Enhancement of Iron Melting Rate under the Co-existence of Graphite and Wüstite

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Carburization and melting processes of solid Fe under the co-existence of graphite and wüstite has been investigated based on a confocal laser scanning microscope “in-situ” observation of the movement of the interface between Fe–C melt and solid Fe at 1523 K. In the experiments, strong stirring flow at the surface of the Fe–C melt is observed. This flow is found to be Marangoni flow and is introduced by the surface tension gradient due to the difference of oxygen concentration between the Fe–C melt interface with graphite and solid iron. The velocity of Marangoni flow is measured from the moving velocities of bubbles at the molten Fe–C surface. The melting rate of Fe is analyzed by computational fluid flow simulations of the Fe–C melt. Based on these results, it is confirmed that the carburization and melting rate of solid Fe can be enhanced by allowing Fe–C melt to come into contact with wüstite and graphite simultaneously.

KEY WORDS: melting rate; carburization; in-situ observation; surface tension; solutal Marangoni flow.

1. Introduction

One of the hottest issues in ironmaking and steelmaking industry at this moment is the reduction of CO₂ emission and energy consumption. During steel production, the ironmaking process discharges most of total CO₂ emission as it uses coke as a reducing agent and a heating source. Hence one of the practical ways to reduce CO₂ emission is the reduction of energy consumption or improvement of energy efficiency. The ironmaking process comprises four processes such as heating, reduction, carburization and melting process. Among them, the carburization of the reduced iron could be the critical stage to determine the energy consumption because the melting temperature of Fe–C alloy can be lowered by increasing the carbon content in it. Therefore, to reduce the energy consumption in the ironmaking processes, the enhancement of the carburization rate can be a key technology.

A newly developed ironmaking process such as COREX and FINEX are based on a smelting reduction technology. COREX and FINEX process consists of pre-reduction and smelting units. Pre-reduced iron ore compacts, generally called direct reduced iron (DRI) which are charged to the smelter and come into contact with a carbonaceous material. Carbon composite agglomerates (CCA) have been also used for coal-based new ironmaking processes such as FASTMET and ITmk3. Many investigations have been carried out to understand the reduction, carburization and melting phenomena occurring in the CCA. In a microscopic view, particles of iron oxides, metallic Fe and carbonaceous material are mixed together and contacted with each other in the DRI and CCA. The reactions occurring in the DRI and CCA must be very complex. Despite the importance of the carburization-melting among them, quite few studies have been carried out for it in the liquid state occurring in the CCA and DRI.

If solid iron contacts graphite over the eutectic temperature of Fe–C binary system, it is transformed to Fe–C melt at the contact points between them by direct carburization process. The carburization-melting process of solid iron is simply controlled by the diffusion process at the interface between the melt and the solid phase. Without the convection flow in the Fe–C melt, the diffusion flux of carbon can be proportional to \( \frac{C_{gr} - C_{li}}{L} \) at the interface. \( C_{gr} \) is the carbon concentration at the interface between carbon and liquid phase and \( C_{li} \) is the carbon concentration at the interface between solid and liquid phases. \( L \) is the distance between two interfaces. \( L \) gradually increases with increase of the carburizing time. Then, the transport rate of carbon atoms from graphite to solid iron gradually decrease with increase of \( L \) since \( C_{gr} \) and \( C_{li} \) are constant at a particular temperature. Accordingly, in order to keep high melting rate, the decrease of the gradient of carbon concentration at the interface between the melt and the solid phase during the carburization-melting process must be avoided.

It is supposed that the residual unreduced iron oxide in the CCA or DRI may be disadvantageous for the iron carburization-melting process because the dissolved carbon in the melt is consumed by iron oxides so that the carbon concentration is decreased. Thus, it has generally been believed that all the iron oxide in iron ores should be fully reduced for the effective carburization. However, Murakami et al. have
reported that the melting rate of the iron plate was enhanced when it had oxide scales on the surface. Their result implies the possibility of the enhancement of reduced iron melting rate by intentional introduction of unreduced iron oxide to DRI and CCA in a smelter. However, they did not establish the exact mechanism of the melting rate enhancement of iron by iron oxide scale. They could not observe the surface of the melt clearly because the most of surface area was covered with the solid wüstite scale. Although several researchers have investigated the kinetics of the reduction of iron oxide with iron–carbon melts, there has been no detailed description of the phenomena near the interface.

Belton and Fruehan said that wüstite leads the super-saturation of iron–carbon melts with oxygen if the oxide exists in Fe–C melts. This local accumulation of dissolved oxygen near the interface between Fe–C melt and wüstite will possibly develop the solutal Marangoni flow and this flow so-called solutal Marangoni flow could be another source to induce the stirring flow in the melt. Yin et al. observed the surface flow near the solid–liquid interface of Fe–C alloy during solidification that was driven by the oxygen concentration gradient. This may be a plausible mechanism to introduce the stirring flow during the melting process of CCA and DRI. It is necessary to evaluate the distribution of oxygen and carbon in the melt as well as roles of wüstite on the carburization-melting process in order to understand the exact mechanism of iron carburization-melting enhancement by the solutal Marangoni flow if it exists.

