1. Introduction

In recent years, the particle size and grade of fine ore used in the production of sintered ore have decline. Decreasing particle size of the fine ore used as a raw material decreases permeability in the sintering bed, and as a result, the productivity of sintered ore decreases. On the other hand, if lower grade ore is used, for example, ore with a higher Al2O3 content, the melting temperature of the ores increases and the melt tends to be inadequate, which impedes the sintering reaction and reduces sinter strength and yield. To meet increasing global demand for steel, it is necessary to maintain and improve sintered ore productivity.

As factors that affect sintered ore productivity, permeability in the sintering bed and product yield may be mentioned. Because the unit wind volume necessary in the production of sintered ore is substantially constant, increasing the wind volume by improving permeability in the sintering bed is important for improving productivity. Increasing product yield increases the percentage of sintered ore that is sent to the blast furnace as product from the sinter cake, and thus increases productivity. In the past, much research and development was carried out to improving the permeability of the sintering bed, product yield, or both.

In order to improve the strength and yield of sintered ore, the authors developed a hydrogen gaseous fuel (hereinafter, gaseous fuel) injection technology in the sintering process. In this technology, injection of the gaseous fuel together with air sucked from above the sintering machine makes it possible to hold the temperature in the sintering bed in the temperature zone between 1473 K and 1673 K, which is proper for the sintering reaction to form the calcium ferrite texture by the gaseous fuel and oxygen injection through the actual plant test. Oxygen enrichment shifted ignition position of coke and gaseous fuel to lower temperature side and the proper temperature zone was expanded. These results denoted the same tendency of the laboratory test results. Moreover, the calcium ferrite ratio of sintered ore increased in the actual plant. As these results, the effects of gaseous fuel and oxygen injection technology were confirmed in the actual machine similarly to the laboratory test.

KEY WORDS: sinter; gaseous fuel; oxygen enrichment; injection; heat pattern; combustion rate.
which the oxygen concentration decreases accompanying combustion of carbonaceous material. As a result, very little is known about oxygen enrichment to concentrations higher than that of atmospheric air. In the present research, the effect of oxygen enrichment above the oxygen concentration of air (21 vol%) on the mineral texture of sintered ore was studied, for combined injection of gaseous fuel and oxygen.

After confirming the combined gaseous fuel and oxygen injection technology in a sintering test (hereinafter, laboratory test) in an electric furnace, the effects of combined gaseous fuel and oxygen injection were quantified in an actual sintering machine (Chiba No. 4 sintering machine). Temperature measurements of the sintering bed at the actual sintering machine, sampling analysis of the product sintered ore, and operational tests were carried out, and the results were compared with those of the laboratory test. The results of this research are reported in the following.

2. Experimental Method

2.1. Sintering Test in Electric Furnace

It has been reported that since the texture of sintered ore consists of a matrix part and a porous part, the strength of sintered ore can be predicted by applying the theory of the strength of porous bodies, and the strength of the matrix can be evaluated by macro strength, and the strength of the component minerals themselves can be estimated and predicted by ensemble average of their existence ratios.12) In the present study, the effect of oxygen enrichment on the mineral texture composition of the sintered ore matrix was investigated by an electric furnace experiment. The experiment was conducted using an electric furnace in which the sintering atmosphere can be controlled. Figure 1 shows the experimental electric furnace. The experimental sample was blended using reagents so that the SiO₂ content was 5% and basicity (CaO/SiO₂) was 2, as shown in Table 1. After the materials were blended, water was added, and the sample was granulated to 10 mm by using a hand roll. The granulated particles were placed on an alumina boat with a platinum sheet fixed on its inner side and sintered at the prescribed temperature. The gas flow rate in the electric furnace was 5 L/min, and the oxygen concentration was adjusted by controlling the ratio of oxygen and nitrogen.

First, the effects of oxygen concentration and temperature on mineral texture formation were investigated. The temperature condition was set to 1548 K, 1598 K, or 1648 K, and sintering was performed for 300 s while increasing the oxygen concentration from 11% to 36% in steps of 5%. Next, the effect of sintering time was investigated by shortening the sintering time to 200 s and 100 s under the same temperature and oxygen concentration conditions.

