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Interfacial Phenomena and Reaction Kinetics between High Al Molten Steel and CaO-SiO₂-Type Flux

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Abstract: To understand the reaction mechanism between high Mn-high Al steel and slag, the reaction experiment of Fe-Mn-Al melts with CaO-SiO₂-type flux was carried out in MgO crucible at 1873 K. The evolution of the morphology of interface was inspected firstly, and then the global reaction kinetics was modeled in consideration of the effect of dynamic interfacial phenomena. The results show that in the reaction of Fe-5 mass % Al alloy with high SiO₂ or low SiO₂ protective slag, the strong chemical affinity between the metal and flux leads to strong spontaneous emulsification and attenuated with the progression of the reaction. Combined with the change of interfacial area caused by emulsification, it is found that the global reaction kinetics can be described satisfactorily by the mass transfer model of Al in liquid steel, and the determined mass transfer coefficient was about $k_{[Al]} = 4.46 \times 10^{-5}$ m/s. However, the emulsification phenomenon in the reaction of Fe-13%Mn-5%Al alloy with low SiO₂ slag did not disappear with the reaction, which can be attributed to the decreasing of the interfacial tension with Mn addition and the accumulation of C on the interface. This reaction process can be modeled by assuming the mass transfer of SiO₂ in the slag as the rate-controlling step with the estimated transfer coefficient of $k_{(SiO_2)} = 5.12 \times 10^{-6}$ m/s.

Keywords: high Mn-high Al steel; dynamic interfacial phenomena; reaction kinetics; process efficiency

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1. Introduction

Twin-induced plasticity (TWIP) steel has attracted much attention because of its high strength and excellent ductility. As the essential alloying element of TWIP steel, a large amount of Al needs to be added to increase the stacking fault energy and affect the deformation mechanism [1–3]. At the same time, the added Al can refine the austenite grain [4], increase the yield stress, and enhance the ductility [5]. Especially, the large amount addition of Al can reduce the density of steel remarkably, so high Al steel is extremely desirable in the automobile industry in favor of reducing weight.

However, there are very serious technological problems in the production process of high Al TWIP steel. Especially in the process of continuous casting, the Al in molten steel will react with SiO₂ in flux at the interface between slag and metal. It will not only reduce the content of Al in molten steel, but also change the Al₂O₃/SiO₂ ratio of mold flux [6–8]. This greatly deteriorates the physical chemistry properties of mold flux, and then affects the quality of continuous casting billet [9–13].

To ameliorate this unfavorable interfacial reaction, many studies concerning the interfacial reaction mechanism and kinetics have been carried out from the fundamental point of view [14,15]. Wang [16] and Yu [17] studied the continuous casting process of high Mn-high Al steel, and a model equation to predict the change of Al₂O₃ content in mold flux was developed on the assumption that the mass transfer of Al₂O₃ in slag is the rate-controlling step. While the studies performed by Kim et al. [18–20] indicated that the mass transfer of Al in molten steel was the rate-controlling step when the content of Al is less than 1.77 wt%, with the increase of the concentration of Al in steel, the reaction seemed to be disturbed

by the formed solid product layer MgAl_2O_4 , but the accumulation rate of Al_2O_3 in molten mold flux still can be modeled by the mass transfer of Al in boundary layer combined with the consideration of dynamic mass balance. To estimate the reaction rate in a wide range of Al content, Park et al. [21] developed two models separately corresponding to mass transport in metal only and mixed mass transfer of metal and slag. Then, by comparing with the experimental results, they concluded that the rate of reaction follows the mixed control model at the low SiO_2 content, and consideration of the mass transport in the slag species should not be omitted.

Considering the interfacial reaction between liquid Fe-Al metal and CaO- SiO_2 -based slags, another noteworthy aspect is the dynamic interfacial phenomenon. Because it is suggested that intensive interfacial reaction may induce Marangoni and natural convection at the slag-metal interface, this interfacial flow will give rise to interfacial waves due to a Kelvin-Helmholtz instability, and the waves grow, become unstable, and lead to spontaneous emulsification of slag in steel and steel in slag [22]. Coley et al. [23] investigated the spontaneous emulsification of Fe-Al droplets in CaO- SiO_2 - Al_2O_3 slag, it was revealed that the interfacial area increases linearly with the initial rate, and the increase of interfacial area in turn affects the global rate. Sridhar et al. [24] investigated the spontaneous emulsification of Fe-P drop immersed in a basic oxygen furnace type slag by using X-ray computerized tomography method to determine the surface area. The results showed that the surface area of the metal drop rapidly increases by over one order of magnitude during the first 60 s of the reaction. Therefore, for the describing and modeling of the kinetic reaction process between high-Al steel and slag, it is extremely necessary to take the change of interfacial area caused by spontaneous emulsification into account. However, concerning the reported studies on the reaction between high Mn-high Al steel and mold flux, the dynamic interfacial phenomenon is seldom considered.

