Reduction of CaO–Fe₂O₃ Series Compounds by CO

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The isothermal reduction kinetics of C₂F, CF, and CF₂ by 30% CO and 70% N₂ at 1 123 K (850°C), 1 173 K (900°C), and 1 223 K (950°C) were investigated by thermogravimetric analysis in this study. Results indicated that the maximum reduction degree increased and its corresponding reduction time decreased by the order of C₂F, CF, and CF₂. The reduction rate analysis by peak fitting based on the Gauss rule revealed that the C₂F, CF, and CF₂ reductions were typical one-step, two-step, and three-step reactions, respectively. Fe₂O₃ to FeO stage overlaps with the following FeO to Fe stage and tends to approach the previous Fe₂O₃ to FeO₂ stage in reduction of CaO–Fe₂O₃ system with an increase in Fe₂O₃ content. The apparent activation energy of the sample C₂F, CF, and CF₂ reductions were 51.74, 46.89, and 34.37 kJ/mol, respectively, indicating that reduction proceeds more easily for them. The In-In and Sharp analysis implied that the C₂F reduction was described by the Avrami–Erofeev function, thus appeared as a 2D reaction during the whole reaction, whereas the CF and CF₂ reductions were expressed initially by a 2D reaction when α<0.5 and subsequently by a 3D reaction when α>0.5. In the new proposed reduction model, the Fe₂O₃ content increases in the CaO–Fe₂O₃ system from C₂F to CF₂ and the gradual promotion of the reduction rate leads to the reduction process of the C₂F, CF, and CF₂ samples occurring by a 2D tending to 3D reaction mechanism.

KEY WORDS: C₂F; CF; CF₂; isothermal reduction kinetics; apparent activation energy; reduction model.

1. Introduction

Clarifying the reducibility of fluxed iron ore sinters, which are the significant burden in a blast furnace, is necessary. As the main bonding phases in fluxed sinters, the reducibility of the CaO–Fe₂O₃–SiO₂–Al₂O₃ quaternary calcium ferrite (SFCA) was investigated by many previous studies. In the 1950s and 1960s, the CaO–Fe₂O₃ system was found as the highlight of the bonding phase in the sintering process instead of the silicate system. Studies on the CaO–Fe₂O₃ system performed composition characterizations, macroscopic properties and micro-morphology. The CaO–Fe₂O₃ system principally comprises dicalcium ferrite (2CaO·Fe₂O₃, C₂F), calcium ferrite (CaO·Fe₂O₃, CF), and calcium diferrite (CaO·2Fe₂O₃, CF₂). To characterize the ternary or even quaternary calcium ferrite, study on binary CaO–Fe₂O₃ systems, which contain simplified phase compositions appears so vital. The phase structure and morphology of C₂F, CF, and CF₂ were extensively discussed, and some consensus was reached in previous work. The reducibility of C₂F, CF, and CF₂ was essentially caused by the chemical composition and micro-structure of the contained multi-phases. The analysis of the reduction behavior of C₂F, CF, and CF₂ under the atmosphere condition in the upper area of the blast furnace requires further research.

The reaction rate and the apparent activation energy of the C₂F, CF, and CF₂ reductions under the CO–N₂ gas mixtures through thermogravimetric analysis (TGA) were rarely discussed intensively. Furthermore, the use of thermal analysis kinetics to reveal the reduction mechanism was almost never intensively explored.

The reduction of the C₂F, CF, and CF₂ bonding phases in iron ore sinters in the blast furnace was a typical gas–solid reaction. Maeda clarified the reduction equilibria of ternary calcium ferrite with CO–CO₂ gas mixture, reduction sequence, and the reaction equilibria in different CO/CO₂ ratios were fully investigated. Ganguly examined the C₂F reduction to calcium oxide and metallic iron in a single reaction step below 1 343 K (1 070°C) compared with those of CF and CF₂ in a number of reaction steps. The investigations also indicated that the product morphologies and reduction kinetics were dependent on the rates of the chemical reactions, rates of calcium and iron diffusion (surface and bulk), oxygen potential of the reducing gas, and inherent structural and surface defects of the samples. Du studied the reduction kinetics of C₂F, CF, and CF₂ and compared their reduction rates at elevated temperatures. Furthermore, the study revealed that the expansion of binary calcium ferrite increases with the increasing Fe₂O₃ content in ferrite.

The previous work focused on the larger particles (>1 mm) of pellet sample from which the reduction process was generally described by shrinking core model. In blast furnace production, powdered sinters and iron ores account...
for iron oxide sources charged into a blast furnace. Therefore, investigation on powdered state of calcium ferrites which are seen as main reduction phases in fluxed sinters appeared to be extremely important. The reduction behaviors of ultrafine powder of C\textsubscript{2}F, CF, and CF\textsubscript{2} were not fully discussed and even the reduction model was not studied. This study attempted to develop model and mechanism of the powder reduction of calcium ferrites, and reduction kinetics of powdered samples of C\textsubscript{2}F, CF, and CF\textsubscript{2} by 30\% CO and 70\% N\textsubscript{2} (blast furnace top atmosphere) were discussed by thermal analysis.

