



Article Study of Thermodynamic for Low-Reactive CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O Mold Flux Based on the Model of Ion and Molecular Coexistence Theory

Maoguo Zhao, Gang Li, Zhirong Li, Qiangqiang Wang * and Shengping He *

College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China; maoguozhao@163.com (M.Z.); ligang93yu@163.com (G.L.); cqulzr@cqu.edu.cn (Z.L.)

* Correspondence: wtfwawj@163.com (Q.W.); heshp@cqu.edu.cn (S.H.); Tel.: +86-023-6510-2469 (Q.W.); +86-023-6510-2469 (S.H.)

Abstract: A thermodynamic model was proposed to calculate the activity of components in lowreactive CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O mold flux, which was chosen to improve the castability of high Al steel, based on the ion and molecular coexistence theory. The model was indirectly validated, and the effects of the mass ratio of Al₂O₃/SiO₂, contents of CaF₂ and Li₂O on the reactivity of components were discussed. The results reveal that the reactivity of mold flux attenuated with the increase in the mass ratio of Al₂O₃/SiO₂. The decrease in reactivity was insignificant as the mass ratio was over 3.5. The steel–slag reaction experiment confirmed that the reactivity of mold flux is weakened when the content of SiO₂ below 8 wt%. The reactivity of mold flux increased nearly linearly with the increase in CaF₂ content, indicating that the proportion of CaF₂ should be kept to a minimum in the flux. In addition, the compositional regions involving around 6 wt% Li₂O should be avoided to develop low-reactive mold flux.

Keywords: thermodynamic model; activity; low reactivity; mold flux; reactivity

1. Introduction

Advanced high-strength steels with high content of aluminum have attracted much attention in the automobile industry owing to low density, high ductility, and strength for the sake of passenger safety and environmental friendliness [1–3]. However, aluminum in molten steel ([Al]) is prone to react with silicon dioxide in traditional CaO-SiO₂-based mold flux ((SiO₂)), resulting in sharply varied content of SiO₂ and Al₂O₃. The compositional variation of the mold flux leads to an increase in melting temperature and viscosity, consequently deteriorating its performances, such as heat transfer and lubrication [4–7]. Therefore, it is essential to develop a specified mold flux having low reactivity with high-Mn, high-Al molten steel [8,9]. Taking the reaction between [Al] and (SiO₂) for example:

$$4[A1] + 3(SiO_2) \to 2(Al_2O_3) + 3[Si]$$
(1)

$$\Delta G = \Delta G^{\theta} + RT \ln \frac{a_{\rm (Al_2O_3)}^2 a_{\rm [Si]}^3}{a_{\rm (SiO_2)}^3 a_{\rm [Al]}^4} \tag{2}$$

where ΔG , ΔG^{θ} , *R*, *T*, *a_i* are the reaction Gibbs free energy change, standard reaction Gibbs free energy change, gas constant (8.314 J/(mol·K)), temperature, and activity of component *i*, respectively. Thus, for a certain steel, the activities of various components in mold flux are crucial parameters to determine the extent of reaction at the steel–slag interface. Currently, the application of thermodynamic software is a preferred approach to predict the activities of components in mold flux. However, the thermodynamic software has limited scope because of the lack of some databases. In order to make up for the shortcomings of the



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). thermodynamic software, the ion and molecular coexistence theory (IMCT) was proposed by Chuiko. N.M. in 1960s [10], which could predict the activity of each component of multi-component flux system. When using IMCT, the activity of each component in the flux can be expressed by the mass action concentration [10]. The accuracy to predict activities of components has been confirmed for flux melts, such as FeO-Fe₂O₃-SiO₂ [10], CaO-SiO₂-Al₂O₃-MgO [10], Na₂O-SiO₂ [10], NiO-MgO [11], CaO-Al₂O₃-Ce₂O₃ [12], and CaO-SiO₂-Al₂O₃-FeO-CaF₂-La₂O₃-Nb₂O₅-TiO₂ [13]. Our previous studies [14] indicated that the flux system of CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O as a low-reactive flux system is expected to be applied for continuous casting of high-Mn high-Al steel. To deeply understand during the contact of steel and flux, the obtainment of activity data in flux melts is urgent. In this study, a thermodynamic model is established to calculate the activity of the components in CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O mold flux based on IMCT (Ion and molecular coexistence theory) at 1773 K. In addition, the steel–slag contact experiment was conducted to verify the accuracy of the prediction. The effects of mass ratio of Al₂O₃/SiO₂ and content of CaF₂ and Li₂O were discussed.

2. Methodology

2.1. Structural Units and Mass Action Concentration

IMCT assumed that structural units of molten flux consisted of simple ions, simple and complex molecules. The simple ions participate in the formation of complex molecules in the form of ion couples, and each pair of cation and anion occupies one structural unit. For CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O system, Ca²⁺, Ba²⁺, Li⁺, F⁻, and O²⁻ as simple ions, and SiO₂ and Al₂O₃ as simple molecules existed. On the basis of ternary phase diagrams of CaO-SiO₂-Al₂O₃, BaO-SiO₂-Al₂O₃, CaO-Al₂O₃-CaF₂, CaO-SiO₂-CaF₂, and Al₂O₃-SiO₂-Li₂O, and binary phase diagrams of CaO-SiO₂, CaO-Al₂O₃, BaO-SiO₂, BaO-Al₂O₃, Li₂O-SiO₂, and Li₂O-Al₂O₃ [15–17], there are 33 major species of complex molecules that form within the temperature range of 1673–1823 K. The structural units and corresponding mole numbers are listed in Table 1. According to IMCT, free Me⁺/Me²⁺ and F⁻/O²⁻ remain independent, whereas ion couples (Me²⁺ + O²⁻) occupy two structural units and (2Me⁺ + O²⁻) or (Me²⁺ + 2F⁻) occupy three structural units (where Me²⁺ refers to Ca²⁺ or Ba²⁺ and Me⁺ refers to Li⁺). For the flux with six kinds of components, the ion couples include (Ca²⁺ + O²⁻), (Ba²⁺ + O²⁻), (2Li⁺ + O²⁻), and (Ca²⁺ + 2F⁻). Thus, the total mole number of structural units can be expressed as follows:

$$\sum n_i = 2n_{\text{CaO}} + 2n_{\text{BaO}} + n_{\text{Al}_2\text{O}_3} + n_{\text{SiO}_2} + 3n_{\text{CaF}_2} + 3n_{\text{Li}_2\text{O}} + n_7 + \dots + n_{39}$$
(3)

where n_i is the mole number of structural units for product *i*.

