A Chemical Reaction-Fluid Dynamics Coupled Model for Al Reoxidation in Tundish by Open Eye Formation

Yong-Min Cho¹, Dong-Jun Lee¹, Min-Chul Lim², Jae-Seop Jo², Chang-Won Kim², Hyun-Jin Cho³, Wan-Yi Kim³, Sang-Woo Han³, and Youn-Bae Kang¹

¹Pohang University of Science and Technology
77 Chengamro, Namgu, Pohang, Gyeongbuk, Rep. of Korea, 37673
Phone: +82-54-279-9032
E-mail: ybkang@postech.ac.kr

²Metalgentech Co. Ltd.
219 GasanDigital-1ro, Geumcheongu, Seoul, Rep. of Korea, 08501

³Technical Research Laboratories, POSCO
6261 Donghaeanro, Namgu, Pohang, Gyeongbuk, Rep. of Korea, 37859

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1. INTRODUCTION
Reoxidation of liquid steel deteriorates the cleanliness of steel, even though the steelmakers put in a great deal of effort to improve the cleanliness of steel. Reoxidation of the steel can take place at several locations where the refined steel contacts with other phases including air, slag, flux, and refractories. One of the most well-recognized locations is Tundish Open Eye (TOE). Often the tundish flux fails to cover the surface of the steel, and the TOE forms. The liquid steel then contacts with the outer atmosphere so they might interact.[1-5] Among the interactions between the liquid steel and air, the infiltration of O₂ gas into the liquid steel and the generation of oxide inclusion are most concerned, as it generates suspending inclusions in the liquid steel.[4,5] Some researchers reported their prediction of the behavior of inclusion via growth and agglomeration, and removal.[6-8] Also, the others focused on the mechanical movement of inclusions suspending in the liquid steel.[9,10] but those studies are generally insufficient for the quantitative evaluation of inclusions considering the deoxidation reaction. In the present study, a model was developed to predict the reoxidation behavior, in view of alumina inclusion generation due to the TOE by combining chemical reaction and Computational Fluid Dynamics (CFD). This model targets not only to describe the infiltration rate of O₂ in the air, but also to foresee the amount of oxide inclusion originating from the reoxidation phenomena.

2. MODEL DESCRIPTION
In order to get analysis results based on the CFD calculation, a commercial CFD software, ANSYS Fluent™ was utilized. The logical procedure of this model is divided into three stage, the one is reflecting reoxidation phenomena by utilizing User-Defined Function (UDF) and the others are calculating fluid dynamics employing intrinsic function of Fluent™, as described below. The schematic of the present model was illustrated in Figure 1. An ultra-low C steel was considered in the present study, and for the sake of simplicity, the steel system was confined to Fe-Al-O ternary system.
2.1. Stage 1: Construction of Reoxidation Phenomena to CFD Utilizing UDF

This stage targets to materialize the reoxidation phenomena based on the experimental results and the knowledge based on the metallurgical theory. The form of materialization is UDF code, which is an extended function of Fluent™ in a form of C++ code. Especially, the present study targets the reflection of reoxidation phenomena caused by the infiltration of O2 from the air. This stage is classified into 3 steps, which are described in detail below.

**Step A: Reflecting Infiltration of O2 From the Air to the Liquid Steel**

In the vicinity of the TOE, although the supply rate of O2 gas to the surface of liquid steel would be affected by not only diffusion but also convection in the gas phase, the contribution of both forced convection and natural convection to the surface of liquid steel might be neglected, because the reoxidation happens by the air residing on the TOE, not by the air injection. Therefore, the present model assumes that the supply rate of O2 molecule is governed by only the diffusional rate. On the other hand, the diffusion rate of O2 molecule is proportional to not only the diffusivity of O2 in the air but also the difference of partial pressures of O2 at the bulk air and that at the surface of liquid steel.\[11\] According to the two-film theory, describing heterogeneous reaction between different two phases, it is thought that the diffusion rate is inversely proportional to the thickness of the diffusion layer (δ).\[12\] Therefore, the molar flux of O2 (\(J_{\text{O}_2}\)) from the bulk air to the surface of liquid steel (\(\text{O}_2(g) = 2\text{O}\)) is derived like the following:

