Effects of Slag Content and Composition on the Reducibility of Iron Oxide Including CaO–SiO$_2$–Fe$_x$O Slag

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In the sintering with lower slag ratio, the melt quantity decreases, and the agglomeration do not progress sufficiently. It is necessary to secure the melt quantity by silicate melt mainly composed of Fe$_x$O–SiO$_2$ system and to control ideally the composition and the generation place of the melt. In the present study, iron ore sinter is simulated by an iron oxide pellet added with (CaO–)SiO$_2$–Fe$_x$O slag particles, and the effects of the slag content, the composition, the holding time at 1 573 K and the slag particle size on the hydrogen reduction behavior of the iron oxide pellet including (CaO–)SiO$_2$–Fe$_x$O slag particles have been investigated at 1 173 K. In the initial stage of reduction, the fractional reduction is higher when the slag content is higher. With proceeding the reduction, the fractional reduction of the sample with the higher slag content becomes lower than the sample with the lower slag content. The reduction rate decreases with the increase of the slag content. The ratio of the pore area with over 100 $\mu$m pore size increases with the increase of slag content. On the other hand, the final fractional reduction decreases with the increase of the slag content. From this fact, it is considered that the increase of macro pore over 100 $\mu$m does not affect on the improvement of reducibility, and the microporosity under 100 $\mu$m may become an influential factor. On the slag sintering, the final fractional reduction of the pellet including Fe$_x$O–SiO$_2$ slag is better. This is because that the silicate slag is difficult to permeate nor block up the pore.

KEY WORDS: ironmaking; reducibility; iron oxide; pore; permeation; iron ore sinter.

1. Introduction

From the recent raw material circumstances of iron and steel industries in Japan, the use of iron ores with high crystal water from Australia increases year by year. There is a trend to increase an import amount of Marra Mamba ore with higher powdered ore rate, instead of pisolite ore with higher Al$_2$O$_3$ and SiO$_2$ contents, in particular. When the use of the limonite increases, the ratio of iron ore sinter increases, since the yield of the lump ore is worse and the strength of iron ore sinter drastically lower for the decrease in the microporosity, although it is effective in maintaining the yield and the strength of iron ore sinter.$^4$ On the other hand, when the use of iron ores with high crystal water is increased, the improvement in the reducibility can be expected from the increase in the microporosity.

In the present study, iron ore sinter is simulated by an iron oxide pellet added with (CaO–)SiO$_2$–Fe$_x$O slag particles, and the experiment on the reducibility is carried out. Namely, the effects of the slag content and composition on the reducibility of iron oxide including (CaO–)SiO$_2$–Fe$_x$O slag have been investigated.

2. Experimental

From the distributions of temperature and chemical composition in sinter layer$^5$ and the Fe–O phase diagram,$^6$ the experimental conditions were determined as follows: $P_{O_2}$ (oxygen partial pressure) = 1.8×10$^{-6}$ atm and H.T. (holding temperature of molten slag at high temperature) = 1 573 K. The compositions of slag included in the iron oxide pellet are shown in Table 1. The compositions in Table 1 are also plotted in Fig. 1, which shows the reducibility of CaO–SiO$_2$–Fe$_x$O slag$^7$ summarized on the isothermal section of CaO–SiO$_2$–Fe$_x$O diagram$^8$ at 1 573 K and $P_{O_2}$=1.8×10$^{-6}$ atm. The slag compositions are on the liquidus at 1 573 K. The slag samples were made as follows: The reagent grade
The chemical compositions of (CaO–)SiO₂–Fe₃O pellet included in the Fe₂O₃ pellet.

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₃O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20.5</td>
<td>18.3</td>
<td>61.2</td>
</tr>
<tr>
<td>B</td>
<td>11.2</td>
<td>6.1</td>
<td>82.7</td>
</tr>
<tr>
<td>C</td>
<td>23.4</td>
<td>7.6</td>
<td>76.6</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. The Surface and Cross-sectional Observation of the Sample

The surfaces of the samples including Slag B after reduction are shown in Fig. 4. The cracks are found in the samples, and the amount of crack tends to increase with increasing the slag content, the holding time at 1 573 K and the slag particle size. Approximately, similar cracks were found in the samples including Slag A or C. On the slag particle size, the larger cracks are found when dₛ (diameter of slag) = 1.0 to 1.7 mm in comparison to dₛ = 0.3 to 1.0 mm. The cause is considered that the macro pores with larger pore size form by the penetration of molten slag when the diameter of slag is larger. From these facts, it is considered that the stress in the circumference of the slag particle occurred by the contraction of sample in the cooling and the formation of macro pore by the penetration of molten slag become the very influential factors on
the generation of crack. The cross-sectional view of the sample including 5 mass% of Slag A, B or C after reduction by a laser microscope is shown in Fig. 5 under the conditions of $d_s = 0.3$ to 1.0 mm and $t_{1573}$ (holding time at 1 573 K) = 60 min. The white parts, the black parts, and the gray parts in the pictures show the reduced iron, the pore and the slag, respectively. In Slag A and B, it is observed that the molten slag permeates the pore in the circumference, but the slag does not block up the whole of the pore. Moreover, it is found that the place where the slag originally exists becomes newly a macroscopic pore after the penetration of the molten slag. On the other hand, in slag C, it is observed that the molten slag little permeates the pore in the circumference.

