1. Introduction

Improving the qualities of sintered ores is essential for lowering the coke rates of blast furnaces. Particularly, high-temperature sinter properties above 1 000°C such as shrinkage, softening-melting, dripping are important because they are directly associated with the permeability at the cohesive zone. Many reports highlighted the importance of reducibility as one of the factors determining high-temperature properties. In particular, high-temperature reducibility is important to gain a higher indirect reduction ratio in the furnace because it is accompanied by a structural change at the initial stage due to melt formation during reduction. Influences of chemical compositions of sintered ores on the high-temperature reducibility were investigated. Manufacturing sintered ores with less Al₂O₃, SiO₂, or FeO content with superior high-temperature properties including reducibility has been explored in many plants. However, considering the future trend of natural resources, the depletion of high-grade ore deposits will result in poor chemical compositions of sintered ores and lowering their quality. Therefore, other new methods to enhance high-temperature reducibility apart from controlling the chemical composition of sintered ores, such as controlling heating conditions or effective use of ore characteristics, is necessary. As the strength is another essential property of sintered ores, achieving high reducibility through changing pore structure appears to be a potentially fruitful methodology.

Though reducibility depends both on mineralogy and pores, many investigations reported the importance of pores on reducibility. However, there is disagreement concerning the suitable size of pores. One of the reasons for the disagreement is likely the different behavior of reduction by temperature mentioned above.

One of the authors reported a relationship between reduction degree at 1 000°C and < 15 μm pore volume in sintered ores and pellets made in a laboratory. Similarly, many reports have shown a significant influence of < 10 μm size pores in high-temperature reduction. Therefore, in this study we focused on pores of < 10 μm size and estimated their influence on high-temperature reducibility and permeability at the cohesive zone through improving the softening-melting behavior, resulting in stable operation of the blast furnace at low coke rates. As the depletion of high-grade ore deposits limits control of the chemical composition of sintered ores, small pores less than 10 μm in diameter in the microstructure of sintered ores were focused on to increase the high-temperature reducibility. Sintering conditions for increasing small pores in constant raw material conditions were examined. Furthermore, considering the heterogeneous structure of the sintered ores, reduction behaviors of relict ores and assimilated structures were estimated individually. The contribution of each structure to small pore formation during sintering and their influence on high-temperature reducibility was discussed.

Sintering with a sharp temperature profile led to many small pores in the sintered ores by increasing the amount of relict ores with small pores even in constant raw material conditions. Both, for relict ores and assimilated structures, low-temperature reducibility was determined by the total porosity including large pores, whereas the Al₂O₃ content in gangue minerals, the < 10 μm pore volume fraction, and the amount of gangue mineral influenced high-temperature reducibility. Assimilated structures involving granular hematite contained many small pores, compared with other types of assimilated structures. Results of plant trials for two different methods to increase small pores, in relict ores and in assimilated structures, revealed their potential for improving the high-temperature reducibility of sintered ores without controlling the chemical composition.

KEY WORDS: reduction; softening-melting; melt; pore; gangue minerals; microstructure; assimilation; agglomeration; iron ore.
investigated measures to increase their abundance in sinter microstructures. Not only small pores, but also total porosity including large pores was estimated as well to carefully separate the influence of pore volume and size.

A few cases of improvement in the high-temperature reducibility by increasing small pores have been reported. Hosotani et al.\textsuperscript{10} found that the reduction degree above $1000°C$ was increased due to an increase in pores of $1$ to $30 \mu m$ in size by simultaneously truncating fine particles of limestone and coke breeze. Oyama et al.\textsuperscript{11} also reported an enhancement in reducibility due to an increase in relic ores with pores of size less than $1 \mu m$ size in sinter products by gaseous fuel injection into the sintering strand. However, fundamental information on the formation of such small pores and its relation to the sinter mineralogy is limited.

The origin of small pores less than $10 \mu m$ is classified as relic ores and assimilated structures. However, their quantitative contribution ratio is un-known. Therefore, in this study, to manufacture the sintered ores having superior high-temperature reducibility, pot-sintering tests with various heating conditions and heating tests using model samples were performed and the formation process of small pores less than $10 \mu m$ was discussed. In addition, plant trials were conducted to enhance high-temperature reducibility by increasing small pores less than $10 \mu m$.

2. Experimental Methods

2.1. Pot Tests and Estimation of Pores

Pot tests were conducted using a pot with a $300 \mathrm{~mm}$ of inner diameter. Water was added during granulation and the blending ratio of burnt lime was varied under constant ore blending conditions to focus on the influence of the temperature profile during sintering (sintering time and maximum temperature) on the small pore formation.