\[
J_{\text{O}_2} = \frac{1}{A} \frac{d n_{\text{O}_2}}{dt} = \frac{D_{\text{O}_2}^{\text{diff}}}{\delta} \frac{P_{\text{O}_2}^G}{P_{\text{O}_2}^G} \left( 1 - \frac{P_{\text{O}_2}^G}{P_{\text{O}_2}^G} \right) \quad [\text{mol m}^{-2} \text{s}^{-1}]
\]

where \(A\), \(n_{\text{O}_2}\), \(D_{\text{O}_2}^{\text{diff}}\), \(R\), \(T\), \(P_{\text{O}_2}^G\), and \(P_{\text{O}_2}^G\) are unit surface area (m²), the number of moles of O2 (mol), diffusivity of O2 in heated air (m² s⁻¹), universal gas constant (J mol⁻¹ K⁻¹), absolute temperature (K), O2 partial pressure at the surface of liquid steel, and O2 partial pressure in the bulk air, respectively. Although the O2 molecules diffuse to the surface of liquid steel per unit volume and per unit time, the entire amount of them does not dissolve into the liquid steel. Some parts of them might form the oxide scale at the surface of liquid steel, and the other parts of them might leave without interaction with the liquid steel. In other words, among the entire amount of O2 molar flux, 1) a mass fraction \(\varepsilon_1\) which is the dissolved amount of O into the liquid steel, 2) the other mass fraction \(\varepsilon_2\) which forms oxide scale at the liquid steel surface, and 3) another mass fraction \(\varepsilon_3\) escaped without the interaction were defined. The values of \(\varepsilon_s\) series were determined by an experiment in the present study. The \(\varepsilon_s\) were introduced only as phenomenological parameters, not for having physical meaning. Besides, \(P_{\text{O}_2}^G\) is extremely smaller than \(P_{\text{O}_2}^G\), so the second term in the bracket was neglected.

**Step B: Calculation of Steel Composition Under the Deoxidation Equilibrium**

Once the reoxidation happens, O content in the steel increases. Al in the liquid steel generates Al₂O₃ inclusion by the following reaction:\[13-15\]

\[
2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3(s)
\]

The reoxidation product was assumed to be pure Al₂O₃.\[16\] Several researchers have investigated the equilibrium composition of Fe-Al-O system through both experimental way and thermodynamic modeling.\[13-15, 17-19\] In the present study, the algorithm to calculate the equilibrium composition of Fe-Al-O system was formulated based on Wagner Interaction Parameter Formalism
(WIPF)[20], due to its simplicity. However, a more sophisticated model is being developed and is now under test to expand the applicability of the present model.

**Step C: Describing Forming Rate of Al₂O₃ Inclusion**

According to the previous studies, the reaction rate between the components of liquid steel is controlled by the mass transport of the component. Also, it is generally accepted that the chemical reaction rate between them is fast enough due to the high temperature as long as the steel phase is retained in a liquid form [16, 21, 22]. Because the mass transport including diffusion and convection will be handled by intrinsic CFD calculation, the reaction rate between Al and O can be defined at each location, which is defined for each mesh implying unit volume in the CFD calculation. Therefore, it is assumed that the Al-O equilibrium covered at step B for each position is satisfied in every moment and the reaction rate at each position is fast enough. It implies that the amount of generated Al₂O₃ inclusion per unit volume per unit time has maximum value, corresponding to the mass balance of Al consumption in each position.

2.2. Stage 2: Calculation of Steel Flow on the Intrinsic CFD Function — Parameter Study for δ̄c′G

In order to reflect the model mentioned in the previous stage, the lab scale analysis (2D) was carried out as shown in Figure 2(a). In the 2D analysis, the air inflow was designed to be corresponded to 500 ml min⁻¹ in a 3D case, which is enough flow rate to touch the surface of liquid steel. Through this lab scale analysis, the value of modeling parameter δ̄c′G was evaluated to utilize at the TD scale analysis with comparing the lab-scale experimental results. For example, it can be summarized that larger value of δ̄c′G implies the slower rate of O₂ absorption to the liquid steel.

![Figure 2. The geometry of system to apply the present model (a) 2D lab-scale system to reflect lab-scale experiments (b) 2D TD-scale system to conduct practical analysis results.](image)

2.3. Stage 3: Application to the TD-scale analysis

As the result of the present model, the reoxidation phenomena during the TD operation are predicted. By employing the evaluated δ̄c′G at stage 2, the prediction to model reoxidation phenomena was suggested to use practically as shown in Figure 2(b). In order to reflect the reoxidation phenomena, the air entrainment at the misalignment of the shroud nozzle was set to correspond to 2.5 L min⁻¹ in a 3D case. [23] The present TD modeling is not to fully reflect a practical TD shape yet, but is an example study to describe how this model operates.