To study the effect of interfacial chemical reaction and composition of molten steel on dynamic interfacial phenomena, as well as the kinetic model of the change of Al content in molten steel, the interfacial reaction between high Mn-high Al steel and CaO- SiO_2 flux at 1873 K was designed in argon atmosphere and research carried out from two aspects. Firstly, by tracking the evolution of the morphology of the quenched sample, the effect of the compositions of metal and slag on the spontaneous emulsification was examined. Secondly, by considering the change of interfacial area, the reaction kinetics was described quantitatively.

2. Materials and Methods

Two different composed metals, Fe-5 mass % Al and Fe-13 mass % Mn-5 mass % Al, were reacted with two different composition flux at 1873 K, respectively. The flux was prepared by melting the analytical reagent oxide powder mixture in a graphite crucible at 1723 K for 120 min followed by grinding and sieving. The compositions of the prepared fluxes were further determined by X-Ray Fluorescence (XRF-1800, Japan) measurement, which are shown in Table 1. Due to the graphite crucible adopted to prepare the fluxes, a small amount of C is dissolved in the fluxes, which was measured by infrared carbon-sulfur analyzer, and listed in Table 1.

Table 1. Components of mold flux (wt%).

Slag	CaO	SiO_2	Al_2O_3	MgO	CaF_2	C
High SiO_2 Flux	41.1	36.7	14.7	4.9	-	0.04
Low SiO_2 Flux	37.8	13.0	31.4	10.3	5.8	0.04

In a typical run, 35 g homogeneous metal mixture composed of iron powder (purity of 99 pct) and aluminum powder (purity of 99.99 pct) according to the proportion was firstly placed into a magnesia crucible with diameter of 24 mm and height of 90 mm, and 17g pre-melting flux was put above to cover the metal. Then, the magnesia crucible was

placed into a bigger graphite crucible, and the graphite crucible was hung into the quench chamber, which was mounted on the top of the furnace. The schematic drawing of the furnace is shown in Figure 1.

Figure 1. Vertical reaction furnace with automatic sample lifting device.

After the sample was placed, the gas tightness of the reaction chamber, which was constituted by the quench chamber and alumina tube was checked by vacuuming and backfilling argon gas for three times. Argon is used to protect the composition of molten steel from oxidation by oxygen during the whole experiment. The flow rate of argon (purity 99.999%) was 200 mL/min.

The furnace was heated up with a rate of 3 K/min. After the furnace reached the reaction temperature of 1873 K, the sample held in the quench chamber was lowered slowly into the alumina tube and stayed in the region of about 1273 K for 30 min, and then it was lowered quickly to the even temperature zone of 1873 K. When the sample reached the even temperature zone, the time was counted immediately.

After reacting in the even temperature zone of 1873 K for desired time, the sample was lifted quickly into the quench chamber with lifting time less than 3 s. Then, a larger flow argon was introduced to flush and cool the sample. The cooled sample together with the magnesia crucible was taken out of the furnace, and they were wholly embedded with epoxy resin. After the resin solidified, it was cut into two parts along the longitudinal section of the sample. One part was polished for micro-morphology measurement carried out on a scanning electron microscope (SEM, ULTRA 55, ZEISS, Jena, Germany). The other part was broken to take out the sample, then the slag and the metal were separated and measured by X-ray fluorescence (XRF) and inductively coupled plasma-atomic emission spectrometry (ICP-AES), respectively, to determine their composition.

3. Results and Discussion

3.1. Evolution of Morphology

When the sample was lowered quickly into the even temperature zone of 1873 K, it would be melted quickly, and the reactions between melt and slag occurred. To track the dynamic interfacial phenomenon of this process, the reacting samples at various time intervals were quenched, and the changes of the morphologies of the metal and the slag were inspected through SEM and Energy Dispersive Spectrometer (INCAX-MAX 50, Oxford Instruments, Oxford, UK) measurements.

3.1.1. Fe-5 Mass % Al Alloy and High SiO₂ Flux

At first, the interaction between the high SiO₂ flux and metal mixture composed of 95 mass % Fe powder and 5 mass % Al was investigated. Figure 2 shows the sectional photos of the samples quenched after reacting for 5, 7, and 10 min. From the photos of 5 and 7 min, it is visible by the naked eye that some slags mingled with small metal drops or fractions. With the progress of the reaction, this kind of chaos became weaker and a clear interface can be seen at 10 min.

Figure 2. Sectional photos of the samples (Fe-5 mass % Al Alloy and high SiO₂ flux) quenched after reacting at 1873 K for 5, 7, and 10 min.

To further evaluate the change of the small metal drops or fractions dispersed in slags, the slags were broken and ground, then the metals were magnetically separated. Figure 3 shows the appearance of the metal particles obtained from the samples reacting for 7 min through 10 min. It can be seen clearly that both the size and the amount of the metal particles decreased with the extending of reaction time.