Table 1 showed types\textsuperscript{12} and chemical compositions of ores used in this study. Ores A to D were Australian, Ores E and F were Brazilian, and Ore G was Indian. Ores C (29 wt% in new feed), Ore D (19 wt%), Ore E (8 wt%), Ore G (8 wt%) and Ore H (pellet feed, 16 wt%) were used in the pot tests. Raw materials (70 kg) were mixed for 1 min and subsequently granulated by hand by adding limestone ( $<0.125 \text{mm}$) were mixed to achieve a $\text{CaO/Ore}$ ratio of 0.1 and subsequently granulated by hand by adding water in a small petri dish. Granulated ores were heated at 1275$°C$ then roughly crushed to form 3–5 mm particles. Granulated particles were charged into the pot to attain 600 mm bed height, then ignited for 1.5 min and subsequently sintered at a constant suction pressure of 14.7 kPa.

Bed temperatures were measured at three different heights (450 mm, 300 mm, 100 mm above grate) and estimated as average values. Yield was estimated as the amount of the sinter product above 5 mm in size after dropping sinter cake five times from 2 m height.

Pore volumes of $<10 \mu m$ were measured by mercury intrusion porosimetry using sintered particles of 2 to 3 mm after roughly crushing and sieving the sinter product. Total porosity was estimated as PAC porosity,\textsuperscript{7} including closed pores and large open pores and surface concavities.

2.2. Heating Tests of Model Samples

Model samples were used to clarify the influences on reducibility of relic ores and assimilated structures individually.

Regarding relic ores, preliminarily washed particles (3–5 mm) of each ore shown in Table 1 were heated along the plant heating condition with a maximum temperature of 1300$°C$. For the assimilated structure, a model sample simulating sintered ores comprising relic ores and assimilated structures was made. Washed ore particles (3–5 mm) and limestone ($<0.125 \text{mm}$) were mixed to achieve a $\text{CaO/Ore}$ ratio of 0.1 and subsequently granulated by hand by adding water in a small petri dish. Granulated ores were heated at 1275$°C$ then roughly crushed to form 3–5 mm particles.

Pore volumes of $<10 \mu m$ before and after reduction were measured. The total porosity of the relic ores was estimated as $<400 \mu m$ pore volume by mercury intrusion porosimetry. The total porosity of the assimilated ores was estimated by the water method (JIS K2151). The Area% values of relic ores and assimilated structures were obtained for the area of each phase excluding large pores and voids measured by image analysis. The volume% values of each phase were approximately treated as the area%. Here, identification of relic ores and assimilated structures was made through microstructural observation of samples by referring to the preliminary analysis. For the preliminary work, the relationship between microstructural characteristics and CaO distribution (by SEM-EDS) was analyzed for each ore.

2.3. Reducibility

A small-scale reduction test apparatus\textsuperscript{3} was used to measure reducibility of samples in small quantities (Table 2). Two measurement conditions were applied, a low-constant temperature reduction test (900$°C$, Test 1) and a high-elevation temperature reduction test (1000 to 1300$°C$, Test 2, 3). In Test 1, raw samples in a graphite crucible were heated to 900$°C$ in $N_2$, then reduced by CO/CO$_2$ gas for 60 min without load. In Test 2, 3, samples were preliminarily reduced at 1000$°C$ by CO/CO$_2$ = 50/50 gas for 3 h to attain 33% reduction degree (wustite) to demonstrate the situation of the thermal reserve zone of blast furnaces. Pre-reduced samples in a graphite crucible were heated at a constant heating rate up to 1300$°C$ with loading. During heating, CO–$N_2$ gas was flowed at the temperature range between 1000$°C$ and 1300$°C$. The reduction degree was estimated by analysis of exhaust gas. Sintered ores in plant tests were evaluated by the large-scale test apparatus for softening-melting test (Test 4).\textsuperscript{13}