After sintering, the cross sections of the specimens were observed. Identification of the texture of the obtained images was performed based on brightness analysis, and the porosity of the sintered ore was measured from the area ratio of the texture. Quantification of the mineral texture in the specimens after sintering was performed by the powder X-ray diffraction method (target: Cu, voltage: 40 kV, current: 50 mA). The main minerals in the sintered ore were classified, assuming these minerals can be broadly classified into 4 types, namely, hematite, magnetite, calcium ferrite (hereinafter, CF), and as other minerals, silicate slag (hereinafter, AS).13) In this quantitative analysis, wt% of hematite and CF was obtained by the internal standard method,11) and wt% of magnetite was obtained by the standard addition method, and the balance relative to 100% of that total was considered to be AS.14) As the reference material used in the internal standard method is crystallographically the same as the components being detected, a substance with a crystal grain size and crystallinity near that of the target substance is necessary; therefore, NaF was used in this experiment. For the diffraction lines to be used in the experiment, it is important that the diffraction peaks do not overlap those of other components and the reference material. Therefore, they were hematite (diffraction line: 104, 2θ: 33.3°), magnetite (diffraction line: 400, 2θ: 43.1°), CF (diffraction line: 240, 2θ: 34.4°), and NaF (diffraction line: 200, 2θ: 38.8°).

2.2. Actual Machine Test

The operational tests of the combined gaseous fuel and oxygen injection with an actual sintering machine were carried out at JFE Steel Corporation, East Japan Works Chiba No. 4 sintering plant. Figure 2 shows an outline of the equipment. A gas injection hood was installed in the front part of the strand. In the actual machine test, gasified liquefied natural gas (LNG: CH₄/C₂H₆/C₃H₈=89/5/6 vol%) was used as the gaseous fuel. In the hood, 100 vol% LNG and oxygen were injected from nozzles arranged in the strand direction and diffused in the suction air. The LNG and oxygen concentrations were controlled to the specified

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>73</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>10</td>
</tr>
<tr>
<td>CaO</td>
<td>10</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1. Blending ratio for sintering test with electrical furnace test.
values by adjusting the injection gas flow rate.

First, in order to confirm the effect of combined gaseous fuel and oxygen injection on the temperature distribution in the sintering bed, which was reported in a previous report, a thermocouple was inserted to a distance of 500 mm through a hole provided in the side wall at a position 130 mm below the sintering bed surface. The thermocouple used here was one R sheath type. In order to avoid melting damage by the melt formed by the sintering reaction, the thermocouple was inserted into the sintering bed with the sheath part covered with a mullite protective tube. To confirm only the effect of oxygen enrichment, the raw materials used in the experiment were adjusted so as to be constant.

Table 2 shows the experimental conditions of the temperature measurements in the sintering bed. The base condition of the experiment was the condition in which neither LNG nor oxygen was injected. Under the other conditions, the LNG concentration was 0.4 vol% in all cases, and charging materials in which coke equivalent to 4 times the heating value of the injected LNG was reduced were used. As the oxygen concentration, the experiment was conducted in the range from the 21 vol% oxygen concentration of atmospheric air to 30 vol%. Sintered ore was sampled under conditions T1, T2, and T4 in Table 2, and quantification of the mineral texture was performed by the same method as in the above-mentioned electric furnace test.

In order to quantify the effects of oxygen enrichment on the gaseous fuel injection method, a comparative test was carried out under conditions with and without oxygen enrichment. The LNG concentration was constant at 0.4 vol%, and the oxygen concentration under the condition with oxygen enrichment was set at 27 vol% of the suction air. The main raw material conditions were all the same, as the test was performed with materials in the same pile. The layer thickness and pallet speed were constant, and operation was adjusted so as to obtain a constant total production.

3. Experimental Results

3.1. Results of Electric Furnace Test

Figure 3 shows examples of photographs of the texture in the sintered ore at each oxygen concentration when sintering was performed at 1548 K for 300 s in the electric furnace. With the oxygen concentration of 11 vol%, CF formed between hematite textures. In addition, a large amount of the slag texture was observed. At 21 vol%, formation of the CF texture between some hematite was confirmed, but the majority existed as a large CF texture. At the oxygen concentration of 26 vol%, a large amount of CF texture that had grown to a large size was observed. The results shown in these photographs confirmed that the CF texture increases accompanying increased oxygen concentration.

