Mathematical Modelling Study of Dynamic Composition Change of Steel and Mold Flux in Continuous Casting of Steel

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A kinetic model was developed to describe multicomponent reactions and mass transfer at the steel/molten flux interface under the effect of the interfacial tension. This model mainly describes the following interfacial physicochemical phenomena: i) Silica decomposition and oxygen adsorption at the interface, ii) Oxygen and titanium reactions at the interface, iii) Oxygen and aluminum reaction at the interface, iv) Silica mass transfer from the flux bulk to the interface, and v) Dissolution of the formed titanium dioxide and alumina into the flux and its transfer in flux. With this model, the dynamic changes of the mold flux composition, steel composition, interfacial oxygen content and interfacial tension for different mold flux compositions were predicted. Overall, the dynamic composition changes of the mold fluxes in a casting mold were reproduced. The basicity of the mold flux shows a large influence on the dynamic change of its composition. The initial composition change of the mold flux is fast when the flux with a high basicity was used, compared with the case of the mold flux with a low basicity. The interfacial oxygen content and the interfacial tension were found to reach a constant value after the steel/flux reaches a metastable state. In addition, the interfacial adsorption of oxygen due to the interfacial tension effect was found to significantly accelerate the dynamic change process of the steel/mold flux system.

KEY WORDS: steel-flux interfacial reaction; mass transfer; mold flux; continuous casting; interfacial tension; oxygen adsorption.

1. Introduction

Mold flux plays an important role in the continuous casting of steels to protect the steel from air reoxidation, to lubricate between the solidified steel shell and the copper mold, to control the heat transfer near the meniscus, and to remove the non-metallic inclusions for the last chance in steel production. In general, CaO–SiO$_2$-type mold flux is widely used in steel continuous casting mold due to its good performance for the lubrication. However, the existence of a large amount of SiO$_2$ in the mold flux easily leads to some intensive interfacial reactions between SiO$_2$ and some reductive elements in different steel grades. Chemical reactions will change the composition of the mold flux as well as the mold flux properties during a casting process.$^{1,2}$ The composition change is a very complex process which involves interfacial reactions and mass transfer. In addition, these phenomena might also be influenced by the existence of the interfacial tension between steel and mold flux. During continuous casting process, the changes of mold flux properties may lead to unstable heat transfer and insufficient lubrication, which might result in severe surface defects of the steel products like cracks and depressions.$^{3-5}$ This problem not only exists in high-alloyed steel casting such as transformation induced plasticity (TRIP) steels and twin-induced plasticity (TWIP) steels,$^{1,6}$ but it also exists in the continuous casting of some low-alloyed steels.$^7$ Therefore, it is important to understand the dynamic evolution of the mold flux composition during the continuous casting of steel, and to minimize this change to realize a stable casting process.

In the past, many experimental studies have been carried out to reveal the dynamic process of the composition change of slag/flux and steel.$^{8-14}$ These efforts aim to understand the mechanism as well as the controlling step for the dynamic composition change process. Furthermore, it is also a basis to find the proper way to realize different purposes in steel production process, either stabilizing the interface or enhancing the mixing of steel and slag. Ooi et al.$^8$ found that SiO$_2$ reduction at the steel/slag interface was the rate-controlling step in Fe-4Al steel alloy. However, the mass transfer of Al in liquid steel was found to be the rate-controlling step of the dynamic change of the flux composition.$^{9-11}$ Park et al.$^{12}$ found that the steel/slag interfacial kinetics was a mixed control process when SiO$_2$ content in slag is low, where the mass transfer both in steel and in slag should be considered. A recent study by Kim...
et al.\textsuperscript{13} suggested that the mass transport of Al in liquid steel does not control the reaction rate any more when the Al content in steel is high such as 5.2 wt% in their study, and the mass transport in the flux phase probably becomes the reaction rate controlling step. In addition, the mass transfer coefficients of Al in steel have been measured in some studies which have been summarized by Kim et al.\textsuperscript{13} However, the values from different studies show a large difference. Besides the experimental investigations, kinetic models were also developed based on the single Al transfer, single SiO\textsubscript{2} transfer or combined transfer as the controlling step.\textsuperscript{12,13} In addition, some kinetic models were also developed to describe the steel/slag reaction during metal refining process.\textsuperscript{14–16} This kind of kinetic model is based on the groundbreaking kinetic model-coupled reaction model, which was developed by Robertson et al.\textsuperscript{14} in 1984 and now are widely used to predict the process kinetics in metallurgical field. These models are based on the assumption that the mass flux balance and the reaction equilibrium exist at the interface. In addition, the effect of the interfacial tension between steel and slag/mold flux on the interfacial reaction and mass transfer was not considered.

A direct observation of this dynamic process due to steel/flux reaction can be found from the measurement of the contact angle change as well as interfacial tension change between steel and mold flux.\textsuperscript{2} The mechanism of this dynamic change has previously been reported. Riboud and Lucas\textsuperscript{17} and Gaye et al.\textsuperscript{18} proposed the following steps to describe the dynamic composition change of steel and flux: i) the oxygen flux from the flux to the interface, ii) the oxidizable element flux towards the interface, iii) the reactions at the interface, and iv) the diffusion of the reaction products to the flux phase. During the process, the interfacial tension decreases sharply as the mass transfer is intense, while it recovers to a high value as soon as the mass transfer slows down.\textsuperscript{17,18} Tanaka et al.\textsuperscript{2} proposed a mechanism to describe the dynamic change of the interfacial tension due to the adsorption and desorption of oxygen at an interface. This dynamic change of the interfacial tension was suggested to occur in the following steps: i) an oxygen element transfer from the flux to the interface, ii) an oxygen element adsorption at the interface due to the interfacial tension, iii) an oxygen desorption from the interface to the steel bulk, iv) an oxygen reaction with the reductive elements, and v) the transfer and dissolution of the reaction products into a flux phase. Based on the above proposed mechanism by Tanaka et al.,\textsuperscript{2} Ni et al.\textsuperscript{19} developed a kinetic model to describe this kind of dynamic change behaviors of the interfacial oxygen content as well as the interfacial tension, where the silica decomposition at the interface, the oxygen adsorption and desorption at the interface and the mass transfer in the steel and flux phase were considered. Later on, aluminum reaction with the interfacial oxygen was included in the kinetic model.\textsuperscript{20} Therefore, it is a complete model which considered both the chemical reaction and the mass transfer. Furthermore, to our knowledge, this is the first kinetic model to describe the dynamic interfacial phenomena of steel and flux, where the effect of the interfacial tension on the interfacial reaction and mass transfer was included. This makes the kinetic model special with respect to describing the kinetics of the steel/flux system close to the reality where the interfacial tension exists, compared to some previously reported kinetic models.\textsuperscript{12–16}

