearly same progress of reaction can be observed in other runs.

3-2. Effect of temperature

Figure 1 shows the effect of temperature on the reduction rate of Cr_2O_3 in slag for runs B-3

and B-6. It is evident from Fig. 1 that the reduction rate of Cr_2O_3 strongly depends on the experimental temperature. According to the thermodynamic equilibrium relation, the reduction of Cr_2O_3 is an endothermic reaction, and therefore, it is considered that a rising temperature causes a considerable increase in the reduction rate of Cr_2O_3 . Higher temperature also favors the reduction reaction of SiO_2 , and therefore, it is seen that the final silicon content in liquid iron is higher in a run at higher temperature.

3-3. Effect of slag compositions

Figure 2 shows the effect of CaF_2 content in slag on the reduction rate of Cr_2O_3 in slag for runs A-1, B-1 and C-1 at 1600 C. It is found that the reduction rate of Cr_2O_3 and the final chromium content in liquid iron increase with increasing the CaF_2 content in slag, and also that the lower the CaF_2 content in slag is, the higher the final silicon content in liquid iron is. Since the viscosity of slag tends to decrease with addition of CaF_2 to slag, such an increase in the reduction rate of Cr_2O_3 may be attributed to the mass transport coefficient in the slag.

Figure 3 shows the effect of Cr_2O_3 content in slag on the reduction rate of Cr_2O_3 in slag for runs I-1, B-2 and J-2 at 1600 C. It is found that the initial reduction rate of Cr_2O_3 is essentially independent of Cr_2O_3 contents in slag, because the slags are saturated with Cr_2O_3 at the beginning of the reaction.

Figure 4 shows the effect of CaO/SiO_2 ratio of slag on the reduction rate of Cr_2O_3 in slag for runs H-1, G-1 and F-1 at 1600 C. It is found that the reduction rate of Cr_2O_3 increases in order of slag G, F, H used. The difference between these runs may be attributed to an decrease of the activity coefficient of Cr_2O_3 in the slag in the case of slag F, because the higher the CaO/SiO_2 ratio of slag is, the lower the activity coefficient of Cr_2O_3 in the slag is^[4], and to an increase of the viscosity in the case of slag H, because SiO_2 content in the slag is high. Consequently, the reduction rate of Cr_2O_3 was the fastest in the case of slag G ($\text{CaO}/\text{SiO}_2 = 1.11$) in these runs.

3-4. Effect of metal compositions

Figure 5 shows the effect of silicon and sulfur in liquid iron on the reduction rate of Cr_2O_3 in slag for runs B-6, B-7 and B-8 at 1500 C. It is found from the comparison of the results of B-6 and B-7 that the reduction rate of Cr_2O_3 and the final chromium content in liquid iron increase remarkably with addition of silicon to liquid iron, which indicates that addition of silicon to liquid iron is effective in the reduction of Cr_2O_3 . It is also found that a decrease of the carbon content is smaller in the case of addition of silicon in liquid iron, which is considered that silicon in liquid iron is oxidized prior to carbon in liquid iron, because the reducing power of silicon in liquid iron is superior to that of carbon in liquid iron under the present experimental conditions, and then the reaction of carbon is suppressed. On the other hand, it is found from the comparison of the results of B-6 and B-8 that the reduction rate of

Cr₂O₃ decreases with addition of sulfur in liquid iron, which is considered that sulfur does not directly involve in the reduction of Cr₂O₃, but the surface active sulfur adsorbed on the slag-metal interface leads to a decrease in the effective reaction area, and then the reduction reaction of Cr₂O₃ is suppressed.

3-5. X-ray diffraction analysis

In order to examine the state of chromium oxide in slag, the X-ray diffraction analysis was made on the initial and the final slag samples. Examples of the diffraction patterns of these slags are shown in Fig. 6. From this figure, the peak of Cr₂O₃ is observed for the initial slag. This fact shows that some Cr₂O₃ existed as undissolved particles owing to the low solubility of Cr₂O₃ in CaO-SiO₂-Al₂O₃ slags, and therefore, slags used in this study were saturated with Cr₂O₃ at the beginning of the reaction. On the other hand, the peak of Cr₂O₃ is not observed for the final slag, but the peak of Al₂O₃ is observed. Al₂O₃ content of the final slags was usually 30~50mass% from the chemical analysis, and therefore, it is considered that the dissolution of crucible material, Al₂O₃, into the liquid slag occurred, and Al₂O₃ content was close to its saturation value, and Al₂O₃ precipitated on cooling.

4. DISCUSSION

4-1. Rate equations

On the basis of the two-film theory, a kinetic reaction model has been developed as follows and has been applied to the analysis of the present experimental results.

