**Article**

**Effect of Al$_2$O$_3$ on the Formation of Calcium Ferrite in the Solid State**

Kaikai Bai®, Jiangwei Shen, Zhenglu Zhu, Haibin Zuo *, Yuzhu Pan, Jingsong Wang and Qingguo Xue

State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China; bk668666@163.com (K.B.); sjw2014ustb@163.com (J.S.); 18810375810@163.com (Z.Z.); panyuzhuustb@163.com (Y.P.); wangjingsong@ustb.edu.cn (J.W.); xueqingguo@ustb.edu.cn (Q.X.)

* Correspondence: zuohaibin@ustb.edu.cn; Tel.: +86-139-1094-9735

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**Abstract:** Pure chemical reagents Fe$_2$O$_3$, Al$_2$O$_3$, and Ca(OH)$_2$ were used to investigate the formation of calcium ferrite in the solid state. The phase composition of the prepared samples was determined using X-ray powder diffraction and by SEM. The TG-DSC analysis was performed to analyze the decomposition behavior and formation of calcium ferrites. The formation rate of calcium ferrite was determined by in-situ X-ray diffraction (XRD) and by the K-value method. The X-ray diffraction analysis was performed using Pt as the internal standard for application of the K-value method. The formation of Ca$_2$Fe$_2$O$_5$ (C$_2$F) occurred much earlier than the formation of CaFeO$_4$ (CF). C$_2$F and CF were formed at approximately 600 °C and 700–800 °C, respectively. With an increase of Al$_2$O$_3$ content, there was a tendency to decrease the melting temperature. There was a heating scheme in this study (i.e., 10 °C per minute to 1250 °C under a flowing atmosphere of high-purity air). The total amount of CF increased with an increase of the Al$_2$O$_3$ content, and the Al$_2$O$_3$ content reaching the maximum value of CF was 1.4%. As the Al$_2$O$_3$ content increased from 1.4% to 2.8%, the total amount of CF reduced slightly. When the Al$_2$O$_3$ concentration was greater than 2.8%, the content of CF generated significantly decreased with the increase of Al$_2$O$_3$.

**Keywords:** calcium ferrite; TG-DSC; in-situ XRD; K-value method; the formation rate of CF

1. **Introduction**

Currently, with increasing costs and decreasing profits, iron and steel enterprises are facing tremendous pressure to survive. Low cost smelting has become an important strategy for these enterprises to extricate from the predicament. The guiding ideology of reducing the consumption of traditional production using the fine material route has not been adapted to the current situation and high-quality iron ore resources are shrinking, and therefore this limited material is commanding higher prices. Consequently, a new fine material concept has been proposed which aims to lower costs by considering energy and resource consumption. Currently, in many enterprises, instead of high-quality iron ore, iron ore with high alumina is widely put into production due to its low price. China imports several million tons of high alumina iron ore from Australia, India, South East Asia, and Africa every year, driven by the continued massive growth of steel production in China which is expected to continue for years to come [1]. Theory and practice have demonstrated that alumina cannot be reduced in a blast furnace, therefore, it cannot stain the hot metal and does no harm to steelmaking. The presence of alumina in iron ore mainly affects the sinter and slag properties, which leads to difficulties and instability during the blast furnace operation. Increased levels of high aluminum ore during ironmaking leads to problems which include decreased grade of the sinter, metallurgical performance deterioration, reduced blast furnace permeability in smelting, increased slag
ratio, and increased coke rate [2,3]. Without finding solutions to these problems, the production costs will continue to increase. Accordingly, rational and efficient use of high aluminum ore has become an urgent issue for the steel enterprises. In past decades, many studies have been conducted on the effect of aluminum on sintering production, the sintering ore quality, and blast furnace smelting and operation. Some countermeasures have been proposed for sinter production and blast furnace smelting of materials with high alumina content. However, the majority of these controlling strategies were proposed to address specific production conditions, without considering the action of alumina, which has led to less than ideal results when indiscriminately applied. The silicoferrite of calcium and aluminum (SFCA) phases are considered the most desirable bonding phases in iron ore sinter because of their high reducibility [4], high mechanical strength, and low reduction degradation [5,6], all of which are significant factors in determining the productivity and efficiency of the blast furnace. The theoretical system of formation characteristics, microstructure, and metallurgical properties of the main binder phase of sintered ore with high aluminum content remains poorly understood.

