Reducibilities of Wüstite and Calcio-wüstite in Terms of High Temperature X-ray Diffraction Analysis

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Reducibilities of wüstite and calcio-wüstite have been examined using high temperature X-ray diffraction analysis including the effect of hydrogen on the reducibility. Fe_2O_3 reagent powders and hematite ore powders were used for reduction of wüstite (denoted as FeO) and sintered ore powders were used for reduction of FeO and calcio-wüstite (denoted as CW). High-temperature X-ray diffraction was applied to these samples in a flow of $\text{CO-CO}_2\text{-He}$ mixtures with and without 3.9 vol% of hydrogen during the heating cycle which simulates a blast furnace condition. The diffraction angle was scanned in the range from 33° to 55° . In experiment on sintered ore powders without hydrogen, the main peak around 48.5° shifted to lower angles with increasing temperature. This shift also continued while temperature was kept at $1\,000^\circ\text{C}$ where wüstite was saturated with iron; on the contrary, the peak shift did not take place for hematite ore powders. This main peak is associated with wüstite (200), which is actually composed of peaks due to FeO and CW for sintered ore powders. The peak shift reflects that the peak intensity of CW increases relative to that of FeO, which suggests that the reduction of FeO proceeds faster than that of CW, and the reducibility of FeO is higher. In contrast, the peak shift did not take place in experiment on sintered ore powders with hydrogen additions. This suggests that the reducibility of CW is comparable to that of FeO in the presence of hydrogen.

KEY WORDS: sintered ore; wüstite; calcio-wüstite; high temperature X-ray diffraction; reduction; hydrogen addition.

1. Introduction

Reducibility of sintered ores is one of crucial factors affecting operation stability of a blast furnace^{1–3)} because sintered ores are the main iron source for the furnace. Sintered ores typically consist of four phases: hematite (Fe_2O_3), magnetite (Fe_3O_4), calcium ferrite (denoted as CF, mainly silico-ferrite of calcium and aluminium (SFCA)) and slag phases; among them, Fe_2O_3 and CF are in main proportion. Reduction of sintered ores in a blast furnace is very complex because temperature as well as gas components change depending on the position of the furnace. This reduction normally proceeds via two steps: (i) Fe_2O_3 , Fe_3O_4 and CF are reduced to wüstite in the lower temperature zone and (ii) wüstite is reduced to metallic iron in the thermal reserve zone and in the even higher temperature zone. The second step is of particular importance in practice because the reaction rate at higher temperatures dominates the overall reduction efficiency of a blast furnace.^{4–6)}

There are two types of wüstite in reduced sintered ores: one is wüstite (denoted as FeO) reduced from hematite containing less impurities and the other is calcio-wüstite (denoted as CW) reduced from CF: both FeO and CW have the rock-salt structure. CW contains CaO and other gang components such as MgO, SiO_2 and Al_2O_3 as solutes, and thus its reducibility could be different from that of FeO. Moreover, the phase structure around wüstite would also affect the reducibility of wüstite. For example, wüstite in sintered ores is mostly adhesive to the slag phase, which is an obstacle against reducing gas penetration to wüstite and worsens the reducibility. Thus, it is important to know the effective reducibilities of FeO and CW in practical sintered ores.

Many studies have been made on the reducibilities of FeO and CW. Most researchers have concluded that the reduction rate of wüstite is accelerated in the presence of CaO.^{7–11)} For example, Inoue *et al.*⁸⁾ have reported that the reduction rate of wüstite at 900°C and $1\,000^\circ\text{C}$ by CO-CO_2 gas mixture increases with increasing CaO content in wüstite up to 1 mass%, beyond which it becomes almost constant. They have suggested that the higher reducibility of CW may be

