Reduction and Disintegration Behavior of Sinter under $\text{N}_2\text{--CO--CO}_2\text{--H}_2\text{--H}_2\text{O}$ Gas at 773 K

Taichi MURAKAMI,* Takeyuki KODAIRA and Eiki KASAI

Graduate School of Environmental Studies, Tohoku University, 6-6-02, Aramaki-aza Aoba, Aoba-ku, Sendai, Miyagi, 980-8579 Japan.

(Received on September 30, 2014; accepted on December 11, 2014)

Reduction of CO_2 emissions is recognized as an urgent issue for the iron and steel industry. One of the feasible methods for the reduction of CO_2 emissions may be the use of H_2 gas as a reducing agent in blast furnaces for ironmaking. In order to keep the conditions of the blast furnace stable under high H_2 concentration, it is necessary to understand the effects of H_2 and H_2O gases on the disintegration of the iron ore sinter in the upper part of the blast furnace. Therefore, the effects of the concentration of the reducing gas and of the reduction time on the reduction and disintegration behavior of actual sinters are examined in the present work.

Reduction experiments were carried out under $\text{N}_2\text{--}20\%\text{ CO--}20\%\text{ CO}_2$ (CO gas) and under $\text{N}_2\text{--}12\%\text{ CO--}17.7\%\text{ CO}_2\text{--}8\%\text{ H}_2\text{--}2.3\%\text{ H}_2\text{O}$ (CO- H_2 gas) at 773 K. The reduction degree of the sinter reduced under CO- H_2 gas increased with time. On the other hand, it was once retarded when reduced under CO gas. For the same value of reduction degree, however, the value of the reduction-disintegration index, RDI, for the sinter reduced under CO gas was higher than that of the sinter processed under CO- H_2 gas. When reducing hematite to magnetite for long time, e.g., 3.6 ks under CO- H_2 gas, the reduction degree calculated from the weight change was larger than that obtained on the basis of the change in the XRD peak intensity.

KEY WORDS: hematite; magnetite; disintegration; reduction; hydrogen; calcium ferrite.

1. Introduction

The iron and steel making industry is responsible for around 14% of the CO_2 gas emissions in Japan, with the contribution from the ironmaking process being particularly large. However, it is essential to utilize fossil fuel energy, especially coal, in the conventional ironmaking process, because carbon is required for heat generation, reduction of iron oxide and carburization. Ironmaking processes based on large scale blast furnaces have been well-established and are characterized by efficient energy consumption. Therefore, further drastic decrease in the CO_2 emissions seems to be difficult.

The use of H_2 as a reducing agent in blast furnaces may be a potential solution to overcome this problem. To realize it, a constant and secure source of H_2 and a better understanding of the H_2 effects on the blast furnace operation are required. A potential source of H_2 in a steel plant could be the coke oven gas (COG). However, the reduction of iron oxide by H_2 is an endothermic reaction; thus, an increase in H_2 would lead to a significant change in the distribution of the temperature in the blast furnace.¹⁾ Moreover, a change in the permeability of the blast furnace is expected, due to a change in the reduction disintegration behavior of the

sinter at low temperature and in the shape of the cohesive zone. The behavior of the reduction disintegration of sinter at low temperature became a big problem when limestone was utilized as auxiliary material in the sintering. Many researchers have investigated the mechanism of disintegration and the methods to prevent it. It is well known that disintegration under CO gas occurs in a significant amount at around 800 K.^{2,3)} The main cause for disintegration is the volumetric expansion of the iron oxide phase, due to its reduction from hematite to magnetite.²⁾ In addition, the sinter consists of hematite with various phases, each having a different effect on the disintegration. Inazumi *et al.* reported that the value of RDI for skeletal hematite may reach approximately 30%.³⁾

Terui *et al.* described the disintegration behavior of sinter reduced by H_2 gas using the experimental apparatus based on Linder methods.⁴⁾ The strength of the sinter reduced by $\text{H}_2\text{--H}_2\text{O}$ gas at 823 K decreased. However, if compared with a CO- CO_2 gas with the same oxygen potential of $\text{H}_2\text{--H}_2\text{O}$ gas, the decrease in the strength was relatively small. Asada *et al.* reported that no crack formation occurred in the sinter produced by the reduction of skeletal hematite with H_2 gas at 733 K, contrarily to that observed in case of CO reduction.⁵⁾ In this paper, reduction and crack formation behaviors of skeletal hematite were discussed in detail, but this discussion does not reach to the behavior of sinter particle. Furthermore, these experiments were car-