In the present study, to evaluate the effect of iron oxides on the carburization-melting rate of the reduced iron, the reaction phenomena on Fe–C melt near wüstite were directly observed by a confocal laser-scanning microscope (CLSM) and the melting rates were evaluated based on the movement of the liquid-solid Fe–C interface. Additionally, the effects of Marangoni flow on the melting rate were quantitatively analyzed by the method of computational simulation.

2. Experimental

Prepared sample assembly was heated up to 1523 K for 5 min under purified Ar atmosphere in an image furnace. Reaction phenomena and melting behavior were observed by using a confocal laser-scanning microscope. All observations were recorded in a personal computer. Two kinds of experiments were carried out in the present research.

The first experiment was carried out to confirm the existence of Marangoni flow in Fe–C melt at the vicinity of wüstite. For the introduction of the oxygen concentration gradient in Fe–C melt to induce the flow, the arrangement of Fe sheet, graphite and wüstite blocks was shown in Fig. 1. The thin iron sheet rapidly melts by carbon diffusion after it has reached over the eutectic temperature of Fe–C alloy. The formed liquid Fe–C film is contacted with graphite and wüstite simultaneously. Therefore the dissolved oxygen concentration at the interface with graphite can be different from that with wüstite. The thickness of an iron plate sample (purity: 99.99 mass% Fe) was 180 μm. Wüstite and graphite (ash~400 ppm) samples were cut into a block (L×W×H: 3.5 mm×2.5 mm×1.5 mm). Alumina crucible (D: 7.8–8.0 mm, H: 3 mm) was used to hold the assembly of graphite, iron foil and wüstite.

In the next experiment, sample assembly was prepared as shown in Figs. 2(a) and 2(b). As depicted in Fig. 2(a), three different kinds of sample height, 0.5 mm, 1.0 mm and 1.5 mm, were used for the analysis of the height effect on the melting rate. 99.99%-purity iron was used. In addition, two different graphites, standard (ash=400 ppm) and high pure graphite (ash<20 ppm), were used for the investigation of the effect of the ash content. Graphite was fixed on an alumina plate by alumina cement. Iron was initially separated from graphite. When temperature reached 1523 K, we made iron come into contact with graphite by using a Pt fine rod as shown Fig. 2(a). In the assembly shown in Fig. 2(b), Fe–C melt can come into contact with graphite and wüstite simultaneously. Since the iron oxide sample does not cover the surface of the Fe–C melt, the melting rate could be easily measured. Only the 1.5-mm-thick layer of iron and standard graphite were used. The melting rate was evaluated by measuring the movement of the interface between the melt and the solid iron.

3. Results and Discussion

3.1. Surface Flow on Fe–C Melt Near the Interface with Wüstite

Of the sample assembly in Fig. 1, the iron film transformed to iron–carbon melt at 1523 K forming link between graphite and wüstite. The carbon concentration of
the melt at the interface with the graphite could be assumed to be saturated at this temperature. The produced Fe–C melts can react with wüsite. Carbon was supplied from graphite to Fe–C melt and was consumed at the interface with wüsite. Wüsite reduction produces CO gas bubbles. Figure 3 shows the bubble movement in the melt near the interface with wüsite after iron film melted. The diameter of bubbles was about 10 μm. The arrow indicates one of bubbles in the melt. It was observed that the bubbles generally move toward the graphite. With increase of the reaction time, chaotic flow was observed near the interface with wüsite. The velocity of the bubble was measured from displacement of its position in the sequential frames of 1/30 s interval. Nine bubbles were randomly selected. The velocity of the bubbles ranges from 266 to 893 μm/s. Murakami suggested in his researches \(^1\),\(^9\) that the Fe–C melt might be agitated by CO bubbling. However, he could not observe the surface of the melt in the vicinity of wüsite scale. Therefore it is necessary to confirm if the bubbling could drive such a strong flow in Fe–C melt or if there would be another driving force of the flow.

Supposed that the migration of bubbles was driven by buoyancy force, terminal velocity of a buoyant bubble in a stagnant fluid is calculated by the balance between buoyancy force and viscous drag force as described in Eq. (1).

\[
\frac{4}{3} \pi R^3 (\rho_{\text{Melt}} - \rho_{\text{CO}}) = 4\pi R \mu_{\text{Melt}} U_{\text{terminal}} \quad \ldots \ldots \ldots (1)
\]

where, \( R \) is 5 μm radius of the bubble, \( \rho_{\text{Melt}} \) is 7 000 kg/m\(^3\) density of Fe–C melt, \( \rho_{\text{CO}} \) is CO gas density which is negligible, \( \mu_{\text{Melt}} \) is 0.008 Pa·s viscosity of Fe–C melt and \( U_{\text{terminal}} \) is the terminal velocity of the bubble. The rising speed of a bubble with 5 μm radius is calculated to be approximately 7.3 μm/s. But it was impossible for buoyancy force to induce the bubble to rise with 7.3 μm/s of velocity and migrate laterally with more than 200 μm/s of speed.