3. EXPERIMENTAL

As mentioned in 2.1 Step A, a series of experiments to measure ε, which are the ratio of O distribution along the entire amount of supplied O₂ with the air, was carried out. Electrolytic iron (50 g) was charged into the alumina crucible. Then, it was heated up to about 1873 K by a high-frequency induction furnace equipped with the water-cooled jacket at the upper part of endcap. The atmosphere of the furnace was filled with purified Ar, and a tip of a lance to supply air was located at the surface of liquid steel. Once the preparation to make a composition Fe-0.04% Al with homogenization was completed, some part of liquid steel was sampled by using a quartz tube. Subsequently, the predetermined flow rate of the air was blown through the lance onto the surface of liquid steel during the predetermined duration, and the specimen was quenched at the upper part of endcap and retrieved. This was intended not to break the inert atmosphere inside the chamber. The specimen sampled prior to the air supply was named as ‘Ι’, which is well Al-deoxidized. After the air blowing onto the liquid steel was finished, the specimen was cut to the parts having one-third height, named as ‘Τ’ that is the most top part, ‘Μ’ is the middle part, and ‘Β’ is the bottom part. These samples were used to carry out the chemical analysis and inclusion image analysis. On the other hand, the specimen
from the tundish, at Gwangyang works of POSCO, was obtained and analyzed in a similar way, as reported previously by the present authors.[24]

4. RESULTS

4.1. Characteristic of Specimens With the Air Supply — Lab-Scale Experiments
The composition of inclusion was pure Al₂O₃ during the flow rate of the air was up to 300 ml min⁻¹, regardless of the supply duration. However, the inclusion was FeAl₂O₄ or Fe-oxide when the flow rate of the air was 500 ml min⁻¹ without respect to the supply duration. Within the range of flow rate which shows Al₂O₃ inclusion, [pct. T. O] (total oxygen) increase solely was shown at the ‘T’ specimen, so the quantitative evaluation of O absorption was carried out by employing the composition of T specimen. However, [pct. S. Al] (soluble aluminum) did not show meaningful differences along with the specimen height. Detailed evaluation for the value of ε will be discussed in the discussion part, 5.1.

4.2. Composition of TD Specimen
Based on the analysis result of the previous study of the present authors, the composition of TD specimen was 20 for [ppm S. O] (soluble oxygen), 3 for [ppm I. O] (insoluble oxygen as a form of Al₂O₃ inclusion), and 0.034 for [pct. S. Al] for the case of ultra-low C steel.[24] The location of sampling TD specimen, where ascending straight up from the submerged entry nozzle (SEN) was illustrated as ‘C’ in Figure 2(b). The inclusions suspending in the liquid steel at the tundish process were pure Al₂O₃, and they have a size distribution which was smaller than 5 μm, which does not flow against the flow of liquid steel. Thus, the size effect for the behavior of inclusion such as a buoyancy force was neglected in this model.

4.3. Examples for Lab-Scale Analyses
Through Stage 1 to 2, the parameter study to get the range of δ₀⁻攮 was carried out through a series of lab-scale analyses as shown in Figure 3. The increasing rate of oxygen content in liquid steel near the surface was quite different from the value of δ₀⁻攮. Similar to the experimental results, the increment of oxygen content was concentrated on the surface, corresponding to the ‘T’ specimen in the lab-scale experimental result.

![Figure 3. The examples for the lab-scale parameter study. The liquid steel was oxidized by air blowing until 25 sec.](image)

DISCUSSIONS

5.1. Measurement of ε, O₂ Absorption Ratio of the Al Deoxidized Liquid Steel
From the experimental results, it was found that ε₁ and ε₂ decreased and ε₃ increased with the increase of O₂ mass supplied by the air injection. The tendency for both ε₁ and ε₂ implies that the efficiency of absorption reaction is low with increasing gas flow rate or time to supply gas. Since the air interacting with the liquid steel at the TOE is not injected with a definite flow rate, it was assumed that all the ε₁, ε₂, and ε₃ used in the present model were those obtained at 0 O₂ mass supplied by extrapolating the tendencies. That is, although the εs were evaluated by the experimental results, the representative value should be extracted to be utilized in a present model, especially in the step A. As mentioned in the description for step A, the amount of O₂ contributing to the reoxidation phenomena is caused by only diffusional mass transport. It implies that a condition when the amount of supplied O₂ is the smallest can reflect the reoxidation phenomena at the TOE. This fact gives a condition when the supplied O₂ mass is approximately zero, as the method to select a representative value of ε. Additionally, the mass balance of O element showed good consistency among the series of εs.
5.2. The Optimization of $\delta_{G'G}$ for the Absorption Rate of O$_2$