Items	Structural Units	Mole Number	Mass Action Concentration
	$(Ca^{2+} + O^{2-})$	$n_1 = 2n_{\text{CaO}}$	$N_1 = n_1 / \sum n_i$
Ion couples	$(Ba^{2+} + O^{2-})$	$n_2 = 2n_{\text{BaO}}$	$N_2 = n_2 / \sum n_i$
ion couples	$(Ca^{2+} + 2F^{-})$	$n_5 = 3n_{\text{CaF}_2}$	$N_5 = n_5 / \sum n_i$
	$(2Li^+ + O^{2-})$	$n_6 = 3n_{\text{Li}_2\text{O}}$	$N_6 = n_6 / \sum n_i$
Simple molecules	Al ₂ O ₃	n_3	$N_3 = n_3 / \sum n_i$
Simple molecules	SiO ₂	n_4	$N_4 = n_4 / \sum n_i$
	CaO·SiO ₂	<i>n</i> ₇	$N_7 = n_7 / \sum n_i$
	$2CaO \cdot SiO_2$	n_8	$N_8 = n_8 / \sum n_i$
	$3CaO \cdot SiO_2$	<i>n</i> 9	$N_9 = n_9 / \sum n_i$
Complex molecules	$3CaO \cdot 2SiO_2$	n_{10}	$N_{10} = n_{10} / \sum n_i$
Complex molecules	$CaO \cdot Al_2O_3$	n_{11}	$N_{11} = n_{11} / \sum n_i$
	$CaO \cdot 2Al_2O_3$	<i>n</i> ₁₂	$N_{12} = n_{12} / \sum n_i$
	$CaO \cdot 6Al_2O_3$	<i>n</i> ₁₃	$N_{13} = n_{13} / \sum n_i$
	$3CaO \cdot Al_2O_3$	n_{14}	$N_{14} = n_{14} / \sum n_i$

Table 1. Mole number and mass action concentration of the structural units.

Items	Structural Units	Mole Number	Mass Action Concentration
	12CaO·7Al ₂ O ₃	n ₁₅	$N_{15} = n_{15} / \sum n_i$
	$BaO \cdot SiO_2$	n ₁₆	$N_{16} = n_{16} / \sum n_i$
	$BaO \cdot 2SiO_2$	n ₁₇	$N_{17} = n_{17} / \sum n_i$
	$2BaO \cdot SiO_2$	<i>n</i> ₁₈	$N_{18} = n_{18} / \sum n_i$
	2BaO·3SiO ₂	<i>n</i> ₁₉	$N_{19} = n_{19} / \sum n_i$
	$BaO \cdot Al_2O_3$	<i>n</i> ₂₀	$N_{20} = n_{20} / \sum n_i$
	BaO·6Al ₂ O ₃	<i>n</i> ₂₁	$N_{21} = n_{21} / \sum n_i$
	$3BaO \cdot Al_2O_3$	n ₂₂	$N_{22} = n_{22} / \sum n_i$
	$3Al_2O_3 \cdot 2SiO_2$	n ₂₃	$N_{23} = n_{23} / \sum n_i$
	$Li_2O \cdot SiO_2$	n ₂₄	$N_{24} = n_{24} / \sum n_i$
	$Li_2O \cdot 2SiO_2$	<i>n</i> ₂₅	$N_{25} = n_{25} / \sum n_i$
	$2Li_2O \cdot SiO_2$	n ₂₆	$N_{26} = n_{26} / \sum n_i$
	$Li_2O \cdot Al_2O_3$	n ₂₇	$N_{27} = n_{27} / \sum n_i$
	$BaO.3CaO.2SiO_2$	n ₂₈	$N_{28} = n_{28} / \sum n_i$
	$2BaO \cdot 4CaO \cdot 3SiO_2$	n ₂₉	$N_{29} = n_{29} / \sum n_i$
	BaO·2CaO·4Al ₂ O ₃	<i>n</i> ₃₀	$N_{30} = n_{30} / \sum n_i$
	3BaO·CaO·Al ₂ O ₃	<i>n</i> ₃₁	$N_{31} = n_{31} / \sum n_i$
	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	n ₃₂	$N_{32} = n_{32} / \sum n_i$
	$2CaO \cdot Al_2O_3 \cdot SiO_2$	<i>n</i> ₃₃	$N_{33} = n_{33} / \sum n_i$
	$BaO \cdot Al_2O_3 \cdot 2SiO_2$	n ₃₄	$N_{34} = n_{34} / \sum n_i$
	$3CaO \cdot 2SiO_2 \cdot CaF_2$	n ₃₅	$N_{35} = n_{35} / \sum n_i$
	$3CaO \cdot 3Al_2O_3 \cdot CaF_2$	<i>n</i> ₃₆	$N_{36} = n_{36} / \sum n_i$
	$11CaO\cdot7Al_2O_3\cdotCaF_2$	n ₃₇	$N_{37} = n_{37} / \sum n_i$
	$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	n ₃₈	$N_{38} = n_{38} / \sum n_i$
	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	n ₃₉	$N_{39} = n_{39} / \sum n_i$

Table 1. Cont.

