Effect of Alumina on Crystallization Behavior of Calcium Ferrite in Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ System

Rui-Feng Xin, Yu Du * and Xing-Min Guo *

State Key Laboratory of Advanced Metallurgy and School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
* Correspondence: yudu930413@163.com (Y.D.); guoxm@ustb.edu.cn (X.-M.G.)

Abstract: Al$_2$O$_3$ is a gangue component in iron ores, significantly influencing the formation and crystallization of calcium ferrite in the sintering process. But the mechanism of the Al$_2$O$_3$ effect on the crystallization of calcium ferrite is rarely reported. In this work, a crystallization device was designed to investigate the crystallization behavior of calcium ferrite in Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ melt under non-isothermal conditions. XRD, SEM-EDS, and optical microscopy were used to identify the crystalline phase and the microstructure of samples. The result shows that the crystal morphology of SFCA changed in the order of strip, column, and needle as the Al$_2$O$_3$ content increased. The crystallization sequence of samples containing Al$_2$O$_3$ was observed as Ca$_4$Fe$_{14}$O$_{25}$ (CF) → Fe$_2$O$_3$ → Ca$_3$Al$_{18}$Fe$_{15.48}$Al$_{1.34}$O$_{36}$ (SFCA-I) → CaFe$_4$O$_4$ (CF) → Ca$_5$Si$_2$(Fe, Al)$_{18}$O$_{36}$ (SFCA) → γ-Ca$_3$SiO$_4$ (C$_2$S). The generation pathway of SFCA-I was found to be $4Fe^{3+}$ + $4Si^{4+}$ + $3Al^{3+}$ → SFCA-I. Increasing the cooling rate can promote the formation of $C_F$ and SFCA-I, Fe$_2$O$_3$, and the amorphous phase. However, it prevented the crystallization of CF and SFCA while inhibiting the transformation of β-C$_3$S to γ-C$_3$S. When the Al$_2$O$_3$ content reached or exceeded 2.5 mass pct, the viscosity of Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ melt increased sharply, resulting in the decrease in the crystal size of calcium ferrite.

Keywords: sinter; binding phase; calcium ferrite; crystallization; alumina

1. Introduction

High-basicity sinter is mainly utilized as a critical iron-containing material for blast furnace ironmaking, where calcium ferrite is the predominant binding phase [1,2]. The mineral composition and microstructure of the binding phase has an important influence on the quality of the sinter [3–5]. Most of the binding phase is mainly complex calcium ferrite.

Recently, with the increasing consumption of high-alumina iron ores, the investigations focused on the role of Al$_2$O$_3$ in the formation and crystallization of the binding phase have increased substantially [6–8]. Researchers [9–11] have found that adding a moderate quantity of Al$_2$O$_3$ can promote the formation of complex calcium ferrite.

In sinter, some studies [12–15] revealed two primary crystal forms of complex calcium ferrite as SFCA (Ca$_5$Si$_2$(Fe, Al)$_{18}$O$_{36}$) and SFCA-I (Ca$_3$Al$_{18}$Fe$_{15.48}$Al$_{1.34}$O$_{36}$). Compared to SFCA (column and lath), needle-shaped SFCA-I is more favorable for releasing internal stress to improve the strength of the sinter [16]. Furthermore, the microstructure and morphology of complex calcium ferrite also have an important influence on the strength of sinter [17]. Webster et al. [18] investigated the effect of Al$_2$O$_3$ on the formation process and thermodynamic stability of complex calcium ferrite. Liles et al. [19] investigated SFCA using the structural refinement approach, finding that Fe$^{3+}$, Si$^{4+}$, and Al$^{3+}$ tended to occupy the tetrahedral positions of SFCA, while Fe$^{3+}$, Ca$^{2+}$ in the octahedral locations. The ion replacement is $2(Fe^{3+} + Al^{3+}) = Ca^{2+} + Si^{4+}$ on electric neutrality. In addition, lowering the temperature is aided in replacing Al$^{3+}$ ↔ Fe$^{3+}$.

Ding et al. [20] studied the crystallization kinetics of the CaO-Fe$_2$O$_3$ binary system by the DSC method using Avrami and Mo models. In addition, the crystalline surface
activation energies of Ca$_2$Fe$_2$O$_5$ (C$_2$F) and CaFe$_2$O$_4$ (CF) were calculated using the Kissinger model. It was found that the crystallization rate of C$_2$F is faster than that of CF, while when the cooling rate increases, the crystallization of CF is accelerated, where inversely the crystallization of C$_2$F is inhibited. Yang et al. [21] investigated the role of Al$_2$O$_3$ in the crystallization behavior of the Fe$_2$O$_3$-CaO-Al$_2$O$_3$ melt during the cooling process. It was found that adding a tiny quantity of Al$_2$O$_3$ can improve the preferred orientation of solid solution in CaFe$_2$O$_4$, at the same time significantly affecting the fracture toughness of the sample. Park et al. [22] revealed the influence of Al$_2$O$_3$ on the reduction performance of the Fe$_2$O$_3$-CaO-Al$_2$O$_3$-SiO$_2$ pseudo-quaternary system through in situ observation by high temperature confocal laser scanning micro-scope, finding that the increase of Al$_2$O$_3$ led to the crystallization of Fe$_2$O$_3$. With the increase of cooling rate, the crystallization of SFCA was promoted, and the reducibility was improved.

In this study, the crystallization mechanism of Al$_2$O$_3$ on the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ system was examined in the non-equilibrium state. A crystallization device was introduced where the cooling rate can be precisely measured, and this approach may assure that the crystallization morphology and composition of the sample are more realistic. The finding of this study is benefit to understand the phase transition of the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ system during the crystallization process. It lays a foundation for promoting the crystallization of SFCA to improve the quality of sinter.

2. Experimental Procedures

2.1. Preparation of Samples

Analytical grade reagents of Fe$_2$O$_3$ (≥99.9 pct, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), CaCO$_3$ (≥99.5 pct, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), SiO$_2$ (≥99.9 pct, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and Al$_2$O$_3$ (≥99.9 pct, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used to prepare the samples. The chemical composition of the initial samples is shown in Table 1. A study revealed that [23], when the molar ratio of Fe$_2$O$_3$ to CaO in the binding phase is in the range of 1.25 to 1.59 in the actual sintering process, more liquid phase and the acicular-shape, column-shaped or columnar calcium ferrite would be generated. Therefore, the Fe$_2$O$_3$ to CaO molar ratio in this study was set at 1.3. In addition, 4.0 mass pct SiO$_2$ was chosen as the gangue in the iron ores, with Al$_2$O$_3$ content range from 0 to 3.0 mass pct. To ensure that the entire crystallization process was carried out in the pure liquid phase, the liquidus temperature (LT) of each sample was calculated using FactSage 8.2 software [24].

