

Article

# The Effects of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the Formation Process of Silico-Ferrite of Calcium and Aluminum (SFCA) by Solid-State Reactions

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**Abstract:** The silico-ferrite of calcium and aluminum (SFCA) is a significant crystalline phase that bonds in high basicity sinter. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> play an important role in the formation of SFCA in the Fe<sub>2</sub>O<sub>3</sub>–CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system, but the effect mechanism of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the formation of SFCA is unclear. To investigate this effect, sintering experiments were carried out with different temperatures and different times. It was found that the reaction of Al<sub>2</sub>O<sub>3</sub> with CaFe<sub>2</sub>O<sub>4</sub> (CF) as an initial product was easier to form during the calcium iron aluminum oxide (CFA) than that of SiO<sub>2</sub> with CF to form SFC. This was due to the former directly forming to CFA while the latter initially formed Ca<sub>2</sub>SiO<sub>4</sub> (C<sub>2</sub>S) and Ca<sub>2.5</sub>Fe<sub>15.5</sub>O<sub>25</sub>, and then SFC. It was also observed that when Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> existed simultaneously, the Al<sub>2</sub>O<sub>3</sub> initially reacted with CF to form CFA at 1100 °C, while the SiO<sub>2</sub> participated in the formation of SFCA at 1150 °C without the formation of SFC. Moreover, it was understood that these were different effects in that the Al<sub>2</sub>O<sub>3</sub> promoted the transformation from the orthorhombic crystal system to the triclinic crystal system, while the SiO<sub>2</sub> dissolved into CFA to form the SFCA phase when Al<sub>2</sub>O<sub>3</sub> existed.

Keywords: Al<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>; SFCA; formation process; solid-state reactions

## 1. Introduction

Silico-ferrites of calcium and alumina (SFCA) is a vital bonding phase in the high basicity sinter as a main material in blast furnace for iron-making, the formation process of SFCA has been studied by many researchers [1–5]. Inoue and Ikeda [6] first reported that the SFCA was a solid solution of calcium ferrite with CaSiO<sub>3</sub>–Ca(Fe, Al)<sub>6</sub>O<sub>10</sub> which existed in the CaO–Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. Patrick et al. [7] also reported that the chemical composition of SFCA was located on the plane of CaO  $\cdot$  3Fe<sub>2</sub>O<sub>3</sub>–CaO  $\cdot$  3Al<sub>2</sub>O<sub>3</sub>–4CaO  $\cdot$  3SiO<sub>2</sub>. Mumme et al. [8] studied the crystal structure of the SFCA by a method of structure refinement to report that it belongs to a triclinic crystal system with P1 space group. On the other hand, many scholars have also studied the precursor in the formation process of SFCA. In Fe<sub>2</sub>O<sub>3</sub>–CaO–SiO<sub>2</sub> system, Hamilton et al. [9] reported a silico-ferrite of calcium (SFC) phase appeared as an alumina-free equivalent SFC. Furthermore, Ding et al. [10,11] studied the formation mechanism and the crystal structure of SFC in which Fe<sub>2</sub>O<sub>3</sub>, CaFe<sub>2</sub>O<sub>4</sub> (CF) and Ca<sub>2</sub>SiO<sub>4</sub> reacted to form the SFC that belongs to a triclinic crystal structure. In the Fe<sub>2</sub>O<sub>3</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> system, Lister et al. [12] reported a ternary phase in which CaO·3(Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>) appeared in the ternary system. Furthermore, Mumme et al. [13] studied a detailed composition of Ca<sub>5.1</sub>Al<sub>9.3</sub>Fe<sup>3+</sup><sub>18.7</sub>Fe<sup>2+</sup><sub>0.9</sub>O<sub>48</sub> and understood that it belongs to a triclinic crystal structure. Guo et al. [14] reported that the CF and hematite solid solution with the Al<sub>2</sub>O<sub>3</sub> could react to form the CFA. The SFC phase, CFA phase, and SFCA phase had the same crystal structure and similar XRD patterns. This made it difficult to identify and track aluminum



and silicon involved in the formation of SFCA. The SFC and the CFA were considered as a precursor of the SFCA formation [15], but it was unclear as to how to transform CF, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to SFCA. For example, Scarlett et al. [16,17] reported that CF appeared as an original in the calcium ferrite phase before the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> participated in the formation of SFCA. Webster et al. [18] reported that C<sub>2</sub>F, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> reacted to form CFA and then SFCA. The possibility of SFC and CFA formation as precursors has an important effect on SFCA formation. Therefore, it is necessary to compare the formation process of SFC and CFA under the same conditions. In this work, the effect of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the SFCA formation process was investigated by XRD, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). Rietveld quantitative methods were used to study the reaction rate of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with CF. These results are helpful in understanding the important role of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the SFCA formation process.