2. Experimental

2.1. Samples Preparations

The C\textsubscript{2}F, CF, and CF\textsubscript{2} samples were prepared from CaCO\textsubscript{3} (≥99.99\%, < 100 μm) and Fe\textsubscript{2}O\textsubscript{3} (α-Fe\textsubscript{2}O\textsubscript{3}, ≥99.99\%, < 100 μm) with 2:1, 1:1, 1:2 molar ratios, respectively. The powdery raw materials were uniformly mixed and then pressed into cylindrical-shaped samples (10 mm high, 10 mm diameter). The samples were roasted in the furnace with the heating element MoSi\textsubscript{2} at 1 173 K (900 °C) for 1 h for the full decomposition of CaCO\textsubscript{3} to CaO, and then increased to 1 473 K (1 200 °C) for 20 h to allow the complete formation of C\textsubscript{2}F, CF, and CF\textsubscript{2}. The entire process was performed in air. The samples were ground into powder (200 mesh, < 74 μm) in vibration mills for the next investigations. The more operation details of samples preparation were shown in Fig. 1.

X-ray diffraction (XRD) (Model D/max2500/PC (Cu K\textsubscript{α})) analysis was performed to ensure the phase composition of samples. Scanning was performed at an angular range of 10° to 90° with a scan rate of 4°/min. MDI Jade 6.5 was utilized to analyze the intensity data obtained by the XRD measurement. The patterns of samples 1, 2, and 3 and the standard patterns of C\textsubscript{2}F, CF, and CF\textsubscript{2} are shown in Fig. 2. The results indicate that samples 1, 2, and 3 mainly comprise C\textsubscript{2}F, CF, and CF\textsubscript{2}, respectively.

The powder sizes of the C\textsubscript{2}F, CF, and CF\textsubscript{2} samples obtained through laser particle test are shown in Fig. 3. The sizes were almost lower than 74 μm, and most of them were less than 1 μm. As the size of particles under 1 μm tend to achieve nanoscale (1–100 nm), this size range of particles can get agglomeration with time going on in the laser particle test, that is, the particles of size larger than 1 μm are almost agglomerated particles, that is why two peaks were shown in the distribution of powder size.

2.2. TG Analysis

TG measurement of C\textsubscript{2}F, CF, and CF\textsubscript{2} reduction was conducted by using a Setaram analyzer (Model Setsys Evo TG-DTA 1750, Setaram Instrumentation) shown in Fig. 4. Samples (20 mg) were heated from room temperature to 1 123 K (850 °C), 1 173 K (900 °C), and 1 223 K (950 °C) in N\textsubscript{2} (≥99.999\%) atmosphere at a heating rate of 15 K/min, then switching to gas mixtures of 30\% CO (≥99.999\%) and 70\% N\textsubscript{2} at a flow rate of 20 ml/min (equals to 176.9 mm/ min of line velocity) for 70 min to enable complete reaction with the samples at the isothermal stage. To exclude the influence of the system error from the thermal analyzer and the buoyance force from the gas mixtures, a blank test was conducted under the same elimination conditions with only empty alumina crucibles. Weight loss were obtained during the isothermal reduction stage, from which the TG data of the blank test were deduced. Gas mixtures at 30 ml/min was blown into the samples to evaluate the effect of external diffusion on the reduction of C\textsubscript{2}F, CF, and CF\textsubscript{2}. The difference
values of TG data reduced at 20 and 30 ml/min are not more than 2% for all the samples reduction. The results indicate the experimental schedule of samples reduced by gas mixtures at 20 ml/min can nearly exclude the effect of external diffusion on the reduction processes.

3. Results and Discussion

3.1. Reduction Degree and Reduction Rate

Reduction degree is defined as the ratio of removed oxygen mass at a fixed time $t$ to the theoretically removed oxygen mass from the iron oxide. It can be expressed as follows:

$$\alpha = \frac{\Delta m_t}{\Delta m_0}, \text{...........................(1)}$$

where $\alpha$ is the reduction degree; and $\Delta m_t$ and $\Delta m_0$ refer to the removed oxygen mass at fixed time $t$ and the theoretically removed oxygen mass from the iron oxide, respectively. $\Delta m_0$ was originated from the oxygen atoms combined with the iron atoms. For instance, the theoretically removed oxygen mass of C$_2$F, CF and CF$_2$ accounts for 17.65%, 22.22% and 25.53% of total mass.

The reduction degrees of the C$_2$F, CF, and CF$_2$ samples at 1123 K (850°C), 1173 K (900°C), and 1223 K (950°C) are shown in Fig. 5. The maximum reduction degrees of the samples and their corresponding time are shown in Table 1. The results indicated that the reduction degree obviously increased in the middle of the reduction stages for all the samples. It reached a higher reduction degree by the order of C$_2$F, CF, and CF$_2$ at the same temperature, and the time to reach the maximum reduction degree decreased. Namely, for the reduction at 1223 K (950°C), the maximum reduction degrees achieved were 0.90, 0.94, and 0.96 and the reduction times were 56.8, 42.6, and 42.5 min for the C$_2$F, CF, and CF$_2$ samples, respectively. As the addition of Fe$_2$O$_3$ increases in the CaO–Fe$_2$O$_3$ system, from C$_2$F to CF$_2$, the reducibility of the sample is enhanced gradually. The reduction of samples progressed during the isothermal stage under 30% CO and 70% N$_2$ gas mixture transformed from the pure N$_2$ atmosphere, therefore, at the beginning of the reaction, the concentration of the reducing atmosphere is 0. Therefore, the reduction rate is almost 0 at $\alpha=0$ ($t=0$).