Table 1. Chemical Compositions of samples (mass pct).

| Samples | Fe$_2$O$_3$ | CaO | SiO$_2$ | Al$_2$O$_3$ | LT (°C) |
|---------|------------|-----|---------|-------------|---------|
| No.1    | 75.64      | 20.36 | 4       | 0           | 1261    |
| No.2    | 75.45      | 20.31 | 3.99    | 0.25        | 1259    |
| No.3    | 75.26      | 20.26 | 3.98    | 0.50        | 1257    |
| No.4    | 75.07      | 20.21 | 3.97    | 0.75        | 1256    |
| No.5    | 74.88      | 20.16 | 3.96    | 1.00        | 1254    |
| No.6    | 74.51      | 20.05 | 3.94    | 1.50        | 1250    |
| No.7    | 74.13      | 19.95 | 3.92    | 2.00        | 1256    |
| No.8    | 73.75      | 19.85 | 3.90    | 2.50        | 1276    |
| No.9    | 73.37      | 19.75 | 3.88    | 3.00        | 1293    |

2.2. Sinter Process

At room temperature, Fe$_2$O$_3$, CaO, SiO$_2$, and Al$_2$O$_3$ were mixed evenly, as stated in Table 1. For improving precision, CaCO$_3$ was used to replace CaO with an equal-molar quantity for precise weighing. 20.0 g of sample and an appropriate amount of anhydrous ethanol (≥99.7 pct, Sinopharm Chemical Reagent Co., Ltd.) were mixed evenly, then roasted at 200 °C for 3 h in a drying oven under an air atmosphere. The sample was compressed into a cylindrical shape (Ø 20 × 20 mm) and sintered in a platinum crucible.
From the previous research [25–27] it was found that if the sample was held above the TL for 2 h, a molten equilibrium liquid phase would be formed.

In this experiment, in order to obtain a complete equilibrium liquid phase, the sample was heated to 1350 °C at a heating rate of 5 °C/min and held for 4 h in air atmosphere. Subsequently, the samples were treated under the condition of various cooling rates (0.02 °C/s, 5 °C/s, 15 °C/s, and 65 °C/s.) [28] as presented in Figure 1.

![Schematic diagram of cooling crystallization device.](image)

Figure 1. Schematic diagram of cooling crystallization device.

For obtaining the order of different crystallization phases, once the samples were cooled to the target temperature at a cooling rate of 0.02 °C/s, water cooling was conducted to obtain an instantaneous mineral composition at the corresponding temperature.

2.3. Phase Determination

A part in each sample was ground to a particle size of less than 50 μm passing through the sieve completely for XRD determination. The mineral phase of the crystalline powder samples was identified using a Rigaku SmartLab X-ray diffractometer (Rigaku Corporation, Tokyo, Japan). Cu Kα was used as the radiation source (40 kV, 150 mA) with a graphite curved monochromator in the diffracted beam path. The wavelength is 0.15406 nm, with a scanning speed of 10°/min, a scanning step length of 0.02°, and a scanning range (2θ) from 10° to 100°. XRD data were matched using Crystallographica Search-Match software (CSM3.0, Oxford Cryosystems Ltd., UK, Oxford).

The other part of the samples was embedded into the ethylenediamine-doping epoxy resin and polished for the microstructure observation. The mineral morphology and structure were observed by optical microscope (Optical Instrument Fifth Factory Co., Ltd., Shanghai, China) and scanning electron microscope (Zeiss GeminiSEM500, Berlin, Germany). The device is equipped with EDS (Ultim Max 170, Berlin, Germany) to detect elemental composition.

3. Results and Discussion

3.1. Effect of Al₂O₃

The composition change of the sample in equilibrium cooling process was obtained by heating to 1350 °C for 4 h and then cooling to room temperature at a rate of 0.02 °C/s. Figures 2–4 and Table 2 depicts the XRD patterns, optical micrograph, SEM, and EDS results of the crystalline samples containing varying amounts of Al₂O₃, respectively.
3. Results and Discussion
3.1. Effect of Al₂O₃

The composition change of the sample in equilibrium cooling process was obtained by heating to 1350 °C for 4 h and then cooling to room temperature at a rate of 0.02 °C/s. Figures 2–4 and Table 2 depict the XRD patterns, optical micrograph, SEM, and EDS results of the crystalline samples containing varying amounts of Al₂O₃, respectively.

**Figure 2.** XRD patterns of samples cooled at 0.02 °C/s.

**Figure 3.** Optical photos of the samples cooled at 0.02 °C/s (CF: CaFe₂O₄; C₄F₁₄: Ca₄Fe₁₄O₂₅; SFCA-Ι (CFA): Ca₃.₁₈Fe₁₅.₄₈Al₁.₃₄O₃₆; SFCA: Ca₅Si₂(Fe, Al)₁₈O₃₆; γ-C₂S: γ-Ca₂SiO₄; H: Fe₂O₃).

