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Influence of calcium aluminate flux on reoxidation behaviour of molten steel during continuous casting process

Tae Sung Kim^a, Lauri Holappa^b and Joo Hyun Park^a

^a Department of Materials Engineering, Hanyang University, Ansan 15588, Korea

^b School of Chemical Engineering, Aalto University, Espoo, Finland

CONTACT Joo Hyun Park ; basicity@hanyang.ac.kr

ABSTRACT

It is an important issue to prevent molten steel in tundish from being reoxidized during continuous casting process for improving the cleanliness of steel products. Rice husk ash (RHA) is an excellent insulation powder to prevent heat loss of the molten steel in the tundish. The addition of RHA increases the silica activity in molten slag layer, which can cause reoxidation of molten steel. Therefore, the effect of calcium aluminate-based flux (CA-flux) on reoxidation behavior was investigated with different ratios of CA-flux to RHA+CA-flux (=RCA). The silicon and oxygen pick-up, which is caused by the self-dissociation of silica at the slag-metal interface was suppressed with increasing RCA, and hence the number of inclusions formed by reoxidation in the molten steel was reduced at high RCA. The evolution of inclusions with different RCA was investigated by comparing experimental results with predictions from a refractory-slag-metal-inclusion (ReSMI) multiphase reaction simulation. Finally, the inclusion formation behavior in tundish was investigated using a ReSMI simulation with different RCA and including the temperature drop of the steel melts in the ladle during casting.

KEYWORDS Reoxidation, Tundish, Cleanliness, Rice husk ash, Calcium aluminate flux, Refractory-Slag-Metal-Inclusion (ReSMI) model.

Introduction

Because the continuous casting tundish is the last metallurgical reactor for removing non-metallic inclusions before distributing molten steel into casting strands, it is essential to control reoxidation of molten steel in the tundish for manufacturing high cleanliness steel products [1]. The entrapment of carryover ladle slag, reaction with tundish flux, degradation of the refractory, reaction with ladle well packing materials, and/or oxidation by air contaminate molten steel in the tundish [1-4].

The reoxidation of molten steel in the tundish can occur at either the initial teeming stage at the beginning of casting or the transition period or even at the stable teeming stage. During the initial teeming stage, the molten steel becomes exposed to ambient air, which oxidizes the molten steel as the steel is devoid of tundish flux under condition of turbulent flow [5-8]. The reoxidation of molten steel during the initial teeming stage can be suppressed with Ar protection [9]. Moreover, oxidation by air is less significant after the molten steel is covered by tundish flux at the stable teeming stage [5].

Because the molten steel in a tundish can react with tundish flux, it is necessary to control the contents of iron oxide, manganese oxide and/or silica, which could be oxygen source by slag-metal reaction. Nevertheless, the molten steel in the tundish is commonly covered by rice husk ash (RHA), which mainly consists of SiO_2 , because the RHA has an excellent thermal insulation property [10]. In a previous study [11], the effect of RHA not only on the corrosion of magnesia refractory but also on the reoxidation of molten steel was investigated by the present authors. The increase in silica activity of the molten slag by the dissolution of SiO_2 from RHA causes an interfacial reaction between aluminum in Al-killed steel and silicate in the slag:

Several authors have performed kinetic analysis of the interfacial reaction in Eq. (1) [11-19]. The transfer of oxygen from slag-metal interface to bulk metal, which is caused by self-dissociation of SiO_2 into $[\text{Si}]$ and $[\text{O}]$ at the interface due to high silica content in tundish flux, could result in supersaturated soluble oxygen level in the molten steel. The supersaturated oxygen then reacts with dissolved aluminum resulting in formation of Al_2O_3 clusters [11,19-22]. To predict the formation behavior of inclusions in the tundish, both an equilibrium study and a kinetic study are necessary.

Many researchers have evolved the different kinetic models to understand the phenomena that occur in various steelmaking processes such as vacuum oxygen decarburization (VOD) [23], RH refining [24], ladle furnace (LF) [25-34], and continuous casting tundish and mold [17,35,36]. Ren et al. [35] investigated the evolution of steel chemistry and the composition of inclusions caused by reoxidation of Al-killed steel in the tundish using FactSage™ software. However, the reaction model used in this study is limited because it only considers reoxidation by incoming air during the cast start and ladle change periods without considering the chemical reactions between tundish flux and molten steel.

Recently, Shin et al. [31-33] developed the refractory-slag-metal-inclusion (ReSMI) multiphase reaction model based on the effective equilibrium reaction zone (EERZ) model in conjunction with FactSage™ for kinetic analysis and the prediction of inclusion evolution during the ladle refining process [34,36]. The ReSMI reaction model is convenient and flexible in that it can be extended to various metallurgical processes because the model only employs the effective reaction volume in the metal and slag phase in conjunction with mass transfer coefficient of MgO in the slag phase at the slag-refractory interface.

Consequently, the effect of calcium aluminate based tundish flux (CA-flux) on the reoxidation behavior of molten steel was investigated by employing computational simulations based on the ReSMI reaction model to predict inclusion evolution. The simulation was adopted to predict the reoxidation of molten steel in tundish during a continuous casting process.