Figure 3. Shape and number of metal droplets dispersed in slag after reacting at 1873 K for various time intervals.

In Figure 4, two micrographs of the sample reacted after 7 min are presented. One was taken at the interfacial vicinity; the other was taken in the interior of the slag. From these micrographs, both the emulsification of slag in metal and metal in slag existed, and the sizes of metal drops and slag fragments were in the level of 10 microns.

Figure 4. The interface morphology between Fe-5Al alloy and high SiO₂ flux after reacted at 1873 K for 7 min.

Regarding the dynamic interfacial phenomena, it is generally considered as a direct result of the gradients of surface and interfacial tension, which drive the Marangoni flow/convection. As for the gradients of surface and interfacial tension itself may stem from three aspects: a gradient of temperature (thermocapillary), a gradient of electrical potential (electrocapillary), and a gradient of surface-active solutes (solutocapillary). These three factors can present simultaneously, but the dominant factor may differ from one system to another. For example, M. A. Rhamdhani et al. [25] released a Fe-Al droplets onto a melted CaO-SiO₂-Al₂O₃ slag, and the dominant source was evaluated by calculating the thermocapillary, solutocapillary, and electrocapillary effects from kinetic data. They concluded that the electrocapillary effect was the dominant source, which contributed approximately 85 pct of the maximum interfacial depression, while the solutocapillarity contributed 15 pct, the thermocapillary effect was negligible. However, in the present study, the sample including both slag and metal mixture was melted simultaneously. If the emulsification of slag in metal and metal in slag observed in the present study related to the melting process, i.e., if some micropores formed during the melting process that caused the emulsification? To estimate this possibility, pure Fe powder was used to replace the Fe-Al mixture and the same experiments were carried out. In Figure 5, the micrographs of quenched samples after melted for 5 and 7 min are presented. By comparing Figures 4 and 5, no emulsification phenomena can be found in the sample constituted of pure Fe and high SiO₂ flux. This implies that the emulsification phenomena are mainly caused by the interfacial reactions between metal and slag.

Figure 5. The interface morphology between pure Fe and high SiO₂ flux after reacted at 1873 K for (a) 5 min and (b) 7 min, respectively.

Accompanying with the occurrence of spontaneous emulsification, there is a significant increase in interfacial area, which in turn affects the global reaction rate. It has been reported that the increase can be up to 300 to 500 pct of the original value. M. A. Rhamdhani [26] evaluated the surface area of the metal droplet, and found that, with the progress of the reaction, the interfacial area increased sharply to a maximum value and then decreased gradually close to the initial value. In the present study, the change of the interfacial area was also estimated by using the ImageProPlus software to calculate the surface area of metal droplet. Through the calculation of the value of the interfacial area at different times, the result is shown in Figure 6. It was found that the interfacial area decreased gradually after 5 min. The quick increase of the interfacial area was not monitored, this implies that the dynamic interfacial phenomena occurred intensively, and the emulsification can reach maximum extent in the initial five minutes.

Figure 6. Change of interfacial area during the reaction of Fe-5Al alloy with high SiO_2 slag.

3.1.2. Fe-5Al Alloy and Low SiO_2 Flux

With the lowering of the content of SiO_2 in the flux, the intensity of interfacial reaction between Fe-Al melt and flux can be depressed, and the dynamic interfacial phenomena will also be weakened. To inspect the extent and effect of SiO_2 content on the spontaneous emulsification, the melting and reacting process of the sample composed of Fe-5 mass % Al and low SiO_2 flux was investigated.

Figure 7 shows the interfacial morphology of the sample quenched after reacting for 7 min. As a comparison, a micrograph of the interface between pure Fe melt and the low SiO_2 flux are presented together. It can be seen that the emulsification still occurred, but the extent and intensity became less serious than the high SiO_2 flux. Firstly, the amount of metal droplet emulsified in the slag decreased dramatically, only emulsification of slag droplet in slag can be observed apparently. Secondly, the thickness or range of emulsification occurring became smaller, only in the vicinity very close to the interface can the emulsification be found.

Figure 7. Interfacial morphology of alloy and low SiO₂ slag at 7 min: (a) Fe-5Al; (b) Fe.

Considering the micro-morphology and composition change in the vicinity very close to the interface, the typical micrographs are presented in Figures 8 and 9. From the element mapping shown in Figure 8, it can be found that the distribution of Al and Si in the metal phase are relatively uniform, whereas the element distribution in slag is uneven. Especially, Mg in slag was found to be gathered, which indicates that with the progress of the reaction a considerable number of aluminum-magnesium spinel was formed along the interface. In Figure 9, the micro-morphology of the interface is exhibited perspicuously, and the compositions of the emulsified metal droplets and slag fractions are presented. It can be seen that the slag fractions emulsified in metal are mainly composed of Al, Mg, and O, which means that a considerable amount of aluminum-magnesium spinel was also formed in the emulsified slag fractions, whereas the emulsified metal droplets are with low Al and high Si contents.