The following reactions are considered to take place simultaneously at the slag-metal interface. The equilibrium constant, K, for each reaction is given as function of temperature as follows:



$$\log K_{\text{Cr}} = \log \frac{a_{\text{Cr}} a_{\text{O}}^{1.5}}{a_{\text{CrO}_{1.5}}} = - \frac{22020}{T} + 9.71 \quad (2)$$



$$\log K_{\text{C}} = \log \frac{P_{\text{CO}}}{a_{\text{C}} a_{\text{O}}} = \frac{1160}{T} + 2.003 \quad (4)$$



$$\log K_{\text{Si}} = \log \frac{a_{\text{Si}} a_{\text{O}}^2}{a_{\text{SiO}_2}} = - \frac{30110}{T} + 11.40 \quad (6)$$



$$\log K_{\text{Fe}} = \log \frac{a_{\text{Fe}} a_{\text{O}}}{a_{\text{FeO}}} = - \frac{6150}{T} + 2.604 \quad (8)$$

Here, because the activity of oxygen in liquid iron is used in the later simulation of the kinetic behavior, an electrochemical expression is used for the reaction of sulfur, and the equilibrium relation of which can be given with the sulfide capacity, C'_S , defined by Eq. (10). The sulfide capacity, C_S , defined by Richardson et al.^[5] was used for the evaluation of C'_S in this study.



$$\begin{aligned} \log C'_S &= \log \frac{(\%S) a_{\text{O}}}{a_{\text{S}}} \\ &= \log C_S - \frac{769}{T} + 1.30 \end{aligned} \quad (10)$$

$$\begin{aligned} \log C_S &= \log \frac{(\%S) P_{\text{O}_2}^{1/2}}{P_{\text{S}_2}^{1/2}} \\ &= 1.35 \times \frac{1.79(\% \text{CaO}) + 1.24(\% \text{MgO})}{1.66(\% \text{SiO}_2) + 0.33(\% \text{Al}_2\text{O}_3)} - \frac{6911}{T} - 1.649 \end{aligned} \quad (11)$$

Several researches^[6-8] on the kinetics of the slag-metal reactions have suggested that the reaction of carbon monoxide formation is controlled by the chemical reaction at the slag-metal interface, and other reactions are controlled by the mass transport in the slag and/or metal phases. In this study, the mass transport of carbon in the metal phase, and the dissociation reaction of oxides at the slag-metal interface for chromium and silicon, were also taken into consideration. The changes of chromium, carbon, silicon, sulfur and oxygen contents in the metal, and iron oxide content in the slag with reaction time can be given by the following equations:

$$\frac{d[\% \text{Cr}]}{dt} = \frac{A}{W_m} k_{\text{Cr sat}} \left\{ \frac{1}{K_{\text{Cr}}} - f_{\text{Cr}}[\% \text{Cr}] a_{\text{O}}^{*1.5} \right\} \quad (12)$$

$$\frac{1}{k_{\text{Cr sat}}} = \frac{1}{k_{\text{r, Cr sat}}} + \frac{f_{\text{Cr}} a_{\text{O}}^{*1.5}}{k_m \rho_m} \quad (13)$$

$$\frac{d[\% \text{Cr}]}{dt} = \frac{A}{W_m} k_{\text{Cr}} \left\{ (\% \text{Cr}) - B_{\text{Cr}}[\% \text{Cr}] a_{\text{O}}^{*1.5} \right\} \quad (14)$$

$$\frac{1}{k_{\text{Cr}}} = \frac{1}{k_s \rho_s} + \frac{1}{k_{\text{r, Cr}}} + \frac{B_{\text{Cr}} a_{\text{O}}^{*1.5}}{k_m \rho_m} \quad (15)$$

$$- \frac{d[\% \text{C}]}{dt} = \frac{A}{W_m} k_{\text{C}} \left\{ f_{\text{C}}[\% \text{C}] a_{\text{O}}^* - \frac{P_{\text{CO}}^*}{K_{\text{C}}} \right\} \quad (16)$$

$$\frac{1}{k_C} = \frac{1}{k_{r,C}} + \frac{f_C a_O^*}{k_m \rho_m} \quad (17)$$

$$\frac{d[\%Si]}{dt} = \frac{A}{W_m} k_{Si} \{ (\%Si) - B_{Si} [\%Si] a_O^{*2} \} \quad (18)$$

$$\frac{1}{k_{Si}} = \frac{1}{k_s \rho_s} + \frac{1}{k_{r,Si}} + \frac{B_{Si} a_O^{*2}}{k_m \rho_m} \quad (19)$$

$$-\frac{d[\%S]}{dt} = \frac{A}{W_m} k_S \left\{ \frac{[\%S] B_S}{a_O^*} - (\%S) \right\} \quad (20)$$

$$\frac{1}{k_S} = \frac{1}{k_s \rho_s} + \frac{B_S}{k_m \rho_m a_O^*} \quad (21)$$

$$\frac{d[\%O]}{dt} = \frac{A}{W_m} k_m \rho_m \left\{ \frac{a_O^*}{f_O} - [\%O] \right\} \quad (22)$$

$$-\frac{d(\%FeO)}{dt} = \frac{A}{W_s} k_s \rho_s \{ (\%FeO) - B_{Fe} a_{Fe} a_O^* \} \quad (23)$$

where

A = slag-metal interface area, cross-sectional area of crucible, cm² ;

T = absolute temperature, K; P = partial pressure, atm; t = reaction time, sec;

W_m, W_s = weight of metal and slag, g; ρ_m, ρ_s = density of metal and slag, g cm⁻³;

a = activity; f = activity coefficient in metal;

k_m, k_s = mass transport coefficient in metal and slag, cm sec⁻¹;

k_{r,Crsat}, k_{r,Cr}, k_{r,C}, k_{r,Si} = rate constant for each reaction, g cm⁻² sec⁻¹;

k_{Crsat}, k_{Cr}, k_C, k_{Si}, k_S = overall mass transport coefficient for each reaction, g cm⁻² sec⁻¹;

K = equilibrium constant; B = apparent equilibrium constant;

m, s, * = metal, slag and quantity at the slag-metal interface;

[], () = component in metal and slag phase.