#### 2. Experimental Section

#### 2.1. Sample Preparation

The materials used were analytical grade hematite (Fe<sub>2</sub>O<sub>3</sub>), calcium hydroxide (Ca(OH)<sub>2</sub>), silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>). The materials were ground to a particle size of less than 50  $\mu$ m in an agate mortar to enable full contact in the mixing process. The starting material composition of the sintering experiments are listed in Table 1. The CF was considered to be the initial bonding phase that appeared during the formation of SFCA [19–21]. In order to compare the effect of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the formation of the precursor, the sintering experiment of CF reacted with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was carried out. The CF was prepared by an equal molar ratio of Ca(OH)<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> at 1200 °C for 2 h [11]. The XRD confirmed it to be a pure phase, and then the sintered CF was crushed into particles with size less than 50  $\mu$ m. The molar ratio of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to CF was selected as 0.5 and 1 respectively. The mole ratio of Si<sup>4+</sup> to Al<sup>3+</sup> was 1, which was consistent with the ratio of Si<sup>4+</sup> to Al<sup>3+</sup> in SFCA for comparing the effect of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the precursor formation. The powdered sample was homogenized in an agate mortar with anhydrous ethanol for 30 min, and then pressed to 8 mm in diameter and 2 mm in thickness under a pressure of 5 MPa in a die. The samples were sintered for different periods of time (5 min, 15 min and 60 min) at 1100 °C and 1150 °C respectively in a resistance furnace.

The composition of SFCA varied in iron ore sinters [22]. The composition of SFCA contained 60–76 mass % Fe<sub>2</sub>O<sub>3</sub>, 3–10 mass % SiO<sub>2</sub>, 13–16 mass % CaO, 4–10 mass % Al<sub>2</sub>O<sub>3</sub> and 0.7–1.5 mass % MgO in industrial sinters [23,24]. In order to remain consistent with the experiments of CF reactions with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, a molar ratio of 2:1 (SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub>) was selected for comparing the competitive effect of Si<sup>4+</sup> and Al<sup>3+</sup> entered into the SFCA. The powdery sample was homogenized in an agate mortar with anhydrous ethanol for 30 min, and then pressed 8 mm in diameter and 2 mm in thickness under a pressure of 5 MPa in a die. Part of the pressed samples were put into a cylindrical Pt crucible, and sintered at different temperatures (800 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C) in a resistance furnace by a solid-state reaction. The sintering time was set at 120 min to ensure the reaction was complete as our previous research [25]. The remaining part of the samples were sintered in Pt crucibles at 1200 °C at different times (2 min, 4 min, 6 min, 8 min, 10 min, 12 min, 15 min, 30 min and 60 min) in the same furnace.

In order to study the composition of the phase at the temperature, all sintered samples were quenched in liquid nitrogen. The sintering experiments were conducted under constant air pressure.

Sample	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	CaFe <sub>2</sub> O <sub>4</sub>
А		23.44			76.56
В				20.65	79.35
С	70.34	6.60	17.45	5.61	

Table 1. Composition of the starting sample (mass percent).

#### 2.2. Phase Determination (XRD, SEM and EDS)

A portion of the sintered sample was ground to less than 50  $\mu$ m for XRD analysis. The X-ray powder diffraction data was collected on a Rigaku D/MAXRB X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu *Ka* radiation ( $\lambda = 0.15406$  nm) at operating parameters of 40 kV  $\times$  300 mA, a step size of 0.02° and scan rate of 10°/min.

