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Chemical zoning of calcium aluminoferrite formed during melt crystallization in $CaO–SiO_2–Al_2O_3–Fe_2O_3$ pseudoquaternary system

Koichiro Fukuda[a,*], Takahiro Bessho[a], Ken-ichi Matsunaga[a], Hideto Yoshida[b]

[a]Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[b]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

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Abstract

In the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ pseudoquaternary system, the solid solutions of $Ca_2(Al_xFe_{1-x})_2O_5$, with $x < 0.7$ (ferrite), Ca_2SiO_4 (belite), $Ca_3Al_2O_6$ (C_3A) and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), were crystallized out of a complete melt during cooling at 8.3 °C/min. Upon cooling to 1370 °C, both the crystals of ferrite with $x = 0.41$ and belite would start to nucleate from the melt. During further cooling, the x value of the precipitating ferrite would progressively increase and eventually approach 0.7. At ambient temperature, the ferrite crystals had a zonal structure, the x value of which successively increased from the cores toward the rims. The value of 0.45 was confirmed for the cores by EPMA. The chemical formula of the rims was determined to be $Ca_{2.03}[Al_{1.27}Fe_{0.68}Si_{0.02}]_{\Sigma 1.97}O_5$ ($x = 0.65$). As the crystallization of ferrite and belite proceeded, the coexisting melt would become progressively enriched in the aluminate components. After the termination of the ferrite crystallization, the C_3A and belite would immediately crystallize out of the melt, followed by the nucleation of $C_{12}A_7$. The $C_{12}A_7$ accommodated about 2.1 mass% Fe_2O_3 in the chemical formula $Ca_{12.03}[Al_{13.61}Fe_{0.37}]_{\Sigma 13.98}O_{33}$, being free from the other foreign oxides (SiO_2 and P_2O_5).

Keywords: Calcium aluminoferrite; $Ca_3Al_2O_6$; Ca_2SiO_4; $Ca_{12}Al_{14}O_{33}$; Microstructure

1. Introduction

A complete series of calcium aluminoferrite solid solutions (ferrite), $Ca_2(Al_xFe_{1-x})_2O_5$ with $x < 0.7$, is formed at ordinary pressures in the binary $Ca_2Fe_2O_5-Ca_2Al_2O_5$ system [1]. Chemical zoning often occurs during slow crystallization of ferrite from the melt [2,3]. When the complete melt of a composition in the solid solution is cooled, the first formed ferrite crystals will have a lower Al/Fe ratio than the bulk composition; as cooling is continued, the Al/Fe ratio of the deposited crystal progressively increases. Thus, the resultant crystals will be enriched in Fe_2O_3 at the cores and enriched in Al_2O_3 at the rims.

The phase stability in a part of the P_2O_5-bearing pseudoquaternary $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system was investigated over the temperature range of 1700–1360 °C in a previous study [4]. Above 1378 °C, α-Ca_2SiO_4 solid solution (α-belite) and melt coexist in equilibrium, and the α'_H - belite and $Ca_4Al_2Fe_2O_{10}$ (C_4AF) coexisted below 1368 °C. However, at temperatures between 1378 and 1368 °C, the three-phase mixture of the α'_H -belite, ferrite and melt was stable. The chemical compositions of these three phases at 1370 °C are plotted on portions of the quaternary system (Fig. 1). The ferrite is enriched in Fe_2O_3 with respect to Al_2O_3 than C_4AF; thus, the relative composition of the coexisting melt is poor in Fe_2O_3. When the mixture of α-belite and melt is cooled below 1378 °C, the melt is induced to differentiate by the crystallization of ferrite and α'_H -belite. During further cooling below 1368 °C, the aluminate phases were eventually crystallized out of the melt. The resulting phase composition (i.e., belite, ferrite and aluminates) at ambient temperature was therefore distinct from that which is thermodynamically most stable (i.e., belite and ferrite).

In the present study, the zoned ferrite has been examined to determine the concentration distributions of Al_2O_3 and Fe_2O_3 within the crystals. As the concurrent crystallization of the ferrite and belite proceeds during cooling, the Al/Fe ratio of the coexisting melt would successively increase, which results in the crystallization of the aluminates.