Many studies have focused on the properties of calcium ferrite bonding phases, stability, and solid solution limits of SFCA as the major phase in high basicity iron-ore sinter. SFCA was found to be stabilized with the Fe$_2$O$_3$-CaO-Al$_2$O$_3$-SiO$_2$ (FCAS) quaternary, along a plane that connects CF$_3$, CA$_3$, and C$_2$S$_2$ (CCC plane) by Patrick [7,8]. Machida et al. measured the viscosity of melted liquid composed of iron ores and reagents and calculated the viscosity of suspension [9]. Sukenaga investigated viscosity changes of CaFeO$_4$ (CF)-based slags with melting time [10]. Pownceby et al. studied the formation mechanism of calcium ferrite using in-situ X-ray diffraction (XRD), and found that quartz did not react at all with CaO and Fe$_2$O$_3$, remaining essentially inert until SFCA and SFCA-I began to form near 1050 °C. The formation of SFCA-I was associated with the reaction of Fe$_2$O$_3$, C$_2$F, and SiO$_2$. SFCA was initially formed by a reaction of CF, CFA-phase, and SiO$_2$, and its initial formation was related to the formation of CS and a melt phase [11]. Pownceby also determined the reaction sequences involved in the formation of SFCA using in-situ X-ray diffraction (XRD) and determined the content of SFCA by Rietveld-based quantitative phase analysis [12]. Their study indicated that the formation of SFCA was dominated by the solid-state reactions, mainly in the CaO-Fe$_2$O$_3$ system. Kang et al. studied the influence of the oxygen partial pressure on the final sinter phases [13]. Much attention has been given to factors that affect the structure of SFCA including chemical composition, sinter basicity, and the maximum sintering temperature [14]. With an increased availability of Al$_2$O$_3$ iron ore, the influence of Al$_2$O$_3$ on the formation of SFCA during sintering is of interest. Takayuki et al. found that the effects of adding Al$_2$O$_3$ on the formation rate of calcium ferrite melt were to increase the melting rate and reduce the liquid formation temperature of the sample in the calcium ferrite system by the coal ash melting examination method (JIS M 8801-10) [15]. Sinha and Ramna reported that Al$_2$O$_3$ had a predominant effect on the microhardness of hematite and magnetite phases [16]. The effect of Al$_2$O$_3$ on the pore structure of experimental compact sinters was investigated by Lu, Holmes and Manuel. They thought the pore area increased drastically, and the pore shape became more irregular as alumina increased from 1.6% to 2.4% [17]. Kasai et al. examined the assimilation behavior of different iron ores and limestone with different size ranges using a differential thermal analysis (DTA) technique [18]. The results showed that the Al$_2$O$_3$ from different mineralogical phases influenced the endothermic peak, resulting in an incongruent melting of SFCA, suggesting that different sources of alumina may alter the composition of SFCA.

As the major bonding phase, the quantity and quality of calcium ferrite determined the metallurgical properties of the sinter, and therefore it is very important to study the formation of calcium ferrite and its microstructure characteristics. In this study, a new method was used to calculate the content of SFCA. The objective of this study was to investigate the influence of different Al$_2$O$_3$ concentrations on the formation of calcium ferrites by solid-state reaction using TG-DSC (Thermogravimetric Analysis and differential scanning calorimetry) and SEM. Other studies have mainly controlled the content of SiO$_2$ and Al$_2$O$_3$ to study SFCA, but few studies have investigated SFCA by adding pure CF.
2. Experiments

