Mathematical Modelling of Change in Composition of Mold Flux in Continuous Casting of Steels

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A mathematical model of the reaction between mold flux and molten steel has been newly developed to estimate the change in composition of the mold flux during the continuous casting of steels and to design an optimum flux composition. The model takes into account mass transfer in the molten steel and molten flux and equilibrium reaction at the interface. On the reaction, the activities of the practical mold flux components like CaO, SiO₂, Al₂O₃, CaF₂, Na₂O are estimated by a statistical thermodynamic model of slag, called cell model. Comparison of calculated composition change with data obtained in the practical casting experiment of high titanium steel showed that the mathematical model is useful for the estimation of the reaction between the mold flux and the molten steel and for the design of the mold flux composition to minimize change in composition due to that reaction.

KEY WORDS: continuous casting; mold flux; mathematical model; kinetics; high titanium steel; reaction.

1. Introduction

Mold flux in the continuous casting of steels plays important roles mainly for lubrication between the mold and the solidifying steel and for control of heat transfer from the molten steel to the mold. The change in composition of the mold flux due to reaction with molten steel during the casting is great in the continuous casting of steels bearing strong deoxidizing elements such as aluminum and titanium.¹⁻⁴⁾ It is important to minimize this change to prevent crack formation of the solidifying steel. Although several studies^{1,2)} have so far been made on estimation of composition change of the mold flux due to absorption of alumina inclusions, theoretical prediction has not been reported on the change due to reactions between practical molten steel and flux of multi-components.

In this study, a mathematical model of the change in composition of mold flux due to the reaction with molten steel was developed to estimate this change during the continuous casting of steels and to design an optimum flux composition. The validity of the model was examined by comparing the estimated results with data in practical casting experiments of high titanium steel.

2. Mathematical Modelling

Change in composition of mold flux is calculated by taking account of mass transfer between the flux and molten steel and the mass balance of components in both

phases.

Assumptions made in the model are as follows:

(1) Rate determining steps of reaction are the mass transfer of components both in the molten flux and steel phases.

(2) Local equilibrium is established between components of the molten flux phase and those of the molten steel phase.

(3) These two phases are homogeneous.

(4) Change in composition of the mold flux due to absorption of non-metallic inclusions in the molten steel is negligible.

Under these assumptions, mass transfer of Al, Si, Ti, Fe, Mn, P, and O due to reaction between the mold flux and molten steel are calculated.

2.1. Mass Fluxes of Components

Mass flux of each component is calculated by a model based on the coupled reaction model,⁵⁾ which is modified for the calculation of reaction between the molten flux and steel. For the reaction at the interface between the molten flux and steel expressed by Eq. (1), mass flux of component X can be expressed by Eqs. (2) and (3), and that of oxygen by Eq. (4)

$$J_X = \frac{\rho_M k_{M,X}}{100M_X} ([\%X] - [\%X]^*) \quad \dots\dots\dots(2)$$

$$= \frac{\rho_F k_{F, \text{XO}_n}}{100 M_{\text{XO}_n}} ((\% \text{XO}_n)^* - (\% \text{XO}_n)) \dots (3)$$

$$J_O = \frac{\rho_M k_{M, O}}{100 M_O} ([\% O] - [\% O]^*) \dots (4)$$

Regarding mass transfer coefficient in the molten steel, the following equation is approximately used by assuming mean contact time between the molten flux and steel of $W/2v_M$:

$$k_{M, X} = 2 \sqrt{\frac{2Dv_M}{\pi W}} \dots (5)$$

According to the assumption of local equilibrium at the reaction interface, equilibrium constant of reaction in Eq. (1) can be expressed by Eq. (6).

$$K_X = \frac{a_{\text{XO}_n^*}}{a_X^* a_O^{*n}} = \frac{\rho_F \gamma_{\text{XO}_n}}{100 C M_{\text{XO}_n} f_X f_O^n} \cdot \frac{(\% \text{XO}_n)^*}{[\% X]^* [\% O]^*} \dots (6)$$

From mass balance of oxygen at the interface, one can obtain the following relation for the simultaneous reactions:

$$1.5J_{\text{Al}} + 2J_{\text{Si}} + 2J_{\text{Ti}} + J_{\text{Fe}} + J_{\text{Mn}} + 2.5J_{\text{P}} - J_O = 0 \dots (7)$$

Using the above equations, mass flux, J_X , for each component can be calculated.

