A Kinetic Model on Oxygen Transfer at a Steel/Slag Interface under Effect of Interfacial Tension

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A kinetic model was developed to predict the dynamic change of the oxygen content in the sub-interface region as well as the dynamic change of the interfacial tension between molten steel and slag. The dynamic steel/slag interfacial phenomena are very complex, where the combined effect of thermodynamics and kinetics on the interfacial tension needs to be accounted for. As a first step, the current model only considers the SiO₂ decomposition, oxygen adsorption and desorption at the steel/slag interface to realize the modeling of the dynamic change of the steel/slag interface phenomena. The oxygen desorption rate was derived based on the slope of the interfacial tension change over oxygen content. Specifically, the oxygen change with time in a sub-interface was predicted by the current model. The oxygen desorption rate was found to have an important influence on the dynamic change of the oxygen content in the sub-interface region. Furthermore, a low slag viscosity was found to increase the oxygen content at the interface due to the fast supply of SiO₂ from the slag bulk to the interface. In addition, the equilibrium constant for the oxygen adsorption at an interface due to the interfacial tension effect increases the oxygen content in the sub-interface region.

KEY WORDS: steel-slag interface; mass transfer; thermodynamics; interfacial tension; dynamic modeling.

1. Introduction

The interfacial tension between liquid steel and molten slag is an important parameter in steel production. For different steps in production process, the desirable values of steel/slag interfacial tensions may have significant differences in order of magnitudes to realize different production purposes. Specifically, in order to make steel clean, a large value of the interfacial tension is desirable to prevent the entrainment of slag droplets into the liquid steel during steel casting. However, in some refining processes such as the desulfurization process, a small value of steel/slag interfacial tension is desirable, since it is easy to create an unstable interface as well as to create a dispersion of liquid steel and molten slag. This can promote chemical reactions, due to an increased interfacial reaction area when a good mixing can be obtained. Therefore, the steel/slag interfacial tension can not only influence the steel refining efficiency, but it can also influence the steel product quality.

Due to its importance, interfacial tensions between molten steel and molten slag have been vastly investigated for various slag compositions and iron alloys.1–10) It has commonly been shown that the steel/slag interfacial tension shows a dynamic change over time, due to that chemical reactions normally occur at the interface. Figure 1 shows the changes of the interfacial tension between steel and slag with time, which were measured by the sessile drop method.9) It can be seen that the interfacial tension firstly shows a sharp decrease after that the slag droplet touched the steel surface. Then, its value shows a steady increase with time. In addition, the minimum interfacial tension value between steel and a high viscous slag is larger than that for a low viscous slag.

The mechanism for this kind of dynamic steel/slag interfacial tension changes has been discussed in the past. Riboud and Lucas3) and Gaye et al.3) described a mechanism for the interfacial tension change due to the oxygen flux from slag to interface, the oxidizable element flux towards interface, the reactions at interface, and the diffusion of reaction products to the slag phase. The interfacial tension decreases sharply with an intense mass transfer, while it recovers to a high value as soon as the mass transfer slows down.2,3) Sharan and Cramb6) suggested that the difference in oxygen chemical potentials in steel and slag leads to an oxygen mass transfer from slag to steel. Furthermore, this causes a reduction of the interfacial tension. An initial high mass transfer rates results in a drastic reduction of the interfacial tension. As the reaction approaches equilibrium, the mass transfer rate is reduced and the interfacial tension approaches its equilibrium value. Richardson5) suggested that the buildup of interfacial charges during rapid reactions, namely the electrocapillary effect, may lead to the lowering of an interfacial tension due to an increased London forces or dipole interactions across the interface. The electrocapillary effect was later on found to...
be the dominant factor for the dynamic change of interfacial tensions by Rhamdhani et al. In addition, Chung and Cramb suggested that interfacial reactions result in a driven fluid flow due to the Marangoni effect and natural convection. The differences of flow velocities in steel and slag lead to the instability of the interface as well as a spontaneous emulsification of slag and metal.

Although the mechanism of the dynamic change of the interfacial tension between molten steel and molten slag is still not clearly understood, it is generally considered to be resulted from a mass transfer through the interface, especially for the oxygen element. Recently, Tanaka et al. 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 process of the interfacial tension change includes the following steps: i) an oxygen element transfer from the slag 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 reductive elements, and v) the transfer and dissolution of reaction products into a slag phase. Due to the small scale of the interface region and due to that complex chemical and physical phenomena occur in a rapid manner in the interfacial region, it is difficult to carry out direct observations during high-temperature steel/slag experiments. Therefore, modeling becomes a choice to help understand the dynamic interfacial phenomena.

In the past, some kinetic models have been proposed to describe the mass transfer from molten slag to liquid steel. However, the effects of the interfacial tension on both interfacial reactions and the transport of some interface active elements have been neglected. Furthermore, these models are based on the assumption that a mass balance and a reaction equilibrium exist at the interface. Specifically, the mass flux towards the interface is assumed to be equal to the mass flux leaving the interface. Therefore, it is difficult to predict the dynamic change of the concentrations of interface active elements in the near interface region as well as the dynamic change of the interfacial tension as observed in Fig. 1.