Figure 8. Micro-morphology and element mapping of quenched sample (Fe-5Al Alloy and low SiO₂ flux) after reacting at 1873 K for 7 min.

Figure 9. Interfacial morphology and dotting analysis at 10 min between Fe-5Al alloy and low SiO₂ slag.

The change of the interfacial area accompanying the spontaneous emulsification is shown in Figure 10. The interfacial area increases quickly to the maximum value and then decreases. Compared with the interfacial area change shown in Figure 6 for the sample constituted of Fe-5Al alloy and high SiO₂ flux, there are two distinctions. The first is the fragment of the increasing of the interfacial area was observed, the second is that the value of the maximum interfacial area is just about half of that shown in Figure 6. These two distinctions indicate that even though the dynamic interfacial phenomena and spontaneous emulsification still exist apparently, the intensity and the extent of spontaneous emulsification was weakened due to the decrease of the reaction affinity between the metal and the slag.

Figure 10. Change of interfacial area during the reaction of Fe-5Al alloy with low SiO₂ flux.

3.1.3. Fe-13Mn-5Al Alloy and Low SiO₂ Flux

Apart from Al, Mn is also an essential alloying element. Although the adding of Mn into Fe-Al melt cannot affect their reaction affinity with slag significantly, Mn can reduce the surface tension of molten steel [27]. The change of surface tension will definitely affect the dynamic interfacial behavior. Therefore, based on the previous experiments, the spontaneous emulsification between the Fe-13 mass % Mn-5 mass % Al melt and the low SiO₂ flux was further investigated.

Figure 11 shows the macro-morphology of the quenched sample after holding at 1873 K for different time intervals. At 5 min, it can be seen that the metal powder began melting, the interface was irregular and unstable. At 7 min, the metal powder melted completely, and the emulsification of metal droplet in slag can be seen apparently. Until 10 min, the emulsification still can be observed obviously.

Figure 11. The interfacial morphology during the reaction of Fe-13Mn-5Al alloy and low SiO₂ mold flux.

In Figure 12, the micro-morphology of the interface of the quenched sample after reacting for 7 min is presented. It can be seen clearly that a larger number of metal droplets with diameter from 10 to 100 microns emulsified in the slag, and the slag fractions emulsified in the metal. In general, the emulsification phenomena are analogous to the previous cases. However, if the interface was enlarged and inspected carefully. It can be found that C was enriched, and a carbon-rich layer with thickness about 20 microns was formed, which is strikingly distinct from the previous cases.

Figure 12. Interfacial morphology of Fe-13Mn-5Al alloy and low SiO₂ flux when holding 7 min at 1873 K.

To observe the enrichment of C deeply, the surface of emulsified metal droplet was also inspected carefully. Shown in Figure 13 is the micro-morphology of emulsified metal droplet and interface in the sample after reacting for 10 min, as well as the distribution of C at the interface. It can be seen that the surface of emulsified metal droplet is very coarse, and enormous tiny C-rich particles aggregate on the surface. As for in the vicinity of interface, similar carbon-rich layer can still be found.

Figure 13. Interfacial morphology and EDS analysis at 10 min between Fe-13Mn-5Al alloy and low SiO₂ slag.

In addition to the above-mentioned difference, another distinction founded is that the time of maintaining the emulsification state became longer than the previous cases. For example, the spontaneous emulsification phenomena occurred in the previous investigated samples disappeared virtually after reacting for 10 min; whereas, in the sample constituted of Fe-13Mn-5Al and low SiO₂ flux, the spontaneous emulsification phenomena can still be observed clearly after 20 min. To demonstrate this change visually, the emulsified metal droplets in the sample after reacting for 15 and 20 min were separated magnetically and shown graphically in Figure 14. A considerable amount of metal particles still existed even after 20 min.

Figure 14. Alloy morphology and metal particles in slag of Fe-13Mn-5Al alloy and low SiO₂ flux.

Why did the spontaneous emulsification disappear so slowly after the metal phase composed of Fe-5Al was replaced by Fe-13Mn-5Al? The reasons should come from two aspects. Firstly, the addition of Mn in the metal results in the reducing of the surface tension of the metal droplet, which is unfavorable for the tiny metal droplet to return back into the bulk metal because the reduced surface tension means that the force driving the aggregation of tiny metal droplet also becomes smaller. Secondly, the carbon enriched on the surface of the emulsified metal droplets may hinder its movements.

As we have discussed, a significant increase in interfacial area is the direct result of the spontaneous emulsification, and this increase in interfacial area in turn results in the acceleration of the global reaction rate. However, if the emulsified metal droplets cannot come back from the slag to the bulk metal, they will no longer have contributions to the global reaction rate. Therefore, the effect of spontaneous emulsification on the global reaction rate in the sample constituted of Fe-13Mn-5Al should be distinguished from the Fe-5Al sample.

