4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

REDUCTION KINETICS OF CHROMIUM OXIDE IN SLAGS BY DISSOLVED CARBON IN IRON BATH

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Synopsis: Reduction kinetics of Cr_2O_3, Cr_2O_3-flux($CaO-SiO_2-MgO-Al_2O_3$) and chromite ore-flux by dissolved carbon in iron bath were investigated. Their reduction rates are found to be related to activity of CrO in slags. When the slags are saturated with CrO, the reaction is the zeroth-order, otherwise is the first order with respect to activity of CrO in slag. The rate-controlling step is the mass transfer of CrO from bulk slag to slag-metal interface. The temperature dependence of transfer coefficients of CrO are determined for slags with different compositions in the temperature range 1600~1670°C. The effect of CaO/SiO_2 ratio, content of CaF_2, contents of Cr in slags and in melts on the reduction rate of CrO are also determined.

Key words: Reduction kinetics, Chromium oxide in molten slags, Dissolved carbon, Iron bath

* Projects supported by the National Natural Science Foundation of China

1. Introduction

It is paid more and more great attantion to smelting reduction of chromite for production of ferrochrome and direct making of stainless steel. The basic research is developed. The present paper studies the reduction rate of chromium oxide in $MgO-Al_2O_3-SiO_2-CaO$ molten slag by dissolved carbon in carbon saturated liquid iron.

2. Experimental section

The experiments were carried out in a vertical carbon tube furnace. The inside of the furnace was protected by nitrogen gas, Cr_2O_3 was added into the graphite crucible and was mixed uniformly with the slags. The composition of slags are shown in Table 1. The reduction reactions were carried out in the inferface between liquid iron and molten slag in the graphite crucible.

3. Results

3.1 Effect of temperatures and Cr contents in slags

Cr from slag transfers to liquid iron in the reduction process, and

Table 1 Composion of Slags

Slag No	MgO	Al_2O_3	SiO_2	CaO	CaF_2
S-1	28.54	20.08	41.01	10.36	
S-2	28.51	20.06	30.07	20.70	
S-3	28.48	20.04	20.04	31.01	
S-4	27.33	19.24	19.64	29.76	4.03
S-5	26.28	18.49	18.88	28.61	7.74
S-6	25.30	17.80	18.18	27.55	11.18

ΔW_{Cr} shows the transfer mass. The relationship between ΔW_{Cr} and time is linear as Fig.1 when Cr content in the slag is higher (>10%). The slop of linearity increases with the increase of temperatures. The relationship between ΔW_{Cr} and time becomes nonlinear from linearity with decrease of Cr content in the slag. P is the point of transition in Fig.2.

3.2 Effect of composition of molten slags

The rate of reduction reaction decreases with the increase of CaO/SiO_2 ratio as MgO and Al_2O_3 contents in the molten slag keep constant. The reduction rate increases with the increase of CaF_2 content when MgO=30%, Al_2O_3=20% and CaO/SiO_2=1.5 in slags.

4. Discussion

The stable formes of Cr existed in the molten slags are CrO and Cr_2O_3, mainly CrO in reduction atmosphere[1,2]. The reaction between CrO and dissolved carbon in liquid iron is

$$(CrO) + [C] = [Cr] + CO \qquad (1)$$

According to the investigation of the reduction rate between FeO in slag and carbon saturated liquid iron[3], it is supposed that the rate-controlling steps are the CrO diffusion from slag to slag-metal interface and the chemical reaction in slag-metal interface, then $a^*_{(Cr)}=a_{(Cr)}$, $a^*_{[C]}=a_{[C]}$ (* shows the activity in the interface). The reduction rate is

$$-\frac{dn_{Cr}}{dt} = \frac{A}{1/k_m + 1/k^+ a_{[C]}}\left(a_{(CrO)} - \frac{a_{[Cr]}.Pco}{K\,a_{[C]}}\right) \qquad (2)$$