The terms k_{Crsat}, k_{Cr}, k_C, k_{Si} and k_S in these equations are the overall mass transport coefficients for Reactions (1), (3), (5) and (9), respectively, and they are given by Eqs (13), (15), (17), (19) and (21), respectively.

The activity of oxygen in metal, a_O, is referred to infinite dilution. The interaction coefficients, e_i^j, between i and j elements in metal^[9] were used to calculate the activity coefficients of components in metal, f_i. Here, a_{Fe} was assumed to be equal to the mole fraction of iron. For simplification, it was assumed that the mass transport coefficients of each element are equal with each other in the metal or in the slag phase.

Slags used in this study were saturated with Cr₂O₃ at the beginning of the reaction, and

Al₂O₃ at the end of the reaction. In the case when slag is saturated with Cr₂O₃, the activity of Cr₂O₃ in slag is unity, and therefore, the overall reaction rate of chromium reduction was derived from the chemical reaction rate at the slag-metal interface and the mass transport rate in the metal phase. When slag is not saturated with Cr₂O₃, the overall reaction rate of chromium reduction was derived from the chemical reaction rate at the slag-metal interface and the mass transport rate in the slag and metal phases. In the present work, the saturation value of Cr₂O₃ in slag, (%Cr)_{sat}, is necessary for this kinetic analysis, but its value in slag with CaF₂ have not been sufficiently determined, so that it was taken as a fitting parameter. In the calculation, the changes in the composition and weight of slag and metal due to the slag-metal reaction and the dissolution of crucible material into the liquid slag, the rate of which was assumed to be controlled by the mass transport in the slag phase, were also taken into consideration.

4-2. Rate calculation

On the assumption that no accumulation of oxygen at the slag-metal interface occurs, the following mass balance equation of oxygen can be obtained:

$$\begin{aligned} & \frac{3W_m}{2M_{Cr}} \frac{d[\%Cr]}{dt} + \frac{W_m}{M_C} \frac{d[\%C]}{dt} + \frac{2W_m}{M_{Si}} \frac{d[\%Si]}{dt} \\ & = \frac{W_m}{M_S} \frac{d[\%S]}{dt} + \frac{W_m}{M_O} \frac{d[\%O]}{dt} + \frac{W_s}{M_{FeO}} \frac{d(\%FeO)}{dt} \end{aligned} \quad (24)$$

where M is the molecular weight, g mol⁻¹.

Given the values of $k_m \rho_m$, $k_s \rho_s$, $k_{r,Crsat}$, $k_{r,Cr}$, $k_{r,C}$, $k_{r,Si}$, B_{Cr} , B_{Si} , B_{Fe} , B_S and (%Cr)_{sat}, the value of oxygen activity at the slag-metal interface, a_O^* , for the given slag and metal compositions, can be determined from Eq. (24). An example of the change of its value during a run is shown in Fig. 7. It is found from this figure that a_O^* increases with reaction time at the beginning of the reaction, which indicates that the rate of carbon monoxide formation is slower than that of Cr₂O₃ dissociation, so that the oxygen content at the interface becomes oversaturated. But it decreases rapidly after the Cr₂O₃ content decreases less than its saturation.

By using these interfacial values of oxygen activity, concentration changes of each element in the metal and the slag under the given conditions with reaction time can be calculated from Eqs. (12)-(23). The pressure of CO gas evolved at the slag-metal interface, P_{CO}^* , was considered to be 1 atm to solve Eq. (16).

In order to reduce the number of parameters, the values of $k_m \rho_m = 0.14 \text{ g cm}^{-2} \text{ sec}^{-1}$ obtained by Mori et al.^[10] and $B_S = 0.0005$ obtained by Shibata et al.^[11] were used for the mass transport coefficient in the metal phase and the apparent equilibrium constant for sulfur, respectively. The other parameters $k_s \rho_s$, $k_{r,Crsat}$, $k_{r,Cr}$, $k_{r,C}$, $k_{r,Si}$, B_{Cr} , B_{Si} , B_{Fe} and (%Cr)_{sat} were determined by comparing the calculated with the experimental results for each run. For

simplification, it was also assumed that the values of these parameters were constant during the entire period of the reaction.

4-3. Parameters

The parameters determined by modeling calculation are shown in Table 3. The solid lines in Figs. 1 through 5 are the results calculated by using these parameters, and these figures show that the kinetic behavior of Cr₂O₃ reduction can be simulated by the present model.

The values of $k_s \rho_s$, in the range of 0.01 to 0.04 g cm⁻² sec⁻¹, were slightly greater than the literature values. This is believed to be attributed to the decrease in viscosity of slag by addition of CaF₂ to slag, and moreover, the stirring effect of slag by CO gas evolved at the interface. The values of $k_{r,Cr,sat}$ and $k_{r,Cr}$ were not reported, and were obtained in this study, as shown in Table 3. The values of $k_{r,C}$ were generally greater than those obtained in the previous work where the oxidation rates of liquid Fe-C-P-Si-S alloys by MnO and/or FeO in slags were examined. The values of (%Cr)_{sat} were 2.1 ~ 3.8, as shown in Table 3.

