Crystallization Kinetics of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ in the CaO–Fe₂O₃ System

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In this study, the non-isothermal crystallization kinetics of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ were investigated by DSC measurement. Crystallization of CaO–Fe₂O₃ system includes three reactions and can be explained using Fe₂O₃–CaO phase diagram. The mechanisms of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ crystallization were analyzed using Avrami and Mo models. Results of the Avrami model analysis indicated that growth of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ include two stages, which are controlled first by a fibril-like mechanism followed by a spherulitic-type mechanism. The Mo model analysis yielded results similar to those of the Avrami model and further concluded that Avrami exponent/Ozawa exponent is constant despite the changes in cooling rate. Calculations using Kissinger method revealed that the activation energy of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ crystallization were −464.16 kJ·mol⁻¹ and −172.61 kJ·mol⁻¹, respectively.

Moreover, 2CaO·Fe₂O₃ crystallization occurs in a difficult manner but proceeds at a faster rate than CaO·Fe₂O₃ crystallization. Increasing the cooling rate promotes CaO·Fe₂O₃ crystallization but inhibits 2CaO·Fe₂O₃ crystallization, which is beneficial during sintering.

KEY WORDS: sinter; 2CaO·Fe₂O₃; CaO·Fe₂O₃; crystallization kinetics; Avrami model; growth type.

1. Introduction

In the 1960s and 1970s, the CaO–Fe₂O₃ system replaced the silicate system as the focus in fluxed sinter research.¹ Fluxed sinter containing CaO–Fe₂O₃ system as bonding phase demonstrates improved physical and metallurgical performance. Research on calcium ferrite, especially its reduction, is extensive.²⁻⁵ However, crystallization of calcium ferrite has not been intensively investigated. The crystallization behavior and crystal morphology of CaO–Fe₂O₃ system affect various indices, such as strength and reducibility, which are used to evaluate the quality of fluxed sinter. Research on the growth type of CaO–Fe₂O₃ system is useful in indirectly investigating the microstructure of the crystallization phase. Crystallization of the CaO–Fe₂O₃ system has not been reported. With the rapid development in thermal analysis methods, such as thermogravimetry (TG) and differential scanning calorimetry (DSC), thermal analysis kinetics has become an effective method used to describe crystallization behavior.

Sosman and Merwin⁶ initially assessed the phase relationship in the CaO–Fe₂O₃ system in air atmosphere in 1916, however, CaO·2Fe₂O₃ was not considered in their theoretical system, but proven by Tavasci⁷ in 1936. By using phase stability analysis, Malquori and Cirilli⁸ demonstrated that CaO·Fe₂O₃ is more stable than CaO·2Fe₂O₃ in a system equilibrated with Fe₂O₃. Edstrom⁹ reported the temperature interval of phases generated in the CaO–Fe₂O₃ system. Muan¹⁰ finally demonstrated the phase diagram of CaO–Fe₂O₃ in air and at 1 atm O₂ pressure, in which phase stability, Fe₂O₃ decomposition, and 2CaO·Fe₂O₃ melting were fully discussed. The morphology of calcium ferrite is highly relevant to phase analysis but has been rarely studied, especially through thermal analysis. Thus, the present study investigated crystallization by using kinetic methods in thermal analysis. This paper discusses only the binary system. The influence of chemical components on crystallization will be tackled in future work.

The Avrami¹¹⁻¹³, Ozawa¹⁴, and Mo¹⁵⁻¹⁷ models are used to analyze the crystallization of copolymers, minerals, and metals. The present study used these models to analyze the crystallization behavior of the CaO–Fe₂O₃ system. The relationship of conversion ratio to crystallization time and temperature was determined by the kinetics study through thermal analysis. DSC scans with regard to the association of heat flow with enthalpy changes provide a scientific means to assess the relevance of conversion ratio to crystallization time and temperature. The non-isothermal crystallization kinetics of 2CaO·Fe₂O₃ and CaO·Fe₂O₃ are further investigated by DSC measurement with Avrami, Ozawa, and Mo models. Moreover, the activation energy for generating 2CaO·Fe₂O₃ and CaO·Fe₂O₃ are calculated using Kissinger¹⁸ method.