The reduction rates $d\alpha/dt$ for C$_2$F, CF, and CF$_2$ at 1123 K
(850°C), 1 173 K (900°C), and 1 223 K (950°C) are illustrated in Fig. 6. Fe₂O₃ is assumed to be the essential reduced composition existing in C₂F, CF, and CF₂. Therefore, the reduction routes of the CaO–Fe₂O₃ system can be simply expressed as follows:

\[ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \quad \ldots \quad (2) \]

Figure 6 clearly describes that the reduction processes of C₂F, CF, and CF₂ were presented as one-step, two-step, and three-step reactions. Therefore, the Fe₂O₃ to Fe₃O₄, Fe₃O₄ to FeO, and FeO to Fe stages overlap with each other in the reduction of C₂F and show only one rate peak. The theoretical reduction degrees are 0.11 and 0.33 when Fe₂O₃ is fully reduced to Fe₃O₄ and Fe₃O₄ is fully reduced to FeO. Thus, in the reduction of CF, the Fe₂O₃ to Fe₃O₄ stage showed the first one peak, and the Fe₃O₄ to FeO stage tended to approach the following FeO to Fe stage and showed the other rate peak. Three independent rate peaks appeared in the reduction of CF₂. The peak in the Fe₂O₃ to Fe₃O₄ stage was in the reduction degree range of 0 to 0.1. The peak in the Fe₃O₄ to FeO stage occurred during 0.1 to 0.2. The last peak in the FeO to Fe stage occurred between 0.2 to the end. The reduction rates increased for C₂F, CF, and CF₂ because of increasing Fe₂O₃ content. Figure 7 shows the peak fitting based on the Gauss rule of reduction rate for the C₂F, CF, and CF₂ samples at 1 173 K (900°C). The results indicate that three reduction peaks gradually split as the Fe₂O₃ content increased in the CaO–Fe₂O₃ system. Moreover, Fe₃O₄ to FeO stage overlaps with the following FeO to Fe stage and tends to approach the previous Fe₂O₃.
to Fe$_2$O$_3$ stage in reduction of CaO–Fe$_2$O$_3$ system with an increase in Fe$_2$O$_3$ content.

The reducibility of the three calcium ferrites was tested in several researches,\textsuperscript{10,11} all of which except Brunner’s result concluded that CF$_2$ has the best reducibility and C$_2$F the worst. The crystal structures\textsuperscript{12–14} and reduction sequence\textsuperscript{15–17} of C$_2$F, CF, and CF$_2$ were investigated in previous studies, and the reduction kinetics of C$_2$F, CF, and CF$_2$ were also fully studied in previous research, as shown in Table 2. The previous work was short because of the macroscopic description of reduction mechanism. Namely, the model function to reveal the reduction process and its relation to the reduction rate were not included. Moreover, compared with the sample shape and size focusing on pellet and much larger particles (0.15–8 mm) in previous studies, sample particles smaller than 100 $\mu$m were investigated in this study. The reduction rate of C$_2$F, CF, and CF$_2$ obtained here were quite lower than the pellet sample reduction in previous work shown in Table 2.

The crystal structures of C$_2$F, CF, and CF$_2$ were obtained by previous studies, as shown in Fig. 8. The orthorhombic unit cell of C$_2$F was found by Bertaut.\textsuperscript{12} The structure consists of the FeO$_6$-distorted octahedra and FeO$_4$-distorted tetrahedra. The FeO$_6$ octahedra was elongated along b-axis, where two Fe–O bond lengths lay 2.114 Å and four Fe–O bond lengths lay 1.964 Å. The FeO$_4$ tetrahedra comprises two types of Fe–O with bond lengths of 1.837 Å and 1.918 Å. The structure of the CF was reported by Decker\textsuperscript{13} to also be orthorhombic, consisting of the distorted octahedra with an iron atom in the center surrounded by six oxygen atoms, and the Fe–O bond length ranged from 1.98 Å to 2.09 Å. The Fe–O bond length in the crystal structure of CF was longer than that of the C$_2$F and easier to break. Therefore, the oxygen atoms in CF were removed more easily than that in C$_2$F. The crystal structure of CF$_2$ was based on a hexagonal close-packing of oxygen atoms with calcium and iron atoms occupying the octahedral interstices, as investigated by Henry.\textsuperscript{14} Burdese\textsuperscript{17} found that CF$_2$ was first reduced to CF and hematite. Hematite has a hexagonal crystal structure and the best reducibility compared with C$_2$F, CF, and CF$_2$. The reduction of CF$_2$ showed the fastest rate. Moreover, the reduction gas diffused into the crystal structure of C$_2$F and CF appeared to be from six different directions, whereas that of the CF$_2$ was from eight directions. It indicates that CF$_2$ reduced by CO in more contact area than C$_2$F and CF. The relations of reduction with crystal structure were rare even not discussed and elucidated for calcium ferrites in previous studies, our paper attempted to explain the results of reduction rates from viewpoints of microstructures. It appeared like a qualitative and rough conjecture in this study, but had lots of enlightening significance on investigations on evolutions of microstructures and changes of lattice parameters in the reduction process for our and even other’s future researches. It is essential to explain the reduction process based on microstructures of crystals. In the future, studies on this field of work can obtain further improvements.

