Effect of Mineral Composition and Pore Structure on Reducibility of Composite Iron Ore Sinter

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Recently, a new agglomeration concept called MEBIOS (Mosaic EmBedding Iron Ore Sintering) process is proposed. In the process, to utilize the characteristic of the goethite effectively is aimed on the premise of the major use of the goethite ores as a raw material and the low slag content. This is the sintering technology in proportion to the property of the goethite, in which a composite iron ore sinter is formed by arranging the dense pre-granulated pellets properly in the porous induction bed. The use of pisolite and Marra Mamba ores are considered as main components of the porous induction bed and the dense pre-granulated pellets, respectively. In the present study, the composite iron ore sinter, which is composed of the dense pre-granulated pellet and the porous induction bed, is produced experimentally. Only a dense pre-granulated pellet is placed at the center of the porous induction bed. In order to examine what kind of mineral composition and pore structure are desirable from the viewpoint of the reducibility of the composite iron ore sinter, the hydrogen reduction experiments are conducted at 1 173 K. The reduction rate of the composite iron ore sinter, which is composed of the dense pre-granulated pellet and the porous induction bed, is larger than the uniform pellet, of which the whole composition is identical. Moreover, the reduction becomes faster by considering the compositional design between the porous induction bed and the dense pre-granulated pellet. It is desirable to contain CaO and SiO₂ more in the porous induction bed than in the dense pre-granulated pellet. From the measurement of the pore-size distribution by the mercury penetration style porosimeter, the reduction is faster for the samples, of which the accumulation pore volume over 10 μm is larger.

From the components analysis of the mineral phase, the increase of calcium ferrite in the porous induction bed contributes to the improvement in the reducibility of the composite iron ore sinter.

KEY WORDS: agglomeration; reduction; iron ore.

1. Introduction

From the recent raw materials circumstances, the proportion of goethite (pisolite and Marra Mamba) increases to the iron ores imported in Japan. The goethite ores thermally decompose into hematite and water vapor by heating and become porous property. In case they are used for the raw materials of iron ore sinter as fine ores, the thermal decomposition and the porous nature of the raw materials lead to reduced sintering productivity and lower sinter strength. In the process, to utilize the characteristic of the goethite effectively is aimed on the premise of the major use of the goethite ores as a raw material and the low slag content. This is the sintering technology in proportion to the property of the goethite, in which a composite iron ore sinter is formed by arranging the dense pre-granulated pellets properly in the porous induction bed. The use of pisolite and Marra Mamba ores are considered as main components of the porous induction bed and the dense pre-granulated pellets, respectively. On the other hand, it is desirable to lower the contents of slag components in the iron ore sinter as fine ores, the thermal decomposition and the porous nature of the raw materials lead to reduced sintering productivity and lower sinter strength. On the other hand, it is desirable to lower the contents of slag components in the iron ore sinter from the lower demand of blast furnace slag and the security of the permeability in high PCI operation of blast furnace. From the above fact, the development of an agglomerating technology, which the goethite iron ores are efficiently used and the reduction of the slag amount is achieved, is indispensable to overcome the international competition and to aim at the minimization of the environmental loading in the steel industries all over the world. In order to realize the above purpose, a new agglomeration concept called MEBIOS (Mosaic EmBedding Iron Ore Sintering) process is proposed. In the process, to utilize the characteristic of the goethite effectively is aimed on the premise of the major use of the goethite ores as a raw material and the low slag content. This is the sintering technology in proportion to the property of the goethite, in which a composite iron ore sinter is formed by arranging the dense pre-granulated pellets properly in the porous induction bed. The use of pisolite and Marra Mamba ores are considered as main components of the porous induction bed and the dense pre-granulated pellets, respectively. The characteristic features are the grain size design by the void network structure and the fast sintering by the increase of the flow rate around the dense pre-granulated pellets. In the present study, the composite iron ore sinter, which is composed of a dense pre-granulated pellet and porous induction bed, is produced experimentally. The hydrogen reduction behavior of the samples is investigated at 1 173 K. The cross-sectional observation of the sample, the analysis of the components of the mineral phases, the measurement of the pore size distribution are conducted. The purpose of the present study is to examine what kind of mineral composition and pore structure are desirable from the viewpoint of the reducibility of the composite iron ore sinter.
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2. Experimental