This flow could be Marangoni flow which is driven by surface tension gradient. Figure 4 schematically shows the relation between the concentrations of the dissolved carbon and oxygen under different CO pressures. At a particular temperature, the carbon concentration at the interface with graphite, \( C_{gr} \) (carbon-saturated concentration with graphite) is different from that at the interface with wüsite, \( C_L \). As a result, oxygen concentrations (\( \Omega_{gr} \) and \( \Omega \)) at each interface are also different. This difference between the oxygen concentrations induces the surface tension gradient. As shown in Fig. 4, the oxygen concentration difference with \( p_{\text{CO}} \) of 1 atm is much smaller than that with \( p_{\text{CO}} \) of more than 1 atm.

In this experiment, bubbles of the order of micrometers were observed. The pressure of CO inside the bubble can be higher than 1 atm. Carbon concentration around the bubble is reasonably assumed to be \( C_{L} \) as the bubble was formed near the interface with wüsite. \( \Omega_{\text{SUP}} \) is the oxygen concentration corresponding to \( C_{L} \) under the equilibrium with higher \( p_{\text{CO}} \) than 1 atm. As oxygen could be supersaturated near the interface with wüsite, \( \Omega_{\text{SUP}} \) can be larger than \( \Omega \) as shown in Fig. 4.

Presently, there are no practical ways to directly measure the oxygen concentration at the interface between the melt and the FeO. We may evaluate the oxygen concentration from the bubble size in Fe–C melt in the vicinity of wüsite. Its value might be very close to that at the interface. The surface tension of Fe melt with dilute concentration of oxygen can be expressed as \(^{14}\).
\[
\sigma = 2.858 - 0.00051 \times T - 0.28 \times \ln(1 + 170 \times Q) \quad \text{(N/m)}
\]

where \( \sigma \) (N/m) is the surface tension of melt, \( T \) (K) is the absolute temperature of melt and \( Q \) is the bulk concentration (mass\%) of oxygen. The gas pressure inside the bubble could be calculated by Young–Laplace equation.

\[
\Delta p = \frac{2\sigma}{R} \quad \text{..................................(3)}
\]

On the free surface of a bubble, CO gas is in equilibrium with dissolved oxygen and dissolved carbon on the free surface as

\[
C_{\text{eq}} \text{(mass\%)} + Q \text{(mass\%)} = \text{CO (g)} \quad \text{.................(4)}
\]

The equilibrium constant for the reaction (4) is defined as

\[
K = \frac{P_{\text{CO}}}{C_{\text{eq}} \text{(mass\%)} \cdot Q \text{(mass\%)}} \quad \text{...............(5)}
\]

Recommended equations for \( K \) and \( C \) (mass\%) are, respectively, as followings\(^{15,16}\):

\[
\log K = 1106/T + 2.003 \quad \text{..........(6)}
\]

\[
\log C \text{(mass\%)} = -1180/T + 2.20 \quad \text{..........(7)}
\]

Although the Eq. (6) is valid over 1 633 K, the equilibrium constant at 1 523 K was evaluated by using the Eq. (6) as a first approximation. In addition, the effect of carbon on the activity coefficient of oxygen was neglected since the evaluation of the exact carbon concentration near the interface with the solid Fe is quite difficult. From Eqs. (2)–(7) and \( R = 5 \mu \text{m} \), the oxygen concentration could be obtained to about 49.4 ppm by trial-error method. On the other hand, the oxygen concentration at carbon–saturated iron melt under 1 atm of CO is calculated to be 1.21 ppm by Eqs. (5) and (6). The oxygen concentration near the interface with wüstite is supersaturated about 41 times higher than the equilibrium value with \( P_{\text{CO}} \) of 1 atm resulting in higher oxygen gradient than that without wüstite. Based on this result, during the smelting of reduced iron in a CCA or a DRI, it can be expected that the remaining iron oxides could generate the stirring flow in Fe–C melt and enhance the melting rate of the reduced iron. Several assumptions are applied in the present evaluation process, however, these assumptions do not change the fundamental result that the oxygen concentration near the interface with wüstite is much higher than the concentration at the liquidus value with \( P_{\text{CO}} \) of 1 atm.