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due to a larger number of fine pores formed in the reduced layer of CW. Noguchi *et al.*¹⁰⁾ have measured the reduction rate from wüstite to iron at 800°C, 900°C, 1 000°C and 1 100°C by high-purity CO gas using powder mixtures having three different ratios of synthesized SFCA to reagent Fe₂O₃. They have found that below 900°C the reduction rate is faster with increasing ratio of SFCA to Fe₂O₃ but is not dependent on the ratio above 1 000°C. They have implied that the lower reduction rate of FeO is attributed to the formation of the dense iron layer near the surface; however, the dense iron layer is not formed on the surface of CW owing to the simultaneous generation of iron and slag. However, to the best of the authors' knowledge, there are few reports on the effective reducibilities of FeO and CW in practical sintered ores. This may stem from the difficulty in distinguishing between the reducibilities of CW and FeO in practical sintered ores.

In addition, Japanese steel industries are currently developing innovative technology for low reducing agent ratio operation through the Japan's national project COURSE50¹²⁾ to reduce CO₂ emissions. Hydrogen reduction is one of the main technologies in COURSE50.¹²⁾ Hence, the effect of hydrogen on the reducibilities of FeO and CW also needs to be clarified.

The difference between reducibilities of FeO and CW in sintered ores could directly be evaluated using high temperature X-ray diffraction (XRD) analysis because the lattice constant of CW increases with increasing CaO concentration in the solid solution even under a constant oxygen partial pressure,^{13,14)} and the diffraction peaks of FeO and CW can be distinguished from each other to compare the intensities of these diffraction peaks corresponding to the respective concentrations. Consequently, the aim of this study is to clarify the difference between reducibilities of FeO and CW and the effect of hydrogen on the reducibility using high temperature XRD.

2. Experimental

2.1. Sample Preparation

Samples used in this study were Fe₂O₃ reagent powders (diameter: 1 μ m, purity: 99.9%), hematite ores and sintered ores. **Table 1** summarizes the chemical compositions of the sintered ore and the compositions of Fe₂O₃ phase containing SiO₂ and Al₂O₃ in the hematite ore. Electron probe microanalysis (EPMA) revealed that the hematite ore was composed of three different parts of silica (SiO₂), Fe₂O₃ with negligible amounts of gang minerals and Fe₂O₃ containing SiO₂ and Al₂O₃ as solutes. Some of the hematite ore and sintered ore samples were crushed into fine powders using an alumina mortar and a pestle and were subjected to XRD analysis to determine major constituent phases before heating. This XRD analysis was carried out with CoK α radiation at an accelerating voltage of 40 kV and a filament current of 250 mA. The optical system of a parallel beam was employed. The scan range was $2\theta = 20\text{--}80^\circ$ which covered all the compounds in the samples. **Figure 1** shows XRD profiles of the hematite ore (a) and the sintered ore (b). The diffraction peaks due to Fe₂O₃ and SiO₂ are observed for the hematite ore, while the peaks due to Fe₂O₃, Fe₃O₄, CF and dicalcium-silicate (2CaO·SiO₂ denoted as C₂S) are

Table 1. Chemical compositions of the sintered and hematite ores (mass%).

	T.Fe	Fe ₂ O ₃	FeO	SiO ₂	CaO	Al ₂ O ₃	MgO	CaO/SiO ₂
Sintered ore	56.0		8.19	5.27	11.56	1.84	1.27	2.19
Hematite ore		97.3		1.9		0.8

Fig. 1. XRD profiles of hematite ore (a) and sintered ore (b).

observed for the sintered ore.

In order to compare gas reduction rates of the samples, their particle sizes, *i.e.*, their specific surface areas must be identical. It should be noted that the sintered ore is composed of several phases with different strengths and thereby the constituent phases may be different from particle to particle depending on the size. To avoid such a situation, the hematite and sintered ores were crushed and sieved into four different groups with particle size ranges of < 38 μ m, 38–75 μ m, 75–150 μ m and 150–300 μ m, which were subjected to XRD analysis. Actually the XRD profiles depended on the particle size for the samples larger than 75 μ m. Thus, these samples were further ground into particles finer than 75 μ m. As a result, the XRD profiles of the samples were almost the same as those of the samples sized < 38 μ m and 38–75 μ m. In this study, only the hematite and sintered ore samples sized 38–75 μ m were subjected to high temperature XRD analysis.

