Comparison between Reducibilities of Columnar Silico-ferrite of Calcium and Aluminum (SFCA) Covered with Slag and Acicular SFCA with Fine Pores

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Reducibilities of silico-ferrite of calcium and aluminum (SFCA) have been examined using high temperature X-ray diffraction (XRD) analysis including the effect of hydrogen. Two types of sample were prepared: columnar SFCA covered with slag and acicular SFCA with fine pores, denoted by 'Columnar SFCA' and 'Acicular SFCA', respectively. These samples were synthesized using chemical reagents and iron ore powders. XRD analysis was applied to the samples heated in a condition simulating a blast furnace. Oxygen partial pressure was controlled by gas mixtures of CO–CO₂–He, and there were some cases where 3.9 vol% of hydrogen gas was added to the mixture. The microstructures of the samples before and after heating were observed by electron probe microanalysis (EPMA). XRD profiles indicated: (i) both SFCA samples were reduced to Fe *via* calcio-wüstite (CW), (ii) the reduction from 'Acicular SFCA' to CW took place at lower temperatures than that of 'Columnar SFCA' during the heating cycle up to 1 000°C, and (iii) CW produced from 'Acicular SFCA' was reduced to Fe earlier than CW from 'Columnar SFCA' at 1 000°C. These results suggest that SFCA and CW phases in 'Acicular SFCA' have higher reducibility than those in 'Columnar SFCA'. This would be because 'Acicular SFCA' consists of smaller SFCA particles with fine pores. BSE images have revealed that such microstructures still remained even after the reduction to CW. Additions of hydrogen promoted reduction of 'Columnar SFCA' more effectively, and this effect was observed more remarkably in the reduction from CW to Fe than from SFCA to CW.

KEY WORDS: acicular SFCA; columnar SFCA; calcio-wüstite; high temperature X-ray diffraction; reduction; microstructure; hydrogen addition.

1. Introduction

Sinters are the main iron source for a blast furnace, and the reducibility of sinters is one of the crucial factors affecting the operation stability of a blast furnace.^{1–3)} Sint-ers are primarily composed of hematite (Fe₂O₃), magnetite (Fe₃O₄), calcium ferrite (mainly silico-ferrite of calcium and aluminum (SFCA)) and slag phases; among them, Fe₂O₃ and SFCA are in main proportion. Sint-ers are reduced in a blast furnace, which reduction process is very complicated because temperature as well as gas components change depending on the position of the furnace. This reduction normally proceeds *via* two steps: (i) Fe₂O₃, Fe₃O₄ and SFCA are reduced to wüstite in the lower temperature zone and (ii) wüstite is reduced to metallic iron (Fe) in the thermal reserve zone and in the even higher temperature zone. The overall reduction efficiency of a blast furnace is dominated by the second-step reaction rate at higher temperatures.^{4–6)}

It is noted that there are two types of wüstite in reduced sinters: one is wüstite (denoted by FeO) reduced from Fe₂O₃ containing less impurities and the other is calcio-wüstite (denoted by CW) reduced from SFCA - both FeO and CW have the rock-salt structure. In the previous work,⁷⁾ it has been found from high temperature X-ray diffraction (XRD) analysis that the reducibility of FeO is higher than that of CW. Now it should also be noted that there are two types of SFCA that produces CW: one is columnar SFCA covered with slag and the other is acicular SFCA with fine pores.¹⁾ Both types of SFCA are often contained in commercial sinters, and thus it is of great importance to evaluate the difference between the reducibilities of these two types of SFCA to optimize the production process of sinters.

Many studies have been made on the reducibilities of columnar and acicular SFCA, and several researchers have insisted from reduction experiments of practical sinters that the reduction rate of acicular SFCA is greater than that of columnar SFCA.^{1,3,8–11)} For example, Sato *et al.*¹⁾ have evaluated the reducibilities of sinters from the viewpoint of the microstructures. They have found that the sinters mostly

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composed of acicular SFCA with fine pores have higher reduction index (RI) at 900°C than those composed of columnar SFCA covered with slag. Maeda and Ono³⁾ have also focused on the relation between the microstructure and the reducibility of sinters. They have observed the microstructures of two sinters having different phase constituents before and after heating in reducing gas, and have reported that acicular SFCA is reduced much faster than Fe₂O₃ and Fe₃O₄. These previous reports suggest that the reducibility of iron ores is dominated by constituent phases such as Fe₂O₃, Fe₃O₄, SFCA and slags as well as morphologies such as columnar and acicular SFCA. However, it is very difficult to conclude effects of the phases and morphologies on the reducibilities of columnar and acicular SFCA because systematic variation cannot be made for the fraction of constituent phase and its morphology as long as practical iron ores are used as samples.