In this paper, a kinetic model was developed based on the proposed mechanism by Tanaka et al. to describe the dynamic behavior of the oxygen transfer at an interface due to the chemical potential difference between slag and steel. In this model, the influences of the interfacial tension on the interfacial reactions, for example, the decomposition of SiO$_2$ at an interface and on the transport of interfacial active elements were considered. As the first step, the kinetic model only includes the transport of SiO$_2$ from the slag towards the interface, the decomposition of SiO$_2$ at the interface and the adsorption and desorption of oxygen at interface. The aim of the model is to predict the dynamic change of the oxygen content near a steel/slag interface to reveal the mechanism of the dynamic interfacial phenomena.

2. Model Description

At a steel/slag interface, chemical reactions may occur depending on the chemical potentials of the components in steel and slag. These reactions are expected to be greatly affected by the interfacial tension as well as the adsorption of surfactant elements at the interface. The surfactant elements from chemical reactions can either stay at the near-interface region or be transported to the steel bulk. Therefore, adsorption equilibriums of the surfactant elements exist between elements in the steel bulk and in the interface. In addition, there should exist a near-interface region where the effect of the interfacial tension on the transport of surfactant elements is still active. This is assumed to be a short-distance effect, which leads to a small thickness at the near-interface region both in the slag side and in the steel side. Furthermore, the elemental transport from the interface regions to the bulk regions should depend on the chemical potential of interfacial active elements rather than their concentration, as previously has been discussed by Sharan and Cramb. Furthermore, the desorption coefficient for a surfactant element transport from the interface to the bulk should be properly evaluated to include the influence of the interfacial tension. After the elements move far away from the interface, their transports in the bulk are not affected by the interfacial tension. Figure 2 shows the mechanism of the dynamic interfacial phenomena after a slag phase comes in contact with a molten steel phase.

Based on the above explained mechanism, a one-dimensional kinetic model is proposed in this paper. In this model, the steel-slag system can either be divided into many layers parallel to the interface or it can be divided into four layers for a simple case. Figure 3 shows the schematic of the kinetic model with four layers as an example. The steel/slag interface was assumed to be flat to simplify the model. The thickness of the sub-interfacial layer, $h$, is set to be 20 $\mu$m. The mass transfer coefficient of the surfactant elements from the sub-interfacial layer to the bulk is affected by the interfacial tension.
2.1. Element Transport and Chemical Reaction in Interface Regions

SiO$_2$ decomposition reaction can happen at the steel/slag interface as soon as that steel and slag touch each other when the oxygen chemical potential in steel is lower than the equilibrium values corresponding to the SiO$_2$ potential in slag:

$$\text{(SiO}_2\text{)}_{\text{slag}} = [\text{Si}]_{\text{steel}} + 2[\text{O}]_{\text{steel}} \quad \text{(R1)}$$

The reaction kinetics can be expressed by the following equation:

$$\frac{d([\text{SiO}_2])}{dt} = k_r ([\text{SiO}_2]^* - [\text{SiO}_2]^q) \quad \text{(1)}$$

where the superscript * represents the sub-interface layer, $t$ is time, the left term is the rate change of the SiO$_2$ content in the slag, $k_r$ is the reaction constant of reaction (R1), and ([SiO$_2$])$^*$ is the weight percent of SiO$_2$ in the slag sub-interface layer. Furthermore, ([SiO$_2$])$^q$ is the equilibrium content of SiO$_2$ in weight percent, which corresponds to the chemical potential of [O] and [Si] in the steel sub-interface layer. The equilibrium of SiO$_2$ in slag ([SiO$_2$])$^q_{\text{slag}}$ corresponding to [O] and [Si] in steel can be expressed by the following interfacial reaction:

$$[\text{Si}]^* + 2[\text{O}]^* = (\text{SiO}_2)_{\text{slag}} \quad \text{(R2)}$$

where the equilibrium constant $K^*_{\text{SiO}_2}$ is equal to the following expression:

$$K^*_{\text{SiO}_2} = \frac{\gamma_{\text{SiO}_2}(\text{SiO}_2)^q}{f_O^* [\text{Si}]^2} \quad \text{(2)}$$

where $\gamma_{\text{SiO}_2}$ is the activity coefficient of SiO$_2$ in slag, (SiO$_2$)$^q$ is the mole fraction of SiO$_2$ in slag, $f_O^*$ is the activity coefficient of [Si] in the steel sub-interface layer, and [%Si] is the [Si] content in steel sub-interface. Furthermore, $a_O^*$ is the activity of oxygen at the steel sub-interface which can be expressed as follows:

$$a_O^* = f_O^* [\text{O}]^* \quad \text{(3)}$$

The reaction kinetics can be expressed by the following equation:

$$\frac{d([\text{O}])}{dt} = k_r ([\text{O}]^* - [\text{O}]^q) \quad \text{(4)}$$

where $k_r$ is the reaction constant of reaction (R2), and ([O])$^*$ is the weight percent of O in the steel sub-interface layer. The modified equilibrium constant $E^c_{\text{SiO}_2}$ can be obtained as follows to describe the partition ratio between the elements:

$$E^c_{\text{SiO}_2} = \frac{[\text{Si}]^*}{[\text{Si}]} \cdot \frac{[\text{O}]^*}{[\text{O}]} = 100CM_{\text{SiO}_2} \cdot f_O^* K^*_{\text{SiO}_2} \cdot \frac{\rho_s}{\rho_{\text{SiO}_2}} \quad \text{(5)}$$