The mass action concentration of the 39 items in Table 1 are denoted as N_1 , N_2 , N_3 , ..., and N_{39} , respectively. N_i is calculated using Equation (4):

$$N_i = \frac{n_i}{\sum n_i} \tag{4}$$

As complex molecules are derived from simple ion couples and molecules by chemical reactions, the mass action concentration of the complex molecules can be expressed by their corresponding reaction equilibrium constant (K_i) and the values of N_1 , N_2 , N_3 , N_4 , N_5 , and N_6 . K_i can be obtained by:

$$K_i = \exp(-\frac{\Delta G_i^{\theta}}{RT}) \tag{5}$$

2.2. Calculation of Standard Gibbs Free Energy for Complex Molecules

To calculate the standard Gibbs free energy change (ΔG_T^{θ}) for the formation of complex molecule by ion couples and simple molecules, the reactants and products are considered to be in dissolution state. For example, the formation of *m*MeO·*n*SiO₂ proceeds by the following way:

$$m(Me^{2+} + O^{2-}) + n(SiO_2) \rightarrow (mMeO \cdot nSiO_2) \quad \Delta G^{\theta}_{solution}$$
(6)

where *m* and *n* are positive integers and $\Delta G^{\theta}_{\text{solution}}$ is the standard Gibbs free energy change in dissolution state. However, obtaining $\Delta G^{\theta}_{\text{solution}}$ data under such condition is often difficult. In contrast, if the reaction occurs in solid state, as shown in Equation (7), the standard Gibbs free energy change, $\Delta G^{\theta}_{\text{solid}}$, is easier to acquire.

$$m(\mathrm{Me}^{2+} + \mathrm{O}^{2-})_{(s)} + n(\mathrm{SiO}_2)_{(s)} \to (m\mathrm{MeO} \cdot n\mathrm{SiO}_2)_{(s)} \quad \Delta G^{\theta}_{\mathrm{solid}}$$
(7)

It is well known that the dissolution of a certain component into flux melts can be divided into two steps. The first step involves melting the component from solid to liquid state, $\Delta_{fus}G_i^{\theta}$. The second step involves further dissolution into flux melts, $\Delta_{sol}G_i^{\hat{\theta}}$. The changes of the standard Gibbs free energy for the above steps are equal, that is $\Delta_{fus}G_i^{\theta} = -\Delta_{sol}G_i^{\theta}$ [18,19]. Therefore, the following relation can be obtained:

$$\Delta G_{\text{solution}}^{\theta} = \Delta G_{\text{solid}}^{\theta} + \Delta_{\text{fus}} G_{\text{i}}^{\theta} + \Delta_{\text{sol}} G_{\text{i}}^{\theta} = \Delta G_{\text{solid}}^{\theta} \tag{8}$$

Generally, ΔG_T^{θ} could be expressed a function of temperature [20] by:

$$\Delta G_T^{\theta} = \Delta H_{298\mathrm{K}}^{\theta} - T \Delta \Phi_T \tag{9}$$

$$\Delta H_{298K}^{\theta} = \sum \left(n_i \Delta H_{i,298K}^{\theta} \right)_{\text{product}} - \sum \left(n_j \Delta H_{j,298K}^{\theta} \right)_{\text{reactant}}$$
(10)

$$\Delta \Phi_T = \sum \left(n_i \Phi_{i,T} \right)_{\text{product}} - \sum \left(n_j \Phi_{j,T} \right)_{\text{reactant}} \tag{11}$$

where, n_j is the stoichiometric number of reactant j; ΔH_{298K}^{θ} is the standard enthalpy change of reaction at 298 K; $\Delta \Phi_T$ is the standard Gibbs function change of reaction at T; ΔG_T^{θ} in the form of $\Delta G_T^{\theta} = A + BT$ for these reactions are listed in Table 2.

Table 2. Reaction formulas for the formation of complex molecules.