The remaining parts of the samples were embedded into a phenolic moulding powder by a metallographic inlaying machine, and ground with abrasive paper (600, 1000, 1200 and 1500 CW successively), before being polished for observation using SEM. A FEI Quanta 250 scanning electron microscope (FEI Quanta, Hillsboro, OR, USA) was used to observe the microstructure of the sintered sample. A XFlash 5030 EDS detector (Bruker Nano GmbH, Berlin, Germany) was used to determine the chemical composition of the phases.

#### 3. Results and Discussion

#### 3.1. Reactions between CF and SiO<sub>2</sub>, CF and Al<sub>2</sub>O<sub>3</sub>

The XRD patterns of the reaction products between SiO<sub>2</sub> and CF sintered at 1100 °C (a) and 1150 °C (b) for 5 min to 60 min are shown in Figure 1. The phases in each set of samples had been marked by different symbols. It can be seen that SiO<sub>2</sub> and CF had not reacted for 5 min at 1100 °C in Figure 1a. The phases of  $Ca_2SiO_4$  ( $C_2S$ ),  $Ca_{2.5}Fe_{15.5}O_{25}$  (CFF) and  $Fe_2O_3$  appeared at 15 min. It indicated that the SiO<sub>2</sub> reacted with CF to form  $C_2S$  and  $Fe_2O_3$ , then  $Fe_2O_3$  reacted with CF to form  $Ca_{2.5}Fe_{15.5}O_{25}$ . The diffraction peak intensity of  $C_2S$  and  $Fe_2O_3$  increased with the time. It was difficult to find the diffraction peaks of SFC until the reaction time reached 60 min. The diffraction peak intensity of  $Fe_2O_3$ and  $C_2S$  increased with the reaction temperature which indicated that the reaction rate of SiO<sub>2</sub> with CF was very fast. The diffraction peak intensity of SFC was not significant at the reaction temperature rising to 1150 °C. The generation rate of SFC was slow below 1150 °C. The XRD patterns of the reaction products between Al<sub>2</sub>O<sub>3</sub> and CF sintered at 1100  $^{\circ}$ C (a) and 1150  $^{\circ}$ C (b) for 5 min to 60 min are shown in Figure 2. The diffraction peak of CFA and  $Ca_2Fe_2O_5$  ( $C_2F$ ) appeared as products at 1100 °C for 5 min as seen in Figure 2a. It indicated that  $Al_2O_3$  can react directly with CF to form CFA and  $C_2F$ , while SiO<sub>2</sub> reacted with CF to form an intermediate  $C_2S$  and  $Fe_2O_3$ . The appearance of the  $C_2S$  layer inhibited the formation of SFC. Furthermore, the CFA phase appeared when the reaction temperature reached 1150 °C as shown in Figure 2b. The CF phase disappeared when the reaction time reached 60 min. Al<sub>2</sub>O<sub>3</sub> reacted with CF to form CFA completely and the content of CFA reached its maximum.

To compare the generate rate of SFC and CFA under the same conditions, the Rietveld refinement method [26] was used to quantify the fractions of sintered products. The Rietveld refinement technique was an important method for the structure model to contact the actual structure through the GSAS [27] computer program. The pure phase of SFC and CFA were prepared according to Mumme's research [8]. XRD patterns of SFC and CFA as shown in Figure 3, were used as crystal structure data for the Rietveld refinement. The crystal structure data of other mineral components were obtained from the Inorganic Crystal Structure Database (ICSD). The background was fitted with a sixth-order polynomial, and the peak shapes were described by pseudo-Voigt profiles.