### 3.2. Apparent Activation Energy and Rate–determining Step for C$_2$F, CF, and CF$_2$ Reduction

The basic kinetic equation\textsuperscript{22} that describes the relation-

### Table 2. Comparisons on reduction kinetics of C$_2$F, CF and CF$_2$ from this study and previous researches.

<table>
<thead>
<tr>
<th>Research</th>
<th>Sample size and shape</th>
<th>Porosity (%)</th>
<th>Temperature (°C)</th>
<th>Reduction Gas</th>
<th>Gas flow rate (ml·min$^{-1}$)</th>
<th>Reduction rate (mg·cm$^{-2}$·min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edstrom\textsuperscript{(5)}</td>
<td>4<em>4</em>4 mm, 0.15 mm Φ</td>
<td>25</td>
<td>1000</td>
<td>–</td>
<td>–</td>
<td>11.49</td>
</tr>
<tr>
<td>Rueckl\textsuperscript{(8)}</td>
<td>100 mg, 0.15 mm Φ</td>
<td>30</td>
<td>980</td>
<td>CO</td>
<td>2500</td>
<td>3.19</td>
</tr>
<tr>
<td>Watanabe\textsuperscript{(9)}</td>
<td>8–10 mesh, 2.36 mm Φ</td>
<td>–</td>
<td>900</td>
<td>H$_2$</td>
<td>150</td>
<td>1.08</td>
</tr>
<tr>
<td>Brunner\textsuperscript{(20)}</td>
<td>6<em>7</em>8 mm, 1.5 mm thick</td>
<td>5</td>
<td>1000</td>
<td>CO</td>
<td>1000</td>
<td>1.97</td>
</tr>
<tr>
<td>Taguchi\textsuperscript{(16)}</td>
<td>9 mm Φ, 1.5 mm thick</td>
<td>–</td>
<td>900</td>
<td>CO</td>
<td>100</td>
<td>1.96</td>
</tr>
<tr>
<td>Ono\textsuperscript{(21)}</td>
<td>5 mm Φ, 8 mm thick</td>
<td>28</td>
<td>1000</td>
<td>CO</td>
<td>2000</td>
<td>4.11</td>
</tr>
</tbody>
</table>

This study

| <100 $\mu$m Φ, 2 mm thick | – | 900 | CO | 20 | 1.04 | 1.18 | 1.29 |
|<100 $\mu$m Φ, 2 mm thick | – | 950 | CO | 1.05 | 1.40 | 1.41 |

Fig. 8. Crystal structures of C$_2$F, CF, and CF$_2$ (C$_2$F, CF: orthorhombic, CF$_2$: hexagonal).
ship between the reduction rate and time can be expressed as follows:

\[
\frac{d\alpha}{dt} = k(T) f(\alpha), \quad \text{........................ (3)}
\]

where \( d\alpha/dt \) is the reduction rate and \( k(T) \) and \( f(\alpha) \) are the rate constant and model function of the reduction reaction, respectively. \( f(\alpha) \) is influenced by the reaction mechanism, and \( k(T) \) is determined by the following Arrhenius equation:

\[
k(T) = A \exp \left( \frac{-E}{RT} \right), \quad \text{........................ (4)}
\]

where \( A \) is the pre-exponential factor, \( E \) is the apparent activation energy, and \( R \) is the gas constant [8.314 J/(mol·K)]. Equation (3) can be further expressed as follows:

\[
\frac{d\alpha}{dt} = A \exp \left( \frac{-E}{RT} \right) f(\alpha). \quad \text{........................ (5)}
\]

Given that the reduction degree \( \alpha \) is a constant, \( \ln f(\alpha) \) remains unchanged. Therefore, the activation energy can be calculated as follows:

\[
E = R \left( \frac{1}{\alpha} \frac{d\ln \alpha}{dt} \right), \quad \text{........................ (6)}
\]

The apparent activation energy can be calculated by the slope of the plots of \( \ln(d\alpha/dt) \) against 1/T, and the results are shown in Table 3. The activation energy increased with the increase of the reduction degrees for C2F, CF, and CF2, and the average values of activation energy for the C2F, CF, and CF2 reductions were 51.74, 46.89, and 34.37 kJ/mol, respectively, indicating that reduction proceeds more easily for C2F, CF, and CF2. For each sample, as the reaction progresses, the reaction becomes more difficult as the activation energy increases with the increasing reduction degree.

