Quantitative Analysis of Mineral Phases in Sinter Ore by XRD-Rietveld Method

Toru TAKAYAMA*

Reiko MURAO

Abstract

Quantitative analysis of mineral phases in sinter ore by micro-texture observation is difficult, due to inhomogeneous distribution of multi phases. Although powder X-ray diffraction is one solution, other options include identification of calcium ferrite phases with complex and similar crystal structure. In this study, the Rietveld method was applied for the quantification of sinter ore, which is based on the least-square fitting of the entire XRD pattern using crystal structure models and refinements of the crystal structure parameters. As a result, identification of several calcium-ferrite phases in sinter ore and quantification of mineral phases including calcium-ferrites in sinter ore were successfully conducted. These values are influenced by the history of the sintering reaction.

1. Introduction

Deterioration in the quality of sinter ore due to the influence of degradation in the quality of the iron ore resource is an issue in the iron-making process. Since the characteristics of sinter ore (strength, reducibility, reduction of degradation etc.) are influenced by sinter microstructures such as mineral phase, particle size, pore etc., accurate estimation of the influence of raw iron ore variation on sinter quality is required. In the case of a sinter ore which has inhomogeneous microstructure, it is difficult to obtain representative data by microscopic observation.

This study investigated the quantification of the crystalline phase in sinter ore by powder X-ray diffraction through the development of quantitative analysis techniques for the mineral phase. The major mineral phases that are composed of sinter ore microstructure are: hematite (α -Fe₂O₃), magnetite (Fe₃O₄), calcium ferrite and silicate slag. These phases are complexly distributed together with pores, and are responsible for the development of sinter ore characteristics. In particular, understanding the calcium-ferrite phase that is formed from calcium ferrite melt and bonds the nucleus particles of iron ore is important to clarify the quality and the formation reaction kinetics of sinter ore.^{1–10)} The calcium-ferrites in sinter ore are multi-component continuous solid solutions containing gangue compositions such as silica and alumina. The silico-ferrite of calcium and aluminum (SFCA) {Ca₂(Ca, Fe, Al)₆(Fe, Al, Si)₆O₂₀} and its homolog as SFCA-I {Ca₃(Ca, Fe) (Fe, Al)₁₆O₂₈} and SFCA-II {Ca₄(Fe, Al)₂₀O₃₆} have chemical compositions and crystalline structures that are different from those of SFCA.^{4,5)}

The crystalline structures of these phases are complicated, resemble each other, and their compositions in sinter ore (type and volume of dissolved element) are wide-ranging, thus rendering them different from the materials registered in the crystalline structure database. Accordingly, it is difficult to identify and determine the quantity of these calcium ferrites in sinter ore by the conventional powder X-ray diffraction method. Therefore, little quantitative analysis of mineral phases that contained multicomponent calcium ferrites in actual sinter ore has been conducted.

Therefore, in this study, the Rietveld method,^{11, 12)} an analysis technique that uses powder XRD patterns to determine the crystal structure and quantify the co-existing crystalline phases, is performed to evaluate the sinter microstructure. The Rietveld method calculates the crystal structure parameters of mineral phases based on initial crystalline structure models including lattice constants, atomic coordinates and their mass fractions. Then the entire simulated XRD patterns is compared with the calculated one, and these parameters are determined by the least square method so that the residual of them is minimum. This method is characterized by its ability to accurately determine the quantity of the mass fraction of the respective mineral phase in a material with multi phases, the diffraction peaks of which overlap each other. Furthermore, this method can determine the crystalline structure of materials that are continu-

^{*} Researcher, Materials Characterization Research Lab., Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

ous solid solutions having a complicated crystalline structure and a wide solid solution range such as multi-component calcium ferrites by refining the crystalline structure factors such as the lattice constant and atomic coordinates of a mineral phase. In addition, the results of the Rietveld method exhibit high repeatability and low arbitrariness as far as using the same initial model and the fitting procedure.

In this study, the effectiveness of Rietveld analysis for the quantitative evaluation of mineral phases in sinter ore was verified by analysis of the sinter ore samples with different mechanical strengths. Then, the mass fraction or crystal structure parameters of mineral phases in sinter ore was conducted to compare the chemical composition or the mechanical strength with them.

2. Experiment

2.1 Preparation of sample

The sinter ore sample was prepared by charging materials to a cylindrical sintering pot of 300mm in diameter and 600mm in height carefully to avoid grain size segregation, and then by burning (Fig. 1(a)). The quasiparticles of the starting material were prepared in the following manner. Lime stone was blended so that CaO is contained by 8.2 mass%, silica stone and olivine were added so that the basicity of CaO/SiO₂ becomes 1.6 (weight ratio), and coke of 4.5 mass% and water of 7.0 mass% were added outside the above figures. These materials were granulated in a five-minute drum-mixer operation. The weight and density of the quasiparticle were 60 kg and 1.62 t/m³, respectively. The top surface layer of the sample in the sinter pot was heated for 90 seconds by burners and the exhaust gas was suctioned by a blower at a constant negative pressure of 8kPa. The heating patterns of the sinter ore at the top layer (Sample A), middle layer (Sample B) and the bottom layer (Sample C) measured by thermocouples are shown in Fig. 1(b).

After burning, the sinter cake was removed from the sintering pot and was divided into three layers evenly in the height direction, and a shatter index test (JIS M 8711) was performed using each layer sample (**Table 1**). Samples with particle sizes of 5 mm or above were taken from each layer and were pulverized to particles of an average 10μ m in size by a vibration mill. The powder sinter ore samples were subjected to powder XRD measurement and chemical composition analysis. The chemical composition was determined by the following methods: Iron ores-Determination of the total iron content (JIS M 8212), Iron ores-Method for determination of the acid soluble iron (II) content (JIS M 8213), Iron ores-Method for determination of the calcium content (JIS M 8214) and Iron ores-Method for determination of the aluminum content (JIS M



Fig. 1 (a) Schematic illustration of the sinter pot test, and (b) Heating patterns of each layer in the pot¹⁹

Table 1 Results of a snutter test of each layer	r ¹⁹
---	-----------------

Sample	SI /mass%
Sample A	73.3
Sample B	85.9
Sample C	89.7

*SI: Weight of grains over +5 mm after shatter test / total sample weight

8220).

