1 Introduction

Steelmaking industry consumes about 12% of total energy consumption in Japan, and most of the consumption is due to the blast furnace process. The most important factors that affect energy consumption in the blast furnace are reduction of iron ore and carburization of reduced iron at high temperature. If it is possible to accelerate the rates of iron ore smelting reduction and the succeeding carburization at low temperature, the technology will be very valuable to lower energy consumption in the blast furnace.

It is well known that phenomena during smelting reduction are very complicated and the mechanism has not yet been clarified. Therefore, “in-situ” observation of smelting reduction and carburization of iron sample were carried out in our previous work. It was confirmed from the results that iron was carburized without a direct contact with carbonaceous material during smelting reduction. The mechanisms of this unique carburization were discussed and it was obtained a conclusion that formation rate of Fe–C particles caused by smelting reduction mainly determined the overall rate of iron carburization reaction.

KEY WORDS: smelting reduction; carburization of reduced iron; “in-situ” observation; laser microscope; kinetics.

2. Experimental

The phenomena in cohesive zone would be complex due to the presence of reduced iron, formed slag and residual carbon phases. In the present work, “in-situ” observation of the reactions between carbon, slag and iron was made at the ironmaking temperature by a laser microscope with a special assembly, where iron and carbon did not contact directly with each other and molten slag was placed between them. A confocal laser-scanning microscope was combined with an infrared image-heating furnace, which enabled us to make microscopic “in-situ” observation at high temperature.\(^5\)

![Fig. 1. Illustration of carburization phenomena at the cohesive zone.](image)
Electrolytic iron and highly pure graphite rods were used to simulate the reduced iron and the carbonaceous material, respectively. The master slag was prepared by melting the reagent grade oxides mixed to the required composition in a Pt crucible. The composition of this master slag was 44.1mass%CaO–9.8mass%Al₂O₃–44.1mass%SiO₂–2mass%MgO. Four kinds of slag specimen containing 10, 20, 30 and 40 mass% Fe₃O₄ were prepared by adding Fe₃O₄ to master slag and quenching after rapidly heating up to slag melting temperatures using the laser microscope. Iron and carbon rods were held horizontally on a BN outer crucible and an Al₂O₃ inner crucible. The outer ends of these rods were fixed on a BN crucible by Al₂O₃ cement. The iron and carbon rods did not contact each other, and the gap between two rods was adjusted at 0.25 mm as shown in Fig. 2. Approximately 0.5 mg of the glassy slag was placed in the gap between these rods.

This assembly was set in the sample chamber of the infrared image-heating furnace and then heated up to 1 650 K with heating rate of 3.33 K/s (200 K/min) under an argon atmosphere. After the temperature reached at 1 650 K, the sample was kept for 300 s or 1 200 s at this temperature and then quenched by turning the power of the furnace off. The behavior of the slag sample was directly observed with the laser microscope during the entire period of the heating. The iron rod and the slag were polished after the experiment, and the carbon concentration profile in the iron and the carbon content in metallic particles in slag phase were analyzed with a wavelength dispersion type electron probe micro analyzer (EPMA).

3. Results

Liquid slag was suspended between the carbon and iron rods like “liquid bridge” during melting. Typical behavior of the slag observed during the heating was summarized as follows.

Slag was held between iron and carbon rods after melting. Small iron particles and fine gas bubbles were found to be formed at carbon–slag interface just after the slag was melted as shown in Fig. 3.

Since the iron particles seemed to be liquid and the temperature of this period was much lower than the melting point of pure iron, iron should be carburized in some extent. That is, iron oxide in slag was reduced at carbon–slag interface, formation of CO gas and metallic iron occurred simultaneously due to the smelting reduction, and the carburization of reduced iron took place on the carbon surface. Continuous flow of molten slag from carbon–slag interface to iron–slag interface was also observed at this moment. This would be due to Marangoni flow caused by the difference of surface tension of slag between the regions near carbon and iron rod. Once Fe–C particles were formed at
carbon–slag interface, they were carried to iron–slag interface by the slag flow as shown in Fig. 4. They did immediately wet the surface of iron rod when they reached to the iron–slag interface.