Reaction	ΔG_T^{Θ}	K _i	N_i	Ref.
$(Ca^{2+} + O^{2-}) + (SiO_2) \rightarrow (CaO \cdot SiO_2)$	-92,500 + 1.25T	$K_7=rac{N_7}{N_1N_4}$	$N_7 = K_7 N_1 N_4$	[10]
$\begin{array}{c} 2(\text{Ca}^{2+} + \text{O}^{2-}) + \\ (\text{SiO}_2) \rightarrow (2\text{CaO} \cdot \text{SiO}_2) \end{array}$	-102,090 - 24.267 <i>T</i>	$K_8 = \frac{N_8}{N_1^2 N_4}$	$N_8 = K_8 N_1^2 N_4$	[21]
$3(Ca^{2+} + O^{2-}) + (SiO_2) \rightarrow (3CaO \cdot SiO_2)$	-118,826 - 6.694T	$K_9 = \frac{N_9}{N_1^3 N_4}$	$N_9 = K_9 N_1^3 N_4$	[21]
$3(Ca^{2+} + O^{2-}) + 2(SiO_2) \rightarrow (3CaO \cdot 2SiO_2)$	-236,814 + 9.623T	$K_{10} = rac{N_{10}}{N_1^3 N_4^2}$	$N_{10} = K_{10} N_1{}^3 N_4{}^2$	[21]
$(Ca^{2+} + O^{2-}) + (Al_2O_3) \rightarrow (CaO \cdot Al_2O_3)$	59,413 – 59.413 <i>T</i>	$K_{11} = \frac{N_{11}}{N_1 N_3}$	$N_{11} = K_{11}N_1N_3$	[21]
$\begin{array}{c} (\mathrm{Ca}^{2+} + \mathrm{O}^{2-}) + \\ 2(\mathrm{Al}_2\mathrm{O}_3) \rightarrow (\mathrm{Ca}\mathrm{O} \cdot 2\mathrm{Al}_2\mathrm{O}_3) \end{array}$	-16,736 - 25.522 <i>T</i>	$K_{12} = \frac{N_{12}}{N_1 N_3^2}$	$N_{12} = K_{11} N_1 N_3^2$	[21]
$\begin{array}{c} (\mathrm{Ca}^{2+} + \mathrm{O}^{2-}) + \\ 6(\mathrm{Al}_2\mathrm{O}_3) \rightarrow (\mathrm{CaO} \cdot 6\mathrm{Al}_2\mathrm{O}_3) \end{array}$	-22,594 - 31.798 <i>T</i>	$K_{13} = \frac{N_{13}}{N_1 N_3^6}$	$N_{13} = K_{13} N_1 N_3^6$	[21]
$3(Ca^{2+} + O^{2-}) + (Al_2O_3) \rightarrow (3CaO \cdot Al_2O_3)$	-21,757 - 29.288 <i>T</i>	$K_{14} = \frac{N_{14}}{N_1^3 N_3}$	$N_{14} = K_{14} N_1{}^3 N_3$	[21]
$12(Ca^{2+} + O^{2-}) + 7(Al_2O_3) \rightarrow (12CaO \cdot 7Al_2O_3)$	617,977 – 612.119 T	$K_{15} = \frac{N_{15}}{N_1^{12}N_3^7}$	$N_{15} = K_{15} N_1^{\ 12} N_3^{\ 7}$	[21]
$(Ba^{2+} + O^{2-}) + (SiO_2) \rightarrow (BaO \cdot SiO_2)$	-154,238 - 2.926T	$K_{16} = \frac{N_{16}}{N_2 N_4}$	$N_{16} = K_{16} N_2 N_4$	[22]
$\begin{array}{c} (\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ 2(\mathrm{SiO}_2) \rightarrow (\mathrm{BaO} \cdot 2\mathrm{SiO}_2) \end{array}$	-169,365 + 1.496T	$K_{17} = \frac{N_{17}}{N_2 N_4^2}$	$N_{17} = K_{17} N_2 N_4^2$	[22]
$\begin{array}{c} 2(\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ (\mathrm{SiO}_2) \rightarrow (2\mathrm{BaO} \cdot \mathrm{SiO}_2) \end{array}$	-264,183 - 3.395T	$K_{18} = rac{N_{18}}{N_2^2 N_4}$	$N_{18} = K_{18} N_2^2 N_4$	[22]
$\begin{array}{c} 2(\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ 3(\mathrm{SiO}_2) \rightarrow (2\mathrm{BaO} \cdot 3\mathrm{SiO}_2) \end{array}$	-337,580 + 7.039T	$K_{19} = \frac{N_{19}}{N_2^2 N_4^3}$	$N_{19} = K_{19} N_2^2 N_4^3$	[22]
$\begin{array}{c} (\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ (\mathrm{Al}_2\mathrm{O}_3) \rightarrow (\mathrm{BaO} \cdot \mathrm{Al}_2\mathrm{O}_3) \end{array}$	-99,760 - 25.413 <i>T</i>	$K_{20} = \frac{N_{20}}{N_2 N_3}$	$N_{20} = K_{20} N_2 N_3$	[22]
$\begin{array}{c} (\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ 6(\mathrm{Al}_2\mathrm{O}_3) \rightarrow (\mathrm{BaO} \cdot 6\mathrm{Al}_2\mathrm{O}_3) \end{array}$	-126,813 - 24.293T	$K_{21} = \frac{N_{21}}{N_2 N_3^6}$	$N_{21} = K_{21} N_2 N_3^6$	[22]
$\begin{array}{c} 3(\mathrm{Ba}^{2+} + \mathrm{O}^{2-}) + \\ (\mathrm{Al}_2\mathrm{O}_3) \rightarrow (3\mathrm{Ba}\mathrm{O}\cdot\mathrm{Al}_2\mathrm{O}_3) \end{array}$	-187,633 - 37.528T	$K_{22} = \frac{N_{22}}{N_2^3 N_3}$	$N_{22} = K_{22} N_2{}^3 N_3$	[23]
$\begin{array}{c} 3(\mathrm{Al}_2\mathrm{O}_3) + \\ 2(\mathrm{SiO}_2) \rightarrow (3\mathrm{Al}_2\mathrm{O}_3 \cdot 2\mathrm{SiO}_2) \end{array}$	-4354 - 10.467T	$K_{23} = \frac{N_{23}}{N_3^3 N_4^2}$	$N_{23} = K_{23}N_3{}^3N_4{}^2$	[22]
$\begin{array}{c} (2\mathrm{Li}^{+} + \mathrm{O}^{2-}) + \\ (\mathrm{SiO}_{2}) \rightarrow (\mathrm{Li}_{2}\mathrm{O} \cdot \mathrm{SiO}_{2}) \end{array}$	-143,757 + 3.796T	$K_{24} = \frac{N_{24}}{N_6 N_4}$	$N_{24} = K_{24}N_6N_4$	[22]
$\begin{array}{c}(2\mathrm{Li^{+}}+\mathrm{O^{2-}})+\\2(\mathrm{SiO}_{2})\rightarrow(\mathrm{Li}_{2}\mathrm{O}{\cdot}2\mathrm{SiO}_{2})\end{array}$	-145,174 - 1.372T	$K_{25} = \frac{N_{25}}{N_6 N_4^2}$	$N_{25} = K_{25} N_6 N_4^2$	[22]
$\begin{array}{c} 2(2\text{Li}^{+} + \text{O}^{2-}) + \\ (\text{SiO}_2) \rightarrow (2\text{Li}_2\text{O} \cdot \text{SiO}_2) \end{array}$	-230,237 + 15.442 <i>T</i>	$K_{26} = \frac{N_{26}}{N_6^2 N_4}$	$N_{26} = K_{26} N_6^2 N_4$	[22]