### 3.2. Carburizing and Melting Process of Fe by Graphite without the Existence of Wüstite

Using the sample assembly without wüstite shown in Fig. 2(a), the increase of the width of Fe–C melt as a function of time up to 6 s was measured. The height of the sample is 0.5 mm. The result was shown in Fig. 5. The obtained experimental results are compared with that by Murakami \textit{et al.}\(^{1,9}\) The solid line is the best-fit regression line of our experimental results. The dotted line is the result by Murakami \textit{et al.}\(^{9}\) Two results agreed well each other. Based on the mass balance of carbon, the melting rate, or the speed of the moving interface in between Fe–C melt and solid iron could be expressed mathematically as following:

\[
(C_{L} - C_{S}) \frac{dL}{dt} = -D_{L}^{C} \left( \frac{\partial C}{\partial n} \right)_{L} + D_{S}^{C} \left( \frac{\partial C}{\partial n} \right)_{S} \quad \text{...............(8)}
\]

where \( L \) is the length of Fe–C melt, \( D_{L}^{C} \) and \( D_{S}^{C} \) is carbon diffusion coefficients in Fe–C melt and in solid iron, and \( C_{L} \) and \( C_{S} \) are carbon concentration at Fe–C melt side of the interface and at solid iron side of the interface, respectively. \( C_{L} \) and \( C_{S} \) are the same as the concentrations of liquidus and solidus. \( n \) is normal vector of the interface. The first term in the right side means carbon flux from Fe–C melt to the interface between the melt and solid iron. The second term is carbon flux from the interface to the solid phase but it is negligible because carbon diffusivity is much smaller in solid than in Fe–C melt. Thus,

\[
(C_{L} - C_{S}) \frac{dL}{dt} = -D_{L}^{C} \left( \frac{\partial C}{\partial n} \right)_{L} \quad \text{...............(8)'}
\]

As a first approximation, the first term in the right side in Eq. (8)' can be simply replaced by \(-D_{L}^{C}(C_{L} - C_{\text{eq}})/L\) where \( C_{\text{eq}} \) is saturated carbon concentration at the interface between Fe–C melt and graphite if the convection flow is not existed. Then Eq. (8)' is integrated from \( t = 0 \) and \( L = 0 \) to \( t = t \) and \( L = L \), respectively.

\[
L = \sqrt{k_{p}t} \quad \text{..................(9)}
\]

\[
k_{p} = \frac{2D_{L}^{C}(C_{gr} - C_{L})}{C_{L} - C_{S}} \quad \text{...............(10)}
\]

From Eq. (9), it is expected that the melt length will be proportional to \( t^{1/2} \) if process is controlled by carbon diffusion. The melt length as function of \( t^{1/2} \) is plotted in Fig. 6. It shows a good linear correlation. It means that the melting rate of iron is mainly controlled by the liquid phase carbon diffusion to iron. Namely, the contribution of the convective Marangoni flow to the carburization process is negligible at least up to 6 s despite of the existence of Marangoni surface flow.
From the slope of the plots in Fig. 6, \( k_p \) is calculated to be \( 2.84 \times 10^{-3} \text{ m}^2/\text{s} \). At 1523 K, \( C_{O_{\text{eq}}} = 4.5 \text{ mass}\% \), \( C_{C_{\text{eq}}} = 3.4 \text{ mass}\% \) and \( C_{O_{\text{eq}}} = 1.6 \text{ mass}\% \). Thus, \( D_L^C \) is \( 2.32 \times 10^{-3} \text{ m}^2/\text{s} \). This value is lower than those of previously reported value of \( 1.0 \times 10^{-8} - 2.2 \times 10^{-8} \text{ m}^2/\text{s} \) at 1523 K. In the evaluation of \( D_L^C \), \( C_{O_{\text{eq}}} \) of 1.6 mass\% was used. If the melting rate is much larger than the carbon diffusion rate in the solid phase, however, the carbon concentration at the solid Fe surface may not be able to reach to the equilibrium \( C_{O_{\text{eq}}} \) of 1.6 mass\%, or it can be much smaller value. Equation (10) can be modified to

\[
D_L^C = \left( \frac{k_p}{2} \frac{1}{(C_{O_{\text{eq}}} - C_{C_{\text{eq}}}))(C_{C_{\text{eq}}} - C_{C_{\text{eq}}})} \right) \cdots \cdots (10)'
\]

From Eq. (10)', with smaller concentration of \( C_{O_{\text{eq}}} \), larger value of \( D_L^C \) can be obtained. Unfortunately, it is practically impossible to directly measure the carbon concentration at the solid Fe surface during melting process. The good linear correlation shown in Fig. 6 suggests that the solid phase carbon diffusion process is possibly negligible or \( C_{O_{\text{eq}}} \approx 0 \) since the relation is obtained by neglecting the solid phase carbon diffusion process. In this case, \( D_L^C \) will be about \( 4.39 \times 10^{-3} \text{ m}^2/\text{s} \). The present experimental set up could not be strict enough for the reliable diffusivity measurement. Thus, the agreement between the reported values and our estimated value within a factor of two is quite acceptable. It is noted that the melting rate \( dL/dt \) does not change with the value of \( D_L^C \) since the ratio of \( D_L^C/(C_{O_{\text{eq}}} - C_{C_{\text{eq}}}) \) is constant with \( C_{C_{\text{eq}}} \) in the Eq. (8)'.