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* Corresponding author. Tel.: +81-52-735-5289; fax: +81-52-735-5289.

E-mail address: fukuda.koichiro@nitech.ac.jp (K. Fukuda).

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2. Experimental

2.1. Materials

In a previous study [4], crystals of ferrite and belite coexisted in equilibrium with a melt at 1370 °C. The present specimen was prepared from the appropriate amounts of reagent-grade chemicals (Table 1), the bulk chemical composition of which is the same as that of this particular melt. The mixture was pressed into pellets (12 mm diameter and 3 mm thick), heated to 1500 °C at 26.7 °C/min, completely melted for 1 h, cooled to 1000 °C at 8.3 °C/min, then quenched in air. During the slow cooling, the ferrite crystals developed, in the presence of melt, together with much smaller amounts of belite and aluminate crystals. A small amount of P_2O_5 was added to suppress the β-to-γ phase transition during quenching and prevent the disintegration of the belite crystals.

2.2. Characterization

A polished thin section was prepared and the micro-texture was observed with both transmitted and reflected light. Backscattered electron micrograph and concentration distribution maps for Al_2O_3, Fe_2O_3, CaO, SiO_2 and P_2O_5 were obtained using an electron probe microanalyzer (EPMA, Model JXA-8900L, JEOL, Tokyo, Japan). The area of analysis on the sample was 300 × 300 μm with 600 × 600 pixels and the dwell time was 15 ms. The accelerating voltage was 15 kV, the probe current was 0.012 μA and the electron probe diameter was approximately 1 μm. Quantitative spot analyses were made within the same area. The corrections were made by ZAF routines.

Table 1
Preparation of raw mixture

Reagent	Bulk composition (mass%)
SiO_2	4.69
Fe_2O_3	17.66
Al_2O_3	13.42
$CaHPO_4\ 2H_2O$	0.38
$CaCO_3$	63.84
Total	100
Substance	**Bulk composition (mass%)[a]**
SiO_2	6.53
Fe_2O_3	24.59
Al_2O_3	18.69
P_2O_5	0.22
CaO	49.97
Total	100
SiO_2*	6.72
	Atomic ratio
Al/Fe	1.19
Al/(Al + Fe)	0.54

[a] Recalculated for nonvolatile components. The amounts of P_2O_5 are added to those of SiO_2 as $0.847P_2O_5$; the total $[SiO_2 + 0.847P_2O_5]$ is denoted by SiO_2.

3. Results and discussion

3.1. Zonal structure of ferrite crystal

The lath-shaped phenocrysts shown in Fig. 2 are of ferrite. They showed, in transmitted light, a zonal structure