Experimental procedure

Electrolytic iron, metal silicon and reagent grade carbon were used for aiming target steel composition (Fe-0.2C-0.1Si, wt-%). The Fe-C-Si steel (500g) was heated using a high-frequency induction furnace equipped with quartz reaction tube and a graphite heating element. After the temperature of the Fe-C-Si steel reached 1550 °C, Fe-16%Al alloy was added for aiming [Al] = 0.003 wt-%. The detailed experimental apparatus and experimental procedure are shown elsewhere [11].

The compositions of the commercial CA-flux and the RHA powder are listed in Table 1. The total quantity of RHA and CA-flux amounted to 50 g. Experiments were carried out that varied the ratio of CA-flux to total RHA and CA-flux mass ($=[\text{CA-flux}]/[\text{RHA} + \text{CA-flux}] = \text{RCA}$ = 0.5, 0.75, 0.83, 0.87, 0.90). A steel sample was taken at 5 and 10 min from the start of the experiment.

Table 1. Initial composition of the commercial calcium aluminate-based flux (CA-flux) and rice husk ash (RHA) powder used in the present experiments (wt-%).

Type	CaO	Al ₂ O ₃	SiO ₂	MgO	Na ₂ O	Fe ₂ O ₃	C
CA-flux	55	35	4	4	1	1	-
RHA	4	7	73	1	-	-	15

The total oxygen and nitrogen contents in the steel samples were analyzed by combustion analysis method (NO, TC-300, LECO). The total amount of Si and Al in the steel were analyzed by inductively coupled plasma - atomic emission spectroscopy (ICP-AES, ACROS, SPECTRO). The field-emission scanning electron microscopy with an energy dispersive X-ray spectroscope (FE-SEM EDS, JSM-7800, JEOL) combined with automatic

feature analysis (AFA) was utilized to quantitatively characterize the observed inclusions in the steel samples taken at 5 min in terms of the number density, morphology and composition. The accelerating voltage was 15 kV, the magnification was 500 $\times$, the pixel size was 0.5 μm pixel, and the inclusions were detected with a 1 μm limit diameter in a 2.4 mm $\times$ 2 mm area.

Basic concept of simulation

Application of ReSMI multiphase reaction model

RHA powder is poured onto CA-flux for reducing heat loss of molten steel in tundish because RHA has excellent insulation properties. Several phenomena (R1-R4 in [Figure 1](#)) must be considered, when attempting to predict the reoxidation behavior between tundish flux and molten steel during the simulations. RHA will continuously dissolve into molten slag due to a gradient in SiO_2 concentration in CA-flux (R1), which results in composition changes in the molten slag phase. The changes to the slag resulting from the dissolution of RHA causes variation in the chemical composition of molten steel from the oxidation-reduction reactions at the slag-metal interface (R2). The increase in MgO content of the molten slag, which is caused by dissolution of MgO from magnesia refractory hot face (R3), is also considered to predict the compositional changes of molten steel. Consequently, the local equilibrium in inclusion-metal reaction (R4) draws the evolution of the inclusions in the molten steel during the refractory-slag-metal reactions in each time step. A schematic of these phenomena is shown in [Figure 1](#). In the present study, we rarely considered the chemical reaction between magnesia refractory and molten steel because the Mg pick-up introduced from the slag-metal reaction is considerably faster than that from refractory-metal from a kinetics standpoint.

The reaction zone mass per unit step is necessary to calculate slag-metal reaction kinetics, instead of using the general flux density equations. That is, a constant volume of

metal from the bulk metal and a constant volume of slag from the bulk slag enter the metal-slag reaction zone at a fixed time interval. The reaction zone volume per unit step for metal and slag phase can be described as follows:

$$V_M^t = \frac{w_M^t}{\rho_M} = d_M \cdot A \cdot \Delta t, \quad (2)$$

$$V_S^t = \frac{w_S^t}{\rho_S} = d_S \cdot A \cdot \Delta t, \quad (3)$$

where the subscripts M and S represent the metal and slag phases, respectively, W represents reaction zone mass per unit step (g), d_M and d_S represent the effective reaction zone depths per time interval (m/s), ρ_M and ρ_S represent the densities of each phase (g/m³), and A represents the interface area between the metal and slag phase (m²).

Figure 1. Schematic of the dissolution of RHA (R1), the slag-metal reaction (R2), the refractory-slag reaction (R3), and the inclusion-metal reaction (R4) in the ReSMI modeling system employed.

The multicomponent and multiphase equilibria at the reaction zone in the ReSMI simulation have been calculated using the FactSageTM software (version 7.3) [37,38]. The

'FTmisc' database and 'FToxid' database were adopted for liquid steel and oxide solutions for the tundish flux and inclusions, respectively. The FactSageTM software has been successfully employed to estimate the thermodynamic equilibria for gas-slag-metal-refractory multiphase reactions in ferrous and nonferrous metallurgical systems [39-45].