2.2. High Temperature XRD Analysis

Figure 2 shows a schematic diagram of the high-temperature X-ray diffractometer used in this study. About 400 mg of sample powders were mounted into a shallow alumina holder (17 mm length $\times$ 9 mm width $\times$ 0.8 mm depth) and

Fig. 2. Schematic diagram of the high-temperature X-ray diffractometer.

Fig. 3. Experimental conditions of temperature and gas compositions.

then the holder was horizontally placed on the heating plate with Pt heating wire. To protect the sample holder from erosion, an iron foil 0.1 mm thick was placed under the power sample. Temperature of a sample was measured by an R-type thermocouple next to the sample with the accuracy of $\pm 0.1^\circ\text{C}$. The sample chamber was sealed by a Ni film to prevent radiation heat transfer and also by a polyimide film to shield the controlled atmosphere from air.

The maximum power of X-ray generator was 10 kW (40 kV and 250 mA) and the $\text{CoK}\alpha$ line was used as the X-ray source. The optical system of a parallel beam was employed, by which accurate data were able to be obtained without systematic errors due to variations in the position and flatness of the sample surface during heating.¹⁵⁾ The scan range was $2\theta = 33\text{--}55^\circ$ covering the peaks of the main compounds. The diffraction scan rate was $5^\circ/\text{min}$ and the scan step was 0.02° . The diffraction angle was calibrated by means of the external standard specimen method using high purity silicon powders at room temperature.

Figure 3 shows experimental conditions of temperature and gas compositions. Oxygen partial pressure in the chamber was adjusted using mixtures of CO/CO_2 , the ratio of

which was changed depending on temperature to simulate a blast furnace condition. In addition, the gas mixture was diluted with 50 vol% of helium gas to improve X-ray diffraction strength and was introduced to the surface of the sample through a Pt tube (inner diameter: 3.5 mm) placed at the center of the front door of the chamber. The total flow rate of the gas mixture was $1.67 \times 10^{-6} \text{ m}^3/\text{s}$ (100 ml/min). The gas mixture was discharged through the hole at the bottom of the reaction chamber to the outside of the system. For reduction experiment with hydrogen, 3.9 vol% of H_2 was also added to the gas mixture. To simulate the condition of the thermal reserve zone, the sample was heated from room temperature to 1000°C with a heating rate of $8.33 \times 10^{-2} \text{ K/s}$ ($5^\circ\text{C}/\text{min}$) (Step I), held at 1000°C for 100 min (Step II) and then heated again up to 1250°C at a heating rate of $8.33 \times 10^{-2} \text{ K/s}$ (Step III). During Steps I and III, temperature continuously increased at a heating rate of $8.33 \times 10^{-2} \text{ K/s}$, resulting in a temperature increment of 24°C per scan covering $2\theta = 33\text{--}55^\circ$.

3. Results

Figures 4, 5 and 6 show XRD profiles of the Fe_2O_3 reagent, hematite ores and sintered ores reduced in atmosphere with no hydrogen addition, respectively, for Step I (4(a), 5(a) and 6(a)), Step II (4(b), 5(b) and 6(b)) and Step III (4(c), 5(c) and 6(c)), where temperature on the right or the left side of Figs. 4(a), 4(c), 5(a), 5(c), 6(a) and 6(c) represents one at which each scan was started for Steps I and III, and time on the left side of Figs. 4(b), 5(b) and 6(b) represents the total time after heating was started. Figure 7 shows XRD profiles of the sintered ores reduced in atmosphere with hydrogen addition for Step I (a), Step II (b) and Step III (c). It can be seen from Figs. 4(a), 5(a), 6(a) and 7(a) for Step I that the peak intensity of Fe_2O_3 becomes higher with increasing temperature although the Fe_2O_3 concentration should not increase in actuality. This is because X-ray absorptivity due to gas decreases with an increase in temperature due to the decrease in gas density. In the case of the sintered ores, the peak due to Fe_2O_3 disappears at temperatures between 462 and 486°C ; instead, the peak due to Fe_3O_4 appears between 414 and 438°C and disappears between 822 and 846°C . More importantly, the wüstite peak starts to appear at 726°C , at which the CF peak disappears; instead, the C_2S peaks seem to appear. This suggests the formation of CW: CaO and SiO_2 dissolved in CF should form C_2S by reaction with the slag phase when CF is reduced to CW. The peak intensity of wüstite starts to decrease 20 min after the onset of Step II; simultaneously, the Fe peak appears. The wüstite peak completely disappears between 1096 and 1120°C , as shown in Fig. 4(c) for Step III.