The connection of the rate-determining step to the activation energy was investigated by Strangway, Nasr, and Geassy, as shown in Table 4. The results concluded that activation energy and rate-determining steps are not decisive but rather indicative. As the relationship between the two is not absolute, this study was only carried out a rough description and not reached conclusions. The apparent activation energy of the C2F, CF, and CF2 reductions lay between 30.34 to 51.90, 20.32 to 86.68, and 5.06 to 86.68 kJ/mol, respectively. The rate-determining steps of the C2F, CF, and CF2 reductions were the first inner gas diffusion, then the interface chemical reaction. During the initial stage of the reduction of the three samples, as the reduction step of Fe2O3 to FeO progressed easily and the reduced gas content has not reached the target value, the CO gas diffusion was the step to limit the reduction rate. When the reaction reached the middle and end stages, the gas flow rate was enough for the reduction, while the interface chemical reaction limited the reduction process.

### 3.3. Model Function Results

Two analysis methods may be applied to target \( G(\alpha) \): \( \ln-\ln \) and Sharp analyses. The two analysis methods established from common gas-solid reactions reflect the relation of reaction degree with time without any other conditions, that is say, theoretically, the reduction kinetics of other ores or under other atmosphere can be characterized by those two methods.

According to the Avrami-Erofeev equation, the reduction degree \( \alpha \) can be expressed by the following relationship of time \( t \) and rate constant \( k \):

\[
1 - \alpha = \exp^{k^{-t}}, \quad \text{........................ (8)}
\]

where \( n \) refers to the Avrami exponent. By obtaining the double natural logarithm on either side of the equal sign of Eq. (8), we can formulate the following equation:

\[
\ln [-\ln(1-\alpha)] = n \ln t + \ln k. \quad \text{........................ (9)}
\]

The Avrami exponent \( n \) can be obtained by the slope of the fitted line of \( \ln [-\ln(1-\alpha)] \) against \( \ln t \). For example,

\[
n = \frac{d}{d\ln t} \left[ \ln [-\ln(1-\alpha)] \right]. \quad \text{........................ (10)}
\]

The value of \( n \) is directly related to \( G(\alpha) \), which means that \( G(\alpha) \) can be determined by first obtaining the value of \( n \). Table 5 shows the corresponding relationship between \( G(\alpha) \) and \( n \) and its reaction mechanism. The Avrami exponent \( n \) is related to the functions corresponding to nine solid-state reactions, which can be expressed as diffusion controlled, reaction-rate controlled, and first-order kinetics controlled in mechanisms or follow the equations of Avrami and Erofeev.

Table 9 shows the relationship between \( \ln [-\ln(1-\alpha)] \) and \( \ln t \) for the C2F, CF, and CF2 samples, and the Avrami exponent \( n \) was calculated in Table 6. The results revealed that the \( n \) corresponding to the C2F sample reduction at 1 123 K (850°C), 1 173 K (900°C), and 1 223 K (950°C) lay at 2.05, 2.06, and 2.08, respectively, thereby indicating the reduction of the C2F sample as described by function

| Table 3. Apparent activation energy of samples C2F, CF, and CF2. |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| \( E(\text{kJ/mol}^{-1}) \) | \( 0.3 \) | \( 0.4 \) | \( 0.5 \) | \( 0.6 \) | \( 0.7 \) | \( 0.8 \) | \( \text{Avg} \) |
| C2F | 30.34 | 31.44 | 45.4 | 73.62 | 77.74 | 51.9 | 51.74 |
| CF | 20.32 | 23.11 | 30.85 | 52.85 | 67.51 | 86.68 | 46.89 |
| CF2 | 5.06 | 6.97 | 13.14 | 21.8 | 72.58 | 86.68 | 34.37 |

| Table 4. Relationship between \( G(\alpha) \) and \( n \) for normal solid reactions and its reaction mechanism. |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| \( E(\text{kJ/mol}) \) | Rate-determining step |
| \( 8-16 \) | Inner gas diffusion |
| \( 29-42 \) | Inner gas diffusion and interface chemical reaction mixed |
| \( 60-67 \) | Interface chemical reaction |
| \( >90 \) | Solid diffusion |
A2. As for CF and CF2 samples, the n values equal to 1.90, 2.01, and 2.24 for CF and 2.41, 2.52, and 2.53 for CF2 at the three temperatures showed that the reductions of CF and CF2 were expressed by function A2 toward A3.

Functions A2 and A3 were obtained from the nucleation process (crystallization) and can also be applied to the reduction reaction. Function A2 can express the 2D reduction reaction and function A3 can express a 3D reaction. Moreover, the reaction determined by A2 appears in a plane, whereas that of A3 is a cylinder.