Figure 7 shows the melt length as a function of time from melting to 50 s for the sample assembly shown in Fig. 2(a). Solid circles are for experimental results. The solid line is obtained by assuming the carbon diffusion control process. It is shown that the experimentally measured melting length starts to deviate from the calculated line after about 10 s as shown in Fig. 7. The melting rate is higher than that expected from the diffusion-controlled melting process. It suggests the development of a convection flow which influences the melting rate of iron. In this experimental assembly, wüstite has not existed, however, there is oxygen concentration gradient in Fe–C melt.

Figure 8(a) shows the equilibrium diagram of dissolved carbon and oxygen under CO gas of 1 atm. The oxygen concentration is determined by the carbon concentration in the equilibrium. The carbon concentration of Fe–C melt at the interface with graphite is higher than that at the interface with solid Fe as described in Fig. 8(b). Thus, the difference of oxygen concentration between two interfaces can exist in Fe–C melt even without wüstite. At 1523 K, the difference of oxygen concentration, \( \Delta O \) is about 0.6 ppm. The computational simulations were carried out to confirm if this small difference of the oxygen concentration could drive a convective flow, and the melting rate could be enhanced, and also to find the reason why the convection flow has no effect on the melting rate until 6 s.

3.2.1. Computational Flow Simulation

The flow in the sample assembly shown in Fig. 2(a) was assumed to be a 2-dimensional flow. The end effect of the sample on flow pattern was neglected. The domain is defined as shown in Fig. 9. The photograph in Fig. 9(c) shows a section of Fe–C melt after quenching the sample. Section is not a perfect rectangle. But it is close to rectangular shape. When the melt is cooled down to solid phase, the shape does not change so much. Therefore the shape of the melt is reasonably assumed to be rectangular. \( H \) is the height of Fe–C melt; \( L \) is the length of the free surface of
the melt; \( W \) is the width of the melt. Boundary I and III are the interface between graphite and Fe–C melt and the interface between Fe–C melt and solid iron, respectively. Boundary II is the free surface of Fe–C melt. Boundary IV is the interface between Fe–C melt and the alumina crucible. All parameters such as concentration, diffusivity and size used in the previous sections were adapted for simulation.

Continuity equation and Navier–Stokes equation which can describe the velocity field of the Marangoni flow in the melt can be expressed as

\[
\nabla \cdot \mathbf{u} = 0 \quad \text{.................................(11)}
\]

\[
\rho \mathbf{u} \cdot \nabla \mathbf{u} = - \nabla p + \mu \nabla^2 \mathbf{u} + \rho g \quad \text{.................................(12)}
\]

where \( g \) is gravitational acceleration. The term about gravitational force could be negligible. The diffusive convective mass transfer equation for carbon is expressed as

\[
\nabla \cdot (-D_C \nabla C_C) = - \mathbf{u} \cdot \nabla C_C \quad \text{.................................(13)}
\]

where \( C_C \) is carbon concentration, \( t \) is melting time and \( D_C \) is carbon diffusivity coefficient. As already mentioned, the estimated value of \( D_C \) varies from \( 2.32 \times 10^{-9} \) to \( 4.17 \times 10^{-9} \) m\(^2\)/s depending on the value of \( C_C \). The melting rate simulations were carried out by using \( D_C \) of \( 2.32 \times 10^{-9} \) m\(^2\)/s and \( 4.17 \times 10^{-9} \) m\(^2\)/s. It was confirmed that there was negligibly small difference between the calculated results with different \( D_C \). Based on these results, all simulations in this study have been carried out by using the \( D_C \) of \( 2.32 \times 10^{-9} \) m\(^2\)/s as an apparent carbon diffusivity coefficient. The diffusive convective mass transfer equation for oxygen is also required and is expressed as

\[
\nabla \cdot (-D_O \nabla C_O) = - \mathbf{u} \cdot \nabla C_O \quad \text{.................................(14)}
\]

where \( C_O \) is oxygen concentration (mass\%) and \( D_O \) is oxygen diffusivity in the melt. \( D_O \) was reported \( 2.3 \times 10^{-9} \) m\(^2\)/s at 1 833 K and \( 2.7 \times 10^{-9} \) m\(^2\)/s at 1 933 K. We extrapolated \( D_O \) to 1 523 K based on the reported values and it was \( 1.24 \times 10^{-9} \) m\(^2\)/s. For the exact simulation of iron melting, the time-transient form of Eqs. (12)–(14) should be solved with a phase change equation from solid phase to liquid one. But the interface speed between solid iron and liquid iron as expressed in Eq. (8)’ is governed by the diffusive flux at the interface. It is slow enough to establish flow pattern and solute distribution of carbon and oxygen in the melt because of high convection flow. Therefore we modified the time-transient equations to the steady equations fixing the melt length, \( L \), under the pseudo steady-state approximation.