Table 2 summarizes temperatures at which the peaks due to Fe_2O_3 , CF, Fe_3O_4 , wüstite and Fe appear and/or disappear for the Fe_2O_3 reagent powder, hematite and sintered ore samples, where (+ H_2) represents the measurements with additions of hydrogen. The table also gives the total heating times in the brackets for the peaks to appear or disappear during Step II. The wüstite peak for Fe_2O_3 reagent powders disappears during Step II while those of hematite and sintered ore samples remain until Step III. The difference would stem from the difference in the particle sizes of

Fig. 4. XRD profiles of the Fe_2O_3 reagent reduced in the atmosphere with no hydrogen addition for Step I (a), Step II (b) and Step III (c).

Fig. 5. XRD profiles of the hematite ores reduced in the atmosphere with no hydrogen addition for Step I (a), Step II (b) and Step III (c).

Fig. 6. XRD profiles of the sintered ores reduced in the atmosphere with no hydrogen addition for Step I (a), Step II (b) and Step III (c).

Fig. 7. XRD profiles of the sintered ores reduced in the atmosphere with hydrogen addition for Step I (a), Step II (b) and Step III (c).

Table 2. Temperatures at which the peaks due to Fe_2O_3 , CF, Fe_3O_4 , wüstite and Fe appear and/or disappear for the Fe_2O_3 reagent powder, hematite and sintered ore, where (+H₂) represents the measurements with additions of hydrogen.

	Fe_2O_3 disappearance	CF* decomposition	Fe_3O_4 appearance/ increase	Fe_3O_4 disappearance	Wüstite appearance	Wüstite disappearance	Metallic iron appearance
Hematite	462–486		390–414	702–726	678–702	1 000 (229 min)	1 000 (214 min)
Hematite (+H ₂)	438–462		383–390	654–678	654–678	1 000 (229 min)	1 000 (200 min)
Hematite ore	438–462.		438–462	822–846	726–750	1 096–1 120	1 000 (219 min)
Sintered ore	462–486	726–750	414–438	822–846	702–726	1 120–1 144	1 000 (229 min)
Sintered ore (+H ₂)	462–486	726–750	414–438	822–846	678–702	1 120–1 144	1 000 (219 min)

sample powders because the particle size generally gives a great effect on the reduction rate: the particle size of Fe_2O_3 sample is 1 μm while those of hematite ore and sintered ore samples are 38–75 μm . Comparison between the results of the measurements with and without hydrogen indicates that wüstite appears at lower temperatures and that Fe also appears earlier in case of hydrogen additions. This indicates that hydrogen promotes reduction for both hematite and sintered ore samples.