3.2. Kinetic Analysis of the Global Slag/Metal Reaction

In all the cases investigated above, the overall reactions occurred between the metal and the slag can be expressed as follows:

where “[]” refers to the element dissolved in the metal phase, whereas “()” refers to the component dissolved in the slag phase. For this heterogeneous reaction, it can be considered as consisting of five steps: (1) Mass transfer of $[Al]$ to slag/metal interface; (2) Mass transfer of (SiO_2) to slag/metal interface; (3) Chemical reaction progressing at the interface; (4) Mass transfer of product Si from interface to bulk steel; (5) Mass transfer of product Al_2O_3 from interface to bulk slag. A number of studies indicated that the interfacial chemical reaction was sufficiently fast due to the high reaction temperature, and global reaction is generally mass transfer-controlled.

However, the factors affecting the mechanism of the interfacial reaction become more complicated in case of having dynamic interfacial phenomena. Such as, the increase of interfacial area caused by spontaneous emulsification, as well as the time of spontaneous emulsification maintained, etc., should all be considered. Therefore, it is worthwhile and meaningful to analyze the kinetics according to the dynamic interfacial characteristic of the reaction system.

3.2.1. Reaction Kinetics between Fe-5Al Metal and Flux

Considering both the reactions of Fe-5Al metal with the high SiO_2 flux and with the low SiO_2 flux, the intensity and extent of the spontaneous emulsification of the two cases are different, the characteristic of the progressing of the spontaneous emulsification is nevertheless similar. That is, the emulsification proceeds quickly to maximum and then dies away. Therefore, by accounting the evolution of interfacial area with the progressing of the spontaneous emulsification, the global reaction kinetics between Fe-5Al metal and high SiO_2 flux, as well as Fe-5Al metal and low SiO_2 flux, was analyzed firstly.

To conduct the kinetic analysis, the bulk compositions of metal and slag of the quenched samples were determined by ICP-AES and XRF measurements, respectively. The contents of Al and Si in metal at various reaction times are shown in Figure 15, and the change of contents of Al_2O_3 and SiO_2 in slag are shown in Figure 16. From these two figures in both cases, the compositions changed abruptly in the initial 10 min, which shows good consistency with the progress of the emulsification. This indicates that the slag/metal reaction is closely connected to the spontaneous emulsification.

Figure 15. Composition change of molten steel during reaction between Fe-5Al alloy and molten flux.

Figure 16. Composition change of mold flux during reaction between Fe-5Al alloy and molten flux.

With the occurrence of spontaneous emulsification, the interfacial area increased tremendously, the slag/metal reaction should still be controlled by the mass transfer step. The mass transfer of SiO₂ in slag is relatively easier due to its high content. Therefore, assuming the reaction was controlled by the mass transfer in metal phase, the diffusion flux can be obtained as follows:

$$J_{[Al]} = -\frac{d[\%Al]}{dt} = \frac{A}{V} k_{[Al]} \{ [\%Al] - [\%Al]^* \} \quad (2)$$

where $[\%Al]$ and $[\%Al]^*$ are the Al contents in the metal at time t and at interface, $k_{[Al]}$ is the mass transfer coefficient, and $A(t)$ is the area of interface at time t . Upon separating the variables, integrating the Equation (2), the following equations can be obtained:

$$\int -\frac{d[\%Al]}{[\%Al] - [\%Al]^*} = \int \frac{k_{[Al]} A}{V_m} dt \quad (3)$$

$$\ln \frac{[\%Al] - [\%Al]^*}{[\%Al]_0 - [\%Al]^*} = -\frac{k_{[Al]}}{V_m} \int_{t_0}^t A(t) dt \quad (4)$$

Let $F(A) = \int_{t_0}^t A(t) dt$, to express the integrated interfacial area, which can be calculated numerically from Figures 6 and 10. Then, the preceding equation can be simplified as:

$$\ln \frac{[\%Al] - [\%Al]^*}{[\%Al]_0 - [\%Al]^*} = -\frac{k_{[Al]}}{V_m} F(A) \quad (5)$$

Because the Al content in interface $[\%Al]^*$ cannot be measured, it was expressed approximately by the final Al content in the metal phase.

According to Equation (5), using the data from Figure 15, the left-hand side of Equation (5) was plotted against the integrated interfacial area, the results are shown in Figure 17. It can be seen obviously that, even though the content of SiO₂ in high SiO₂ flux is much higher than the low SiO₂ flux, their reaction with Fe-5Al melt can be described satisfactorily by Equation (5) simultaneously. This implies that to exclude the mass transfer of SiO₂ in slag phase from the rate limiting steps is plausible.

Figure 17. Relationship between interfacial area integral and logarithm of Al concentration during the reaction of Fe-5Al with CaO-SiO₂-based slag.