* Corresponding author: E-mail: taichi@material.tohoku.ac.jp
DOI: <http://dx.doi.org/10.2355/isijinternational.55.1181>

ried out under a $\text{H}_2\text{-H}_2\text{O}$ gas flow, which was far from the actual blast furnace condition. It is difficult to estimate the behavior of the sinter under a complex gas system, *e.g.*, $\text{N}_2\text{-CO-CO}_2\text{-H}_2\text{-H}_2\text{O}$, because the effects of the concentration of CO and H_2 on the reduction rate are not linear. The authors reported the effects of the concentration of H_2 on the reduction disintegration behavior of the sinter reduced under a $\text{N}_2\text{-CO-CO}_2\text{-H}_2\text{-H}_2\text{O}$ gas at 773 K for 3.6 ks.⁶⁾ While the reduction under the CO gas proceeds topochemically, and large cracks formed at reduced skeletal hematite grow together with net-like fine cracks near the reduced hematite. As a result, the amount of fine cracks formed in the sinter reduced under CO-H_2 gas is lower than that under CO gas.

It is important to widely evaluate the effect of the reduction temperature and time on the reduction and disintegration behaviors, because the temperature distribution in the blast furnace changes when the concentration of H_2 in the reducing gas increases significantly. The structure and properties of the sinter are affected by its production conditions, including the rate of the agglomeration agent and the design of raw materials. In the present study, typical two types of sinter samples having different JIS-RDI were used to examine the effects of the concentration of the reducing gas and of the reduction time on the reduction and disintegration behaviors.

2. Experimental

2.1. Sample Preparation

Two types of sinter samples were supplied by a Japanese steel mill and were crushed and sieved to a grain size between 6.7 and 9.5 mm before use. The composition of the sinters is shown in **Table 1**. Physical and chemical properties such as JIS-RDI (ISO 4696-2), JIS-RI, hematite/magnetite phase ratio, specific surface area, average pore size, apparent density and porosity are shown in **Table 2**. The hematite/magnetite phase ratio was calculated from an internal standard method based on XRD, which is described in detail in section 2.4. The apparent density and porosity of sinter A were similar to those of sinter B. On the other hand, the specific surface area of sinter B was 1.7 times larger than that of sinter A. The average pore size of sinter B was one third of that of sinter A, meaning that sinter B had finer pores than sinter A.

Table 1. Chemical composition of sinter samples (mass%).

	T-Fe	M-Fe	FeO	CaO	SiO ₂	Al ₂ O ₃	MgO	P	S
A	57.0	0.1	6.9	10.1	5.0	1.9	1.5	0.05	0.01
B	57.2	0.2	10.6	9.3	5.7	2.0	0.3	0.08	0.01

Table 2. Mineral composition and physical properties of sinter samples.

Sinter	JIS-RDI	JIS-RI	Hematite (mass%)	Magnetite (mass%)	Total specific surface area (m ² /g)	Average micro pore size (μm)	Apparent density (g/cm ³)	Porosity (%)
A	37.6	73.5	32.40	14.10	2.67	1.02	3.52	14.47
B	30.4	69.2	25.58	46.71	4.56	0.38	3.42	14.58

2.2. Reduction and Drum Tests

A sample made of approximately 25 particles randomly collected, with a total weight of 25 ± 3 g, was inserted in the furnace, as shown in **Fig. 1**.⁶⁾ The sample was heated to 773 K in a N_2 stream with a flow rate of $21.5 \text{ cm}^3/\text{s}$ and kept for 300 s. The temperature of the sample was measured using a thermocouple inserted into the furnace from the top. Subsequently, the gas was changed to a reducing gas, keeping constant the flow rate, and the reduction experiment was carried out for selected times, varying from 1.2 to 9.0 ks. H_2O gas was generated by heating distilled water in the furnace at 573 K. Two reducing gases were used: $\text{N}_2\text{-20\% CO-20\% CO}_2$ (CO reduction) and $\text{N}_2\text{-12\%CO-17.7\%CO}_2\text{-8\%H}_2\text{-2.3\%H}_2\text{O}$ (CO-H_2 reduction). After the reduction experiment, the reducing gas was changed to N_2 again, and then the reduced sample was cooled down to a temperature below 473 K. The reduction degree, R.D._w , was calculated from the weight change before and after reduction, using the equation:

$$\text{R.D.}_w = (W_0 - W_1) / W_s \times 100 \quad (1)$$

where W_0 and W_1 are the weights of the sample before and after reduction, respectively, and W_s is the weight of oxygen coursed by iron oxide in the sinter.