4. Discussion

4.1. Comparison between Reduction Processes from FeO and CW to Metallic Iron

Focus on wüstite (200) peaks to clarify the difference in reducibilities between FeO and CW. **Figure 8** shows close-ups of XRD profiles around wüstite (200) peaks obtained from experiments on Fe_2O_3 reagent and sintered ore samples: the former was recorded at 1 000°C and 14 min after the onset of Step II and the latter at 1 000°C and 29 min after the onset of Step II. It can be seen that the full width of the half maximum of the peak of the sintered ore sample is larger than that of the Fe_2O_3 reagent. This is because Fe_2O_3 reagent is reduced to FeO whereas sintered ore is reduced to FeO and CW which contains considerable amounts of gangue components such as CaO and SiO_2 as solutes. Closer look at the peak obtained in the sintered ore sample indicates that it is recorded as superposition of the FeO and CW peaks centered at ca. 48.25° and ca. 48.5°, the former corresponding to CW because the lattice constant of CW is greater due to the presence of solutes. This finding is supported by a study due to Inami and Suzuki,¹³⁾ who have estimated the solubility limit of CaO in iron saturated wüstite as 5.95 mass% and the difference between peak angles of FeO and CW as 0.55° at maximum at room temperature.

To investigate the reduction progress of FeO and CW, the wüstite (200) peaks of the sintered ore sample should be deconvoluted into two peaks. At the moment, however, this deconvolution has not been made because there are no reference data available for FeO and CW peak positions. In this study, the total profile around (200) peak is regressed to the Pseudo-Voigt function. The profiles fitted to the Pseudo-Voigt function are included in Fig. 8.

Figure 9 shows peak areas of wüstite (200) and Fe (110) in the hematite and sintered ore samples as a function of heating time (t) together with the heating profile: the peak area has been derived from the XRD profile regressed to

Fig. 8. Close-ups of XRD profiles around wüstite (200) peaks obtained from experiments on Fe_2O_3 reagent and sintered ore samples. The profiles fitted to the Pseudo-Voigt function are also included.

Fig. 9. Peak areas of wüstite (200) and Fe (110) in the hematite and sintered ore samples as a function of heating time (t) together with the heating profile.

the Pseudo-Voigt function and is proportional to the amount of each component. For both hematite and sintered ore samples, the wüstite peaks appear around $t = 145$ min, i.e., $T = 725^\circ\text{C}$. The peak areas increase with time and then start to decrease at $t = 219$ min (19 min after the onset of Step II) for the hematite ore sample and at $t = 229$ min (29 min after the onset of Step II) for the sintered ore sample. In addition, Fe peaks start to appear at the same time when the wüstite peaks start to decrease. This indicates that part of wüstite is reduced to metallic iron and is saturated with Fe. Figure 9 also indicates that the reduction of wüstite in the hematite ore sample proceeds faster than that in the

sintered ore sample.

Figure 10 shows changes with time of the diffraction angles of wüstite (200) peaks for the hematite and sintered ore samples together with the heating profile, where the diffraction peak angle has been derived from the XRD profile regressed to the Pseudo-Voigt function. With respect to the hematite ore, the diffraction peak angle decreases with time from $t = 145$ min in Step I at which time wüstite appears to $t = 219$ min in Step II at which time wüstite becomes saturated with iron. During this process, the decrease in diffraction peak angle stems from the thermal expansion of lattice constant as well as the change of non-stoichiometry of FeO, *i.e.*, the decrease in the value of x in Fe_{1-x}O . Subsequently, the diffraction peak angle keeps constant up to the onset of Step III. This is because neither the thermal expansion of lattice constant nor the decrease in the value of x takes place. In Step III, the diffraction peak angle decreases with time again owing to the thermal expansion of lattice constant during the heating cycle. With respect to the sintered ore, in contrast, the diffraction peak angle always decreases even when wüstite is saturated with iron at $1\,000^\circ\text{C}$ although the negative gradient becomes moderate. This decrease in the diffraction peak angle would be associated with the variation in the peak intensities of FeO and CW.