Additionally, the standard specimens of calcium ferrite singlephase used for verification of analytical accuracy of the Rietveld method were synthesized by the conventional powder sintering method.

2.2 X-ray diffraction (XRD) measurement

The sinter ore powder was filled into a sample holder made of glass plate (sample section: 20 mm width × 18 mm height × 0.2 mm depth), and the XRD measurement was conducted by an XRD measurement device (Ultima-III manufactured by Rigaku Corporation). The X-ray source was a Cu K α radiation. The tube current and the tube voltage were set at 40 mA and 40 kV, respectively. The one-dimensional detector (D/teX Ultra, Rigaku) was used with a K β filter and the measurement was conducted by a concentrated optical system.

The measurement was conducted using a stepped scanning method under the condition of a measuring angle range of 2θ =10–140°, step width of ($\Delta 2\theta$)=0.020° and scanning speed=1°/min. The divergence slit (DS) was 2/3° and the vertical divergence limitation slit was10 mm. Under this condition, the width of the radiation range becomes larger than the width of the sample in the range of low angle of 2θ =10–19° (20 mm). However, it was prioritized and determined to obtain a sufficient radiation range area in a high angle range because of the high mineral phase distribution inhomogeneity in the sinter ore sample. All X-rays out of the sample were considered as radiated to the sample and diffracted, and a correction of $1.66 \times 10^{-1}/\sin \theta$ times was rendered to the diffracted ray intensity in the range.

2.3 Rietveld analysis

2.3.1 Outline of Rietveld analysis^{11, 12)}

The Rietveld analysis, which is the least square refreshment technique of powder XRD, optimizes scale factor (*S*), crystal structure factor (F_k), preferred orientations (P_k), and other parameters of each mineral phase by calculating the diffraction intensities in the *i*-th step ($f_i(\mathbf{x})$) of each phase, as given by Eq. (1)^{11, 12}; this analysis is performed until the best fit is obtained between the observed powder diffraction pattern and the sum of the calculated patterns of each phase.^{11, 12}

$$F_{i}(\mathbf{x}) = sS_{R}(\theta_{i})A(\theta_{i})D(\theta_{i})\sum_{k}m_{k}|F_{k}|^{2}P_{k}L(\theta_{i,k})\Phi(\Delta 2\theta_{i,k}) + y_{b}(2\theta_{i})$$
(1)

Where

- *x*: structural parameters (lattice constant, atomic coordinate, atom displacement parameter etc.) used when diffraction angle 2θ and crystalline structure factor are calculated
- s: scale factor
- $S_{R}(\theta_{i})$: correction factor for sample surface roughness
- $A(\theta_i)$: absorption factor
- $D(\theta)$: constant radiation correction factor
- *K*: numerical value indicating the type of reflection contributing to Bragg reflection intensity

 m_{κ} : multiplicity of Bragg reflection at the Kth step

 F_{κ} : crystalline structure factor

 P_{k} : preferred orientation function $L(\theta_{i,k})$: Lorentz polarization factor

 $\theta_{i,K}$: Bragg angle

 $\Phi(\Delta 2\theta_{i,\kappa})$: profile function

 $v_{i}(2\theta)$: background function.

The mass fraction R_h of the *h*th phase is given by Formula (2). $R_h = (s_h Z_h M_h V_h) / (\sum_i s_i Z_i M_i V_i)$ (2)

Where

 s_i, s_j : scale factor of the phases *j* and *h*

 Z_i , Z_i : chemical formula number of phase *j* and *h* in a unit cell

 $\dot{M}_{i}, \ddot{M}_{i}$: chemical formula mass of phase j and h

 V_{i}^{j} , V_{k}^{j} : unit cell volume of component *j* and *h*.

For background correction, B-spline method, and for peak profile function, divided pseudo-Voigt function were used, respectively. In addition, preferred orientation was corrected by the March-Dollase function.

Parameters to be refined in this analysis are the background function, lattice constant, profile function and crystalline structure factor of the respective mineral phase. The secondary profile parameters V and W of the profile function, which are the values that depend on the optical system, were not optimized in this refinement. Similarly, the isotropic temperature factor T of the crystalline structure factors was also not refined. Furthermore, as the number of atoms that constitute SFCA and SFCA-I is large, and the influence of oxygen on the crystalline structure is considered small as compared with positive ions, the coordinate of oxygen atoms was fixed. The fixation of the oxygen atomic coordinate was confirmed as exerting no influence on the phase fraction and other parameters in a separate manner.

The acceptability of the analysis result was judged by the weighted reliability factor R_{wn} and an indicator S (goodness-of-fit indicator). These indicators were given by the following formulae of (3) and (4).

$$R_{wp} = \left[\frac{\sum_{i} w_{i} \{y_{i} - f_{i}(\mathbf{x})\}^{2}}{\sum_{i} w_{i} y_{i}^{2}}\right]^{\frac{1}{2}}$$
(3)

$$S = \left[\frac{\sum_{i} w_i \{y_i - f_i(\mathbf{x})\}^2}{N - P}\right]^2 \tag{4}$$

Where

w: statistical weight

y: observed intensity

N: the number of observation points

P: number of parameters adjusted.

For Rietveld analysis, Rigaku-manufactured powder X-ray analysis software PDXL ver.2.1 was used.