Carbon concentration profile in iron rod was analyzed after the experiment. The typical result on 20 mass% FeO containing slag is shown in Fig. 5. Carbon content in iron rod near the slag–iron interface was found to be much higher than that in the iron bulk in all samples. Therefore, it was confirmed that iron rod was carburized by the iron particle moved form other side.

Carbon content in Fe–C particle found in slag phase was also analyzed after the experiment. The typical result is shown in Fig. 6. Mean value of carbon content in the particle was about 2 mass%. This result indicated that the Fe–C particle contained enough carbon to carburize the iron rod.

4. Discussion

These above-mentioned phenomena have been studied in our previous work,4) and the mechanism of iron carburization during smelting reduction has been roughly considered as follows:

When iron oxide containing slag contacts with carbon, iron oxide is immediately reduced and Fe particles are formed simultaneously accompanied by CO gas bubbles at the interface as illustrated in Fig. 7(a). The Fe particles are simultaneously carburized by carbon and melted at the slag–carbon interface. The molten Fe–C particles are then carried from the slag–carbon interface to the slag–iron interface due to the slag flow driven by Marangoni effect as shown by Fig. 7(b). The molten Fe–C particles immediately
spread on the surface of reduced iron and the reduced iron is carburized by Fe–C particles as indicated in Fig. 7(c). Reduced iron is carburized continuously by the repetition of such sequence.

From above consideration, these sequences of phenomena could be classified into three steps roughly, although the phenomena were very complex. But, it has not been able to be clarified which step determines the overall rate of carburization reaction. Clarification of this carburization rate determining step is the key for decreasing the energy consumption of ironmaking process. Therefore, our former results were reviewed to find which step had the strongest effect on the carburization.

4.1. Carbon Diffusion Coefficient in Iron

At first, carbon diffusion coefficient in the iron rod was estimated from carbon concentration profiles measured in the present work to examine the last step of above-mentioned carburization mechanism as shown in Fig. 7(c). Semi-infinite diffusion in longitudinal-direction from the slag–Fe interface was assumed in the center of iron rod. Fundamental equation, initial condition and boundary condition are shown as follows.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} ......................(1)$$

$$t=0; \quad C=C_0, \quad x=0; \quad C=C_s, \quad x=\infty; \quad C=C_0 ......(2)$$

These equations derived the following solution.

$$\frac{C-C_s}{C_0-C_s} = er\frac{\sqrt{x}}{2\sqrt{Dt}} ......................(3)$$

Curve-fitting between the measured and the calculated carbon profiles was conducted using various values of $D$ as a parameter for determination of carbon diffusion coefficient. As the result, $D=1.2 \times 10^{-10}$ (m²/s) was obtained as shown in Fig. 8. This result showed good agreement with literature values.\(^9\)\(^10\)

This comparison of results indicated that the amounts of carbon supplied by Fe–C particle balanced with the diffused into the iron. In other words, the amounts of Fe–C particles, which carried from carbon–slag interface, were not enough to be piled up at slag–Fe interface. Therefore, this step could not be the rate determining step.

4.2. Velocity of Slag Flow

Next, the flow rate of slag, which was the driving force of Fe–C particle movement, was measured by the “in-situ” observation through Fe–C movement to examine the middle step of the carburization mechanism as shown in Fig. 7(b). The result was shown in Fig. 9.

The velocity of slag flow $u_s$ had strong correlation with initial content of Fe₂O in slag, and the flow was very fast when the distance between carbon and iron rod was consid-
where, \( \sigma \) is surface tension \([\text{N/m}]\), \( \mu \) is viscosity \([\text{Pa} \cdot \text{s}]\), \( \Delta C \) is \( \text{FeO} \) content \([\text{mass\%FeO}]\) difference in \( C_{\text{FeO}(l)} \) and \( C_{\text{FeO}(h)} \). 