The XRD data on the reaction of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with CF at 1150 °C, respectively, were used for the refinement quantitative due to the lack of SFC formation at 1100 °C. The Rietveld refinement sample results of SiO<sub>2</sub> and CF, Al<sub>2</sub>O<sub>3</sub> and CF sintered at 1150 °C for different times are listed in Table 2. It can be seen that the measured pattern fitted well with the calculated pattern by the value of R*p* and *Rwp*. The mass fraction of SFC increased from 2.7 to 9.8 within a timeframe of 5 min to 60 min, while the mass fraction of CFA increased from 7.5 to 57.7 within the same timeframe. The CF and SiO<sub>2</sub> did not completely react while CF could not be detected after CF reacted with Al<sub>2</sub>O<sub>3</sub> for 60 min. It indicated that Al<sub>2</sub>O<sub>3</sub> reacted more easily with CF than SiO<sub>2</sub> under the same experimental conditions. The generation rate of the CFA was faster than the SFC. Our past work [25] reported the effect of SiO<sub>2</sub> on the formation process of SFC by solid-state reactions. Combined with previous research, the schematic diagram of the SiO<sub>2</sub> reaction with CF and the Al<sub>2</sub>O<sub>3</sub> reaction with CF is shown in Figure 4. The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> participated in the formation of calcium ferrites in different forms. The SiO<sub>2</sub> and CF reacted to form Ca<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> whilst Al<sub>2</sub>O<sub>3</sub> and CF reacted to form the precursor CFA phase and C<sub>2</sub>F. That was due to the Ca<sub>2</sub>SiO<sub>4</sub> (C<sub>2</sub>S) formed from the SiO<sub>2</sub> and CF, and the C<sub>2</sub>S reacting with Fe<sub>2</sub>O<sub>3</sub> or CF to form a small amount of SFC while the Al<sub>2</sub>O<sub>3</sub> and CF formed directly to the CFA.



**Figure 1.** XRD patterns of the reaction products between SiO<sub>2</sub> and CF sintered at 1100 °C (**a**) and 1150 °C (**b**) for 5 min, 15 min and 60 min respectively.



**Figure 2.** XRD patterns of the reaction products between  $Al_2O_3$  and CF sintered at 1100 °C (**a**) and 1150 °C (**b**) for 5 min, 15 min and 60 min respectively.



Figure 3. XRD patterns of SFC and CFA sintered at 1200 °C for 8 h.

Sample	Phase Fractions (Mass Percent)								R <sub>n</sub> (%)	Rwn (%)	
	CFA	$C_2F$	$Al_2O_3$	SFC	CF	Fe <sub>2</sub> O <sub>3</sub>	$Ca_2SiO_4$	$SiO_2$	CFF	P · · ·	up i i
$CF + SiO_2$ (5 min)	-	-	-	2.7	63.0	6.8	3.3	22.6	1.6	10.3	13.5
$CF + SiO_2$ (15 min)	-	-	-	4.9	50.2	14.1	7.1	21.5	2.2	9.5	12.2
$CF + SiO_2$ (60 min)	-	-	-	9.8	34.7	25.1	8.6	18.9	2.9	9.7	12.9
$CF + Al_2O_3$ (5 min)	7.5	5.5	18.2	-	68.8	-	-	-	-	8.9	11.2
$CF + Al_2O_3$ (15 min)	20.9	18.4	14.6	-	46.1	-	-	-	-	8.6	12.3
$CF + Al_2O_3$ (60 min)	57.7	36.8	5.5	-	0	-	-	-	-	8.3	11.4

**Table 2.** Phase fractions of the sintering samples  $CF + Al_2O_3$  and  $CF + SiO_2$  determined by the Rietveld method.



Figure 4. Schematic diagram of solid-state reactions (a) SiO<sub>2</sub> + CF; (b) Al<sub>2</sub>O<sub>3</sub> + CF.

#### 3.2. Phase Composition of Calcium Ferrites Formation with Temperature

The XRD patterns of sample C sintered at different temperatures for 2 h are shown in Figure 5. Different phases at each temperature are represented by numbers in the figure. It was difficult to observe the diffraction peak of  $C_2F$  in the process of SFCA formation because the  $C_2F$  transformed to CF at 2 h. Initially, the diffraction peak of CF appeared at 800 °C and then the diffraction approached the maximum at 1000 °C. Subsequently, the diffraction peak intensity of CF decreased while peak intensity of SiO<sub>2</sub> remained unchanged. It indicated that the Al<sub>2</sub>O<sub>3</sub> reacted with CF when the temperature was over 1000 °C. Additionally, SiO<sub>2</sub> did not react with other phases when the temperature was below 1150 °C. The diffraction peaks of CFA transformed to SFCA as the diffraction peaks of SiO<sub>2</sub> disappeared at 1200 °C. Therefore, it was deduced that the SiO<sub>2</sub> participated in the formation of SFCA at 1150 °C. The microscopic photos of the quenched sample C, sintered at different temperatures are shown in Figure 6. Different mineral compositions could be distinguished by the reflectance of minerals. The CF was light grey, which was easy to distinguish from Fe<sub>2</sub>O<sub>3</sub> at 1000 °C.