2.3.2 Selection of crystalline structural model to be applied to sinter ore

To execute profile-fitting in Rietveld analysis, the major mineral phases and their initial models of crystalline structure factors contained in the sample are to be determined. The mineral phases and the crystalline structure database number (ICDD) of the crystalline structure factors determined for the initial model are shown in Table 2

 α -Fe₂O₂¹³), Fe₂O₄¹⁴), SFCA phase³) and SFCA-I phase⁴) of multi-

Table 2-1 Crystal lattice constants of major mineral phases used for minar structural models	attice constants of major mineral phases used for initial structural mode	s used for initial structural	phases used	jor mineral	of major	constants o	Crystal lattice	Table 2-1
--	---	-------------------------------	-------------	-------------	----------	-------------	-----------------	-----------

			Major phases		
Crystal phase	a-Fe ₂ O ₃	$\mathrm{Fe_{3}O_{4}}$	$Ca_{2.8}Fe_{8.7}Al_{1.2}Si_{0.8}O_{20}$ (SFCA)	Ca _{3.14} Fe _{15.48} Al _{1.34} O ₂₈ (SFCA-I)	Ca ₂ SiO ₄
	Space Group: R-3c,	Space Group: Fd-3m,	Space Group: $P\overline{l}$,	Space Group: $P\overline{I}$,	Space Group: P21/n,
	<i>a</i> =0.50352 nm,	<i>a</i> =0.84045 nm,	<i>a</i> =0.90610 nm,	<i>a</i> =1.03922 nm,	<i>a</i> =0.55160 nm,
Crystal	<i>b</i> =0.50352 nm,	<i>b</i> =0.84045 nm,	<i>b</i> =1.00200 nm,	<i>b</i> =1.05945 nm,	<i>b</i> =0.67620 nm,
	$c = 1.37508 \mathrm{nm},$	$c = 0.84045 \mathrm{nm},$	c=1.09200 nm,	$c = 1.17452 \mathrm{nm},$	$c = 0.93292 \mathrm{nm},$
structure	$\alpha = 90.000^{\circ}, \beta = 90.000^{\circ},$	<i>α</i> =90.000°, <i>β</i> =90.000°,	<i>α</i> =60.300°, <i>β</i> =73.680°,	$\alpha = 94.308^{\circ}, \beta = 111.293^{\circ},$	<i>α</i> =90.000°, <i>β</i> =94.313°,
	γ=120.000°,	γ=90.000°,	γ=65.810°,	γ=109.647°,	γ=90.000°,
	$V = 0.301921 \mathrm{nm^3}$	$V = 0.593657 \mathrm{nm^3}$	$V = 0.781762 \mathrm{nm^3}$	$V = 1.105700 \mathrm{nm^3}$	$V = 0.346991 \mathrm{nm^3}$
Pafaranaas	Perkins et al.13)	Fjellvåg et al.14)	Hamilton et al.3)	Mumme et al.4)	Mori et al.15)
Kererences	(ICDD:01-080-2377)	(ICDD: 01-089-0688)	(ICDD: 01-080-0850)	(ICDD: 00-052-1258)	(ICDD: 01-076-3608)

Table 2-2 Crystal lattice constants of miner mineral phases used for initial structural models¹⁹)

	Miner phases									
Crystal phase	Fe _{0.925} O (FeO)	Ca ₂ Fe _{15.51} O ₂₅ (CFF)	Ca ₂ Fe ₂ O ₅	α -SiO ₂						
	Space Group: <i>Fm-3m</i> ,	Space Group: R32,	Space Group: Icmm,	Space Group: P1,						
	$a = 0.43064 \mathrm{nm}, b = 0.43064 \mathrm{nm},$	<i>a</i> =0.60110 nm, <i>b</i> =0.60110 nm,	<i>a</i> =0.56432 nm, <i>b</i> =1.50701 nm,	<i>a</i> =0.49160 nm, <i>b</i> =0.49170 nm,						
Crystal	<i>c</i> =0.43064 nm,	<i>c</i> =9.46900 nm,	$c = 0.54859 \mathrm{nm},$	c=0.54070 nm,						
structure	$\alpha = 90.000^{\circ}, \beta = 90.000^{\circ},$	<i>α</i> =90.000°, <i>β</i> =90.000°,	<i>α</i> =90.000°, <i>β</i> =90.000°,	<i>α</i> =90.000°, <i>β</i> =90.000°,						
	γ=90.000°,	<i>γ</i> =120.000°,	γ=90.000°,	<i>γ</i> =120.000°,						
	$V = 0.079863 \mathrm{nm^3}$	$V = 2.962977 \mathrm{nm^3}$	$V = 0.466541 \mathrm{nm^3}$	V=0.113118 nm ³						
Pafaranaas	Fjellvåg et al. ¹⁴⁾	Karpinskii et al.16)	Berastegui et al.17)	Pakhomov et al. ¹⁸⁾						
References	(ICDD: 01-089-0686)	(ICDD: 01-078-2301)	(ICDD: 01-089-8668)	(ICDD: 01-077-1060)						

component calcium ferrites and dicalcium silicate $(Ca_2SiO_4)^{15}$ of silicate slag were selected as the major composition phases in sinter ore.

Furthermore, although not clearly observed in microstructure observation by using XRD and/or a microscope, the following phases were added as minor mineral phases. They are: wustite $(FeO_x)^{14}$ that may be formed in the neighborhood of coke in a strong reducing atmosphere, dicalcium ferrite $(Ca_2Fe_{2O_3})^{16}$ and CFF $(Ca_2Fe_{15.51}O_{25})^{17}$ of pseudo two composition systems that may be formed under a condition wherein gangue scarcely dissolves into the melt of calcium ferrites. In addition, α -SiO₂ that originated from gangue in iron ore, and/or from silica stone added for basicity adjustment was added.