In this paper, a new kinetic model was further developed based on the previous model developed by Ni et al.\textsuperscript{19,20} to include the multicomponent reactions with oxygen in the interfacial region in a continuous casting mold. This new model considers the following mechanisms: i) silica decomposition and oxygen adsorption at the interface, ii) reaction between oxygen and reductive elements in steel at the interface, iii) oxygen desorption from the interface to the steel bulk, iv) silica mass transfer from the molten flux to the interface, v) dissolution of the formed interfacial reaction products into the flux and their transfer in the flux. The dynamic changes of the mold flux composition, steel composition, interfacial oxygen content and interfacial tension for different mold fluxes were predicted. Furthermore, the influence of the interfacial adsorption, due to the interfacial tension effect, on the dynamic change of the steel and mold flux compositions was investigated.

2. Model Description

Due to the chemical potential difference of the components in a steel and mold flux, chemical reactions can happen as soon as that the mold flux comes in contact with steel in a continuous casting mold. Therefore, the interfacial phenomena between steel and mold flux are coupled with interfacial reactions and mass transfers under the effect of the interfacial tension. A one-dimensional multicomponent kinetic model was developed in this paper, based on the previously developed models.\textsuperscript{19,20} Figure 1 shows the schematic of the four-layer kinetic model for multicomponent interfacial reactions and mass transfers. It is impossible to solve the dynamic composition change directly at an interface. Instead, a small thickness of the steel interfacial layer, \( h_{\text{steel}} \), assumed to be 1 \( \mu \)m was used as the interfacial tension active region. The slag interfacial layer, \( h_{\text{flux}} \), is equal to \( h_{\text{steel}}/(k_{\text{si}}/k_{\text{si}}} \), where \( k_{\text{si}} \) and \( k_{\text{si}} \) represent the mass transfer coefficient in metal and in flux, respectively. Thus, the ratio of \( h_{\text{si}}/h_{\text{flux}} \) is equal to the ratio of \( k_{\text{si}}/k_{\text{si}} \). The real thickness of the interfacial layer is unknown, which may be in the size of several atom layers. To solve the thickness in the size of several atoms is impossible for a macroscale model. Therefore, the thickness value of 1 \( \mu \)m was used as a first step in this study. The steel/flux interface was assumed to

![Fig. 1. Schematic of the kinetic model with four layers. (Online version in color.)](image-url)
be flat to simplify the model. The whole dynamic process is described as below.

2.1. SiO\textsubscript{2} Decomposition and Oxygen Adsorption at Interface\textsuperscript{19}

SiO\textsubscript{2} decomposition reaction can happen at the steel/flux interface as soon as that steel and flux are in contact with each other and when the oxygen chemical potential in steel is lower than the equilibrium value corresponding to the SiO\textsubscript{2} potential in flux. The SiO\textsubscript{2} decomposition rate at the interface has been described in detail in our previous study\textsuperscript{19} and it can be expressed by the following equations:

\[ \Delta \beta = \beta_{\text{mixing-flux}} \cdot k_{\text{Si}} \left( \beta_{\text{Si}} \beta_{\text{O}} - E_{\text{SiO}} \beta_{\text{Si}} \beta_{\text{O}} \right) \cdots (1) \]

where the superscript * represents the sub-interface layer, \( \Delta \beta \) is the weight percent change in the flux sub-interface at each time step, \( \Delta \) is the time step, \( k_{\text{Si}} \) is the apparent reaction rate of the SiO\textsubscript{2} decomposition, \( \beta_{\text{Si}} \) and \( \beta_{\text{O}} \) are the oxygen activity in the steel sub-interface, and \( \beta_{\text{SiO}} \) is the mass transfer coefficient of SiO\textsubscript{2} in flux.

\[ E_{\text{SiO}} = \frac{(\%\text{SiO}_2)^{\text{eq}} f_{\text{Si}}^{\text{eq}} [\text{Si}]}{f_{\text{SiO}}^{\text{eq}} [\text{SiO}_2]} = \frac{100C_{\text{SiO}_2} K_{\text{SiO}_2}}{\rho_{\text{SiO}_2}} \cdots (2) \]

\[ \Delta G^\circ = -RT \ln K_{\text{SiO}_2} = -581900 + 221.8T \cdots (4) \]

\[ [\text{O}] = [\text{O}]^* \cdots (3) \]

\[ [\text{Si}] = [\text{Si}]^* \cdots (4) \]

\[ (\text{SiO}_2)^{\text{eq}} f_{\text{SiO}} = (\text{SiO}_2)^{\text{eq}} f_{\text{SiO}} \cdots (5) \]

where the superscript \( b \) represents bulk, the equilibrium constant \( K_{\text{SiO}_2} \) for reaction (R2) is known from Eq. (4) when pure SiO\textsubscript{2} was selected as the standard state,\textsuperscript{21} and the equilibrium constant \( K_{\text{O}} \) for the oxygen adsorption in reaction (R3) is unknown. The interfacial adsorption of oxygen can reduce the interfacial energy of steel and flux. Furthermore, the equilibrium constants for reactions (R4) and (R5) are assumed to be one. This means that their distributions do not influence the interfacial tension. Therefore, the equilibrium constant \( K_{\text{SiO}_2}^{\star} \) for reaction (R1), \( K_{\text{SiO}_2} \) for reaction (R2) and \( K_{\text{O}} \) for reaction (R3) can be described by the following relationship:

\[ K_{\text{SiO}_2}^{\star} = \frac{K_{\text{SiO}_2}}{K_{\text{O}}^2} \cdots (5) \]

At every time step, only a part of SiO\textsubscript{2} in the flux sub-interface can reach the steel/flux interface. This means that not all the SiO\textsubscript{2} in the flux sub-interface take part in the reaction. Therefore, the parameter \( \beta_{\text{mixing-flux}} \) was used to describe the ratio of SiO\textsubscript{2} in the flux sub-interface, which takes part in the reaction at each time step as a result of the mass transfer effect. In addition, the brackets term on the right side of Eq. (1) is the driving force for the SiO\textsubscript{2} decomposition due to its chemical potential difference.