Determination of ReSMI model parameters for slag-metal reaction kinetics

Because RHA will continuously dissolve into the molten slag layer (R1), it should be considered that the dissolution rate of SiO₂ from RHA to slag layer for understanding slag-metal reaction kinetics. Feichtinger et al. [46] concluded that the dissolution rate of silica into the CaO-SiO₂-Al₂O₃ slag is strongly proportional to fluidity of the molten slag (1/η). The dissolution rate of silica was measured as 11.0×10⁻⁶ m/s at which the viscosity was about 0.5 Pa·s at 1450 °C. Because the viscosity of CaO-Al₂O₃-SiO₂-MgO (C/A=1.8, SiO₂=7 and MgO=5 wt-%), which is similar in composition to CA-flux, is about 0.1 to 0.2 Pa·s at 1550 °C [47], it can be assumed that the SiO₂ in RHA layer could be rapidly dissolved into the molten slag layer under the present experimental conditions. Therefore, we assumed that RHA is completely dissolved into molten slag before calculating the oxidation-reduction reactions at slag-metal interface (R2).

As shown in Eqs. (2) and (3), it is important to determine the effective reaction zone depth for accurate modeling of ReSMI multiphase reaction kinetics. The value of effective reaction zone depth of metal and slag (d_M and d_S) could be deduced from the mass transfer coefficients in the metal and slag phase.

The reaction rate of Al in metal phase for Eq. (1) can be represented by Eq. (4):

$$-\ln \frac{[\text{wt}\% \text{ Al}]_t - [\text{wt}\% \text{ Al}]_e}{[\text{wt}\% \text{ Al}]_0 - [\text{wt}\% \text{ Al}]_e} = k_{Al} \frac{A}{V_M} \left(\frac{[\text{wt}\% \text{ Al}]_0}{[\text{wt}\% \text{ Al}]_0 - [\text{wt}\% \text{ Al}]_e} \right) t, \quad (4)$$

where k_{Al} is the mass transfer coefficient of Al in the metal phase (m/s), V_M is the volume of

metal (m^3), and A is the reaction area between the slag and the metal (m^2), which is assumed to be the inner cross-sectional area of the crucible. Subscripts t , e , and 0 represent specific time, equilibrium, and initial condition, respectively.

The concentration of Al in the metal phase at specific time, $[wt\% Al]_t$, can be determined by considering the mass balance of aluminum as follows:

$$[wt\% Al]_t = \frac{[wt\% Al]_0 \cdot (W_M - W_M^t) + [wt\% Al]_e \cdot W_M^t}{W_M}, \quad (5)$$

where $[wt\% Al]_0$ is the initial concentration of Al in the metal, $[wt\% Al]_e$ is the equilibrium concentration in the metal, and W_M is total weight of metal. The effective reaction zone mass of metal phase per unit step can be obtained from rearranging Eq. (5):

$$W_M^t = \frac{([wt\% Al]_t - [wt\% Al]_0)}{([wt\% Al]_e - [wt\% Al]_0)} \cdot W_M. \quad (6)$$

The effective reaction zone depth of metal phase per unit time interval (d_M) can be calculated by combining Eqs. (2) and (6) if the concentration of Al in the metal at specific time is obtained. The effective reaction zone depth of slag phase per unit time interval (d_S) can be deduced in a similar way. Therefore, the effective reaction zone depths can be deduced from the mass transfer coefficients in the metal and slag phases.

Rhamdhani et al. [13] and Kang et al. [15] presented that the mass transfer of Al in metal phase is the rate determining step for the interfacial reaction kinetics between Al-killed steel ($Al < 4$ wt-%) and molten slag. Rhamdhani et al. [13] suggested that $k_{Al}=1.7 \times 10^{-6}$ m/s at 1650 °C, while Kang et al. [15] reported that $k_{Al}=0.9-1.2 \times 10^{-4}$ m/s at 1500 °C. In a previous study carried out with similar conditions to those in the present study, the obtained mass transfer coefficient for Al in the metal phase was in the range of $1.5-2.0 \times 10^{-4}$ m/s at 1550 °C [11]. A value of $k_{Al}=2.0 \times 10^{-4}$ m/s was chosen for the present study.

Kim et al. [18] found that the reaction given in Eq. (1) between high Mn-high Al steel (Mn = 20.8 and Al = 5.2 wt-%) and CaO-SiO₂ type molten flux at 1450 °C is controlled by mass transfer in the slag phase. This study also reports that the mass transfer coefficients of Al₂O₃ and SiO₂ in the slag phase are in the ranges of 5-10×10⁻⁶ m/s and 4-8×10⁻⁶ m/s, respectively. The mass transfer coefficient in slag phase was determined to be 5.0×10⁻⁶ m/s in the present study. Consequently, the effective reaction zone depths of $d_M=2.0\times10^{-4}$ m/s and $d_S=3.5\times10^{-5}$ m/s were obtained.

The dissolution rate of MgO from refractory to the molten slag phase could be described by a gradient between the saturation value of MgO, (wt-% MgO)_{sat}, and the actual MgO content in the bulk slag at time t , (wt-% MgO) _{t} , when the mass transfer of MgO in the slag phase is the rate determining step. In the present study, the rate equation of MgO dissolution is then given as follow:

$$-\ln \left[\frac{(\text{wt}\% \text{ MgO})_{\text{sat}} - (\text{wt}\% \text{ MgO})_t}{(\text{wt}\% \text{ MgO})_{\text{sat}} - (\text{wt}\% \text{ MgO})_0} \right] \cdot \left(\frac{W_S}{\rho_S \cdot A_{\text{slag/ref}}} \right) = k_{\text{MgO}} \cdot t, \quad (7)$$