Rietveld analysis was conducted by refining stepwise the crystalline structure factors and profile function of the respective mineral phase. In the first place, in the order from α -Fe₂O₃ to α -SiO₂ as shown in Table 2, the lattice constant and profile function were refined simultaneously. After that, the crystalline structure factors of the major mineral phases were refined in the order from α -Fe₂O₃ to Ca₂SiO₄ sequentially. Refining for the minor mineral phase was limited to the lattice constant and profile function.

3. Result and Discussions

3.1 Evaluation of quantitative analysis accuracy of Rietveld method

Using the single phase sample of di-calcium ferrite (2CaO- Fe_2O_2) and mono-calcium ferrite (CaO-Fe_2O_2) composed by the powder sintering method, quantitative analysis accuracy of Rietveld analysis was evaluated. Phase fraction was sought by using XRD measurement and Rietveld analysis regarding the mixture of samples wherein the ratio of the single phase samples was varied, and the result was compared with the nominal weight fraction of the mixture. In Rietveld analysis, only lattice constant and profile parameters were refined. In Fig. 2, the relationship between the prepared composition ratios and the phase fractions determined by Rietveld analysis is shown. There was a mean relative deviation of about 7% between the phase fraction of di-calcium ferrite determined by Rietveld analysis and the actual nominal weight fraction. In the samples with the prepared mix ratios of less than 10%, the quantification accuracy decreased and the relative deviation increased to 10%-25%, which is allowable for comparative quantification analysis.

3.2 Result of quantification of phase fraction of constituent phase of sinter ore sample

XRD patterns of Sample A, B and C and the identification re-

sults of diffraction peaks of major mineral phases are shown in **Fig. 3**. The differences among the peak intensities of calcium ferrites of each sample are small, and the quantification and the refinement of the crystalline structure of the respective mineral phase only by comparing the peak intensity are difficult. Rietveld analysis was applied to these diffraction patterns and the obtained results are shown in **Fig. 4** and **Table 3**. Figure 4 shows the measured XRD pattern and the calculated XRD pattern refined by Rietveld analysis (shown in the upper section) and the residual difference between the two



Fig. 2 Relationship of nominal mass fraction of mixture of Ca₂Fe₂O₅ and CaFe₂O₄, and its quantitative value determined by Rietveld method¹⁹



Fig. 3 XRD patterns of sinter samples A, B and C¹⁹⁾ •: α -Fe₂O₃, \circ :Fe₃O₄, \diamond :SFCA, \diamond :SFCA-I, \diamond :Ca₂SiO₄, \odot :FeO, **=**:CFF, \diamond :SiO,



Fig. 4 Comparison of the measured (solid line) and the calculated (dotted line) XRD patterns of sinter samples A, B and C¹⁹) Differential of the profiles were shown in the bottom region of the figure.

					Quantita	ative value	e /mass%					
Sample	α-Fe O	Fe O	SECA	SFCA-I	Ca SiO	FeO	CFF	Ca Fe O	a-SiO	Total calcium ferrites (SFCA+SFCA-I	$R_{_{\!$	S
	or 1 v ₂ or 3	1°3°4	51 011	51 011 1	20104	100	011	04210205	0. D10 ₂	$+CFF+Ca_2Fe_2O_5)$		
Sample A	44.1(1)	15.5(1)	19.5(3)	8.6(2)	6.3(2)	1.7(1)	2.5(2)	0.1(1)	1.6(1)	30.7	1.81	1.01
Sample B	37.0(1)	18.9(1)	20.7(3)	11.0(3)	7.9(5)	1.2(1)	1.6(2)	n.d.	1.7(1)	33.3	1.89	1.03
Sample C	33.0(1)	23.0(1)	21.8(4)	9.3(3)	8.5(6)	1.8(1)	1.5(2)	n.d.	1.2(1)	32.6	2.03	1.06

Table 3 Quantitative value of mineral phases in sample A, B and C determined by Rietveld method¹⁹⁾

Table 4 Chemical compositions of samples A, B and C obtained by chemical and Rietveld method¹⁹⁾

Samula	Mathad	Quantitative value /mass%						
Sample	Method -	T.Fe	CaO	SiO ₂	Al ₂ O ₃			
Sample A	Chemical analysis	58.18	9.72	5.49	1.28			
	Rietveld analysis (initial)	59.8	8.6	4.8	1.6			
	Rietveld analysis (EDS)	58.9	10.0	5.8	1.2			
Sample B	Chemical analysis	56.51	10.95	6.75	1.29			
	Rietveld analysis (initial)	58.2	9.9	5.5	1.7			
	Rietveld analysis (EDS)	58.9	10.2	5.6	1.4			
	Chemical analysis	57.39	10.33	6.01	1.45			
Sample C	Rietveld analysis (initial)	58.4	10.3	5.2	1.7			
	Rietveld analysis (EDS)	59.5	9.8	5.7	1.3			
Relative deviatio	n of Rietveld analysis (initial)	2.5%	-7.3%	-14.9%	25.3%			
Relative deviation	on of Rietveld analysis (EDS)	3.1%	-2.8%	-5.6%	-5.8%			

(shown in the section below). Table 3 shows the mass fractions of the mineral phases obtained by Rietveld analysis and the reliability factor (R_{wn}, S) of the respective sample.

Rietveld analysis provided us with mass fractions of not only the main constituents, such as α -Fe₂O₃, Fe₃O₄, SFCA, SFCA-I, Ca₂SiO₄, but also the less than 5 mass% minor mineral phases such as FeO_x, CFF and α -SiO₂. In the samples, the iron oxides, α -Fe₂O₃ and Fe₃O₄occupied slightly over 50 mass% of the entire mass, and the multi-component calcium ferrites (SFCA+SFCA-I) occupied 35 mass% of the in the sinter ore samples, and less than 10 mass% slag (Ca₂SiO₄+ α -SiO₂) was present. In the subject samples, Ca₂Fe₂O₅ was scarcely formed. In any samples, R_{wp} is below 2.0% and the *S* value is about 1.1. Statistically, the fitting is judged as good.¹²

Table 4 shows the chemical analysis values of Sample A, B and C, and the compositions obtained by multiplying the mass fractions of mineral phases determined by Rietveld analysis with the compositions of the initial structural model (denoted as "initial" in Table 4). In the utmost bottom column of Table 4, the average values of relative error between the compositions by Rietveld analysis results and the chemical analysis values are shown for the three samples.