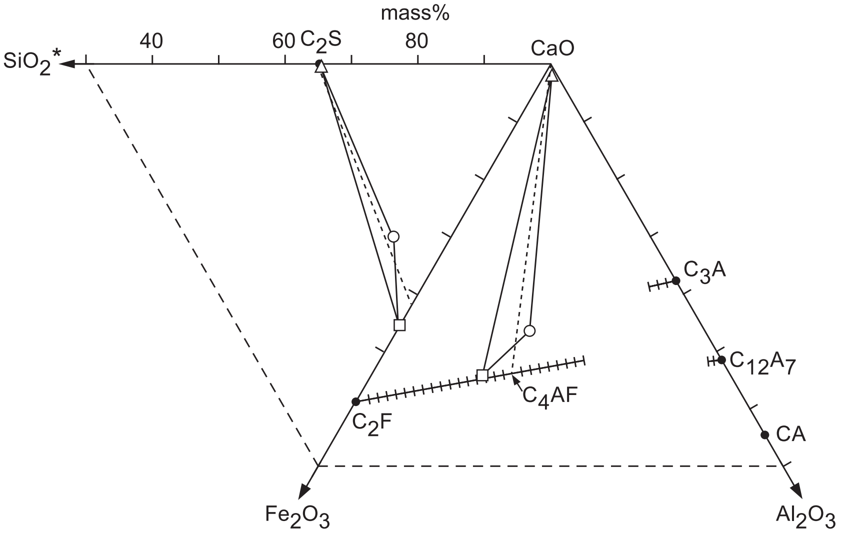

Fig. 1. Compositions of melt (○), ferrite (□) and belite (△) on portions of the quaternary system $CaO-Al_2O_3-Fe_2O_3-SiO_2$* [4]. The three phases coexist in equilibrium at 1370 °C. The amounts of P_2O_5 are added to those of SiO_2 as $0.847P_2O_5$ and the total $[SiO_2 + 0.847P_2O_5]$ is denoted by SiO_2* [4]. The hatched lines indicate solid solutions in the formulas $Ca_2(Al_xFe_{1-x})_2O_5$ with x between 0 and 0.7 [1], and $Ca_3(Al_{1-y}Fe_y)_2O_6$ with y between 0 and 0.077. The limit of the latter solid solution is 4.5 mass% Fe_2O_3 [5].

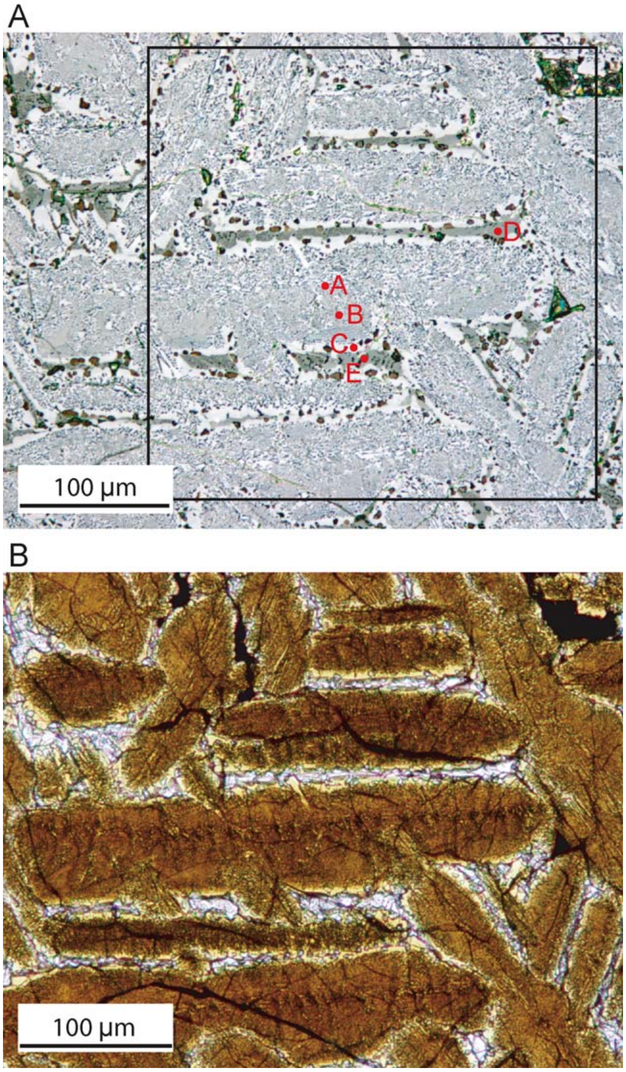

Fig. 2. Optical micrograph of lath-shaped ferrite phenocrysts and much smaller crystals of belite and aluminates. Polished thin section etched with nital. (A) Reflected light and (B) transmitted light. The zonal structure from the cores toward the rims is clearly recognized for the ferrite phenocrysts by the change in color from dark brown to yellowish pale brown in (B). Red closed circles mark the locations of the electron probe microanalyses referred to in the text.

with a color varying from dark brown at the cores to yellowish pale brown toward the rims (Fig. 2B). The crystallization was accompanied by the intergrowth of minute (< 1 μm) crystals of belite, rendering the entire phenocrysts grayish rather than white in reflected light (Fig. 2A). However, the rims of the phenocrysts were completely free from the minute crystals of belite. Thus, the ferrite rims impart a white color in reflected light and are transparent in transmitted light (Figs. 2 and 3). The belite crystals within the rims were much larger (up to 10 μm) than those in the inner regions (Fig. 3).