Disintegration tests were conducted on the reduced samples on the basis of the ISO 4696-2 norm, using a tumbling drum with an inner diameter of 130 mm, at a rotation speed of 30 rpm, for 1.8 ks. Then, the sample was sieved with a 2.8 mm mesh, to determine the weight of the particles having a size larger than 2.8 mm in the sample. Finally, the RDI value was calculated using the following equation:

$$\text{RDI} = (1 - W_2 / W_1) \times 100 \quad (2)$$

Fig. 1. Schematic diagram of the experimental apparatus for reduction experiment.⁶⁾

where W_2 is the weight of particles larger than 2.8 mm. Further, the particles smaller than 2.8 mm were sieved using a series of meshes with a size of 0–0.1, 0.1–0.25, 0.25–0.5, 0.5–1.0, and 1.0–1.7 mm, in order to measure the particle size distribution of the sample. In addition, the microstructure of the sample before and after reduction was observed using an optical microscope.

2.3. Sample Analysis

After reduction, the sample was ground well with a mortar, obtaining a powder. This was well mixed with the NaF reagent in a 9:1 ratio, for the quantitative analysis of the compounds performed by the internal standard method based on XRD. NaF was selected because its peak is far from that of hematite and magnetite. The XRD analysis was carried out in the range of 10° – 80° .

3. Results

3.1. Effects of the Reducing Gas on the Reduction and Disintegration Behavior of the Sinter

Figures 2 and 3 show the changes in the reduction degree and RDI value of sinter A and B with time, under CO and CO–H₂. The plots show the average values, and the error bars show both the maximum and minimum values of the reduction degree measured from multiple experiments. The reduction degree of both sinters is larger in case of CO–H₂

Fig. 2. Effect of reduction time on reduction degree and RDI value of sinter A reduced under $N_2 - 20\%CO - 20\%CO_2$ and $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$.

Fig. 3. Effect of reduction time on reduction degree and RDI value of sinter B reduced under $N_2 - 20\%CO - 20\%CO_2$ and $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$.

reduction than that of CO reduction. In particular, in case of CO reduction, the increase in the reduction of sinter A and B becomes less significant with passing reduction time from 1.8 to 3.6 ks and from 3.6 to 5.4 ks, respectively. The RDI value of sinter A under CO reduction is lower than under CO–H₂ reduction. Also, the RDI value of sinter B under CO reduction is lower than under CO–H₂ reduction after 1.8 ks. After 3.6 ks, however, it is higher than that found under CO–H₂ gas, although the two values are difficult to be directly compared, because the associated reduction degree is different.

Figure 4 shows the relationship between the RDI value and the reduction degree. In case of CO reduction, the RDI value increased linearly with increasing the reduction degree. Takamoto reported that there is a linear relation between the RDI value and the reduction degree of sinter reduced at 823 K under a CO/CO₂ gas with equal amounts of CO and CO₂,⁷⁾ which agrees with the relation found in the present study. In case of CO–H₂ reduction, also the RDI value increased linearly. For the same reduction degree, the RDI value under CO–H₂ reduction was lower than that under CO reduction.

3.2. Microstructure of Sinter and Particle Size

The typical microstructure for both sinters after reduction for selected times is shown in Figs. 5 and 6. After 1.8 ks, the reduction was evident near the surface of the sinter in both cases. After 3.6 ks, the reduction extended also towards the center of the sinter. This trend was particularly evident in case of CO–H₂ reduction, reasonably because the diffusion coefficient of H₂ is larger than that of CO.^{8,9)} The reduction of fine hematite, which has a minor effect on the reduction disintegration of the sinter,³⁾ began after 5.4 ks. This corresponds qualitatively to the fact that the RDI value changes negligibly when the reduction degree increases under CO reduction, as described in chapter 3.1. Also, in case of sinter B the fine hematite was partly reduced after 5.4 ks under CO and CO–H₂ gas. After 7.2 ks of reduction, however, just a few fine hematite phases were observed.