The slope of the fitting line in Figure 17 is $-\frac{k_{Al}}{V_m} = -9.7\text{m}^{-2}\cdot\text{s}^{-1}$. The volume of metal phase $V_m = W_m/\rho_m = 4.6 \times 10^{-6}\text{m}^3$, and the mass transfer coefficient of [Al] in molten steel can be determined as: $k_{[Al]} = 4.46 \times 10^{-5}\text{m/s}$. However, it is worthwhile to note that, if the chemical reaction follows first-order kinetics with respect to Al in metal, the chemical reaction controlled kinetic equation will be the same as Equation (5). That is to say, Equation (5) is equally applied to the case separately controlled by chemical reaction or by the mass transfer of Al in metal phase. However, the interfacial chemical reaction takes place rapidly at high temperature, and the chemical reaction rate constant is much larger than the mass transfer coefficient. Therefore, it is more accurate to assume that the mass transfer of Al in molten steel is a speed control step.

3.2.2. Reaction Kinetics between Fe-13Mn-5Al Metal and Flux

As shown previously, the evolution of the interfacial morphology between Fe-13Mn-5Al and flux exhibited considerable difference from the reaction between Fe-5Al alloy and flux. This will definitely result in different global reaction kinetics. The change of the contents of Al, Si, and Mn in metal are shown in Figure 18, and the change of contents of Al₂O₃ and SiO₂ in slag are shown in Figure 19. It can be seen apparently that the reaction rate between Fe-13Mn-5Al alloy and mold slag is obviously slower than that of Fe-5Al alloy. The main reasons can be accounted for by two aspects. One is the minor effect of the dynamic interfacial phenomena on the change of its interfacial area. The other is the carbon-enrichment occurred at the interface and the spinel layer formed in the slag phase, which may hinder the mass transfer of component in slag. Moreover, the SiO₂ content of the protective slag used in the experiment is low. Therefore, the reaction process can be described more accurately by using the speed control of SiO₂ mass transfer.

Figure 18. Composition change of molten steel during reaction between Fe-13Mn-5Al alloy and molten flux.

Figure 19. Composition change of mold flux during reaction between Fe-13Mn-5Al alloy and molten flux.

Similar to the above derivation, the diffusion flux in slag can also be expressed as:

$$J_{(\text{SiO}_2)} = -\frac{d(\%\text{SiO}_2)}{dt} = \frac{A}{V_s} k_{(\text{SiO}_2)} \{(\%\text{SiO}_2) - (\%\text{SiO}_2)^*\} \quad (6)$$

where $(\%\text{SiO}_2)$ and $(\%\text{SiO}_2)^*$ are the contents of SiO_2 in the bulk slag at time t and at interface, $k_{(\text{SiO}_2)}$ is the mass transfer coefficient in slag. Integrating of Equation (6) yields the following Equations (7) and (8).

$$\int -\frac{d(\%\text{SiO}_2)}{(\%\text{SiO}_2) - (\%\text{SiO}_2)^*} = \int \frac{k_{(\text{SiO}_2)} A}{V_s} dt \quad (7)$$

$$\ln \frac{(\%\text{SiO}_2) - (\%\text{SiO}_2)^*}{(\%\text{SiO}_2)_0 - (\%\text{SiO}_2)^*} = -\frac{k_{(\text{SiO}_2)} A}{V_s} t \quad (8)$$

According to Equation (8), using the data shown Figure 19 and assuming the interfacial concentration of SiO_2 , the left-hand side of Equation (8) was plotted against reaction time t , the results are shown in Figure 20.

The slope of the fitted line is $-\frac{k_{\text{SiO}_2} A}{V_s} = -5.87 \times 10^{-4} \text{ s}^{-1}$. The volume of molten slag was $V_s = W_s / \rho_s = 5.9 \times 10^{-6} \text{ m}^3$. About the interfacial area, a constant value of 1.5 times of the cross-section area of crucible $A = 6.78 \times 10^{-4} \text{ m}^2$ was adopted. Then, the mass transfer coefficient of $k_{(\text{SiO}_2)}$ can be obtained as $5.11 \times 10^{-6} \text{ m/s}$.

Figure 20. Relationship between interfacial area integral and logarithm of SiO_2 concentration during the reaction of Fe-13Mn-5Al with low SiO_2 slag.

