

Article

Formation of Calcium Ferrite Containing Aluminum (CFA) in Sintering of Iron Ore Fines

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Abstract: Calcium ferrite containing aluminum (CFA) is a precursor of the low-temperature bonding phase in the sintering process of iron ore fines for blast furnace ironmaking. Thus, improving the formation of CFA at lower temperature is very important for saving energy, improving efficiency and production. In this paper, the formation process of CFA was investigated at 1200 °C by reactions of alumina (Al₂O₃), respectively with a mixture of calcium oxide (CaO) and hematite (Fe₂O₃) and monocalcium ferrite (CF) as a recognized initial product, as well as reaction of Al-containing hematite (H_{ss}) with CF. The result confirmed that CF is an intermediate product formed easily in the sintering process, and it may react with excessive Fe₂O₃ to generate an alpha-calcium iron oxide (Ca₂Fe_{15.50}O₂₅) as a new phase. It was found that CFA can be formed directly by reactions of CF with H_{ss} and Ca₂Fe_{15.50}O₂₅ with Al₂O₃, while the reaction of CF with Al₂O₃ is more helpful in generating Ca₂Fe_{15.5}O₂₅ rather than CFA, simultaneously forming a calcium aluminum oxide (CaAl₂O₄, CA; CaAl₄O₇, CA₂). It was revealed that the appearance of CA and CA₂ is a main reason to hinder CFA formation in the sintering process of iron ore fines.

Keywords: CFA; calcium ferrite; formation; sintering; DFT



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1. Introduction

Iron ore sinter is a main charge material in blast furnaces for ironmaking [1–4]. Specially, high-basicity sinter is well received due to the low sintering temperature, high product strength, and good reducibility in blast furnaces [5–8]. As metallurgical production progresses, iron ore fines with high quality are becoming scarcer, causing an increase in gangue content like Al₂O₃ and SiO₂ in raw materials for the sintering process [9–16]. So, attention is being paid to the effect of gangue on the formation mechanism of complex calcium ferrite (SFCA) as a bonding phase of high-basicity sinter.

Patrick et al. [17] reported that SFCA is a stable phase possessing the chemical composition plane that connects the members of CaO·3Fe₂O₃ (CF₃), CaO·3Al₂O₃ (CA₃), and 4CaO·3SiO₂ (C₄S₃), where the limitation of substitution ratio for Al³⁺ to Fe³⁺ was 31.5% of its mass.

Scarlett et al. [18] investigated the formation process of SFCA using an in situ X-ray diffraction method, indicating that CaO·Fe₂O₃ (CF) is a precursor of SFCA formation, and the formation of SFCA can be promoted by adding Al₂O₃.

Webster et al. [19] found that ternary calcium ferrite (CFA) is also a precursor of SFCA formation. Actually, CFA was discovered decades ago. It was observed earlier by Yamauchi [20] as a ternary compound in the CaO-Al₂O₃-Fe₂O₃-SiO₂ system. Lister et al. [21] defined this compound as “ternary phase” (TP) and pointed out that the chemical formula is CaAl₂Fe₄O₁₀ (CAF₂). Subsequently, Mumme et al. [22] determined the structure of CFA in Ca_{5.1}Al_{9.3}Fe³⁺_{18.7}Fe²⁺_{0.9}O₄₈. As accordingly verified, CFA provides a basis for SFCA formation due to it having the same structure as triclinic crystal. According to

previous studies, CFA is a solid solution formed by the reaction of Al_2O_3 with CF [23]. Webster et al. [24] also confirmed the formation of CFA using gibbsite ($\text{Al}(\text{OH})_3$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), and aluminous goethite, respectively, in the sintering process of iron ore fines, and simultaneously observed that alumina in kaolinite or aluminous goethite provide a better condition for the formation of CFA at lower temperatures than gibbsite. In our previous works, it was reported [25] that alumina dissolved into hematite (H_{ss}) could promote the formation of CFA in a reaction with CaCO_3 . Moreover, it was found [26] that the reaction of Al_2O_3 with CaFe_2O_4 (CF) to form CFA is easier than using SiO_2 to form calcium ferrite containing silica (SFC), as a precursor for the formation of SFCA. Other work [27] also indicated that the simultaneous appearance of CFA and CF could be conducive to producing a liquid phase with a lower melting temperature than CF. So, it is very important to understand the formation of CFA in the sintering process of iron ore fines.

However, there still exist many questions, as follows: What are the reactions in the transformation process from CF to CFA? Why does the formation rate of CFA show a great difference in the sintering process of iron ore fines with different Al_2O_3 materials? These have also been paid attention to in recent years [28–31]. In this work, the mole ratio of Fe_2O_3 to CaO with 3:1 and 4.0% Al_2O_3 were used to simulate the chemical composition of sintering materials to investigate the transformation process of CF to CFA at 1200 °C for revealing the formation mechanism at low temperature; simultaneously, the reactions of CF with Al-containing hematite solid solution (H_{ss}), a mixture of Fe_2O_3 and Al_2O_3 , and only 4.0% Al_2O_3 , respectively, at different times were investigated to ascertain the reason for different CFA formation rates by different Al-containing materials for improving the sintering process of iron ore fines.