Figure 11 shows a conceptual illustration to explain how the diffraction peak angle decreases owing to the variation of the peak intensities of FeO and CW. As aforementioned, the total peak of wüstite (200) consists of the peaks of FeO and CW and the diffraction angle of the CW peak is smaller than that of the FeO peak. Now consider that the decreasing rate of the peak intensity of FeO is larger than that of CW, as shown in Fig. 8, which indicates that the diffraction angle of the total peak shifts to lower angles. As a consequence, the decrease in the diffraction peak angle during Step II for the sintered ore sample in Fig. 7 is due to the increase in the peak intensity of CW relative to that of FeO, suggesting that a considerable amount of CW still remained during Step II. Both Figs. 10 and 11 suggest that the reduction of FeO proceeds faster than that of CW, *i.e.*, the reducibility of FeO is higher than that of CW. This result is inconsistent with the most previous studies: As aforementioned, Noguchi *et al.*¹⁰⁾ have reported that the reduction rates of CW and FeO are almost the same above $1\,000^\circ\text{C}$. The reason for this inconsistency may be due to the fact that the effective reducibilities of FeO and CW are measured for practical sintered

ores in this study. In fact, the phase structure around wüstite would affect the reducibility of wüstite. It is known that skeleton hematite in sintered ores causes the pulverization of ores around 400 to 700°C in a blast furnace because of the volume expansion from Fe_2O_3 to Fe_3O_4 .¹⁶⁾ Adhesive slag surrounding Fe_2O_3 might be cracked, and open pores might be formed so as to enable the reducing gas to directly reach the FeO phase. However, the reason why the reducibility of FeO is higher than that of CW should be studied based on the structural observations.

4.2. Effect of Hydrogen Additions on Reduction Process from FeO and CW to Metallic Iron

Figure 12 shows peak areas of wüstite (200) and Fe (110) for the sintered ore samples as a function of heating time, obtained in reduction experiments with and without hydrogen additions, together with the heating profile: the

Fig. 11. Conceptual illustration to explain how the diffraction peak angle decreases owing to the variation of the peak intensities of FeO and CW.

Fig. 10. Changes with time of the diffraction angles of wüstite (200) peaks for the hematite and sintered ore samples together with the heating profile.

Fig. 12. Peak areas of wüstite (200) and Fe (110) for the sintered ore samples as a function of heating time, obtained in reduction experiments with and without hydrogen additions, together with the heating profile.

Fig. 13. Changes with time in the diffraction angles of wüstite (200) peaks derived from reduction experiments on the sintered ore samples with and without hydrogen additions.

peak area has been derived from the XRD profile regressed to the Pseudo-Voigt function. It can be seen that the relative area of the wüstite peak reaches the maximum in about 10 min earlier with hydrogen additions than without hydrogen additions. Besides, it can also be seen that the reduction rate of wüstite with hydrogen additions is faster than that without hydrogen additions. These results suggest the possibility that hydrogen additions promote the reducibility of sintered ores. To examine the effect of hydrogen additions from the viewpoint of the peak shift in the same manner as Fig. 10, the changes with time in the diffraction angles of wüstite (200) peaks are compared in Fig. 13, which shows the data derived from reduction experiments on the sintered ore samples with and without hydrogen additions, where the diffraction peak angle has been derived from the XRD profile regressed to the Pseudo-Voigt function.

In case of no hydrogen additions, as mentioned in 4.1, the diffraction peak angle always decreases even after wüstite is saturated with iron at 1 000°C, suggesting that a considerable amount of CW still remained during Step II. In case of hydrogen additions, in contrast, the diffraction peak angle does keep constant for the same period. This indicates that the reduction rate of CW is comparable to that of FeO, which suggests that the reduction of CW is accelerated by hydrogen additions, *i.e.*, the reducibility of CW is comparable to that of FeO in the presence of hydrogen. Sasaki and Hida have reported that the needle like calcium ferrite that is a type of calcium ferrites is surrounded by fine pores.¹⁷⁾ It is considered that hydrogen more easily penetrates through such fine pores rather than carbon monoxide owing to the smaller molecular size of hydrogen.

5. Conclusions

High-temperature X-ray diffraction analysis has been applied to Fe₂O₃ reagent powders, hematite ore powders and sintered ore powders to examine the reducibilities of FeO and CW in CO–CO₂–He with and without hydrogen. Examination was carried out based on the fact that wüstite produced from Fe₂O₃ reagent and hematite ore powders contains only FeO whereas wüstite produced from sintered ore powders contains both FeO and CW. The samples were heated up to 1 000°C at a rate of 8.33×10^{-2} K/s (Step I),

held at 1 000°C for 100 min (Step II) and then increased up to 1 250°C at a rate of 8.33×10^{-2} K/s (Step III) to simulate a blast furnace condition.