2. Theoretical Basis

2.1. Avrami Model

Studies on thermal analysis kinetics have gradually shifted
from the use of isothermal methods to non-isothermal methods. 19) In particular, the Avrami model was derived from the isothermal system and extended to the non-isothermal system by substituting crystallization time to temperature. Other non-isothermal models, such as the Ozawa and Mo models, have also been widely employed.

The conversion ratio can be described as follows:

$$X(T) = \frac{S_T^x}{S_T^0} \quad \cdots \quad (1)$$

where $X(T)$ is the conversion ratio that corresponds to temperature $T$. $S_T^x$ is the area surrounded by the DSC curve and the baseline from the onset temperature $T_0$ to a fixed temperature $T$. $S_T^0$ is the total area from the onset temperature to the final temperature $T_f$. $X(T)$ can be also expressed as Fig. 1.

During crystallization under a fixed cooling rate $\beta$, the relationship between time and temperature can be described as follows:

$$t = \frac{T_0 - T}{\beta} \quad \cdots \quad (2)$$

the Avrami model was formulated using the conversion ratio as a function of time and can be described as follows:

$$1 - X(t) = \exp \left(-Kt^n\right) \quad \cdots \quad (3)$$

where $X(t)$ is the conversion ratio at a given temperature at time $t$, $K$ is the rate constant of crystallization, and $n$ is the Avrami exponent, which is determined by using the conversion ratio to temperature. $X(T)$ is related to crystallization time, the Avrami model, in which the conversion ratio is related to crystallization time, the Ozawa model was established based on the evolution of conversion ratio as a function of temperature.

$$1 - X(T) = \exp \left(-\frac{P(T)}{K\beta^n}\right) \quad \cdots \quad (4)$$

$K$ is the modified rate constant based on the non-isothermal process.

### 2.2. Mo Model

The Ozawa model is another kinetics equation derived from the Avrami model based on Evans 22) equation to describe non-isothermal crystallization. Compared with the Avrami model, in which the conversion ratio is related to crystallization time, the Ozawa model was established based on the evolution of conversion ratio as a function of temperature.

$$1 - X(T) = \exp \left(-\frac{P(T)}{\beta^n}\right) \quad \cdots \quad (5)$$

where $P(T)$ is a function of temperature related to nucleation mode, nucleation rate, and growth rate. The meaning of $m$ is similar to that of $n$, that is, $m$ reflects a type of nucleation and growth mechanism. 15, 21-25 $m$ is determined by the conversion ratio $X(T)$ and time $T$ by plotting $\ln[-\ln(1-X(T))]$ against $\ln t$ as follows:

$$\ln\left[-\ln(1-X(T))\right] = P(T) - m \ln|\beta| \quad (7)$$

$K$ and $c$ as follows:

$$\ln\left[-\ln(1-X(T))\right] = \ln K + n \ln t \quad \cdots \quad (8)$$

The Mo model is a combination of the Avrami and Ozawa models. 26-29 The Avrami model describes the relationship of conversion ratio to time, whereas the Ozawa model describes the relationship of conversion ratio to temperature. As shown in Eq. (2), crystallization time can be expressed as a function of temperature for crystallization under a constant cooling rate. Hence, a certain time should correspond to a certain temperature at the same conversion ratio. That is, when $X(t) = X(T)$, the following equation can be obtained:

$$\ln\left[-\ln(1-X(T))\right] = \ln F(T) - a \ln t \quad \cdots \quad (9)$$

This equation can be transformed into

$$\ln K + n \ln t = \ln F(T) - m \ln|\beta| \quad \cdots \quad (10)$$

then,

$$\ln|\beta| = \ln F(T) - a \ln t \quad \cdots \quad (11)$$

where $F(T) = \left(\frac{P(T)}{\beta^n}\right)^{\frac{1}{m}}$ and $a = \frac{n}{m}$, where $F(T)$ corresponds to the cooling rate at unit crystallization time when reaching a certain value of conversion ratio; this parameter represents the crystallization rate at a certain conversion ratio. A low $F(T)$ value indicates a fast cooling rate. Hence, a certain time should correspond to a certain temperature at the same conversion ratio. That is, when $X(t) = X(T)$, the following equation can be obtained:

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$$\ln\left[-\ln(1-X(T))\right] = \ln F(T) - a \ln t \quad \cdots \quad (9)$$

This equation can be transformed into

$$\ln K + n \ln t = \ln F(T) - m \ln|\beta| \quad \cdots \quad (10)$$

then,
\[
\ln \frac{\beta_i}{T_{pi}} = \ln \frac{AR}{E} - \frac{E}{RT_{pi}} (i = 1, 2, 3\ldots) \quad (11)
\]

where \(T_{pi}\) is the peak temperature at a fixing cooling rate, \(A\) is the pre-exponential coefficient, and \(E\) is the activation energy of the crystallization.