2.2. Interfacial Reactions of Reductive Elements with Oxygen

After a SiO\textsubscript{2} decomposition, the oxygen potential in the steel sub-interface becomes larger, compared to the value before the steel and flux contacts. In case that the oxygen chemical potential is higher than the value which is in equilibrium with the contents of reductive elements in the steel sub-interface such as aluminum, the chemical reaction between aluminum and oxygen may occur towards the buildup of a new equilibrium in the sub-interface. The new equilibrium compositions in the steel sub-interface are the target compositions, where the whole system automatically tends to reach to minimize the system Gibbs energy. However, this dynamic change process requires different times depending on the reaction rate and the element transport or mixing in the sub-interface. In this paper, Newton-Raphson method was used to calculate the equilibrium contents of aluminum, titanium and oxygen in the steel sub-interface at each time step.

2.2.1. Aluminum Reaction with Oxygen in the Steel Sub-Interface\textsuperscript{20}

The aluminum and oxygen reaction and the equilibrium distribution of aluminum in the steel bulk and in the interface can be expressed as follows:\textsuperscript{21}

\[ 2[\text{Al}]^{\circ} + 3[\text{O}]^{\circ} = (\text{Al}_2\text{O}_3)^{\text{eq}} \cdots (6) \]

\[ \Delta G^\circ = -RT \ln K_{\text{Al}_2\text{O}_3} = -1205115 + 386.7T \cdots (6) \]

\[ [\text{Al}]^{\circ} = [\text{Al}]^{\star} \cdots (7) \]

where \( K_{\text{Al}_2\text{O}_3} \) is the equilibrium constant for reaction (R6) when pure Al\textsubscript{2}O\textsubscript{3} is selected as the standard state. With the combination of reaction (R3), (R6) and (R7), the aluminum and oxygen reaction at the interface can be written as follows:

\[ 2[\text{Al}]^{\circ} + 3[\text{O}]^{\circ} = (\text{Al}_2\text{O}_3)^{\text{eq}} \cdots (8) \]

With the assumption that the interfacial tension does not have an influence on the aluminum distribution in steel, namely the equilibrium constant value of one for reaction (R7), the equilibrium constant of reaction (R8) can be calculated by using the following relationship:
where $a_{Al/O_2}$ is the alumina activity, $f_{Al}$ is the activity coefficient of aluminum, $E_{Al/O_2}$ is the modified equilibrium constant for reaction (R8), and [%Al] is the weight percent of Al in steel. As mentioned in a previous study, the reaction nucleation can occur in three different ways, namely i) a nucleation in steel, ii) a nucleation at the steel/flux interface and iii) a nucleation at the surface of Al$_2$O$_3$ inclusions in steel. The apparent reaction rate due to the first mechanism might be related to the excess amount of [Al] and [O] in steel. For the second and the third mechanism, the chance of the [Al] and [O] elements to come in contact with the nucleation site is proportional to the element concentration. Since the apparent reaction rate is related to the number of the effective nucleation sites, the apparent reaction rate might also be related to the element concentration. In this model, we simply relate the apparent reaction rate to the excessive product of [Al] and [O] by using the following relationship:

$$k_{r_{Al}} = \left[ \lambda_{Al} \times (1.0 - E_{Al/O_2}' / E_{Real,Al}) \right] E_{Al/O_2}' < E_{Real,Al}$$

where $\lambda_{Al}$ is a general coefficient, and $E_{Real,Al}$ is the product of the chemical potentials of [Al] and [O] in the steel sub-interface at each time step. Therefore, the apparent reaction rate increases with an increased element content. Finally, the change of the aluminum content in the steel sub-interface can be obtained by using the following equation:

$$\Delta[Al] = \beta_{mixing-steel} \cdot k_{r_{Al}} \cdot \Delta t \cdot \left[ \%Al \right] \cdot \left[ \%Al^{eq} \right]$$

where $\beta_{mixing-steel}$ is the parameter that describes the mixing characteristics of [Al] and [O] in the steel interfacial layer, and $\phi$ is a general coefficient. Furthermore, when $\beta_{mixing-steel} \cdot k_{r_{Al}} \cdot \Delta t$ is equal to 1, the reaction equilibrium condition is instantly obtained. In addition, the term in the brackets of Eq. (10) is the driving force for the Al reaction with oxygen towards an equilibrium state.

2.2.2. Titanium Reaction with Oxygen in the Steel Sub-Interface

The reaction of titanium and oxygen, and the equilibrium distribution of titanium in steel bulk and at the interface can be expressed as follows:

$$[Ti]^0 + 2[O]^0 = (TiO_2)^b_{eq} \quad (R9)$$

$$\Delta G^0 = -RT \ln K_{TiO_2} = -673.360 + 227.1T \quad (J/mol) \quad (R10)$$

where $K_{TiO_2}$ is the equilibrium constant for reaction (R9) when pure TiO$_2$ is selected as the standard state. With the combination of reaction (R3), (R9) and (R10), the titanium and oxygen reaction at the interface can be written as follows:

$$[Ti]^0 + 2[O]^0 = (TiO_2)_{eq} \quad (R11)$$

where $a_{TiO_2}$ is the TiO$_2$ activity, $f_{TiO_2}$ is the activity coefficient of titanium, $E_{TiO_2}$ is the modified equilibrium constant for reaction (R11), and $[\%Ti]$ is the weight percent of Ti in steel. The apparent reaction rate of titanium and oxygen has a similar form as that for the reaction of aluminum and oxygen as follows:

$$k_{r_{Ti}} = \left[ \lambda_{Ti} \times (1.0 - E_{TiO_2}' / E_{Real,ti}) \right] E_{TiO_2}' < E_{Real,ti}$$

where $\lambda_{Ti}$ is a general coefficient, and $E_{Real,ti}$ is the product of the chemical potentials of [Ti] and [O] in the steel sub-interface at each time step. Therefore, the change of the titanium content in the steel sub-interface for each time step can be obtained by using the following equation:

$$\Delta[\%Ti] = \beta_{mixing-steel} \cdot k_{r_{Ti}} \cdot \Delta t \cdot \left[ \%Ti \right] \cdot \left[ -[\%Ti]^{eq} \right]$$

where $[\%Ti]^{eq}$ is the new equilibrium content of titanium in the steel sub-interface. Furthermore, the value of $\beta_{mixing-steel} \cdot k_{r_{Ti}} \cdot \Delta t$ equal to 1 represents that an reaction equilibrium condition was obtained. In addition, the term in the brackets of Eq. (16) is the driving force for the titanium reaction with oxygen towards an equilibrium state.