Carbon, oxygen and flow velocity conditions at each boundary could be defined as followings:

On boundary I (interface with graphite),

\[
C_C = C_{gr} \quad \text{.................................(15)}
\]

\[
C_{Ox} = Q_{gr} \quad \text{.................................(16)}
\]

\[
u = v = 0 \quad \text{.................................(17)}
\]

where \( C_{gr} \) is carbon-saturated concentration and \( Q_{gr} \) is the oxygen concentration corresponding to \( C_{gr} \). In addition, \( u \) and \( v \) are \( x \)- and \( y \)-component of flow velocity \( \mathbf{u} \), respectively.

On boundary II (free surface of Fe–C melt),

\[
\frac{\partial C_C}{\partial y} = \frac{\partial C_{Ox}}{\partial y} = 0 \quad \text{.................................(18)}
\]

\[
\mu \frac{\partial u}{\partial y} = \sigma \frac{\partial C_{Ox}}{\partial x} \quad \text{.................................(19)}
\]

where \( \sigma \) is \( -\partial \sigma/\partial Q \). Surface tension gradient drives surface flow on the free surface. Marangoni flow can be introduced by the Eq. (19).

On boundary III (interface with wüstite),

\[
C = C_l \quad \text{.................................(20)}
\]

\[
O = Q_{gr} + \Delta O \quad \text{.................................(21)}
\]

\[
u = v = 0 \quad \text{.................................(22)}
\]

where \( C_l \) is carbon concentration of liquidus and \( \Delta O \) is set at 0.6 ppm as calculated earlier.

On boundary IV (bottom of Fe–C melt),

\[
\frac{\partial C_C}{\partial y} = \frac{\partial C_{Ox}}{\partial y} = 0 \quad \text{.................................(23)}
\]

\[
u = v = 0 \quad \text{.................................(24)}
\]
Melting rate is determined by the carbon flux at the interface as described in Eq. (8). The carbon flux was integrated along with the interface (boundary III) to obtain the average carbon flux, $F_{av}$. The average flux, $F_{av}$, is defined

$$F_{av} = \frac{1}{H} \int_{\text{Interface} \cdot L} - D_C \frac{\partial C}{\partial n} \, \frac{\partial \nu}{\partial \nu}$$

where $H$ is the height of the melt. $H$ is equal to 0.5 mm. Each average flux was obtained when $L/H > 0.01, 0.02, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8, 1.0$ mm. The computational simulation was conducted by using commercial software, COMSOL Multiphysics 3.5 a.\(^{19}\) The numerical algorithm of this numerical solver is based on the finite element method. We used quadratic triangle elements. The total number of elements was more or less 12 000 but mesh was highly refined at both corners on the boundary II as well as along the boundary I and III.

The iron melting rate obtained by the computational simulation was compared with the experimental result in Fig. 10. The melting rate is plotted in a logarithmic scale. $x$-axis is the length $L$ of iron melt. $y$-axis is the melting rate of iron. The solid line is the theoretical melting rate of iron controlled by the carbon diffusion. On the other hand, the broken line is the melting rate of iron obtained by the computational simulation considering not only the diffusion process but also the flow convection by the solutal Marangoni flow driven by the $\Delta O$ of 0.6 ppm. Solid and open circles are the experimental results: solid circles for the experiment results using pure graphite; open circles for the experiment results using standard graphite. The computational simulation reasonably well agreed with the experimental results. Around the region (A) shown in Fig. 10, there was no difference between the melting rate controlled by only diffusion and that controlled by Marangoni flow. As the melt length, $L$, increases, the enhancement of melting rate by Marangoni flow appeared in the region of (B) and (C). (A), (B) and (C) are corresponding to (a), (b) and (c) in Figs. 11 and 12, respectively.

The Figs. 11 and 12 show the contours of carbon concentration (mass%) and the streamlines of the flow and in Fe–C melt at $L/H > 0.01, 0.1$ and 0.5 with $H=0.5$ mm, respectively. These results can explain the reason why the convection effect on the melting rate does not appear distinctly at the initial period of iron melting. The carbon concentration (mass%) distribution is perturbed only near the free surface when $L$ is 0.01 as shown in Fig. 11(a). Referring the flow pattern of Fig. 12(a), the convection effect of the
Marangoni flow does not influence the whole of the melt. Therefore the agitation of solutal Marangoni flow cannot enhance the melting rate. However, as $L$ increases, the effectively stirred area driven by solutal Marangoni flow becomes deeper and deeper from the free surface as shown in Figs. 11(b) and 11(c). When $L$ is equal to 0.5 mm, the carbon concentration profile was totally changed by the Marangoni flow, as shown in Fig. 11(c). It was deduced from the streamlines described in Fig. 12(c) that the whole melt could be stirred by the Marangoni flow.

Figure 13 shows the carbon concentration profile along the dotted line in Fig. 11(c). In this figure, the expected carbon concentration profile under the carbon diffusion control condition is also shown as a linear solid line. At the interface, the slope of the dotted curve is much larger than that of the solid line. Thus we can say that the carbon flux at the interface with Marangoni convection flow is distinctly larger than that without convection. It means that the carbon mass transfer to the solid Fe interface is enhanced by Marangoni flow so that the melting rate of solid iron is also enhanced. It is noted that the small oxygen difference of 0.6 ppm could induce such effective convection flow to agitate the melt even if wüstite is not introduced.