The Kissinger method can be further converted to

\[
\frac{d}{dT} \left( \ln \frac{\beta_i}{T_{pi}^2} \right) = \frac{E}{R} \quad (12)
\]

activation energy \(E\) can be calculated using the slope of the plot of \(\ln \frac{\beta_i}{T_{pi}^2}\) against \(\frac{1}{T_{pi}}\).

3. Experimental Procedure

3.1. Materials

Testing samples were prepared by mixing CaCO\(_3\) (99.99% purity) and Fe\(_2\)O\(_3\) (\(\alpha\)-Fe\(_2\)O\(_3\), 99.99% purity) at a mole ratio of 1:1 for 30 min. The mixture was pressed into a cylindrical shape under 10 MPa to obtain a homogenous sample. The samples were heated from room temperature up to 900°C, which was maintained for 1 h to ensure the decomposition of CaCO\(_3\). The temperature was further increased to 1200°C and maintained for 10 h to generate CaO·Fe\(_2\)O\(_3\). The samples were pulverized in a vibration mill.

Qualitative and quantitative analyses of X-ray diffraction (XRD) patterns (Model D/max2500/PC; Cu K\(\alpha\)\) were performed before thermal analysis to verify the presence of CaO·Fe\(_2\)O\(_3\) in the samples after roasting and cooling. The XRD patterns of the samples were compared with those of CaO·Fe\(_2\)O\(_3\) in the standard PDF card.

The results (Fig. 2) show that the XRD pattern of the samples fitted well with that of CaO·Fe\(_2\)O\(_3\) in the standard PDF card, and other impurity peaks are not evident; this finding reflects that the CaO·Fe\(_2\)O\(_3\) phase accounts for the majority of the sample phases. Furthermore, XRD quantitative analysis shows that the CaO·Fe\(_2\)O\(_3\) content reaches 93%, confirming that the thermal analysis test is based on the crystallization phase of CaO·Fe\(_2\)O\(_3\).

3.2. Non-isothermal DSC Investigation

Non-isothermal DSC investigation was conducted by using a Netzsch thermal analyzer (Model STA 449C). Samples (10 mg) were tiled in a Pt crucible, with an Al\(_2\)O\(_3\) crucible containing air as reference. The samples were heated to 1300°C at 20 K/min and then cooled to 1100°C at a cooling rate of 10, 15, 20, and 25 K/min in air atmosphere.

4. Results and Discussion

4.1. DSC Curves

Figure 3 shows the DSC curves of the samples at various cooling rates (10, 15, 20, and 25 K/min). As the temperature decreases from 1300°C to 1100°C, three exothermic peaks mainly appear in order. According to the Fe\(_2\)O\(_3\)–CaO phase diagram\(^{10}\), three crystallization reactions are generated at \(n(\text{Fe}_2\text{O}_3)/n(\text{CaO}) = 1:1\) when the temperature decreases from 1300°C to 1100°C; these reactions match the three peaks shown on the DSC curves. The experimental crystallization temperature is lower than the theoretical temperature because of the crystallization undercooling effect. The crystallization processes are described in Figs. 4 and 5 and correspond to Eq. (13). The amount of product at various cooling rates remains constant.
The samples are initially in the full liquid phase from the start of cooling from point A. The first peak (peak 1) indicates the liquid–solid transition, in which $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ precipitates from the liquid phase when the temperature decreases between points A and B. CaO·Fe$_2$O$_3$ is then generated by the peritectic reaction at the interface of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and the liquid phase at the beginning of temperature B, which corresponds to peak 2. Meanwhile, $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and the liquid phase gradually disappear. CaO·Fe$_2$O$_3$ is generated on adhesion of the $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ surface and inhibits the contact of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ to the liquid phase. Thus, the peritectic reaction cannot proceed completely, and the liquid phase remains low when the peritectic reaction is completed. The remaining liquid phase is cooled from points C to D. A eutectic reaction is generated, in which CaO·Fe$_2$O$_3$ and CaO·$2\text{Fe}_2\text{O}_3$ precipitate from the total liquid phase when the temperature decreases at point D. The temperature in this process is apparently similar to that during peritectic reaction, and the heat release for this part corresponds to peak 2. The generated CaO·Fe$_2$O$_3$ adds to the CaO·Fe$_2$O$_3$ produced from the peritectic reaction. CaO·$2\text{Fe}_2\text{O}_3$ is further cooled from points E to F. Eutectoid reaction then occurs, in which CaO·$2\text{Fe}_2\text{O}_3$ is transformed into CaO·Fe$_2$O$_3$ and Fe$_2$O$_3$ and corresponds to peak 3. The final phases for the entire process are CaO·Fe$_2$O$_3$ and Fe$_2$O$_3$. The entire crystallization is described by Eq. (13).