For most solid-state reaction, the model function \( G(\alpha) \) can be calculated by multiplying \( k(T) \) by \( t \) as shown in Eq. (7). \( G(\alpha) \) can also be described by the following form:

\[
G(\alpha) = c \cdot \frac{t}{t_{0.5}}, \quad \text{.................. (11)}
\]

Sharp analysis defines a non-dimensional parameter \( y(\alpha) \) as follows:

\[
y(\alpha) = \frac{G(\alpha)}{G(0.5)} = \frac{kt}{k_{0.5}t_{0.5}} = \frac{t}{t_{0.5}}, \quad \text{.................. (12)}
\]

where \( c \) is a calculated parameter based on the function \( f(\alpha) \), \( G(0.5) \) refers to a fixed \( G(\alpha) \) with \( \alpha = 0.5 \), and \( t_{0.5} \) is the time corresponding to \( \alpha = 0.5 \). The curves described by the plots of \( y(\alpha) \) against \( \alpha \) were based on the normal solid reactions, which are called standard curves. Experimental data \( [\alpha, t/t_{0.5}, i = 1, 2, ... j] \) can be easily obtained through TGA. The corresponding \( G(\alpha) \) can be identified when the experimental data match one of the standard curves.

The standard curves and experimental data based on Sharp analysis for the CF2, CF, and CF3 samples are shown in Fig. 10. The experimental data \( y(\alpha) \) values for the CF2 reduction mostly lay at the standard curve corresponding to Function A2. The \( y(\alpha) \) values for the CF and CF2 reductions lay at the curve based on Function A2, and then gradually tended to lay at the curve based on Function A3. Furthermore, the \( y(\alpha) \) values for the CF reduction were closer to function A2, whereas those for CF2 were closer to function A3. The Sharp analysis results markedly agree with the In-In analysis results.

### 3.4. New Proposed Reduction Model for CF2, CF, and CF3 Powdered Samples

Shrinking core model was adopted to describe the reduction process of the pellet samples of iron ore. However, powdered samples were tested in this study. Gas diffusion appears more smoothly in powders than in pellets. In the shrinking core model, the three reduction stages, namely, Fe2O3 to Fe3O4, Fe3O4 to FeO, and FeO to Fe, overlapped with each other and caused the reduction rate to show only one peak because the CO diffusion was blocked by the dense pellet, the reduction Fe2O3 to FeO3 cannot completes when the reduction Fe2O3 to FeO, and FeO to Fe occur. In this study, the three stages in the reduction process were more stratiﬁed, especially for CF and CF2, as shown in Fig. 6. Powdered samples reduction in this study can be described as three independent stages which shows that nearly all the Fe2O3 transformed to Fe3O4, all the Fe3O4 to FeO, and then all the FeO to Fe. It’s still an ideal powdered reaction process for the sample of reduction rate reaching high, the reduction processes of CF and CF2 are close to the phenomena of ideal powdered reduction model expressed above, and the reduction process of reactant with lower reducibility could progress with multi-stage overlapping.

The powdered samples tiled at the bottom of the aluminia crucible are shown in Fig. 11, and the samples were reduced by 30% CO and 70% N2 gas mixtures at a flow rate of 20 mL/min (radius of reactor is 12 mm, linear speed of gas mixture was calculated as 1769 m/min). The order of the reduction rate of the CF2, CF, and CF3 samples was CF < CF < CF2, as shown in Fig. 6. That is, the reduction of CF2 appeared the fastest, and that of CF the slowest at the same conditions. The reducibility of CF2, CF, and CF3 was essentially determined by the Fe2O3 content that was added in the CaO–Fe2O3 system.

A new reduction model was proposed to express the reduction process of powdered samples. In the new reduction model, the CO-diffused distance and thickness of the unreacted layer were defined as L and D. As for the CF2