2.1. Starting Sinter Mixture Preparation

The pure chemical reagents Fe$_2$O$_3$, Al$_2$O$_3$, and Ca(OH)$_2$ were used as test materials. Considering the stability of CaO in the mixture under 600 °C and eliminating the weighing error caused by water absorption of CaO, Ca(OH)$_2$ was used instead of CaO. The reagents were mixed with acetone at the desired ratio and ground using a mortar and pestle to ensure homogeneity. The sample compositions of the solid-state reaction experiments are shown in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition/g</th>
<th>wt(Fe$_2$O$_3$)%</th>
<th>wt(Al$_2$O$_3$)%</th>
<th>wt(Ca(OH)$_2$)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5128</td>
<td>0.2372</td>
<td>68.37</td>
<td>31.63</td>
</tr>
<tr>
<td>2</td>
<td>0.5056</td>
<td>0.2399</td>
<td>67.41</td>
<td>31.19</td>
</tr>
<tr>
<td>3</td>
<td>0.4985</td>
<td>0.2305</td>
<td>66.47</td>
<td>30.73</td>
</tr>
<tr>
<td>4</td>
<td>0.4913</td>
<td>0.2272</td>
<td>65.51</td>
<td>30.29</td>
</tr>
<tr>
<td>5</td>
<td>0.4841</td>
<td>0.2239</td>
<td>64.55</td>
<td>29.85</td>
</tr>
</tbody>
</table>

All the tests and experiments reported in this study were conducted in air atmosphere. In the TG-DSC tests, mixed powders were directly used as test samples. All the tests were carried out with a Q600 SDT TG-DSC thermal analyzer (TA Instruments, New Castle, USA) using a heating rate of 20 °C/min from room temperature to 1523 K.

The samples were mixed for 30 min using a three-dimensional mixer (Sujia Powder Machinery Co., Ltd., Shanghai, China), to ensure homogeneity of composition and particle size. Mixed powders of 3–5 µm particle size accounted for more than 90% of the samples. The mixed powders were pressed into columns with a diameter of 6 mm and a length of 21–25 mm in a stainless module under a pressure of 15 MPa. The samples were heated in a muffle furnace. The temperature adjacent to the crucible was measured using a Pt/PtRh13 pct thermocouple connected to the top of the muffle furnace. For experiments where the samples were held at the desired temperature for 90 min, the temperature fluctuation range was controlled accurately between ±5 K. The samples were water quenched and then crushed, and a small piece was collected from each sample and prepared for scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Quantitative chemical microanalyses of the phases were performed by SEM-EDS (FEI company, Hillsboro, OR, USA) and chemical compositions of the various mineralogical constituents were evaluated.

A FEI Quanta 400 field emission environmental SEM (FEI Corporation, Hong Kong, China) was employed in this study and the SEM was operated at an accelerating voltage of 30 kV and a working distance of 10 mm. Energy-dispersive spectroscopy (EDS) was performed on this instrument using a Bruker X-Flash 5010 Si-drift EDS detector (Bruker AXS, Madison, WI, USA).

2.2. In-Situ XRD

In-situ XRD experiments were performed using a SmartLab diffractometer (Rigaku, Tokyo, Japan) that incorporated a sensitive detector allowing simultaneous collection of up to 160° 2θ of diffraction data. The X-ray tube was operated at 45 kV and 200 mA. A tungsten resistance strip was equipped to heat the samples. The sinter sample mixture was prepared and placed into the corundum crucible, which was 15 mm in diameter and 0.8 mm in height. To reduce the error of corundum crucible, a platinum sheet with 15 mm diameter was padded at the bottom of the crucible.

The temperature of the samples was increased at a heating rate of 20 K-min$^{-1}$ from 298 K to 1423 K (approaching the decomposition temperature of CF) during the CF phase formation. The temperature was measured using a Pt/PtRh10% thermocouple placed under the platinum pad. In-situ XRD data
were collected throughout the heating procedure, with individual datasets recorded at an interval of 50 °C from 973 K to 1423 K.