Figure 4 shows the change in the mineral composition ratio under various oxygen concentrations at various temperature conditions. Under all temperature conditions, the ratios of the CF texture and hematite texture increased as the oxygen concentration increased, and accompanying this change, the ratios of the magnetite texture and AS texture decreased. The largest amount of the CF texture formed at 1598 K, and the smallest amount was at 1648 K. The hematite texture decreased as the sintering temperature increased. The largest amount of the magnetite texture formed at 1648 K. The largest amount of the AS texture also formed at 1648 K, and the smallest amount was observed at 1548 K.
Figure 5 shows the relationship diagram of the CF ratio in the mineral texture and sintering time at 1598 K. At all oxygen concentrations, an increasing tendency in the CF ratio could be seen with increasing sintering time. In comparison with the CF ratio at the oxygen concentration of 21 vol%, no effect of the oxygen concentration could be observed with the holding time of 100 s, but with the holding time of 200 s, the highest CF ratio was observed with the oxygen concentration of 31 vol%. And at 300 s, the highest ratio was observed with 26 vol%, though the difference between the CF ratio at 26 vol% and at 31 vol% was slight.

3.2. Results of Sintering Bed Temperature Measurements in Actual Machine

Figure 6 shows the results of temperature measurements by the thermocouple inserted 130 mm below the surface of the sintering bed. As reported in a previous report, it is considered possible to improve both strength and reducibility by holding the sintering bed temperature at 1473 K–1673 K for an extended time. Therefore, the holding time of the sintering bed in this 1473 K–1673 K temperature zone was measured. Under the T2 condition, in which LNG injection was performed so as to obtain an LNG concentration of 0.4 vol%, the holding time at 1473 K–1673 K increased from 130 s to 190 s, or an increase of 60 s in comparison with the base condition T1. Under the T3 condition, in which the oxygen concentration was enriched to 25 vol%, the holding time at this temperature increased by 100 s in comparison with T2. Under the T4 condition with the oxygen concentration of 27 vol%, the holding time at 1473 K–1673 K was 406 s, or an increase of 116 s in comparison with the T3 condition. However, under the T5 condition, in which the oxygen concentration was 30 vol%, the holding time at 1473 K–1673 K was 414 s, which was only a negligible increase in comparison with T4.

Figure 7 shows cross-sectional photographs of the sintered ore sampled under conditions T1, T2, and T4. Under T1, that is, without LNG injection or oxygen enrichment, there are many angular shaped, skeletal type hematite (secondary hematite) which did not originate from the original ore but rather, crystallized once from the melt. A scattered large AS texture could also be observed. On the other hand, under condition T2 with LNG injection, a large portion of the hematite texture could be observed; however, this hematite was primary hematite from the original ore, and it displayed a roundish shape. A fine CF texture could also
be seen, and the AS texture could be observed between the AS. Under condition T4, i.e., with oxygen enrichment to 27 vol%, a texture in which primary hematite and secondary hematite coexisted could be observed. The sintered ore porosity obtained by image analysis of the cross-sectional photographs was T1: 7.3%, T2: 7.2%, and T4: 7.8%.

Figure 8 shows the results of a quantitative analysis of the mineral composition ratios of the sampled sintered ore by powder X-ray diffractometry. In comparison with T1, the percentages of the hematite texture and AS texture in T2 were approximately the same, but the magnetite texture decreased by 1.2 points and the CF texture increased by 2.1 points. In comparison with T2, in T4, the hematite texture increased by 7.7 points and the CF texture also increased by 2.1 points, whereas the magnetite texture decreased by 1.9 points and the AS texture decreased by 8.1 points.