The temperatures for peaks 1 and 2 are nearly similar to each other; thus, the two crystallization peaks overlap. The peak should be separated using the Gauss rule to obtain the two complete peak patterns of the crystallization of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and CaO·Fe$_2$O$_3$. This study mainly analyzed the kinetics of the two crystallization processes, which correspond to peaks 1 and 2. Figures 6 and 7 show the DSC curves of the two individual peaks at different cooling rates.

Figure 3 shows that the generation temperature of the reaction D ($\text{CaFe}_3\text{O}_7$ = Fe$_2$O$_3$ + CaFe$_2$O$_4$), which corresponds to peak 3, reaches approximately 1160°C. We used FactSage to prove our results, and the “reaction” module can reveal the thermodynamic condition of reaction D being generated; the results show that the theoretical generation temperature of reaction D ranges from 1156°C to 1157°C, where Gibbs free energy ($\Delta$G) is < 0. The enthalpy change in reaction D shows a negative value (~21.8 kJ·mol$^{-1}$); thus, exothermic peaks appear on the DSC curve but not on the endothermic peaks.

\[
\text{liquid} \xrightarrow{\text{Liquid–solid reaction, peak 1}} 2\text{CaO} \cdot \text{Fe}_2\text{O}_3(S) + \text{liquid} \\
\xrightarrow{\text{Peritectic reaction, peak 2}} \text{CaO} \cdot \text{Fe}_2\text{O}_3(S, 1) + \text{CaO} \cdot \text{Fe}_2\text{O}_3(S, 1) \\
\xrightarrow{\text{Eutectic reaction}} \xrightarrow{\text{Eutectic reaction, peak 3}} \text{CaO} \cdot \text{Fe}_2\text{O}_3(S, 1) + \text{CaO} \cdot \text{Fe}_2\text{O}_3(S, 1) + \text{Fe}_2\text{O}_3(S) \\
\text{................................. (13)}
\]

4.2. Avrami Model

The relationship between conversion ratio and time can be determined using the DSC curves of the two crystallization reactions (Fig. 8).

According to the Avrami model, $K_c$ and $n$ are determined by the intercept and slope of plotting $\ln[-\ln(1-X(t))]$ against $\ln t$ (Fig. 9). The Avrami kinetic parameters of the two reactions are shown in Table 2.

The two reactions include two stages, which were analyzed in this study. $K_c$ increases with increasing cooling
rates, indicating that raising the cooling rate increases the crystallization rate; this conclusion is consistent with the actual situation. The $K_c$ values of peak 1 are higher than those of peak 2 at the same cooling rate, demonstrating that $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ crystallization occurs faster than $\text{CaO} \cdot \text{Fe}_2\text{O}_3$. In addition, the $n$ values of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ crystallization are between 1 and 2 for stage 1 and between 3 and 4 for stage 2. This finding indicates that $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ crystallization is controlled first by a fibril-like and then by a spherulitic-type mechanism. The $n$ values of peak 2 also lie nearly between 1 and 2 for stage 1 and between 3 and 4 for stage 2, showing that $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ crystallization is also controlled first by a fibril-like and then by a spherulitic-type mechanism.

### 4.3. Mo Model

$X(t)$ (20%, 40%, 60%, and 80%) was selected to determine the corresponding crystallization times of the four cooling rates in the two crystallization processes. Fitting the plots of $\ln[-\ln(1-X(t))]$ against $\ln t$ based on the Avrami model for the two peaks.