2.1. Sample Preparation

Calcium oxide was made by calcining a reagent grade of CaCO$_3$ at 1273 K. The samples were prepared by mixing the CaO, a reagent grade of Fe$_2$O$_3$ and a reagent grade of SiO$_2$ at the fixed proportions for the dense pre-granulated pellet and the porous induction bed, respectively. The schematic cross section of the sample prepared in the present study, which simulated the composite iron ore sinter, is shown in Fig. 1. The pellet which is located at the central part of the sample simulates the dense pre-granulated pellet, and the layer arranged around the dense pre-granulated pellet corresponds to the porous induction bed. Only a dense pre-granulated pellet was placed at the center of the porous induction bed on the samples prepared in the present study. The Fe$_2$O$_3$, CaO and SiO$_2$ compositions of samples prepared in the present study are shown in Table 1. The dense pre-granulated pellet set the contents of CaO and SiO$_2$ lower in comparison with the porous induction bed in order to avoid the rapid melting by increasing temperature and to progress the soft sintering. The CaO/SiO$_2$ ratios (C/S) of the dense pre-granulated pellet and of the whole sample were fixed C/S = 1 and 2, respectively. The mass ratio of the dense pre-granulated pellet and the porous induction bed were fixed 2:3. Moreover, for samples A and B, the CaO/SiO$_2$ ratio of the porous induction bed was set C/S = 3. For samples B and C, the whole composition of the sample was set Fe$_2$O$_3$–9.6mass%CaO–4.8mass%SiO$_2$ with reference to the product of iron ore sinter. The samples PA and PB are the uniform pellets made by a hand-rolling without dividing into the dense pre-granulated pellet and the porous induction bed. The compositions of PA and PB are the same as the whole compositions of samples A and B (or C), respectively. The samples A’ and B’ are the composite iron ore sinter, of which both compositions of the dense pre-granulated pellet and the porous induction bed are identical. The compositions of the samples A’ and B’ are the same as the whole compositions of samples A and B, respectively.

The dense pre-granulated pellet was prepared as follows: The green pellet was made of the mixed powder of Fe$_2$O$_3$, CaO and SiO$_2$ by adding the ethanol of the proper quantity and by the hand-rolling, and it was dried over 1 h at 378 K in a drying apparatus. The diameter of the pellet is about 10 mm. Then, the pellet was put in an alumina crucible (O.D. 25 mm, I.D. 20 mm, Height 35 mm), as shown in Fig. 1, and was sintered by being held for 1.5 h in an electric resistance furnace in air at temperatures ranging from 1503 to 1573 K. The heat pattern of the synthesizing is shown in Fig. 2. The mass of the whole sample is about 6.5 g.

2.2. Experimental Procedure

The hydrogen reduction experiments were conducted using an electric resistance furnace with a thermobalance. After the sample weight was measured by an electric balance, it was hung in a platinum chain. Then, it was heated to 1173 K in N$_2$ (3.3×10$^{-6}$ m$^3$/s (s.t.p.)) atmosphere at the heating rate of about 10 K/min. After reaching 1173 K, the N$_2$ gas was switched to the H$_2$ gas at a flow rate of 1.7×10$^{-5}$ m$^3$/s (s.t.p.), and the reduction experiments was started at the constant temperature of 1173 K. The mass change of the sample by the reduction was measured by using a strain gauge type load converter, and was recorded continuously by using pen-recorder. The experiments were finished when the mass change of the sample became under 0.05 g during 3 min. After the experiments, the ingoing gas was switched to the N$_2$ gas. The sample was cooled by decreasing the furnace temperature.