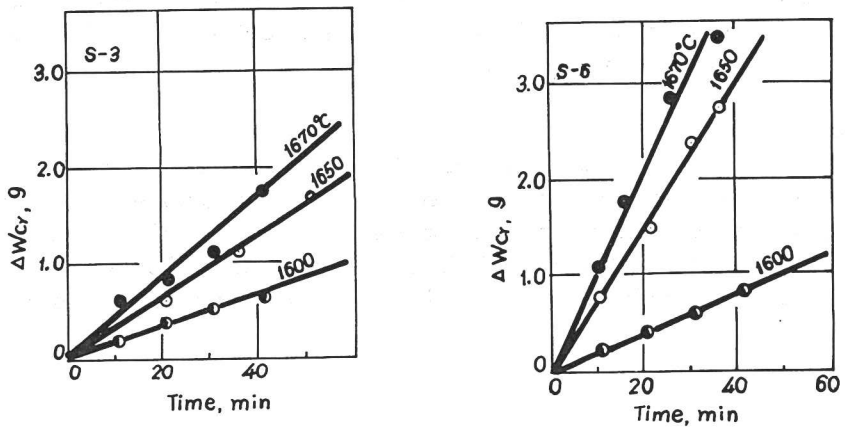

Fig.1 Reduction rate of chromium oxide in slag

here, k_m represents the transfer coefficient (mol. $min^{-1}cm^{-2}$) of CrO in slags, k^+ and K are the positive rate constant ($mol.min^{-1}cm^{-2}$) and the equilibrium constant of reaction (1). The activities of these constituents in equation (2) take the saturated concentration as the standard state, then $a_{[C]}=1$, $a_{[Cr]} \leqslant 1$, values of K are 38.32 and 66.95 at 1600 and 1670°C respectively. Pco=0.1 MPa, $a_{[Cr]}Pco/K\ a_{[C]} \ll a_{CrO}$ when CrO in slag is approaching to saturation, so that equation (2) can be simplified as

$$\frac{d\,n_{Cr}}{d\,t} = \frac{A}{1/k_m + 1/k^+} a_{(CrO)} \qquad (3)$$

It is suggested from equation (3) that the reduction rate keeps constant when the temperature is definite and CrO in the slag is saturated, $a_{(CrO)}=1$. It is in agreement with the experimental results, as shown in Fig.1.

There is $1/k_m = 0$ when Cr oxide reacts with carbon saturated liquid iron. The experimental data are worked out and values of k^+ are 1.225×10^{-3} and 1.183×10^{-3} $mol.min^{-1}cm^{-2}$ respectively at 1650 and 1600°C. The viscosity of the slag influences the rate of the reduction reaction between Cr oxide in the slag and carbon saturated liquid iron. The melting point of $MgO-Al_2O_3-SiO_2-CaO$ slag increases with the increase of CaO/SiO_2 as the contents of MgO and Al_2O_3 are definite[4]. The increase of the viscosity of the slag at a definite temperature leads to increase the diffusion resistance ($1/k_m$) of CrO in the slag, as shown in Fig.3a. At 1670°C, CaO/SiO_2 ratio increases from 0.25 to 1.5, as well as k_m decreases from 1.08×10^{-4} to 6.38×10^{-5} $mol.min^{-1}cm^{-2}$. Addition of CaF_2 to the slag can decrease the viscosity of the slag, which is in favour of the diffusion of CrO in the slag, as shown in Fig.3b. When the content of CaF_2 in molten slag increases from 0 to 11%, the values of k_m increase from 6.38×10^{-5} to 1.87×10^{-4} $mol.min^{-1}cm^{-2}$. It is clear in comparsion k^+ with k_m that the transfer of CrO in the slag is the rate-controlling step of the reduction reaction.

Using the CrO activity coefficient ($\gamma=1/(\%CrO)s$) in CrO saturated slag instead of the activity coefficient of CrO, approaching to saturation in slag, then the activity of CrO is shown as

$$a_{(CrO)} \approx \frac{(\%CrO)}{(\%CrO)s} = \frac{(\%Cr)}{(\%Cr)s} \qquad (4)$$

If the weight percent concentration of Cr in the slag represents the reduction rate, integrating with equation (3) and (4), it gives