where the k_{MgO} represents the mass transfer coefficient of MgO in the slag phase, $A_{\text{slag/ref}}$ represents the interfacial area between slag and refractory phase and the (wt% MgO)₀ is the initial content of MgO in the slag. Here, the actual MgO content in the slag at time t , (wt% MgO) _{t} , has the following relationship with the mass of MgO in the slag at time t (W_{MgO}^t):

$$W_{\text{MgO}}^t = \frac{(\text{wt}\% \text{ MgO})_t}{100 - (\text{wt}\% \text{ MgO})_t} \cdot W_{\text{S,total}}^{t-1}, \quad (8)$$

where $W_{\text{S,total}}^{t-1}$ represents the total mass of the slag right before the time t . Combining Eqs. (7) and (8), W_{MgO}^t can be obtained. The saturation value of MgO of the present slag system was calculated using the FactSage™ 7.3 software, and $W_{\text{S,total}}^{t-1}$ could be obtained in the ReSMI

multiphase reaction model at each step. In the present study, $k_{\text{MgO}}=5.0\times10^{-6}$ m/s was adopted as the mass transfer coefficient of MgO, a value obtained in the previous studies for ReSML multiphase reaction simulations [32].

The required simulation conditions are listed in Table 2. The simulation was carried out following similar steps to previous studies using the ReSML multiphase reaction model. The slag-metal reaction at the effective reaction zone was calculated, for which the reaction volumes of metal and slag phases were calculated using Eqs. (2) and (3). Next, the effective reaction zone of slag and bulk slag was mixed for the homogenization of the slag phase, from which the value of the total amount of slag was deduced. This amount was then used for calculation of the increase in MgO content to describe the MgO dissolution from the refractory using Eq. (7). This result was used as the input in the equilibrium calculation of the slag phase, from which the slag composition at time t was obtained. Simultaneously, the effective reaction zone of metal and bulk metal was mixed for the homogenization of the metal phase, from which the composition of molten steel at time t , and thus the inclusion information, could be finally obtained. This procedure was one step of the calculation, and the above procedure was repeated until the time t reached the desired final time. The calculated results of slag and metal phase at each step were consecutively inputted to variables for the next step in the calculation.

Table 2. Simulation conditions.

Parameters	Value (unit)
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Total weight of slag (W_S)	50 (g)
Weight of metal (W_M)	500 (g)
Diameter of crucible	50 (mm)
Density of molten steel	6.96 (g/cm ³)
Density of molten slag	2.50 (g/cm ³)
Temperature	1550 (°C)
Effective reaction zone depth of metal phase (d_M)	2.0×10^{-4} (m/s)
Effective reaction zone depth of slag phase (d_S)	3.5×10^{-5} (m/s)
Mass transfer coefficient of MgO (k_{MgO})	5.0×10^{-6} (m/s)
Time per unit step	60 (s)
Total number of steps	10 (-)
Total time	600 (s)

Results and Discussion

Comparison of experimental data and simulation results for reoxidation of Al-killed steel by slag-metal reaction

The total oxygen content in the Al-killed steel with different RCA as a function of reaction time at 1550 °C is shown in [Figure 2](#). The initial content of oxygen of the Al-killed steel was about 15(±3) ppm. The oxygen content in the steel drastically changed throughout the experiment as the relatively large amounts of RHA with a RCA of 0.50 were added. The oxygen pick-up (ΔO) within 10 min continuously decreased with increasing RCA and the oxygen content remained almost unchanged when the RCA was over 0.85. The solid lines in [Figure 2](#) represent the calculated results from the ReSMI multiphase reaction model. The calculated results showed similar trends as the experimental results, specifically a decrease in oxygen pick-up with increasing RCA, despite some scatter between the experimental and calculated results.

Figure 2. Total oxygen content in the steel melt as a function of reaction time with different RCA.

The change of Al and Si concentration in the steel as a function of reaction time and RCA at 1550 °C is shown in [Figure 3](#). The initial contents of Al and Si were about 0.03 and 0.1 wt-%, respectively. The solid lines in [Figure 3](#) represent the calculated results from the ReSMI multiphase reaction model. As soon as the CA-flux and the RHA were added on the molten steel, Al concentration in the steel decreases within 10 min, as shown in [Figure 3\(a\)](#). The oxidation rate of Al within 10 min is very fast at RCA=0.50, while it decreases with increasing RCA. The calculated results for Al content in the steel showed similar trends to the changes of Al content in the experimental results.

Figure 3. Changes to the concentration of (a) Al and (b) Si in the steel melt as a function of reaction time with different RCA.

The content of Si in the steel remained almost unchanged at relatively high RCA (i.e., greater than 0.8), while the Si pick-up was more serious at relatively low RCA (less than 0.8), as shown in Figure 3(b). The calculated results were in good agreement with the experimental results with the exceptions of the 10 min steel samples at relatively low RCA. In a previous study [11], it was observed that the increase of RHA addition to the slag enhances the reduction of SiO_2 compared to the oxidation of Al from Eq. (1).