2. Materials and Methods

2.1. Reactions of CFA Formation

Analytical reagents of CaCO_3 , Fe_2O_3 , and Al_2O_3 (purity above 98%) were used to prepare CF and Al-containing H_{ss} , respectively, based on our previous work [25,32]. The chemical compositions and sintering conditions for the synthesis of CF and H_{ss} are shown in Table 1. The analytical reagents were first weighed and homogenized in a mortar grinder for 60 min under air atmosphere, and pressed into a tablet approximately 15 mm in diameter and 5 mm in height under 5 MPa pressure using an electric briquetting machine. Then, the samples were sintered in a tubular resistance furnace at the given temperature for different durations in air atmosphere and taken out, followed by air cooling. XRD patterns of synthesized CF and H_{ss} are shown in Figure 1. It can be seen that the diffraction peaks of synthesized CF and H_{ss} matched well with the stand card of CF and Fe_2O_3 , without diffraction peaks of Al_2O_3 .

Table 1. Chemical compositions (wt%) and sintering conditions for the synthesis of CF and H_{ss} .

Materials	Fe_2O_3	CaCO_3	Al_2O_3	Sintering Time	Sintering Temperature
CF	61.5	38.5		480 min	1200 °C
H_{ss}	96.0		4.0	240 min	1250 °C

To investigate the generation order of intermediate products in the formation of CFA, three kinds of reactions, including Fe_2O_3 - CaCO_3 - Al_2O_3 , CF- Fe_2O_3 - Al_2O_3 , and H_{ss} -CF, were conducted, and the corresponding mass fraction of reactants are listed in Table 2. To simulate the environment of the actual sintering process, the mole ratio of Fe_2O_3 to CaO was set at around 3:1. The reactants including Fe_2O_3 , CaCO_3 , and Al_2O_3 were first weighed, homogenized in a mortar grinder (Fritsch Pulverisette 2, Idar-Oberstein, Germany) for 30 min, and pressed into a tablet of 5 mm in diameter and approximately 5 mm in height at 5 MPa, and sintered at 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C for 60 min in the

air atmosphere, followed by liquid nitrogen cooling. Similarly, based on the experimental results above, the reactions including CF with Fe_2O_3 , Al_2O_3 , and H_{ss} with CF were also weighed, homogenized, pressed, and sintered at 1200 °C for different durations in the air atmosphere, followed by liquid nitrogen cooling. Afterwards, each sample was cut into two pieces along the radial line, where one was polished for microstructure observation and element quantification using SEM-EDS and optical microscope methods, and the other was grinded into small particles less than 50 μm for mineral composition identification using the XRD method.

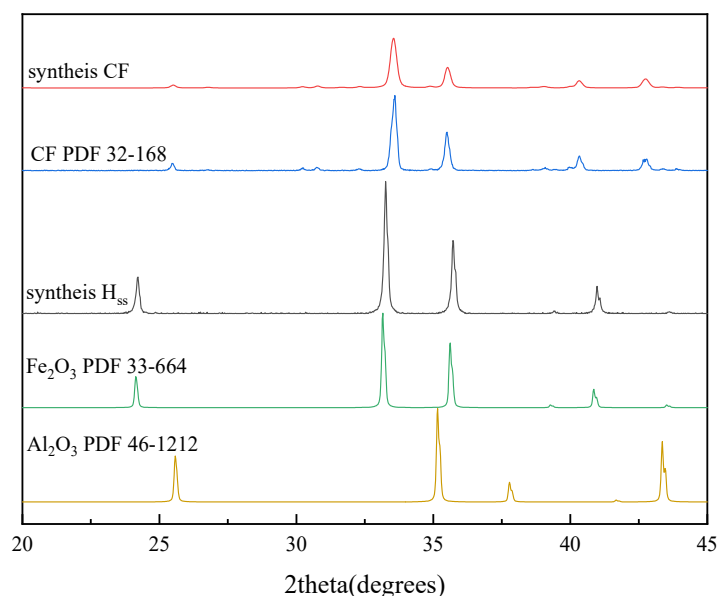


Figure 1. XRD patterns of synthesized CF and H_{ss} .

Table 2. Mass fraction (%) of reactants in various reactions for the formation of CFA.

Reaction	Fe_2O_3	CaCO_3	Al_2O_3	H_{ss}	CF
$\text{Fe}_2\text{O}_3\text{-CaCO}_3\text{-Al}_2\text{O}_3$	79.42	16.58	4		
$\text{CF-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$	57.3		4		38.7
$\text{H}_{\text{ss}}\text{-CF}$	59.7			40.3	

Reactions of CF with Al_2O_3 and CF with Fe_2O_3 were also conducted to investigate the formation of calcium aluminate and alpha-calcium iron oxide. For the reactions of CF with Al_2O_3 , 96 wt% of CF and 4 wt% Al_2O_3 were also weighed, homogenized, pressed, and sintered at 1200 °C for different durations, followed by liquid nitrogen cooling. For the reactions of CF with Fe_2O_3 , the mole ratios of CF and Fe_2O_3 were set at 1:0.5, 1:0.9, 1:0.95, 1:0.98, 1:1, and 1:1.5. Similarly, samples of CF with different ratios of Fe_2O_3 were also weighed, homogenized, pressed, and sintered at 1200 °C for different durations, followed by liquid nitrogen cooling. Afterwards, the synthesized alpha-calcium iron oxide was also homogenized with 5 wt% and 10 wt% Al_2O_3 , pressed, and sintered at 1200 °C for 10 h in the air atmosphere, followed by liquid nitrogen cooling. Afterwards, the cooled samples were also analyzed using the XRD and SEM-EDS methods.