Because both the lab-scale analysis and TD-scale analysis should be elucidated by the unified value of $\delta_{G'G}$, the exact value could not be suggested, but the unified order of $\delta_{G'G}$ is meaningful. As shown in Fig 3, the absorption rate of O$_2$ was evaluated by comparing the result of this parameter study and the experimental result, the value of $\delta_{G'G}$ would be less than 0.01 m. Also, the detailed order might be approximately 0.001 m. If the value of $\delta_{G'G}$ is larger than 0.01 m, the infiltration rate of oxygen into liquid steel will be set very slowly.

5.3. Application of the Present Model to TD-Scale

The result of TD-scale analysis utilizing the values of the parameter previously mentioned was shown in Figure 4. The air bubbles from the end of the shroud nozzle go downward to the bottom of the tundish. Afterward, they float up to the surface of liquid steel and contribute to making slag open eye with the upflow of liquid steel. While the bubble flows, the air filling the bubble acts as an O$_2$ source. Thus, there are oxygen sources not only at the slag open eye but also at the air bubble in the shroud nozzle. This contribution was reflected partially oxidized region in the shroud nozzle. As a quantitative analysis, the composition of liquid steel for both at the end of shroud nozzle marked as ‘A’ in Figure 2(b) and at the entry of SEN marked as ‘B’ reached a steady-state within 25 seconds, as shown in Figure 4, except for Al$_2$O$_3$. The composition of liquid steel at the location ‘B’ represents the status of entering material into casting mold, through the SEN. As regard to the location to take a sample marked as ‘C’, the result of TD-scale analysis is similar in that the composition of the tundish specimen as mentioned at 4.2 is matched with the composition of TD specimen with a reasonable range. This implies that this model seems to work to predict for the reoxidation behavior in the tundish operations, employing the parameter from lab-scale comparison. In the present study, the geometry of the tundish does not correspond to a real tundish, but it means applicable potential of the present model.

The present analysis was based on a 2D-modeling. This implies that the reoxidation behavior might be over-estimated because the width-directional dissipation of reactant was neglected. Due to this characteristic, the system for this reaction modeling can be extended into 3D-modeling, which has more realistic shape of tundish.

5.4. Possibility to extend the present model

The present model targets to reflect reoxidation phenomena of ultra-low C steel during the tundish operation. In particular, this model reflects not only the interfacial (heterogeneous) reaction between gas component and liquid steel, but also the homogeneous reaction forming other phase such as suspending oxide inclusion. Thus, the extension of the present model can be thought such as followings: 1) modifying the reaction model from Al-killed steel to other species such as Si-killed steel, 2) altering the reactant from O$_2$ gas to other gas such as CO or N$_2$ gas, and 3) changing the system from the tundish to ladle process involving bottom bubbling. The first can be realized by modifying both the interaction parameter formalism to a more sophisticated deoxidation model to get equilibrium composition and stoichiometry of deoxidation reaction and reaction product. The second can be reflected by employing other values of absorption efficiency such as $\varepsilon$ to be obtained by the experimental-similar way. The last can be achieved by changing the system to carry out CFD calculation from the tundish to the other operation, such as ladle with bottom bubbling. In other words, the present model has a good expandability to the other system and operations.
CONCLUSION

The model to predict reoxidation phenomena of Al-killed liquid steel at the TOE was organized on the basis of CFD method with respect to the chemical reaction mechanism. It targets to reflect not only O2 absorption from the air into liquid steel in the vicinity of the TOE but also arrival to the deoxidation equilibrium with the formation of Al2O3 inclusion. In order to evaluate consistency between the present model and real phenomena, the optimization of the parameter in the present model was carried out through the experimental method. The usage of the present model can be expanded to reflect the reoxidation behavior for not only the other system such as an application for Si-killed steel or absorption of CO gas, but also each secondary refining process. Thus, this work can contribute to not only an industrial usage, but also a theoretical aspect such as methodology combining CFD and metallurgical understanding.

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