Reaction	ΔG_T^{Θ}	K_i	N_i	Ref.
$\begin{array}{c}(2\mathrm{Li}^{+}+\mathrm{O}^{2-})+\\(\mathrm{Al}_{2}\mathrm{O}_{3}){\rightarrow}(\mathrm{Li}_{2}\mathrm{O}{\cdot}\mathrm{Al}_{2}\mathrm{O}_{3})\end{array}$	-106 , 327 - 16.567 <i>T</i>	$K_{27} = rac{N_{27}}{N_6 N_3}$	$N_{27} = K_{27} N_6 N_3$	[22]
$(Ba^{2+} + O^{2-}) + 3(Ca^{2+} + O^{2-}) + 2(SiO_2) \rightarrow (BaO \cdot 3CaO \cdot 2SiO_2)$	-376,298 + 8.751 <i>T</i>	$K_{28} = \frac{N_{28}}{N_2 N_1^3 N_4^2}$	$N_{28} = K_{28} N_2 N_1^3 N_4^2$	[22]
$2(Ba^{2+} + O^{2-}) + 4(Ca^{2+} + O^{2-}) + 3(SiO_2) \rightarrow (2BaO \cdot 4CaO \cdot 3SiO_2)$	-533,550 + 269.292 <i>T</i>	$K_{29} = \frac{N_{29}}{N_2^2 N_1^4 N_4^3}$	$N_{29} = K_{29} N_2^2 N_1^4 N_4^3$	[22]
$(Ba^{2+} + O^{2-}) + 2(Ca^{2+} + O^{2-}) + 4(Al_2O_3) \rightarrow (BaO \cdot 2CaO \cdot 4Al_2O_3)$	-157,255 - 85.113T	$K_{30} = \frac{N_{30}}{N_2 N_1^2 N_3^4}$	$N_{30} = K_{30} N_2 N_1^2 N_3^4$	[22]
$3(Ba^{2+} + O^{2-}) + (Ca^{2+} + O^{2-}) + (Al_2O_3) \rightarrow (3BaO \cdot CaO \cdot Al_2O_3)$	-139,905 - 42.192T	$K_{31} = \frac{N_{31}}{N_2^3 N_1 N_3}$	$N_{31} = K_{31} N_2{}^3 N_1 N_3$	[22]
$(Ca^{2+} + O^{2-}) + (Al_2O_3) + 2(SiO_2) \rightarrow (CaO \cdot Al_2O_3 \cdot 2SiO_2)$	-4184 - 73.638T	$K_{32} = \frac{N_{32}}{N_1 N_3 N_4^2}$	$N_{32} = K_{32} N_1 N_3 N_4^2$	[23,24]
$2(Ca^{2+} + O^{2-}) + (Al_2O_3) + (SiO_2) \rightarrow (2CaO \cdot Al_2O_3 \cdot SiO_2)$	-116,315 - 38.911 <i>T</i>	$K_{33} = \frac{N_{33}}{N_1^2 N_3 N_4}$	$N_{33} = K_{33} N_1^2 N_3 N_4$	[23,24]
$(Ba^{2+} + O^{2-}) + (Al_2O_3) +$ 2(SiO ₂) \rightarrow (BaO·Al ₂ O ₃ ·2SiO ₂)	-198,791 - 38.497T	$K_{34} = \frac{N_{34}}{N_2 N_3 N_4^2}$	$N_{34} = K_{34} N_2 N_3 N_4{}^2$	[22]
$3(Ca^{2+} + O^{2-}) + 2(SiO_2) + (Ca^{2+} + 2F^{-}) \rightarrow (3CaO \cdot 2SiO_2 \cdot CaF_2)$	-255,180 - 8.20T	$K_{35} = \frac{N_{35}}{N_1^3 N_4^2 N_5}$	$N_{35} = K_{35} N_1{}^3 N_4{}^2 N_5$	[23,24]
$3(Ca^{2+} + O^{2-}) + 3(Al_2O_3) + (Ca^{2+} + 2F^{-}) \rightarrow (3CaO_3Al_2O_3) - (CaF_2)$	-44,492 - 73.15T	$K_{36} = \frac{N_{36}}{N_1^3 N_2^3 N_2^3 N_2}$	$N_{36} = K_{36} N_1{}^3 N_3{}^3 N_5$	[23,24]
$11(Ca^{2+} + O^{2-}) + 7(Al_2O_3) + (Ca^{2+})$ + 2E ⁻) $\times (11C_2O_2O_2O_2O_2O_2O_2O_2O_2O_2O_2O_2O_2O_$	-228,760 - 155.8T	$K_{37} = \frac{N_{37}}{N \cdot 11 N \cdot 7 N}$	$N_{37} = K_{37} N_1^{11} N_3^7 N_5$	[23,24]
$(2Li^{+} + O^{2-}) + (Al_2O_3) + (SiO_2) \rightarrow (I i_2O_3 Al_2O_3) + (Al_2O_3) + $	-136,270 - 37.516T	$K_{38} = \frac{N_{38}}{N_{1}N_{1}N_{2}}$	$N_{38} = K_{38} N_6 N_3 N_4^2$	[19]
$(2\text{Li}^{+} + O^{2-}) + (Al_2O_3 + 2SiO_2)$ $(2\text{Li}^{+} + O^{2-}) + (Al_2O_3) + 4(SiO_2) \rightarrow (\text{Li}_2O \cdot Al_2O_3 \cdot 4SiO_2)$	-128,739 - 48.253T	$K_{39} = \frac{N_{39}}{N_6 N_3 N_4 4}$	$N_{39} = K_{39} N_6 N_3 N_4^4$	[19]

Table 2. Cont.

2.3. Mass Action Concentration for Structural Units and Ion Couples

The initial mole contents of CaO, BaO, Al₂O₃, SiO₂, CaF₂, and Li₂O are denoted as a_1 , a_2 , a_3 , a_4 , a_5 , and a_6 , respectively. Based on the principle of mass conservation:

$$a_{1} = (0.5N_{1} + N_{7} + 2N_{8} + 3N_{9} + 3N_{10} + N_{11} + N_{12} + N_{13} + 3N_{14} + 12N_{15} + 3N_{28} + 4N_{29} + 2N_{30} + N_{31} + N_{32} + 2N_{33} + 3N_{35} + 3N_{36} + 11N_{37})\sum n_{i}$$
(12)

$$a_{2} = (0.5N_{2} + N_{16} + N_{17} + 2N_{18} + 2N_{19} + N_{20} + N_{21} + 3N_{22} + N_{28} + 2N_{29} + N_{30} + 3N_{31} + N_{34})\sum n_{i}$$

$$(13)$$

$$a_{3} = (N_{3} + N_{11} + 2N_{12} + 6N_{13} + N_{14} + 7N_{15} + N_{20} + 6N_{21} + N_{22} + 3N_{23} + N_{27} + 4N_{30} + N_{31} + N_{32} + N_{33} + N_{34} + 3N_{36} + 7N_{37} + N_{38} + N_{39})\sum n_{i}$$

$$(14)$$

$$a_{4} = (N_{4} + N_{7} + N_{8} + N_{9} + 2N_{10} + N_{16} + 2N_{17} + N_{18} + 3N_{19} + 2N_{23} + N_{24} + 2N_{25} + N_{26} + 2N_{26} + 3N_{29} + 2N_{32} + N_{33} + 2N_{34} + 2N_{35} + 2N_{38} + 4N_{39})\sum n_{i}$$

$$(15)$$

$$a_5 = (1/3N_5 + N_{35} + N_{36} + N_{37})\sum n_i \tag{16}$$

$$a_6 = (1/3N_6 + N_{24} + N_{25} + 2N_{26} + N_{27} + N_{38} + N_{39}) \sum n_i$$
(17)

To solve Equations (12)–(17), Matlab software was subsequently used for further calculations, and the unique solutions of N_1 , N_2 , N_3 , N_4 , N_5 , and N_6 were obtained. Thus, the activity calculation model for CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O mold flux system could be developed.