3. Results and Discussion

3.1. Cross-sectional Observation

The cross-sectional image for each sample sintered at temperatures ranging from 1503 to 1573 K is shown in Fig. 3. The mass ratio of liquid phase in the dense pre-granulated pellet and in the porous induction bed for each sample is calculated from the isothermal section of Fe$_2$O$_3$–CaO–SiO$_2$ ternary diagram at each sintering temperature and is shown in Table 2. From Fig. 3, in each sample of composite iron ore sinter except for those sintered at 1573 K (B2, C2, A’2 and B’2), it is observed that the
The porous induction bed includes the dense pre-granulated pellet located at the central part of the sample, and the boundary can be clearly distinguished. It is considered that, in case of samples B2, C2 and B/H11032, the boundary became indistinct because a large amount of melt forms, as shown in Table 2, and the faster assimilation occurs because of the higher sintered temperature. On the other hand, as to the sample A/H11032, although the amount of melt formation of sample A/H11032 is less than that of sample A, the boundary becomes indistinct. The isothermal section of Fe2O3–CaO–SiO2 ternary system at 1 573 K is shown in Fig. 4. As shown in Fig. 4, there are two lower temperature liquid phase regions, α and β, in Fe2O3–CaO–SiO2 ternary system at 1 573 K is shown in Fig. 4. As shown in Fig. 4, there are two lower temperature liquid phase regions, α and β, in Fe2O3–CaO–SiO2 ternary system. The α region is a silicate melt, of which the primary crystal is 3CaO·2SiO2, and the β region is calcium ferrite (CF) melt, of which the primary crystal is CF. In case of sample A2, the CF melt mainly forms in the porous induction bed, and the silicate melt mainly form in the dense pre-granulated pellet. It is considered that these two melts mix and react with temperature increasing and move toward the uniform composition. However, when the CF melt and the silicate melt physically contact with each other and react at the boundary, the progress of the reaction slows down since the composition of the product material is in the higher-melting point region and the barrier is formed by the crystallization of Fe2O3 at the boundary surface. On the other hand, in case of sample A2, the composition of the porous induction bed is identical to that of the dense pre-granulated pellet, and both of the induction bed and the dense pellet form the CF melt. For this reason, it is considered that the assimilation rate of sample A2 is faster than that of sample A, and the boundary became unclear.

### 3.2 Hydrogen Reduction Experiments

The results of the hydrogen reduction experiments for the samples sintered at 1 523 K (A1, B1, C1, A’1, B’1, PA and PB) are shown in Fig. 5. Similarly, the results of the hydrogen reduction experiments for the samples sintered at 1 573 K (A2, B2, C2, A’2 and B’2) are shown in Fig. 6. From Figs. 5 and 6, on the samples which simulated the composite iron ore sinter, the reduction rate of sample A, of which the total slag content is lower, is the largest, and the reduction rate is larger in the order of samples A/H11022, B/H11022, C. As to the samples sintered at 1 523 K, the reduction rates of all the samples which simulated the composite iron ore sinter are larger than those of the uniform pellets. When the reduction rate is compared among the samples of which the whole composition is identical, the reduction is faster in the order of A1>A’1>PA and B1>C1>B’1>PB in case of the samples sintered at 1 523 K. In case of samples sintered
at 1 573 K, the reduction is faster in the order of \( A_2 > A'2 \) and \( B_2 > C_2 \equiv B'2 \). From this fact, it is found that it is useful to possess the mineral phase and pore structure of the composite iron ore sinter with the porous induction bed for the improvement of the reducibility of the samples. The reducibility of the samples improves further by considering the compositional design between the porous induction bed and the dense pre-granulated pellet. That is to say, it is desirable to contain CaO and SiO\(_2\) more in the porous induction bed than in the dense pre-granulated pellet.