Bonì and Derge\(^{12}\) proposed relationship between surface tension and slag composition.

\[
\sigma = M_iF_i + M_iF_i + \cdots + M_iF_i \quad \text{..........}(5)
\]

Where \( \sigma \) is surface tension, \( M_i \) is mol percent \([\text{mol\%}]\) of the \( i \)th component, and \( F_i \) is its surface tension factor \([\text{N/m} \cdot \text{mol\%}]\). This equation was calculated at 1 673 K on the present experimental condition; the slag included 5 components, \( \text{SiO}_2, \text{CaO}, \text{Al}_2\text{O}_3, \text{MgO} \) and \( \text{FeO} \). As the result, the relationship between surface tension and \( \text{FeO} \) content is shown in Fig. 11. \( \mu \) was referred from literature value. As \( \mu \) is its surface tension factor \([\text{N/m} \cdot \text{mol\%}]\), the second was adopted from this figure in accordance with the present experimental condition. And then, \( W_{\text{FeO}} \) was estimated using Eqs. (6) and (7).

At first, the decreased amount of iron oxide from slag phase, \( W_{\text{FeO}} [\text{iron oxide-kg}] \), by smelting reduction was estimated. The following equation was derived from Eq. (6).

\[
r = -\frac{dW_{\text{FeO}}}{dt} \quad \text{[kg - iron oxide / m}^2 \text{ s]} \quad \text{..........}(6)
\]

Where, \( W_{\text{FeO}} [\text{kg-iron oxide}] \) is atomic weight of oxygen and \( M_{\text{FeO}} [\text{kg}] \) is molecular weight of wustite.

\[
dW_{\text{FeO}} = \frac{d}{dt} \frac{W_{\text{FeO}}}{M_{\text{FeO}}} \quad \text{[kg - iron oxide]} \quad \text{..........}(7)
\]

Where, \( W_{\text{FeO}} [\text{kg}] \) is initial amount of slag.
The rate of smelting reduction, the flow rate of slag and the carbon diffusion coefficient in iron were determined on the present experimental condition to clarify the rate determining step of the iron carburization phenomenon during smelting reduction.

The rate of Fe–C particle movement, which decided from the direct observed measurement of the slag flow rate, was very fast. Marangoni flow could consider as driving force of the slag flow.

The assumption on the carbon diffusion coefficient, in which carbon content at slag–iron interface was the concentration on solidus, agreed well with literature values. The amount of carbon supplied by Fe–C particle balanced with that diffused into the iron.

The estimated rate of smelting reduction by solid carbon through the observed carburization rate showed fair agreement with literature values.

The above discussion indicates that the acceleration of this carburization phenomenon needs large amount of Fe–C particle formation due to smelting reduction. In other words, search of favorable slag composition, which would increase of carbon concentration in iron rod could be derived from amounts of Fe–C particles moved from carbon–slag interface, and these amounts of the particles could compare with \( W_O \) caused by smelting reduction of iron oxide. It was confirmed from the previous work \(^5\) that carbon concentration distribution in iron rod existed also in radius direction. Hence, carburization from not only slag–Fe interface but also circumference was considered when the amounts of carbon in iron rod were analyzed at 1 200 s as follows.

\[
W_O^\text{Experimental} = 1.44 \times 10^{-7} \text{ [kg-oxygen]} \quad ..........(13)
\]

Where, \( W_O^\text{Experimental} \) was amounts of removed oxygen, and they were estimated from experimental values in the present work. And also, \( k^{2nd} \) was derived from \( W_O^\text{Experimental} \) using Eqs. (6) and (7), and it was plotted in Fig. 13.

Therefore, \( W_O \) values estimated by Eqs. (12) and (13) showed fair agreement. However, \( W_O^\text{Experimental} \) is little larger than \( W_O^\text{Theoretical} \). It could be considered that this difference between \( W_O \) values caused due to over estimation of iron carburization value when \( W_O^\text{Experimental} \) was calculated, because it has the possibility that wetted area on surface of iron sample by molten Fe–C particle was greatly estimated too much. The difference of \( k^{2nd} \) values among this work and literatures could be explained, in the same way.

These estimations indicated that assumptions to estimate \( W_O \) were considerable. In other words, carbon mass transfer rate through slag phase was very fast, and so carbon amounts in Fe–C particles formed balanced with those of diffused carbon in iron rod.

5. Conclusions

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