The Role of Molten Slag in Iron Melting Process for the Direct Contact Carburization: Wetting and Separation

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Rapid iron melting initiation and molten slag separation which take place in carbon composite iron ores are quite interesting phenomena, but their mechanisms have not been established yet. Since the size of carbonaceous material and iron ore particles is tiny in carbon composite iron ores, molten slag can dynamically play a critical role in the iron melting initiation and the slag separation. The behavior of the molten slag was clarified by direct observation of phenomena occurring in a simplified carbon composite agglomerate sample (iron disk–slag particle–graphite or coke particle) via a confocal laser scanning microscope combined with an image furnace. It was found that the molten slag wetting induced the iron melting initiation by attracting graphite or coke to iron and the molten slag separation took place with iron melting propagation. However, the high content of coke ash could suppress the iron melting initiation. In addition, the mechanism of molten slag separation from Fe–C melt was verified by phase field modeling.

KEY WORDS: iron melting initiation; slag wetting; slag separation; coke ash; carbon composite iron ore; confocal laser scanning microscope; phase field method.

1. Introduction

For the issues of environment, energy and resources, new ironmaking processes have been developed by using the composites of mixture of fine iron ore with fine carbonaceous materials because of its much shorter iron production time than the conventional iron making process. Several researchers have investigated the carburization and melting of iron in the mixture of powdery carbonaceous materials and iron ores. It has been known that iron melting rate is very high because of the direct contact of the iron with carbonaceous material as well as the small size of reduced iron particles. It has been confirmed that iron could be most rapidly carburized by direct contact with carbonaceous materials. However, it has not been clear yet how the direct contact of iron with carbonaceous materials can be brought about that would cause the iron melting initiation. Molten slag can play a critical role in this initiation process. However, the role has not yet been confirmed. Matsui et al. found that reduced iron could not come into contact with coals until the gangue layer surrounding the iron was liquidized. Thus, the fusion of slag could be related to the direct contact of iron with coals. After gangue layer was liquidized, the iron and the carbon may come to be close to each other, further explanation is needed to elucidate the mechanism of the direct contact while the liquid layer still exists between them.

Ohno et al. showed that the iron carburization could occur through the slag even if the iron was separated from the graphite. That is, the existence of liquid slag mediates the transport of molten Fe–C particle from the interface with the graphite to that with the iron. However, since iron carburization through the slag is much lower than that through the direct contact with the carbon, the latter must occur in the composite of fine iron ore and fine carbonaceous material. Thus, another mechanism for the enhancement of the direct contact must exist.

Moreover, molten slag separation as well as slag wetting is also quite interesting phenomenon after completion of iron melting of carbon composite iron ores. Some authors have found the separation of CaO–SiO₂–Al₂O₃ molten slag from pig iron, while others reported the covering of FeO containing slag with it. It implies that the composition of a molten slag may determine the behavior of a molten slag separation from molten iron. However, details of the mechanism of molten slag separation have not been established. Since graphite and coke have their own characteristics, molten slag behaviors can be different between them, and especially coke ash may influence the slag behavior.

In the present study, we observe the behavior of the slag between iron and carbonaceous materials (graphite and coke) by using a confocal laser scanning microscope combined with an image furnace. This direct observation for the molten slag behaviors can inform us of the exact mechanisms of iron melting initiation and slag separation. We simplify such a complex system as carbon composite iron ores into an assembly of iron, slag and graphite. In addition, in order to understand the behavior of molten slag with reduced iron clearly, wetting and separation processes are simulated by using a phase field method.
2. Experimental

Iron disks (diameter: 1.0 mm, purity: 99.99%) were prepared by polishing sliced iron particles from an iron rod. Thickness of the iron disks was 0.5 mm. Graphite disks (diameter: 1 mm, high purity) were made by punching a graphite plate (thickness: 0.5 mm). Cokes fragments (mesh: <1.0 mm) were prepared by crushing the original cokes (mesh: <60 mm), whose composition is given in Table 1. In order to know the ash effect on the wetting behavior, higher ash content containing cokes were made by the reaction of the broken cokes particles with CO₂ gas at 1 273 K for 20 min. Slag was prepared by heating mixture of oxide powders (CaO: 22.2%, Al₂O₃: 15.1%, SiO₂: 62.7%) up to 1 673 K in a platinum crucible by using a muffle furnace. According to a literature, the melting temperature of the slag is around the eutectic temperature, 1 446 K, which was confirmed by direct observation via a confocal laser scanning microscope. A piece of, approximately, 0.8 mg slag was positioned between an iron disk and a graphite disk or a fragment of coke on an alumina plate as shown in Fig. 1(a). The plate was slightly coated with boron nitride by a BN spray in order to prevent the slag from reacting with the alumina crucible. "In-situ" observation of the phenomena within iron, slag and carbonaceous material was conducted.