Subsequently, the reduction behavior of the samples sintered under various conditions was compared for every sample with identical composition. The results of the hydrogen reduction experiments for Series A (samples A1, A2, A'1, A'2 and PA) are shown in Fig. 7. Similarly, the results of the hydrogen reduction experiments for Series B (sample B1, B2, B'1, B'2 and PB) and Series C (sample C1, C2, C3, B'1, B'2 and PB) are shown in Figs. 8 and 9, respectively. From Figs. 7 and 8, on Series A and B, the reduction rate is generally larger in the order of \( A1 > A'1 > A2 > A'2 > PA \) and \( B1 > B'1 > B2 > B'2 > PB \). It is found that the reduction rates of Samples A1 and B1, which are sintered at 1 523 K, are faster than those of the other samples, in particular. On the other hand, from Fig. 9, on Series C, the reduction is faster in the order of \( C3 > C1 \equiv B'1 > B'2 > C2 > PB \). In particular, the reduction of Sample C3, which is sintered at 1 503 K, is faster than the other samples.

3.3. Measurement of Pore-size Distribution

The pore volume and the pore size distribution were measured using a mercury penetration style porosimeter. The pore size distribution for each sample is shown in Fig. 10. It is found that the pore volume with over 10 \( \mu \)m pore size tends to increase for the samples of which the reduction rate is larger, for example, samples A1 and B1 sintered at 1 523 K and sample C3 sintered at 1 503 K. The fractional reduction after 20 min from the beginning of the reduction experiment is in the range of 0.7 to 0.95 for each sample in the present study. In the stage, the reduction of the dense pre-granulated pellet proceeds for all samples, and the difference of the reduction rate for each composite iron ore sinter is appeared. It is considered suitable to compare the reducibility for each sample. For this reason, we introduce the fractional reduction after 20 min from the beginning of the reduction experiment as an index of the reducibility for each sample in order to investigate the relation with the reducibility. The index, \( F_{20\text{h} \rightarrow Fe} \), is plotted against (a) total pore volume and (b) accumulated pore volume with pore size over 10 \( \mu \)m for each sample. The relationship is shown in Fig. 11. It is found from Fig. 11 that the correlation of the fractional reduction after 20 min with accumulated pore volume with pore size over 10 \( \mu \)m is stronger than that with total pore volume. Moreover, when
we consider the reducibility of the uniform pellets, which are shown by a circle seal in Fig. 11(b), it is found that their reducibility is worse although they have comparatively much pore volume.

### 3.4. Analysis of the Components of the Mineral Phase

The components of the mineral phase were analyzed from the microscopic photograph of the sample cross section (magnification: ×200), using an image analysis appliance. In the analysis, the sample was divided into the dense pre-granulated pellet and the porous induction bed. The microscopic photograph of the cross section for each sample is shown in Fig. 12. The composition of the mineral phases of the samples sintered in the present study is shown in Table 3. All samples are composed of hematite (Fe₂O₃), CF and ‘slag’, where ‘slag’ is not ‘silicate slag’ in general but the generic name of ‘amorphous substance’.

From Fig. 12, it is found that the mineral phase of the porous induction bed is much different from those of the dense pre-granulated pellet. Moreover, it is found the mineral phase also changes by the difference of the sintering temperature, even if the composition of samples is identical. A large part of the dense pre-granulated pellet of the sample sintered at 1 523 K is composed of hematite. The existence of CF is also partly confirmed around the hematite. It is found the crystallization of hematite and slag from the melt. On the other hand, the porous induction bed is composed of more CF and the hematite has also mainly remained, in comparison to the dense pre-granulated pellet. The dense pre-granulated pellets of the samples sintered at 1 573 K are largely composed of hematite. The existence of CF is partly found around the hematite. It is proven that a large amount of melt formed during the sintering from the texture mainly crystallized from the melt. The crystallization of hematite, slag and CF is confirmed from the melt. On the other hand, the porous induction bed is composed of more CF and less hematite in comparison to the dense pre-granulated pellet. In addition, many voids are found.