The chemical zoning of ferrite was confirmed by the concentration distribution maps for Al_2O_3 and Fe_2O_3 (Fig. 4). The cores were richer in Fe_2O_3 than the rims, while the concentration of Al_2O_3 was inversely distributed in agreement with a previous study [2,3]. These two maps, as well as the quantitative spot analyses at points A, B and C in Fig. 3, reveal that the Al/Fe ratio gradually increased from the core to the rim (Table 2). The chemical compositions determined at points A and B are for the mixtures of ferrite and belite. Thus, their chemical data lie between the two phases when plotted as mass ratios on the $CaO-Al_2O_3-Fe_2O_3-SiO_2$ quaternary diagram (Fig. 5). Because the concentrations of both Al_2O_3 and Fe_2O_3 are much higher for the ferrite than for the belite, the values for their relative concentrations are almost identical to those of the ferrite. Accordingly, the Al/(Al + Fe) values of the ferrite would be 0.45 at point A, and 0.50 at point B (Table 2). The composition at point C was representative of the ferrite rim; it had the chemical formula $Ca_{2.03}(Al_{1.27}Fe_{0.68}Si_{0.02})_{1.97}O_5$, the Al/(Al + Fe) value of which is 0.65 (Table 2). As a result, the zonal structure of the ferrite phenocryst was characterized by the progressive increase in the Al/(Al + Fe) value from 0.45 at the cores to 0.65 at the rims. The chemical zoning of the ferrite was also clearly demonstrated in the backscattered electron micrograph in Fig. 6.

3.2. Crystallization of aluminates and belite

Between the ferrite phenocrysts, viewed under reflected light, dark gray regions occur consisting of aluminates (Fig. 2A). They were adjacent to the ferrite rims with sharp interface boundaries. Each region was revealed under magnification to be subdivided into two areas, the fields with and without the minute crystals of belite (Fig. 3). The area indicated by point D in Fig. 2A was completely free from the belite crystals and rich in the Al_2O_3 component, as demonstrated by the concentration distribution map for

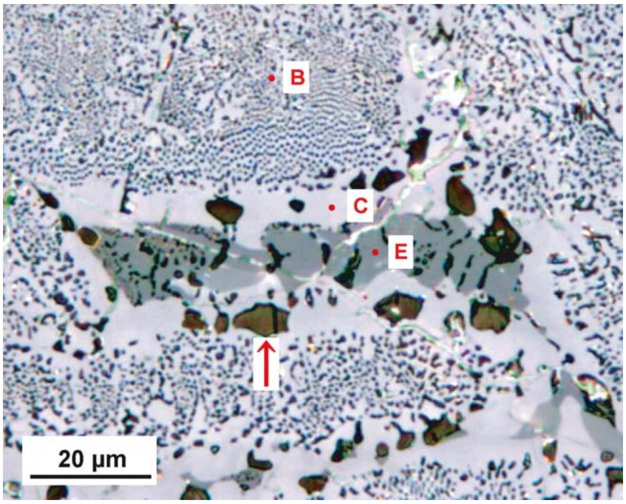

Fig. 3. Magnification of a part of the area in Fig. 2A. Red closed circles, the diameter of which corresponds to 1 μm, mark the locations of the electron probe microanalyses referred to in the text. One of the large belite crystals within the ferrite rims is indicated by an arrow.