**Figure 4.** SEM photos of the samples cooled at 0.02 °C/s.
### Table 2. EDS results of the crystallized phases in the samples under 0.02 °C/s.

| Sample No. | Marked Points | Crystal Phase | Elements (at Pct) |
|------------|---------------|---------------|------------------|
|            |               |               | Fe   | Ca   | Si   | Al   | O    |
| 0mass%     | P₁            | C₄F₁₄         | 46.20 | 13.54 | 1.97 | 0.74 | 37.72 |
|            | P₂            | CF            | 39.38 | 21.93 | 1.38 | 0.94 | 36.37 |
|            | P₃            | γ-C₂S         | 0.61  | 40.07 | 20.33| 0.24 | 38.75 |
|            | P₄            | Fe₂O₃         | 62.63 | 0.06  | 1.45 | 0.95 | 34.91 |
| 1.0mass%   | P₂            | CF            | 41.42 | 23.82 | 0.00 | 0.10 | 34.67 |
|            | P₃            | γ-C₂S         | 0.48  | 41.01 | 19.91| 0.31 | 38.29 |
|            | P₄            | Fe₂O₃         | 67.98 | 0.14  | 0.42 | 0.91 | 30.54 |
|            | P₅            | SFCA-I        | 47.64 | 14.79 | 2.42 | 2.15 | 33.01 |
| 1.5mass%   | P₂            | CF            | 38.51 | 22.76 | 0.31 | 0.29 | 36.31 |
|            | P₃            | γ-C₂S         | 0.86  | 37.95 | 17.98| 0.26 | 38.12 |
|            | P₄            | Fe₂O₃         | 64.33 | 0.00  | 0.42 | 0.72 | 34.67 |
|            | P₅            | SFCA-I        | 43.01 | 14.34 | 3.83 | 3.65 | 35.16 |
| 2.0mass%   | P₂            | CF            | 41.02 | 24.77 | 1.40 | 1.32 | 31.49 |
|            | P₃            | γ-C₂S         | 0.64  | 42.53 | 21.15| 0.35 | 35.33 |
|            | P₄            | Fe₂O₃         | 68.94 | 0.00  | 0.42 | 0.92 | 30.10 |
|            | P₅            | SFCA-I        | 47.06 | 14.56 | 3.20 | 3.20 | 31.98 |
| 2.5mass%   | P₂            | CF            | 39.31 | 24.09 | 0.01 | 0.28 | 36.31 |
|            | P₃            | γ-C₂S         | 0.35  | 39.08 | 19.78| 0.16 | 40.63 |
|            | P₄            | Fe₂O₃         | 62.79 | 0.28  | 0.00 | 0.84 | 36.09 |
|            | P₅            | SFCA          | 41.35 | 13.26 | 3.83 | 5.00 | 36.56 |
| 3.0mass%   | P₂            | CF            | 41.32 | 26.74 | 0.00 | 0.40 | 31.53 |
|            | P₃            | γ-C₂S         | 0.94  | 45.13 | 17.11| 0.00 | 36.82 |
|            | P₆            | SFCA          | 42.86 | 13.37 | 4.17 | 7.19 | 32.41 |

It is indicated that Ca₄Fe₁₄O₂₅(C₄F₁₄), CF, γ-Ca₂SiO₄(γ-C₂S), SFCA-I, SFCA and Fe₂O₃ were crystallized. The increase of Al₂O₃ content led to the gradual decreases of C₄F₁₄, Fe₂O₃, and γ-C₂S. SFCA-I first increased and then decreased. CF and SFCA increased gradually. The detailed result is as follows:

1. When Al₂O₃ was not added, Ca²⁺ reacted with Fe³⁺ and O²⁻ to form C₄F₁₄ and CF, while Ca²⁺ reacted with Si⁴⁺ and O²⁻ to form γ-C₂S;
2. When Al₂O₃ reached 0.5 mass pct, C₄F₁₄ disappeared, and CF had gradually increased, indicating that the preferentially crystallized C₄F₁₄ reacted with Al³⁺ and Si⁴⁺ to form SFCA-I;
3. When Al₂O₃ reached 2.0 mass pct, CF and Fe₂O₃ had gradually decreased, γ-C₂S had not changed significantly, and SFCA-I increased gradually. It shows that CF also participated in the generation of SFCA-I;
4. When Al₂O₃ reached 2.5 mass pct, the iron-rich SFCA-I was transformed into SFCA (high Si, high Al). Simultaneously, it promoted the precipitation of Fe₂O₃, Fe₂O₃ and CF increased, and Si⁴⁺ was mainly involved in generating SFCA, resulting in the decrease of γ-C₂S.
5. When Al₂O₃ reached 3.0 mass pct, CF and SFCA continued to increase, while γ-C₂S decreased and Fe₂O₃ disappeared.

### 3.2. The Sequence of Crystallization Phase

Due to the strong crystallization ability of calcium ferrite, the crystallization order in the liquid phase cooling process has yet to be understood. For obtaining the sequence of various phases crystallized in the Fe₂O₃-CaO-SiO₂-Al₂O₃ system, samples of No.1, No.6, and No.9 (0, 1.5, and 3.0 Al₂O₃ mass pct) were selected to further research as cooled to the different target temperature at a cooling rate of 0.02 °C/s, and followed by water cooling. Figure 5 depicts the XRD patterns of the collected samples. It shows that adding Al₂O₃...
inhibited the formation of $C_4F_{14}$ and SFC, while it promoted the formation of Fe$_2$O$_3$, CF, and $\gamma$-C$_2$S simultaneous to the transformation of SFCA-I into SFCA. The detailed result is as follows:

(1) When Al$_2$O$_3$ was not added, the crystalline phase of quenched samples was Fe$_2$O$_3$ and $C_4F_{14}$ at 1350 °C, while Fe$_2$O$_3$ and $C_4F_{14}$ increased at 1300 °C, simultaneously CF appeared; Fe$_2$O$_3$ and $C_4F_{14}$ increased at 1280 °C, while Fe$_2$O$_3$ decreased. CF increased at 1250 °C, simultaneously SFC and $\gamma$-C$_2$S appeared while Fe$_2$O$_3$ disappeared; CF increased at 1200 °C, and CF, SFC, and $\gamma$-C$_2$S increased at 1150 °C. So it can be considered the crystallization sequence was (Fe$_2$O$_3$, $C_4F_{14}$) → CF → (SFC, $\gamma$-C$_2$S).

(2) When Al$_2$O$_3$ reached 1.5 mass pct, the crystalline phase of quenched samples was Fe$_2$O$_3$ and $C_4F_{14}$ at 1350 °C; SFCA-I appeared, simultaneously Fe$_2$O$_3$ increased at 1300 °C, but $C_4F_{14}$ disappeared; Fe$_2$O$_3$ and SFCA-I increased at 1280 °C; SFCA and CF appeared at 1250 °C, simultaneously Fe$_2$O$_3$ and SFCA-I decreased. At this time, SFCA was formed by the preferentially precipitated SFCA-I and Al$^{3+}$ and Si$^{4+}$ in the melt; CF and SFCA increased at 1200 °C, simultaneously $\gamma$-C$_2$S appeared; CF, SFCA, and $\gamma$-C$_2$S increased at 1150 °C. So it can be considered the crystallization sequence was (Fe$_2$O$_3$, $C_4F_{14}$) → SFCA-I → CF → SFCA → $\gamma$-C$_2$S.