The findings and conclusions obtained are summarized as follows:

(1) The wüstite peak for Fe₂O₃ reagent powders disappears during Step II while those of hematite and sintered ore samples remain until Step III. The difference would stem from the difference in the particle sizes of sample powders (the particle size of Fe₂O₃ sample is about 1 μm while those of hematite ore and sintered ore samples are in the range 38–75 μm).

(2) The diffraction peak of wüstite (200) reduced from sintered ore consists of those of FeO and CW. The relative intensities of these peaks affect the diffraction angle of the total peak of wüstite, which shifts to lower angles even while wüstite is saturated with iron at 1 000°C (Step II) where the peak intensity of CW increases relative to that of FeO.

(3) In reduction experiment on the sintered ore sample with no hydrogen additions, the diffraction peak angle decreases even while wüstite is saturated with iron at 1 000°C (Step II), suggesting that the reduction of FeO proceeds faster than that of CW and that the reducibility of FeO is higher.

(4) In reduction experiment on the sintered ore sample with hydrogen additions, the diffraction peak angle keeps almost constant while wüstite is saturated with iron at 1 000°C, suggesting that the reducibility of FeO is comparable to that of CW in the presence of hydrogen.

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REFERENCES

- 1) K. Sato, S. Suzuki, Y. Sawamura and K. Ono: *Tetsu-to-Hagané*, **68** (1982), 2215.
- 2) N. Sakamoto, H. Fukuyo, Y. Iwata and T. Miyashita: *Tetsu-to-Hagané*, **70** (1984), 504.
- 3) T. Maeda and Y. Ono: *Trans. Iron Steel Inst. Jpn.*, **25** (1985), 1191.
- 4) Y. Yamaoka, H. Hotta and S. Kajikawa: *Tetsu-to-Hagané*, **66** (1980), 1850.
- 5) K. Mori, R. Hidaka and Y. Kawai: *Tetsu-to-Hagané*, **66** (1980), 1287.
- 6) H. Kokubu, A. Sasaki, S. Taguchi and N. Tsuchiya: *Tetsu-to-Hagané*, **68** (1982), 2338.
- 7) S. Khalafalla and P. Weston: *Trans. TMS-AIME*, **239** (1967), 1494.
- 8) H. Inoue, Y. Kiritani and Y. Takahashi: *Bull. Res. Inst. Miner. Dressin. Metall.*, **31** (1975), 118.
- 9) M. Moukassi, M. Gougeon, P. Steinmetz, B. Dupre and C. Gleitzer: *Metall. Trans. B*, **15B** (1984), 383.
- 10) D. Noguchi, K. Ohno, T. Maeda, K. Nishioka and M. Shimizu: *Tetsu-to-Hagané*, **98** (2012), 55.
- 11) Y. Iguchi and S. Hayashi: *Tetsu-to-Hagané*, **79** (1993), 431.
- 12) T. Miwa, H. Okuda, M. Osame, S. Watakabe and K. Saito: *EECR-METEC InSteelCon 2011*, Steel Institute VDEh, Düsseldorf, (2011), Session 1, CD-ROM.
- 13) T. Inami and K. Suzuki: *ISIJ Int.*, **42** (2002), 150.
- 14) T. Inami and K. Suzuki: *ISIJ Int.*, **43** (2003), 314.
- 15) T. Mitsunaga and M. Saigo: *Powder Diff.*, **3** (2002), 173.
- 16) H. Nogami, Y. Ueki, T. Murakami and S. Ueda: *Tetsu-to-Hagané*, **100** (2014), 227.
- 17) M. Sasaki and Y. Hida: *Tetsu-to-Hagané*, **68** (1982), 563.