2.3. Quantitative Method of the Mineralogical Phase

In quantitative X-ray diffraction phase analysis, for the internal standard method, the doping method [19] requires standard substance to be added to the sample to make the working curve and the added standard phase leads to more overlapping opportunities for the spectral lines. Although no standard phase is needed for the external standard method, it has lower measuring accuracy as compared with the internal standard method. The quantitative phase analysis method without standard and the Rietveld full-pattern fitting method are superior in accuracy; the Rietveld full-pattern fitting method is suitable for the quantitative analysis of complex samples. The K-value method is easy to understand and operate, each method has clear physical interpretation and operation steps, and it is suitable for samples with few phase types. In our experiment, considering the explicit phase composition and easy obtainability of the pure measuring phase calcium ferrite (CF), the matrix flushing method, usually called K-value method, was applied. The content of the measured mineral phase is described as follows:

\[ X_J = \frac{1}{K} \cdot \frac{X_S}{1 - X_S} \cdot \frac{I_{1J}}{I_{1S}} \]

where, \( X_J \) and \( X_S \) are the mass fractions of the measured phase and reference phase, respectively, and \( I_{1J} \) and \( I_{1S} \) are the strongest diffraction peak intensity of the measured phase and the inner standard phase, respectively. \( K \) is the reference intensity, which is independent of the amount and only corresponding to the type of inner standard substance. In this method the inner standard substance is mixed with the measured sample as a cleaning agent to “clean” off the matrix effect. The cleaning agent is actually the internal standard substance with characteristics of high purity, good chemical stability, and without the preferred orientation. A variety of reagents were tried, and consequently, the platinum was proven to meet the experimental demands as the cleaning reagent.

To obtain the \( K \) value, pure calcium ferrites were prepared in the laboratory according to the following process. The pure reagents Ca(OH)\(_2\) (99.99% purity) and Fe\(_2\)O\(_3\) (\(\alpha\)-Fe\(_2\)O\(_3\), 99.99% purity) were mixed evenly at a molar ratio of 1:1 for 30 min, then pressed into a cylinder shape under 10 MPa to obtain a homogenous sample. The samples were heated from room temperature to 1200 °C with a heating rate of 20 °C/min in the muffle furnace, holding for 8 h in air atmosphere to react completely and generate pure calcium ferrites. The samples were pulverized in a vibration mill.

Five standard samples composing of CF, Pt, and Fe\(_2\)O\(_3\) were carefully prepared according to the desired ratio as shown in Table 2 to eliminate possible measuring error.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>70</td>
<td>60</td>
<td>50</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Pt</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Through XRD pattern at room temperature, the diffraction peak intensity ratio \( \frac{I_{CF}}{I_{Pt}} \) corresponding to the chemical composition was obtained. According to the definition of \( K \): \( \frac{I_{CF}}{I_{Pt}} = K \frac{X_{CF}}{X_{Pt}} \), make linear fitting to get the slope, which represented the \( K \) value at room temperature, named \( K_1 \). The XRD patterns show that the diffraction peak intensity of Pt at high temperature is different from the diffraction peak intensity of Pt at room temperature, while the diffraction peak shape of Fe\(_2\)O\(_3\) has no evident change. Accordingly, this difference can be revised through the ratio of \( \frac{I_{Fe_2O_3}}{I_{Pt}} \) at 25 °C and 700 °C, named \( K_2 \), the reference intensity \( K = K_1/K_2 \). Using Equation (1), the content of CF in the sample can be determined.
3. Results and Discussion

3.1. The TG-DSC Analysis of Sintering Mixture with Different Al₂O₃ Content

Figure 1 shows the TG-DSC curves of the samples at various Al₂O₃ contents (0, 1.4%, 2.8%, 4.2%, and 5.6%). The molar ratio of Ca(OH)₂ and Fe₂O₃ in these five tests is 1:1. As temperature increases from room temperature to 1250 °C, three endothermic peaks mainly appear in order. For these five tests, an obvious endothermic peak appears at around 400 °C, where the decomposition reaction of Ca(OH)₂ occurs. Comparing the dehydration temperatures of Ca(OH)₂ with different Al₂O₃ contents shows that an increase in the amount of Al₂O₃ has no effect on the decomposition of Ca(OH)₂, and this finding reflects that no reaction between Al₂O₃ and CaO happens at this temperature.