(3) When Al$_2$O$_3$ reached 3.0 mass pct, the crystalline phase of quenched samples was Fe$_2$O$_3$ and SFCA-I at 1350 °C; SFCA-I increased while Fe$_2$O$_3$ decreased, simultaneously CF appeared at 1300 °C; Fe$_2$O$_3$ and SFCA-I decreased at 1280 °C while CF increased, simultaneously SFCA appeared; CF and SFCA increased at 1250 °C while SFCA-I decreased, simultaneously Fe$_2$O$_3$ disappeared; SFCA-I decreased at 1200 °C while CF and SFCA increased, simultaneously $\gamma$-C$_2$S appeared; SFCA-I decreased at 1150 °C while CF, SFCA, and $\gamma$-C$_2$S increased. So it can be considered the crystallization sequence was (Fe$_2$O$_3$, SFCA-I) → CF → SFCA → $\gamma$-C$_2$S.

Thermodynamically, the Gibbs free energy of formation of C$_2$S is lower than that of CF [27], and the reactions are as Equations (1) and (2), respectively. It shows that C$_2$S is more stable to form easier than CF. However, since the added SiO$_2$ content of 4mass pct is much smaller than Fe$_2$O$_3$, resulting in the probability of Si$^{4+}$ reacting with Ca$^{2+}$ is relatively small, simultaneously Si$^{4+}$ also participates in the formation of SFC, SFCA-I, and SFCA. Therefore, the crystallization sequence of C$_2$S was late. Since the Gibbs free energy of $C_4F_{14}$, SFC, SFCA-I, and SFCA formations are not existing in the thermodynamic database, unfortunately it cannot be compared with other crystalline phases.

\[
2\text{CaO} + \text{SiO}_2 = 2\text{CaO-SiO}_2 \quad \Delta_G^0 = -118899 - 11.3T \text{ (J/mol)} \quad (1)
\]

\[
\text{CaO} + \text{Fe}_2\text{O}_3 = \text{CaO-Fe}_2\text{O}_3 \quad \Delta_G^0 = -29700 - 4.81T \text{ (J/mol)} \quad (2)
\]

From the crystallization order of different samples containing Al$_2$O$_3$, a new generation path of SFCA-I was found in the crystallization process of the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ quaternary system. The $C_4F_{14}$ reacts with Si$^{4+}$ and Al$^{3+}$ in the melt to form SFCA-I ($C_4F_{14}$ + Si$^{4+}$ + Al$^{3+}$ → SFCA-I), and SFCA-I reacts with Si$^{4+}$ and Al$^{3+}$ to form SFCA (SFCA-I + Si$^{4+}$ + Al$^{3+}$ → SFCA).

Figure 6 shows the corresponding cross-sectional optical micrograph, where the experimental results are consistent with the XRD results. Seven phases of Fe$_2$O$_3$, $C_4F_{14}$, CF, SFC, $\gamma$-C$_2$S, SFCA-I, and SFCA were co-precipitated in the melt. When the quenched temperature was lowered, equivalent to prolonging the crystallization time, the Fe$_2$O$_3$ grew up in a lump, and calcium ferrite (CF, $C_4F_{14}$, SFC) developed from strip to short column. Simultaneously needle-shaped SFCA-I transformed into column-shaped SFCA, and $\gamma$-C$_2$S developed from block to strip. $\gamma$-C$_2$S was generated at 1200 °C while degraded when lowered to 1150 °C.
Figure 5. XRD patterns of water-cooled (65 °C/s) samples at different target temperatures (a) 0mass% Al₂O₃; (b) 1.5mass% Al₂O₃; (c) 3mass% Al₂O₃. (The bold contents were the first formed phases in the corresponding temperature).
Figure 6. Optical micrographs of cross-sections of water-cooled samples with Al₂O₃ addition at different temperatures. CF: CaFe₂O₄; C₄F₁₄(Ca₄Fe₁₄O₂₅); SFC: Ca₂.₇₃Fe₂⁺₀.₀₄Fe³⁺₁₀.₅₆Si₀.₆₆O₂₈; SFCA-I: Ca₃.₁₈Fe₁₅.₄₈Al₁.₃₄O₃₆; SFCA: Ca₅Si₂(Fe Al)₁₈O₃₆; H: Fe₂O₃; γ-C₂S: γ-Ca₂SiO₄.

Figure 7 and Table 3 show the SEM photos and EDS results of the samples, confirming the XRD results. With the increase of the mass percentage of Al₂O₃ in the melt, the crystalline phase would change, and Al₂O₃ promoted the transition from SFCA-I to SFCA while inhibiting the formation of C₄F₁₄.

Table 3. EDS results of the crystallized phases in the samples with different mass pct of Al₂O₃.

| Sample No. | Marked Points | Phase          | Elements |
|------------|---------------|----------------|----------|
|            |               |                | Fe  | Ca  | Si  | Al  | O  |
| 0mass%     | P₁            | Fe₂O₃          | 68.63| 0.49| 1.36| 0   | 28.94|
|            | P₂            | C₄F₁₄          | 51.13| 14.23| 1.16| 0   | 33.48|
|            | P₃            | Slag phase     | 35.81| 22.88| 5.90| 0   | 35.41|
| 1.5mass%   | P₁            | C₄F₁₄          | 47.25| 12.37| 0.00| 1.08| 39.30|
|            | P₂            | SFCA-I         | 44.04| 12.68| 1.08| 2.20| 39.99|
|            | P₃            | Slag phase     | 44.52| 15.88| 2.71| 2.55| 34.34|
| 3.0mass%   | P₁            | Fe₂O₃          | 54.96| 0.62| 0.00| 1.10| 43.32|
|            | P₂            | SFCA-I         | 39.52| 11.80| 2.31| 4.84| 41.53|
|            | P₃            | Slag phase     | 36.85| 15.91| 3.18| 4.12| 39.95|
Figure 7 and Table 3 show the SEM photos and EDS results of the samples, confirming the XRD results. With the increase of the mass percentage of Al$_2$O$_3$ in the melt, the crystalline phase would change, and Al$_2$O$_3$ promoted the transition from SFCA-I to SFCA while inhibiting the formation of C$_4$F$_{14}$.