The values of B_{Cr}, B_{Si}, B_S and B_{Fe} can be theoretically calculated from the thermodynamic data. Using the equilibrium constants or capacity and the activity coefficients in slag and metal, the theoretical values of B_{Cr}, B_{Si}, B_S and B_{Fe} are given as follows:

$$B_{Cr} = \frac{M_{Cr} f_{Cr} \sum \frac{MO_x}{M_{MO_x}}}{K_{Cr} \gamma_{CrO_{1.5}}} \quad (25)$$

$$B_{Si} = \frac{M_{Si} f_{Si} \sum \frac{MO_x}{M_{MO_x}}}{K_{Si} \gamma_{SiO_2}} \quad (26)$$

$$B_{Fe} = \frac{M_{FeO} \sum \frac{MO_x}{M_{MO_x}}}{K_{FeO} \gamma_{FeO}} \quad (27)$$

$$B_S = C'_S f_S \quad (28)$$

where MO_x indicates oxides and fluoride (Cr₂O₃, CaO, SiO₂, Al₂O₃, CaF₂ and FeO) in slag, and γ_{MO_x} is the activity coefficient of oxide in slag.

B_{Si} and B_S were calculated using the initial and final compositions of slag due to the difference in the initial and the final compositions of slag. The values of $\gamma_{CrO_{1.5}}$ and γ_{SiO_2} in the initial slags were estimated from the literature values^[12], and the values of γ_{SiO_2} and γ_{FeO} in the final slags were estimated from the following relation based on the regular solution model for slag.

$$RT \ln \gamma_i = \sum_j \alpha_{ij} N_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) N_j N_k \quad (29)$$

where i, j and k indicate oxides (CaO, SiO₂, Al₂O₃ and FeO) in slag, and N is the mole fraction of oxides in slag. α_{ij} are the ion-ion interaction energies in slag suggested by Banya^[13], and were used in this calculation. CaF₂ was also taken into consideration as the calcium ion.

Figure 8 shows the comparison of the values obtained from the present work, B(para), with the theoretical values calculated from Eqs. (25)-(28) using the thermodynamic data, B(theo). As seen in Figure 8, the theoretical and the calculated values agree well with each other, although the values of B_{Cr} deviate slightly for the lack of the literature values of $\gamma_{CrO_{1.5}}$ in slag studied.

4-4. Rate-controlling steps

The total resistance for the transfer reaction of each element i (i = Cr_{sat}, Cr, C, Si, S) between slag and metal, R_i, is defined by the reciprocal of the overall mass transport coefficient, k_i, i.e.,

$$R_i = \frac{1}{k_i} \quad (30)$$

The relative contributions to the total resistance of the transport in the slag phase, R_i^s, and that in the metal phase, R_i^m, and the chemical reaction at the slag-metal interface, R_i^r, are defined by the following equations, respectively:

$$R_{Cr_{sat}}^r = \frac{1}{k_{r,Crsat} R_{Cr_{sat}}}, \quad R_{Cr_{sat}}^m = \frac{f_{Cr} a_O^{*1.5}}{k_m \rho_m R_{Cr_{sat}}} \quad (31)$$

$$R_{Cr}^s = \frac{1}{k_s \rho_s R_{Cr}}, \quad R_{Cr}^r = \frac{1}{k_{r,Cr} R_{Cr}}, \quad R_{Cr}^m = \frac{B_{Cr} a_O^{*1.5}}{k_m \rho_m R_{Cr}} \quad (32)$$

$$R_C^r = \frac{1}{k_{r,C} R_C}, \quad R_C^m = \frac{f_{Ca} a_O^*}{k_m \rho_m R_C} \quad (33)$$

$$R_{Si}^s = \frac{1}{k_s \rho_s R_{Si}}, \quad R_{Si}^r = \frac{1}{k_{r,Si} R_{Si}}, \quad R_{Si}^m = \frac{B_{Si} a_O^{*2}}{k_m \rho_m R_{Si}} \quad (34)$$

$$R_S^s = \frac{1}{k_s \rho_s R_S}, \quad R_S^m = \frac{B_S}{k_m \rho_m a_O^* R_S} \quad (35)$$

The comparison of these relative contributions for each element, R_i^s, R_i^r, R_i^m, gives a good suggestion on which step(s) controls the overall reaction. For an example, R_{Cr_{sat}}^r was about 1.0 during the time when slag was saturated with Cr₂O₃, this fact indicates that the overall rate of Cr₂O₃ reduction is controlled by the chemical reaction at the slag-metal interface. But at

the later stage when slag was unsaturated with Cr_2O_3 , R_{Cr}^s is much larger than R_{Cr}^r and R_{Cr}^m , so that it can be said that the overall rate is controlled by the mass transport in the slag phase at that time. It also suggests that the rates of CO formation and SiO_2 reduction are controlled by the chemical reaction at the slag-metal interface, but the rate of Reaction (9) on sulfur is controlled by the mass transport in the slag phase.