Figure 7 shows the change in weight ratio of particles with a size lower than 2.8 mm after the drum test. There is no typical change in the weight ratio of particles reduced under CO gas with time. In case of CO–H₂ reduction, on the other hand, the weight ratio of particles having a size

Fig. 4. Relationship between reduction degree and RDI of sinter reduced under $N_2 - 20\%CO - 20\%CO_2$ and $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$.

Fig. 5. Microstructures of sinter A reduced under a) $N_2 - 20\%CO - 20\%CO_2$ and b) $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$ at 773 K for 1) 1.8 ks, near the surface; 2) 3.6 ks, near the surface; 3) 3.6 ks, inner 4) 5.4 ks, inner. FH: Fine Hematite, SH: Skeletal Hematite.

Fig. 6. Microstructures of the center part of sinter B reduced under a) $N_2 - 20\%CO - 20\%CO_2$ and b) $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$ at 773 K for 1) 5.4 ks, and 2) 7.2 ks.

Fig. 7. Change in weight ratio of particle of reduced sinter A and B after drum test with time. The gas concentrations are a) $N_2 - 20\%CO - 20\%CO_2$ and b) $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$ gas.

Fig. 8. Relationship between average particle size (+2.8 mm) after drum test of sinter B reduced under $N_2 - 20\%CO - 20\%CO_2$ and $N_2 - 12\%CO - 17.7\%CO_2 - 8\%H_2 - 2.3\%H_2O$ and reduction degree.

lower than $0.25 \mu m$ decreases with increasing the reduction time. This is reasonable because the H_2 reduction causes the sinter to break into particles having a larger size with respect to CO reduction.⁶⁾ **Figure 8** shows the relationship between an average particle with a size above 2.8 mm and the reduction degree. The particle size was calculated from a binary image analysis of each sample. Therefore, reduction degree shows different value from that shown in Fig. 3, which is the average value. The average particle size of the sample subject to CO- H_2 reduction is larger than that of the sample subject to CO reduction, at a parity of reduction degree. Even if the RDI value became the same after 7.2 ks, the average particle size is larger.

The findings described above show that the average size of the particles formed under CO- H_2 reduction was larger than that achieved under CO reduction for every considered condition.

Fig. 9. Optical microscope images of a particle of sinter A reduced at 773 K for 1.8, 3.6, and 5.4 ks under a) $\text{N}_2 - 20\%\text{CO} - 20\%\text{CO}_2$ and b) $\text{N}_2 - 12\%\text{CO} - 17.7\%\text{CO}_2 - 8\%\text{H}_2 - 2.3\%\text{H}_2\text{O}$.

Fig. 10. Effect of reducing time on the crack density of sinter A after reduction under a) $\text{N}_2 - 20\%\text{CO} - 20\%\text{CO}_2$ and b) $\text{N}_2 - 12\%\text{CO} - 17.7\%\text{CO}_2 - 8\%\text{H}_2 - 2.3\%\text{H}_2\text{O}$.

Fig. 11. Effect of reduction time on the weight ratio of particle size of sinter A after drum test.

3.3. Relation between Disintegration and Reduction under CO Gas

The reduction rate under CO slowed down, whereas the RDI value increased. After a while, the reduction rate increased again. On the other hand, the behavior under CO-H_2 reduction was different. In order to clarify such a difference, optical microscope images of sinter A after reduction for 1.8, 3.6 and 5.4 ks under CO and CO-H_2 are shown in **Fig. 9**. After 1.8 ks, few cracks appeared in the center of the sinter particle, and some cracks near the surface are observed. After 3.6 ks, many large cracks are observed and they reach the center of the sinter particle. Images of cracks after 5.4 ks are similar to those after 3.6 ks, meaning that the crack propagation was complete after 3.6 ks.

To quantify the formation of cracks, the change in the density of cracks formed by ruptures in the bulk is shown in **Fig. 10**. The density of cracks was calculated as the difference between the number of all the cracks and the number of the fine and intercrystalline cracks only, using a microstructural analysis based on the observation of 4–13 pictures for each condition. There is no difference between the two gas conditions. The crack density increases with increasing the reduction time up to 3.6 ks. After that, it reaches a constant value. This indicates that the cracks reached the center of the sinter particle after 3.6 ks under both gas conditions. It can be concluded that, under CO gas, the sinter broke even if reduction reaction hardly proceed.