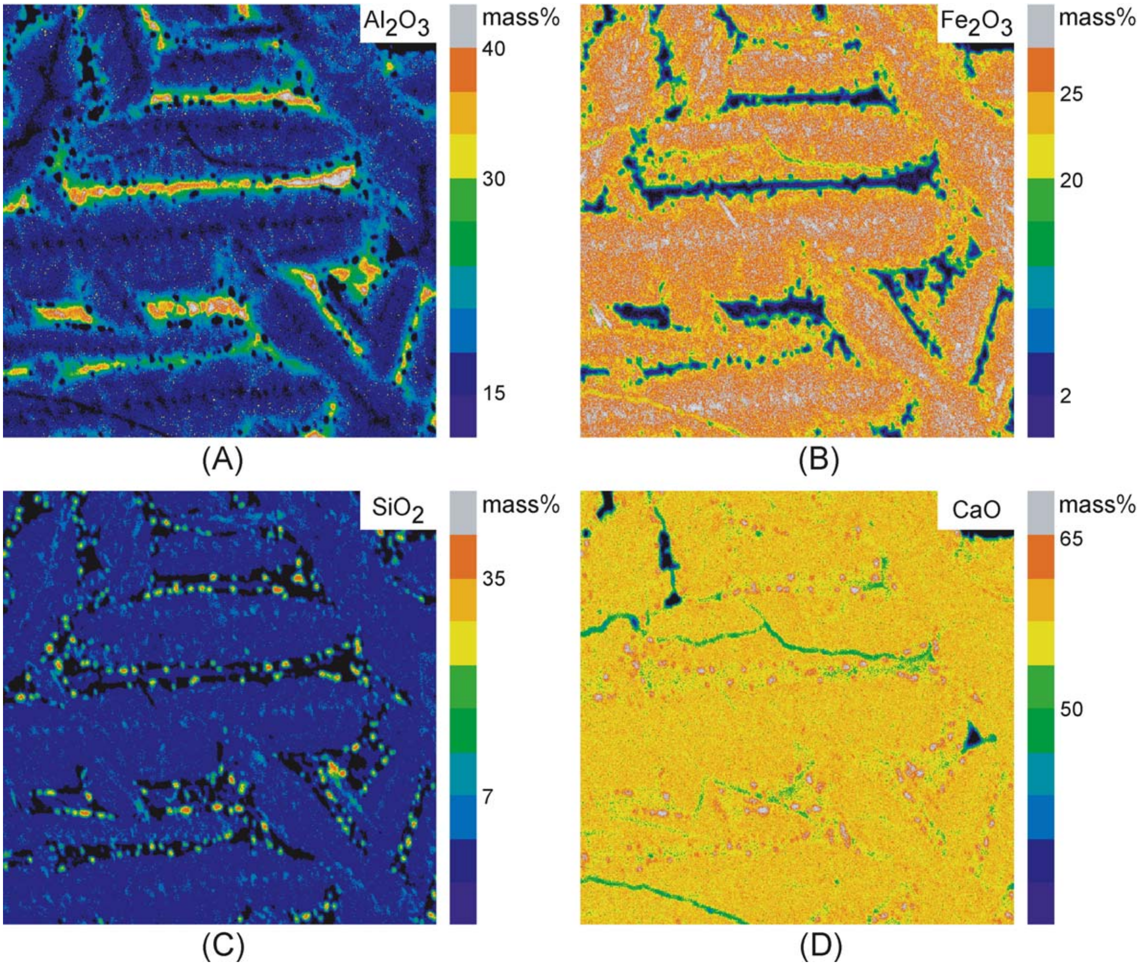

Fig. 4. Concentration distribution maps for (A) Al_2O_3, (B) Fe_2O_3, (C) SiO_2 and (D) CaO in the area depicted by the open square in Fig. 2A. The figures beside the color columns represent the mass percentage of the relevant oxides.

Al_2O_3 (Fig. 4A). The quantitative analysis at this point showed that this area was exclusively composed of the $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) solid solution, which accommodated about 2.1 mass% Fe_2O_3, while other oxides, SiO_2 and P_2O_5, were not detectable (Table 2). The solid solution range of the $C_{12}A_7$ in Fig. 5 is depicted based on this result. The quantitative chemical data at sampling point E (Table 2) lies, when plotted as mass ratios on the $CaO-Al_2O_3-Fe_2O_3$ ternary diagram (Fig. 5), between the two hatched lines indicating the solid solutions of $Ca_3Al_2O_6$ (C_3A; approximately 38 mass% Al_2O_3) and $C_{12}A_7$ (approximately 50 mass% Al_2O_3). These imply that the two compounds were actually formed in those regions, and the crystals of the C_3A solid solution were always formed along with the belite.