Figure 1. Curves of the mixed powders with different Al₂O₃ contents. (a) 0, (b) 1.4%, (c) 2.8%, (d) 4.2%, (e) 5.6%.
As the temperature increases from the ending temperature of Ca(OH)\(_2\) decomposition to about 1000 °C, no obvious endothermic or exothermic peak appears, and the DSC curve goes up but not evenly. Because there are only a few Al\(_2\)O\(_3\) in the sample, the effect of the formation of CaO-Al\(_2\)O\(_3\) and CaO-2Al\(_2\)O\(_3\) are ignored. Accordingly, the uneven going up perhaps contributes to the slow formation of C\(_2\)F (Ca\(_2\)Fe\(_2\)O\(_5\)) which is an endothermic reaction. This result was also proven by Yin [20]. Another reason is the heat capacity of C\(_2\)F (Ca\(_2\)Fe\(_2\)O\(_5\)) is much larger than that of calcium oxide and ferric oxide [21], leading to an increase in the overall heat capacity of the mixed sample.

As the temperature increases, there is a small peak that appears at around 1050 °C on the DSC curves for all samples. The temperature range of the peak is where the calcium ferrites generate rapidly, and the temperature of the peak point represents the maximal generation speed temperature. The peak point temperature is different from that of Yin, who reported the peak point temperature at around 985 °C. The increase of the peak temperature attributes to the thermal hysteresis phenomena caused by the higher heating rate, 20 K/min versus 10 K/min. According to the results analyzed by PeakFit software (Informer Technologies, Inc., Version 4.04), when the Al\(_2\)O\(_3\) content is lower than 4.2%, the endothermic peak area varies in accordance with the Al\(_2\)O\(_3\) content in the mixture, indicating that with an increase of Al\(_2\)O\(_3\), the amount of calcium ferrite is promoted. Meanwhile, the maximal generation speed temperature of calcium ferrite decreases when Al\(_2\)O\(_3\) content increases, implying that Al\(_2\)O\(_3\) plays a positive role in the generation of calcium ferrite. Increasing the Al\(_2\)O\(_3\) content to 5.6%, the amount of calcium ferrite reduces and the maximal generation speed temperature increases, and Al\(_2\)O\(_3\) begins to reveal a negative effect on the formation of calcium ferrite. The third endothermic peak corresponds to the melting process of calcium ferrite. As the Al\(_2\)O\(_3\) content increases, there is a tendency to decrease the melting temperature. Aluminum solid solution calcium ferrite is the main binder phase of high alkalinity sinter, which has a low melting point phase. Because its content increases greatly with the increase of aluminum content, the content of the low melting point binder phase is high under high aluminum conditions [22].

Figure 2 shows the TG-DSC curves for different concentrations of Al\(_2\)O\(_3\) with 50% CF addition, and the third endothermic peak in the figure is the one located at about 1220 °C. The CF addition reduces the temperature of the maximum production rate of the calcium ferrite and sample melting. The endothermic peak area decreased, which indicates that the addition of CF decreases the maximum formation rate of the calcium ferrite.

![Figure 2. Cont.](image-url)
The Gibbs free energy of the 4 groups were negative and increased with an increase of temperature. Variation curves of reaction type (2) to reaction type (5) were calculated and are shown in Figure 3.

As the temperature increased to 1200 °C, and the melt vermicular calcium ferrite CF increased. The acicular calcium ferrite C2F disappeared and Fe2O3 at 1000 °C, and the shape of C2F differed from that at 900 °C. The melt vermicular calcium ferrite CF occurred by the reaction of C2F and Fe2O3. The needlelike calcium ferrite decreased at 1100 °C, as the temperature increased to 1200 °C.

From a structural perspective, the needle-like C2F was produced by the reaction between CaO and Fe2O3, and Fe2O3 at 1000 °C, and the shape of C2F differed from that at 900 °C. The melt vermicular calcium ferrite CF occurred by the reaction of C2F and Fe2O3. The needlelike calcium ferrite decreased at 1100 °C, and the melt vermicular calcium ferrite CF increased. The acicular calcium ferrite C2F disappeared as the temperature increased to 1200 °C.