From Table 3, the CF content of dense pre-granulated pellet is smaller than that of porous induction bed in all the samples. This is because the composition of the dense pre-
granulated pellet is set to be a lower basicity of CaO/SiO$_2$. In case of the samples sintered at 1573 K, the difference of mineral phases composition between the dense pre-granulated pellet and the porous induction bed becomes smaller by the progress of the assimilation, which is caused by the larger amount of melt formation. When the composition of the samples is identical, the CF content decreases as the sintering temperature increasing. This is because the CF decomposes as increasing temperature. The decomposition of CF is also observed in the microscopic photograph for the samples sintered at 1573 K (A2, B2 and C2), which is shown in Fig. 12.

The reduction rate is larger for the samples A1 and A2 sintered at 1523 K and the sample C3 sintered at 1503 K. The CF content of the porous induction bed of these samples is larger. The clear difference is not observed in the composition of mineral phases of the dense pre-granulated pellet. Accordingly, in order to investigate what kind of mineral composition and pore structure are desirable from the viewpoint of the reducibility of the composite iron ore sinter, the fractional reduction after 20 min, \( F_{20}^{b-Fe} \), is plotted against the content of CF in the porous induction bed in Fig. 13. From Fig. 13, it is found that the increase of the CF content in the porous induction bed contributes to the improvement of the reducibility of the composite iron ore sinter.

### 4. Conclusions

The composite iron ore sinter, which is composed of the dense pre-granulated pellet and the porous induction bed, is produced experimentally. Only a dense pre-granulated pellet is placed at the center of the porous induction bed. In order to examine what kind of mineral composition and pore structure are desirable from the viewpoint of the reducibility of the composite iron ore sinter, the hydrogen reduction experiments are conducted at 1173 K. The cross-sectional observation of the sample, the analysis of the

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**Table 3.** The composition of mineral phases of samples sintered in the present study.

<table>
<thead>
<tr>
<th>Sintering temperature (K)</th>
<th>Composition of dense pellet</th>
<th>Composition of induction bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>CF</td>
</tr>
<tr>
<td>A1</td>
<td>1523</td>
<td>81.2</td>
</tr>
<tr>
<td>A2</td>
<td>1573</td>
<td>76.2</td>
</tr>
<tr>
<td>B1</td>
<td>1523</td>
<td>73.9</td>
</tr>
<tr>
<td>B2</td>
<td>1573</td>
<td>76.4</td>
</tr>
<tr>
<td>C1</td>
<td>1523</td>
<td>79.4</td>
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<tr>
<td>C2</td>
<td>1573</td>
<td>76.7</td>
</tr>
<tr>
<td>C3</td>
<td>1503</td>
<td>77.6</td>
</tr>
</tbody>
</table>

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**Fig. 12.** The cross sectional pictures of samples by optical microscope (diameter: ×200).

**Fig. 13.** Relationship between fractional reduction after 20 min, \( F_{20}^{b-Fe} \), and content of CF in porous induction bed.
components of mineral phases and the measurement of the pore size distribution are conducted. The conclusions are as follows:

1) The reduction rate of the composite iron ore sinter, which is composed of the dense pre-granulated pellet and the porous induction bed, is larger than the uniform pellet, of which the whole composition is identical. Moreover, the reduction becomes faster by considering the compositional design between the porous induction bed and the dense pre-granulated pellet. It is desirable to contain CaO and SiO₂ more in the porous induction bed than in the dense pre-granulated pellet.

2) From the measurement of the pore-size distribution by the mercury penetration style porosimeter, the reduction is faster for the samples, of which the accumulation pore volume over 10 μm is larger.

3) From the components analysis of the mineral phase, the increase of CF in the porous induction bed contributes to the improvement in the reducibility of the composite iron ore sinter.

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