**Figure 7.** SEM-EDS mapping of the samples, morphology, and distribution of main elements.

### 3.3. Effect of Cooling Rate on Crystallization

Figures 8–10 present the variations of XRD profiles of crystallized samples with different Al$_2$O$_3$ content under the cooling rates of 5 °C/s, 15 °C/s, and 65 °C/s, respectively. The corresponding optical micrographs of crystallized phases are presented in Figure 11. Table 4 shows six phases as CF, C$_4$F$_{14}$, SFCA-I, SFCA, Fe$_2$O$_3$, and β-C$_2$S.

It can be seen that CF, C$_4$F$_{14}$, and Fe$_2$O$_3$ were generated without Al$_2$O$_3$. With the increase of the Al$_2$O$_3$ content, the crystallographic phase transformed significantly as follows. C$_4$F$_{14}$ had gradually decreased as C$_4$F$_{14}$ reacted with Al$^{3+}$ and Si$^{4+}$ to form columnar SFCA-I. With further increasing the content of Al$_2$O$_3$, SFCA-I transformed to SFCA. Compared with SFCA, SFCA-I had a higher ratio of Fe$_2$O$_3$ to CaO in chemical composition. The crystallization of C$_4$F$_{14}$ and Fe$_2$O$_3$ was promoted during the transformation. Moreover, with the increase of Al$_2$O$_3$ content, the complex calcium ferrite first increased and then decreased. The two-dimensional crystal morphology of the minerals shows that CF was skeletal or corroded. Meanwhile, C$_4$F$_{14}$, Fe$_2$O$_3$, SFCA-I, and SFCA were existed in the morphology of strip, irregular block, column and needle, and short column, respectively.
3.3. Effect of Cooling Rate on Crystallization

Figures 8–10 present the variations of XRD profiles of crystallized samples with different Al$_2$O$_3$ content under the cooling rates of 5 °C/s, 15 °C/s, and 65 °C/s, respectively. The corresponding optical micrographs of crystallized phases are presented in Figure 11. Table 4 shows six phases as CF, C$_4$F$_{14}$, SFCA-I, SFCA, Fe$_2$O$_3$, and β-C$_2$S.

Figure 8. XRD patterns of samples with different Al$_2$O$_3$ content cooled at 5 °C/s.

Figure 9. XRD patterns of samples with different Al$_2$O$_3$ content cooled at 15 °C/s.
Figure 10. XRD patterns of samples with different Al₂O₃ content cooled at 65 °C/s.

Table 4. The crystalline phase of the corresponding samples in Figures 8–10.

| Cooling Rate (°C/s) | Al₂O₃ (Mass Pct) |
|---------------------|------------------|
|                     | 0    | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    |
| 5                   | CF   | CF   | CF   | CF   | CF   | CF   | CF   |
|                     | C₄F₁₄ | SFCA-I | SFCA-I | SFCA-I | SFCA-I | SFCA-I | SFCA-I |
|                     | Fe₂O₃ | Fe₂O₃ | β-C₂S | β-C₂S | β-C₂S | β-C₂S | β-C₂S |
| 15                  | CF   | CF   | CF   | CF   | CF   | CF   | CF   |
|                     | C₄F₁₄ | SFCA-I | SFCA-I | SFCA-I | SFCA-I | SFCA-I | SFCA-I |
|                     | Fe₂O₃ | Fe₂O₃ | β-C₂S | β-C₂S | β-C₂S | β-C₂S | β-C₂S |
| 65                  | CF   | CF   | CF   | CF   | CF   | CF   | CF   |
|                     | C₄F₁₄ | C₄F₁₄ | C₄F₁₄ | C₄F₁₄ | C₄F₁₄ | C₄F₁₄ | C₄F₁₄ |
|                     | Fe₂O₃ | Fe₂O₃ | Fe₂O₃ | Fe₂O₃ | Fe₂O₃ | Fe₂O₃ | Fe₂O₃ |
|                     | β-C₂S | β-C₂S | β-C₂S | β-C₂S | β-C₂S | β-C₂S | β-C₂S |

It can be found that as increasing the cooling rate it shortens the crystal growth time, so the crystalline of some minerals would be inhibited, while the crystalline phase and morphology were also changed significantly. On the one hand, the crystal size would be narrowed. On the other hand, the formation of complex calcium ferrite and the conversion of SFCA-I to SFCA would be promoted, while the formation of SFC and γ-C₂S would be inhibited. It also promoted the formation of C₄F₁₄, Fe₂O₃, and the amorphous phase that filled around the complex calcium ferrite in an imperfect crystallization state. But when the cooling rate reaches 65 °C/s, it was found that C₄F₁₄ was easier to form than Fe₂O₃, so C₄F₁₄ should be crystallized with Fe₂O₃ first in the crystallization sequence. Therefore, the crystallization order of samples in the Fe₂O₃-CaO-SiO₂-Al₂O₃ melt containing Al₂O₃ should be C₄F₁₄ → Fe₂O₃ → SFCA-I → CF → SFCA → γ-C₂S.
Figure 11. Optical micrographs of cross-sections of crystalline samples with Al$_2$O$_3$ addition at various cooling rates. C$_4$F$_{14}$: (Ca$_4$Fe$_{14}$O$_{25}$); CF: CaFe$_2$O$_4$; SFCA-I: Ca$_3.18$Fe$_{15.48}$Al$_{1.34}$O$_{36}$; SFCA: Ca$_5$Si$_2$(FeAl)$_{18}$O$_{36}$; H: Fe$_2$O$_3$; P: Pore.