As compared with the relative error of total Fe (T.Fe) of the major compositions, the relative error of quantified values of Ca, Si and Al, which are contained both in the major mineral phases and minor mineral phases, was large. This is considered to be attributed to the difference between the initial model compositions of SFCA and SF-CA-I phases and the compositions of multiple calcium ferrite phases formed during the actual sintering operation. Furthermore, the influence of amorphous slag is considered for the error of Si composition.

For the mineral phase's mass fractions of Sample A, B and C, trends of decrease in α -Fe₂O₃ and increase in Fe₃O₄ in the direction from the top layer to the bottom layer were observed. It is inferred

that the sintering reaction in the lower layer proceeded at higher temperature and longer time than those in the upper layers. Moreover, the measured O_2 gas concentration values in the exhaust gas are 15% in the upper layer and 12% in the lower layer. Another factor that supports this trend is that the oxygen partial pressure is lower in the lower layer and Fe₃O₄ is prone to be produced more easily.

Regarding the total amount of calcium ferrites that are considered to correspond to the amount of the melt at a high temperature, there were no significant differences among samples when the quantification errors are taken into consideration. It is considered that the +5mm diameter grain sinter ore used for the analysis sample in this research has the minimum strength, and the low strength section wherein less of the calcium ferrite melt is produced was removed. It is considered that, if the entire sinter ore before the strength test is used for analysis, the lower layer is sintered at a higher temperature and the amount of the melt increases therein, and the increase in the absolute amount of calcium ferrites could be obtained as a result.

The above result shows that the mass fractions of mineral phases determined by Rietveld analysis explain the sintering reaction process. The sinter ore properties such as mechanical strength etc. are contributed by other factors such as pores, the particle size and the shape of a mineral phase in addition to the mineral phase fraction. To define the influence of these factors quantitatively, the quantification of a mineral phase by Rietveld analysis is considered to be an important step.

3.3 Crystal structure of calcium ferrite optimized by Rietveld methoed

Next, the difference in crystalline structure parameters of calcium ferrites among samples was discussed. A calcium ferrite is a continuous solid solution consisting of multi-component systems that dissolve gangue compositions,¹⁾ and the crystal structure varies depending on the composition.^{2–6)} First, to define the amount of the

solid solution of gangue on an experimental basis, the electron micrographs of the high gangue-containing calcium-ferrite microstructure (a), and of the low gangue-containing calcium ferrite microstructure (b) of Sample B shown in Fig. 5 were analyzed for the amounts of Fe, Ca, Si and Al by EDS (energy disperse X-ray spectrometry). The mean compositions at the measurement points of EDS in Fig. 5 were calculated, and based on the elemental compositions, the microstructure in Fig. 5(a) was assumed as the SFCA phase and the microstructure in Fig. 5(b) with a higher Fe concentration was assumed as the SFCA-I phase. The compositional formula of the SFCA phase corrected with the mean compositions based on EDS analysis is $Ca_{2,3}Fe_{10,3}Al_{0,6}Si_{0,8}O_{20}$ for the SFCA phase and $Ca_{3,6}Fe_{15,1}A_{10,6}Si_{0,7}O_{28}$ for the SFCA-I phase. The Al content of each phase was lower than that of the crystal structure models used in the present research.



Fig. 5 Electron micrographs of calcium ferrites and chemical compositions in sample¹⁹

(a) Calcium ferrite with high gangue $(Ca_{2,3}Fe_{10,3}Al_{0,6}Si_{0,8}O_{20})$ (b) Calcium ferrite with low gangue (Ca_{3.6}Fe_{15.1}Al_{0.6}Si_{0.7}O₂₈)

Next, to apply the compositions obtained by EDS analysis to the crystalline structural models of SFCA and SFCA-I, the occupancy rate of the cation sites in the respective crystalline structural model was modified, the result of which is shown in Table 5. We assume that the atoms at the octahedral-coordinated cation sites in the SFCA and SFCA-I phases are substituted by Fe and Ca and the tetrahedral-coordinated cation sites in the SFCA and that SFCA-I phases are substituted by Fe, Al, and Si. In the case of the SFCA phase, the occupancies of cation sites were corrected to fit to the chemical composition by making the following assumptions (the changed site occupancies are shown in bold in Table 5). Ca preferentially substitutes sites with longer oxygen bond distances in SFCA. Therefore, the occupancy of Ca/Fe12 site was changed to fit the Ca composition. Next, Si in SFCA preferentially substitutes the tetrahedral site with the shortest oxygen bond distance. Therefore, the occupancy of Si/Al15 site was changed to fit the Si composition. Al prefers to distribute to the Si/Al15 sites and the Al/Fe6 sites with the next shortest oxygen bond distance, so the site occupancies of these sites were changed to fit the Al composition. In the case of the SFCA-I phase, it was assumed that Si statically distributed at the Al substituted the tetrahedral-coordinated cation sites because Si was not contained in the initial models

The respective mineral phase fraction determined by Rietveld analysis is shown in Table 6, and the crystalline structure factors of SFCA and SFCA-I are shown in Table 7, and the parameters such as atomic coordinates of the SFCA phase of each sample are shown in Table 8, respectively. When the atomic coordinates of the initial structural model of SFCA (Table 5(a)) and those of the structural model after refining by Rietveld analysis (Table 8) are compared, particularly in the Al/Fe6 and Ca/Fe12 sites wherein the occupancy rate was modified by the EDS analysis values, changes in atomic coordinates took place after refining. This is attributed to the influ-