2.3. SiO$_2$, Al$_2$O$_3$ and TiO$_2$ Transfer between Flux Bulk to Flux Sub-interface

Due to the SiO$_2$ decomposition, its content in the flux sub-interface decreases. Therefore, SiO$_2$ will transfer from the flux bulk to the flux sub-interface due to the chemical potential difference. Thus, at each time step, the amount of SiO$_2$ moving into the flux sub-interface can be expressed by the following equation:

$$\Delta[SiO_2]^b = \Delta \cdot A \cdot k_{SiO_2} \cdot \left[ \frac{(\%SiO_2)^b - (\%SiO_2)^s}{V_s} \right]$$

where the term $(\%SiO_2)^b$ is the weight percent of SiO$_2$ in the flux bulk.

Due to the interfacial reactions, TiO$_2$ and Al$_2$O$_3$ are formed. In a continuous casting mold, the interfacial velocity due to the steel flow in mold was supposed to increase the dissolution of these formed oxides into the flux phase. Therefore, the blockage of these formed oxides on the SiO$_2$ transfer which has been considered in a previous study was not considered in the current study. These formed oxides were supposed to be directly dissolved into the flux sub-interface. Their transfer between the flux sub-interface
and the flux bulk can be described by using the following equations:

\[ \Delta(\%\text{Al}_2\text{O}_3) = \Delta \cdot A \cdot k_{\text{Al}_2\text{O}_3} \cdot \left( \frac{\left(\%\text{Al}_2\text{O}_3\right)^* - \left(\%\text{Al}_2\text{O}_3\right)^b}{V} \right) \]  

(18)

\[ \Delta(\%\text{TiO}_2) = \Delta \cdot A \cdot k_{\text{TiO}_2} \cdot \left( \frac{\left(\%\text{TiO}_2\right)^* - \left(\%\text{TiO}_2\right)^b}{V} \right) \]  

(19)

where \(\%\text{Al}_2\text{O}_3\)^b and \(\%\text{Al}_2\text{O}_3\)^* is the weight percent of \(\text{Al}_2\text{O}_3\) in the flux bulk and sub-interface, respectively. Furthermore, \(\%\text{TiO}_2\)^b and \(\%\text{TiO}_2\)^* is the weight percent of \(\text{TiO}_2\) in the flux bulk and sub-interface. \(k_{\text{Al}_2\text{O}_3}\)

and \(k_{\text{TiO}_2}\) are the mass transfer coefficient of \(\text{Al}_2\text{O}_3\) and \(\text{TiO}_2\) in flux, respectively.

2.4. Elements Transfer between Steel Sub-interface and Steel Bulk

Silicon, aluminum and titanium are supposed not to be a surfactant element. Therefore, their mass transfer coefficients from the sub-interface to the bulk are assumed not to be influenced by the interfacial tension. However, oxygen is a surfactant element. Thus, its desorption from the interfacial region to the steel bulk might be slow when the oxygen content is very low in the sub-interfacial region. Finally, the weight percent change of oxygen and silicon in the flux bulk and sub-interface can be expressed by using the following equations, respectively:

\[ \Delta(\%\text{Si}) = \Delta \cdot k_{\text{Si}} \cdot A \cdot \left( \frac{\left(\%\text{Si}\right)^* - \left(\%\text{Si}\right)^b}{V} \right) \]  

(20)

\[ \Delta(\%\text{O}) = \Delta \cdot k_{\text{O}} \cdot A \cdot \left( \frac{\left(\%\text{O}\right)^* - \left(\%\text{O}\right)^b}{V} \right) \]  

(21)

\[ \Delta(\%\text{Ti}) = \Delta \cdot k_{\text{Ti}} \cdot A \cdot \left( \frac{\left(\%\text{Ti}\right)^* - \left(\%\text{Ti}\right)^b}{V} \right) \]  

(22)

\[ \Delta(\%\text{Al}) = \Delta \cdot k_{\text{Al}} \cdot A \cdot \left( \frac{\left(\%\text{Al}\right)^* - \left(\%\text{Al}\right)^b}{V} \right) \]  

(23)

where \(k_{\text{Si}}\) is the mass transfer coefficient of metal m in steel, and \(k_{\text{O}}\) is the desorption rate of oxygen from the steel sub-interface to the bulk. Furthermore, \(\%\text{O}\)^b is the oxygen content in steel bulk which is in equilibrium with the interfacial oxygen content \(\%\text{O}\)^*. The parameter \(\%\text{O}\)^b can be obtained based on the reaction as follows:

\[ [\text{O}]^b_{\text{eq}} = [\text{O}]^* \]  

(R12)

\[ K_{\text{O}} = \frac{\alpha_{\text{O}}}{\alpha_{\text{O}}^b} = \frac{f_{\text{O}}(\%\text{O})^b}{f_{\text{O}}(\%\text{O})_{\text{eq}}} \]  

(24)

\[ [\%\text{O}]^b_{\text{eq}} = f_{\text{O}}(\%\text{O})^b / (K_{\text{O}} f_{\text{O}}^b) \]  

(25)

where \(\alpha_{\text{O}}\) and \(\alpha_{\text{O}}^b\) is the oxygen activity in bulk and at interface, respectively. Finally, the transfer of oxygen from the sub-interface to the steel bulk can be obtained as follows by inserting Eq. (25) into Eq. (21):

\[ \Delta(\%\text{O}) = \Delta \cdot k_{\text{O}} \cdot A \cdot \left( \frac{f_{\text{O}}(\%\text{O})^b / (K_{\text{O}} f_{\text{O}}^b) - \left(\%\text{O}\right)^b}{V} \right) \]  

(26)

2.5. Estimation of Oxygen Desorption Rate from Interface to Bulk\(^{19}\)

The surfactant element tends to stay at the locations where a large interfacial tension exists. Therefore, the oxygen desorption rate from the interface should properly be evaluated to include the influence of the interfacial tension on this value. This has been described in our previous study\(^{19}\) where the oxygen desorption rate was related to the slope of the interfacial tension change as a function of the interfacial oxygen activity. The dependence of the interfacial tension, \(\sigma\), on the interfacial oxygen activity, at a constant temperature, is as follows based on the relationship between the interfacial tension and the bulk oxygen activity in the literature:\(^{25}\)

\[ \frac{d\sigma}{d\alpha_{\text{O}}^b} = \frac{d\sigma}{d(K_{\text{O}} \alpha_{\text{O}}^b)} = -RT \gamma \frac{\sigma}{(K_{\text{O}} + \gamma \alpha_{\text{O}}^b)} \]  

(27)

where \(R\) is the gas constant, \(\Gamma^0\) is the adsorption at a full coverage, \(\gamma\) is the partition constant under the assumption of an adsorption equilibrium, and \(T\) is temperature. A larger value of \(\frac{d\sigma}{d\alpha_{\text{O}}^b}\) illustrates a higher dependence of the interfacial tension on the interfacial oxygen activity. This means that it is not easy for the oxygen to leave the interface once it reaches there. On the other hand, a smaller value means that the dependence of the interfacial tension on the oxygen content is smaller. In this case, oxygen can easier leave the interface. In an extreme situation, for example with the slope value of 0, the interfacial tension is independent on the element content. Then, the element can pass through the interface without being influenced by the interfacial tension.