To further confirm the phase composition, the SEM-EDS analysis of the sample with a cooling rate of 5 °C/s is shown in Figure 12 and Table 5. When the Al$_2$O$_3$ is not added, only C$_4$F$_{14}$ and CF phases were formed. With Al$_2$O$_3$ content increasing, C$_4$F$_{14}$, CF, SFCA-I, and SFCA appeared, which confirmed the experimental results in Figure 8.
To investigate the influence of cooling rate on the morphology of calcium ferrite (C$_4$F$_{14}$, SFCA-I, and SFCA) in the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ melt under different Al$_2$O$_3$ content, the grain size of calcium ferrite in each sample in Figure 11 was measured using the Nano Measurer 1.2 software [29]. Thirty positions in each sample were selected, measured, and an averaged value was calculated. Figure 13 illustrates that with the increased cooling rate, the crystal size of calcium ferrite decreased significantly. Furthermore, when the Al$_2$O$_3$ content increased, the crystal size of calcium ferrite increased and subsequently decreased, which demonstrates that adding a small amount of Al$_2$O$_3$ promoted the formation of complex calcium ferrite. At different cooling speeds (5 °C/s, 15 °C/s, and 65 °C/s), the grain size achieved the maximum value (corresponding to 22.15 μm, 13.85 μm, and 9.25 μm, respectively) when the Al$_2$O$_3$ reached 2.0 mass pct. After Al$_2$O$_3$ reached 2.5 mass pct, it would increase a viscosity of the melt, which could be a primary reason for the decrease in the crystal size of calcium ferrite.

| Al$_2$O$_3$ (Mass Pct) | Marked Points | Phase    | Elements (at Pct) |
|------------------------|--------------|----------|-------------------|
|                        |              | Fe       | Ca    | Si    | Al   | O     |
| 0                      | P$_1$        | C$_4$F$_{14}$ | 52.06 | 12.37 | 0.79 | 0     | 34.78 |
|                        | P$_2$        | CF       | 40.74 | 19.59 | 3.96 | 0     | 35.72 |
|                        | P$_3$        | Slag phase | 37.10 | 20.93 | 6.93 | 0     | 35.04 |
| 1.0                    | P$_2$        | CF       | 40.49 | 21.60 | 4.95 | 1.77  | 31.20 |
|                        | P$_4$        | SFCA-I   | 48.28 | 14.24 | 2.09 | 0.92  | 34.48 |
| 1.5                    | P$_2$        | CF       | 42.16 | 19.75 | 4.89 | 2.06  | 31.14 |
|                        | P$_4$        | SFCA-I   | 49.19 | 14.77 | 2.94 | 2.77  | 30.33 |
| 2.0                    | P$_2$        | CF       | 43.43 | 26.11 | 0    | 0.69  | 29.77 |
|                        | P$_5$        | SFCA     | 47.35 | 14.22 | 3.40 | 4.42  | 30.62 |
| 2.5                    | P$_2$        | CF       | 39.39 | 21.58 | 4.51 | 3.94  | 30.58 |
|                        | P$_5$        | SFCA     | 43.77 | 12.73 | 4.28 | 6.27  | 32.95 |
| 3.0                    | P$_2$        | CF       | 39.39 | 21.58 | 4.51 | 3.94  | 30.58 |
|                        | P$_5$        | SFCA     | 40.10 | 13.17 | 4.26 | 6.25  | 36.22 |

Table 5. The EDS results of the corresponding marked points in Figure 12.

Figure 12. SEM image of the cross-section of the sample after cooling at 5 °C/s.
3.4. Discussion on Crystallization Mechanism

To further explain the effect of Al$_2$O$_3$ on the crystallization of calcium ferrite, FactSage 8.2 software was used to perform thermodynamic equilibrium calculations on the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ system, even though C$_4$F$_{14}$, SFCA-I, and SFCA are lacking in the thermodynamic database. Future metallurgical workers are required to improve it.

Figure 14 and Table 6 show the primary crystallization temperature and crystallization amount of the thermodynamic equilibrium phase with different Al$_2$O$_3$ content. The result shows that without adding Al$_2$O$_3$, the phases are M$_2$O$_3$ ($\geq 99.50$ mass pct Fe$_2$O$_3$ and $\leq 0.50$ mass pct Al$_2$O$_3$), $\alpha'$-Ca$_2$SiO$_4$($\alpha'$-C$_2$S), and CaFe$_2$O$_7$(CF$_2$). With the Al$_2$O$_3$ content increasing, CF$_2$ disappeared while CF appeared. When Al$_2$O$_3$ content reached 2.0 mass pct, the primary crystallization phase transformed from M$_2$O$_3$ to $\alpha'$-C$_2$S, and the transition temperature was 1250 °C. When Al$_2$O$_3$ content reached 3.0 mass pct, CF and Ca(Al, Fe)$_6$O$_{10}$ appeared.

The corresponding crystallization amounts of M$_2$O$_3$, $\alpha'$-C$_2$S, and CF decreased from 39.01 to 24.19 mass pct, 11.41 to 11.12 mass pct, and 49.00 to 35.76 mass pct, respectively. Ca(Al, Fe)$_6$O$_{10}$ increased from 0.579 to 28.924 mass pct.

As shown in Figure 11, many spherical holes appeared in samples when the Al$_2$O$_3$ content reached 2.5 and 3.0 mass pct, which increased with the increase of the Al$_2$O$_3$ content and the cooling rate. Simultaneously, the crystalline size of minerals decreased. It can be considered that the increase of the melt viscosity resulted in a slow crystalline rate due to the hard mass transferring.

Table 6. Changes of primary crystallization phase and temperature after adding Al$_2$O$_3$.

| Al$_2$O$_3$ Content (Mass Pct) | Primary Phase | Primary Crystallization Temperature (°C) |
|--------------------------------|--------------|----------------------------------------|
| 0                              | M$_2$O$_3$   | 1261                                   |
| 0.5                            | M$_2$O$_3$   | 1258                                   |
| 1.0                            | M$_2$O$_3$   | 1253                                   |
| 1.5                            | M$_2$O$_3$   | 1250                                   |
| 2.0                            | $\alpha'$-C$_2$S | 1251                                  |
| 2.5                            | $\alpha'$-C$_2$S | 1252                                  |
| 3.0                            | $\alpha'$-C$_2$S | 1253                                  |
Figure 14. Theoretical crystal phase composition of Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ slag during cooling.