2.4. Steel-Slag Contact Experiment

The schematic of the apparatus to conduct steel–slag contact experiment is shown in Figure 1. The compositions of mold flux and steel are listed in Table 3. Total content of Al_2O_3 and SiO_2 in the flux is designed to be constant as 27 wt%. The content of Al in steel is 1.49 wt%, which belongs to grades of high-Mn, high-Al steels. Before the contact experiment, 80 g of each mold flux was prepared using chemically pure reagents, and pre-melted in a silica-molybdenum furnace at 1573 K for compositional homogeneity. After cooling, the mold flux was ground into fine powder. For each run, approximately 320 g of steel sample was placed in a MgO crucible and heated. Then, the molten steel was

maintained isothermally at 1773 K for 20 min. Subsequently, 80 g of pre-melted flux was dispensed onto the top surface of the molten steel, at which moment was recorded as the start time of steel–slag reaction. To avoid the effect of oxygen, the contact experiments were conducted under Ar atmosphere at a flow rate of 1 L/min. After the reaction time reached 12 min, the MgO crucible with molten steel and flux was taken out and cooled at room temperature. The compositions of mold flux before and after contact experiment were analyzed by the methods of ICP-OES (ICAP 6300 Duo made by Thermo Scientific IRIS Intrepid II, MA, USA) and XRF (ARL Perform X made by Thermo Fisher).



Figure 1. Schematic of apparatus for the steel-slag reaction.

		CaO	BaO	Al ₂ O ₃	SiO ₂	F	Li ₂ O
S	S-1	36.5	24	21	6	8	4.5
171	S-2	36.5	24	19	8	8	4.5
Fluxes	S-3	36.5	24	17	10	8	4.5
	S-4	36.5	24	15	12	8	4.5
Ste	el	C 0.17	Al 1.49	Mn 22.7	Si 0.22	S 0.02	Fe Bal.

Table 3. Initial composition of mold fluxes and steel for the contact experiment (wt%).

3. Model Validation

To validate the accuracy of established model to predict the activity of various components in flux melts, the comparisons between the prediction by the current study and the calculation by Factsage and the literature [17,25–28] were made on the activity of the reactive component, SiO₂. The flux melts were CaO-Al₂O₃-SiO₂-CaF₂, CaO-BaO-Al₂O₃-SiO₂, and Li₂O-SiO₂, respectively. It should be noted that the accuracy of the current model was indirectly validated, and all components in Table 3 were taken into consideration. At present, Factsage is a popular thermodynamic software to calculate the activity for simple flux systems with 2–4 components. However, as the data of BaO and CaF₂ belong to two separate databases, the activities of the components in the CaO-Al₂O₃-SiO₂-CaF₂ and CaO -Al₂O₃-SiO₂-BaO systems were validated, respectively. Rey [27] and Charles [28] have obtained the activity data of SiO₂ in Li₂O-SiO₂ binary system with the SRS model (sub-regular solution model).

CaO-Al₂O₃-SiO₂-BaO and CaO-Al₂O₃-SiO₂-CaF₂

Table 4 summarizes the compositions of the CaO-Al₂O₃-SiO₂-BaO and the CaO-Al₂O₃-SiO₂-CaF₂ quaternary flux systems and the corresponding activity of SiO₂. The deviation (ΔX) for the difference between IMCT model and Factsage was calculated by Equation (18), 0.5% to 24.2% for CaO-Al₂O₃-SiO₂-BaO melt, and 0.2% to 11.0% for

 $CaO-Al_2O_3-SiO_2-CaF_2$ melt. The close agreement indicates that the IMCT model is reliable for quaternary flux system.

$$\Delta X = \frac{\left|k_{i,cal} - k_{i,fit}\right|}{\left|k_{i,fit}\right|} \times 100\%$$
(18)

where N represents the number of the samples; $k_{i,cal}$ is the value calculated from Factsage; $k_{i,fit}$ is the fitted value derived from the relationship between calculated values of Factsage and IMCT model.

Table 4. Composition of the CaO-Al₂O₃-SiO₂-BaO/CaF₂ quaternary flux system (wt%) and activity of SiO₂.

	CaO	BaO	Al ₂ O ₃	SiO ₂	CaF ₂	k _{i,cal}	k _{i,fit}	ΔX
	20	30	10	40	0	-0.670	-0.884	0.242
	20	40	10	30	0	-1.241	-1.549	0.199
	20	50	10	20	0	-2.378	-2.234	0.064
	30	30	10	30	0	-1.494	-1.711	0.127
CaO-Al ₂ O ₃ -SiO ₂ -BaO	40	20	10	30	0	-1.763	-1.943	0.093
	50	10	10	30	0	-2.093	-2.411	0.132
	50	20	20	10	0	-4.632	-4.653	0.005
	40	20	30	10	0	-3.983	-4.049	0.016
	30	20	40	10	0	-2.851	-3.383	0.157
	36	0	16	40	8	-0.969	-1.006	0.037
	40	0	16	36	8	-1.297	-1.294	0.002
	40	0	22	30	8	-1.734	-1.623	0.068
	40	0	34	18	8	-2.552	-2.627	0.029
	40	0	40	12	8	-2.879	-3.236	0.110
$CaO-AI_2O_3-SIO_2-CaF_2$	36	0	8	40	16	-0.876	-0.846	0.035
	40	0	8	36	16	-1.188	-1.111	0.069
	40	0	14	30	16	-1.729	-1.529	0.131
	40	0	26	18	16	-2.731	-2.795	0.023
	40	0	32	12	16	-3.106	-3.302	0.059