<table>
<thead>
<tr>
<th>Function</th>
<th>( G(\alpha) )</th>
<th>( n )</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0(\alpha) )</td>
<td>( \alpha^2 = kt )</td>
<td>0.62</td>
<td>One-dimensional diffusion</td>
</tr>
<tr>
<td>( D_2(\alpha) )</td>
<td>( (1 - \alpha) \ln(1 - \alpha) - \alpha = kt )</td>
<td>0.57</td>
<td>Two-dimensional diffusion (bidimensional particle shape)</td>
</tr>
<tr>
<td>( D_3(\alpha) )</td>
<td>( [1 - (1 - \alpha)^{\frac{1}{3}}]^2 = kt )</td>
<td>0.54</td>
<td>Three-dimensional diffusion (tridimensional particle shape)</td>
</tr>
<tr>
<td>( D_4(\alpha) )</td>
<td>( (1 - 2/3\alpha)(1 - \alpha)^{\frac{1}{3}} = kt )</td>
<td>0.57</td>
<td>Three-dimensional diffusion (tridimensional particle shape)</td>
</tr>
<tr>
<td>( F_s(\alpha) )</td>
<td>( -\ln(1 - \alpha) = kt )</td>
<td>1</td>
<td>Bimolecular decay law (instantaneous nucleation and unidimensional growth)</td>
</tr>
<tr>
<td>( R_\alpha(\alpha) )</td>
<td>( 1 - (1 - \alpha)^{\frac{1}{3}} = kt )</td>
<td>1.11</td>
<td>Phase boundary controlled reaction (contracting area, i.e., bidimensional shape)</td>
</tr>
<tr>
<td>( R_\alpha(\alpha) )</td>
<td>( 1 - (1 - \alpha)^{\frac{1}{3}} = kt )</td>
<td>1.07</td>
<td>Phase boundary controlled reaction (contracting volume, i.e., tridimensional shape)</td>
</tr>
<tr>
<td>( A_2(\alpha) )</td>
<td>( [-\ln(1 - \alpha)^{\frac{1}{3}} = kt] )</td>
<td>2</td>
<td>Random instant nucleation and two-dimensional growth of nuclei (Avrami-Erofeev equation)</td>
</tr>
<tr>
<td>( A_3(\alpha) )</td>
<td>( [-\ln(1 - \alpha)^{\frac{1}{3}} = kt] )</td>
<td>3</td>
<td>Random instant nucleation and three-dimensional growth of nuclei (Avrami-Erofeev equation)</td>
</tr>
</tbody>
</table>
reduction, when \( L \) was much higher than \( D \), CO was diffused more deeply into the sample to react with \( \text{Fe}_2\text{O}_3 \) in the interphase layers, and some no-reduced \( \text{CF}_2 \) and \( \text{Fe}_2\text{O}_3 \) were still behind the diffusion front in the iron product layers. The reduction reaction was composed of the strong reduction of a large amount of \( \text{Fe}_2\text{O}_3 \) in the diffusion front and the weak reduction of a small amount of \( \text{Fe}_2\text{O}_3 \) remaining in the iron product layers, and the reduction process proceeded in the thick samples layers like a 3D reaction, which was described by function \( A_3 \). As for the \( \text{C}_2\text{F} \) and \( \text{CF} \) reductions, when \( L \) was much lower than \( D \), the \( \text{Fe}_2\text{O}_3 \) content was lower than that of \( \text{CF}_2 \), thus the CO diffusion progressed slowly in the unreacted layers, and the reduction process occurred like a 2D reaction. In this study, the model functions of the three sample reductions were obtained by the ln-ln method and Sharp analysis, and the results implied that \( \text{C}_2\text{F} \) reduction was described by a 2D plane reduction mechanism, whereas...
the CF and CF$_2$ reductions were expressed by a reduction mechanism from the 2D plane toward a 3D cylinder.

Szekely$^{34}$ generalized the results of previous studies on shrinking core model for the gaseous reduction that the reduction time can be calculated as:

$$\frac{d\alpha}{dt} = \frac{k'}{m_1(\alpha) + m_2(\alpha)}$$

where

$$k' = \frac{3(c_0 - c_e)}{\rho_0 r_0}$$

is the comprehensive reaction rate constant, $m_1(\alpha) = \frac{r_0}{D_e} \left(1 - \alpha\right)^{-1/3} - 1$ and

$$m_2(\alpha) = \frac{K}{k(1 + K) \left(1 - \alpha\right)^{2/3}}$$

the resistance of the reaction rate determined by inner gas diffusion and chemical reaction. $r_0$ is the initial radius of pellet, $m$; $\rho_0$ the oxygen concentration in pellet, mol·m$^{-3}$; $c_0$ the initial concentration of reducing agent, mol·m$^{-3}$; $c_e$ the equilibrium concentration of reducing agent, mol·m$^{-3}$; $k$ the reaction rate constant, m·s$^{-1}$; $D_e$ the effective diffusion coefficient of gaseous species, m$^2$·s$^{-1}$; and $K$ the equilibrium constant of chemical reaction. In this situation, the external gas diffusion was excluded. Functions $m_1$ and $m_2$ increase as $\alpha$ (or $t$) increases. Therefore, in the shrinking core model, reaction rates $d\alpha/dt$ always decrease when $\alpha$ (or $t$) increases. However, a reaction based on shrinking core model always starts from an induction period with gradual improvement of reaction rate and undergoes a catalytic period with reaction rate accelerating.

In this study, the kinetics equations of C$_2$F, CF, and CF$_2$ reduction were described as function $A_2$ and $A_3$, the overall reaction rate can be expressed as:

$$\frac{d\alpha}{dt} = g_1 f_1(\alpha) + g_2 f_2(\alpha)$$

Table 7. Shrinking core model and the new proposed model.