Figure 15 shows the viscosity diagrams of Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ melts with Al$_2$O$_3$ content at different temperatures, which is calculated using thermodynamical software, simultaneously combined by the Einstein-Roscoe formula (Equation (3)) [30], where the mass fraction of the solid phase was obtained as shown in Figure 14. The result shows that at all temperatures, the viscosity value increased with the increase of Al$_2$O$_3$ content. The viscosity value increased obviously. The viscosity increase would hinder the crystallization and mass transfer of complex calcium ferrite in the melt, resulting in poor crystalline morphology. Specially, after Al$_2$O$_3$ reached 2.5 mass pct, the viscosity of the melt increased sharply, which could be the main reason for the decrease in the crystal size of calcium ferrite.

$$\eta = \eta^0 (1 - c)^{-2.5}$$

$\eta$—solid-liquid mixing viscosity;  
$\eta^0$—viscosity of pure liquid phase;  
$c$—a mass fraction of solid phase.
at all temperatures, the viscosity value increased with the increase of Al$_2$O$_3$ content. The viscosity value increased obviously. The viscosity increase would hinder the crystallization and mass transfer of complex calcium ferrite in the melt, resulting in poor crystalline morphology. Specially, after Al$_2$O$_3$ reached 2.5 mass pct, the viscosity of the melt increased sharply, which could be the main reason for the decrease in the crystal size of calcium ferrite.

$$\eta = \eta_0 (1 - c)^{-2.5}$$

$\eta$—solid-liquid mixing viscosity;
$\eta_0$—viscosity of pure liquid phase;
$c$—a mass fraction of solid phase.

Figure 15. Viscosity diagrams of samples with Al$_2$O$_3$ addition at different temperatures.

The isothermal cross-sections of Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ systems with varying Al$_2$O$_3$ content at different temperatures are shown in Figure 16. With the Al$_2$O$_3$ content increasing, the liquid phase is divided into three regions, named L$_\alpha$, L$_\alpha$ + L$_\beta$, and L$_\beta$, where the content of Al$_2$O$_3$ increased from 1.0 to 3.0 mass pct. When the red component point is at 1250 °C, the primary crystal region is transformed from L$_\alpha$ + M$_2$O$_3$ to L$_\alpha$ + L$_\beta$ + $\alpha'$-C$_2$S. There may be two reasons for the deterioration of crystallization. On the one hand, the viscosity of L$_\alpha$ + L$_\beta$ + $\alpha'$-C$_2$S is higher than that of L$_\alpha$ +M$_2$O$_3$. In addition, the crystallization of $\alpha'$-C$_2$S leads to the reducing of initial Ca$^{2+}$ and Si$^{4+}$ in the melt, which is not conducive to the crystallization of complex calcium ferrite. It can be seen from Figure 16 that when Al$_2$O$_3$ is 2.0 mass pct, not only a certain amount of liquid phase is retained, but also Ca$^{2+}$ and Si$^{4+}$ are not reduced too much. This also explains that when Al$_2$O$_3$ was 2.0 mass pct, the crystal size of calcium ferrite was the largest, as shown in Figure 13.
4. Conclusions

In this work the influences of Al$_2$O$_3$ content, cooling rate and the crystallization sequence of the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ system during the cooling process were investigated. On this basis, the influence mechanism of Al$_2$O$_3$ content and cooling rate on the crystallization of complex calcium ferrite (C$_4$F$_{14}$, SFCA-I, SFCA) was also proposed. The main conclusions are as follows:

1. Al$_2$O$_3$ has an important effect on the composition of the crystal phase of the Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ system. Adding alumina promoted the crystallization of Fe$_2$O$_3$, γ-C$_2$S, SFCA-I, and SFCA, while it inhibited the crystallization of C$_4$F$_{14}$ and SFC. However, the content of CF first decreased and then increased. This is mainly because of the formation of complex calcium ferrite and the transformation of SFCA-I to SFCA.

2. The crystallization sequence in Fe$_2$O$_3$-CaO-SiO$_2$-Al$_2$O$_3$ melt under different Al$_2$O$_3$ content was investigated, where the corresponding crystalline order is (Fe$_2$O$_3$, C$_4$F$_{14}$) → CF → (SFC, γ-C$_2$S), (Fe$_2$O$_3$, C$_4$F$_{14}$) → SFCA-I → CF → SFCA → γ-C$_2$S, and (Fe$_2$O$_3$, SFCA-I) → CF → SFCA → γ-C$_2$S under the Al$_2$O$_3$ content of 0 mass pct, 1.5 mass pct, and 3.0 mass pct respectively. It can be concluded that the C$_4$F$_{14}$ reacts with Si$^{4+}$ and Al$^{3+}$ in the melt to form SFCA-I (C$_4$F$_{14}$ + Si$^{4+}$ + Al$^{3+}$ → SFCA-I), and then SFCA-I reacts with Si$^{4+}$ and Al$^{3+}$ to form SFCA (SFCA-I + Si$^{4+}$ + Al$^{3+}$ → SFCA).