Bessho et al. [1] reported that contamination of the molten steel in tundish is dependent

on the silica activity in tundish flux. The Si pick-up was suppressed at low silica activity ($a_{\text{SiO}_2} < 0.008$). Tanaka et al. [19,22] proposed a mechanism for the dynamic interfacial phenomena at the slag-metal interface influenced by the chemical reaction in Eq. (1). The released [Si] from SiO_2 dissociation at the slag-metal interface directly diffuses into steel bulk, while the released [O] tends to be absorbed at the slag-metal interface and then diffuses into steel bulk after the interface is saturated. Some researchers also found that [Si] and [O] dissociated from SiO_2 at the slag-metal interface transfer into the Al-containing alloy, where [O] further reacts to form Al_2O_3 clusters in the alloys [11,20,21]. It is not concluded that the ReSMI multiphase reaction model fully describes the silicon pick-up caused by dynamic interfacial phenomena at the slag-metal interface because all phases within the effective reaction zone at the slag-metal interface are assumed to reach local equilibrium in the model.

Characterization of inclusions in molten steel at initial stage of reoxidation reaction

The inclusions morphology observed in the steel sample at 5 min using SEM are shown in Figure 4. Three types of inclusions are shown: Al_2O_3 -rich ($\text{Al}_2\text{O}_3 > 80$ wt-%, spinel-type (mainly MgAl_2O_4) and monoxide (Mg,Ca)O inclusions. The total number of inclusions per unit area in the 5 min steel samples continuously decreased with increasing RCA and dramatically fell in the experiments with the two highest RCA heats (0.87, 0.9), as shown in Figure 5. The experimental and calculated variation of the relative fraction (population) of the inclusions in the 5 min steel samples is shown as a function of RCA in Figure 6. It is interesting that the calculations reveal a similar tendency for inclusion evolution as a function of RCA as that obtained from the experiment. The relative fraction of Al_2O_3 -rich inclusions dramatically decreased and that of spinel-type inclusions was evaluated when the RCA was over 0.8. The spinel-type inclusions were formed from the reaction between Al_2O_3 inclusions and magnesium that originated from the slag phase. The related reactions are as follows [11,32-35,48].

Figure 4. Typical SEM micrograph of the inclusions in the steel sample at 5 min: (a) spinel type, (b) monoxide, and (c) Al₂O₃-rich inclusions.

Figure 5. Number of inclusions per unit area in 5 min experiments at different RCA.

(a)

(b)

Figure 6. (a) Experimental and (b) calculated changes to the relative fraction of the inclusions in molten steel at 5 min as a function of RCA.

The size distribution and the average diameter of Al₂O₃-rich (including spinel-type) inclusions in the 5 min steel samples are shown in Figure 7. When the RCA was 0.5, the observed Al₂O₃-rich inclusions were larger than 3.0 μm . However, the relative population of fine (smaller than 2.5 μm) Al₂O₃-rich inclusions sharply increased simultaneously with decreases in the proportion of inclusions larger than 2.5 μm when the RCA was greater than 0.8. Therefore, the average size of the inclusions decreased with increasing the RCA, which indicates that the reoxidation of molten steel is suppressed by large amounts of CA-flux.

Figure 7. Size distribution and average size of Al_2O_3 -rich (including spinel-type) inclusions at 5 min as a function of RCA.

The mean composition ranges of inclusions with RCA of 0.50, 0.75, 0.83, 0.87 and 0.90 are shown in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-5\%SiO}_2$ phase diagram at 1550 °C in [Figure 8](#). The composition of the inclusions at a RCA of 0.50 is mainly located in the Al_2O_3 -corner. As the RCA increased over 0.8, the Al_2O_3 content in the inclusions continuously decreased because the increase in RCA suppressed the oxygen pick-up from the slag into the metal. The solid red circles mean the calculated average composition of inclusions at 5 min with different RCA. The trend of the solid red circles with increasing RCA was similar to that of the observed mean composition of inclusions relative to RCA.

Figure 8. Composition of the inclusions at different RCA.

Prediction of reoxidation behavior of molten steel during continuous casting process

It might be expected that the temperature of molten steel in a ladle continuously decreases during pouring of the molten steel into the continuous casting tundish. The temperature drop of the steel influences on the thermodynamic equilibrium of Al deoxidation in the steel. Hence, the temperature drop of the steel melts in ladle would also cause the simultaneous formation of non-metallic inclusions. The molten steel poured from ladle stays in the tundish for a few minutes before solidifying in the continuous casting mold. Therefore, the chemical reaction between the molten steel and tundish flux as well as the temperature drop of molten steel in ladle could result in the formation of alumina inclusions in the ladle and the tundish simultaneously (Figure 9).

Figure 9. Schematic of the (a) initial and (b) last stage in continuous casting process.

The computational simulations of the reoxidation behavior of molten steel during continuous casting were carried out based on the ReSMI multiphase reaction model for tundish process, which is discussed in the previous section, and the ladle process. To simplify the model and the calculations, the following assumptions were made: (1) the

reoxidation of molten steel by air is negligible, (2) there is steady state flow of molten steel in the ladle and tundish during casting, and (3) the temperature of the molten steel in the ladle linearly decreases from 1600 to 1550 °C during casting. One hundred tons of molten steel is teemed from the ladle into the tundish with a casting rate of 2.5 tons per min. The molten steel teemed from ladle remains in the tundish for 5 min during casting. Detailed simulation conditions used in the ReSMI multiphase reaction model are listed in [Table 3](#). The similar compositions of steel, CA-flux and RHA, which were discussed in the previous section, and the typical composition of ladle slag (45CaO-35Al₂O₃-10SiO₂-5MgO-5CaF₂, wt-%) were used for the simulation.