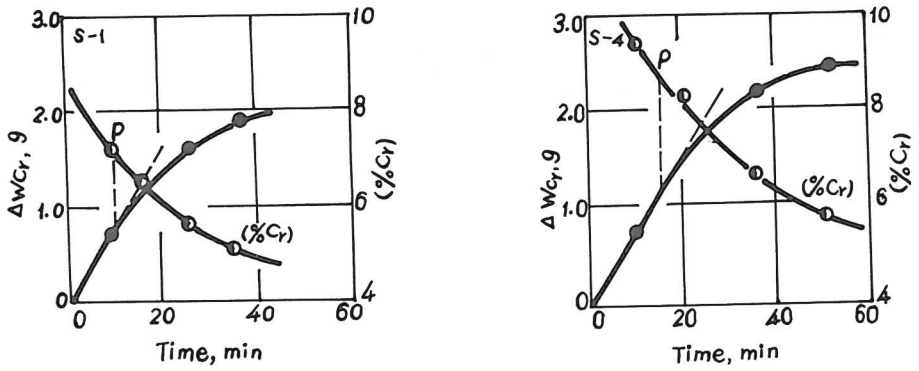

Fig.2 Effect of Cr content in slag on reduction rate at 1670°C

$$\ln \frac{(\%Cr)s}{(\%Cr)} = k\,A\,t \tag{5}$$

$$k = \frac{M_{Cr}}{V\ \rho} \cdot \frac{1}{1/k_m + 1/k^+} \cdot \frac{1}{(\%Cr)s} \tag{6}$$

V and ρ in equation (6) are shown as volume and density of molten slags. Using the relative concentration at P point in Fig.2 as (%Cr)s, k is calculated to be $1.29\sim1.68\times10^{-3}$ mol.min^{-1}cm^{-2}. Equation (5) is in agreement with the research result by a rotating crucible method[1], but the value of k, obtained by the rotating crucible method is ten times magnitude than the present work, which is mainly the effects of stirring function and of the different composition of slags.

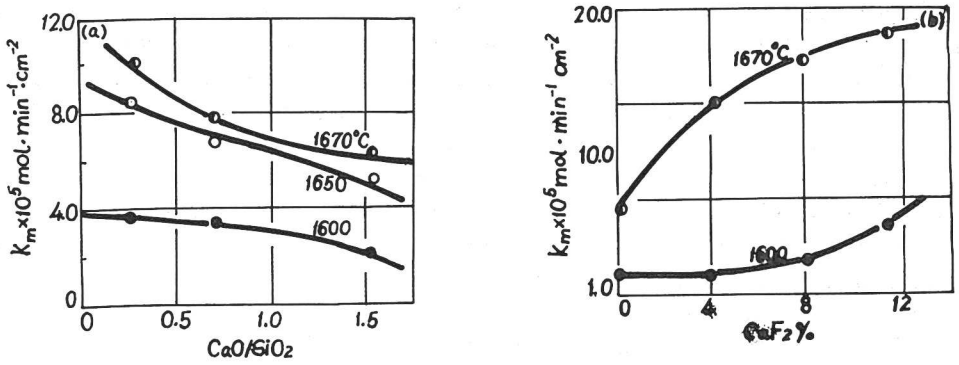

Fig.3 Effect of CaO/SiO_2 (a) and CaF_2 (b) in slag on k_m

5. conclusions

5.1 Reduction kinetics of pure Cr_2O_3, Cr_2O_3-flux($CaO-SiO_2-MgO-Al_2O_3$) and chromite ore-flux by dissolved carbon in iron bath were researched. Their reduction rates are found to be related to activity of CrO in slags. When the slag are saturated with CrO, the reaction is the zeroth-order, otherwise is the first order with respect to activity of CrO in slag. The rate-controlling step is the mass transfer of CrO from bulk slag to slag-metal interface. The transfer coefficients of CrO are determined as $10^{-5}\sim10^{-4}$ mol.min^{-1}cm^{-2} for slags with different compositions in the temperature range 1600~1670°C.

5.2 The effect of CaO/SiO_2 ratio, content of CaF_2 in molten slag on the reduction rate of CrO are determined as Fig.3. At 1670°C, CaO/SiO_2 ratio increases from 0.25 to 1.5, as well as the transfer coefficients of CrO decrease from 1.08×10^{-4} to 6.38×10^{-5} mol.min^{-1}cm^{-2}. When the content of CaF_2 in molten slag increases from 0 to 11%, the transfer coefficients of CrO increase from 6.38×10^{-5} to 1.87×10^{-4} mol.min^{-1}cm^{-2}.

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