Due to the lack of measured activities for Li_2O-SiO_2 binary system, the calculated activity of (SiO_2) by the IMCT model was compared with those estimated by SRS model [27,28], as shown in Figure 2. When the Li_2O content was below 20 wt%, the values of SiO_2 activity predicted by SRS model were slightly higher than those predicted by the current study. When the Li_2O content was higher than 25%, the values of SiO_2 activity predicted by the IMCT model agreed more closely with those predicted by Ref. [27]. The comparison in Figure 2 indicated that the IMCT model has acceptable credibility to predict the SiO_2 activity in melts containing Li_2O .



Figure 2. Activities of SiO₂ estimated by the IMCT model and sub-regular solution model for Li₂O-SiO₂ binary system.

In summary, the reliability of the established thermodynamic model based on IMCT was indirectly confirmed by separately validating three flux systems that contained all six interested components in Table 3.

4. Contact Experiment of Steel-Slag Reaction

The compositions of mold fluxes before and after the contact experiment are listed in Table 5. It is clearly shown that as the initial content of SiO_2 increased from 6.07% to 12.18%, the reduced content of SiO_2 after the contact experiment also increased from 1.02% to 3.60%. Because high content of SiO₂ favors the reaction between [Al] and (SiO₂) at the steel-slag interface, the oxidized Al₂O₃ dissolves into flux and the reduced Si enters into the steel pool. As the duration time of 12 min was short, the content of typical volatile components $(Li_2O \text{ and } F^-)$ attenuated slightly (less than 1%). The detection of MgO was caused by the erosion of MgO crucible at a high temperature. Figure 3 shows the variation of SiO₂ and Al_2O_3 in the mold flux before and after contact experiments. When the content of SiO₂ in mold flux was no more than 8%, the increment of Al_2O_3 (ΔAl_2O_3) was approximately 7.1%, and the decrement of SiO_2 (ΔSiO_2) was approximately 16.8%. As soon as the content of SiO_2 rose to 10% and even higher, ΔAl_2O_3 changed obviously from 18.4% to more than 34.2%, and ΔSiO_2 reached 30%. The variation of ΔAl_2O_3 and ΔSiO_2 indicated clearly that critical content of components may play a part in determining the extent of steel-slag reaction. Some references reported that the steel-slag reaction did not occur once the content of (SiO_2) was less than 7 wt% [4] or in the range of 5–10 wt% [9] for conventional CaO-Al₂O₃-based flux.

Table 5. Composition of mold flux before and after steel-slag reaction (wt%).

Mold Flux	Before/After	CaO	BaO *	Al_2O_3	SiO ₂	F	Li ₂ O	MgO
S-1	Initial	36.70	24.00	20.82	6.07	8.00	4.08	0.00
	Final	35.20	23.00	22.31	5.05	7.60	3.78	2.55
S-2	Initial	36.41	24.00	19.12	8.21	6.90	4.12	0.00
	Final	35.80	23.00	21.01	6.90	6.80	3.81	2.46
S-3	Initial	36.23	24.00	17.09	10.11	7.20	4.05	0.00
	Final	35.10	23.00	20.24	7.09	7.00	3.35	2.32
S-4	Initial	36.15	24.00	15.24	12.18	7.00	4.07	0.00
	Final	33.71	23.00	20.45	8.58	6.80	3.74	2.89

* The BaO content is the analytical reference value.



Figure 3. Variations of Al_2O_3 and SiO_2 before and after steel–slag reaction.

5. Effect of Different Factors

Equation (1) can be expressed in the form of Equation (19):

$$\Delta G = \Delta G^{\theta} + RT \ln \frac{a_{\rm [Si]}^3}{a_{\rm [Al]}^4} + \Delta G_{\rm react}^{\theta}$$
(19)

$$\Delta G_{react}^{\theta} = RT \ln \frac{a_{(Al_2O_3)}^2}{a_{(SiO_2)}^3}$$
(20)

where $\Delta G_{\text{react}}^{\theta}$ denotes the Gibbs free energy change involving the activities of (SiO₂) and (Al₂O₃) in mold flux, and is a parameter characterizing the reactivity of mold flux.

5.1. Mass Ratio of Al₂O₃/SiO₂

When the CaO-SiO₂-based flux is applied to cast high-Mn, high-Al steel, the content of (SiO_2) decreases and that of (Al_2O_3) increases continuously during casting, resulting in changes in the composition of flux and the deterioration of physical properties of flux. Change in the flux composition is mainly related to the substitution of SiO_2 with Al_2O_3 , that is, the change of Al_2O_3/SiO_2 ratio. In the present study, a promising flux for casting high-Mn, high-Al steel was selected as the original flux [29] and SiO₂ was gradually replaced with Al_2O_3 (the Al_2O_3/SiO_2 ratio ranges from 0.29 to 8.00) to investigate variations in the activities of (SiO_2) and (Al_2O_3) and the reactivity of mold flux. The contents of the other components in the original flux are listed in Table 6. Figure 4 shows that with the increase in mass ratio of Al₂O₃/SiO₂ from 0.29 to 8.0, the activity of (SiO₂) first decreased rapidly, and then decreased slowly when the mass ratio of the Al_2O_3/SiO_2 was beyond 3.5, and the activity of (Al₂O₃) changed slightly. Meanwhile, the decrease in the reactivity of flux was similar to that trend of (SiO_2) . Figure 4 also demonstrates that increasing the mass ratio of Al₂O₃/SiO₂ could effectively weaken the reactivity of flux contacting steel with high content of [Al]. Although with further increase above 3.5, the effect on weakening the reactivity of mold flux was extremely limited, indicating that the reactivity of flux approached to the minimum. Therefore, for this six-component flux system, the mass ratio of Al_2O_3/SiO_2 of 3.5 can be regarded as the critical value, below which the reactivity of mold flux is prominent and the reaction between [Al] and (SiO₂) at the steel–slag interface occurs easily.