On the other hand, Sakamoto *et al.*⁸⁾ have synthesized samples with a single sinter structure from chemical reagents. They have concluded that the sample composed of fine Fe₂O₃ and fine SFCA particles has higher reducibility than the sample with columnar SFCA covered with slag, which has been explained by faster diffusion of reducing gas through the sample having smaller particle sizes and less slag volume. As is the case with many other studies, Sakamoto *et al.* have carried out the reduction experiments at 900°C, which is the same as that used for RI measurement. However, the reduction reaction from FeO or CW to Fe mostly proceeds at higher temperatures than 900°C in a blast furnace. Accordingly, to totally understand the reducibility of SFCA, reduction experiments should be made using samples with homogeneous microstructures at changing temperatures and oxygen partial pressures simulating a blast furnace condition, including the reduction process from CW to Fe. Against this background, this study aims to compare the reducibilities between two types of SFCA, *i.e.*, columnar SFCA covered with slag and acicular SFCA with fine pores, using high temperature X-ray diffraction (XRD) analysis to discuss from the perspective of microstructure. In addition, hydrogen effect on the reducibility is also examined.

2. Experimental

2.1. Preparation of SFCA Samples

Samples used in this study were two types of synthesized samples having homogeneous structures: columnar SFCA covered with slag ('Columnar SFCA') and acicular SFCA with fine pores ('Acicular SFCA'). **Table 1** shows the nominal compositions of these samples. 'Columnar SFCA' samples were synthesized according to the method conducted by Maeda and Ono.¹²⁾ Reagent grade powders of Fe₂O₃, CaCO₃, SiO₂ and Al₂O₃ were weighed to the desired compositions and mixed in an alumina mortar. The mixed

powder was calcined at 1 000°C for 3 h, and then crushed and mixed again. The calcining, crushing and mixing processes were repeated three times. About 12 g of the powder was then charged into an alumina crucible and melted in air at 1 300°C for 0.5 h. Subsequently, the sample was cooled down to 1 100°C at a cooling rate of 4.9°C/s, and then quenched into an ice-water mixture.

'Acicular SFCA' samples were synthesized using an iron ore and reagent grade CaCO₃. The iron ore was crushed and sieved to obtain particles sized under 90 μm. The CaCO₃ reagent was calcined in air for 24 h to obtain CaO. Powdery iron ore and CaO were weighed so that the CaO/SiO₂ ratio was 2, and then mixed in an alumina mortar. About 0.45 g of mixed powders were uniaxially pressed into a shape of disc using a piston cylinder die of 10 mm in diameter. The compaction pressure of 40 MPa was applied for 30 s. The prepared sample was heated in air at 1 275°C for 10 min, and then cooled down to room temperature in air.

Both 'Columnar SFCA' and 'Acicular SFCA' samples were crushed and sieved to obtain particles in the range 38–75 μm in diameter to be subjected to reduction experiments in a high temperature XRD apparatus.

2.2. Characterization of Synthesized Samples

Electron probe microanalysis (EPMA) was used to observe microstructures of synthesized SFCA samples, and the compositions of the phases were quantitatively analyzed by point analysis, where the beam diameter was about 1 μm. An accelerating voltage of 15 kV and a probe current of 20 nA were used. For quantitative analysis, standard samples were prepared: Fe₂O₃ was used for Fe, and a homogeneous glassy sample of 12.5(mass%)Fe₂O₃-41.7CaO-33.3SiO₂-12.5Al₂O₃ for Si, Ca, Al and O.

Some of columnar and acicular SFCA samples were crushed into fine powders using an alumina mortar and a pestle and were subjected to XRD analysis to identify major constituent phases before heating. This XRD analysis was carried out with CoKα 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 diffraction-scanning rate was 0.5°/min, and the scan range of 2θ was between 10° and 80° covering all the compounds in the samples.