The present experiment consisted of two sub-experiments. The first one was designed that the wetting behaviors of CaO–Al₂O₃–SiO₂ slag would be compared for different types of carbonaceous material: graphite, coke and reacted coke. Since ash in coke plays a critical role in slag wetting at the interface between the slag and the coke, each surface of the original coke and the reacted coke was analyzed by a field emission scanning electron microscope (FE-SEM) and an energy dispersive spectroscopy (EDS). For the purpose of obtaining clear images for cokes surface, instead of the fragments, a coke brick was used, which was obtained by grinding and polishing its surface. The preparation method of the reacted coke brick was the same as that of the reacted coke fragment.

Secondly, the shape of Fe changes from disk-like to sphere-like shape after Fe is melted by carburization. In order to know the effect of the shape change on the slag wetting on the iron, a sphere-like iron particle was prepared by quenching the iron particle after heating it up to over the melting temperature, 1 833 K. Then, the behavior of the slag wetting to the sphere-like iron was observed at 1 523 K. The sample arrangement is shown in Fig. 1(b).

3. Results and Discussion

3.1. Molten CaO–Al₂O₃–SiO₂ Slag Wetting for Iron Melting Initiation under the Existence of Graphite

At 1 473 K, lower than the experiment temperature condition, the slag already transformed to transparent liquid phase between iron and graphite. Figures 2(a)–2(f) show the behavior of the liquid slag. And Figs. 3(a)–3(f) are schematics for Figs. 2(a)–2(f), respectively. When the liquid slag came into contact with the solid iron, it began wetting the surface of iron and subsequently covered the whole surface of the solid iron. It shows the good wettability of the molten slag with solid Fe. Interestingly, even though the wettability of the slag to graphite does not seem to be good
as shown in Figs. 2 and 3 (contact angle is larger than $\pi/2$), the graphite was being dragged by the slag. It has been known that molten slag gets better wettability to graphite with time due to the reduction of silica at the interface\textsuperscript{12,13} and the increase in the silica content of slag improves the wetting.\textsuperscript{14} The silica composition of the slag used in the present experiment was 62.7%. But, sometimes, the graphite was detached from the slag possibly due to the friction between the graphite and the bottom plate, and iron melting was not initiated. Figures 2(c) and 3(c) show that the graphite disk located very close to the slag covering iron disk. Figures 2(d) and 3(d) show the initiation of iron melting between them. Once the iron began to melt by direct contact with graphite, it never lost the contact with graphite. In Fig. 2(e) and Fig. 3(e), the propagation of iron melting was observed. As the transformation of iron to Fe–C melt proceeded, the slag which had covered the molten iron was peeled off from its surface as shown in Fig. 2(f) and Fig. 3(f). It clearly reveals the process of slag separation during molten iron production from carbon composite iron ores, which has not been verified by the previous studies.\textsuperscript{1,2,5} The change of the contact angle from small value to large one means that the interface energy between slag and Fe must be increased after Fe melting. Namely, the change of the interfacial energy of iron/slag due to the Fe melting could determine the molten slag behavior. However, there is another variation. When the iron disk melted, its shape changed to sphere-like. The shape change means the surface area change. Therefore it is necessary to check whether the slag behavior to a sphere-like solid iron is different from that to a solid iron disk or not. If the slag has good wettability to the sphere-like solid iron and covers the whole iron, it could be concluded that the main cause of the slag separation is not the shape change of the solid iron during the iron melting.

Figures 4(a)–4(c) show that the liquid slag behavior to a sphere-like solid iron particle. The weight of the sphere-like iron particle was the same as that of the disk-like iron particle, 3.1 mg, that is, the surface area of the sphere-like solid iron was approximately the same as that of the liquid Fe–C particle transformed from the disk-like iron particle. It was observed that the molten slag wetted almost the whole surface of the solid iron sphere. Thus, it can be said that the molten slag behavior is not influenced by the iron shape change from disk-like to sphere-like during iron melting. Therefore the interfacial energy change can be the main driving force to cause the slag separation.