where C is the total molar concentration of the elements in the slag, $\rho_s$ is slag density, and $M_{\text{SiO}_2}$ is the molecular weight of SiO$_2$. In order to calculate the value of $E^c_{\text{SiO}_2}$, the equilibrium constant $K^*_{\text{SiO}_2}$ including the effect of the interfacial tension for reaction (R2) is required. The reaction (R2) can be obtained by combining the following reactions from (R3) to (R6):

$$[\text{Si}]^* + 2[\text{O}]^* = (\text{SiO}_2)_{\text{slag}} \quad \text{(R3)}$$

$$\Delta G^o = -RT \ln K_{\text{SiO}_2} = -581900 + 221.8 T \quad \text{(5)}$$

$$[\text{O}]^* = [\text{O}]^+ \quad \text{(R4)}$$

$$[\text{Si}]^* = [\text{Si}]^+ \quad \text{(R5)}$$

$$(\text{SiO}_2)_{\text{slag}} = (\text{SiO}_2)_{\text{slag}} \quad \text{(R6)}$$

where the equilibrium constant $K_{\text{SiO}_2}$ for reaction (R3) is known from Eq. (5)$^{10}$ and the equilibrium constant $K_O$ for the oxygen adsorption in reaction (R4) is unknown. The contact angle between SiO$_2$ and iron is not significantly smaller than that between either CaO or Al$_2$O$_3$ and iron. Therefore, SiO$_2$ is assumed not to be a surfactant component in slag. The interfacial tension between Fe–Si alloy and Al$_2$O$_3$–SiO$_2$–CaO slag showed almost a linear decrease of...
around 20% when the silicon content in iron increases from 0 to 20 wt%.

Therefore, silicon can reduce the interfacial tension between iron and Al2O3–SiO2–CaO type slag. However, its influence is much smaller compared to the influence of oxygen, where the addition of 0.05 wt% oxygen content in pure iron can reduce the iron/slag interfacial tension by around 35%.

Furthermore, the silicon content in the current system is very small. Therefore, its influence on the steel/slag interfacial tension is expected to be very small and was not considered in this study. With this assumption, the Gibbs energy changes for reaction (R5) and (R6) are equal to zero. Therefore, the equilibrium constant $K_{\text{SiO}_2}$ for reaction (R2), $K_{\text{SiO}_2}$, for reaction (R3) and $K_{O}$ for reaction (R4) have the following relationship:

$$K_{\text{SiO}_2} = \frac{K_{\text{SiO}_2}}{K_{O}} \quad \text{..............(6)}$$

Therefore, (\%SiO$_2$)$_{eq}$ can be obtained based on Eq. (4) by the following equation:

$$(\%\text{SiO}_2)_{eq} = E_{\text{SiO}_2} - E_{\text{SiO}_2} \left[ \%\text{Si} \right] f_{O^2}^* \left[ \%\text{O} \right]^2 \quad \text{..............(7)}$$

Finally, the reaction rate in the sub-interfacial region can be obtained by inserting Eq. (7) into Eq. (1) as follows:

$$\frac{d(\%\text{SiO}_2)}{dt} = k \left\{ (\%\text{SiO}_2)_{eq} - E_{\text{SiO}_2} \left[ \%\text{Si} \right] f_{O^2}^* \left[ \%\text{O} \right]^2 \right\} \quad \text{..............(8)}$$

However, at every time step, only a part of SiO$_2$ in the slag sub-interface can reach the interface. This means that not all the SiO$_2$ in the slag sub-interface take part in the reaction. Therefore, the diffusion of SiO$_2$ inside the slag sub-interface to the steel/slag interface, where reaction happens, should also be a parameter that accounts for the SiO$_2$ decomposition rate. The maximum time required for the SiO$_2$ in slag sub-interface to the interface is $t_{\text{max}} = h/\kappa_{\text{SiO}_2}$, namely the sub-interface thickness divided by the mass transfer coefficient. Therefore, the ratio of SiO$_2$ which takes part in reactions at every time step is $\beta = \Delta t / t_{\text{max}}$. Finally, the weight percent change of SiO$_2$ in the slag sub-interface can be expressed by the following equation:

$$\Delta(\%\text{SiO}_2) = \Delta \cdot \beta \cdot k_{O} \left\{ (\%\text{SiO}_2)_{eq} - E_{\text{SiO}_2} \left[ \%\text{Si} \right] f_{O^2}^* \left[ \%\text{O} \right]^2 \right\} \quad \text{..............(9)}$$

where $\Delta(\%\text{SiO}_2)$ is the weight percent change in the sub-interface at each time step, and $\Delta$ is the time step. The apparent reaction rate constant $k_{O}$ in Eq. (9) is assumed to be 0.8 s$^{-1}$ in this paper, where a value of 1.0 represents a full decomposition of the over-amount SiO$_2$ per second, compared to the equilibrium amount, which arrived at the interface.

2.2. Diffusion from Slag Bulk to Slag Sub-interface Layer

For the SiO$_2$ transport from the slag bulk to the sub-interfacial layer, the effect of the interfacial tension on its mass transfer coefficient is not considered. This is due to the fact that the contact angle between SiO$_2$ and iron is not significantly smaller than that between either CaO or Al$_2$O$_3$ and iron. Therefore, SiO$_2$ is assumed not to be a surfactant component in slag. Thus, at each time step, the amount of SiO$_2$ moving into the sub-interface can be expressed by the following equation:

$$\Delta(\%\text{SiO}_2) = \Delta \cdot \kappa_{O} \cdot \left\{ \frac{1}{V} \right\} \left( \%\text{SiO}_2 \right)^{\text{b}} - \left( \%\text{SiO}_2 \right)^{\text{b}} \quad \text{..............(10)}$$

where the superscript b represents the bulk, $\kappa$ is the interfacial area among different layers which is equal to the steel/slag interfacial area, $\kappa_{O}$ is the apparent mass transfer coefficient of SiO$_2$ in slag, and $V$ is the volume of the sub-interface layer. Finally, the term (\%SiO$_2$)$^b$ is the weight percent of SiO$_2$ in the slag bulk.