2.2. Minerals Determination

The mineral phase of samples was identified using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, Japan). Cu K α was used as a radiation source (40 kV, 400 mA) with a graphite monochromator in the diffraction beam path. The XRD data were collected using continuous scanning mode, for which the scanning speed was 10°/min. The XRD data were analyzed using Crystallographica Search-Match software 2.1.1.0 (Oxford Cryosystems Ltd. Oxford, UK).

A piece of each sample was embedded with phenolic powders, molded by a metallographic molding machine, and polished for SEM and optical observations. Mineral morphology and microstructure observation were performed using an FEI Quanta 250 scanning electron microscope (FEI Corporation, Hillsboro, OR, USA) with an accelerating voltage of 20 kV. The chemical composition of elements was obtained on this instrument using an XFlash 5030 EDS detector (Bruker Nano GmbH, Berlin, Germany). Moreover, the element distribution was obtained through an EPMA detector (EPMA-1720H, Shimadzu, Kyoto, Japan).

2.3. Calculations of Formation Energy for Products

First-principles calculations were used to investigate the thermodynamical stability of the products of the above reactions [33,34]; where structural models were constructed, the formation energy (FE) of products was calculated using the density functional theory (DFT) in Materials Studio. The forces on every atom were converged within 0.05 eV/Å. The corresponding calculation parameters are presented in Table 3.

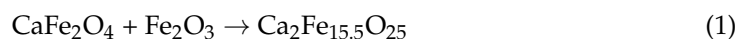
Table 3. The calculating parameters of formation energy using DFT.

Modules	Functional Used	Plane Wave Basis Set Cut-Off	k-Point	Relativistic Treatment	Pseudopotentials
CASTEP	Perdew–Burke–Ernzerhof	489.8000 eV	1 × 1 × 1	Koelling–Harmon	OTFG ultrasoft

3. Results and Discussion

3.1. Effect of Temperature on CFA Formation

The XRD patterns of samples of Fe₂O₃, CaCO₃, and Al₂O₃ reacted for 60 min at different temperatures lower than 1200 °C are shown in Figure 2a. It can be seen that CaCO₃ corresponding to PDF 5-586 decomposed completely at 900 °C after sintering for 60min, while CaO corresponding to PDF 37-1497 had also not appeared, which indicates that the CaO had already participated in the reaction to generate other products. As the temperature increased to 1100 °C, Ca₂Fe₂O₅ (C₂F) corresponding to PDF 47-1744, CFA (Ca_{3.18}Fe_{15.48}Al_{1.34}O₂₈) corresponding to PDF 52-1258, and CF corresponding to PDF 32-168 successively appeared. However, it can easily be seen that the diffraction peak intensity of CF decreased, while the diffraction peak intensity of CFA and Ca₂Fe_{15.5}O₂₅ corresponding to PDF 78-1669 increased when the temperature increased to 1200 °C. In more detail, for diffraction angles ranging from 33.5° to 35.4°, as shown in Figure 2b, the first strong peaks of CF (3 2 0), CFA (0 -2 4), and Ca₂Fe_{15.5}O₂₅ (1 1 18) clearly exited, and this phenomenon had already appeared above 1000 °C. Amazingly, the diffraction peak of CaO (2 0 0) appeared at 1200 °C, corresponding to the first strong peak, as shown in Figure 2a. According to above result, it can be considered that CF transformed to Ca₂Fe_{15.5}O₂₅ and CFA at 1200 °C, as follows:



However, a large amount of Fe₂O₃ corresponding to PDF 33-664 still remained in samples at 1200 °C. In addition, CaAl₂O₄ possibly also appeared at 1200 °C, corresponding to the first strong peak (2 2 0) of PDF 23-1036, as shown in Figure 2a, but it was very week.

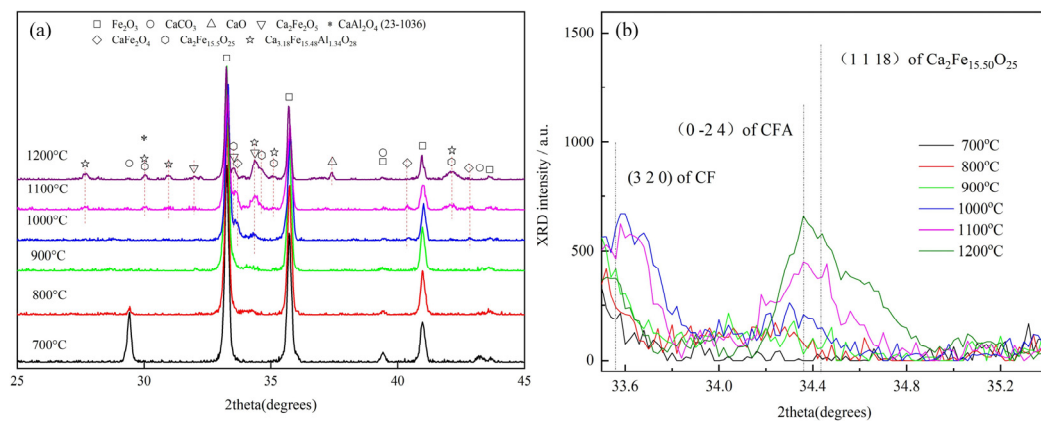


Figure 2. XRD patterns of Fe_2O_3 - CaO - Al_2O_3 sample sintered for 60 min at different temperatures: (a) full spectrum; (b) partial spectrum.