3.2.2. Effect of Graphite Purity on Iron Melting Rate

Solutal Marangoni flow is a surface flow. If graphite contains relatively high amount of oxides as impurities, the oxides float up to the surface after melting and may interfere with the surface flow of the melt. Therefore the oxide content in graphite could be another factor to change the melting rate of iron.

Figure 10 shows melting rate with pure graphite which seems to be slightly higher than that with standard graphite, and also both results slightly deviate from the computational result which does not consider the floating oxides on the surface.

If a liquid contains concentrated dispersion particles, viscosity of the liquid is altered. Viscosity of the surface of Fe–C melt where there are floating ashes is plausibly different from that of Fe–C melt without them. Einstein has derived the viscosity equation for dilute dispersions of spherical particles. Some researchers extended the Einstein viscosity equation to the viscosity of concentrated dispersions of particles. The extension of Einstein’s viscosity equation was adapted to modify the viscosity of the surface of Fe–C melt on which concentrated oxides floated as following:

\[
\mu_{\text{eff}} \frac{\partial u}{\partial y} = \sigma \frac{\partial Q}{\partial x} \quad \text{(26)}
\]

\[
\mu_{\text{eff}} = \frac{\mu(1-0.5\phi)}{(1-\phi)^3} \quad \text{(27)}
\]

where $\mu$ is the viscosity of Fe–C melt and $\phi$ is the volume fraction of the floating particles in the surface layer. For the evaluation of impurities, we used Eqs. (26) and (27) in the calculation instead of Eq. (19). In this case, the viscosity on the surface is larger than that of the bulk of Fe–C melt. The driving force of Marangoni flow could be suppressed by higher viscosity. Consequently, the flow stirring effects can be reduced and the enhancement of the melting rate of iron is decreased.

Figure 14(a) shows that decrease in the melting rate with increase in the volume fraction of floating ash from $\phi=0.0$ to $\phi=0.8$ when $\Delta O$ was equal to 0.6 ppm and $H$ was 0.5 mm. Experimental results with pure graphite and with standard graphite distribute around $\phi=0.2$ and 0.5, respectively. It was observed as shown in Fig. 14(b) some floating matters exist on the surface of the melt but their density could not be measured quantitatively. From the computa-
tional simulation, it was deduced that there were more floating oxides on the surface of iron which came into contact with standard graphite. Effective viscosity could describe the effect of the floating oxide on the melting rate of iron. As higher ash containing cokes are used in ironmaking process, the melting rate of iron with cokes would be retarded more than the results of the present research. It is necessary to study the effect of ash content in cokes on the melting rate of iron in future.

### 3.2.3. Effect of Sample Height on Iron Melting Rate

As discussed previously, it was assessed that the enhancement of iron melting rate was influenced by melt length, $L$, at constant sample height $H=0.5$ mm. The melting rate pattern would be altered by the sample height $H$ for a melting length $L$.

**Figure 15** shows the melting rate of iron for three different heights, 0.5, 1.0 and 1.5 obtained for standard graphite and the computational results. Computational results show the melting rate decreases for a melt length $L$ as sample height $H$ increases from 0.5 to 1.5 mm. In the simulation, the volume fraction of the floating particles in the surface layer, $\phi$, was set 0.5. The difference between the melting rate with $H=0.5$ mm and that with $H=1.0$ mm obtained from the experiments was relatively small, but the former looks slightly higher than the latter. The melting rate with $H=1.5$ mm was rather lower than the others. It deviated from the melting rate obtained from the computational simulation. This suggests that the fraction of floating particles on the surface layer, $\phi$, was probably much larger than 0.5 at $H=1.5$. At constant melt length, the volume of the melt with the aspect ratio of 1.5 is larger than those with the aspect ratio of 0.5 and 1.0, which proves that this melt contained more oxides than others if the oxides were considered to be homogeneously distributed. Thus the number of floating particles on the surface of the melt with the aspect ratio of 1.5 can be expected to be much larger than those with 0.5 and 1.0. These results show that the aspect ratio could be one of the parameters to determine the melting rate of iron.