<table>
<thead>
<tr>
<th>Reduction model</th>
<th>Sample size and shape</th>
<th>Reduction rate</th>
<th>Reduction kinetics equation</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>Shrinking core model</td>
<td>$\frac{d\alpha}{dt} = \frac{k'}{m_1(\alpha) + m_2(\alpha)}$</td>
<td>Shrink core</td>
<td></td>
</tr>
<tr>
<td>Powder, &lt;100 μm</td>
<td>C$_2$F</td>
<td>$\frac{d\alpha}{dt} = f_1(\alpha)$</td>
<td>2D reduction</td>
<td></td>
</tr>
<tr>
<td>Powder, &lt;100 μm</td>
<td>CF</td>
<td>$\frac{d\alpha}{dt} = \begin{cases} g_1 f_1(\alpha) + g_2 f_2(\alpha) &amp; \alpha &lt; 0.5 \ (g_1 &gt; g_2), \alpha &gt; 0.5 &amp; \end{cases}$</td>
<td>2D (more)→3D reduction</td>
<td></td>
</tr>
<tr>
<td>Powder, &lt;100 μm</td>
<td>CF$_2$</td>
<td>$\frac{d\alpha}{dt} = \begin{cases} f_1(\alpha), \alpha &lt; 0.5 \ f_2(\alpha), \alpha &gt; 0.5 &amp; \end{cases}$</td>
<td>2D→3D (more) reduction</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 11. A new model for reduction of samples C$_2$F, CF, and CF$_2$.
where $g_1$ and $g_2$ are adjustment functions influenced by the reduction degree $\alpha=0.5$. $f_i(\alpha)=2k[-\ln(1-\alpha)]^{1/2}(1-\alpha)$, $f_i(\alpha)=3k[-\ln(1-\alpha)]^{3/2}(1-\alpha)$ are reaction rate devoted by function $A_2$ and $A_3$. $f_1$ and $f_2$ appears increases then decreases as $\alpha$ (or $t$) increases. That is why the rate curve of C$_2$F reduction expressed only by function $A_2$ shows one peak whereas those of CF and CF$_2$ expressed by $A_2$ then $A_3$ show more peaks.

As for the C$_2$F, CF, and CF$_2$ reduction, the kinetics equation can be specifically expressed as:

for C$_2$F, when $\alpha<0.5$ or $\alpha>0.5$, $g_1=1>>g_2$,

$$\frac{d\alpha}{dt} = f_i(\alpha); ................................ (15)$$

for CF, when $\alpha<0.5$, $g_1>>g_2$; when $\alpha>0.5$, $g_1>g_2$,

$$\frac{d\alpha}{dt} = \begin{cases} f_i(\alpha), \alpha < 0.5 \\ g_1f_1(\alpha)+g_2f_2(\alpha)(g_1 > g_2), \alpha > 0.5 \end{cases}; ................................ (16)$$

for CF$_2$, when $\alpha<0.5$, $g_1=1>>g_2$; when $\alpha>0.5$, $g_1<<g_2=1$,

$$\frac{d\alpha}{dt} = \begin{cases} f_i(\alpha), \alpha < 0.5 \\ f_2(\alpha), \alpha > 0.5 \end{cases}; ................................ (17)$$

The comparisons of shrinking core model and new proposed reduction model were listed in Table 7.

4. Conclusions

The isothermal reduction kinetics of powdered C$_2$F, CF, and CF$_2$ was investigated via TG measurement with 30% CO and 70% N$_2$ gas mixtures. The reducibility of C$_2$F, CF, and CF$_2$ was implied by revealing the reduction rate and apparent activation energy. The reduction mechanisms of C$_2$F, CF, and CF$_2$ were examined through ln-ln and Sharp analysis. The following conclusions were summarized.

(1) The order of maximum reduction degree is C$_2$F $<$ CF $<$ CF$_2$, and the corresponding reduction time is C$_2$F $>$ CF $>$ CF$_2$.

(2) The reduction rate analysis by peak fitting based on the Gauss rule indicated that the reduction of the C$_2$F, CF, and CF$_2$ samples were typical one-step, two-step, and three-step reactions, respectively. Fe$_3$O$_4$ to FeO stage overlaps with the following FeO to Fe stage and tends to approach the previous Fe$_3$O$_4$ to FeO$_2$ stage in reduction of CaO–Fe$_2$O$_3$ system with an increase in Fe$_3$O$_4$ content.

(3) Under the powdered state ($\leq 74 \mu$m) of samples reduced by 30% CO and 70% N$_2$ gas mixtures, the apparent activation energy values of the reduction process of the C$_2$F, CF, and CF$_2$ were 51.74, 46.89, and 34.37 kJ/mol, indicating that reduction of the C$_2$F, CF, and CF$_2$ proceeded easily.

(4) A new model was proposed to describe the reduction processes of powdered C$_2$F, CF, and CF$_2$ samples by CO. The ln-ln method and the Sharp analysis implied that the reduction of C$_2$F was described by the Avrami–Erofeev function and appeared as a 2D reaction during the whole reaction, whereas the CF and CF$_2$ reductions were expressed initially by a 2D reaction when $\alpha<0.5$ and subsequently by a 3D reaction when $\alpha>0.5$.

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Nomenclature

$\alpha$: reduction degree $[\cdot ]$

$\Delta n_t$ and $\Delta n_0$: removed oxygen mass at a fixed time $t$ and the theoretically removed oxygen mass from iron oxide $[mg]$

$\frac{d\alpha}{dt}$: reduction rate $[min^{-1}]$

$k(T)$: rate constant $[min^{-1}]$

$f(\alpha)$ and $G(\alpha)$: model function

$E$: apparent activation energy $[kJ/mol]$

$A$: pre-exponent $[min^{-1}]$

$R$: gas constant, 8.314 $[J/(mol·K)^{-1}]$

$n$: Avrami exponent $[\cdot ]$

$y(\alpha)$: a defined non-dimensional parameter $[\cdot ]$

$L$ and $D$: diffusion distance of CO, thickness of the unreacted layer, $[mm]$

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