According to a previous experimental study,\(^{26}\) the values of \(RT \gamma\) are equal to 314 and 116, respectively. The dependence of interfacial tensions on the bulk oxygen activity \(a_{\text{O}}^b\) can be expressed as follows:\(^{25,26}\)

\[ \sigma = 1386 - 324ln(1 + 116a_{\text{O}}^b) \]  

(28)

If the relationship in reaction (R3) is considered, the interfacial tension values have the following relationship with the interfacial oxygen activity:\(^{19}\)

\[ \sigma = 1386 - 324ln(1 + 116a_{\text{O}}^b / K_{\text{O}}) \]  

(29)

Equation (29) was used in this paper to calculate the interfacial tension value after the interfacial oxygen content was predicted by the current model. Finally, the oxygen desorption rate from the interface was expressed by the following equation:\(^{19}\)

\[ k_{\text{O}} = k_0 \cdot \left(1 - \frac{1}{\left(1 + \frac{\gamma \alpha_{\text{O}}^b}{K_{\text{O}}}\right)}\right) \]  

(30)

where \(\alpha\) is a general coefficient and the \(k_0^b\) is the mass transfer coefficient of oxygen in steel bulk. The brackets part represents the modified factor to include the interfacial tension effect. With the slope definition in Eq. (27), the oxygen desorption rate coefficient can be obtained as follows:

\[ k_{\text{O}} = \alpha \cdot \left[ \frac{\frac{d\sigma}{d\alpha_{\text{O}}^b}_{\%\text{O}=0} - \frac{d\sigma}{d\alpha_{\text{O}}^b}_{\%\text{O}=0}}{\frac{d\sigma}{d\alpha_{\text{O}}^b}} \right] \cdot k_0^b \]  

(31)
2.6. Model Solving Procedures

The procedure to solve the kinetic model is shown in Fig. 2. The solving order on Ti reaction with oxygen and Al reaction with oxygen did not influence the solution in this study. In order to get a stable solution, a small time step is required and the value was set to 0.00005 s in this study. This guarantees a small composition change in the sub-interface layer at each time step. The liquid steel and molten flux were assumed to be in contact with each other at the time of 0 s. In addition, the values of parameters used in the model are shown in Table 1. The oxygen adsorption equilibrium constant and the oxygen desorption coefficient are not known and they were assumed to 50 and 0.2, respectively. Oxide activities change with time due to the flux composition change in reactions. As a first step, constant values of them were used. According to calculations by using FactSage 7.1 based on the flux composition changes in a real casting process,7) the activities of TiO$_2$ in high basicity flux 1 and low basicity flux 2 after the reaction are 0.087 and 0.127, respectively. Since the TiO$_2$ amount in sub-interfacial flux layer must be higher than that in the flux bulk, higher values of activities were used in this study, namely 0.1 and 0.2 for flux 1 and flux 2, respectively. The activities of Al$_2$O$_3$ in these two fluxes are very small, and the value of

![Fig. 2. Solution procedure for the kinetic model.](image)

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<table>
<thead>
<tr>
<th>Properties</th>
<th>Symbol</th>
<th>Mold Flux 1</th>
<th>Mold Flux 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial flux composition (both in Sub interface and in Bulk), wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(%CaO)</td>
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<td>19</td>
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<td>(%SiO$_2$)</td>
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<td>4</td>
<td></td>
</tr>
<tr>
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<td>12</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>(%CaF$_2$)</td>
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<td>13</td>
<td></td>
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<tr>
<td>Initial steel composition (Bulk and Sub-interface), wt%</td>
<td>[%Si]</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>[%Mn]</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[%Al]</td>
<td>0.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[%Ti]</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[%O]</td>
<td>0.0015</td>
<td></td>
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<tr>
<td>Flux density, g/mm$^3$</td>
<td>$\rho$</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td>Metal density, g/mm$^3$</td>
<td>$\rho_m$</td>
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<td></td>
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<tr>
<td>Flux weight, g</td>
<td>$W_f$</td>
<td>1 875</td>
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<tr>
<td>Flux volume, mm$^3$</td>
<td>$V_f$</td>
<td>750 000</td>
<td></td>
</tr>
<tr>
<td>Metal volume, mm$^3$</td>
<td>$V_m$</td>
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<tr>
<td>Metal weight, g</td>
<td>$W_m$</td>
<td>36 750</td>
<td></td>
</tr>
<tr>
<td>Total molar concentration in flux, mol/mm$^3$</td>
<td>C</td>
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<tr>
<td>SiO$_2$ mole weight, g/mol</td>
<td>$M_{SiO_2}$</td>
<td>60</td>
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<tr>
<td>Interfacial area, mm$^2$</td>
<td>A</td>
<td>150 000</td>
<td></td>
</tr>
<tr>
<td>Interfacial oxygen adsorption Equilibrium Constant</td>
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<tr>
<td>Interface oxygen partition coefficient</td>
<td>$\gamma$</td>
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<td></td>
</tr>
<tr>
<td>Mass-transfer coefficient in steel, mm/s</td>
<td>$k_{Al} = k_{Ti} = k_{Si} = k_{Bu}$</td>
<td>0.3</td>
<td>0.15</td>
</tr>
<tr>
<td>Mass-transfer coefficient in flux, mm/s</td>
<td>$k_{SiO_2} = k_{TiO_2} = k_{Al_2O_3} = k_s$</td>
<td>0.03</td>
<td>0.015</td>
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<tr>
<td>SiO$_2$ decomposition rate coefficient, s$^{-1}$</td>
<td>$k_{Si}$</td>
<td>3 000</td>
<td>1 500</td>
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<tr>
<td>Equilibrium Constant for SiO$_2$ decomposition</td>
<td>$K_{SiO_2}$</td>
<td>$1.22 \times 10^9$ at 1 823 K</td>
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<tr>
<td>Equilibrium Constant for Al$_2$O$_3$ decomposition</td>
<td>$K_{Al_2O_3}$</td>
<td>$2.14 \times 10^{14}$ at 1 823 K</td>
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</tr>
<tr>
<td>Equilibrium Constant for TiO$_2$ decomposition</td>
<td>$K_{TiO_2}$</td>
<td>$2.7 \times 10^7$ at 1 823 K</td>
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<tr>
<td>Activity of Al$_2$O$_3$</td>
<td>$a_{Al_2O_3}$</td>
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<tr>
<td>Activity of TiO$_2$</td>
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<td>0.2</td>
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<tr>
<td>SiO$_2$ activity coefficient</td>
<td>$\gamma_{SiO_2}$</td>
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<td></td>
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<tr>
<td>O desorption coefficient in Eq. (31)</td>
<td>$\alpha$</td>
<td>0.2</td>
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<tr>
<td>[O] activity coefficient</td>
<td>$f_{O} = f_{O}^*$</td>
<td>First-order Interaction coefficient</td>
<td></td>
</tr>
<tr>
<td>[Al] activity coefficient</td>
<td>$f_{Al} = f_{Al}^*$</td>
<td>First-order Interaction coefficient</td>
<td></td>
</tr>
<tr>
<td>[Ti] activity coefficient</td>
<td>$f_{Ti} = f_{Ti}^*$</td>
<td>First-order Interaction coefficient</td>
<td></td>
</tr>
<tr>
<td>[Si] activity coefficient</td>
<td>$f_{Si} = f_{Si}^*$</td>
<td>First-order Interaction coefficient</td>
<td></td>
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<tr>
<td>Al reaction coefficient in Eq. (9)</td>
<td>$\lambda_{Al}$</td>
<td>6 000</td>
<td></td>
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<tr>
<td>Ti reaction coefficient in Eq. (15)</td>
<td>$\lambda_{Ti}$</td>
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<tr>
<td>General coefficient for mixing</td>
<td>$\phi$</td>
<td>15</td>
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</tbody>
</table>