3.2. Phase Evolution

For the tested samples, the possible chemical reactions during heating are listed as follows:

\[
\begin{align*}
\text{Ca(OH)}_2(s) & \rightarrow \text{CaO} (s) + \text{H}_2\text{O(g)} && (1) \\
\text{CaO(s)} + \text{Al}_2\text{O}_3(s) & \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3(s) && (2) \\
\text{CaO(s)} + 2\text{Al}_2\text{O}_3(s) & \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3(s) && (3) \\
2\text{CaO(s)} + \text{Fe}_2\text{O}_3(s) & \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5(s) && (4) \\
\text{CaO(s)} + \text{Fe}_2\text{O}_3(s) & \rightarrow \text{CaFe}_2\text{O}_4(s) && (5)
\end{align*}
\]

Referring to published inorganic thermodynamic data, the Gibbs free energy and temperature variation curves of reaction type (2) to reaction type (5) were calculated and are shown in Figure 3. The Gibbs free energy of the 4 groups were negative and increased with an increase of temperature. Ca2Fe2O5 is the most easily formed, and CaFe2O4 is the most difficult to form.

It is clearly seen by the b-2 in Figure 4 that taking the particles of CaO as the center, CaO is surrounded by C2F and wrapped with CF. C2F occurs first by the reaction between CaO and Fe2O3, and C2F and CF are generated subsequently. CF is not directly generated, which is consistent with the research of Xiang Ding et al. [23].

To compare the effects of different amounts of Al2O3 on the morphology of calcium ferrite, electron microscopy was performed on samples containing 1.4% Al2O3 or 5.6% Al2O3, as shown in Figure 4. From a structural perspective, the needle-like C2F was produced by the reaction of CaO and Fe2O3 at 1000 °C, and the shape of C2F differed from that at 900 °C. The melt vermicular calcium ferrite CF occurred by the reaction of C2F and Fe2O3. The needlelike calcium ferrite decreased at 1100 °C, and the melt vermicular calcium ferrite CF increased. The acicular calcium ferrite C2F disappeared as the temperature increased to 1200 °C.
**Figure 3.** The Gibbs free energy and temperature variation curves of the reaction type (2) to reaction type (5) over the range 800 K to 1500 K (527 °C to 1227 °C).

**Figure 4.** Cont.
3.3. Effect of Al₂O₃ Content on Formation Rate of CF

The calcium ferrites were prepared and subjected to XRD analysis. The results (Figure 5) show that the XRD pattern of the prepared sample fits well with that of CaO-Fe₂O₃ in the standard PDF card, and that other impurity peaks are not obvious. These findings reflect that the prepared sample is composed of pure calcium ferrite, meeting the demands of standard sample used for determining the reference intensity, $K$.

![X-ray diffraction (XRD) patterns of samples and CaO-Fe₂O₃ in standard PDF card.](image)

**Figure 5.** X-ray diffraction (XRD) patterns of samples and CaO-Fe₂O₃ in standard PDF card.
The XRD patterns at room temperature of five standard samples (the chemical compositions of the samples are listed in Table 2) are shown in Figure 6. The value of $I_{CF}/I_{Pt}$, the area ratio of the strongest peak of CF and Pt, was obtained using PeakFit software. According to the definition of $K$, $I_{CF}/I_{Pt}$ and $X_{CF}/X_{Pt}$ should show a basic linear relationship, as shown in Figure 7. $K_1$ is the slope of the fitting line according to the formula $K = K_1/K_2$ and its value is 0.08292. Because the peak shape of Pt at room temperature is different from that at high temperature, it needs to be modified. On the basis that Fe$_2$O$_3$ hardly reacts at 700 °C and has the same peak shape at 700 °C and room temperature, consequently, the $K$ at high temperature was modified by the aid of the peak intensity of Fe$_2$O$_3$. Figure 8 shows the relationship of $I_{Pt700°C}/I_{PtHT}$ between room temperature and 700 °C, where the slope named $K_2$ indicates the value of $I_{Pt700°C}/I_{PtHT}$. According to Figure 8, $K_2$ is 0.73499. Furthermore, the modified $K$ at high temperature can be obtained through $K = K_1/K_2$, and the result is 0.112818.