The reduction degree at 900$°C$ and 1300$°C$ was evaluated

<table>
<thead>
<tr>
<th>Classification</th>
<th>Type</th>
<th>T.Fe</th>
<th>FeO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore A</td>
<td>Channel iron deposit</td>
<td>High Al$_2$O$_3$</td>
<td>57.50</td>
<td>0.12</td>
<td>4.99</td>
<td>2.47</td>
</tr>
<tr>
<td>Ore B</td>
<td>Low Al$_2$O$_3$</td>
<td>58.56</td>
<td>0.26</td>
<td>5.05</td>
<td>0.95</td>
<td>8.32</td>
</tr>
<tr>
<td>Ore C</td>
<td>MH</td>
<td>63.89</td>
<td>0.14</td>
<td>3.16</td>
<td>1.77</td>
<td>2.76</td>
</tr>
<tr>
<td>Ore D</td>
<td>MH</td>
<td>64.44</td>
<td>0.14</td>
<td>3.90</td>
<td>1.50</td>
<td>1.76</td>
</tr>
<tr>
<td>Ore E</td>
<td>H</td>
<td>66.78</td>
<td>0.22</td>
<td>2.01</td>
<td>0.90</td>
<td>1.06</td>
</tr>
<tr>
<td>Ore F</td>
<td>MH</td>
<td>67.68</td>
<td>0.17</td>
<td>4.44</td>
<td>0.68</td>
<td>1.17</td>
</tr>
<tr>
<td>Ore G</td>
<td>MH</td>
<td>60.18</td>
<td>0.14</td>
<td>2.90</td>
<td>2.51</td>
<td>6.51</td>
</tr>
<tr>
<td>Ore H</td>
<td>IF conc.</td>
<td>67.90</td>
<td>0.13</td>
<td>1.38</td>
<td>0.55</td>
<td>0.49</td>
</tr>
</tbody>
</table>
in the small-scale reduction tests (Test 1 to 3). The reduction degree at 1 200°C was evaluated in the large-scale reduction tests (Test 4) to detect accurately reduction behavior of sintered ores at high-temperatures accompanied with melt formation within large ore layers during the tests. Hereafter, they are denoted as R900, R1300, and R1200, respectively.

3. Results and Discussion

3.1. Influence of Heating Condition on <10 μm Pore Formation

Figure 1 shows changes in sintering time (t), productivity, and Tmax by moisture content and burnt lime rate in pot tests. A and B indicates sinter A and sinter B shown in Fig. 3.

Table 2. Reduction test conditions and evaluation index.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample condition</th>
<th>Reduction condition</th>
<th>Evaluation index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (mm)</td>
<td>Weight (gram)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Test 1</td>
<td>3–5</td>
<td>50</td>
<td>900</td>
</tr>
<tr>
<td>Test 2</td>
<td>3–5</td>
<td>20</td>
<td>1 000 to 1 300</td>
</tr>
<tr>
<td>Test 3</td>
<td>10–15</td>
<td>620–697 (70 mm bed height)</td>
<td>800 to 1 200</td>
</tr>
<tr>
<td>Test 4</td>
<td>10–15</td>
<td>620–697 (70 mm bed height)</td>
<td></td>
</tr>
</tbody>
</table>

Optical microscopic observation of <10 μm pores in the temperature profile with a shorter duration and/or lower heating temperature. Therefore, too low Tmax·t less than 20×10³°C·min resulted in low yield. However, if we focused on data showing high yield above 80 wt%, the less the 40×10³°C·min of Tmax·t, the more the <10 μm pore volume increased. In contrast, the influence of the temperature profile on total porosity was unclear.

Figure 3 shows reduction curves of sinters A and B shown in Figs. 1 and 2 (Test 3). Sinter A with abundant <10 μm pores showed a higher R1300 (66.5%) than that of sinter B (65.1%). In particular, the reduction rate of sinter A was maintained higher at temperatures above 1 200°C. These results coincided with the past investigation showing an increase of R1300 with an increase of <15 μm pore by 2 mm³/g, as a result of forming a sharper temperature profile (decrease in Tmax·t from 42 to 35×10³°C·min) by simultaneously truncating fine particles of limestone and coke breeze. ¹⁰

In this study, only “open” pores measured by mercury intrusion porosimetry were estimated. However, the estimated pore size is effective for high-temperature reduction due to the following reasons: 1) Most of the closed pores in the sinter structure were released by pre-treatment crushing of the sinter product to 2–3 mm particles prior to measurement. 2) The remainder of the closed pores transforms to “open” pores during reduction by the formation of cracks or small pores as described in Subsection 3.2.1.

Optical microscopic observation of <10 μm pores in
sinter A containing much <10 μm pores than other sinters was performed (Fig. 4). Many <10 μm pores were observed in relict ores than in assimilated structures in the sintered ores. Therefore, pores in relict ores were namely focused on. Many <10 μm sized pores were observed in relict Ore D (1 in the figure). Although the dense part of relict Ore G had few pores (2), large cracks and <10 μm pores were observed in the goethite part of relict Ore G (3). Relict Ore E had 5 μm pores, however, the quantity was small (4). In contrast, the goethite part of relict Ore E formed large pores of 50 μm (5). Only a few <10 μm pores were found in assimilated structure (6: coexisting structure of magnetite and columnar SFCA (Silico-Ferrite of Calcium and Aluminum)).