Note: b and * represent bulk and sub-interface.
0.01 was used in the calculation. The activity coefficients of SiO$_2$ changed from 0.33 (before reaction) to 0.22 (after reaction) for flux 1, and changed from 0.26 to 0.29 for flux 2. Thus, the constant value of 0.27 was used in this study. Based on these parameters, the reaction coefficients $\lambda_{\text{Al}}$, $\lambda_{\text{Ti}}$, and $k_{\text{Si}}$ were determined to fit with the experimental data.\(^{7)}\)

In order to know the chemical potential of elements, first order activity interaction coefficients of elements in steel were used and shown in Table 2. The compositions of the mold flux and steel, the weight of the flux and the value of the interfacial area in the current model are set to be the same as that in a real casting mold in a previous study,\(^{7)}\) since the model predictions were compared to the industrial measurements to show the model performance.

### 3. Results and Discussion

#### 3.1. Dynamic Change Characteristics of Steel/Mold Flux

The dynamic change of the mold flux composition has been predicted with the parameters shown in Tables 1 and 2 by using the multicomponent kinetic model. Figure 3 shows the predicted bulk composition changes of different mold fluxes and their comparison to the experimental data.\(^{7)}\) It can be seen that the kinetic model reproduces the composition change of the mold flux in a real continuous casting process. Specifically, SiO$_2$ content in mold flux decreased with time, with the value from 43 wt% decreasing to around 30 wt% for mold flux 1 in Fig. 3(a) and the value from 51 wt% decreasing to around 42 wt% in Fig. 3(b). Due to the interfacial reaction, TiO$_2$ content in mold flux increased with time, with the value from 0 wt% to around 15 wt% and 10 wt% for flux 1 and flux 2, respectively. Al$_2$O$_3$ content in mold flux has only a slight increase at the initial moment. This is a similar situation for these two mold flux. Figure 4 shows the dynamic changes of flux compositions in the sub-interface layer. It can be seen that in the initial period, the

<table>
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<tr>
<th>$e_{ij}$</th>
<th>O</th>
<th>Al</th>
<th>Ti</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
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<td>O</td>
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<td>−0.021</td>
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<td>Ti</td>
<td>−1.8</td>
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<td>0.013</td>
<td>−0.043</td>
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<td>−0.165</td>
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<td>Mn</td>
<td>−0.083</td>
<td>0</td>
<td>−0.05</td>
<td>0</td>
<td>0</td>
<td>−0.07</td>
</tr>
<tr>
<td>Si</td>
<td>−0.23</td>
<td>0.058</td>
<td>0.002</td>
<td>0.11</td>
<td>0.18</td>
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</table>

Table 2. First-order Activity interaction coefficient of elements in steel.\(^{27,28)}\)

![Fig. 3. Model predicted composition change of the mold flux bulk with time and its comparison with experimental data,\(^{7)}\) (a) Mold flux 1 with a high basicity and (b) Mold flux 2 with a low basicity. (Online version in color.)](https://example.com/fig3)

![Fig. 4. Model predicted composition change of the mold flux in sub-interface with time and its comparison with experimental data,\(^{7)}\) (a) Mold flux 1 with a high basicity and (b) Mold flux 2 with a low basicity. (Online version in color.)](https://example.com/fig4)
oxide content in the flux sub-interface is higher than that in the bulk. However, the difference almost disappeared when the metastable stage was reached.

The time required to reach a metastable state is different for different mold flux systems. For mold flux 1 with a high basicity, the time required to reach a metastable state is around 600 s, while the value for mold flux 2 with a low basicity is around 1 000 s. The flux basicity influences the mass transfer in the molten flux. Furthermore, it will influence the interfacial flow behavior as well as the mixing behavior of steel and molten flux in a mold during a continuous casting. This might in turn affect the mass transfer and chemical reaction in the interfacial region. In the molten flux with a low basicity, SiO$_2$ may exist in the form of some large networks. The decomposition rate of SiO$_2$ in the form of a large network may be different from that with a short network as well as a high basicity. Therefore, different steel volumes, SiO$_2$ decomposition rate depending on the flux basicity, and mass transfer coefficients in molten flux were used in the calculations for different flux compositions. In summary, with the parameters shown in Tables 1 and 2, the developed kinetic model reproduced the dynamic changes of the mold flux compositions in a steel continuous casting process.