The distribution of the belite crystals is well shown by the concentration map for SiO_2 (Fig. 4C), because this component is mainly present in belite. The inner regions of the ferrite phenocrysts showed a relatively high concentration of SiO_2 (above 7 mass%) due to the coexistence of the minute belite crystals. The CaO component was distributed almost uniformly over the entire constituent phases, showing a slight concentration effect in the belite (Fig. 4D). The P_2O_5 component also showed a tendency to concentrate in belite. However, the extremely low concentration of P_2O_5 provided a low resolution for the distribution map, which was therefore omitted in the present paper.

3.3. Crystallization sequence of the melt during cooling

Upon cooling a melt from 1500 °C, both ferrite and belite would start to crystallize at around 1370 °C. The Al/(Al + Fe) value of the initial ferrite is expected to be 0.41, because this value is of that particular ferrite which was in equilibrium with the melt at 1370 °C. Actually, the comparable value of 0.45 was determined for the cores of the ferrite phenocrysts. Upon further cooling, the Al/(Al + Fe) value of the precipitating ferrite would progressively increase and ultimately approach the extreme value of 0.7. For the ferrite rims, the value of 0.65 was actually determined. At this stage of the ferrite crystallization, its Al/(Al + Fe) value would remain essentially fixed at around 0.7. Both the ferrite with this particular composition and belite would continue to crystallize out of the melt. The large size belite crystals within the ferrite rims were most probably formed during this

Table 2
Chemical compositions determined at sampling points A–E in Fig. 2A

Substance	Chemical composition (mass%)[a]				
	Point A	Point B	Point C[b]	Point D[c]	Point E
SiO_2	7.90	7.31	0.41	ND	5.00
Fe_2O_3	27.67	25.78	23.19	2.12	2.09
Al_2O_3	14.49	16.71	27.67	49.61	42.40
P_2O_5	0.17	0.14	ND	ND	ND
CaO	49.77	50.06	48.73	48.27	50.50
Total	100	100	100	100	100
SiO_2 *	8.04	7.43	0.41		5.00
	Atomic ratio				
Al/Fe	0.82	1.02	1.87	36.70	31.70
Al/(Al + Fe)	0.45	0.50	0.65	0.97	0.97

ND is not detectable.
The amounts of P_2O_5 are added to those of SiO_2 as $0.84P_2O_5$; The total $[SiO_2 + 0.847P_2O_5]$ is denoted by SiO_2.

[a] Total is normalized to be 100 mass%.

[b] Atomic ratios are derived based on five oxygen atoms, leading to the chemical formula of ferrite as $Ca_{2.03}[Al_{1.27}Fe_{0.68}Si_{0.02}]_{\Sigma 1.97}O_5$.

[c] Atomic ratios are derived based on 33 oxygen atoms, leading to the chemical formula of $C_{12}A_7$ solid solution as $Ca_{12.03}[Al_{13.61}Fe_{0.37}]_{\Sigma 13.98}O_{33}$.

period, which would be long enough for the belite crystals to undergo ripening. During subsequent cooling, equilibrium within the ferrite crystals is not attained, and hence the zonal structure is preserved to ambient temperature.

As the simultaneous crystallization of ferrite and belite proceeds, the coexisting melt would become progressively enriched in the aluminate components. Immediately after the termination of the crystallization of ferrite, the aluminates and belite would start to precipitate out of the residual melt. Accordingly, the regions composed of the aluminates and belite were necessarily adjacent to the ferrite rims with sharp interface boundaries. The crystallization probably comprises two stages; the concurrent crystallization of C_3A and belite, followed by the nucleation of $C_{12}A_7$. The end result would therefore be the mixture of the two areas with different phase compositions, one is composed of both C_3A and belite, and the other is mainly made up of $C_{12}A_7$.