3.2. Phase Field Modeling for the Molten Slag Separation from Fe–C Melt

To understand the slags’ wetting and separation process, the evaluation of interface energy between molten slag and Fe is essential. However, the measurement of the interfacial energy is generally difficult. Thus, it is quite effective if the contact angle instead of the interfacial energy can be used to describe the slags’ wetting and separation process since
the measurement of contact angles is relatively easy.

Under equilibrium condition, the surface tension of molten slag is balanced by the surface tension of iron and the interfacial tension between molten slag and iron at the triple point of slag, iron and gas phases. Contact angles of the molten slag for solid iron and liquid iron, $\theta$ and $\theta'$ are expressed as, respectively:

\[
\gamma_{lv} \cos \theta = \gamma_{il} - \gamma_{il} \cos \theta' \quad (1)
\]

\[
\gamma_{lv} \cos \theta' = \gamma_{lv} - \gamma_{il} \cos \theta \quad (1')
\]

where $\gamma_{ij}$ means the interfacial tension of $i$ and $j$ phase ($I$: solid iron; $L$: Fe–C melt; $V$: molten slag; $G$: gas). Since the contact angle is strongly related to the relative values of $\gamma_{ij}$, the molten slag wetting behavior can be described based on the change the contact angles.

Thus, we used the phase field method to simulate the molten slag wetting behavior on a Fe–C melt drop by using the contact angle as a parameter. Phase field method is a sort of diffuse-interface models. The interface between molten slag and Ar atmosphere is regarded as a smooth diffuse-interface. This diffuse-interface model has attracted much interest recently because it has advantages for getting numerical solutions to multiphase-flow problems. The interfacial layer is expressed by a phase field variable, $\phi$, which ranges from $-1$ to $1$. In the present phase field method, the free surface of the molten slag is regarded as a diffuse-interface. The surface tension force of the free surface is applied by its addition to a body force of the Navier–Stokes equation, which is multiplication of the chemical potential is expressed as15):

\[
\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla \{ \mu [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \} + G \nabla \phi
\]

\[= \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \gamma \nabla G
\]

where $\rho$ is molten slag density and $\mu$ is molten slag viscosity and $\mathbf{u}$ is flow velocity field and $G$ is the chemical potential.

Phase field, $\phi$, is governed by the 4th-order PDE of Cahn–Hilliard equation15):

\[
\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \gamma \nabla G
\]

where $\gamma$ is the mobility ($m^3 \cdot s/kg$). The mobility determines the time scale of the Cahn–Hilliard diffusion and must be large enough to retain a constant interfacial thickness but small enough so that the convective terms are not overly damped. The chemical potential is expressed as15):

\[
G = \lambda \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\varepsilon^2} \right]
\]

where $\lambda$ and $\varepsilon$ are the interfacial energy density and capillary width, respectively.

The surface tension of the molten slag could be expressed as15):

\[
\sigma = \frac{2\sqrt{2}}{3} \frac{\lambda}{\varepsilon}
\]

Phase field parameter $\phi$ has a value of 1 or $-1$ except in a very thin region on the fluid/fluid interface by the Cahn–Hilliard equation.

The boundary conditions for the interface between the slag and the iron are as followings16):

\[
u = 0 \quad \text{(No-slip condition)}
\]

\[
n \cdot \varepsilon \nabla \phi = \varepsilon^2 \tan(\pi/2 - \theta) \left[ \nabla \phi - (n \cdot \nabla \phi) \mathbf{n} \right]
\]

where $\theta$ is the contact angle between the molten slag and the iron.

For the computational simulation, we used a finite-element commercial package ‘Comsol Multiphysics 3.5a’16). Figure 5 schematically shows in plan-view that molten slag wets the surface of a solid iron sphere. The molten slag covers the whole surface of solid iron before the direct contact of iron with graphite as described by the dotted-line circle but this slag covering is disturbed by the Fe–C melt formation from a point A after initiation of the direct contact at the point as described by the solid-line circle. We investigate the molten slag behavior when all solid iron transforms to Fe–C melt. The radii, $R_1$ and $R_2$, of iron and slag are simply set to be 0.5 mm and 0.6 mm, respectively. The molten slag volume described by the red area is $3.8 \times 10^{-4} \text{cm}^3$ and the Fe–C melt volume is $5.2 \times 10^{-5} \text{cm}^3$. Contact angle $\theta$ between the molten slag and the Fe–C melt is defined as the angle difference between the respect tangent lines to the molten slag and the Fe–C melt at the point B. The molten slag wetting is simulated as a function of the final equilibrium contact angle from $\pi/6$ to $2\pi/3$.