2.3. Reduction Experiments in High Temperature XRD Apparatus

About 400 mg of sample powders were mounted into a shallow flat alumina holder (17 mm length × 9 mm width × 0.8 mm depth). The holder was horizontally placed on the heating plate with a Pt heating element in the center of the furnace. To protect the sample powders from reacting with the holder, an iron foil 0.1 mm thick was placed under the sample powders. The iron foil is not considered to affect the experimental system because it has been confirmed after the experiment that the iron foil is not reacted with the sample powders. The furnace was installed in the sample chamber (Φ 116 mm × 102 mm depth) of a high temperature X-ray diffractometer as shown in **Fig. 1**.⁷⁾ The X-ray generator had the maximum power of 10 kW (40 kV and 250 mA). The Co-Kα line was used as the X-ray source. The optical system of a parallel beam was employed. The scan range of

Table 1. Nominal compositions of columnar and acicular SFCA samples (mass%).

	Fe ₂ O ₃	SiO ₂	CaO	Al ₂ O ₃	CaO/SiO ₂
Columnar	65.0	7.8	23.3	3.9	3.0
Acicular	80.5	6.2	12.3	1.0	2.0

Fig. 1. Schematic diagram of the high-temperature X-ray diffractometer.

2θ was $33\text{--}55^\circ$ covering the peaks of the main compounds. The diffraction scan rate was $5^\circ/\text{min}$ and the scan step was 0.02° . To know the relative amounts of SFCA and CW, diffraction peak areas were derived from XRD profiles. To evaluate the change with time in the peak area more accurately, a diffraction scan rate of $1^\circ/\text{min}$ and a scan step of 0.02° were employed in the 2θ range of $39.3\text{--}41.6^\circ$ and $47.2\text{--}49.5^\circ$, respectively, for SFCA and CW. The diffraction angle was calibrated by means of the external standard specimen method using high purity silicon powders at room temperature. Temperature of samples was measured by an R-type thermocouple placed in the vicinity of the sample with the accuracy of $\pm 0.1^\circ\text{C}$.

Figure 2 shows the experimental conditions of temperature and gas composition in the present study, which are the same as in the previous work.⁷⁾ Oxygen partial pressure in the furnace was adjusted using gas mixtures of CO–CO₂, the ratio of which was changed depending on temperature to simulate a blast furnace condition. To improve X-ray diffraction intensity, the gas mixture was further diluted with 50 vol% of helium gas although there is no helium gas added in the actual blast furnace condition. The ratio of CO/CO₂ is set to be the same as not added so as for the oxygen partial pressure to be the same as that in the blast furnace condition. The gas mixture was introduced to the surface of the sample through a Pt tube (3.5 mm inner diameter) placed at the center of the front door of the furnace. 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 furnace to the outside of the system. To simulate the condition of the thermal reserve zone, the sample was heated from room temperature to $1\,000^\circ\text{C}$ with a heating rate of $5^\circ\text{C}/\text{min}$ (Step I), held at $1\,000^\circ\text{C}$ for 100 min (Step II) and then heated again up to $1\,250^\circ\text{C}$ at a heating rate of $5^\circ\text{C}/\text{min}$ (Step III). During Steps I and III, temperature continuously increased at a heating rate of $5^\circ\text{C}/\text{min}$, resulting in a temperature increment of 24°C per scan covering the 2θ range of $33\text{--}55^\circ$. Preliminary experiment examines whether the current flow rate is gas supply rate

Fig. 2. Experimental conditions of temperature and gas composition.

controlling: Two sintered ore powder samples were used for reduction under the same heating history above-mentioned with the total flow rate of $1.67 \times 10^{-6} \text{ m}^3/\text{s}$ (100 ml/min) and $3.34 \times 10^{-6} \text{ m}^3/\text{s}$ (200 ml/min) respectively. The same results were obtained in both samples. Consequently, the current flow rate of $1.67 \times 10^{-6} \text{ m}^3/\text{s}$ is not supply rate controlling. These reduction experiments were repeated four times for ‘Columnar SFCA’ and twice for ‘Acicular SFCA’. For reduction experiments with hydrogen, 3.9 vol% of H₂ was also added to the gas mixture. As a result, the total flow of gas mixture was $1.73 \times 10^{-6} \text{ m}^3/\text{s}$ (103.9 ml/min). According to the FactSage thermodynamical software and databases, the calculated oxygen partial pressures with and without hydrogen addition are almost identical: For example, the oxygen partial pressures at $1\,000^\circ\text{C}$ are $6.6 \times 10^{-16} \text{ atm}$ and $5.0 \times 10^{-16} \text{ atm}$ for with and without hydrogen addition, respectively.