Table 3. Simulation conditions for reoxidation behavior of molten steel during continuous casting.

Parameters	Value (unit)
Weight of slag in ladle	1 (ton)
Weight of metal in ladle	100 (ton)
Diameter of ladle	4 (m)
Total weight of tundish flux in tundish	200 (kg)
Area of slag-metal interface in tundish	1 (m ²)
Weight of steel in tundish	12.5 (ton)
Density of molten steel	6.96 (g/cm ³)
Density of molten slag	2.50 (g/cm ³)
Temperature in ladle	1600 to 1550 (°C)
Temperature in tundish	1550 (°C)
Casting rate	2.5 (ton/min)
Duration of molten steel in tundish	5 (min)
Casting time	30 (min)

The calculation results for reoxidation behavior of molten steel with different RCA in the tundish as a function of casting time during continuous casting are shown in [Figure 10](#). The number of inclusions formed by the chemical reaction between tundish flux and molten steel

declined with increasing RCA. It is noteworthy that the number of inclusions in the molten steel suddenly rose near the end of the casting time. As the temperature of the steel melts in the ladle continuously decrease with casting time, the inclusions are formed by the gradient of oxygen solubility in Al-killed steel melts with different temperature. Therefore, the chemical composition of tundish slag in the tundish and the temperature drop in ladle seriously affect the alumina formation behavior in molten steel during continuous casting.

Figure 10. Variation in the number of inclusions in the molten steel at the end of tundish process and the temperature of the molten steel in the ladle as a function of casting time during continuous casting.

In tundish conditions, dissolution of inclusions into the slag phase can be the rate controlling step for the entire removal of inclusions, changes to the physicochemical properties of the molten slag determine the removal rate of inclusions from the steel melts [49,50]. The present calculations do not consider the effect of these physicochemical properties and only reflect the chemical slag-metal reaction by varying temperatures. Thus, it is necessary to investigate the relationship between the physicochemical properties of slag and the removal rate of inclusions at different temperatures for a better understanding of the reoxidation (and inclusion removal) phenomena during continuous casting process.

Conclusions

We investigated the effect of calcium-aluminate (CA) flux and rice husk ash (RHA) on the reoxidation of molten steel experimentally in tundish conditions. Further the computational simulation based on ReSMI multiphase reaction model was applied for predicting the reoxidation of molten steel in continuous casting process. The results of this study can be summarized as follows.

1. The reoxidation of the steel was very pronounced when a relatively large amount of RHA (RCA=0.50) was added, resulting in significant oxygen pick-up. With increasing RCA, the reoxidation declined and almost ceased when RCA was increased over 0.8 (i.e., 80%CA + 20%RHA).
2. The increase of the silica activity in the slag layer with increasing RHA content caused silicon and oxygen pick-up by the self-dissociation of silica from the slag layer (i.e., $\text{SiO}_2 = [\text{Si}] + 2[\text{O}]$), which resulted in reoxidation of the molten steel. The addition of sufficient amount of CA-flux suppressed the reoxidation of the molten steel, resulting in a decrease in the total number of inclusions.
3. The relative fraction of Al_2O_3 -rich inclusions formed by reoxidation of molten steel continuously decreased with increasing RCA. Simulations based on a ReSMI multiphase reaction model for the evolution of inclusions with different RCA were in good agreement with the experimental results.
4. For the computational simulation, it was noteworthy that not only tundish flux but also the temperature drop of molten steel in ladle deteriorates the cleanliness of Al-killed steel at the end of casting period during continuous casting.