It is expected that propagation of the cracks affects the size of the powder formed after the drum test. **Figure 11** shows the change in the weight ratio of disintegrated sinter A with an average particle size under 0.25 mm (small size) and with an average particle size between 1.7 and 2.8 mm (large size), together with the relative RDI value. W_1 indicates the weight of the sample before the drum test, it means just after reduction. The weight ratio of the large size powder obtained by the CO reduced sinter is smaller than that obtained by the CO-H_2 reduced sinter. The weight ratio increases with time, similarly to the behavior of the RDI value. The amount of large and small size powders increases from 1.8 to 3.6 ks, whereas the reduction rate became lower. This can be explained by the reduction of skeletal hematite and by the occurrence of cracks generated by the stress due to volume expansion.

3.4. Change of Mineral Phases in Sinter during Reduction

Figure 12 shows the XRD profiles of the sinter B reduced under CO gas for specified times. A decrease in the peak of hematite and an increase in that of magnetite with time are observed. No peak corresponding to a new phase appeared after reduction. This result was consistent for all the experimental conditions. Therefore, the reduction degree was calculated from the peak change of hematite using the following equation:

$$R.D._{XRD} (\%) = 100 \times (B_i - B_{ii}) / (B_{iii} + B_{iv}) \dots\dots (3)$$

where B_i and B_{ii} indicate the amount of oxygen, in moles, calculated from the peak intensity of hematite before and after reduction, respectively; whereas B_{iii} and B_{iv} indicate the amount of Fe^{3+} and Fe^{2+} moles, respectively, which was calculated from the chemical composition of sinter. If the reduction degree calculated from Eq. (3) is the same as the one calculated from Eq. (1), the reduction only involves a transformation from hematite to magnetite.

Changes in the reduction degree with time, calculated from Eqs. (1) and (3), are shown in **Figs. 13** and **14**. The dashed line indicates the reduction degree expected in

case the hematite in the sinter is completely reduced to magnetite. In case of CO reduction of sinter A, $R.D._{XRD}$ shows a similar value to the $R.D._w$ measured after 3.6 ks. However, the value of $R.D._{XRD}$ becomes lower than $R.D._w$ after a further reduction. In case of CO–H₂ reduction, this trend is evident already at shorter times. $R.D._w$ exceeds the dashed line for a longer reduction, while $R.D._{XRD}$ is lower than the line for all the experimental conditions. In case of sinter B, the behavior of these two values is similar to that observed for CO reduction of sinter A. $R.D._{XRD}$ increases with increasing the reduction time, coming close to the dashed line. The difference in the behavior of $R.D._{XRD}$ is reasonably caused by the specific surface area of sinter B, which is higher than that of sinter A.

These results indicate that the weight of the sinter, except for the reduction from hematite to magnetite, keeps decreasing with the reduction time. **Figure 15** shows the microstructure of sinter A reduced for 1.8, 5.4 ks, and before reduction. Magnetite, the product of the reduction of skeletal hematite, and a phase derived from calcium ferrite, are observed after reduction. A number of pores, not evident before reduction, are observed at the interface between the original skeletal hematite and the original calcium ferrite. Further, numerous cracks are observed in the phase which was calcium ferrite before reduction. Consequently, a long reduction caused the calcium ferrite phase to change.

The reduction behavior of quaternary calcium ferrite, whose system was Fe_2O_3 –CaO–SiO₂–Al₂O₃, SFCA, was reported by Taguchi *et al.*¹⁰⁾ Above 1 073 K, the following

Fig. 12. X-ray diffraction pattern of sinter B reduced under N₂ – 20%CO – 20%CO₂.

Fig. 13. Effect of reduction time on reduction degree from XRD of sinter A reduced under a) N₂ – 20%CO – 20%CO₂ (CO reduction) and b) N₂ – 12%CO – 17.7%CO₂ – 8%H₂ – 2.3%H₂O (CO–H₂ reduction).