2.2. Equation of Mass Balance

Equation of mass balance for each component in each phase can be expressed as follows:

For the molten flux phase:

$$\begin{aligned} & \frac{\rho_F V_F}{100 M_{\text{XO}_n}} \cdot \frac{d(\% \text{XO}_n)}{dt} \\ &= \frac{\rho_F Q_F}{100 M_{\text{XO}_n}} ((\% \text{XO}_n)^o - (\% \text{XO}_n)) + AJ_X \dots (8) \end{aligned}$$

For the molten steel phase:

$$\frac{\rho_M V_M}{100 M_X} \cdot \frac{d[\% X]}{dt} = \frac{\rho_M Q_M}{100 M_X} ([\% X]^o - [\% X]) - AJ_X \dots (9)$$

Mass balance for Al, Si, Ti, Fe, Mn, P and O is taken into account.

2.3. Data Used for Calculations

The present model was applied to estimation of the composition change of mold flux for continuous casting of high titanium steel. The problem in continuous casting of this steel is that the changes in viscosity and thermal conductivity of the mold flux due to the composition change during casting often cause a breakout or crack of the solidifying shell.

Data used for calculations are given in Table 1. Equilibrium constant of reaction K_X is estimated from thermodynamic data,^{6,7)} activity coefficients f_X and f_O are estimated from interaction parameters,⁶⁾ and γ_{XO_n} is estimated using the cell model.⁸⁾ Volume of the molten flux phase is calculated from the area of cross section of mold and thickness of the molten flux layer. Volume of the molten steel phase is assumed to be the same as that

Table 1. Data used for calculations.

Casting condition					
Consumption of mold flux			0.45 kg/ton-steel		
Thickness of molten flux layer			0.005 m		
Casting velocity			0.7 m/min		
Size of bloom			0.5 m × 0.3 m		
Temperature			1550 ℃		
Composition of mold flux (mass%)					
	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	CaF ₂
A	26	43	5	12	14
B	19	51	4	13	13
Composition of molten steel (mass%)					
C	Si	Mn	Al	Ti	O
0.03	0.34	0.34	0.044	0.33	0.0015

of the molten flux phase. In the calculation, effect of volume of the molten steel phase on changes in composition of the flux and steel is small, even if the volume of the molten steel phase is varied from 1/10 to 10 times as large as that of the flux phase. Mass transfer coefficient of each component in the molten steel phase is estimated from Eq. (5) with data of diffusion coefficient in molten steel,⁹⁾ width of mold, and flow velocity of molten steel at meniscus in mold, which is assumed to be 0.2 m/s. Mass transfer coefficient of each component in the molten flux phase is estimated as 1/10 of that in molten steel.¹⁰⁾

3. Experimental

To investigate the composition change of mold flux and to validate the proposed model, practical casting experiments were conducted on high titanium steel. The experimental conditions are listed in Table 1. Two kinds of mold flux were used in the casting experiment: the ratio of %CaO to %SiO₂ (hereafter, written as C/S) in the mold flux is 0.6 (A) and 0.38 (B).

4. Results and Discussion

Figure 1 shows a comparison of calculated change in composition of the mold flux with that observed for high titanium steel. The concentration of TiO₂ in molten flux increases and that of SiO₂ decreases, because SiO₂ in the flux is reduced by Ti in the molten steel during the casting. In this case, there is little change in the concentration of Al₂O₃. The calculated result is in good agreement with the observed one. Change in composition of the mold flux becomes small after 20 min in the casting period, because the concentration of each component in molten flux changes as a result of the reaction so that it is close to a value in equilibrium with the molten steel by the reaction under a constant feeding rate of the mold flux. Calculated change in composition of molten steel and that in concentration of components except SiO₂, TiO₂ and Al₂O₃ in the flux are negligible, which is confirmed by the casting experiment.

Fig. 1. Comparison of calculated composition change of mold flux during continuous casting of high titanium steel with observed one.

Fig. 2. Comparison between calculated composition change of mold flux and observed one for C/S of 0.38.

Because the calculated result of the effect of C/S in mold flux on increase in concentration of TiO_2 suggested that the composition change in the mold flux for high titanium steel could be suppressed by decreasing the value of C/S, as described below, mold flux for C/S of 0.38 was used in a casting experiment. Observed and calculated changes in composition of the mold flux with C/S of 0.38 for high titanium steel are shown in Fig. 2. Open marks and solid lines represent the observed and the calculated values, respectively. The change in composition of the mold flux is smaller for C/S of 0.38 than for C/S of 0.6. It is seen in Fig. 2 that the calculated values are in good agreement with the observed ones.