The SEM images and EDS results of sample C sintered at 1100 °C (a) and 1150 °C (b) for 2 h are shown in Figure 7. It can be seen that the main phases (light gray area) were  $CaFe_2O_4$  (a-1) and CFA (a-2) in Figure 7a. The aluminum entered into the calcium ferrites to form CFA, whilst the silicon was undetected in the calcium ferrites. The aluminum entered into the CFA in the form of  $Al^{3+}$  and

replaced Fe<sup>3+</sup> due to the same valence states and their similar ionic radius. The CFA (b-1) and SFCA (b-2) were observed when the temperature reached 1150 °C. It indicated that the silicon first entered into CFA at 1150 °C. Therefore, it was confirmed that the Al<sub>2</sub>O<sub>3</sub> participated in the formation of SFCA at a lower temperature than the SiO<sub>2</sub>.



Figure 5. XRD patterns of the sample C sintered at different temperature for 2 h by solid-state reactions.



20µm

**Figure 6.** Microscopic photos of sample C sintered at different temperatures for 2 h. F:  $Fe_2O_3$ , S:  $SiO_2$ , A:  $Al_2O_3$ , CF: CaFe<sub>2</sub>O<sub>4</sub>, CFA: calcium iron aluminum oxide, SFCA: silico-ferrite of calcium and aluminum, P = pore.



**Figure 7.** The SEM and EDS results of the quenched sample C sintered at (**a**) 1100 °C and (**b**) 1150 °C for 2 h.

#### 3.3. Order of Calcium Ferrite Formation with Time at 1200 °C

The XRD patterns of sample C sintered at 1200 °C at different times are shown in Figure 8. It can be seen the CF first appeared at 2 min, and the CFA phase appeared when the time reached 4 min, while the diffraction peak intensity of SiO<sub>2</sub> was unchanged. The Al<sub>2</sub>O<sub>3</sub> reacted with CF to form CFA as the reaction time increased. The diffraction peak intensity of SiO<sub>2</sub> was unchanged until the appearance of SFCA at 8 min when Fe<sub>2</sub>O<sub>3</sub> reacted almost completely with CaO to form CF. The CFA peak at 32.15° gradually transformed to a high angle as a small amount of Si<sup>4+</sup> dissolved into CFA during the timeframe from 6 min to 10 min. The diffraction peak position of CFA was similar to that of SFCA due to their similar crystal structure. The diffraction peaks (34.25°) widened due to the superposition of the CFA and SFCA peaks. The diffraction peak position of 32.7° and 35.9° were clearly distinguished between CFA and SFCA. The SiO<sub>2</sub> continuously dissolved into SFCA, resulting in that the diffraction peak position of SFCA also gradually transformed to a higher angle. The deflection of the diffraction peak was due to smaller size Si<sup>4+</sup> (radius, 0.040 nm) substituted for Fe<sup>3+</sup> (radius, 0.064 nm) or Al<sup>3+</sup> (radius, 0.054 nm).

Under experimental conditions, the SFC, CFA and SFCA were considered thermodynamically stable. Ding [10] compared the Gibbs free energy of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> reacting with CaO respectively. Ca<sub>2</sub>SiO<sub>4</sub> had a greater negative value comparing with that of the formation reaction of CF. SiO<sub>2</sub> would react with CaO to form Ca<sub>2</sub>SiO<sub>4</sub> before the formation of SFCA. The formation of the Ca<sub>2</sub>SiO<sub>4</sub> layer inhibited contact between SiO<sub>2</sub> and CF, thus inhibiting the formation of SFC. However, Al<sub>2</sub>O<sub>3</sub> reacted directly with CF to form CFA. Al<sup>3+</sup> replaced Fe<sup>3+</sup> into calcium ferrite due to their identical valence states and similar ionic radius. Subsequently, Si<sup>4+</sup> diffused into CFA and dissolved into CFA to form SFCA.