**Figure 6.** The X-ray diffraction patterns of standard samples.

**Figure 7.** The relationship between the accumulation intensity ratio $I_{CF}/I_{Pt}$ of the diffraction peak and the mass fraction ratio $X_{CF}/X_{Pt}$ at room temperature.
Figure 8. Relationship between the accumulation intensity ratio $I_{CF}/I_{Pt}$ of the diffraction peak at room temperature and 700 °C.

In-situ XRD patterns of samples with different $\text{Al}_2\text{O}_3$ contents were collected every 50 °C from 700 °C to 1150 °C as shown in Figure 9. The peak of CF emerges at about 800 °C and the intensity enhances gradually as the roasting temperature increased. Correspondingly, the peak intensity of $\text{Fe}_2\text{O}_3$ decreases. CF occurred at 700–800 °C as indicated by the X-ray diffraction patterns, which differs from the study by Scarlett. Scarlett et al. reported that the formation of $\text{C}_2\text{F}$ and CF were observed at approximately 750 °C and 1000 °C, respectively. However, that study used a different heating scheme (10 °C per minute to 600 °C, and then, 5 °C per min to approximately 1260 °C under a flowing atmosphere of high-purity air). They reported that the occurrence of CF started at about 968–979 °C (varied with the addition of $\text{Al}_2\text{O}_3$) by using a heating rate of 20 °C/min from 25 °C to 600 °C and 10 °C/min from 600 °C to 1350 °C under a continuous gas flow of $\text{N}_2$ and $\text{O}_2$ ($p_{\text{O}_2} = 5 \times 10^{-3}$ atm).

Figure 9. Cont.
The thermodynamics is more strongly combined with that of Fe$_2$O$_3$. Under the push of this chemical difference, it is easy to enter simple CF or C$_2$F [25], forming the aluminum solid solution composite calcium ferrite.

A set of straight lines following the data in Figure 10 were generated using OrginPro8 software (Microcal Co., Northampton, MA, USA), and the average generation rates of CF in the temperature range of 800–1150 °C were obtained. The generation rates were 0.185%/°C, 0.218%/°C, 0.171%/°C, 0.194%/°C, 0.218%/°C, 0.171%/°C, 0.194%/°C, and 0.157%/°C corresponding, respectively, to the different Al$_2$O$_3$ content of 0, 1.4%, 2.8%, 4.2%, and 5.6%. The total amount of CF increased with an increase in Al$_2$O$_3$ levels, and the Al$_2$O$_3$ concentration for the maximum value of CF was 1.4%. As Al$_2$O$_3$ content increased from 1.4% to 2.8%, the total amount of CF reduced slightly. At Al$_2$O$_3$ levels greater than 2.8%, the content of CF generated significantly decreased with an increase of Al$_2$O$_3$ content. With an increase of Al$_2$O$_3$ content, the chemical composition of the composite calcium ferrite ore also changed greatly. When the Al$_2$O$_3$ content increased from 1.5% to 3.0%, the chemical composition changed from 7.7CaO·13.6Fe$_2$O$_3$·Al$_2$O$_3$·3.4SiO$_2$ to 4.8CaO·11.4Fe$_2$O$_3$·Al$_2$O$_3$·2SiO$_2$ [24]. With an increase of Al$_2$O$_3$ content, the activity of Al$_2$O$_3$ increases, and it is most similar to Fe$_2$O$_3$ in this system. The thermodynamics is more strongly combined with that of Fe$_2$O$_3$. Under the push of this chemical difference, it is easy to enter simple CF or C$_2$F [25], forming the aluminum solid solution composite calcium ferrite.

**Figure 9.** In-situ XRD data collected for samples with different Al$_2$O$_3$ concentrations over the range 973 K to 1423 K (700 °C to 1150 °C) and 30° < 2θ < 45°, showing the formation of CF. (a) 0 Al$_2$O$_3$, (b) 1.4% Al$_2$O$_3$, (c) 2.8% Al$_2$O$_3$, (d) 4.2% Al$_2$O$_3$, (e) 5.6% Al$_2$O$_3$.

