1. Introduction

Sinter ore is one of the main charge materials in blast furnace operation. Productivity of blast furnace is governed by the sinter qualities such as reducibility and mechanical strength. These sinter qualities are governed by its microstructure. Iron ore sinter is composed of iron oxides, ferrites (mostly SFCA), and glassy phases and the mineralogy of sinter significantly depends on its chemistry and many process factors. Silico-ferrite of calcium and aluminum (SFCA) is believed to be the most desirable main bonding phase in sinter ore because of its high reducibility and sufficient mechanical strength which may enhance the blast furnace productivity and efficiency.

Since the properties of iron ore sinter mainly depend on sinter mineralogy, understanding of the mineralogical characteristics of sinter is necessary to design the optimum sinter microstructure, especially about that of SFCA. However, due to the complexity of the sintering process caused by its inhomogeneous and non-equilibrium nature, the formation mechanism of iron ore sinter is not fully understood yet. Furthermore, the sinter mineralogy also has a very complicated nature, and its behaviors are significantly varying and depending on various factors.1–3)

In sintering process, since the main source of heat energy is the combustion of coke breeze, the sinter mix is heated in a reducing atmosphere and cooled in an oxidizing atmosphere.4) As schematically shown in Fig. 1, the reactions during sintering process can be divided to two solid state steps and one liquid state step. Firstly, during the heating stage, calcium ferrite phases are formed from iron oxides which contained in iron ore and lime calcined from calcite and they react with gangue materials in solid state. In the following liquid step, gangue materials start to dissolve into the melt. Finally, in the cooling stage, the development of sinter microstructure is completed through solidification and precipitation.1)
be considered. Solid phases which do not pass through the melt may possibly exist in the final sinter microstructure. The existence of relict hematite in the final product of sinter supports this assumption. As the first step to study the initial solid state reaction of sintering process, the solid state calcium ferrites formation reactions from different iron oxides and CaO are investigated at 1 273 K. As the intermediate phase appears during the formation of SFCA, clarifying the calcium ferrites formation mechanism is the prerequisite step before inquiry into the SFCA formation mechanism. Since coke breeze is charged in sinter mix as a main heat source, it may cause local different atmosphere or different oxygen potentials. Therefore, different kinds of iron oxide can exist in the sinter mix during the heating stage. Since each iron oxide has different characteristics, there should be different reaction behaviors between different iron oxides and CaO.

In this study, solid state calcium ferrite formation reactions between different kinds of iron oxides and CaO were investigated under various $p_{O_2}$ at 1 273 K by using thermogravimetric analysis (TGA) and X-ray diffraction method (XRD) in order to determine the development processes of calcium ferrite phases and to establish the mechanism of calcium ferrite formation corresponding to the early stage of sintering process.

2. Experimental Design to Evaluate Calcium Ferrite Formation Process under Constant $p_{O_2}$

To investigate the solid state calcium ferrite formation process from iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$ and wüstite) and CaO under various $p_{O_2}$ at a particular temperature, the reaction between iron oxides and CaO during the heating process from room temperature to the particular experimental temperature must be avoided. Furthermore, $p_{O_2}$ required to stabilize each iron oxide changes with temperature as shown in Fig. 2. To solve these two problems, CaCO$_3$ and Fe$_2$O$_3$ have been used as starting materials in the present study.

The CaCO$_3$ decomposition reaction is given by

$$\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \quad \Delta G^\circ = 161 \, 300 - 137.2 \, T \quad \text{J/mol}^6$$

Based on the thermodynamic evaluation, the decomposition of CaCO$_3$ theoretically starts at 1 114, 1 168 and 1 176 K under the partial pressure of 40%, 90% and 100% CO$_2$, respectively. The result of thermogravimetric analysis of CaCO$_3$ decomposition under CO–40%CO$_2$ is shown in Fig. 3. In our experimental condition, the decomposition of CaCO$_3$ starts after reaching 1 173 K slightly higher than the calculated one. In the case of mixture of iron oxides and CaCO$_3$, however, the decomposition starts at lower temperature of around 1 073 K in all cases. Under the present TGA experimental condition, the reduction of wüstite with CO–40%CO$_2$ and Fe$_3$O$_4$ with CO–90%CO$_2$ were found to be almost completed before reaching at 1 073 K. It means that the calcinations of CaCO$_3$ will start at least after the iron oxide reduction process is almost finished. It has been also confirmed that CaCO$_3$ do not react with wüstite, Fe$_3$O$_4$ and Fe$_2$O$_3$.