The microscopic photos of sample C sintered at 1200 °C at different times are shown in Figure 9.  $SiO_2$  participated in the formation of SFCA after CF and CFA formed. It can be seen that the surface of  $SiO_2$  gradually decomposed, and  $SiO_2$  slowly reacted with the surrounding CFA or CF.



Figure 8. XRD patterns of sample C sintered at 1200 °C at different times by solid-state reactions.



20µm

**Figure 9.** Microscopic photos of the sample C sintered at 1200 °C for different time. F: Fe<sub>2</sub>O<sub>3</sub>, S: SiO<sub>2</sub>, CF: CaFe<sub>2</sub>O<sub>4</sub>, CFA: calcium iron aluminum oxide, SFCA: silico-ferrite of calcium and aluminum, P: pore.

The SEM images and EDS results of sample C sintered at 1200 °C at different times are shown in Figure 10. The CFA phase was detected at 4 min in Figure 10a1. The aluminum content in CFA increased when reaction time reached 6 min as shown in Figure 10b1,b2. The SiO<sub>2</sub> had a relatively complete profile and was not detected in calcium ferrites. The SiO<sub>2</sub> did not react with the surrounding CF whilst Al<sub>2</sub>O<sub>3</sub> gradually dissolved into CF to form CFA. The SiO<sub>2</sub> participated in the formation of SFCA at 8 min, and the external profile of  $SiO_2$  gradually blurred. The  $SiO_2$  began to react with the surrounding CaO and CF to form Ca<sub>2</sub>SiO<sub>4</sub>. When the silicon entered into the CFA, it prompted the transformation from the CFA phase to the SFCA phase. At 10 min, Al<sub>2</sub>O<sub>3</sub> was hard to be observed whilst the  $SiO_2$  still existed. The silicon content in SFCA increased more at 10 min than 8 min. It indicated that the Si<sup>4+</sup> continuously entered into the SFCA crystal structure. The Al<sub>2</sub>O<sub>3</sub> participated in the formation of SFCA earlier in the form of CFA in the Fe<sub>2</sub>O<sub>3</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system whilst SiO<sub>2</sub> promoted the transformation of CFA to SFCA in the form of dissolving into SFCA after the formation of CFA. As mentioned in the previous section, Ca<sub>2</sub>SiO<sub>4</sub> was used as a precursor for SiO<sub>2</sub> to participate in the SFCA reaction, whilst Al<sub>2</sub>O<sub>3</sub> reacted directly with CF to form CFA. The generation rate of the CFA was faster than SFC, resulting in CFA becoming the main precursor in the formation process of SFCA. The SFC had not been detected, indicating that silicon dissolved into CFA before the formation of SFC. The  $Al_2O_3$  promoted the transformation from the orthogonal crystal structure to the triclinic crystal structure, which provided the structural basis for the silicon dissolving.









**Figure 10.** SEM and EDS results of sample C sintered at 1200 °C at different times (**a**) 4 min (**b**) 6 min (**c**) 8 min (**d**) 10 min.

#### 4. Conclusions

To investigate the competitive effects of  $Al_2O_3$  and  $SiO_2$  on the formation process of silico-ferrite of calcium and aluminum (SFCA) by solid-state reactions,  $SiO_2$  and CF,  $Al_2O_3$  and CF reactions were carried out at 1100 °C and 1150 °C in different timeframes. The quantitative method of Rietveld refinement was used to calculate the amount of SFC and CFA at 1150 °C. The experiments on the SFCA formation mechanism with different temperatures and different times were carried out in a resistance furnace. The results are summarized as follows:

- (1) Al<sub>2</sub>O<sub>3</sub> reacted with CF to form CFA and C<sub>2</sub>F, while SiO<sub>2</sub> initially reacted with CF to form Ca<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> before SFC; the reaction rate of CFA formation is faster than that of SFC under the same conditions.
- (2) The CFA as a precursor participated in the SFCA formation at 1100 °C, while SiO<sub>2</sub> participated in the SFCA formation until the temperature reached 1150 °C.
- (3) Al<sub>2</sub>O<sub>3</sub> participated in the formation of SFCA in the form of CFA, while SiO<sub>2</sub> dissolved into CFA and promoted the formation of SFCA.

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