The computational domain of Fig. 5 is simplified by axial symmetry condition as show in Fig. 6. The maximum mesh element size is $2.0 \times 10^{-2} \text{mm}$ and the total number of mesh elements is 17664. The motion of the interface between molten slag and Ar atmosphere is simulated. The phase field parameters for molten slag and Ar are equal to 1 and $-1$, respectively. There are no reported exact values of

![Fig. 5. Sketch for good wetting of molten slag to a solid iron sphere at $r<0$.](image)
density and viscosity of the molten slag (CaO: 22.2%, Al₂O₃: 15.1%, SiO₂: 62.7%) at 1 523 K. The density (ρ) and viscosity (μ) of the molten slag can be approximately set to be 2 600 kg/m³ and 10 Pa·s, respectively, based on literatures. The surface energy of the slag, γLV (or γs) can be extrapolated to 0.40 N/m at 1 523 K. We would like to see the behavior of molten slag when a solid iron in Fig. 4 (or the white sphere in Fig. 5) is suddenly changed to a Fe–C melt drop by using this computational simulation.

Figure 7 shows the molten slag behavior for the various contact angles which range from π/6 to 2π/3. Red and blue colors mean the molten slag and the Ar atmosphere, respectively. The initial contact angle θ was set to be 0.027π (4.8°) as shown in Fig. 5 and the interfacial tension γIV of the molten slag and the solid iron could be calculated to be 1.68 N/m based on Eq. (1) where γLV=0.4 N/m (surface tension of molten slag) and γIV=2.08 N/m (surface tension of solid Fe) at 1 523 K. These values correspond the situation before melting (t<0) and stands for good wetting of molten slag on solid iron. The molten slag covers almost the whole iron as in Fig. 6. It represents the condition that the molten slag wets a sphere-like solid iron particle shown in Fig. 4(c). t=0 s means the moment when the solid iron transforms to the Fe–C melt. After t=0 s, the contact angle was suddenly changed to a particular value of the equilibrium contact angle (from π/6 to 2π/3). As the contact angle of the molten slag to the iron in Eq. (7) was set to increase, the molten slag separation starts to take place. For examples, for θ=π/6, the final slag behavior converges to the state that the molten slag covers the half of the surface of the Fe–C melt. On the other hand, for θ=2π/3, the molten slag goes to the state of separation from the Fe–C melt. Figure 8 shows the final state of the slag behavior which was observed by a confocal laser scanning microscope. The contacting line of slag/melt is indicated by the dotted line in the photomicrograph. It is away from the center of the Fe–C melt. This situation is corresponding to the slag behavior of θ≈π/3 shown in Fig. 7. For θ=π/3, π/2 and 2π/3, γLV is calculated to be 1.88, 2.08 and 2.28 N/m, respectively, by using Eq. (1) and (1'). These values means the interfacial tension of the iron and the molten slag increases to 12%, 24% and 36% during the iron melting compared with the value 1.68 N/m (interfacial tension before melting). Based on this simulated results, the driving force of the molten slag separation from the molten iron occurred in a carbon composite iron ore can be the increase of the interfacial energy between molten slag and Fe due to Fe melting.
3.3. Molten Slag Behavior During Iron Melting Process under Existence of Cokes

The behavior of the slag to the original coke was not so much different from that to the graphite as mentioned before. Figures 9(a)–9(d) describe the molten slag wetting drives the attraction between an iron particle and an original coke particle. Even though the contact area between slag and coke was so small, the coke could be dragged toward the iron particle. Figures 9(a)–9(c) show the slag wetting and the iron melting initiation, which are not so much different from those described in the Sec. 3.1. The wetted molten slag was separated from Fe–C melt drop as shown in Fig. 9(d). This separation process seemed to be the same as that discussed in the Sec. 3.1 where graphite was used. We also found floating matters on the Fe–C melt drop as shown in Fig. 9(d). This was not yet identified but might be oxide particles coming from the cokes.