Figure 4 shows the theoretical weight changes of materials through the reactions under (a) pure CO$_2$, (b) CO–90%CO$_2$ and (c) CO–40%CO$_2$. Two grams of sample mixture contains 0.8875 g of Fe$_2$O$_3$ and 1.1125 g of CaCO$_3$. Reductions of Fe$_2$O$_3$ to Fe$_3$O$_4$ and Fe$_3$O$_4$ to wüstite (‘FeO’) cause 3.36% (−0.030 g) and 6.89% (−0.059 g) weight decrease, respectively. Calcinations of CaCO$_3$ causes 43.98% (−0.4893 g) weight decrease. The formation of Ca$_2$Fe$_2$O$_5$ from Fe$_3$O$_4$, Fe$_2$O$_3$ and ‘FeO’ causes 0%, 2.01% (+0.030 g) and 6.25% (+0.089 g) weight increase, respec-
3. Experimental Details

3.1. Sample Preparation

The reagent grade powder of Fe₂O₃ was pressed at 20 MPa and sintered at 1 273 K in air for 10 h. It was crushed into powder, whose mean diameter was about 3.5 μm, and mixed with reagent grade powder of CaCO₃. The determination of average particle diameter of starting iron oxides was carried out using commercial particle size analyzer. Mixture of Fe₂O₃ and CaCO₃ was prepared to be cylinders of 10 mm diameter were produced by pressing 2 g of the mixtures at 20 MPa into a cylindrical mold. The pressed samples were placed in a crucible and heated to 1 273 K with heating rate of 10 K/min under various pO₂ adjusted by CO₂/CO ratio. The sample was held for 2 h at 1 273 K and then quenched by opening a separable furnace and introducing helium gas at the same time.

3.2. Experimental System and Procedure

The experimental apparatus is shown in Fig. 6. The specimen was placed in alumina crucible which is 15 mm in diameter and 20 mm in height with 13 holes of 1.5 mm diameter at the bottom to enhance gas permeability. It was suspended on the magnetic balance by Pt wire. All gases used in the experiment were purified by passing through a drying unit filled with CaSO₄ as a desiccant. Additionally, Ar and CO₂ gases were passed through the deoxidizing unit filled with magnesium chips at 723 K, while CO gas was passed through the CO₂ absorption unit filled with NaOH granules. The flow rate of the individual gases was controlled by mass flow controller and the total gas flow rate was 500 ml/min in each experiment. Prior to the calcium ferrite formation experiment, argon gas purging of the reactor was carried out for 20 min.

In the present experiments, the controlled pO₂ of 0, 10, 20, 30, 50 and 60 vol% CO with CO₂ balance were designated to 0 CO (pO₂=5.91×10⁻⁶), 10 CO (pO₂=6.02×10⁻¹⁰), 20 CO (pO₂=1.19×10⁻⁰³), 30 CO (pO₂=4.05×10⁻¹⁴), 50 CO (pO₂=7.44×10⁻¹⁵) and 60 CO (pO₂=3.30×10⁻¹⁵), respectively. As already mentioned, under reductive condition, initial hematite (Fe₂O₃) in mixtures will be reduced to magnetite (Fe₃O₄) or wüstite (‘FeO’) before calcinations start depending on the pO₂ setting.

3.3. Phase Analysis

The final and intermediate products at several reaction intervals after completion of calcinations were checked by using XRD in each case. The 0 min was defined as the apparent completion of CaCO₃ decomposition. Its definition...
can be discussed in the Sec. 4.4. For the calcium ferrite formation from CaO and Fe₂O₃, there is no weight change during the formation of calcium ferrite phase. Therefore, the fractions of phases were checked at 5 min, 30 min, 1 h and 2 h after completion of CaCO₃ decomposition to estimate the calcium ferrite phase formation rate. In the case of the calcium ferrite formation from CaO and ‘FeO’ or Fe₃O₄, the intermediate products were checked at 30 min and 2 h after the completion of calcinations and at 10 min and 30 min after the completion of calcinations, respectively. From the basis of these XRD results, quantitative phase analyses were carried out using Rietveld method. The quality of refinement can be checked by the chi-squared value, \( \chi^2 \). It approaches 1 for a perfect fit, but in general, a value below 3.0 indicates a well refined pattern. The range of these values in this study was 2.24–2.97, which may ensure the refinement results. During the quantification, it is assumed that all phases in the system were identified and considered as a crystalline phase.

4. Results and Discussion

4.1. Calcium Ferrite Formation from Fe₂O₃ and CaO

Figure 7 and Fig. 8 show TGA and XRD results for 0 CO. There was no weight change before calcinations which means there was no reduction of Fe₂O₃. After calcinations resulting to 43.98% weight decrease of CaCO₃ (≈0.49 g), there was no further weight change which means the reaction occurred without oxygen employing from the ambient atmosphere. The intermediate products at 5 min, 30 min and 1 h and the final product at 2 h after the calcinations consisted of Ca₂Fe₂O₅, CaFe₂O₄ and CaO phases. The phase Fe₂O₃ was detected at 5 and 30 min. From the XRD and quantitative phase analysis results, the amount of Ca₂Fe₂O₅ increased as the reaction time increases, while the amounts of CaFe₂O₄ and CaO decreased (Table 1). This result suggests that the reaction of Fe₂O₃ and CaO forms CaFe₂O₄ initially, followed by it reacts with CaO to form Ca₂Fe₂O₅.