2.3. Diffusion of Elements from Steel Sub-interface to Steel Bulk

As previously mentioned, silicon is supposed not to be a surfactant element. Therefore, its transfer from the sub-interface to the bulk is assumed not to be influenced by the interfacial tension between steel and slag. However, oxygen is a surfactant element. Thus, its desorption from the interfacial region to the steel bulk should be significantly influenced by the interfacial tension. This appears at a slow rate for the oxygen transfer, especially when the oxygen content is very small in the sub-interfacial region. Furthermore, the differences between oxygen chemical potentials in different regions should be evaluated in order to calculate the oxygen transfer. Finally, the weight percent change of oxygen and silicon at the sub-interface can be expressed by the following equations, respectively:

$$\Delta(\%\text{Si}) = \Delta \cdot k_{\text{Si}} \cdot \left\{ \frac{1}{V} \right\} \left( \%\text{Si} \right)^{\text{b}} - \left( \%\text{Si} \right)^{\text{b}} \quad \text{..............(11)}$$

$$\Delta(\%\text{O}) = \Delta \cdot k_{O} \cdot \left\{ \frac{1}{V} \right\} \left( \%\text{O} \right)^{\text{b}} - \left( \%\text{O} \right)^{\text{b}} \quad \text{..............(12)}$$

where $k_{\text{Si}}$ is the mass transfer coefficient of silicon in steel, $k_{O}$ is the desorption rate of oxygen from steel sub-interface to bulk, and $\left( \%\text{Si} \right)^{\text{b}}$ is the silicon content in the sub-interface.

Furthermore, (\%O$^b$)$_{eq}$ is the equilibrium content of [O] without considering the interfacial tension effect as in the steel bulk. This corresponds to the same chemical potential of the oxygen in the sub-interfacial region, where the interfacial tension effect is considered. It can be obtained based on the previously shown reaction (R4):

$$\left( \%\text{O} \right)^{\text{eq}} = \left[ \%\text{O} \right] \quad \text{..............(R7)}$$

$$K_{O} = \frac{a_{O}^{\text{eq}}}{a_{O}^{b}} = \frac{f_{O}^{\text{eq}}}{f_{O}^{b}} \quad \text{..............(13)}$$

$$\left[ \%\text{O} \right]^{\text{eq}} = f_{O}^{b} \left[ \%\text{O} \right]^{\text{b}} / (K_{O} f_{O}^{b}) \quad \text{..............(14)}$$

where $f_{O}^{b}$ is the activity coefficient of [O] in steel bulk. Finally, the desorption of oxygen from the sub-interface to the steel bulk can be obtained as follows by inserting Eq. (14) into Eq. (12):

$$\Delta(\%\text{O}) = \Delta \cdot k_{O} \cdot \left\{ f_{O}^{\text{eq}} \left[ \%\text{O} \right]^{\text{b}} / (K_{O} f_{O}^{b}) \right\} / V \quad \text{..............(15)}$$

2.4. Estimation of Oxygen Desorption Rate from Interface to Bulk

Due to the existence of an interfacial tension, the rate of oxygen desorption from a sub-interface to a steel bulk...
should be decreased compared to its transport rate in the steel bulk. This is due to the fact that the surfactant element tends to stay at the locations where a large interfacial tension exists. The mass transfer coefficient of oxygen in steel bulk is related to the physical properties of iron atoms and oxygen atoms, such as the atom size. Furthermore, the mass transfer coefficient of some elements in liquid steel have been known. Therefore, a proper way to obtain \( k_0 \) values should be based on the mass transfer coefficient of oxygen in steel bulk, namely \( k_0^b \). However, it must be modified to include the interfacial tension effect. According to the literature, the relationship between the surface tension and the bulk oxygen activity is as follows:

\[
\frac{d\sigma}{d\ln a_0^a} = -RT\Gamma^0 \tag{16}
\]

where \( \sigma \) is the surface tension, \( a_0^a \) is the bulk oxygen activity, \( R \) is the gas constant, \( \Gamma^0 \) is the adsorption at a full coverage and \( T \) is the temperature. The connection between the oxygen activity in the bulk and the oxygen coverage fraction at the interface can be expressed by using the Langmuir isotherm, which arises from the assumption that the energy of adsorption of the species is independent of the coverage or the atomic arrangement of the species on the surface. Furthermore, it is most simply expressed as follows at a constant temperature for a single solute and for single site occupancy:

\[
\frac{\theta}{1-\theta} = \gamma a_0^b \tag{17}
\]

where \( \gamma \) is the partition constant under the assumption of an adsorption equilibrium. This constant is different from the equilibrium constant \( K_0 \) for the oxygen adsorption in reaction (R4). Therefore, \( \theta \) can be calculated by using the following equation:

\[
\theta = \frac{\gamma a_0^b}{1 + \gamma a_0^b} \tag{18}
\]