3. As the cooling rate increase, C$_4$F$_{14}$, SFCA-I, Fe$_2$O$_3$, β-C$_2$S, and the amorphous phases are increased while CF and SFCA are reduced, and the crystal transformation from
3. Yang, L.X.; Loo, C.E. Structure of Sinters Formed from Complex Chinese Iron Ores. ISIJ Int. 1993, 33, 462–473. [CrossRef]
4. Guo, H.; Guo, X.M. Effect of Aluminum Dissolved in Hematite on Formation of Calcium Ferrites at 1473 K. Metall. Mater. Trans. B 2018, 49, 1974–1984. [CrossRef]
5. Yang, L.X.; Loo, C.E. Structure of Sinters Formed from Complex Chinese Iron Ores. ISIJ Int. 1997, 37, 449–457. [CrossRef]
6. Nicol, S.; Chen, J.; Pownceby, M.I.; Webster, N.A.S. A Review of the Chemistry, Structure and Formation Conditions of Silico-Ferrite of Calcium and Aluminum (SFCA) Phases. ISIJ Int. 2018, 58, 2157–2172. [CrossRef]
7. Sato, S.; Kawaguuchi, T.; Ichidate, M.; Yoshinaga, M. Mineral Forming and Its Composition Model for Iron Ore Sinter. Tetsu-to-Hagane 1987, 73, 964. [CrossRef]
8. Bristow, N.J.; Loo, C.E. Sintering Properties of Iron Ore Mixes Containing Titanium. ISIJ Int. 1992, 32, 819–828. [CrossRef]
9. Nyembwe, A.M.; Garbers-Craig, A.M. Study of iron ore sinter when fine ore is replaced with coarse ore, using infrared furnace and sinter pot tests. Ironmak. Steelmak. 2014, 41, 173–181. [CrossRef]
10. Wang, Z.; Pinson, D.; Chew, S.; Monaghan, B.J.; Rogers, H.; Zhang, G.Q. Mineral Phase Formation and Zinc Removal during Sintering of Filter Cake Wastes. ISIJ Int. 2016, 56, 505–512. [CrossRef]
11. Scarlett, N.V.Y.; Pownceby, M.I.; Madsen, I.C.; Christensen, A.N. Reaction sequences in the formation of silico-ferrites of calcium and aluminum in iron ore sinter. Metall. Mater. Trans. B 2004, 35, 929–936. [CrossRef]
12. Guo, X.M. The Formation and Mineralogy of Calcium Ferrite in Sintering Process; Metallurgical Industry Press: Beijing, China, 1999; pp. 143–146.
13. Patrick, T.R.C.; Pownceby, M.I. Stability of silico-ferrite of calcium and aluminum (SFCA) in air-solid solution limits between 1240 °C and 1390 °C and phase relationships within the Fe2O3-CaO-Al2O3-SiO2 (FCAS) system. Metall. Mater. Trans. B 2002, 33, 79–89. [CrossRef]
14. Webster, N.A.S.; Pownceby, M.I.; Madsen, I.C.; Kimpton, J.A. Silico-ferrite of Calcium and Aluminum (SFCA) Iron Ore Sinter Bonding Phases: New Insights into Their Formation During Heating and Cooling. Metall. Mater. Trans. B 2012, 43, 1344–1357. [CrossRef]
15. Webster, N.A.S.; Churchill, J.G.; Tufaile, F.; Pownceby, M.I.; Manuel, J.R.; Kimpton, J.A. Fundamentals of Silico-Ferrite of Calcium and Aluminum (SFCA) and SFCA-I Iron Ore Sinter Bonding Phase Formation: Effects of Titanomagnetite-based Ironsand and Titanium Addition. ISIJ Int. 2016, 56, 1715–1722. [CrossRef]
16. Hsieh, L.H.; Whiteman, J.A. Effect of Raw Material Composition on the Mineral Phases in Lime-fluxed Iron Ore Sinter. ISIJ Int. 1993, 33, 462–473. [CrossRef]
17. Cai, B.; Watanabe, T.; Kamijo, C.; Sasa, M.; Hayashi, M. Comparison between Reducibilities of Columnar Silico-ferrite of Calcium and Aluminum (SFCA) Covered with Slag and Acicular SFCA with Fine Pores. ISIJ Int. 2018, 58, 642–651. [CrossRef]
18. Webster, N.A.S.; O’Dea, D.P.; Ellis, B.G.; Pownceby, M.I. Effects of Gibbsite, Kaolinite and Al-rich Goethite as Alumina Sources on Silico-Ferrite of Calcium and Aluminum (SFCA) and SFCA-I Iron Ore Sinter Bonding Phase Formation. ISIJ Int. 2017, 57, 41–47. [CrossRef]
19. Liles, D.C.; Villiers, J.P.R.; Kahlenberg, V. Refinement of iron ore sinter phases: A silico-ferrite of calcium and aluminium (SFCA) and an Al-free SFC, and the effect on phase quantification by X-ray diffraction. Mineral. Petrol. 2016, 110, 141–147. [CrossRef]

20. Ding, C.Y.; Lv, X.W.; Chen, Y.; Bai, C.G. Crystallization Kinetics of 2CaO·Fe2O3 and CaO·Fe2O3 in the CaO–Fe2O3 System. ISIJ Int. 2016, 56, 1157–1163. [CrossRef]

21. Yang, D.W.; Wang, W.; Li, J.X.; Xu, R.S.; Wang, X.Z.; Wang, G. Effect and Mechanism of Alumina on the Morphology and Mechanical Properties of Calcium Ferrite. Metall. Mater. Trans. B 2020, 51, 776–785. [CrossRef]

22. Park, T.J.; Choi, J.S.; Min., D.J. Influence of Al2O3 Content and Cooling Rate on Crystallization in Fe2O3–CaO–SiO2–Al2O3 Systems. Met. Mater. Int. 2021. [CrossRef]

23. Fan, X.H. Principle and Technology of Optimum Blending of Iron Ore Sintering; Metallurgical Industry Press: Beijing, China, 2013; pp. 62–65.

24. Wang, B.; Zhao, W.; Zhang, X.H.; Hu, S.Y.; Guo, H.W.; Chu, M.S. Revealing the Softening-Melting Behaviors and Slag Characteristics of Vanadium-Titaniun Magnetite Burden with Various MgO Addition. Minerals 2022, 12, 842. [CrossRef]

25. Wang, Z.J.; Sun, Y.Q.; Sridhar, S.; Zhang, M.; Zhang, Z.T. Selective Crystallization Behavior of CaO-SiO2-Al2O3-MgO-Fe3O-P2O5 Steelmaking Slags Modified through P2O5 and Al2O3. Metall. Mater. Trans. B 2015, 46, 2246–2254. [CrossRef]

26. Wang, Z.J.; Sun, Y.Q.; Sridrar, S.; Zhang, M.; Zhang, Z.T. Investigation on Viscosity and Nonisothermal Crystallization Behavior of P-Bearing Steelmaking Slags with Varying TiO2 Content. Metall. Mater. Trans. B 2017, 48, 527–537. [CrossRef]

27. Wang, W.; Yang, D.W.; Ou-Yang, Z.L.; Xu, R.S.; Song, M.M. Effect of SiO2 on the Formation of Acicular Calcium Ferrite in Sinter. Metall. Mater. Trans. B 2019, 50, 678–687. [CrossRef]

28. Xin, R.F.; Guo, X.M. Effect of SiO2 on Crystallization of Calcium Ferrites in Fe2O3–CaO–SiO2–Al2O3 System in Cooling Process. Metall. Mater. Trans. B 2022, 53, 1904–1919. [CrossRef]

29. Chang, R.G.; Yan, Y.T.; Zhang, J.Y.; Zhu, Z.L.; Gu, J.H. Large-grain and smooth cesium doped CH3NH3PbI3 perovskite films by cesium iodide post-treatment for improved solar cells. Thin Solid Films. 2020, 712, 138279. [CrossRef]

30. Roscoe, R. The viscosity of suspensions of rigid spheres. Br. J. Appl. Phys. 1952, 3, 267. [CrossRef]