In another experiment, a reacted coke particle was used. The reacted coke particle was prepared by introducing CO₂ over the glowing coke particle. The surface of coke after reaction is schematically illustrated in Fig. 10. Its wetting behavior to the slag was found to be totally different from the original coke. Figure 11(a) shows the contact area between the slag and the reacted coke is larger than that between the slag and the original coke. There must have been higher density of oxides on the reacted coke. The ash was apt to improve the wettability of the slag to the coke better. But, in spite of its good wettability, the initiation of the iron melting has never been observed as shown in Fig. 11(b). There may be two possible reasons for the different behavior of the reacted coke from the original coke: 1) enlarged pore size of the reacted coke; 2) oxides layer on the surface of the reacted coke. Figures 12(a) and 12(b) show each surface of the original coke and the reacted one, respectively. In this magnification, the bigger pores were observed in the reacted coke of (b). It means the area of carbon matrix of reacted coke was decreased. Even though the contact area between coke’s carbon matrix and solid iron is very tiny, it can induce the iron melting as explained by the authors. Therefore the effect of the pore size enlargement is not considerable. On the other hand, once some amount of carbon matrix disappears from the surface, the oxide layer is exposed and becomes the dominant part of the coke surface. Figures 13(a) and 13(b) are FE-SEM images of the surfaces of the original coke (a) and the reacted coke (b). The surface of original coke mainly consists of carbon matrix as shown in Fig. 13(a). At the surface of the reacted coke, more oxide particles were observed as shown in Fig. 13(b).
comparing with that of the original one shown in Fig. 13(a). The coke contained ash about 12.1 mass% according to the composition given in Table 1. Recently, Gupta et al. investigated various kinds of minerals existing on the surface of coke. They found Al–silicate, iron oxide and silicate, etc. in the cokes. Figures 14 and 15 show respective EDS images for the original cokes of Fig. 13(a) and the reacted one of Fig. 13(b). In the original coke of Fig. 14, a few oxides such as alumina, silicates and iron oxides were detected. White arrows indicate them as shown in Fig. 14. On the other hand, in the case of the reacted coke of Fig. 15, very concentrated Al–silicates and iron oxides were detected on the surface. In order to contact the carbon matrix behind the oxides with iron, the oxides should be dissolved into the slag. However, according to CaO–SiO$_2$–Al$_2$O$_3$ phase diagram shown in Fig. 16(a), the slag was already saturated with silicate and alumina since the liquidus temperature of the slag is between the eutectic temperature,
1 446 K and the experimental temperature, 1 523 K, which is marked 1. Even if small amount of Al–silicates is dissolved into the liquid slag, the slag composition 1 shifts to 2 in Fig. 16(a) and thus the solidified shell may form in the vicinity of the oxides as described in Fig. 16(b). As a result, Al–silicates oxides could not be dissolved into the slag. Consequently, the ash blocks the direct contact of the iron with the reacted coke. Thus, for the enhancement of the carburization or melting of reduced Fe in CCA, the design of appropriate composition of slag for the effective dissolution of the ash content in coke is very critical.

4. Conclusions

The exact role of molten slag had not been clarified in iron melting initiation, neither had slag separation process been in a carbon composite iron ore. In this research, the roles of the molten slag were clarified by “in-situ” observation of the behavior of molten slag on the process of iron melting and slag separation process using a confocal laser scanning microscope. In addition, the phase field modeling for the behavior of molten slag confirmed that the increment of the interfacial tension of Fe–C melt/molten slag was the driving force of the molten slag separation from the melt. In addition, the effect of coke ash on iron melting initiation was investigated. The findings are as followings:

(1) It is molten slag wetting that brings about an attractive force between carbon and iron so as to make them come into contact with each other, and consequently iron melting can take place.

(2) Wetted CaO–Al₂O₃–SiO₂ molten slag is separated from Fe–C melt after iron melting due to the interfacial energy increase between slag and iron.

(3) The change of the interfacial tension of Fe–C melt and molten slag determines the wetting or de-wetting behavior of the molten slag during iron melting process.

(4) Higher ash-density of coke has better wettability with Fe, but is unfavorable for the initiation of the iron melting coke, since it interrupts the direct contact of iron with carbon matrix if slags with appropriate composition for ash dissolution does not exist.

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