3.2. Effect of Different Types of Al-Containing Materials on CFA Formation

The XRD patterns of samples sintered at 1200 °C for different durations in reactions of CF with mixtures of hematite and alumina (Fe_2O_3 - Al_2O_3) and Al-containing hematite solid solution (H_{ss}), respectively, are shown in Figure 3. It can be seen that the diffraction peaks of $\text{Ca}_2\text{Fe}_{15.5}\text{O}_{25}$ and CFA appeared in the CF- Fe_2O_3 - Al_2O_3 sample sintered for 30 min; then, the corresponding diffraction peak intensity increased as time went on, but the former increased much more than the latter, indicating that the reaction is conducive to promoting the formation of $\text{Ca}_2\text{Fe}_{15.5}\text{O}_{25}$, while the diffraction peak of CFA appeared in the CF- H_{ss} sample sintered for 5 min, which was far earlier than that of the CF- Fe_2O_3 - Al_2O_3 sample; the intensity increased with time; simultaneously, the diffraction peak intensity of CF decreased, but the diffraction peak of $\text{Ca}_2\text{Fe}_{15.5}\text{O}_{25}$ was not observed, indicating the reaction is evidently conducive to promoting the formation of CFA.

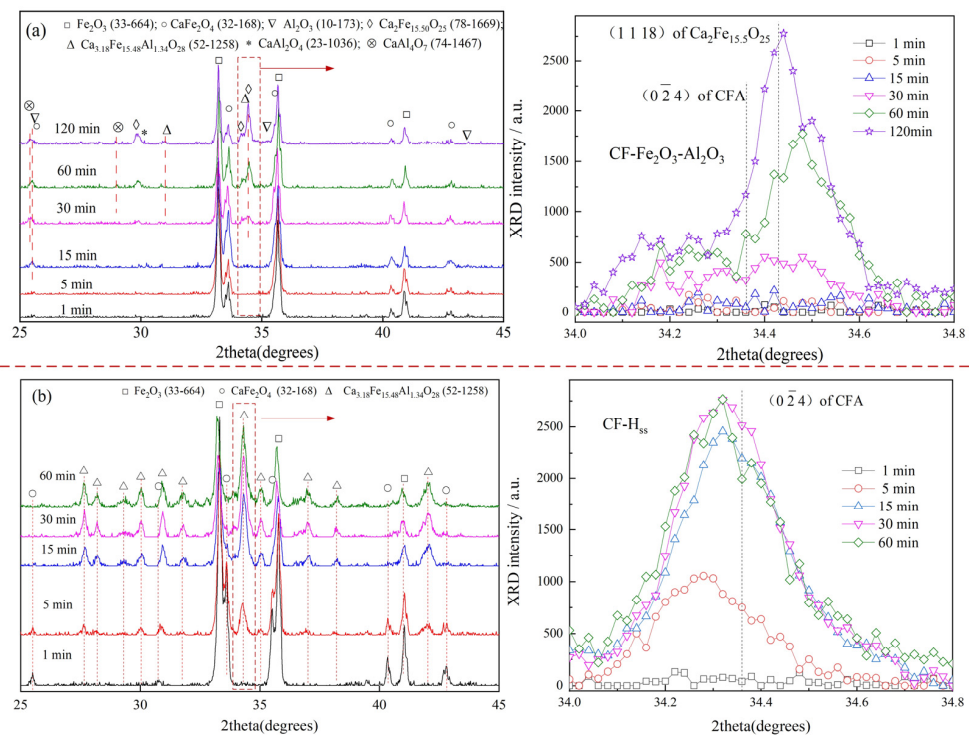


Figure 3. XRD patterns of samples for reactions of CF, respectively, with mixtures of Fe_2O_3 - Al_2O_3 (a) and H_{ss} (b) for different durations at 1200 °C.

In order to reveal the reason for the obvious difference in the formation of CFA in the two reactions, XRD patterns of the CF-Fe₂O₃-Al₂O₃ sample and CF-H_{ss} sample ranging from 34° to 34.8° were investigated. It was obvious that the diffraction peaks of CaAl₄O₇ and CaAl₂O₄ appeared in the CF-Fe₂O₃-Al₂O₃ sample, respectively, corresponding to PDF 23-1037 and PDF 23-1036. To verify the reason, the geometrical structure characteristic of Al-containing materials was further investigated. The results of SEM and EDS on the section of the CF-H_{ss} sample sintered at 1200 °C for 60 min and the CF-Fe₂O₃-Al₂O₃ sample sintered at 1200 °C for 120 min, respectively, are shown in Figure 4 and Table 4.