These results implied that increasing the amount of relict ores containing many <10 μm pores by forming a sharp temperature profile increased <10 μm pores in the sinter A. Therefore, the influence of relict ores and assimilated structure in sintered ores on its reduction behavior was individually investigated in the next section.

3.2. Influence of Ore Types on Reducibility

3.2.1. Reducibility of Relict Ores

Table 3 shows a summary of results of reduction tests of model samples. R900 of ores after heat treatment (Test 1) was correlated with total porosity (<400 μm pore volume) (Fig. 5). The influence of <10 μm pores on R900 was negligible. Bristow et al.14 conducted similar experimental work and reported that goethite ores, corresponding to Ore B in this study, had higher R900 due to their small pores less than 250 μm. However, in this study, R900 was simply correlated with total porosity including large pores, similar to other investigations.6,7 In contrast, R1300 of ores after heat treatment (Test 2) was correlated with SiO2 content after dehydration (Fig. 6). SiO2 was dominant grange mineral after dehydration of ores (Table 1). However, Ore G represented higher R1300, mostly due to abundant <400 μm pores in particularly, 10 to 400 μm. The influence of Al2O3 content on R1300 was negligible. In Test 2, samples were preliminarily reduced at 1000°C to attain the wustite phase. A significant change in small pore structure during reduction is well known.35 Hence, pore volumes before reduction, after pre-reduction,
and after reduction at 1 300°C were compared (Table 3). The <10 μm pore volume fraction increased after pre-reduction in every ore mostly due to an increase in small pores concentrated in magnetite phases, crack formation in assimilated structures and shrinkage of iron oxide grains. In contrast, <10 μm pore volume tended to decrease during reduction at 1 300°C. Figure 7 shows a relationship between the <10 μm pore volume after reduction at 1 300°C and SiO2 content after ore dehydration. The greater the ore SiO2 content, the more decrease of the <10 μm pore volume fraction after reduction. In such high SiO2 ores (Ore A, B), coexisting phases of FeO and slag were observed after reduction (Fig. 8). These results implied that the <10 μm pores preferentially occluded during reduction up to 1 300°C. In the FeO–SiO2 system, small pore occlusion and retardation of
reduction due to an increase in melt with increasing SiO₂ content was reported.¹⁷) Maeda et al.¹⁸) reported that ores containing finely distributed SiO₂ preferentially formed 2FeO·SiO₂ leading to low reducibly at high temperatures. These findings coincided with the results in this study.

Ore D had larger < 10 μm pore volume than Ore A and Ore B as it contained less SiO₂ content after dehydration, in spite of its smaller < 10 μm pore volume after pre-reduction. The reason of the smaller <10 μm pore volume after pre-reduction in Ore D seems to relate with the mineralogical change during pre-reduction, however, further study is required to clarify the influence of ore type on the pore structural change during pre-reduction.

3.2.2. Reducibility of Samples after Assimilation

R900 values of every sample after assimilation were higher than those of relict ores (Table 3). Bristow et al.'s¹⁹) reported similar results and implied that the reason for the enhancement of reducibility by assimilation was the formation of small pores less than 1 μm during reduction of SFCA. In this study, a correlation between R900 and total porosity was found (Fig. 9), implying that the reason for the enhancement in reducibility by assimilation was the increase in large pores with diameters up to a few mm.

R1300 after assimilation was higher than those of relict ores for most ores (Table 3). This implies that the influence of assimilated structure on the high-temperature reducibility is large in addition to the influence of relict ores. R1300 was determined namely by Al₂O₃ content in gangue (Fig. 10). The influences of the <10 μm pore volume and gangue quantity (CaO+SiO₂+Al₂O₃) were also observed in Ore E and Ore B, respectively. The negative influence of Al₂O₃ in sintered ores on high-temperature reducibility due to an increase in melt volume during reduction was reported by many investigations.³,⁴) For the reason of the influence, eutectic melting at 1 250°C in 2CaO·SiO₂–2CaO·Al₂O₃·SiO₂–FeO system and increasing melt volume at lower temperature due to a retardation of dissolution of olivine melts into 2CaO·SiO₂ and recrystallization are proposed.⁴)