By inserting Eq. (18) into Eq. (16), the following equation can be obtained:

\[
\frac{d\sigma}{d\ln a_0^a} = -RT\Gamma^0 \frac{\gamma a_0^b}{1 + \gamma a_0^b} \tag{19}
\]

Thus, the dependence of the surface tension on the bulk oxygen activity can be obtained as follows:

\[
\frac{d\sigma}{d a_0^b} = -RT\Gamma^0 \frac{\gamma}{1 + \gamma a_0^b} \tag{20}
\]

This equation for the surface tension can also be used to describe the interfacial tension change with the oxygen content.\(^{16} \) According to a previous experimental study,\(^{17} \) the values of \( RT\Gamma^0 \) and \( \gamma \) are equal to 314 and 116, respectively. In order to obtain a good fit with experimental data, the dependence of interfacial tensions on the bulk oxygen activity \( a_0^b \) can be expressed as follows, after integrating Eq. (20) with pure iron as one integration limit: \(^{16,17} \)

\[
\sigma = 1386 - 324\ln\left(1 + 116a_0^a / K_0\right) \tag{21}
\]

If the relationship in reaction (R4) is considered, the interfacial tension values have the following relationship with the interfacial oxygen activity:

\[
\sigma = 1386 - 324\ln\left(1 + 116a_0^a / K_0\right) \tag{21}
\]

By using the relationship between oxygen activity in bulk and at interface shown in Eq. (13), the dependence of interfacial tension on the oxygen activity at interface, at a constant temperature, can be obtained as follows based on Eq. (20):

\[
\frac{d\sigma}{da_0^b} = -\frac{d\sigma}{da_0^a} = -RT\Gamma^0 \frac{\gamma}{K_0 + \gamma a_0^a} \tag{22}
\]

A larger value of \( \frac{d\sigma}{da_0^a} \) illustrates a higher dependence of the interfacial tension on the interfacial oxygen activity. This means that it is not easy for oxygen to leave the interface once it reaches it. On the other hand, smaller values mean 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. To describe the diffusion or desorption of an element from an interface into the bulk, the mass transfer coefficient should be modified based on the value in a material bulk to include the interfacial tension effect. Therefore, the following equation was proposed in this paper to describe the desorption coefficient of oxygen from an interfacial region to the bulk:

\[
k_0^b = \alpha \cdot \left[ \frac{d\sigma}{da_0^a} \right]_{\text{[O]-a}} \tag{23}
\]

where \( \alpha \) is a general coefficient and the \( k_0^b \) is the mass transfer coefficient of oxygen in steel bulk. The bracket part represents the modified factor to include the interfacial tension effect. It is the maximum value of \( \frac{d\sigma}{da_0^a} \) at an oxygen content of zero minus its value at an oxygen content, and divided by the maximum value. This guarantees that the mass transfer coefficient will obtain a value of zero when the oxygen content approaches zero. Also, this term becomes dimensionless. Finally, the following expression for the oxygen mass transfer coefficient can be obtained:

\[
k_0^b = \alpha \cdot \left[ \frac{1}{1 + \frac{\gamma}{K_0 a_0^a}} \right] \cdot k_0^b \tag{24}
\]

where \( k_0^b \) has the same unit as \( k_0^b \).

2.5. Model Solving Procedures

The procedure to solve the kinetic model is shown in Fig. 4. In order to get a stable solution, a very small time step is required. Specifically, the value was set to 0.0001 s in this study. This guarantees a small composition change in the sub-interface layer at each time step. Therefore, the time step should decrease with a decreased thickness of the sub-interface. In this paper, the thickness value of 20 \( \mu \)m was used to avoid too large computational times. In addition, the thermodynamics and kinetics parameters used in
the model are shown in Table 1. The weights of the slag and steel and the value of the interfacial area are based on results from an experimental study, since the model predictions will be compared to the experimental data later.

3. Results and Discussion

3.1. Comparison of Model Predictions and Experimental Data

The dynamic change of oxygen concentration in steel sub-interface layer was predicted by the kinetic model based on the parameters shown in Table 1. Figure 5 shows the predicted change of oxygen content with time and the calculated interfacial tension by using Eq. (22) based on the oxygen content predicted by the current model. The liquid steel and molten slag were assumed to be in contact with each other at the time of 0 s. Figure 5(a) shows that the oxygen content in the sub-interfacial layer first sharply increases with time to a peak value and then it steadily decreases with time. The initial rapid increase is due to the fact that some SiO_2 in the slag immediately touch the liquid steel once the steel and slag come in touch with each other. These SiO_2 are supposed to decompose rapidly to release oxygen, because of a low oxygen chemical potential in steel. Due to the interfacial tension effect, the released oxygen tends to stay in the interfacial region in order to reduce the interfacial tension rather than to diffuse into the steel bulk. As time passes, the SiO_2 content in the slag sub-interface decreases and the supply rate of SiO_2 to the interface depends on its mass transfer coefficient in slag, namely the k_{SiO_2} value. At the same time, the amount of oxygen in the sub-interface increases. The possibility of the oxygen atom desorption from the interface to the steel bulk increases, since its influence on the interfacial tension becomes smaller with an increased oxygen content. At a moment, a peak value of oxygen content was

![Fig. 4. Procedure for solving the kinetic model.](image)