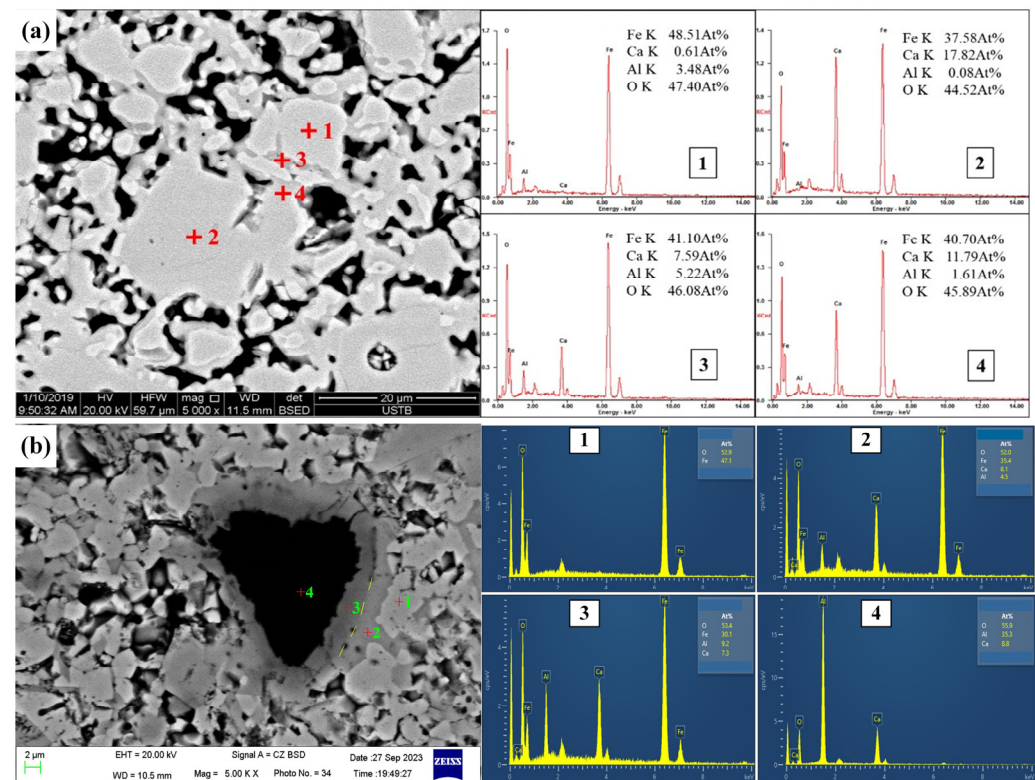


Figure 4. SEM and EDS images of samples for the reactions of CF, respectively, with mixtures of Fe₂O₃-Al₂O₃ (a) and H_{ss} (b) for different durations at 1200 °C.

Table 4. EDS results of samples for the reactions of CF, respectively, with the mixtures of Fe₂O₃-Al₂O₃ and H_{ss} for different durations at 1200 °C.

Position	Fe	Ca	Al	O	Minerals
Figure 4(a1)	48.51	0.61	3.48	47.40	H _{ss}
Figure 4(a2)	37.58	17.82	0.08	44.52	CF
Figure 4(a3)	41.10	7.59	6.22	46.08	CFA
Figure 4(a4)	40.70	11.79	1.61	45.89	CFA
Figure 4(b1)	47.06			52.94	Fe ₂ O ₃
Figure 4(b2)	35.40	8.12	4.50	51.97	Ca ₂ Fe _{15.50} O ₂₅
Figure 4(b3)	30.14	7.28	9.22	53.36	CFA
Figure 4(b4)		8.20	36.16	55.64	CA ₂

As shown in Figure 4a, combined with the EDS results as shown in Table 4, it can be confirmed that there are samples of H_{ss} with light gray and CF and CFA with dark gray in which the CFA and CF were hard to identify by SEM, and we could only rely on EDS due

to having a near-reflected electron color. The CF was directly surrounded by the CFA, and so it can be deduced that CFA was generated between CF and H_{ss} directly, as follows:



Then, the amount of CFA increased via the diffusion of Fe³⁺, Al³⁺, and Ca²⁺ in the CFA layer between the CF and H_{ss}.

As shown in Figure 4b, similarly, the phases CA₂, CFA, Ca₂Fe_{15.5}O₂₅, and Fe₂O₃ can be confirmed through the EDS results and XRD patterns. It can be seen that there was a clear layering structure in order of CA₂, CFA, Ca₂Fe_{15.5}O₂₅, and Fe₂O₃, where Al₂O₃ disappeared. To further confirm this result, it was characterized by EPMA, and the corresponding image and Al, Fe, and Ca mappings are shown in Figure 5. The Al, Fe, and Ca elements were distributed around the CA₂, corresponding to CFA, Ca₂Fe_{15.5}O₂₅, and Fe₂O₃, respectively, which is consistent with the result in Figure 4b. This can be seen in the result of Reactions (1), (2), and (4), in which Al₂O₃ reacted with CaO after Reaction (2) to generate calcium aluminum oxide (CA or CA₂) as follows:

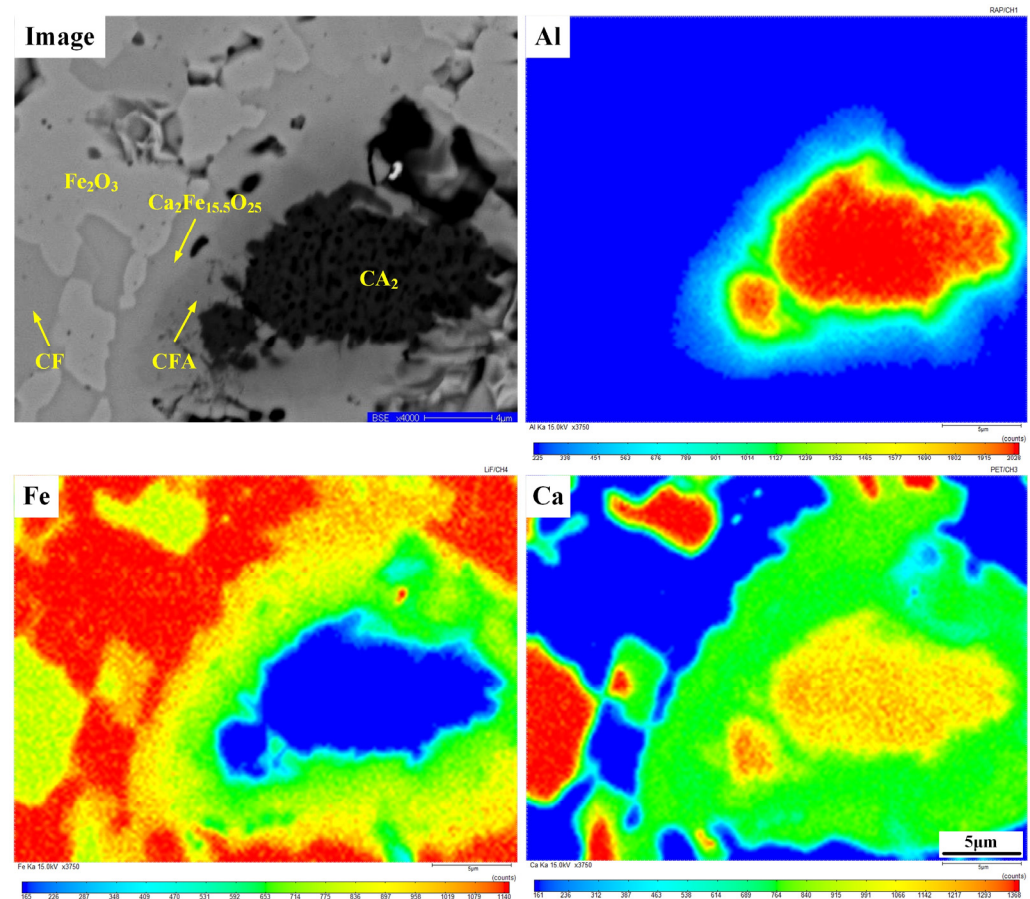
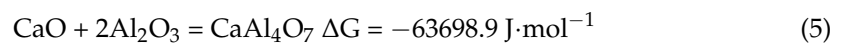
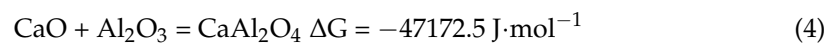


Figure 5. EPMA image and Al, Fe, and Ca mappings of CF-Fe₂O₃-Al₂O₃ sample section sintered at 1200 °C for 120 min.

Reactions (4) and (5) first occurred, respectively, due to the strong binding force and low Gibbs free energy for the formation of CA and CA₂. Afterwards, the Fe³⁺ in Fe₂O₃ and the Al³⁺ in Al₂O₃ diffused in opposite directions; simultaneously, the Ca²⁺ and Fe³⁺ in the CF diffused in the Fe₂O₃ and Al₂O₃ directions under the chemical potential until the CF and Al₂O₃ disappeared, forming the layering structure shown in Figure 5.

3.3. Reaction of CF with Fe_2O_3

$\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ is the product of Reaction (1) according to the XRD result, in which there is some doubt in the chemical composition. Karpinskii et al. reported several similar formulas like $\text{Ca}_2\text{Fe}_{15.51}\text{O}_{25}$ (PDF 78-2301), $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ (PDF 78-1669), and $\text{Ca}_{2.5}\text{Fe}_{15.5}\text{O}_{25}$ (PDF 79-440) as rhombohedral structures [29,30], and simultaneously reported $\text{Ca}_2\text{Fe}_{15.6}\text{O}_{25}$ (PDF 78-1184) and $\text{Ca}_2\text{Fe}_{15.588}\text{O}_{25}$ (PDF 78-1675) as hexagonal structures, two crystal structures that are also very similar [31]. These seem very difficult to understand with regard to experimental accuracy. For this reason, the chemical composition was verified by using the CF- Fe_2O_3 (CF-F) sample sintered at 1200 °C, respectively, for 5 h and 10 h in air by changing the Fe_2O_3 content. The XRD patterns of the CF-F samples are shown in Figure 6, indicating only $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ as a product at 1200 °C for 5 h and 10 h. In addition, it was observed that for 5h, the amount of CF in the samples increased with the increase in mole ratio of CF to Fe_2O_3 in the raw materials, as shown in Figure 6a. After sintering for 10 h, as shown in Figure 6b, the CF and Fe_2O_3 in the samples simultaneously disappeared when the mole ratio of CF to Fe_2O_3 in the raw materials was 1: 0.98, and the $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ formed completely. This indicates the formula corresponding to $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ should be $\text{CaFe}_{3.96}\text{O}_{6.94}$ ($\text{CF}_{1.98}$), similar to the chemical composition of CaFe_4O_7 . If the $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ as crystal structure is true, there will be a lot of Fe^{3+} and O^{2-} vacancies in $\text{CF}_{1.98}$, which is beneficial for its internal diffusion.