2.4. Confirmation of Microstructure Change in SFCA Samples

Two ‘Acicular SFCA’ samples and two ‘Columnar SFCA’ samples were employed. About 38 mg of sample powders were mounted into an alumina crucible (4 mm diameter $\times$ 3 mm height), and the crucible was horizontally placed in the center of an infrared image furnace. The samples were heated up to $1\,000^\circ\text{C}$ in the same reducing atmosphere as in Fig. 2; in 220 min and 235 min for ‘Acicular SFCA’ samples and in 240 min and 280 min for ‘Columnar SFCA’ samples, these samples were cooled down to room temperature, where temperature decreased down to 500°C in 25 s and to 150°C in another 70 s. Temperature of the furnace was controlled using a B-type thermocouple placed at the sample holder. Temperature of the sample surface was calibrated using the melting point of Au, which was placed at the same position as SFCA samples; resultantly, the temperature uniformity of the sample was within $\pm 5^\circ\text{C}$. Finally, these samples were subjected to EPMA observation.

3. Results

3.1. Microstructures and Phases of Synthesized Samples

Figure 3 shows two typical back-scattered electron (BSE) images of a ‘Columnar SFCA’ sample, where Fig. 3(a) contains skeleton hematite and slag observed near the alumina crucible, and Fig. 3(b) contains columnar SFCA phases

Fig. 3. Two typical back-scattered electron (BSE) images of a 'Columnar SFCA' sample. a: Near the alumina crucible b: Inside the sample far from the crucible.

Fig. 4. A typical BSE image of an 'Acicular SFCA' sample. a: Bulk b: Powder after sieving.

(typically 60 μm in major axis $\times$ 10 μm in minor axis), which are closely covered with slag phase and observed inside the sample far from the crucible. This difference in microstructures may stem from the sample composition change due to alumina pick-up from the crucible, which would lead to the formation of skeleton hematite. Meanwhile, XRD cannot distinguish between Fe_2O_3 -origin FeO

Table 2. Chemical compositions of the SFCA and slag phases in the 'Columnar SFCA' sample and of the SFCA phase in the 'Acicular SFCA' sample (mass%). The numbers in parentheses are the standard deviations of 5 point analyses for each phase.

Phase	Fe_2O_3	CaO	SiO_2	Al_2O_3	CaO/SiO ₂	$\text{Al}_2\text{O}_3/\text{SiO}_2$
SFCA in 'Columnar SFCA'	79.22 (1.47)	12.17 (0.31)	3.62 (0.16)	4.99 (0.11)	3.36 (0.07)	1.38 (0.07)
Slag in 'Columnar SFCA'	1.25 (0.13)	56.76 (1.24)	36.61 (0.47)	5.38 (0.14)	1.55 (0.03)	0.15 (0.04)
SFCA in 'Acicular SFCA'	82.48 (2.10)	11.55 (0.28)	4.86 (0.15)	1.11 (0.09)	2.38 (0.06)	0.23 (0.11)

Fig. 5. XRD profiles measured at room temperature (a) for 'Columnar SFCA' and (b) for 'Acicular SFCA'.

peaks and SFCA-origin CW peaks. To avoid such a situation, the outer part of the sample was removed as much as possible before reduction experiment.

Figure 4(a) shows a typical BSE image of an 'Acicular SFCA' sample. There are three different phases observed: acicular SFCA, granular Fe_2O_3 and SiO_2 . However, Fe_2O_3 phase is a minor part of SFCA and this sample is reasonable for examining the reducibility of SFCA. **Figure 4(b)** shows a BSE image for 'Acicular SFCA' powder after sieving. It can be seen more clearly that SFCA is in an acicular (or plate-like) shape (typically 10 μm in major axis $\times$ 0.5 μm in minor axis) and that 'Acicular SFCA' have many fine pores around SFCA phase.