![Fig. 5. Predicted dynamic change with time of (a) oxygen content and (b) interfacial tension with its comparison with experimentally determined data.](image)

| Properties | Symbol | Values |
|------------|--------|--------|
| Metal weight, g | W_m | 80 |
| Slag weight, g | W_s | 0.8 |
| Metal density, g/mm^3 | \rho_m | 0.007 |
| Slag density, g/mm^3 | \rho_s | 0.0025 |
| Metal viscosity, Pa·s | \mu_m | 0.006 |
| Slag viscosity, Pa·s | \mu_s | 0.434 |
| Total molar concentration in slag, mol/mm^3 | C | 3.94×10^{-5} |
| Mass-transfer rate constants, mm/s | k_{SiO_2} = k_{O_{b}} = k_{m} | 0.6 |
| | k_{exn} | 0.05 |
| Interface area, mm^2 | A | 95 |
| Initial metal composition (Bulk and Sub-interface), wt% | [%Si] | 0 |
| | [%O] | 0.001 |
| | [%Fe] | 100 |
| Initial slag composition (Sub interface and Bulk), wt% | (%CaO) | 40 |
| | (%SiO_2) | 40 |
| | (%Al_2O_3) | 20 |
| Interface oxygen adsorption | K_O | 10 |
| Interface oxygen partition coefficient (^1) | \gamma | 116 |
| Interface [O] activity coefficient(^1) | f^{O} | log f^{O} = -0.17 × [%O] |
| Bulk [O] activity coefficient | f^{O}_{b} | log f^{O}_{b} = -0.17 × [%O] |
| Interface [Si] activity coefficient | f^{Si} | 1 |
| Equilibrium Constant for SiO_2 decomposition(^1) | K_{SiO_2} | 1.22×10^5 at 1 823 K |
| Bulk (SiO_2) activity coefficient | \gamma_{SiO_2} | 0.15 |
| SiO_2 mole weight, g/mol | M_{SiO_2} | 60 |
| SiO_2 decomposition rate constant | k_d | 0.8 |
| O desorption coefficient | \alpha | 0.005 |
observed when the supply rate of oxygen in the form of SiO₂ from the slag is equal to the oxygen desorption rate from the interface to the steel bulk. After this, the supply rate of oxygen from the slag is smaller than the desorption rate of oxygen which tends to reach the same oxygen potential at interface and in steel bulk. A steady decrease of oxygen content in the sub-interface was expected. Therefore, a dynamic change of the oxygen content in Fig. 5(a) was observed.

A direct measurement of the oxygen content in a sub-interface region is impossible today, since it is a very small area and due to that this interfacial phenomenon changes fast. Therefore, there are no experimental data which can directly validate the current model predictions. However, the dynamic change of the interfacial tension between the steel and the slag was measured in some studies. Figure 5(b) shows the calculated interfacial tension by using Eq. (22) based on the predicted interface oxygen content in Fig. 5(a) and a comparison of predictions with experimental data.9) It can be seen that the trend of the change of the interfacial tension is quite similar. However, the magnitudes of the predicted interfacial tension and experimental data show a tension is quite similar. However, the magnitudes of the predicted interfacial tension and experimental data show a tension is not possible to be observed. This is due to that the interfacial tension effect, oxygen tends to stay at the interfacial region which will result in a low interfacial tension. Therefore, an equilibrium state exists when the oxygen contents in the steel bulk and at the interface do not change any more. This equilibrium was described by reaction (R4). Therefore, the equilibrium constant is an important parameter. This is due to that it directly determines the distribution of oxygen. In part 3.1, a K₀ value of 10 was assumed. Figure 7(a) shows the influence of different K₀ values on the predicted oxygen content in sub-interface region. It can be seen that the oxygen content increases with an increased K₀ value. With different K₀ values, a similar trend of the oxygen content change was observed. Specifically, the oxygen content first rapidly increases to a peak value and then it decreases steadily.

3.2. Parameter Study

Due to the small scale of interfacial regions, direct observations or measurements are difficult. This is especially true for the steel/slag system, which has a very high temperature around 1 823 K. Therefore, knowledge about the interfacial thermodynamics and kinetics are still limited. In this paper, a parameter study was carried out to show their influence on the dynamic interfacial phenomena.

3.2.1. Thermodynamic Parameter Influence

Due to the interfacial tension effect, oxygen tends to stay at the interfacial region which will result in a low interfacial tension. Therefore, an equilibrium state exists when the oxygen contents in the steel bulk and at the interface do not change any more. This equilibrium was described by reaction (R4). Therefore, the equilibrium constant is an important parameter. This is due to that it directly determines the distribution of oxygen. In part 3.1, a K₀ value of 10 was assumed. Figure 7(a) shows the influence of different K₀ values on the predicted oxygen content in sub-interface region. It can be seen that the oxygen content increases with an increased K₀ value. With different K₀ values, a similar trend of the oxygen content change was observed. Specifically, the oxygen content first rapidly increases to a peak value and then it decreases steadily. Figure 7(b) shows the calculated interfacial tension based on the predicted oxygen contents given in Fig. 7(a) along with experimental data.9) It can be seen that the K₀ value only slightly influences the interfacial tension during the initial moment. After that, its influence on the interfacial tension is not possible to be observed. This is due to that the interfacial oxygen activity divided by K₀, namely aO/K₀, do not change significantly. This ratio is used to calculate the interfacial tension in Eq. (22). In addition, all the curves in Fig. 7(b) show a similar trend as the experimental data. Due to the lack of the experimental data on the oxygen content in sub-interface region, a K₀ value of 10 is selected in the
following parameter studies.