Table 5	Structural	model of	f SFCA ³⁾ a	nd SFCA-I ⁴⁾	based on	EDS analysis ¹⁹⁾
---------	------------	----------	------------------------	-------------------------	----------	-----------------------------

(a)	SFCA ³⁾
-----	--------------------

Atom	Coodinate	Atomi	c coodina	Occupancy		
Atom	number	х	у	Z	Ref ³)	This study
Fe1	6	0.441	0.596	0.348	1	1
Fe2	6	0.758	0.003	0.254	1	1
Fe3	6	0.669	0.693	0.458	1	1
Fe4	4	0.737	0.217	0.434	1	1
Fe5	4	0.849	0.030	0.741	1	1
Al/Fe6	4	0.837	0.529	0.235	1/0	0.4/0.6
Fe7	6	0.349	0.782	0.049	1	1
Fe8	4	0.934	0.359	0.691	1	1
Fe9	4	0.547	0.635	0.799	1	1
Fe10	6	0.000	0.000	0.000	0.5	0.5
Fe11	6	0.500	0.000	0.500	0.5	0.5
Ca/Fe12	6	0.556	0.904	0.156	0.8/0.2	0.3/0.7
Ca13	7	0.114	0.206	0.420	1	1
Ca14	7	0.127	0.664	0.951	1	1
Si/Al15	4	0.728	0.731	0.929	0.8/0.2	0.8/0.2

(b) SFCA-	$I^{4)}$					
Atom	Coodinate	Atom	ic coodin	ates	Occi	ipancy
Atom	number	х	у	Z	Ref ³⁾	This study
Cal	6	0.088	0.688	0.079	1	1
Ca2	6	0.4736	0.113	0.920	1	1
Ca3	6	0.0976	0.155	0.181	1	1
Fe4	6	0.3153	0.033	0.632	1	1
Fe5	6	0.1777	0.463	0.354	1	1
Fe/Ca6	6	0.5413	0.399	0.088	0.82/0.18	0.4/0.6
Fe7	6	0.0755	0.789	0.644	1	1
Fe/Al/Si8	4	0.0076	0.088	0.632	0.98/0.02	0.98/0.01/0.01
Fe/Al/Si9	4	0.3767	0.022	0.371	0.96/0.04	0.96/0.02/0.02
Fe10	6	0.2438	0.745	0.489	1	1
Fe11	6	0.622	0.676	0.223	1	1
Fe12	6	0.2457	0.250	0.491	1	1
Fe13	6	0.6021	0.189	0.228	1	1
Fe/Al/Si14	4	0.1316	0.473	0.636	0.84/0.16/0	0.84/0.08/0.08
Fe/Al/Si15	4	0.2404	0.477	0.082	0.9/0.1/0	0.9/0.05/0.05
Fe/Al/Si16	4	0.4955	0.407	0.366	0.94/0.06/0	0.94/0.03/0.03
Fe/Al/Si17	4	0.8431	0.3225	0.091	0.8/0.2/0	0.8/0.1/0.1
Fe/Al/Si18	4	0.1707	0.1876	0.9266	0.7/0.3/0	0.7/0.15/0.15
Fe/Al/Si19	4	0.2484	0.9721	0.0794	0.54/0.46/0	0.54/0.23/0.23
Fe20	6	0.4324	0.7142	0.3574	1	1

					Quantita	tive value	e /mass%					
Sample										Total calcium ferrites	D /0/-	c
name	α -Fe ₂ O ₃	Fe ₃ O ₄	SFCA	SFCA-I	Ca ₂ SiO ₄	FeO	CFF	Ca ₂ Fe ₂ O ₅	α -SiO ₂	(SFCA+SFCA-I+	$\Lambda_{wp}^{\prime}/70$	3
										$CFF + Ca_2Fe_2O_5)$		
Sample A	42.4(1)	14.1(1)	20.8(3)	8.2(2)	7.6(2)	1.7(1)	2.6(2)	0.8(1)	1.9(1)	32.4	1.74	0.93
Sample B	35.9(1)	19.7(1)	21.3(3)	9.6(3)	7.0(2)	1.5(1)	2.3(2)	1.2(1)	1.6(1)	34.4	1.88	1.02
Sample C	33.5(1)	23.9(1)	18.2(2)	9.2(2)	8.8(2)	1.8(1)	2.5(1)	0.9(1)	1.3(1)	30.8	1.88	0.97

Table 6 Quantitative value of mineral phases in samples A, B and C determined by Rietveld method (using modified models by EDS results)¹⁹⁾

Table 7 Crystal lattice constants of SFCA and SFCA-I refined by Rietveld method¹⁹⁾