Table 2 summarizes the chemical compositions of the SFCA and slag phases in the 'Columnar SFCA' sample and of the SFCA phase in the 'Acicular SFCA' sample. The compositions are the averages for five positions in cross-sectional areas. The numbers in parentheses are the standard deviations of 5 point analyses for each phase. Table 2 indi-

cates that the SFCA phases in both samples are quaternary calcium ferrite, the compositions of which are close to each other. **Figures 5(a)** and **5(b)** show XRD profiles measured at room temperature (a) for ‘Columnar SFCA’ and (b) for ‘Acicular SFCA’. It can be seen that both samples have the XRD peaks at the angles where the diffraction peaks due to SFCA should be observed. It is generally known that acicular calcium ferrite has a different crystalline structure from columnar calcium called SFCA-I.^{13–17} It has been reported that the content of SiO₂ in SFCA-I is around 1 mass%.¹⁷ However, the SFCA obtained in this study contains ca. 3.62 mass% SiO₂. Therefore, the acicular SFCA observed in this study is considered to be different from the SFCA-I reported by the previous studies. The intensities of Fe₂O₃ peaks in Fig. 5(a) are smaller than in Fig. 5(b), suggesting that the volume fraction of Fe₂O₃ phase in ‘Columnar SFCA’ is smaller than in ‘Acicular SFCA’. Accordingly, the ‘Columnar SFCA’ sample can also be used for the purpose of the present work. Thus, the SFCA phases in both samples are very close to each other in terms of chemical composition and crystal structure but different in terms of the morphology of SFCA and the presence of fine pores around it.

3.2. Reduction Process in Terms of High Temperature XRD Analysis

Figures 6 and **7** show typical XRD profiles of the columnar and acicular SFCA samples reduced in atmosphere with no hydrogen addition, respectively, for Step I (Figs. 6(a) and 7(a)), Step II (Figs. 6(b) and 7(b)) and Step III (Figs. 6(c) and 7(c)), where temperature on the right or the left side of Figs. 6(a), 6(c), 7(a) and 7(c) represents one at which each

scan was started for Steps I and III, and time on the left side of Figs. 6(b) and 7(b) represents the total time after heating was started. **Figures 8** and **9** show XRD profiles of the columnar and acicular SFCA samples reduced in atmosphere with hydrogen addition for Step I (Figs. 8(a) and 9(a)), Step II (Figs. 8(b) and 9(b)) and Step III (Figs. 8(c) and 9(c)). On the basis of these four figures, **Table 3** summarizes temperatures at which peaks due to Fe₂O₃, Fe₃O₄, SFCA, dicalcium-silicate (2CaO·SiO₂ denoted as C₂S), CW and Fe appear or disappear in both ‘Columnar SFCA’ and ‘Acicular SFCA’, where the time in the bracket represents when CW disappear and Fe appear at 1 000°C, and (+H₂) represents the reduction with hydrogen additions. Repeated experiments have revealed that all these data are reproducible within $\pm 5^\circ\text{C}$ for temperature in Step I and within ± 1 min for time in Step II. It is found from Table 3 that in case of no hydrogen additions, SFCA and CW phases in ‘Acicular SFCA’ disappear at lower temperatures than those in ‘Columnar SFCA’. In addition, it seems that hydrogen additions promote disappearance of SFCA and CW more effectively in ‘Columnar SFCA’. These results are discussed in detail in the discussion section.

3.3. Microstructure of Reduced Sample

Figures 10(a) and **10(b)** shows BSE images of ‘Columnar SFCA’ powders after reduction where the samples were quenched at (a) 240 min and (b) 280 min in Step II. The microstructure in Fig. 10(a) consists of three phases, *i.e.*, CW reduced from columnar SFCA, Fe and slag phases. Small amount of columnar SFCA is reduced to Fe and residual columnar SFCA is reduced to CW at 240 min. At

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

Fig. 7. Typical XRD profiles of the acicular SFCA sample reduced in atmosphere with no hydrogen addition for Step I (a), Step II (b) and Step III (c).