Figure 4. Effect of mass ratio of Al_2O_3/SiO_2 on the activities of Al_2O_3 and SiO_2 and the reactivity of mold flux.

Variable	CaO	BaO	Al ₂ O ₃	SiO ₂	CaF ₂	Li ₂ O	Sum	Interval
Al ₂ O ₃ , SiO ₂	20	20	8–32	28-4	16	8	100	4
CaF_2	CaO:Ba	aO = 1:1	24	12	4-28	8	100	4
Li ₂ O	CaO:Ba	aO = 1:1	24	12	16	2–14	100	2

Table 6. Composition of various flux systems for investigating the effect of components on the activities of Al_2O_3 and SiO_2 (wt%).

Figure 5 shows the mole fraction of complex molecules that rank the top three in amount as a function of the mass ratio of Al_2O_3/SiO_2 . The top three were all silicates, when the content of Al_2O_3 was low and the ratio was 0.29. As the mass ratio of Al_2O_3/SiO_2 increased from 0.29 to 8.0, the total mole fraction of silicates decreased sharply, and aluminates ($Li_2O \cdot Al_2O_3$, and $3BaO \cdot Al_2O_3$) became the main units whose mole fraction reached 17.8%. The increase in the proportion of aluminate-type complex molecules also attributed to the relative stable activity of (Al_2O_3) with the increase in the mass ratio of Al_2O_3/SiO_2 in Figure 4. The variation of silicates and aluminates demonstrates that the flux system gradually transformed from CaO-SiO₂-based to CaO-Al₂O₃-based mold flux.



Figure 5. Mole fraction of the top three complex molecules as a function of mass ratio of Al₂O₃/SiO₂.

5.2. Content of CaF₂

CaF₂ is a common fluxing agent that can greatly reduce the viscosity of flux. Moreover, it can form cuspidine $(3CaO \cdot 2SiO_2 \cdot CaF_2)$ combining with CaO and SiO₂ and favor decreasing the horizontal heat transfer between the solidify strand and mold. The content of F^- in commercial flux typically ranges from 2 to 14 wt% [30], corresponding to a CaF₂ content range of 4-28 wt%. Figure 6 shows the effect of CaF₂ content on the activities of (SiO_2) and (Al_2O_3) and the reactivity of mold flux. The increased activities of (SiO_2) and (Al_2O_3) and the reactivity of flux indicated that the reaction between [Al] and (SiO_2) was enhanced with the addition of CaF₂. The decreased viscosity with CaF₂ addition is expected to intensify the kinetic condition of the steel-slag reaction. Hence, there is a need to keep the content of CaF_2 as low as possible, while ensuring appropriate lubrication and heat transfer of mold flux. Figure 7 shows the top three complex molecules with different contents of CaF₂. For the current flux system with fixed contents of 24 wt% Al₂O₃ and 12 wt% SiO₂, the main structure units were $Li_2O \cdot Al_2O_3$ and $2CaO \cdot SiO_2$, while both of their contents attenuated gradually with increased content of CaF₂ from 4 wt% to 28 wt%. The decreased content of silicates and aluminates was consistent with the predicted increased activities of simple molecule (Al_2O_3 and SiO_2), indicating that the number of free SiO₂ and Al₂O₃ was enhanced with increased addition of CaF₂.



Figure 6. Effect of CaF₂ content on the activities of Al₂O₃ and SiO₂ and the reactivity of mold flux.



Figure 7. Mole fraction of the top three complex molecules as a function of CaF₂ content.

5.3. Content of Li₂O

It is well known that the common fluxing agents, Na₂O and B₂O₃, can react with [Al], whereas Li₂O does not participate in the steel–slag reaction, and is able to reduce the melting temperature and viscosity of mold flux [31]. Thus, Li₂O is a promising fluxing agent for designing low-reactivity flux. Figure 8 shows the effect of Li₂O content. The activities of (SiO₂) and (Al₂O₃) and the reactivity of mold flux decreased gradually, which indicated that the reactivity between [Al] and (SiO₂) was weakened. As the content of Li₂O increased from 2 wt% to 14 wt%, the reactivity of flux increased first and then decreased with a maximum at 6 wt%, indicating the compositional region around 6 wt% Li₂O should be avoided in the development of low-reactivity flux. Figure 9 lists the top three complex molecules. The increased addition of Li₂O made the mole fraction of silicate and aluminate containing Li₂O be enlarged obviously, and the mole fraction of (2CaO·SiO₂) and (BaO·Al₂O₃) decreased gradually.



Figure 8. Effect of Li_2O content on the activities of Al_2O_3 and SiO_2 and the reactivity of mold flux.



Figure 9. Mole fraction of the top three complex molecules as a function of Li₂O content.

6. Conclusions

A thermodynamic model to predict the activities of components in low-reactive CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O mold flux was established based on IMCT. The conclusions can be summarized as follows:

- 1. The results calculated by IMCT model are good accordance to the experiment results and Factsage calculation. The thermodynamic model based on IMCT could predict the activity of each component in the low-reactive CaO-BaO-Al₂O₃-SiO₂-CaF₂-Li₂O mold flux accurately and has good reliability.
- With the increase in mass ratio of Al₂O₃/SiO₂, the decreases in the activity of SiO₂ and the reactivity of mold flux had a turning point when the ratio of Al₂O₃/SiO₂ was 3.5, where the content of SiO₂ was 8 wt%.
- 3. The activities of SiO₂ and Al₂O₃ and the reactivity of mold flux increased continuously with an increase in the content of CaF₂, which is unfavorable for developing low-reactivity mold flux. However, to avoid compromising other physical properties, the CaF₂ should be kept to a minimum.
- 4. The activities of SiO₂ and Al₂O₃ decreased with an increase in Li₂O content, whereas the reactivity of mold flux had a maximum with 6 wt% Li₂O content, indicating that the compositional regions involving around 6 wt% Li₂O content should be avoided to design the low-reactive flux system.

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