Fig. 14. Effect of reduction time on reduction degree from XRD of sinter B reduced under a) N₂ – 20%CO – 20%CO₂ (CO reduction) and b) N₂ – 12%CO – 17.7%CO₂ – 8%H₂ – 2.3%H₂O (CO–H₂ reduction).

Fig. 15. Morphology of calcium ferrite in sinter A reduced under a) N₂ – 20%CO – 20%CO₂ (CO reduction) and b) N₂ – 12%CO – 17.7%CO₂ – 8%H₂ – 2.3%H₂O (CO–H₂ reduction) at 773 K.

phase change was observed:

where C, W, and F are CaO, FeO, and Fe₂O₃, respectively. The structure of SFCA is very complicated and difficult to analyze because a sinter from a real steel mill was used in the present study. There is a possibility for the change in calcium ferrite without any phase transformation, for example a reduction not involving phase transformation. In this case, it is expected that the calcium ferrite phase would become more brittle.

Because of the volume expansion caused on the skeletal hematite phase by reduction, the calcium ferrite phase occurring in the skeletal hematite becomes more compressed. The progressive embrittlement of the calcium ferrite phase may lead to its rupture. The sample was polished before observation by optical microscope and, during polishing, it was observed that this brittle and weak phase easily detached. It is thus expected that the calcium ferrite phase would disintegrate during reduction in the blast furnace. However, it is not easy to quantitatively evaluate the disintegration behavior of calcium ferrite, which is proposed as a further development of the present research.

4. Conclusion

The effects of the reducing gas composition, reduction time, and type of sinter on the reduction disintegration behavior were examined. The obtained results can be summarized as follows:

(1) The reduction rate of sinter under CO gas is at first relatively low, although the RDI value increases constantly from the beginning. This may be attributed to an increasing stress occurring in the secondary (skeletal) hematite phase and causing the formation and growth of large cracks. When

the reducing gas contains H₂ (CO–H₂ gas), there is no retard in the reduction because H₂ diffuses through the inside of the sinter particles and reduces the iron oxide. For the same reduction degree, the RDI value of the sinter reduced under CO–H₂ gas is lower than that of the sinter reduced under CO gas.

(2) The size distribution of the particles formed from the reduced sinter does not change with time when the sinter is reduced under CO gas. When reduced under CO–H₂ gas, on the contrary, the ratio of fine particles (–0.25 mm) to the total weight of reduced sinter decreases, although the ratio of larger particles (between 0.25 and 1.7 mm) to the total weight of reduced sinter increases with time.

(3) For a long time reduction, in case of a reduction under CO–H₂ gas, e.g., for 3.6 ks, the reduction degree calculated from the weight change is larger than that calculated from the change in the XRD peak of hematite. This indicates that the reaction causing weight change occurred without causing a reduction from hematite to magnetite. Many pores were observed in the calcium ferrite phase near the skeletal hematite, indicating that some changes occurred in calcium ferrite, and this could be the subject of further investigation.

REFERENCES

- 1) H. Nogami, Y. Kashiwaya and D. Yamada: *CAMP-ISIJ*, **24** (2011), 584.
- 2) N. Sawamoto, H. Fukuyo, Y. Miyata and T. Miyasita: *Tetsu-to-Hagané*, **70** (1984), 512.
- 3) T. Iazumi, K. Shinada and M. Kawabe: *Tetsu-to-Hagané*, **68** (1982), 2207.
- 4) T. Terui, R. Takahashi, J. Yagi and Y. Omori: *Bull. Res. Inst. Miner. Dressin. Metall. (SENKEN IHO)*, **29** (1973), 37.
- 5) M. Asada, S. Masashi and Y. Omori: *Tetsu-to-Hagané*, **73** (1987), 1901.
- 6) T. Murakami, Y. Kamiya, T. Kodaira and E. Kasai: *ISIJ Int.*, **52** (2012), 1447.
- 7) Y. Takamoto: *CAMP-ISIJ*, **15** (2002), 114.
- 8) T. Usui, M. Ohmi, Y. Oshima and Y. Horikawa: *Tetsu-to-Hagané*, **72** (1986), S895.
- 9) T. Usui, M. Ohmi, S. Hiroshima and N. Kitagawa: *Tetsu-to-Hagané*, **73** (1987), 1956.
- 10) N. Taguchi and T. Otomo: *J. Soc. Mater. Eng. Resour.*, **11** (1998), 51.