4. Conclusions

By micro-morphological measurements combined with macro-kinetic analysis, the effect of dynamic interfacial phenomena on the global reaction between high Al molten steel and CaO- SiO_2 -type fluxes was elucidated. The following conclusions can be drawn:

- (1) For the reaction either between high Al steel and high SiO_2 flux or between high Al steel and low SiO_2 flux, the spontaneous emulsification of metal droplets in slag and slag fractions in metal, as well fluctuation of interface, occur abruptly at the beginning of the reaction. Although the intensity for the case of low SiO_2 flux is lower relatively, it still can be observed apparently.
- (2) The duration of these dynamic interfacial phenomena is affected distinctively by the reaction system. The dynamic interfacial phenomena occurred in the system composed of Fe-5Al alloy and flux can disappear rapidly with the progressing of reaction, whereas for the case of reaction between Fe-13Mn-5Al alloy and flux, the emulsified metal droplets and slag fractions can maintain and stay stably.
- (3) For different reaction systems, the dynamic interfacial phenomena have significant and specific effect on the global reaction kinetics and reaction mechanism. As for the reaction between Fe-5Al alloy and flux, the dynamic interfacial phenomena result in a considerable increment of interfacial area, which consequently causes an extremely rapid global reaction controlled by the mass transfer of $[\text{Al}]$ in molten steel with a mass transfer coefficient of $k_{[\text{Al}]} = 4.46 \times 10^{-5} \text{ m/s}$. However, the reaction between Fe-13Mn-5Al alloy and flux is comparatively very slow due to the trivial effect or contribution from the dynamic interfacial phenomena, and its rate-controlling step may be the transfer of (SiO_2) in molten slag with a mass transfer coefficient of $k_{(\text{SiO}_2)} = 5.11 \times 10^{-6} \text{ m/s}$.
- (4) Through the kinetic analysis, we have a better understanding of the reaction mechanism between CaO- SiO_2 flux in molten steel with high Al content. It is helpful to predict the changing trend of flux composition in the process of continuous casting of high Mn-high Al steel and improve the production efficiency. Additionally, it is meaningful to analyze which type of mold powder is more suitable for continuous casting operation. However, to predict well the change of mold powder composition in the continuous casting process, more continuous casting process reaction models need to be established based on multi-component reaction model, and the accuracy of the continuous casting model should be verified by actual production.