Fig. 8. XRD profiles of the columnar SFCA sample reduced in atmosphere with hydrogen addition for Step I (a), Step II (b) and Step III (c).

280 min in Step II, as shown in Fig. 10(b), the microstructure consists of CW, Fe, slag and silicates originating from gangue minerals originally contained in SFCA (hereinafter

denoted as ‘silicate’). Most parts of CW have been reduced to Fe at 280 min.

Figures 11(a) and 11(b) shows BSE images of ‘Acicular

Fig. 9. XRD profiles of the acicular SFCA sample reduced in atmosphere with hydrogen addition for Step I (a), Step II (b) and Step III (c).

Table 3. Temperatures (°C) at which peaks due to Fe₂O₃, Fe₃O₄, SFCA, C₂S, CW and Fe appear or disappear in both ‘Columnar SFCA’ and ‘Acicular SFCA’, where the time in the bracket represents when CW disappear and Fe appear at 1 000°C, and (+H₂) represents the reduction with hydrogen additions.

	Columnar SFCA	Columnar SFCA (+H ₂)	Acicular SFCA	Acicular SFCA (+H ₂)
Fe ₂ O ₃ disappear	495	457	495	495
Fe ₃ O ₄ appear	471	435	495	495
Fe ₃ O ₄ disappear	807	753	759	759
SFCA disappear	855	816	815	815
C ₂ S appear	789	750	750	750
CW appear	789	750	750	748
CW disappear	1 046	1 000 (264 min)	1 000 (239 min)	1 000 (234 min)
Fe appear	1 000 (239 min)	1 000 (214 min)	1 000 (219 min)	1 000 (214 min)

SFCA' powders after reduction where the samples were quenched at (a) 220 min and (b) 235 min in Step II. The microstructure before reduction shown in Fig. 4(b) contains only SFCA and Fe_2O_3 phases; in contrast, the microstructure in Fig. 11(a) consists of four phases, *i.e.*, CW reduced from acicular SFCA, FeO reduced from Fe_2O_3 , Fe and 'silicate' phases. Parts of acicular SFCA and Fe_2O_3 phases

Fig. 10. BSE images of 'Columnar SFCA' powders after reduction where the samples were quenched at (a) 240 min and (b) 280 min in Step II.

Fig. 11. BSE images of 'Acicular SFCA' powders after reduction where the samples were quenched at (a) 220 min and (b) 235 min in Step II.

are reduced to Fe at 220 min. It should be noted that most parts of CW phase still keep the same structure as acicular SFCA and have fine pores nearby. At 235 min in Step II, as shown in Fig. 11(b), the microstructure consists of CW, Fe and 'silicate' phases but most parts of CW and FeO are reduced to Fe. At this stage, 'silicate' formed by heating fills parts of fine pores; however, fine pores still remain around CW phase originating from SFCA phase.

4. Discussion

4.1. Reduction from SFCA to CW

To evaluate the reducibility of SFCA, XRD profiles shown in Figs. 6–9 are examined in more detail for SFCA, Fe_2O_3 , Fe_3O_4 and CW phases. For example, **Figs. 12(a)** and **12(b)** are more accurate XRD profiles around (a) SFCA (311) peak and (b) Fe_3O_4 (400) peak for 'Columnar SFCA': the former was recorded at 702°C and the latter at 712°C. The peak area corresponds to the relative amount of each phase present when measuring. To evaluate the relative amount of the phase, the XRD profiles relevant to SFCA (311), Fe_2O_3 (104), Fe_3O_4 (400) and CW (200) peaks are regressed to the Pseudo-Voigt function,⁷⁾ as shown in Fig. 12, to derive the peak areas.

Figures 13 and **14** show the change with time in the relative amounts of SFCA, Fe_2O_3 , Fe_3O_4 and CW phases in 'Columnar SFCA' and 'Acicular SFCA', respectively, together with the temperature history. The relative amount means the value of the peak areas calculated by

Fig. 12. Close-ups of XRD profiles around (a) SFCA (311) peak and (b) Fe_3O_4 (400) peak for 'Columnar SFCA': the former was recorded at 702°C and the latter at 712°C. The profiles fitted to the Pseudo-Voigt function are also included.