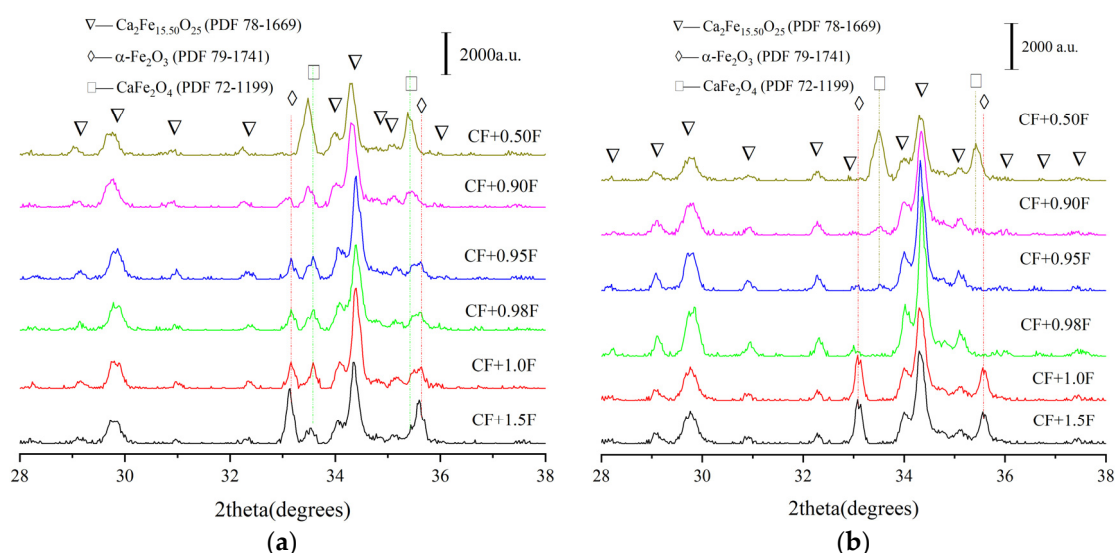


Figure 6. XRD patterns of CF- Fe_2O_3 (F) samples sintered at 1200 °C for different durations by changing the raw material composition: (a) 5 h; (b) 10 h.

For further reactions of $\text{CF}_{1.98}$, 5% Al_2O_3 and 10% Al_2O_3 were added, respectively, to $\text{CF}_{1.98}$, homogenized, pressed, and sintered at 1200 °C for 10 h. The XRD patterns of $\text{CF}_{1.98}\text{-Al}_2\text{O}_3$ samples are shown in Figure 7. It can be seen that the products of the reaction after adding of 5% Al_2O_3 and 10% Al_2O_3 into $\text{CF}_{1.98}$ were all CFA, indicating that the CFA was a solid solution with the same crystal structure although with differences in Al^{3+} content. The reaction is as follows:



$\text{CF}_{1.98}$ was also confirmed as a precursor of CFA formation.

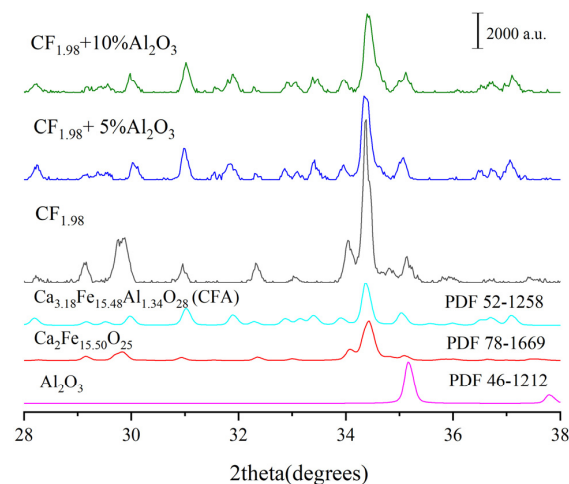


Figure 7. XRD patterns of $\text{CF}_{1.98}\text{-Al}_2\text{O}_3$ samples sintered at $1200\text{ }^\circ\text{C}$ for 10 h.

3.4. Reaction of CF with Al_2O_3

To further verify Reaction (2) with the $\text{CF-4\%Al}_2\text{O}_3$ sample sintered at $1200\text{ }^\circ\text{C}$ for different durations, the XRD patterns are shown in Figure 8. It can be seen that $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$, CaAl_2O_4 , CaAl_4O_7 , and a little CFA were products of sintering process in which the CaAl_2O_4 transformed to CaAl_4O_7 , and disappeared for 60min; simultaneously, the $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ increased with time, while the CF decreased. The result is consistent with Reaction (2); the diffraction peak intensities of $\text{Ca}_2\text{Fe}_{15.50}\text{O}_{25}$ and CFA in the $\text{CF-Al}_2\text{O}_3$ sample, as shown in Figure 8b, are clearly inferior to those in the $\text{CF-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ sample. As shown in Figure 3, the Fe_2O_3 could act as a conductive layer of Al^{3+} ; instead, the Al_2O_3 captured Ca^{2+} from the CF to generate CA and CA_2 . It can be considered that the CA or CA_2 was determined by the activity of Ca^{2+} (or CaO) at the interface between the Al_2O_3 and CF, but CaO was not observed as it was in the $\text{CF-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ sample. This further revealed that the appearance of CA or CA_2 is a main reason to decrease the rate of CFA formation.