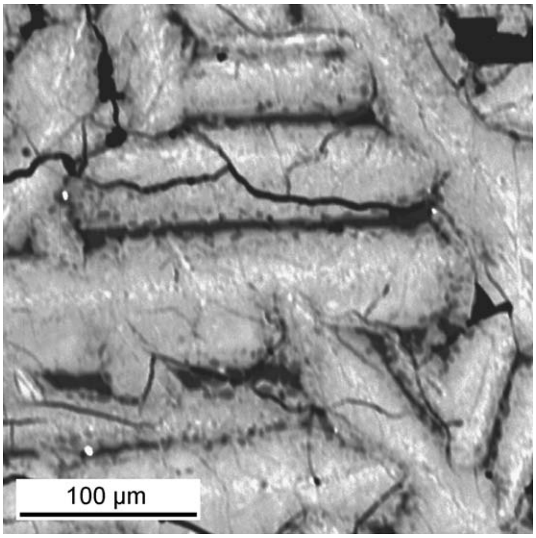

Fig. 6. Backscattered electron micrograph showing the zonal structure of ferrite phenocrysts in the area depicted by the open square in Fig. 2A. The brightness in the ferrite phenocrysts gradually decreases from the cores toward the rims, which corresponds to the progressive increase in the Al/Fe ratio.

4. Conclusions

(1) Upon cooling to 1370 °C, both the ferrite with Al/(Al + Fe) = 0.41 and belite would simultaneously crystallize out of the complete melt. During further cool-

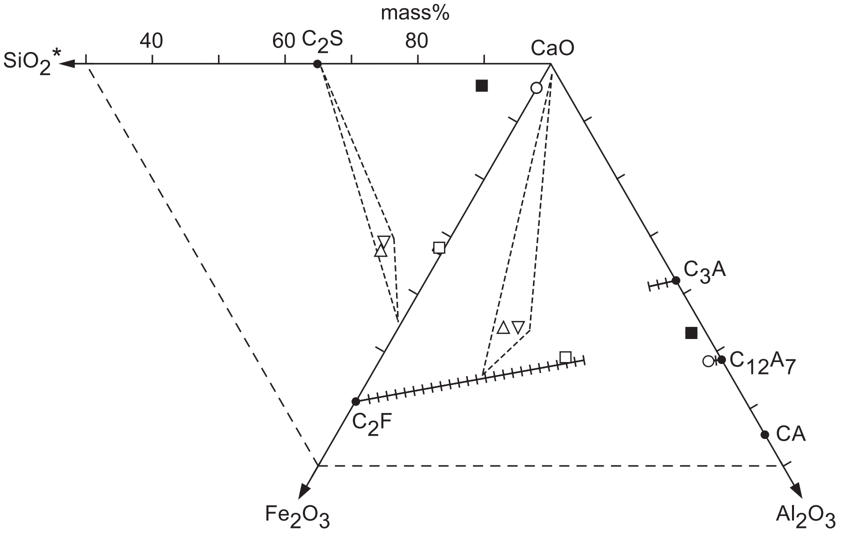

Fig. 5. Analytical data for sampling points A (△), B (▽), C (□), D (○), and E (■) in Fig. 2A. Compositions are plotted on portions of the quaternary system $CaO–Al_2O_3–Fe_2O_3–SiO_2$*. The hatched lines indicate solid solutions. Analysis connected by broken lines is coexisting melt, ferrite and belite at 1370 °C [4]. The amounts of P_2O_5 are added to those of SiO_2 as $0.847P_2O_5$ and the total $[SiO_2 + 0.847P_2O_5]$ is denoted by SiO_2*.

ing, the Al/(Al + Fe) value of the precipitating ferrite would progressively increase and become approximately 0.7.

(2) At ambient temperature, the ferrite phenocrysts showed a zonal structure, the Al/(Al + Fe) value of which successively increased from the cores toward the rims. The value of 0.45 was confirmed for the cores, and the chemical formula was determined to be $Ca_{2.03}[Al_{1.27}Fe_{0.68}Si_{0.02}]_{\Sigma 1.97}O_5$ [Al/(Al + Fe) = 0.65] for the rims.

(3) As the crystallization of the ferrite and belite proceeded, the coexisting melt would become enriched in the aluminate components. Immediately after the termination of the crystallization of ferrite, the C_3A and belite would start to crystallize out of the residual melt, followed by the crystallization of $C_{12}A_7$.

(4) The $C_{12}A_7$ accommodated about 2.1 mass% Fe_2O_3 in the chemical formula $Ca_{12.03}[Al_{13.61}Fe_{0.37}]_{\Sigma 13.98}O_{33}$, being free from the other foreign oxides (SiO_2 and P_2O_5).

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