The dynamic change of the interfacial oxygen content as well as the interfacial tension values with the casting time in mold were also predicted by the current model based on the micro interfacial region concept near the steel/flux interface, and they are shown in Fig. 5. It can be seen that the interfacial oxygen content fast reaches a high level with the value of around 0.03 wt% for both fluxes as soon as steel and flux come in touch with each other as shown in Fig. 5(a). Then, it first slowly increases and later on fast increases to constant values, with the values of around 0.065 wt% for the high basicity flux and 0.08 wt% for the low basicity flux. The time required to reach such a constant oxygen content namely metastable state is different for different flux basicity, where a high basicity flux requires a shorter time than that with a low basicity flux. When the flux basicity is low, the oxygen content initially is low compared to that with a high flux basicity. However, the final constant value is around 0.015 wt% larger than that with a high basicity flux. This is probably due to that, in the low basicity flux, the total amount of the SiO$_2$ is large. This low basicity flux can still provide oxygen from the SiO$_2$ decomposition after a long reaction time compared to that in the high basicity flux with a low SiO$_2$ content. With the interfacial oxygen content in Fig. 5(a), the interfacial tension value was calculated by using Eq. (29). It can be seen that the change behavior of the interfacial tension value is different for these two mold fluxes. However, the value difference after reaching the final constant level is only around 7 mN/m for these two fluxes.

Due to the interfacial reaction between the molten flux and the steel, steel compositions also undergo significant changes. Figure 6 shows the changes of Ti, Si and Al con-

![Fig. 5. Change of oxygen content in the interfacial region (a) and interfacial tension (b) with time. (Online version in color.)](image)

![Fig. 6. Changes of Si, Ti and Al content in steel bulk (a) and its comparison with that in steel sub-interface (b) with time for different fluxes. (Online version in color.)](image)
tent in steel bulk and sub-interface with the casting time. It can be seen that Si content show a large increase from 0.34 wt% to around 0.57 wt% and Ti content shows a large decrease from 0.33 wt% to around 0.005 wt%, for both of these two mold fluxes. Therefore, the metastable contents of these two elements for different fluxes are similar. However, the initial change trend shows a significant difference for different mold fluxes, where the change rate in the case of the high basicity flux is much larger than that with a low basicity flux. Furthermore, the aluminum content only shows a small decrease at the initial 500 s for the both cases. In addition, Fig. 6(b) shows that the comparison of the composition changes in steel bulk and in sub-interface layer. It can be seen that the composition change in the sub-interface at the initial moment is much faster than that in bulk, due to the immediate reaction between steel and flux after they come in contact with each other. Furthermore, Ti content in the sub-interface is smaller than that in steel bulk due to the interfacial reaction. This means that the supply of Ti from the bulk to the sub-interface layer also influences the interface reaction in the initial 1 000 s for flux 1 and the initial 1 500 s for flux 2. In addition, the total amount of Ti in steel decrease with the reaction going on. These may be the reason of the second period of the fast increase of the oxygen content as previously observed in Fig. 5(a).

3.2. Effect of Interfacial Adsorption on Dynamic Composition Change of Steel/Flux

The adsorption of some surfactant elements at the inter-face of the steel and mold flux might influence the interfacial phenomena, such as mass transfer across the interface. However, this has commonly been ignored in some reported kinetic models. The adsorption of oxygen at an interface has been described in Eq. (R3), which occurs to lower the interfacial tension between the steel and the mold flux. The intensity of the influence of such an adsorption is reflected by the value of the equilibrium constant Ko of Eq. (R3).

Figure 7 shows the dynamic composition changes of the mold flux 1 under different Ko values. It can be seen that the flux composition change becomes faster when a larger value of Ko was used. This means that interfacial adsorption can significantly influence the dynamic change of the interfacial behavior. With the Ko value of 1, the adsorption phenomenon does not occur. When the Ko value increased from 1 to 5, the dynamic change of the flux composition shows a large difference, with the maximum composition difference of around 7 wt% for SiO\textsubscript{2} and 8 wt% for TiO\textsubscript{2}. With a further increase of the Ko value from 5 to 20, it can be observed that the difference of the flux composition change becomes small, with the maximum difference smaller than around 3 wt% for SiO\textsubscript{2} and around 5 wt% for TiO\textsubscript{2}. With the Ko value increasing from 20 to 100, the difference further reduces, and a similar result was obtained for Ko values of 50 and 100. In addition, the influence of the adsorption on the Al\textsubscript{2}O\textsubscript{3} content change was very small, compared to its influence on SiO\textsubscript{2} and TiO\textsubscript{2}. This is due to that the aluminum content in steel is low and its reaction with oxygen is not the dominant reaction in the current steel-flux system.

![Figure 7](image-url)
can be seen from the composition change of Al$_2$O$_3$ content in flux that only around 2.5 wt% of Al$_2$O$_3$ was produced through the aluminum reaction with oxygen.

Figure 8 shows the dynamic change of the interfacial oxygen content and interfacial tension under different adsorption constant Ko values. It can be seen from Fig. 8(a) that the adsorption of oxygen at interface can directly influence both the interfacial oxygen content and the dynamic change behavior, where the oxygen content increases with an increased adsorption equilibrium constant value. Specifically, the maximum interfacial oxygen contents are in the level of around 0.0017 wt%, 0.0064 wt%, 0.013 wt%, 0.026 wt%, 0.067 wt% and 0.144 wt% for Ko values of 1, 5, 10, 20, 50 and 100, respectively. Figure 8(b) shows the dynamic changes of the interfacial tension with different Ko values. It can be seen that the interfacial tension changes show different behaviors for different Ko values, especially in the initial 500 s. However, the difference of the predicted interfacial tensions becomes smaller with time going on. Among these different Ko values, the values of 50 and 100 obtained a similar change behavior of interfacial tensions. When there is no interfacial adsorption influence, namely Ko=1, the interfacial tension change shows a different behavior, with a low interfacial value of around 1 340 mN/m and gradu-

![Fig. 8. Dynamic change of the interfacial oxygen content (a) and interfacial tension (b) under different adsorption constant values for steel/mold flux 1. (Online version in color.)](image_url)

![Fig. 9. Dynamic change of the steel bulk compositions for steel/mold flux 1, (a) Si content, (b) Ti content and (c) Al content. (Online version in color.)](image_url)
ally increasing to around 1 350 mN/m which is close to the predicted interfacial tension values with the other Ko values. The different behaviors induced by different Ko values should result from its influence on the reactions in the sub-interface layers. Figure 9 shows the dynamic changes of the steel bulk compositions under different Ko values. It can be seen that Ko value directly influence the reaction rate in the initial period, which can be found either from the increase of Si content in Fig. 9(a) or from the decrease of the Ti content in Fig. 9(b). However, its influence on the Al content in Fig. 9(c) is small.