![Fig. 8. Conversion ratio corresponding to time at various cooling rates for the crystallization of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (peak 1) and peritectic crystallization of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (peak 2).](image)

![Fig. 9. $\ln[-\ln(1-X(t))]$ against $\ln t$ based on Avrami model for the two peaks.](image)

**Table 2.** Avrami parameters for the $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ generation and peritectic crystallization of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>$\beta$ (K/min)</th>
<th>Stage 1</th>
<th>Stage 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$ $K_c$ $R^2$</td>
<td>$n$ $K_c$ $R^2$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.70</td>
<td>0.73</td>
</tr>
<tr>
<td>15</td>
<td>1.47</td>
<td>0.82</td>
</tr>
<tr>
<td>20</td>
<td>1.09</td>
<td>0.83</td>
</tr>
<tr>
<td>25</td>
<td>1.63</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**Note:** (a): peak 1, (b): peak 2

The $F(T)$ values, which indicate that the cooling rate corresponds to a specific conversion ratio at a unit crystallization time, increase with increasing conversion ratio; this phenomenon follows the crystallization rules. Moreover, the $F(T)$ value of peak 1 is lower than that of peak 2 at the same conversion ratio, indicating that peak 1 requires a low cooling rate to reach a fixed conversion ratio. That is, the crystallization rate of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is faster than $\text{CaO} \cdot \text{Fe}_2\text{O}_3$. This conclusion corresponds to the results of the Avrami model-based analysis. The $a$ values remain nearly constant at peaks 1 and 2. The $a$ values for the crystallization of
2CaO·Fe2O3 and CaO·Fe2O3 are 0.63 and 0.97, respectively. Thus, a certain linear relationship exists between \( n \) and \( m \).

### 4.4. Calculation of Activation Energy Using Kissinger Method

According to Kissinger method, the peak temperature in the DSC curves at various cooling rates must be obtained.

After fitting the plots of \( \ln \beta_i \) against \( 1/T_{pi} \) (Fig. 11), the activation energy \( E \) can be calculated using the slope of the fitted line.

2CaO·Fe2O3 and CaO·Fe2O3 crystallization includes a chemical reaction and a liquid–solid transformation. Therefore, the calculated value of the activation energy includes two energy types, which are derived from chemical and physical processes, as follows:

\[
E_{\text{Tot}} = E_{\text{Chem}} + E_{\text{Phys}} \quad \text{(14)}
\]

where \( E_{\text{Tot}} \) is the apparent energy value; \( E_{\text{Chem}} \) and \( E_{\text{Phys}} \) refer to the apparent activation energy from the chemical reaction and energy change from phase transformation.

The calculated activation energy is the activation energy of the chemical reaction; thus, energy accompanied by the liquid–solid transformation must be deducted from the calculated \( E_{\text{Tot}} \). The changes in energy in the phase transformation of the two processes are \(-557.25 \text{ kJ·mol}^{-1}\) and \(-1 228.7 \text{ kJ·mol}^{-1}\) as revealed by the phase diagram module in FactSage. Table 4 shows that the apparent activation energy of 2CaO·Fe2O3 and CaO·Fe2O3 can be derived as follows:

\[
E = \frac{\Delta H_{\text{f}}}{\beta} \quad \text{(16)}
\]

In Eq. (15), \( n \) refers to the molar quantity of 2CaO·Fe2O3.
by a fibril-like and then by a spherulitic-type mechanism. Mo model analysis confirmed the accuracy of the Avrami results and showed that \( n/m \) is constant despite the changes in cooling rate.

(3) The apparent activation energy of \( 2\text{CaO-Fe}_2\text{O}_3 \) and \( \text{CaO-Fe}_2\text{O}_3 \) crystallization calculated based on the Kissinger method are \(-464.16\, \text{kJ} \cdot \text{mol}^{-1}\) and \(-172.61\, \text{kJ} \cdot \text{mol}^{-1}\), respectively.

(4) \( 2\text{CaO-Fe}_2\text{O}_3 \) crystallization occurs in a difficult manner but proceeds at a faster crystallization rate than \( \text{CaO-Fe}_2\text{O}_3 \) crystallization. Moreover, increasing the cooling rate promotes \( \text{CaO-Fe}_2\text{O}_3 \) crystallization but inhibits \( 2\text{CaO-Fe}_2\text{O}_3 \) crystallization.

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