3.2.2. Kinetic Parameter Influence

The interfacial tension of steel and slag shows a dynamic change due to the change of the oxygen content near the interface. The kinetic parameters should be very important for the transport of oxygen as well as for the dynamic interfacial tension change. For the desorption of oxygen from the interfacial region to the steel bulk, the mass transfer coefficient \( k_{o} \) was previously derived as shown in Eq. (25). Its value depends on the coefficient \( \alpha \), the mass transfer coefficient in steel bulk \( k_{m} \) (\( k_{Si} = k_{O}^b = k_{m} \)), and also the oxygen content in sub-interface region. 

Figure 8 shows the influence of different \( k_{m} \) values on the dynamic change of the oxygen content in the sub-interface layer. It can be seen that the change of oxygen content shows a similar behavior for different \( k_{m} \) values, while it has different magnitudes during different times. With a large value of mass transfer coefficient \( k_{m} \), a small peak value of oxygen content was observed. This is due to that oxygen and silicon atoms from the SiO\(_{2}\) decomposition quickly transfers into the steel bulk when a large mass transfer rate exists. 

Figure 9 shows the effect of the oxygen transport coefficient \( \alpha \) in Eq. (25) on the predicted oxygen contents in the sub-interface layer. A similar behavior of oxygen content change was found for different \( \alpha \) values. A high \( \alpha \) value corresponds to a fast desorption rate of oxygen from the interface region to the steel bulk. When the supply rate of oxygen by the decomposition of silica is equal to the desorption rate of oxygen to the bulk, a peak value was observed. A small \( \alpha \) value represents a slow desorption rate of oxygen, which results in a large peak value of oxygen.

The diffusion of SiO\(_{2}\) towards the interface also influences the dynamic interface behavior. This is normally considered to be one of the rate-controlling steps for the oxygen transfer from slag to steel, since molten slag normally has a large viscosity and thus a slow mass transfer rate. Figure 10(a) shows the influence of the SiO\(_{2}\) mass transfer rate in slag on the oxygen content in the sub-interface layer. It can be seen that a large mass transfer rate leads to a high oxygen content. This is obviously due to that the supply of oxygen from slag is fast with a large value of \( k_{SiO_2} \). Figures 10(b)

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**Fig. 8.** Effect of Si and O mass transfer coefficient in steel on the predicted oxygen content in the sub-interface layer.

**Fig. 9.** Effect of oxygen transport coefficient in steel on the predicted oxygen contents in the sub-interface layer.

**Fig. 10.** Effect of the SiO\(_{2}\) mass transfer coefficient in different viscous slags on the interface phenomena, (a) Predicted oxygen content, (b) Interfacial tension with a low slag viscosity, and (c) Interfacial tension with a high slag viscosity.
and 10(c) shows the comparison of model predictions with $k_{SiO_2}$ values of 0.05 and 0.025 to experimental data\(^9\) for different slag viscosities, respectively. It can be seen that the change trends of the interfacial tensions predicted by the model are similar as the change trend of the interfacial tension measured in experiments for different slag viscosities as well as for different SiO\(_2\) diffusion speeds in slag. This also illustrates that the kinetic model is built on a good physical framework, which can capture the trend of the dynamic interfacial change behavior.

### 3.2.3. Combined Influence by Ko and $\alpha$

From previous investigation in Fig. 7, it is known that the oxygen adsorption equilibrium constant Ko can significantly influence the oxygen content in the sub-interface region. The coefficient $\alpha$ of the oxygen desorption coefficient $k_\alpha$ shows a large influence on both the oxygen content and the interfacial tension, as shown in Figure 9. Therefore, the combined influence of Ko and $\alpha$ on the interfacial tension was investigated. Figure 11 shows the combined influence of Ko and $\alpha$ on the dynamic change of the oxygen content and interfacial tension. It can be seen from Fig. 11(a) that a larger Ko value leads to a larger peak value of oxygen content. Furthermore, a longer time is required to reach a larger value of the peak oxygen content. Therefore, it is observed that the location of the peak oxygen content shifts towards the right direction in Fig. 11(a) with an increased oxygen peak content. This is due to that more SiO\(_2\) is required to release oxygen in sub-interface in order to get a larger value of oxygen content. Figure 11(b) shows that the $\alpha$ value determines the change trend of interfacial tension after reaching the minimum interfacial tension value, and the Ko value can only affect the initial change behavior of the interfacial tension. Specifically, the influence of Ko value on the interfacial tension change was found to be larger when the $\alpha$ value as well as the desorption rate of oxygen is smaller. This is due to the fact that a larger value of transfer rate will lead to a shorter time for the system to reach the metastable state. This can be easily seen from Fig. 11(a) that a smaller value of the peak oxygen content was obtained for the same Ko value when a larger $\alpha$ value is used, and the time required to a lower peak oxygen content is shorter than that with a higher peak oxygen content.