Sample	$Ca_{2,3}Fe_{10,3}Al_{0,6}Si_{0,8}O_{20}$	$Ca_{3,6}Fe_{15,1}Al_{0,6}Si_{0,7}O_{28}$				
	(SFCA)	(SFCA-I)				
	Space Group: P1,	Space Group: P1,				
Sample A	a=0.9102(3) nm, $b=1.0124(2)$ nm, $c=1.0986(2)$ nm,	a = 1.0364(6) nm, $b = 1.0483(5)$ nm, $c = 1.1780(6)$ nm,				
Sample A	$\alpha = 60.30(2)^{\circ}, \beta = 73.42(2)^{\circ}, \gamma = 65.57(2)^{\circ},$	$\alpha = 94.16(2)^{\circ}, \beta = 111.50(3)^{\circ}, \gamma = 110.09(2)^{\circ},$				
	$V = 0.7966(5) \mathrm{nm^3}$	$V = 1.0891(6) \mathrm{nm^3}$				
	Space Group: $P\overline{l}$,	Space Group: $P\overline{I}$,				
Samula D	a=0.9109(2) nm, $b=1.0122(4)$ nm, $c=1.0984(4)$ nm,	a = 1.0406(5) nm, $b = 1.0541(5)$ nm, $c = 1.1733(6)$ nm,				
Sample B	$\alpha = 60.21(2)^{\circ}, \beta = 73.32(2)^{\circ}, \gamma = 65.48(2)^{\circ},$	$\alpha = 94.63(4)^{\circ}, \beta = 110.82(4)^{\circ}, \gamma = 110.05(4)^{\circ},$				
	$V = 0.7955(5) \mathrm{nm^3}$	$V = 1.0993(4) \mathrm{nm^3}$				
	Space Group: $P\overline{l}$,	Space Group: $P\overline{I}$,				
Samula C	a=0.9110(3) nm, $b=1.0110(3)$ nm, $c=1.0983(3)$ nm,	a = 1.0373(4) nm, $b = 1.0540(5)$ nm, $c = 1.1720(6)$ nm,				
Sample C	$\alpha = 60.23(2)^{\circ}, \beta = 73.39(2)^{\circ}, \gamma = 65.48(2)^{\circ},$	$\alpha = 94.25(3)^{\circ}, \beta = 111.51(3)^{\circ}, \gamma = 109.99(3)^{\circ},$				
	$V = 0.7948(4) \mathrm{nm^3}$	$V = 1.0959(8) \mathrm{nm^3}$				

Table 8 Atomic coordinates and occupancies of SFCA phases in (a) Sample A, (b) B and (c) C determined by Rietveld method¹⁹)

(a) Sample A				(b) Sample B				(c) Sample C						
Atom	х	у	Z	Occupancy	Atom	х	у	Z	Occupancy	Atom	х	у	Z	Occupancy
Fe1	0.443	0.573	0.386	1	Fe1	0.455	0.587	0.366	1	Fe1	0.466	0.576	0.359	1
Fe2	0.766	-0.004	0.255	1	Fe2	0.746	0.006	0.259	1	Fe2	0.760	0.003	0.242	1
Fe3	0.661	0.707	0.462	1	Fe3	0.669	0.692	0.468	1	Fe3	0.676	0.684	0.474	1
Fe4	0.761	0.215	0.421	1	Fe4	0.754	0.211	0.434	1	Fe4	0.758	0.189	0.421	1
Fe5	0.842	0.026	0.753	1	Fe5	0.844	0.026	0.733	1	Fe5	0.834	0.022	0.760	1
Al/Fe6	0.832	0.492	0.265	0.4/0.6	Al/Fe6	0.858	0.514	0.239	0.4/0.6	Al/Fe6	0.867	0.529	0.246	0.4/0.6
Fe7	0.365	0.796	0.041	1	Fe7	0.378	0.778	0.054	1	Fe7	0.353	0.782	0.057	1
Fe8	0.909	0.371	0.717	1	Fe8	0.917	0.355	0.697	1	Fe8	0.915	0.370	0.698	1
Fe9	0.535	0.627	0.799	1	Fe9	0.553	0.633	0.788	1	Fe9	0.549	0.625	0.791	1
Fe10	0.000	0.000	0.000	0.5	Fe10	0.000	0.000	0.000	0.5	Fe10	0.000	0.000	0.000	0.5
Fe11	0.500	0.000	0.500	0.5	Fe11	0.500	0.000	0.500	0.5	Fe11	0.500	0.000	0.500	0.5
Ca/Fe12	0.550	0.990	0.153	0.3/0.7	Ca/Fe12	0.546	0.896	0.170	0.3/0.7	Ca/Fe12	0.579	0.877	0.149	0.3/0.7
Ca13	0.119	0.214	0.433	1	Ca13	0.110	0.221	0.425	1	Ca13	0.099	0.227	0.407	1
Ca14	0.153	0.655	0.961	1	Ca14	0.148	0.636	0.957	1	Ca14	0.127	0.683	0.957	1
Si/Al15	0.728	0.731	0.923	0.8/0.2	Si/Al15	0.753	0.720	0.924	0.8/0.2	Si/A115	0.728	0.739	0.945	0.8/0.2

ence of the deformation (distortion) of polyhedrons caused by the occupation of elements with different effective ionic radii as a result of the difference in the occupation rates of occupying elements.

The effective ionic radii of Fe^{3+} and Al^{3+} at the tetrahedral Al/Fe6 sites are 0.039 and 0.049 nm, respectively. The effective ionic radii of Fe^{3+} and Ca^{2+} at the octahedral Al/Fe12 sites are 0.055 and 0.100 nm, respectively, and are significantly different from each other. Therefore, it is considered reasonable to have obtained such results because the coordination structure of the surrounding oxygen changed (polyhedra were distorted) and the atomic positions of cat-

ions in the SFCA phase were different between the initial model and the correction model by EDS. In **Fig. 6**(b), the crystalline structure of SFCA on the $(1\overline{1}1)$ plane is shown. The sites arranged on the same plane as the Ca/Fe12 site are Fe2, Al/Fe6, Fe7, Fe8, Fe9, Fe10, and Fe11. It is highly probable that the change in the site occupancy of the Ca/Fe12 affects the atomic coordinates of these adjacent sites. However, in this research, as the occupation site is assumed and the oxygen position is fixed in executing refinement, further study is required for the determination of the position of the cation.



Fig. 6 Polyhedral representation of the SFCA³ structure¹⁹ (a) Shows stacking of the spinel and the pyroxene modules and (b) Shows the projection along (11) plane S: Spinel module ($M_4T_2O_8$), P: Pyroxene module ($Ca_2M_2T_4O_{12}$), T: Tetrahedral site, M: Octahedral site

In this research, it was confirmed in a separate study that fixation of the oxygen atomic coordinate does not have any influence on the mass fraction and lattice constant of mineral phases. In addition, when the contents of Table 3 and Table 6 are compared, R_{up} values are better when the corrected calcium-ferrite composition is used, and further, the relative error from the chemical analysis values presented in Table 4 has been greatly improved.