3.2.3. <10 μm Pore Volume in Assimilated Structure

Figure 11 shows schematic diagram of macro structure of sintered ores. Samples after assimilation contain relict ores and assimilated structures. Therefore, for the <10 μm pore volume of samples after assimilation (P₉) was divided into <10 μm pore volume of relict ores (P₈) and <10 μm pore volume of assimilated structures (Pₐ) by executing the following Eqs. (1) to (4).

\[
V_R + V_A = 100 \quad \text{(1)}
\]

\[
\rho_A = \frac{100 \cdot \rho_R - V_R \cdot \rho_K}{V_A} \quad \text{(2)}
\]

\[
P_K = p_K \cdot \frac{V_R \cdot \rho_K}{100 \cdot \rho_R} \quad \text{(3)}
\]

\[
P_A = P_T - P_K \quad \text{(4)}
\]

Fig. 7. Relationship between <10 μm pore volume after reduction and SiO₂ content after dehydration of ore. A to G indicates the ore type shown in Table 1.

Fig. 8. Microstructure images of ores after reduction at 1 300°C. M: Metal, P: Pore, W: Wustite, S: Slag.
where V (%) is volume%, ρ (cm³/g) is apparent density, ρ (mm³/g) is <10 μm pore volume per 1 gram of the assimilated structure and suffixes R, A, and T are the relict ores, assimilated structures, and whole sample after assimilation, respectively.

Figure 12 shows the <10 μm pore volume of the assimilated part and relict ores in samples after assimilation test. Numbers denote types of assimilated structure, 1: Granular hematite + glassy silicate and granular hematite + SFCA, 2: Granular hematite + SFCA, 3: Granular hematite + SFCA and single phase of SFCA, 4: Single phase of SFCA.

3.2.4. Increasing Measures of <10 μm Pore Volume in Plants

Two measures to increase <10 μm pore volume in sintered ores were derived from results of the above experimental works, one increasing relict ores containing significant <10 μm pore volume (Ore D in Fig. 1 (1) and Ores C, D, F, and G in Table 3) and the other increasing assimilated structure containing significant <10 μm pore volume (Ores A, B and G in Fig. 12). Therefore, two series of plant test were conducted. Table 4 showed test conditions and results from plant tests.
A plant test to increase relict ores containing <10 μm pore volume in sintered ores by increasing the amount of certain types of ores in the selective granulation line was performed at the Oita No.2 sintering plant. Ore D was chosen, as it had significant <10 μm pore volume after heat treatment. In addition, fine particles of Ore D with high Al₂O₃ content were expected to prevent assimilation of Ore D with melt during sintering by using selective granulation, promoting the formation of relict Ore D in sinter structure. Relict ores and <10 μm pore volume in the sinter product were increased in the test. R1200 was improved even though a change of JIS-RI was insignificant. The reduction behavior of sintered ores through assimilation was examined. Ore type and ore characteristics largely influenced the reduction behavior of sintered ores through their forming pore structure after assimilation. The following results were obtained.

### 4. Conclusions

To increase high-temperature reducibility of sintered ores without changing their chemical composition, a manufacturing technology forming <10 μm pores in their microstructure was examined. Ore type and ore characteristics largely influenced the reduction behavior of sintered ores through assimilation. The following results were obtained:

1. The sharper temperature profile promoted the formation of the <10 μm pore volume in the sinter products. Many relict ores containing <10 μm pores were observed in sinter products with considerable small pores.

2. A reduction degree at 900°C of relict ores was determined by total porosity. In contrast, a reduction degree at 1300°C of relict ores was determined by SiO₂ content and <400 μm pore volume. Both factors influence melt volumes during reduction and are associated with small pore occlusion.

The reduction degree at 900°C of sample after assimilation was determined by total porosity. In contrast, the reduction degree at 1300°C of samples after assimilation was determined namely by Al₂O₃ content in gangue and also by <10 μm pore volume and gangue quantity.

3. The contribution of relict ores and assimilated structures for <10 μm pores varied with assimilation characteristics of the ores. Assimilated structures containing abundant granular hematite and less SFCA had many <10 μm pores.

4. Plant tests to increase relict ore or assimilated structures containing <10 μm pores successfully showed enhancement of high-temperature reducibility via an increase in <10 μm pore volume in sinter products.

### REFERENCES

17. M. Nakanaka, H. Ono-Nakazato, H. Kawabata and T. Usai: Proc. 3rd Int. Conf. on Science and Technology of Ironmaking (ICSTI), Stahlinstitut VDEh, Düsseldorf, (2003), 144.