5. CONCLUSION

In order to clarify the mechanism of Cr_2O_3 reduction, the rate of reduction of Cr_2O_3 in slag by liquid iron containing carbon was investigated in the temperature range of 1500 to 1600 C under an argon atmosphere. Experiments were carried out to examine the effects of temperature, compositions of slag and metal. The reduction rate strongly depended on the experimental temperature. The reduction rate and the final chromium content in liquid iron increased with increasing CaF_2 content, which was attributed to an increase in the mass transport coefficient in the slag. The reduction rate increased remarkably with the addition of silicon to liquid iron, while it decreased with the addition of sulfur, which was attributed to a decrease in the effective reaction area by the adsorption of sulfur to the slag-metal interface. These experimental results were well simulated by the kinetic model developed on the basis of the two-film theory. It was found from the simulation results that the transfer rate of chromium from slag to metal was controlled by the chemical reaction at the slag-metal interface in the early stage of the reaction, but it was controlled by the mass transport in the slag phase in the later stage of the reaction.

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Table 1 Composition of initial slags (mass%).

Slag	Cr ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	CaO/SiO ₂
A	12.2	36.3	41.3	9.66	-	0.88
B	11.7	30.3	36.4	9.65	11.4	0.83
C	10.3	29.2	32.7	9.57	17.8	0.89
F	7.01	33.1	20.9	27.0	11.5	1.58
G	5.74	28.4	25.7	27.5	12.2	1.11
H	5.58	17.8	37.2	27.1	11.9	0.48
I	6.90	33.4	39.0	10.3	9.90	0.86
J	19.7	25.2	30.0	8.84	15.8	0.84

Table 2 Experimental conditions and compositions of the initial and the final iron of each experiment (mass%).

Run No.	Temp. (°C)	Initial			Final			
		[C]	[Si]	[S]	[Cr]	[C]	[Si]	[S]
A-1	1600	3.854	0.0179	-	0.879	3.267	0.1190	-
B-1	1600	3.876	0.0162	-	0.968	3.290	0.0587	-
B-2	1600	0.871	0.0166	-	0.941	0.697	-	-
B-3	1600	2.022	0.0233	-	1.099	1.634	0.0352	-
B-6	1500	1.868	0.0073	-	1.015	1.614	0.0033	-
B-7	1500	1.853	0.7260	-	1.264	1.803	0.2720	-
B-8	1500	1.867	0.0058	0.348	1.164	1.589	0.0037	0.339
C-1	1600	3.981	0.0189	-	1.289	3.342	0.0226	-
F-1	1600	0.799	0.0204	-	0.494	0.627	0.0184	-
G-1	1600	0.796	0.0173	-	0.503	0.585	0.0176	-
H-1	1600	0.786	0.0171	-	0.475	0.702	0.0373	-
I-1	1600	0.798	0.0017	-	0.612	0.676	0.0056	-
J-2	1600	0.970	0.0167	-	1.355	0.734	-	-

Table 3 The parameters determined by modeling calculation.

Run No.	$k_s \rho_s$	$k_{r,Crsat}$	$k_{r,Cr}$	$k_{r,C}$	$k_{r,Si} \times 10^5$	$B_{Cr} / 10^4$	$B_{Si} / 10^8$	$B_{Fe} / 10^2$
	$g\ cm^{-2}\ sec^{-1}$							
A-1	0.02	10	5	1	4	30	2.5	1
B-1	0.03	15	5	1	2	10	10	2
B-2	0.03	15	5	0.6	4	1.6	2.5	1.7
B-3	0.03	20	5	0.3	3	2	0.5	1.5
B-6	0.02	25	1	0.8	1	7	30	6
B-7	0.02	120	1	0.05	8	1	0.3	2
B-8	0.02	13	1	0.1	0.1	1	3	2
C-1	0.03	15	5	0.5	1	1.4	10	2.5
F-1	0.03	8	5	1	4	1	0.3	1
G-1	0.04	12	5	3	4	0.9	0.5	1.3
H-1	0.03	6	5	0.5	2	1.1	0.18	2
I-1	0.04	15	10	0.6	2	1.2	4	1.7
J-2	0.01	15	10	1	1	1	3	5