4. Concluding Discussion

A kinetic model to describe multicomponent interfacial reactions and mass transfers between mold flux and steel under the effect of the interfacial tension has been developed in this study. With the input of the kinetic parameters in Table 1, the dynamic changes of the flux composition, steel composition, interfacial oxygen content and the interfacial tension were predicted. In this study, different values of the kinetic parameters such as the mass transfer coefficients in steel and slag were used for different flux basicity. This is due to that the flux basicity not only affects the mass transfer in flux, but it also affects the steel/slag flow or mixing behavior at the interface. Furthermore, the structure of a flux is closely related to its basicity, which may influence the decomposition rate of SiO$_2$. The main characteristics of the current model are that it includes the interfacial tension effect as well as the interfacial adsorption effect on the mass transfer and the chemical reactions. It was found that the interfacial adsorption can significantly influence the dynamic change characteristics of the steel/flux interface. Furthermore, it is also different from some other kinetic models for which the reaction equilibrium is assumed at the interface. However, experimental study is still required to get accurate kinetic parameters under different situations, such as the values of mass transfer coefficients in molten flux $k_t$ and in steel $k_{int}$, and the reaction rate coefficients for Ti, $\lambda_{Ti}$, and Al, $\lambda_{Al}$, with oxygen. These will influence the evolution speed of the whole steel/flux system. In addition, the oxide component activity in molten flux may change during the reaction process due to the flux composition change. This will be studied in future by combining the thermodynamic software to the kinetic model to update the thermodynamic parameters such as $\alpha_{AlO_2}$ and $\alpha_{TiO_2}$ at each time step.

5. Conclusions

A novel kinetic model was developed to describe multicomponent reactions and mass transfer at the steel/flux interface under the effect of the interfacial tension. This is a further effort based on the previously proposed model towards a more realistic model, where the SiO$_2$ decomposition and oxygen adsorption at an interface, aluminum and titanium reaction with oxygen at an interface, the oxygen desorption from an interface, and the mass transfers in steel and flux were considered. The following specific conclusions can be obtained from this study:

1. The dynamic changes of the mold flux composition were predicted by using the developed kinetic model, which reproduces the experimental data from a real casting mold.

2. The interfacial oxygen content first increases with time, and then reaches a constant value after the metastable state of the steel-flux system is reached. The interfacial tension value shows a decrease due to the interfacial oxygen increase, and then reaches a stable level. In the metastable state, the interfacial oxygen content was found to be larger for a low basicity flux than that with a high basicity flux, probably due to a high SiO$_2$ content in the low basicity flux.

3. Interfacial tension as well as the interfacial adsorption shows a large influence on the dynamic change of the mold flux composition, interfacial oxygen content and the interfacial tension. The interfacial adsorption accelerates the composition change of the mold flux and steel, as well as the steel/flux reaction.

Acknowledgments

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Nomenclature

- $n$: Sub-interface
- $m$: Bulk
- eq: Equilibrium state
- $A$: Metal
- $C$: Total molar concentration of the elements in the flux
- $M$: Volume
- $k_r$: Reaction rate coefficient, s$^{-1}$
- $h_{steel}$: Thickness of steel sub-interface, mm
- $h_{flux}$: Thickness of flux sub-interface, mm
- $\rho$: Flux density, g/mm$^3$
- $t$: Time, s
- $\%$: Weight percent in flux, wt%
- $\%Si$: Si content in steel, wt%
- $%Al$: Al content in steel, wt%
- $%O$: O content in steel, wt%
- $%Ti$: Ti content in steel, wt%
- $%Al_2O_3$: Al$_2$O$_3$ weight percent in flux, wt%
- $%TiO_2$: TiO$_2$ weight percent in flux, wt%
- $M_{SiO_2}$: Molecular weight of SiO$_2$, g/mol
- $k_{Si}$: SiO$_2$ decomposition rate, s$^{-1}$
- $k_{Al}$: Aluminum and oxygen reaction rate, s$^{-1}$
- $k_{Ti}$: Titanium and oxygen reaction rate, s$^{-1}$
- $Y_{SiO_2}$: Activity coefficient of SiO$_2$ in flux
- $Y_{Si}$: Activity coefficient of [Si] in steel
- $Y_{Al}$: Activity coefficient of [Al] in steel
- $Y_{Ti}$: Activity coefficient of [Ti] in steel
- $a_{AlO_2}$: Activity of the formed Al$_2$O$_3$
- $a_{TiO_2}$: Activity of the formed TiO$_2$
- $K_{SiO_2}$: SiO$_2$ decomposition reaction Equilibrium constant
- $K_{Al_2O_3}$: Al$_2$O$_3$ reaction Equilibrium constant

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$K_{\text{TiO}_2}$: TiO$_2$ reaction Equilibrium constant
$E_{\text{SiO}_2}$: Modified Equilibrium constant for SiO$_2$
$E_{\text{Al}_2\text{O}_3}$: Modified Equilibrium constant for Al$_2$O$_3$
$E_{\text{TiO}_2}$: Modified Equilibrium constant for TiO$_2$

$K_G$: Equilibrium constant for the oxygen adsorption at interface

$k_{\text{SiO}_2}$: SiO$_2$ mass transfer coefficient in flux, mm/s
$k_{\text{Al}_2\text{O}_3}$: Al$_2$O$_3$ mass transfer coefficient in flux, mm/s
$k_{\text{TiO}_2}$: TiO$_2$ mass transfer coefficient in flux, mm/s
$k_s$: Mass transfer coefficient of [Si] in steel, mm/s
$k_{\text{Al}}$: Mass transfer coefficient of [Al] in steel, mm/s
$k_{\text{Ti}}$: Mass transfer coefficient of [Ti] in steel, mm/s

$k_G$: Desorption rate of oxygen from steel sub-interface to bulk, mm/s
$k_o$: Mass transfer coefficient of oxygen in steel bulk, mm/s

$\beta_{\text{mixing-flux}}$: Ratio of SiO$_2$ in sub-interface that take part in decomposition reaction

$\beta_{\text{mixing-steel}}$: Mixing parameter in steel sub-interface

$\varphi$: General coefficient for mixing in steel sub-interface

$\sigma$: Surface or Interfacial tension, mN/m
$R$: Gas constant, J/(mol K)
$\Gamma$: Adsorption at a full coverage, mol/m$^2$
$T$: Temperature, K
$\gamma$: Partition constant under the assumption of adsorption equilibrium
$\alpha$: General coefficient for oxygen desorption
$\lambda_{\text{Al}}$: Al reaction coefficient, s$^{-1}$
$\lambda_{\text{Ti}}$: Ti reaction coefficient, s$^{-1}$

REFERENCES