Change in composition of mold flux should be minimized for stable casting operation. An optimum composition of mold flux for high titanium steel for reducing composition change of the mold flux is examined by the present model in the following.

Influence of C/S on this change in composition was calculated, since CaO and SiO_2 are main components of the mold flux. Figure 3 shows the effect of C/S on the increase in concentration of TiO_2 in the mold flux at 40 min after the start of casting; the concentration increases with the increase in C/S, agreeing with results in previous studies.^{3,4)} A sharp increase of TiO_2 in the mold flux can be seen when the value of C/S is larger than 0.5. This result can be examined from the thermodynamic consideration. Iso-activity lines of TiO_2 of the mold flux calculated by the cell model⁸⁾ are shown on a

Fig. 3. Estimated effect of $(\% \text{CaO})/(\% \text{SiO}_2)$ in the mold flux on increase in $(\% \text{TiO}_2)$.

Fig. 4. Estimated iso-activity lines of TiO_2 in mold flux and change in composition of mold flux for high titanium steel on CaO- SiO_2 - TiO_2 quasi-ternary phase diagram.

CaO- SiO_2 - TiO_2 quasi-ternary phase diagram in Fig. 4. The activity of TiO_2 is high when C/S value is below 0.5, but it becomes lower when the value is larger than 0.5 on the condition that concentration of TiO_2 is constant. This is one reason why the increase in concentration of TiO_2 becomes remarkable for a C/S value larger than 0.5. To reduce the composition change of the mold flux for high titanium steel, the value of C/S in the mold flux to be fed should be below 0.5.

The observed changes in composition of the mold flux for C/S of 0.6 and 0.38 are also plotted in Fig. 4 by open and solid marks, respectively, where the change for C/S of 0.38 is clearly smaller than that for C/S of 0.60. When C/S in mold flux is 0.38, there is no precipitation of solid CaTiO_3 phase in the molten flux, which is harmful for stable casting. For optimum design of the mold flux, then, the composition change should be closed in the region without precipitation of CaTiO_3 shown in Fig. 4, by lowering the value of C/S.

The present mathematical model is thus found useful not only for the estimation of the reaction between the mold flux and the molten steel, but also for the design of the mold flux composition to minimize change due to the reaction with molten steel.

5. Conclusion

A mathematical model of change in composition of mold flux due to reaction with molten steel during con-

tinuous casting was developed for the theoretical prediction of the composition change and for an optimum design of mold flux. The model was applied to the continuous casting of high titanium steel.

(1) During the casting of high titanium steel, TiO_2 in the mold flux increases and SiO_2 decreases, because SiO_2 is reduced by Ti in the molten steel. The composition change calculated by the present model is in good agreement with data obtained in the casting of high titanium steel.

(2) According to the model, the composition change of the mold flux for high titanium steel can be suppressed by decreasing the ratio of (%CaO) to (% SiO_2) in the mold flux, which has been confirmed by the practical casting experiment. This comes from that the activity of TiO_2 increases with decreasing the ratio of (%CaO) to (% SiO_2) in the multi-components flux, which was estimated in this study.

(3) The present mathematical model is found useful not only for the estimation of the reaction between the mold flux and the molten steel, but also for the design of the mold flux composition to minimize change due to the reaction with molten steel.

Nomenclature

A :	reaction area (m^2)
a :	activity (—)
C :	total molar concentration of molten flux (mol/m^3)
D :	diffusion coefficient (m^2/s)
f :	activity coefficient in molten steel (—)
J :	mass flux ($\text{mol}/\text{m}^2\text{s}$)
K :	equilibrium constant (—)
k :	mass transfer coefficient (m/s)
M :	molar weight (kg/mol)
Q :	feeding rate (m^3/s)
V :	volume (m^3)
v :	flow velocity of molten steel in mold (m/s)

W : width of mold (m)

$[\%X]$: concentration of component X in molten steel (mass%)

$(\%XO_n)$: concentration of component XO_n in mold flux (mass%)

γ : activity coefficient in mold flux (—)

ρ : density (kg/m^3)

Subscripts:

F: mold flux

M: molten steel

O: oxygen

X: component X in molten steel phase

XO_n : component XO_n in molten flux phase

superscripts

0: initial

*: at reaction interface

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