$k_m \rho_m = 0.14$ $B_S = 0.0005$ $(\%Cr)_{sat} = 2.1 \sim 3.8$

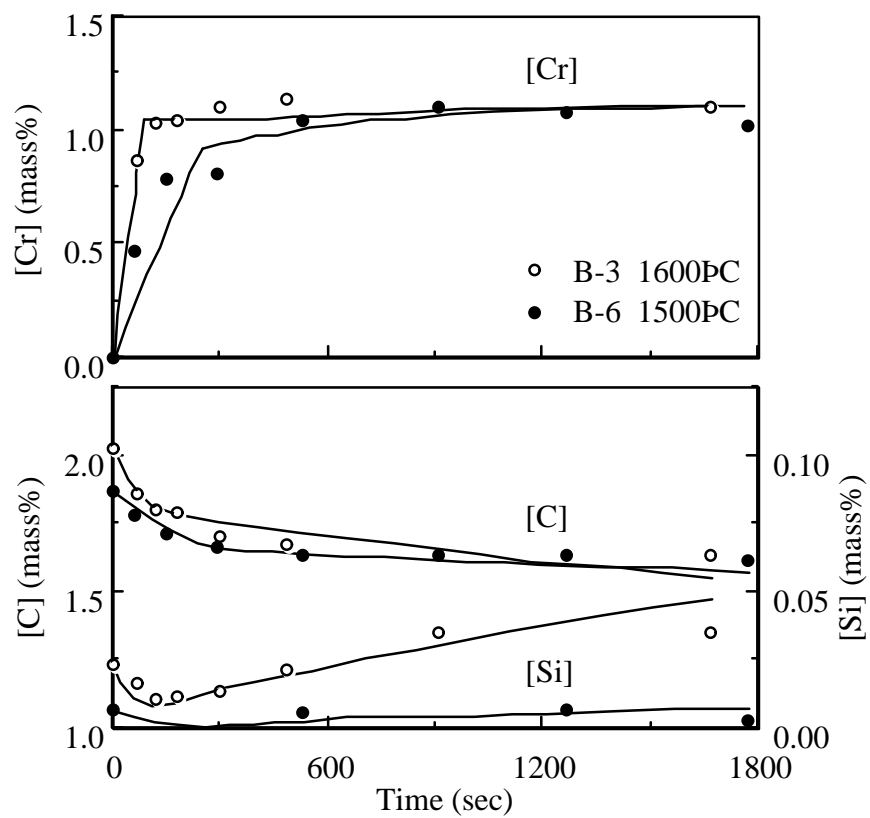


Fig. 1 Effect of temperature on the reduction rate of Cr_2O_3 in slag.

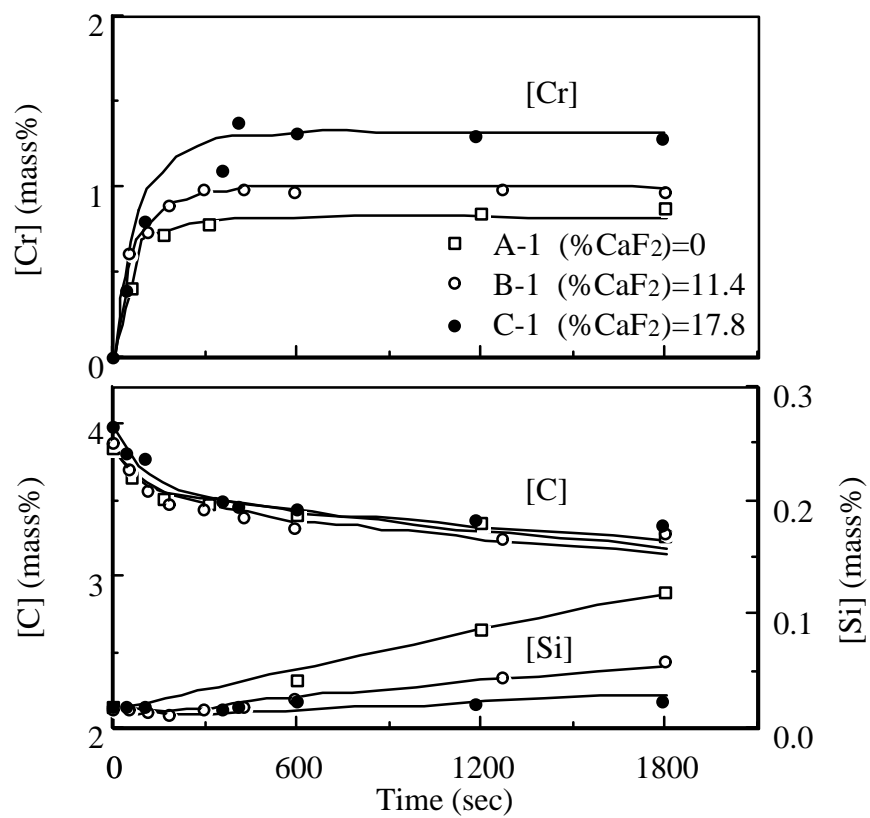


Fig. 2 Effect of CaF₂ content in slag on the reduction rate of Cr₂O₃ in slag at 1600 °C.

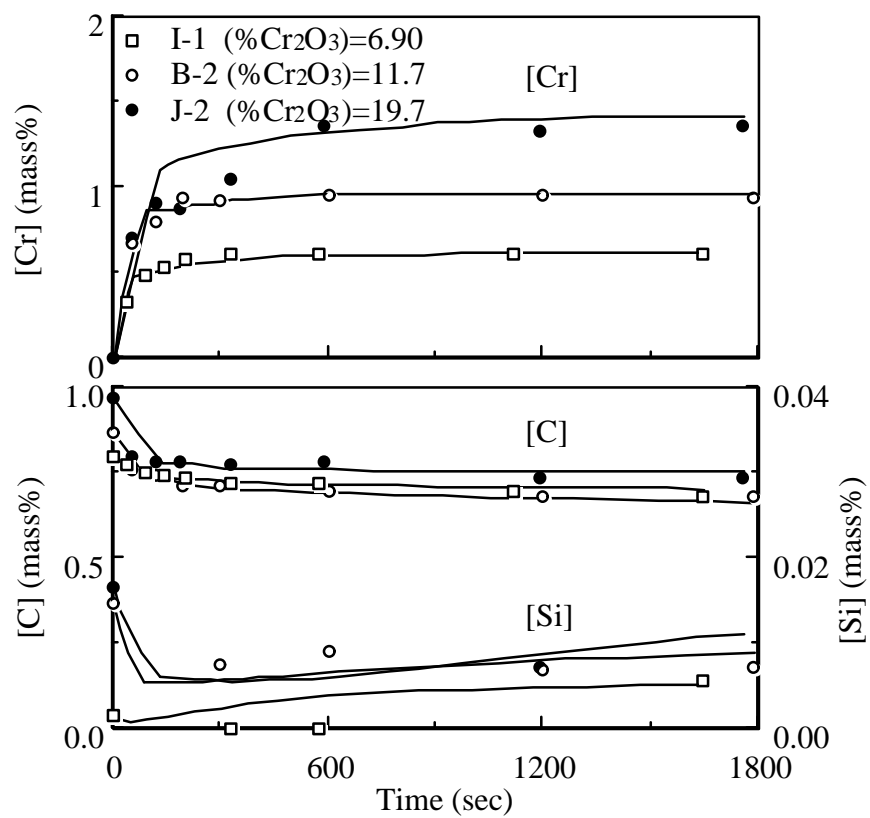


Fig. 3 Effect of Cr₂O₃ content in slag on the reduction rate of Cr₂O₃ in slag at 1600 °C.