3.3. Results of Operational Test in Actual Machine

Figure 9 shows the results of the operational test. The base condition was the condition in which oxygen enrichment was not used and LNG injection was performed so as to obtain the LNG concentration of 0.4 vol%. This base condition was compared with the condition in which oxygen enrichment was performed to the oxygen concentration of 27 vol%. Under a condition of constant total production, the tumbler index (TI) increased from 63.1% to 64.3% accompanying oxygen enrichment. Furthermore, because the sintering speed was increased by oxygen enrichment while the pallet speed was constant, unit consumption of burnt lime decreased from 10 kg/t-s to 8 kg/t-s.

4. Discussion

4.1. Effect of Oxygen Enrichment on Texture Formation of Sintered Ore

As described in section 3.1, the ratios of the hematite texture and the CF texture increased as a result of an increased oxygen concentration in the sintering bed. In general, hematite in the sintering bed is reduced to magnetite by the reducing gas of the coke in the sinter mix during sintering bed temperature rise. Accordingly, the increased hematite texture ratio is considered to be due to suppression of the reduction reaction by a higher oxygen concentration in the sintering bed atmosphere. In addition, some hematite undergoes thermal dissociation and changes to magnetite at high temperature. However, the thermal dissociation temperature of hematite is greatly affected by the oxygen concentration in the sintering bed atmosphere, and it is thought that the
thermal dissociation temperature is increased by higher oxygen concentrations.\textsuperscript{15) Thus, the experimental results described above are thought to be due to the fact that thermal dissociation of hematite to magnetite became difficult as a result of the above-mentioned suppression of the reduction reaction and higher thermal dissociation temperature. Regarding the increased CF texture ratio, it is estimated that CF forms from hematite (Fe$_2$O$_3$) and CaO.\textsuperscript{16,17) It is thought that the area of the reaction interface between hematite and CaO is increased by the increased ratio of the hematite texture due to oxygen enrichment, and as a result, a larger amount of CF forms. Furthermore, based on the fact that hematite particles cannot be observed in the AS in the mineral texture, it is assumed that decomposition of CF occurs in the region where magnetite forms.\textsuperscript{18) From this fact as well, it is thought that decomposition of CF becomes difficult, and as a result, the ratio of the CF texture increases in the region where hematite is stabilized. Regarding the decrease in the magnetite texture, because the Fe content in the sinter mix is constant, it is considered that the amount of magnetite decreases by an amount equivalent to the increase in the hematite texture. As the cause of the decrease in AS, it is thought that decomposition of CF becomes difficult due to stabilization of hematite. CF decomposes to hematite at around 1623 K, and in case of a low partial pressure of oxygen, CF decomposes to magnetite and the slag fraction is released into the melt. In other words, it is thought that the amount of slag component released in the melt decreases as decomposition of CF becomes more difficult, and as a result, the amount of AS texture decreases.

Next, the effect of time on CF formation will be described. As shown in Fig. 5, at all oxygen concentrations, the CF ratio increased with increasing sintering time. This is thought to occur because the CF formation reaction time increases due to the extended holding time at 1473 K–1673 K associated with higher oxygen concentrations, as shown in Fig. 6.

Regarding the effect of sintered ore porosity on strength, Sato et al. gave $(1 - P)^n$ as the coefficient of the sintered ore porosity in the estimation equation for shatter strength. Here, P is the porosity of sintered ore (%) and n is a coefficient, and n=2 was adopted as the closest integer value to the mean slope of the regression equations by type of sintered ore.\textsuperscript{12) Accordingly, the change in strength due to the porosity of sintered ore obtained in this experiment is thought to be small.