### 3.3. Carburizing and Melting Process of Fe by Graphite Under Existence of Wüstite

The oxygen super-saturation possibly increases the strength of the Marangoni flow in the melt. In other words, the value of $\Delta O$ more than 0.6 ppm can make stronger Marangoni flow and thus the iron melting rate is expected to be much faster. To examine the effect of $\Delta O$ on the melting rate, the measurement and the computational simulation of melting rate was carried out by using the sample assembly shown in Fig. 2(b). In the experiments, standard graphite was used, and the height of iron sample $H$ is 1.5 mm. For highly pure graphite, the enhancement of iron melting rate under FeO existence was evaluated by Murakami et al.\(^1\,^9\) The standard graphite containing more ash is closer to cokes or coal than highly pure graphite. **Figure 16** shows the measured Fe–C melting length with time in a logarithmic scale. Open diamonds are the melting rates of iron without wüstite existence (assembly shown in Fig. 2(a)). Open circles are the melting rates of iron under the wüstite existence. It is clearly shown that the melting rates are enhanced under wüstite existence. Solid line means the theoretical melting rate controlled by the carbon diffusion process. It means that the melting rate without wüstite is simply controlled by the carbon diffusion process in this particular experimental condition. Wüstite could induce the strong surface flow on the melt. The developed flow in the sample assembly shown in Fig. 2(b) should be 3-dimension because Fe–C melt has interfaces with wüstite as well as solid iron. However, it is quite difficult to decide the oxygen concentration at the interfaces. Thus, to obtain the exact melting rate, we must calculate the 3-dimensional flow pattern and concentration distribution. Intriguingly, the observed surface flow is essentially from the interface with the solid iron to that with the graphite and is qualitatively the same flow pattern although the velocity can be different. Thus, instead of solving the 3-dimensional flow pattern exactly, it was simulated as a 2-dimensional problem with varying $\Delta O$ to fit the experimental results.

The calculated best-fit line for the experimental results was obtained by using the oxygen concentration difference $\Delta O$ of 10 ppm and is shown as the finely broken line in Fig.

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**Figure 15.** Variation of the convection effect with the height of Fe–C melt, $H=0.5$, 1.0 and 1.5 mm in the logarithmic scale. Open circle, square and diamond stand for the melting rate of the experiment results. Lines are the computational simulation results.

**Figure 16.** Wüstite effect on the melting rate of iron in the logarithmic scale. Open circle and diamond are the experimental results with the sample height $H=1.5$ mm. Finely broken line and normally broken line are the melting rate obtained from the simulation with $\Delta O=10$ and 0.6 ppm, respectively.
The value of $\Delta O$ equal to 10 ppm under existence of wüstite is about 17 times larger than $\Delta O$ equal to 0.6 ppm without wüstite, which is the broken line in Fig. 16. Therefore it can be said that the existence of wüstite is quite effective to enhance the melting process of Fe in the case of relatively impure graphite as well.

Cokes and coals contain impurities such as ashes more than standard graphite does. In this case, the effective enhancement of melting rate may not be introduced since the convective stirring is retarded by the floated particles originated from ashes. However, even when using high ash graphite, the effective stirring flow is developed as shown in Fig. 16 if wüstite exists. Therefore the appropriate amount of iron oxides must be required to effectively increase the melting rate of iron in the CCA or DRI reduction processes. It is well known that the solid inclusions can be absorbed into molten slags. Thus, by the addition of slag with appropriate composition into CCA or DRI, the floated particles may possibly be eliminated.

Just as discussed, unreduced iron oxides can enhance Fe–C alloy melting rate and then the Fe–C melt can reduce the unreduced iron oxide more quickly. In this way, Fe–C melt and wüstite can interact with each other in a good way. Therefore the unreduced iron oxide like wüstite could improve the operation efficiency of melting in an industrial smelter. However, the amount and the distribution of the wüstite and the reduced iron phases should be controlled appropriately. That could be the next subject in the future.

4. Conclusions

The liquid Fe–C formation rate under the condition that Fe–C melt is simultaneously contacted with wüstite and graphite was measured based on a confocal laser scanning microscope “in-situ” observation of the melting process. The results are summarized as follow:

(1) After the melting of solid Fe, the development of surface flow is always observed. This flow is confirmed to be solutal Marangoni flow driven by the difference of oxygen concentration at the each Fe–C melt interface with solid Fe and graphite.

(2) The oxygen concentration at the interface between Fe–C melt and wüstite is oversaturated than that expected from the liquidus carbon concentration. This large oxygen concentration introduced by wüstite makes it possible to develop the strong Marangoni flow on the surface.

(3) The equilibrium oxygen concentrations at the Fe–C melt interfaces with graphite and solid iron are different. This difference introduces the solutal Marangoni flow in the Fe–C melt even without the existence of wüstite.

(4) At the early stage of melting (within 10 s), the melting rate is mainly controlled by the carbon diffusion process because the stirring effect by Marangoni flow is only effective in the thin surface area. With increase of length of the melt, the convective stirring effect due to Marangoni flow becomes dominant in the whole melt and melting rate is enhanced.

(5) The stirring effect of solutal Marangoni flow on the melting rate is dependent on the aspect ratio (melt length $L$ / melt height $H$) of Fe–C melt. When the aspect ratio ($L/H$) is smaller than 1/2, the stirring effect is negligible.

(6) Strength of solutal Marangoni flow is suppressed by floating oxides originated from impurities in graphite and iron. The effect of these oxides on the melting is quantitatively evaluated by introducing “surface viscosity”.

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