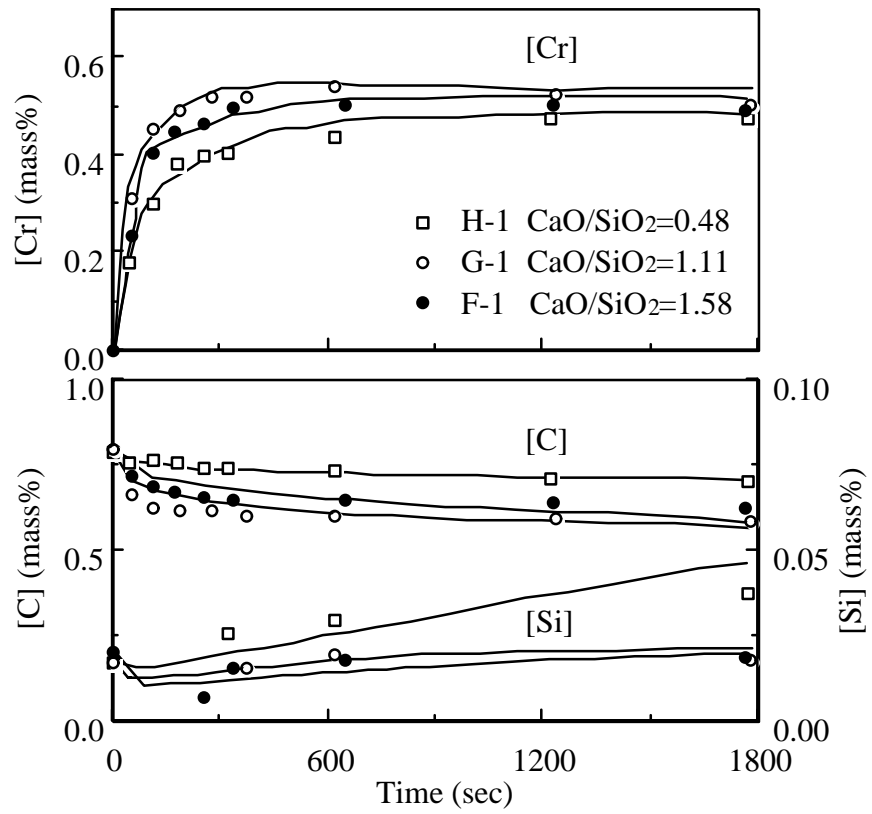


Fig. 4 Effect of CaO/SiO_2 ratio of slag on the reduction rate of Cr_2O_3 in slag at 1600 °C.

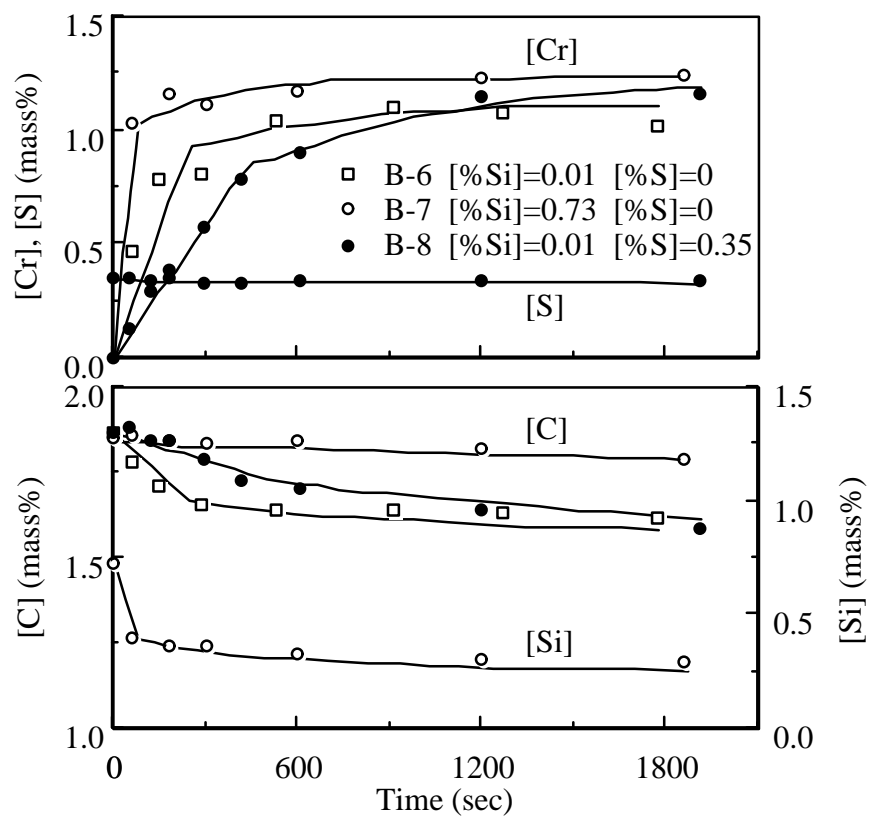


Fig. 5 Effect of Si and S in liquid iron on the reduction rate of Cr_2O_3 in slag at 1500 °C.