**Figure 10.** Comparison of samples with different Al$_2$O$_3$ concentrations on the conversion rate of CF at different temperatures.
The reaction (6) is obtained by combining reactions (2) + (5). The reaction (7) is obtained by combining reactions (3) + (5); The reaction (8) is obtained by combining the reactions (5) + (5). The reactions (6–8) are as follows:

\[2\text{CaO}(s) + \text{Al}_2\text{O}_3(s) + \text{Fe}_2\text{O}_3(s) \rightarrow \text{CaO}·\text{Al}_2\text{O}_3(s) + \text{CaFe}_2\text{O}_4(s)\]  \hspace{1cm} (6)

\[2\text{CaO}(s) + 2\text{Al}_2\text{O}_3(s) + \text{Fe}_2\text{O}_3(s) \rightarrow \text{CaO}·2\text{Al}_2\text{O}_3(s) + \text{CaFe}_2\text{O}_4(s)\]  \hspace{1cm} (7)

\[2\text{CaO}(s) + 2\text{Fe}_2\text{O}_3(s) \rightarrow 2\text{CaFe}_2\text{O}_4(s)\]  \hspace{1cm} (8)

The free energy of Gibbs decreased with increasing amounts of Al\textsubscript{2}O\textsubscript{3} from the thermodynamic point of view, as shown in Figure 11. When the Gibbs free energy of the reaction was lower, the reaction occurred more easily. As the concentration of Al\textsubscript{2}O\textsubscript{3} increased, there was an increased formation of CF. This is in accordance with the findings of other investigators [26, 27], who reported an increase in the formation of calcium ferrite for sinters prepared with the addition of Al\textsubscript{2}O\textsubscript{3}.

High Al\textsubscript{2}O\textsubscript{3} concentrations will hinder the reaction of CaO and Fe\textsubscript{2}O\textsubscript{3} from the point of view of dynamics analysis. At concentrations of Al greater than 2.8%, the dynamics have a significant influence on the reaction, more than thermodynamic effects.

![Figure 11](image-url)  \hspace{1cm} Figure 11. The Gibbs free energy and temperature variation curves of the reaction type (6) to reaction type (8) over the range 800 K to 1500 K (527 °C to 1227 °C).

4. Conclusions

Three pure chemical reagents (Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, and Ca(OH)\textsubscript{2}) were used to study the formation of calcium ferrite in solid state. Phase composition of the samples was determined using X-ray powder diffraction and by SEM. In addition, TG-DSC analysis was also used to determine the decomposition behavior and formation of calcium ferrites at different Al\textsubscript{2}O\textsubscript{3} concentrations at temperatures ≤1250 °C. The formation rate of calcium ferrite was determined by in-situ XRD and by the K-value method.

The following conclusions were drawn from the results:

1. Both Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} and CaFe\textsubscript{2}O\textsubscript{4} were formed at different concentrations of Al\textsubscript{2}O\textsubscript{3}. The formation of Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} (C\textsubscript{2}F) occurred much earlier than CaFe\textsubscript{2}O\textsubscript{4} (CF). The C\textsubscript{2}F and CF formed at approximately 600 °C and 700–800 °C, respectively. As Al\textsubscript{2}O\textsubscript{3} increased, the melting temperature decreased.

2. Pt was used as an internal standard because the chemical properties of Pt at high temperatures are stable, allowing the application of the K-value method: \(X_j = \frac{1}{K} \cdot \frac{X_j}{I_j} \cdot \frac{I_j}{I_j}, K = 0.112818\).
(3) The total amount of CF increased with an increase of Al$_2$O$_3$ concentration, and the Al$_2$O$_3$ content at the maximum value of CF was 1.4%. As the amount of Al$_2$O$_3$ increased from 1.4% to 2.8%, the total amount of CF reduced slightly. At greater than 2.8% Al$_2$O$_3$, the concentration of CF generated significantly decreased as Al$_2$O$_3$ increased.

(4) The free energy of Gibbs decreased with increasing amounts of Al$_2$O$_3$ from the thermodynamic point of view. As the concentration of Al$_2$O$_3$ increased, there was increased formation of CF.

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**References**


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