4.2. Effect of Oxygen Enrichment on Temperature Distribution of Sintering Bed in Actual Machine

In comparison with the conventional sintering method using only solid fuel, it has been confirmed that the holding time in the temperature range from 1473 K to 1673 K, which is proper for the sintering reaction, is extended by the gaseous fuel injection method.\textsuperscript{7) Moreover, in a previous report,\textsuperscript{3) a further extension of this holding time was also possible by simultaneously injecting the gaseous fuel and oxygen. The mechanism of this phenomenon can be explained as follows: Figure 10 shows a schematic diagram of the heat patterns and the positions of solid fuel (coke) and gaseous fuel (LNG) combustion points with the conventional method, the gaseous fuel injection method, and the combined gaseous fuel and oxygen injection method. As shown in Fig. 10(a), in comparison the conventional sintering method using only coke, injection of LNG from the bed surface is an advantage of the LNG injection method. The injected LNG burns above the coke combustion point; this suppresses cooling by convective heat transfer with the sintering bed suction gas, and thereby expands the proper temperature region. Moreover, as shown in Fig. 10(b), with combined gaseous fuel and oxygen injection, oxygen enrichment of the suction gas is performed in addition to LNG injection, and as a result, the respective combustion points shift to the low temperature side due to the higher combustion rates of coke and LNG. As a result of this shift, the distance between the combustion points of the coke and LNG expands, and the proper temperature zone becomes larger than that in LNG injection. Thus, as in the laboratory test, an expansion of the proper temperature zone by oxygen enrichment could also be confirmed in the actual machine test in this research.

Figure 11 shows the relationship between holding time and oxygen concentration at temperatures over 1473 K. At the same time, the figure also shows the relationship between the oxygen concentration and shatter strength, Fig. 10. Schematic diagram of heat pattern and ignition behavior with each condition.
which was confirmed in a previous report.\(^8\) At oxygen concentrations from 21 vol% to 27 vol%, the holding time in the proper temperature zone is greatly extended, but at 30 vol%, there is little change from 27 vol%. This is considered to occur because the oxygen concentration becomes excessively high, causing the distance between the coke and LNG combustion points to become too large, and as a result, increased oxygen enrichment no longer contributes to extending the holding time at 1473 K–1673 K. Although the holding time at 1473 K–1673 K is constant, from the measurement results in Fig. 6, it can be seen that the heat patterns do not agree. Under the condition of the 30 vol% oxygen concentration, there was a difference in the cooling rate in the region under 1473 K in comparison with the 27 vol% condition. This difference in the cooling rate in the region under 1473 K is also attributed to the shift in the combustion point to the low temperature side. In the relationship between sintered ore strength and oxygen concentration, which was confirmed in the laboratory test in the previous report,\(^8\) the maximum effect was observed at an oxygen concentration of approximately 28 vol%, and strength decreased at higher oxygen concentrations than this level. Because a tendency similar to the results of the laboratory test could also be confirmed in this experiment, the longest holding time at 1473 K–1673 K is obtained at an oxygen concentration of 27–28 vol%; this is considered to be the optimum concentration for maximizing sinter strength.

### 5. Conclusions

1. The hematite texture and CF texture in sintered ore increased accompanying increases in the oxygen concentration of the sintering bed atmosphere. This increase of the hematite texture is thought to occur because the reduction reaction and thermal dissociation reaction of hematite were suppressed by the increased oxygen concentration, resulting in stabilization of the hematite texture. The increase of the CF texture is considered to be the result of formation of a larger amount of CF, which contains hematite as a main component, due to the stabilization of hematite. It was also found that the formation rate of the CF texture is accelerated as the oxygen concentration of the atmosphere in the sintering bed increases.

2. Accompanying an increased oxygen concentration in the sintering bed atmosphere, the amounts of magnetite texture and AS texture in the sintered ore decreased. Because T.Fe was constant, the decrease in the magnetite
texture is thought to occur because magnetite formation decreased by an amount equivalent to the increase in hematite. The decrease of the AS texture was attributed to the fact that decomposition of CF became difficult due to stabilization of hematite.

(3) The possibility of holding the sintering bed at 1473 K–1673 K for an extended time by combined gaseous fuel and oxygen injection was confirmed in an actual sintering plant. Up to the oxygen concentration of 27 vol%, the holding time at 1473 K–1673 K was extended as the oxygen concentration increased; however, virtually no further extension of the holding time was observed at 30 vol%. It is thought that the oxygen concentration became excessively high, causing the distance between the combustion points of the coke and LNG to become too large, and as a result, increased oxygen enrichment no longer contributed to extension of the holding time at 1473 K–1673 K.

(4) A strength improvement effect by the combined gaseous fuel and oxygen injection method was confirmed in the actual sintering plant. This improvement is attributed to the formation of a larger amount of melt due to the extended holding time at 1473 K–1673 K, which resulted in the formation of a larger amount of CF.

REFERENCES