#### 4. Concluding Discussion

A kinetic model was developed in this paper to describe the dynamic change of the oxygen content in the sub-interface layer as well as the steel/slag interfacial tension. The model is based on a good physical framework, where the physical meaning of each part is explained in this paper. The developed model aims to qualitatively show the dynamic change trend of the interfacial phenomena and to reveal the mechanism for this kind of complex change. In reality, an interfacial region is a very small volume perhaps in the level of several atomic layers. Therefore, it is difficult to solve such a small region in a kinetic model. In this study, the thickness of the interfacial region is set to 20 $\mu$m to avoid a large computational time. Due to that a parameter $\beta$ was used in the SiO\(_2\) decomposition equation Eq. (9), this thickness is supposed to only have a slight influence on the supply rate of the oxygen from the slag sub-interface to the steel.

Due to the lack of the thermodynamic and kinetic data, a parameter study was carried out to show the influence of each parameter and to show the model performance. In this model, the adsorption equilibrium constant is assumed to have a constant value. In reality, both the partition constant $\gamma$ and adsorption equilibrium constant Ko should be a function of the interfacial tension and temperature. However, studies\(^{10,17}\) showed that reasonable results can be obtained with a constant value of $\gamma$ when they predict the steel/slag interfacial tension under different bulk oxygen activity by Eq. (21). Furthermore, this study shows that Ko value is not a critical parameter to determine the value of the steel/slag interfacial tension. Therefore, a constant Ko value is also reasonable to use when predicting the interfacial tension. In addition, the oxygen activity coefficient in sub-interface is assumed to be equal to that in bulk, due to the lack of the knowledge regarding the interfacial tension effect on it. In order to describe the dynamic oxygen change at the interface, the desorption rate of oxygen from the interface is found to be an important parameter. In the current model, the expression for the oxygen desorption rate from the interface is derived based on the slope of the interfacial tension change over the interfacial oxygen activity.

After oxygen is released from SiO\(_2\) decomposition, it may react with iron or other reductive elements in iron. The oxygen concentration in iron which is in equilibrium with
FeO can be estimated by the following reaction:

$$K_{FeO} = \frac{y_{FeO}(FeO)}{a_{FeO}f_c[O]} = \exp \left[ \frac{14.553.757}{1823} - 6.2999 \right] \quad (26)$$

where $K_{FeO}$ is the equilibrium constant for reaction (R8) at 1823 K. The calculated saturation oxygen content, which is in equilibrium with iron, is around 0.18 wt% when the (FeO) activity value of 1 was used. As shown in Figs. 7–10, the predicted interfacial oxygen content under the interfacial tension effect may temporarily exceed the bulk oxygen solubility limit (with the value of 0.18 wt%) equilibrated with iron oxide. In addition, chemical reactions between the reductive elements in steel and oxygen at interface were currently not considered. These are left for a further study in the future based on the model proposed in this study.

5. Conclusions

In this study, a novel kinetic model was proposed to describe the dynamic change of the oxygen content in the sub-interface layer as well as the dynamic change of the steel/slag interfacial tension. As a first step towards a more realistic model, the current model only considers the SiO$_2$ decomposition reaction at the interface as well as the oxygen adsorption and desorption at the interface. Generally, the model predicted the trend of the oxygen content change in the sub-interface layer. However, experimental results are still required for a quantitative validation of the model predictions. The following specific conclusions can be obtained from this study:

(1) The trend of the oxygen change was predicted with a rapid increase at the initial period and a steady decrease after passing the maximum point.

(2) The equilibrium constant for oxygen adsorption at the interface was found to increase the oxygen content in sub-interface layer, while it only has a slight influence on the interfacial tension predictions.

(3) The oxygen desorption rate was found to be an important factor for the dynamic change of oxygen content in the sub-interface layer as well as for the steel/slag interfacial tension.

(4) A low slag viscosity was found to increase the oxygen content, due to the fast supply of SiO$_2$ from slag bulk to the steel/slag interface.

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Nomenclature

- $*: $ Sublayer
- b: Bulk
- eq: Equilibrium state
- m: Metal
- $\Delta$: Change of the quantity
- C: Total molar concentration of the elements in the slag, mol/mm$^3$
- $A$: Interface area, mm$^2$
- $\rho$: Slag density, g/mm$^3$
- $t$: Time, s
- V: Volume, mm$^3$
- $%$SiO$_2$: SiO$_2$ content in slag, wt%
- $%$O: O content in steel, wt%
- $M_{SiO_2}$: Molecular weight of SiO$_2$, g/mol
- $k_r$: SiO$_2$ decomposition rate coefficient, s$^{-1}$
- $\gamma_{SiO_2}$: Activity coefficient of SiO$_2$ in slag
- $\gamma_{FeO}$: Activity coefficient of FeO in slag
- $f_{Si}$: Activity coefficient of [Si] in steel
- $f_{O}$: Activity coefficient of [O] in steel
- $a_{O}$: Activity of [O] in steel
- $K_{FeO}$: FeO formation reaction Equilibrium constant
- $E_{SiO_2}$: Modified Equilibrium constant
- $K_G$: Equilibrium constant for the oxygen adsorption at interface
- h: Thickness of sub-interface, mm
- $k_{SiO_2}$: SiO$_2$ mass transfer coefficient in slag, mm/s
- $k_S$: Mass transfer coefficient of [Si] in steel, mm/s
- $f_{O}$: Desorption rate of oxygen from steel sub-interface to bulk, mm/s
- $\beta$: Ratio of SiO$_2$ in sub-interface that take part in decomposition reaction
- $\sigma$: Surface or Interfacial tension, m/m
- $R$: Gas constant, J/(mol K)
- $\theta$: Fractional coverage by oxygen at the interface
- $P_0$: 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

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