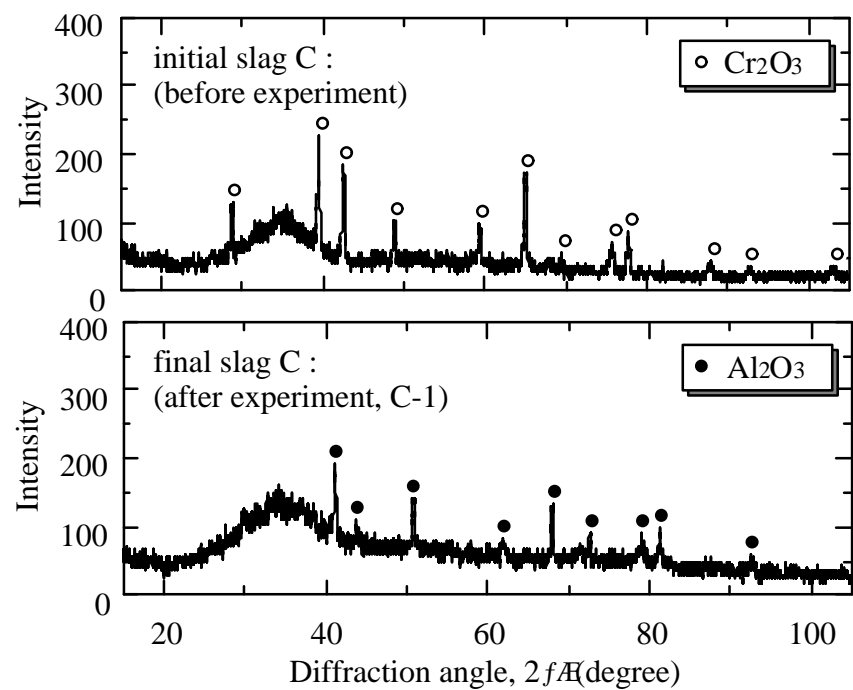


Fig.6 X-ray diffraction patterns of the initial and the final samples.

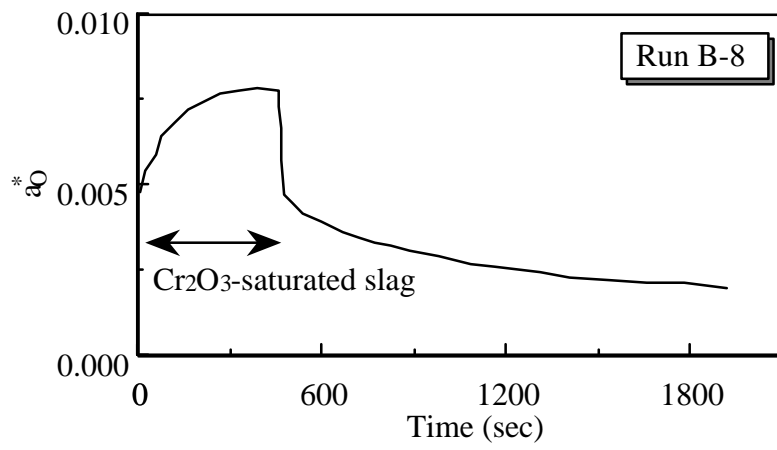


Fig. 7 Variation of calculated oxygen activity at the slag-metal interface with reaction time.

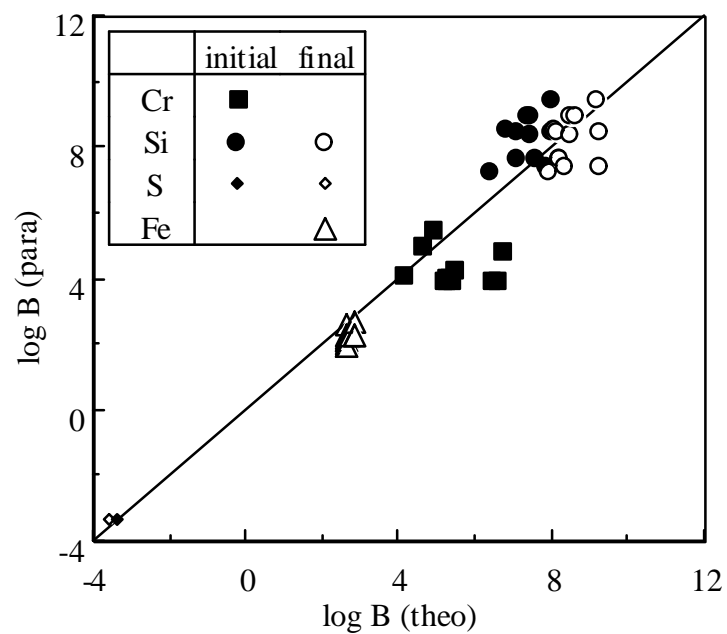


Fig. 8 Comparison of the values obtained from the present work, $B(\text{para})$ with those calculated from the thermodynamic data, $B(\text{theo})$.