Fig. 13. Changes with time in the relative amounts of SFCA, Fe_2O_3 , Fe_3O_4 and CW phases in 'Columnar SFCA' together with the temperature history.

Pseudo-Voigt function. In both figures, SFCA and Fe_2O_3 exist at room temperature; as temperature rises, SFCA starts to decrease; instead, CW starts to appear at 750°C for 'Acicular SFCA' and at 789°C for 'Columnar SFCA'. SFCA finally disappears at 815°C for 'Acicular SFCA' and at 855°C for 'Columnar SFCA'. These results indicate that SFCA is reduced to CW and the differences in temperature suggest that 'Acicular SFCA' has better reducibility than 'Columnar SFCA', which is consistent with the previous studies.^{1,3,8–11)} As mentioned in 3.1, the SFCA phases in both samples are very close to each other in terms of chemical composition and crystal structure but different in terms of the morphology of SFCA and the presence of fine pores

Fig. 14. Changes with time in the relative amounts of SFCA, Fe_2O_3 , Fe_3O_4 and CW phases in 'Acicular SFCA' together with the temperature history.

Fig. 15. Equilibrium relations among SFCA, ' Fe_3O_4 ', CW, Fe and CO-CO_2 gas mixture along with the gas composition change with temperature in the present experimental condition, shown by the dashed line.

around it. As shown in Fig. 4(b), 'Acicular SFCA' have many fine pores around SFCA phases, which would allow the SFCA phases to contact to reducing gas directly. In contrast, as shown in Fig. 3(b), SFCA phases in 'Columnar SFCA' are closely covered with slag phase, which would be an obstacle to reducing gas penetration to SFCA and worsen its reducibility.

Now focus on Fe_2O_3 phase, which disappears at lower temperatures than SFCA; instead Fe_3O_4 appears. This indicates that Fe_2O_3 is reduced to Fe_3O_4 . On the contrary, there are previous reports that SFCA is reduced to Fe_3O_4 containing gangue minerals (denoted as ' Fe_3O_4 ') but not to CW.^{18,19)} The contradiction between the present and previous studies may be interpreted as follows: **Figure 15** shows the equilibrium relations among SFCA, ' Fe_3O_4 ', CW, Fe and CO-CO_2 gas mixture along with the gas composition change with temperature in the present experimental condition, shown by the dashed line. The equilibrium relation between SFCA and ' Fe_3O_4 ' has been reported by Usui *et al.*,²⁰⁾ and those between ' Fe_3O_4 ' and CW and between CW and Fe by Maeda *et al.*¹²⁾ Although the equilibrium phase diagram has not been completely established, it is possible to roughly estimate the temperature range of the stable region for ' Fe_3O_4 ' phase. The stable region is not large on the dashed line, and thus ' Fe_3O_4 ' would exist only for a short time during the reduction process from SFCA to Fe. That is why the diffraction peaks due to ' Fe_3O_4 ' reduced from SFCA have not been observed in this study.

Fig. 16. Changes with time in the relative amounts of CW and Fe in 'Columnar SFCA' and 'Acicular SFCA', together with the temperature history.

4.2. Reduction from CW to Fe

Figure 16 shows the change with time in the relative amounts of CW and Fe in 'Columnar SFCA' and 'Acicular SFCA', together with the temperature history. Fe phase appears almost as soon as CW phase starts to decrease, which indicates that Fe is reduced from CW. It can also be seen that CW starts to decrease at 236 min in Step II for 'Columnar SFCA' and at 213 min for 'Acicular SFCA'. This suggests that CW in 'Acicular SFCA' has better reducibility than that in 'Columnar SFCA'. As shown in Fig. 10, CW phase originating from 'Columnar SFCA' is still surrounded by slag at 1000 °C. On the other hand, some fine pores still remain around CW phases originating from 'Acicular SFCA' even after SFCA is reduced to CW, as shown in Fig. 11. This may be the main reason that CW in 'Acicular SFCA' has better reducibility than that in 'Columnar SFCA'. Taking a close look at the CW phases, it can be seen that some parts of CW reduced from SFCA is surrounded by 'silicate'. This would be an obstacle to reducing gas penetration to CW and worsen its reducibility. However, comparing to CW phases in 'Columnar SFCA', CW phases in 'Acicular SFCA' surrounded by 'silicate' phases still have an advantage in reducibility: As mentioned in 3.1, columnar SFCA phases typically have a size of 60 μm in major axis $\times$ 10 μm in minor axis while acicular SFCA phases typically have a size of 10 μm in major axis $\times$ 0.5 μm in minor axis. The penetration route through slag phase to reach the center of the CW phase is shorter in acicular CW phases than that in columnar CW phases. In general, the reducibility of CW in 'Acicular SFCA' is better than that in 'Columnar SFCA' for the two reasons above-mentioned. To the best of the authors' knowledge, there are no reports about the reducibility of acicular-SFCA-origin CW to Fe from the perspective of the morphology of SFCA.