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References

- [1] Bessho N, Yamasaki H, Fujii T, et al. Removal of inclusion from molten steel in continuous casting tundish. *ISIJ Int.* 1992;32(1):157-163.
- [2] Habu Y, Kitaoka H, Yoshii Y, et al. Origin and removal of large non-metallic inclusions present during continuous casting of wide slabs. *Tetsu-to-Hagane.* 1976;62(14):1803-1812.
- [3] Tanaka H, Nishihara R, Miura R, et al. Technology for cleaning of molten steel in tundish. *ISIJ Int.* 1994;34(11):868-875.
- [4] Sasai K, Mizukami Y. Reoxidation behavior of molten steel in tundish. *ISIJ Int.* 2000;40(1):40-47.
- [5] Kuchar L, Holappa L. Prevention of steel melt reoxidation by covering powders in tundish. *Proc. of 76th Steelmaking Conference, Dallas, TX, USA; 1993*, p. 28-31.
- [6] Tanaka H, Nishihara R, Kitagawa, et al. Quantitative analysis of contamination of liquid steel in tundish. *Tetsu-to-Hagane.* 1993;79(11):1254-1259.
- [7] Manninen V, Lano T, Holappa L. Low reoxidation tundish metallurgy at Fundia Koverhar steel plant. *Scand J Metall.* 2000;29(4):156-165.
- [8] Holappa L, Nurmi S, Louhenkilpi S. Role of slags in steel refining: is it really understood and fully exploited? *Rev de Metall Paris.* 2009;106(1):9-20.
- [9] Higuchi Y, Tago Y, Fukagawa S, et al. Reoxidation behavior in Al-killed steel during casting. *Tetsu-to-Hagane.* 1999;85(5):375-381.
- [10] Sahai Y, Emi T. *Tundish Technology for Clean Steel Production*, World Scientific; 2008, p. 201-202.
- [11] Kim TS, Chung Y, Holappa L, Park, JH. Effect of rice husk ash insulation powder on the reoxidation behavior of molten steel in continuous casting tundish. *Metall Mater Trans B.* 2017;48(3):1736-1747.
- [12] Sun H, Mori, K. Oxidation rate of aluminum in molten iron by CaO-SiO₂-Al₂O₃-FeO-MnO slag. *ISIJ Int.* 1996;36:S34-37.
- [13] Rhamdhani MA, Brooks GA, Coley KS. Kinetics of metal/slag reactions during spontaneous emulsification. *Metall Mater Trans B.* 2005;36(2):219-227.
- [14] Kim DJ, Park JH. Interfacial reaction between CaO-SiO₂-MgO-Al₂O₃ flux and Fe-xMn-yAl (x = 10 and 20 mass pct, y = 1, 3, and 6 mass pct) steel at 1873 K. *Metall Mater Trans B.* 2012;43(4):875-886.
- [15] Kang YB, Kim MS, Lee SW, et al. A reaction between high Mn-high Al steel and CaO-SiO₂-type molten mold flux: Part II. Reaction mechanism, interface morphology, and Al₂O₃ accumulation in molten mold flux. *Metall Mater Trans B.* 2013;44(2):309-316.
- [16] Park J, Sridhar S, Fruehan RJ. Kinetics of reduction of SiO₂ in SiO₂-Al₂O₃-CaO slags by Al in Fe-Al(-Si) melts. *Metall Mater Trans B.* 2014;45(4):1380-1388.
- [17] Kim MS, Kang YB. Development of a multicomponent reaction rate model coupling thermodynamics and kinetics for reaction between high Mn-high Al steel and CaO-SiO₂-type molten mold flux. *Calphad.* 2018;61:105-115.
- [18] Kim MS, Park MS, Kang SE, et al. A reaction between High Mn–High Al steel and CaO-SiO₂-type

- molten mold flux: Reaction mechanism change by high Al content ($[pct Al]_0 = 5.2$) in the steel and accumulation of reaction product at the reaction interface. *ISIJ Int.* 2018;58(4):686-695.
- [19] Ni P, Tanaka T, Suzuki M, et al. A kinetic model of mass transfer and chemical reactions at a steel/slag interface under effect of interfacial tensions. *ISIJ Int.* 2019;59(5):737-748.
- [20] Chung Y. Surface and interfacial phenomena in iron-alloys (Ph.D. Thesis), Carnegie Mellon University, Pittsburgh, PA, USA; 1999.
- [21] Park DC, Jung IH, Rhee PCH, et al. Reoxidation of Al–Ti containing steels by CaO–Al₂O₃–MgO–SiO₂ slag. *ISIJ Int.* 2004;44(10):1669-1678.
- [22] Tanaka T, Goto H, Nakamoto M, et al. Dynamic changes in interfacial tension between liquid Fe alloy and molten slag induced by chemical reactions. *ISIJ Int.* 2016;56(6):944-952.
- [23] Ding R, Blanpain B, Jones PT, et al. Modeling of the vacuum oxygen decarburization refining process. *Metall Mater Trans B.* 2000;31(1):197-206.
- [24] Van Ende MA, Kim YM, Cho MK, et al. A kinetic model for the Ruhrstahl Heraeus (RH) degassing process. *Metall Mater Trans B.* 2011;42(3):477-489.
- [25] Harada A, Maruoka N, Shibata H, et al. A kinetic model to predict the compositions of metal, slag and inclusions during ladle refining: Part 1. Basic concept and application. *ISIJ Int.* 2013;53(12):2110-2117.
- [26] Harada A, Maruoka N, Shibata H, et al. A kinetic model to predict the compositions of metal, slag and inclusions during ladle refining: Part 2. Condition to control the inclusion composition. *ISIJ Int.* 2013;53(12):2118-2125.
- [27] Harada A, Maruoka N, Shibata H, et al. Kinetic analysis of compositional changes in inclusions during ladle refining. *ISIJ Int.* 2014;54(11):2569-2577.
- [28] Hsieh Y, Watanabe Y, Asai S, et al. Effect of recirculating flow rate of molten steel in refining processes. *Tetsu-to-Hagane.* 1983;69(6):596-603.
- [29] Roy D, Pistorius PC, Fruehan RJ. Effect of silicon on the desulfurization of Al-killed steels: Part I. Mathematical model. *Metall Mater Trans B.* 2013;44(5):1086-1094.
- [30] Roy D, Pistorius PC, Fruehan RJ. Effect of silicon on the desulfurization of Al-killed steels: Part II. Experimental results and plant trials. *Metall Mater Trans B.* 2013;44(5):1095-1104.
- [31] Shin JH, Chung Y, Park JH. Refractory–Slag–Metal–Inclusion multiphase reactions modeling using computational thermodynamics: Kinetic model for prediction of inclusion evolution in molten steel. *Metall Mater Trans B.* 2016;48(1):46-59.
- [32] Shin JH, Park JH. Modification of inclusions in molten steel by Mg-Ca transfer from top slag: Experimental confirmation of the ‘Refractory-Slag-Metal-Inclusion (ReSMI)’ multiphase reaction model. *Metall Mater Trans B.* 2017;48(6):2820-25.
- [33] Shin JH, Park JH. Effect of CaO/Al₂O₃ ratio of ladle slag on formation behavior of inclusions in Mn and V alloyed steel. *ISIJ Int.* 2018;58(1):88-97.
- [34] Van Ende MA, Jung IH. A kinetic ladle furnace process simulation model: Effective equilibrium reaction zone model using FactSage macro processing. *Metall Mater Trans B.* 2017;48(1):28-36.
- [35] Ren Y, Zhang L, Ling H, et al. A reaction model for prediction of inclusion evolution during