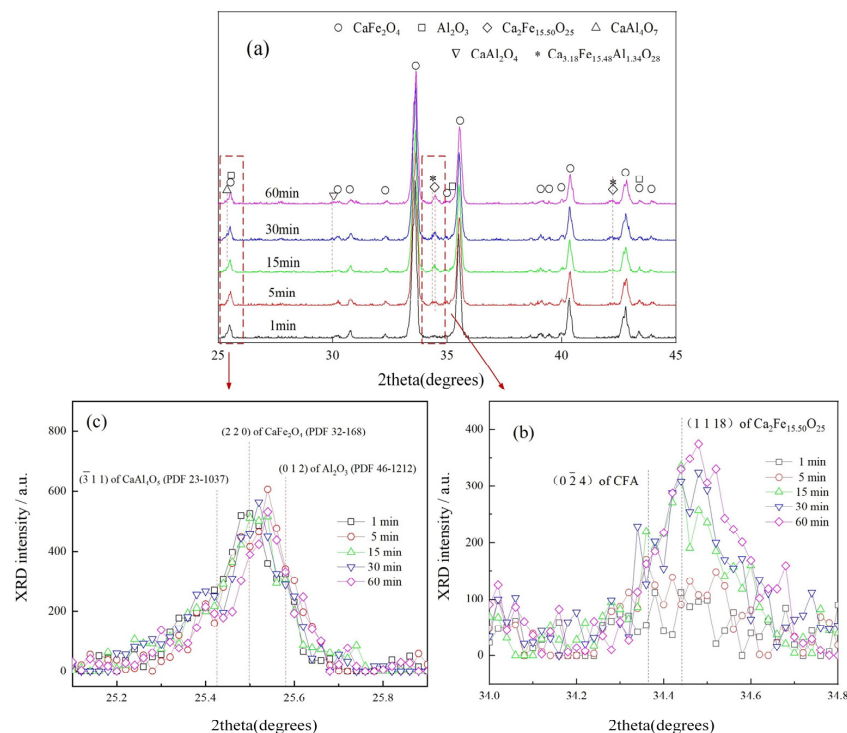


Figure 8. XRD patterns of $\text{CF 4\% Al}_2\text{O}_3$ sample sintered at $1200\text{ }^\circ\text{C}$ for different durations: (a) full spectrum; (b,c) partial spectrums.

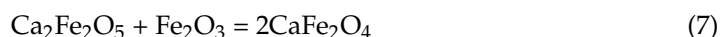
3.5. Stability of Products Generated in Reactions

Because the lack of thermodynamical data for the solid solution, the formation energy of the products was calculated by DFT on first-principles to estimate the stability. The result is listed in Table 5. It shows that the stabilities of CF and CF_{1.98} are lower than those of CFA, while those of CA, C₂F, and CA₂ are higher than those of CFA, indicating that the appearance of CA, C₂F, and CA₂ is not beneficial for CFA formation, simultaneously confirming that CF and CF_{1.98} are thermodynamic precursors of CFA formation.

Table 5. Formation energy of products in the reactions for formation of CFA (eV).

CF	CF _{1.98}	CFA	CA	C ₂ F	CA ₂
53,777	52,281	49,546	35,963	23,753	9092

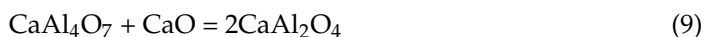
According to the above results, the mechanism of CFA formation in the Fe₂O₃-CaO-Al₂O₃ sample can be considered as follows: First, Fe₂O₃ reacts with CaO to generate CF or C₂F; simultaneously, Al₂O₃ reacts with CaO to generate CA or CA₂, wherein the product is determined by the activity of the reactants. In addition, the contact between Fe₂O₃ and Al₂O₃ may form a solid solution of H_{ss}. Further, CF and C₂F react, respectively, with Fe₂O₃ to generate CF_{1.98} and CF by Reaction (1) and Reaction (7), as follows:



CA reacts with Al₂O₃ to generate CA₂ by Reaction (8), as follows:



while CA₂ reacts with CaO to generate CA by Reaction (9), as follows:



And then, H_{ss} reacts with CF by Reaction (3) to generate CFA; simultaneously, Al₂O₃ reacts with CF_{1.98} by Reaction (6) to also generate CFA.

The above reactions revealed that the formation of CFA is not the same as for the CF, C₂F, CF_{1.98}, CA, and CA₂ generated, respectively, by pairwise direct reactions among Fe₂O₃, CaO, and Al₂O₃; it needs ion diffusion, especially in the case of Al³⁺, to the surface of precursors like CF and CF_{1.98}, in which the best media for diffusion should be a solid solution like CF_{1.98} or CFA with an ion vacancy; secondly CF, C₂F, and Fe₂O₃ have the ability to be replaced by Al³⁺ rather than CA or CA₂.

4. Conclusions

In this work, the formation of CFA in an Fe₂O₃-CaO-Al₂O₃ system was investigated below 1200 °C by reactions among Fe₂O₃, CaO, and Al₂O₃; CF with Fe₂O₃ and Al₂O₃; CF with Al-containing hematite; and CF with Al₂O₃ for promoting the low-temperature bonding phase in the sintering process of iron ore fines. The conclusions are summarized as follows:

- (1) It was observed in the Fe₂O₃-CaO-Al₂O₃ sample sintered below 1200 °C that CF appeared at 1000 °C, while Ca₂Fe_{15.5}O₂₅ and CFA appeared at 1100 °C.
- (2) It was found that CF and Ca₂Fe_{15.5}O₂₅ are the precursors for CFA formation, and the chemical composition of Ca₂Fe_{15.5}O₂₅ phase was determined to be CaFe_{3.96}O_{6.94} (CF_{1.98}), similar to CaFe₄O₇.
- (3) It was revealed that the appearance of CA or CA₂ is a main reason to decrease the rate of CFA formation in Fe₂O₃-CaO-Al₂O₃ samples.

Therefore, Al³⁺ diffusion is promoted in the Fe₂O₃-CaO-Al₂O₃ system, which contributes to an increase in the rate of CFA formation for promoting the low-temperature bonding phase in the sintering process of iron ore fines.

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