4.3. Effect of Hydrogen Additions on Reductions from SFCA to CW and from CW to Fe

Figure 17 compares the changes with time in the relative amounts of CW and Fe in 'Acicular SFCA' obtained in experiments with and without hydrogen additions, together with the temperature history. For both reduction experiments, CW appears around 750 °C, *i.e.*, at 150 min, and Fe appears almost as soon as CW starts to disappear, which indicates that Fe is reduced from CW. CW starts to decrease at 213 min in Step II in case of no hydrogen additions, while CW starts to decrease 5 min earlier than in case of hydrogen

Fig. 17. Changes with time in the relative amounts of CW and Fe in 'Acicular SFCA' obtained in experiments with and without hydrogen additions, together with the temperature history.

Fig. 18. Changes with time in the relative amounts of CW and Fe in 'Columnar SFCA' obtained in experiments with and without hydrogen additions, together with the temperature history.

additions. From these results, there is no effect of hydrogen addition on the reduction from SFCA to CW around 750°C; however, hydrogen can slightly promote the reduction of CW in 'Acicular SFCA' at 1 000°C. It is commonly known that chemical reaction is rate controlling step at lower temperatures and the diffusion of gas in pores is rate controlling step at higher temperatures. In the present study, hydrogen addition has no effect on the CW generation from SFCA probably because the chemical reaction is rate controlling step around 750°C; the effect of hydrogen addition can be seen on the Fe generation from CW because the diffusion in the pores is rate controlling step at 1 000°C.

Figure 18 compares the changes with time in the relative amounts of CW and Fe in 'Columnar SFCA' obtained in experiments with and without hydrogen additions, together with the temperature history. In case of no hydrogen additions, CW phase appears at 789°C, *i.e.*, at 158 min and starts to decrease at 236 min in Step II. In contrast, in case of hydrogen additions, CW phase appears at 750°C, *i.e.*, at 150 min and starts to disappear about 20 min earlier than in case of no hydrogen additions. These results indicate that hydrogen additions can promote the reduction of CW in 'Columnar SFCA' at 1 000°C more effectively than in 'Acicular SFCA'. This difference would be explained as follows: CW in 'Columnar SFCA' is covered with slag phase, and hydrogen can diffuse through slag phase much faster than carbon monoxide, particularly at higher temperatures. On the other hand, CW in 'Acicular SFCA' has many fine pores around them, and the diffusion rate of carbon monoxide

through the pores would be comparable to that of hydrogen.

5. Conclusions

High-temperature X-ray diffraction analysis has been applied to 'Columnar SFCA' and 'Acicular SFCA' to evaluate the reducibilities of the samples in CO–CO₂–He with and without hydrogen additions in the temperature history simulating a blast furnace condition.

The findings and conclusions obtained are summarized as follows:

(1) SFCA and CW phases in 'Acicular SFCA' have better reducibilities than those in 'Columnar SFCA'. This would be because SFCA phases in 'Acicular SFCA' have fine pores around them, which allow SFCA phases to contact to reducing gas directly. Fine pores have also been observed around CW in the samples after reduced to CW.

(2) 'Fe₃O₄' phase reduced from SFCA has not been observed in this study, probably because Fe₃O₄ could be thermodynamically stable only for a short time during the present reduction process.

(3) Hydrogen additions can promote reduction of both 'Columnar SFCA' and 'Acicular SFCA', and this effect is more significant on 'Columnar SFCA'. In particular, hydrogen addition promotes reduction from CW to Fe at 1 000°C more effectively than that from SFCA to CW at lower temperatures.

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