- reoxidation of Ca-treated Al-killed steels in tundish. *Metall Mater Trans B*. 2017;48(3):1433-1438.
- [36] Van Ende MA, Jung IH. Development of a thermodynamic database for mold flux and application to the continuous casting process. *ISIJ Int*. 2014;54(3):489-495.
- [37] Bale CW, Bélisle E, Chartrand P, et al. FactSage thermochemical software and databases - recent developments. *Calphad*. 2009;33:295-311.
- [38] www.factsage.com (accessed August 2019).
- [39] Heo JH, Kim BS, Park JH. Effect of CaO addition on iron recovery from copper smelting slags by solid carbon. *Metall Mater Trans B*. 2013;44(6):1352-1363.
- [40] Kwon SK, Kong YM, Park JH. Effect of Al deoxidation on the formation behavior of inclusions in Ce-added stainless steel melts. *Met Mater Int*. 2014;20(5):959-966.
- [41] Park JS, Park JH. Effect of Mg-Ti deoxidation on the formation behavior of equiaxed crystals during rapid solidification of iron alloys. *Steel Res Int*. 2014;85(8):1303-1309.
- [42] Han YS, Park JH. Thermodynamics of indium dissolution behavior in FeO-bearing metallurgical slags. *Metall Mater Trans B*. 2015;46(1):235-242.
- [43] Han YS, Swinbourne DR, Park JH. Thermodynamics of gold dissolution behavior in CaO-SiO₂-Al₂O₃-MgO_{sat} slag system. *Metall Mater Trans B*. 2015;46(6):2449-2457.
- [44] Kwon SK, Park JS, Park JH. Influence of refractory-steel interfacial reaction on the formation behavior of inclusions in Ce-containing stainless steel. *ISIJ Int*. 2015;55(12):2589-2596.
- [45] Heo JH, Park JH. Manganese recovery by silicothermic reduction of MnO in BaO-MnO-MgO-CaF₂ (-SiO₂) slags. *Metall Mater Trans B*. 2018;49(2):514-518.
- [46] Feichtinger S, Michelic SK, Kang YB, et al. In situ observation of the dissolution of SiO₂ particles in CaO-Al₂O₃-SiO₂ slags and mathematical analysis of its dissolution pattern. *J Am Ceram Soc*. 2014;97(1):316-325.
- [47] Kim TS, Park JH. Structure-Viscosity relationship of low-silica calcium aluminosilicate melts. *ISIJ Int*. 2014;54(9):2031-2038.
- [48] Park JH, Todoroki H. Control of MgO·Al₂O₃ spinel inclusions in stainless steels. *ISIJ Int*. 2010;50(10):1333-1346.
- [49] Valdez M, Shannon GS, Sridhar S. The ability of slags to absorb solid oxide inclusions. *ISIJ Int*. 2006;46(3):450-457.
- [50] Park JS, Park JH. Effect of physicochemical properties of slag and flux on the removal rate of oxide inclusion from molten steel. *Metall Mater Trans B*. 2016;47(6):3225-3230.

List of Figure Captions and Tables

Figure 1. Schematic of the dissolution of RHA (R1), the slag-metal reaction (R2), the refractory-slag reaction (R3), and the inclusion-metal reaction (R4) in the ReSMI modeling system employed.

Figure 2. Total oxygen content in the steel melt as a function of reaction time with different RCA.

Figure 3. Changes to the concentration of (a) Al and (b) Si in the steel melt as a function of reaction time with different RCA.

Figure 4. Typical SEM micrograph of the inclusions in the steel sample at 5 min: (a) spinel type, (b) monoxide, and (c) Al_2O_3 -rich inclusions.

Figure 5. Number of inclusions per unit area in 5 min experiments at different RCA.

Figure 6. (a) Experimental and (b) calculated changes to the relative fraction of the inclusions in molten steel at 5 min as a function of RCA.

Figure 7. Size distribution and average size of Al_2O_3 -rich (including spinel-type) inclusions at 5 min as a function of RCA.

Figure 8. Composition of the inclusions at different RCA.

Figure 9. Schematic of the (a) initial and (b) last stage in continuous casting process.

Figure 10. Variation in the number of inclusions in the molten steel at the end of tundish process and the temperature of the molten steel in the ladle as a function of casting time during continuous casting.

Table 1. Initial composition of the commercial calcium aluminate-based flux (CA-flux) and rice husk ash (RHA) powder used in the present experiments (wt-%).

Table 2. Simulation conditions.

Table 3. Simulation conditions for reoxidation behavior of molten steel during continuous casting.