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References

1. Park, K.K.H.A.; Jin, K.G.; Han, S.H.; Hwang, S.W.; Choi, K.; Lee, C.S. Stacking fault energy and plastic deformation of fully austenitic high manganese steels: Effect of Al addition. *Mater. Sci. Eng. A* **2010**, *527*, 3651–3661. [\[CrossRef\]](#)
2. Frommeyer, G.; Brück, U.; Neumann, P. Supra-Ductile and High-Strength Manganese-TRIP/TWIP Steels for High Energy Absorption Purposes. *ISIJ Int.* **2003**, *43*, 438–446. [\[CrossRef\]](#)
3. Suikkanen, P.P.; Lang, V.T.E.; Somani, M.C. Effect of Silicon and Aluminium on Austenite Static Recrystallization Kinetics in High-strength TRIP-aided Steels. *ISIJ Int.* **2012**, *52*, 471–476. [\[CrossRef\]](#)
4. Chin, K.G.A.; Kang, C.Y.A.; Shin, S.Y.B.; Hong, S.B.; Lee, S.B.; Kim, H.S.B.; Kim, K.H.C.; Kim, N.J.D. Effects of Al addition on deformation and fracture mechanisms in two high manganese TWIP steels. *Mater. Sci. Eng. A* **2011**, *528*, 2922–2928. [\[CrossRef\]](#)
5. Lee, Y.K.; Jin, J.E. Effects of Al on microstructure and tensile properties of C-bearing high Mn TWIP steel. *Acta Mater.* **2012**, *60*, 1680–1688.
6. CHO, J.; BLAZEK, K.; FRAZEE, M. Assessment of CaO–Al₂O₃ Based Mold Flux System for High Aluminum TRIP Casting. *ISIJ Int.* **2013**, *53*, 62–70. [\[CrossRef\]](#)
7. Liu, J.; Cui, H. Simulation for Mass Transfer Kinetics at Slag-Steel Interface during High Al Steel Continuous Casting. *ISIJ Int.* **2019**, *59*, 2256–2263.
8. Zhang, Z.; Wen, G.; Tang, P.; Sridhar, S. The Influence of Al₂O₃/SiO₂ Ratio on the Viscosity of Mold Fluxes. *ISIJ Int.* **2008**, *48*, 739–746. [\[CrossRef\]](#)
9. Yang, J.; Zhang, J.J.Q.Z.; Ostrovski, O.; Sasaki, Y.; Zhang, C.; Cai, D. Dynamic Wetting of High-Al Steel by CaO–SiO₂- and CaO–Al₂O₃-Based Mold Fluxes. *Metall. Mater. Trans. B* **2019**, *50*, 2175–2185. [\[CrossRef\]](#)
10. Liao, J.; Zhang, Y.; Sridhar, S.; Wang, X.; Zhang, Z. Effect of Al₂O₃/SiO₂ Ratio on the Viscosity and Structure of Slags. *ISIJ Int.* **2012**, *52*, 753–758. [\[CrossRef\]](#)
11. Hanao, M.; Kawamoto, M.; Yamanaka, A. Influence of Mold Flux on Initial Solidification of Hypo-Peritectic Steel in a Continuous Casting Mold. *ISIJ Int.* **2012**, *52*, 1310–1319. [\[CrossRef\]](#)
12. Yang, J.; Wang, Q.; Zhang, J. Effect of Al₂O₃/(B₂O₃+Na₂O) Ratio on CaO–Al₂O₃-Based Mold Fluxes: Melting Property, Viscosity, Heat Transfer, and Structure. *Metall. Mater. Trans. B* **2019**, *50*, 2794–2803. [\[CrossRef\]](#)
13. Wang, Z.; Sohn, I. Review on the High-Temperature Thermophysical Properties of Continuous Casting Mold Fluxes for Highly Alloyed Steels. *ISIJ Int.* **2019**, *60*, 2705–2716. [\[CrossRef\]](#)
14. Kim, G.H.; Sohn, I. Interfacial Kinetics of High-Al-Containing Ultra-Lightweight Steels with Calcium Silicate-Based Molten Oxides at High Temperature. *Metall. Mater. Trans. B* **2016**, *47*, 1773–1784. [\[CrossRef\]](#)
15. Brooks, G.A.; Rhamdhani, M.A.; Coley, K.S.; Subagyo; Pan, Y. Transient Kinetics of Slag Metal Reactions. *Metall. Mater. Trans. B* **2009**, *40*, 353–362. [\[CrossRef\]](#)
16. Wang, Q.W.Q.; Qiu, S.Q.S.; Zhao, P.Z.P. Kinetic analysis of alumina change in mold slag for high aluminum steel during continuous casting. *Metall. Mater. Trans. B* **2012**, *43*, 424–430. [\[CrossRef\]](#)
17. Yu, X.Y.X.; Wen, G.W.G.; Tang, P.T.P.; Ma, F.M.F.; Wang, H.W.H. Behavior of Mold Slag Used for 20Mn23Al Nonmagnetic Steel During Casting. *J. Iron Steel Res. Int.* **2011**, *18*, 20–25. [\[CrossRef\]](#)
18. Kim, M.; Lee, S.; Cho, J.; Park, M.; Lee, H.; Kang, Y. A Reaction between High Mn-High Al Steel and CaO–SiO₂-Type Molten Mold Flux: Part I. Composition Evolution in Molten Mold Flux. *Metall. Mater. Trans. B* **2013**, *44*, 299–308. [\[CrossRef\]](#)
19. Kang, Y.B.; Kim, M.S.; Lee, S.W.; Cho, J.W.; Park, M.S.; Lee, H.G. 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*, 309–316. [\[CrossRef\]](#)
20. Kim, M.; Park, M.; Kang, S.; Park, J.; Kang, Y. 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*, 686–695. [\[CrossRef\]](#)
21. Park, J.; Sridhar, S.; Fruehan, R.J. Kinetics of Reduction of SiO₂ in SiO₂–Al₂O₃–CaO Slags by Al in Fe–Al(–Si) Melts. *Metall. Mater. Trans. B* **2014**, *45*, 1380–1388. [\[CrossRef\]](#)

-
22. Chung, Y.; Cramb, A.W. Dynamic and equilibrium interfacial phenomena in liquid steel-slag systems. *Metall. Mater. Trans. B* **2000**, *31*, 957–971. [[CrossRef](#)]
 23. Rhamdhani, M.A.A.B.; Brooks, G.A.D.; Coley, K.S.E. Analysis of interfacial area changes during spontaneous emulsification of metal droplets in slag. *Metall. Mater. Trans. B* **2006**, *37*, 1087–1091. [[CrossRef](#)]
 24. Assis, A.N.A.; Warnett, J.B.; Spooner, S.B.; Fruehan, R.J.A.; Williams, M.A.B.; Sridhar, S.B. Spontaneous Emulsification of a Metal Drop Immersed in Slag Due to Dephosphorization: Surface Area Quantification. *Metall. Mater. Trans. B* **2015**, *46*, 568–576. [[CrossRef](#)]
 25. Rhamdhani, M.A.A.B.; Coley, K.S.C.; Brooks, G.A.D.E. Analysis of the source of dynamic interfacial phenomena during reaction between metal droplets and slag. *Metall. Mater. Trans. B* **2005**, *36*, 591–604. [[CrossRef](#)]
 26. Rhamdhani, M.A.A.; Brooks, G.A.B.C.; Coley, K.S.A. Kinetics of metal/slag reactions during spontaneous emulsification. *Metall. Mater. Trans. B* **2005**, *36*, 219–227. [[CrossRef](#)]
 27. Lee, J.; Le, T.H.; Shin, M. Density and Surface Tension of Liquid Fe-Mn Alloys. *Metall. Mater. Trans. B* **2011**, *42*, 546–549. [[CrossRef](#)]