3.2. The Reducibility of Oxide Pellet Including CaO–SiO$_2$–Fe$_3$O$_5$ Slag Particles

The reduction behavior of the oxide pellet samples including Slag A, B or C is shown in Figs. 6 to 8, respectively, under the conditions of $d_s = 0.3$ to 1.0 mm and $t_{1573} = 10$ or 60 min. Through Figs. 6 to 8, it is found that the reducibility tends to become worse as the slag content increases or the holding time at 1 573 K is longer. It is considered the deterioration of the reducibility is caused by the penetration of the molten slag in the pore. When the pore is blocked, the diffusion of gas is prevented, and the specific surface area for the reduction reaction decreases. Accordingly, the reducibility deteriorates when the slag content is more increased or the holding time is longer because the molten slag can sufficiently permeate the pore. In Fig. 9, the influence of slag content on the fractional reductions at 5 and 20 min is shown under the conditions of $d_s = 0.3$ to 1.0 mm and $t_{1573} = 60$ min. In the initial stage of reduction, the fractional reduction is found to be better when the slag content is higher. This is because many cracks are found in the sample when the slag content is higher. It is observed that these cracks already occur in the stage which cools from 1 573 K (slag penetration temperature) to 1 173 K (reduction temperature). With proceeding the reduction, the fractional reduction of the sample with the higher slag content becomes lower than the sample with the lower slag content. The relationship between the slag content and the final fractional reduction is shown in Fig. 10. The final fractional reduction is defined to be that when the change of the fractional reduction is not found over 3 min in the present study. The final fractional reduction decreases with the increase of slag content and with the decrease of the slag particle size. This is because the diffusion of the reducing gas is prevented and the specific surface area for the reduction reaction decreases by the molten slag, which permeates and blocks up the pore. As the result, with the increase of slag content, the final fractional reduction decreases in spite of the existence of large number of cracks. The relationship between the ratio of the pore area and the slag content on the pore-size distribution is shown in Fig. 11 for the sample including Slag B under the conditions of $d_s = 0.3$ to 1.0 mm and $t_{1573} = 60$ min. The ratio of pore area and the pore-size were investigated by image processing from the cross-sectional observation of the sample. Approximately, a similar relationship was found in the sample including Slag A or C. The ratio of the pore area with over 100 $\mu$m pore size increases with the increase of slag content. On the other hand, the final fractional reduction decreases with the increase of the slag content. From this fact, it is considered that the increase of macro pore over 100 $\mu$m does not affect on the improvement of reducibility, and the microporosity under 100 $\mu$m may become an influential factor. On the slag composition, the final fractional reduction of the pellet including Slag C is better. This is because that Slag C is rather difficult to permeate in comparison to Slag A and B from the viewpoint of viscosity, although the reducibility of Slag C itself is worse than that of slag A.
or B.\textsuperscript{7,13,14} On the other hand, both slag A and B easily permeate the pore, and the reducibility becomes worse. When the reducibility of the pellet including Slag A and B is compared, the reducibility of the pellet including Slag B is a little better than that including Slag A, which is in accordance with the reducibility of slag A and B themselves.\textsuperscript{7,13,14}
4. Conclusions

The effects of the slag content, the composition, the holding time at 1573 K and the slag particle size on the hydrogen reduction behavior of the iron oxide pellet including (CaO–)SiO$_2$–Fe$_3$O$_4$ slag particles have been investigated at 1173 K. The following conclusions are obtained:

(1) In the initial stage of reduction, the fractional reduction is better as the slag content is higher. This is because many cracks exist in the sample when the slag content is higher. With proceeding the reduction, the fractional reduction of the sample with the higher slag content becomes lower than the sample with the lower slag content. The reduction rate decreases with the increase of the slag content.

(2) The ratio of the pore area with over 100 $\mu$m pore size increases with the increase of slag content. On the other hand, the final fractional reduction decreases with the increase of the slag content. From this fact, it is considered that the increase of macro pore over 100 $\mu$m does not affect on the improvement of reducibility, and the microporosity under 100 $\mu$m may become an influential factor.

(3) On the slag composition, the final fractional reduction of the pellet including Fe$_3$O$_4$–SiO$_2$ slag is better. This is because the silicate slag is difficult to permeate nor block up the pore.

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