3.4 Verification of lattice constant of mineral phase

The lattice constants of the respective mineral phases of Samples A, B and C after refining together with values reported in ICDD data (initial) are shown in **Fig. 7**.

The lattice constants of (a) α -Fe₂O₃, (b) Fe₃O₄, and (e) Ca₂SiO₄ among the samples were slightly varied and not significantly different from the reported values. Therefore, the crystalline structures of these phases are considered to be nearly the same among the samples. The lattice constants of Ca_{2.8}Fe_{8.7}Al_{1.2}Si_{0.8}O₂₀ (SFCA) and Ca_{3.14}Fe_{15.48}Al_{1.34}O₂₈ (SFCA-I) of the sinter ore samples differ among samples, and were different from the values reported in ICDD data. This is because the chemical compositions of the calcium ferrites in these sinter ore samples are different from those of the values reported in ICDD data. As shown in Fig. 6(a), SFCA consists of the crystalline structure of the pyroxene layer and spinel layer stacked alternately, and the balance of electric charge and the relaxation of crystalline distortion realized by substitution determine the solid-solution limit of gangue compositions and the substitution site.^{2, 0} The value of the crystalline lattice is considered to be changed by the influence.

When the effective ion radius of the respective atoms is taken into consideration, along with the decrease of the solid-solution amount of gangue elements of Al and Si, the lattice constant of calcium ferrite is considered to increase.⁶⁾ The atomic number ratio value of Fe/(Al+Si) of SFCA in the values reported in ICDD data is $8.7/(0.8+1.2)\approx 4.4$. On the other hand, in the SFCA composition model modified by EDS analysis values, Fe/(Al+Si) equals 10.3/ $(0.6+0.8)\approx 7.4$ and the rates of solid solution of Al and Si is small. Accordingly, the scale of the lattice constant tended to grow larger as compared with the values reported in ICDD data.

On the other hand, the lattice constant of $Ca_{3.14}Fe_{15.48}Al_{1.34}O_{28}$ (SFCA-I) showed a different trend depending on samples. As for the atom number ratio of Fe/(Al+Si), the values reported in ICDD data is Fe/(Al+Si)=15.48/(1.3+0)≈11.6, the EDS analysis value is Fe/ (Al+Si)=15.1/(0.6+0.7)≈11.6, and they are equivalent. Although the values reported in ICDD data do not include Si, as the SFCA-I phase in the sample contains Si, the effective ion radius of which is smaller than that of Al, it may have influenced the lattice constant, causing a change. In this research, a structural model is used by the compositions determined by EDS analysis, it ignores electric charge balance and assumes solid solution of Si to the SFCA-I phase, and the genuine crystalline structure of SFCA-I contained in the actual sinter ore has not yet been clarified. Determination of the crystalline structural model is a subject for future consideration.

4. Conclusion

XRD measurement and Rietveld analysis were applied to sinter ore samples produced in a sintering pot test, and the determination of the respective mass fractions of major mineral phases and minor mineral phases in sinter ore were verified to be practically possible. It is suggested that these mass fractions are influenced by the sintering reaction. Furthermore, it was also confirmed that Rietveld analysis enables refining of crystal parameters such as the lattice constant. Lattice constants of calcium ferrites varied depending on their own compositions. By utilizing the quantified information and crystallography knowledge obtained by Rietveld analysis, further clarification and new knowledge as to sinter ore is expected.

References

- 1) Hancart, J. et al.: CNRM Report. DS 24, 3 (1967)
- 2) Inoue, K. et al.: Tetsu-to-Hagané. 68 (15), 2190 (1982)
- 3) Hamilton, J.D.G. et al.: Neues Jahrb. Mineral. Abh. 161 (1), 1 (1989)
- 4) Mumme, W.G. et al.: N. Jb. Miner. Abh. 173 (1), 93 (1998)
- 5) Mumme, W.: N. Jb. Miner. Abh. 178 (3), 307 (2003)
- 6) Sugiyama, K. et al.: ISIJ Int. 45 (4), 560 (2005)
- 7) Webster, N.A. et al.: ISIJ Int. 43 (4), 500 (2003)
- 7) webster, N.A. et al., 1515 Int. 55 (8), 7/4 (2015)
- 8) Kimura, M. et al.: ISIJ Int. 53 (12), 2047 (2013)
- 9) Sasaki, M. et al.: Tetsu-to-Hagané. 68 (6), 563 (1982)
- 10) Hida, Y. et al.: Tetsu-to-Hagené. 73 (15), 1893 (1987)
- 11) Rietveld, H.: Act Cryst. 22 (1), 151 (1967)
- Young, R.A.: The Rietveld Method (IUCr Monographs on Crystallography-5). Oxford, Oxford University Press, 1993, p. 1
- 13) Perkins, D.A. et al.: J.Chem. Soc., Chem. Commun. (4), 229 (1991)
- 14) Fjellvåg, H. et al.: J. Solid State Chem. 124 (1), 52 (1996)
- 15) Mori, K. et al.: J. Solid State Chem. 179 (11), 3286 (2006)
- 16) Karpinskii, O. et al.: Dokl. Akad. Nauk SSSR. 282 (30), 1139 (1985)
- 17) Berastegui, P. et al.: Mater. Res. Bull. 34 (2), 303 (1999)
- 18) Pakhomov, V.I. et al.: Zh. Neorg. Khim. 38 (12), 44 (1993)
- 19) Takayama, T. et al. : Tetsu-to-Hagané. 103 (6), 397 (2017)



Fig. 7 Comparison of lattice constants refined by Rietveld method of major mineral phases in samples A, B and C, and the one reported in ICDD



Toru TAKAYAMA Researcher Materials Characterization Research Lab. Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Reiko MURAO Researcher, Dr. Eng. Materials Characterization Research Lab. Advanced Technology Research Laboratories