\[
\text{Fe}_2\text{O}_3 + \text{CaO} \rightarrow \text{CaFe}_2\text{O}_4 \quad \quad (2)
\]

\[
\text{CaFe}_2\text{O}_4 + \text{CaO} \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5 \quad \quad (3)
\]

Scarlett et al. studied the formation of SFCA and its intermediate phases using in situ XRD under vacuum condition. They reported that Ca₃Fe₅O₁₀ was the first appearing calcium ferrite phase from the reaction between Fe₂O₃ and CaO with some substitution of Al and Si. And then, CaFe₂O₄ was formed. Their results were inconsistent with this study. The existence of gangue materials (Si and Al) or oxygen potentials may have some effects on the formation and/or stability of calcium ferrite phases. Further work is required to examine the effect of Al₂O₃ or SiO₂ and \( pO_2 \) on the stability of intermediate calcium ferrite formation.

4.2. Calcium Ferrite Formation from Fe₃O₄ and CaO

Figure 9 and Fig. 10 show TGA and XRD results for 10 CO. There was weight change of about 0.03 g decrease before the calcinations which means the reduction of Fe₂O₃ to Fe₃O₄ is occurred as expected. In the following weight decrease step corresponding to the calcinations of CaCO₃, the amount of weight decrease (approximately 0.48 g) was smaller than the theoretically expected one (0.4893 g), since some amount of calcium ferrite was already formed before the completion of the calcinations. After the calcinations of CaCO₃, there was weight increase corresponding to the Ca₂Fe₂O₅ formation. From the basis of this TGA result, it is suggested that extra oxygen from ambient atmosphere

![Fig. 7. Thermogravimetric analysis result of calcium ferrite formation under pure CO₂ (\( pO_2 = 5.91 \times 10^{-5} \)). The open circles are the points where sampled for XRD analysis.](image)

![Fig. 8. XRD patterns of samples under pure CO₂ at 5 min, 30 min, 1 h and 2 h after completion of calcination.](image)

| Table 1. Quantitative phase analysis of samples under pure CO₂. |
|---------------------------------------------------------------|
| \( \chi^2 \) | \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) | \( \text{CaFe}_2\text{O}_4 \) | \( \text{CaO} \) | \( \text{Fe}_2\text{O}_3 \) |
| 5 min | 25.1% | 39.6% | 19.2% | 16.2% | 2.67 |
| 30 min | 35.7% | 45.8% | 15.1% | 3.3% | 2.69 |
| 1 hour | 44.7% | 42.3% | 13.1% | - | 2.97 |
| 2 hours | 61.5% | 28.7% | 9.8% | - | 2.64 |
was employed during the calcinations and the reactions in the last weight increase step. The intermediate and final products after 30 min and 2 h of reaction were composed of Ca$_2$Fe$_2$O$_5$, CaFe$_3$O$_5$, CaO and Fe$_3$O$_4$. The amount of Ca$_2$Fe$_2$O$_5$ increased as the reaction time increases, but the amounts of CaFe$_3$O$_5$, CaO and Fe$_3$O$_4$ decreased after 2 h of reaction time as shown in Table 2. This result simply suggests that the reaction of Fe$_3$O$_4$ and CaO forms CaFe$_3$O$_5$ initially, after that it reacts with CaO to form the Ca$_2$Fe$_2$O$_5$.

\[
\text{Fe}_3\text{O}_4 + \text{CaO} \rightarrow \text{CaFe}_3\text{O}_5 \\
2\text{CaFe}_3\text{O}_5 + 4\text{CaO} + 1/2 \text{O}_2 \rightarrow 3\text{Ca}_2\text{Fe}_2\text{O}_5
\]

4.3. Calcium Ferrite Formation from Wüstite and CaO

Figure 11 and Fig. 12 show TGA and XRD results for 60 CO. There were two steps of weight changes which correspond to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ and the reduction of Fe$_3$O$_4$ to ‘FeO’ just as predicted. In the following weight decrease step corresponding to the calcinations of CaCO$_3$, the amount of weight decrease (approximately 0.43 g) was much smaller than the theoretically expected one (0.4893 g). It means, as same as that of 10 CO, some amount of calcium ferrite was already formed before the completion of the calcinations. However, in this case, the amount of formed calcium ferrite before the completion of calcinations is much larger than that of 10 CO. After the calcinations of CaCO$_3$, there was considerable weight increase corresponding to the Ca$_2$Fe$_2$O$_5$ formation with employment of extra oxygen from ambient atmosphere. The samples after 10 and 30 min of reaction were examined by XRD. Both of them were made up of Ca$_2$Fe$_2$O$_5$, CaO and ‘FeO’. Differing from the case of Fe$_2$O$_3$ or Fe$_3$O$_4$, the intermediate calcium ferrites were not detected. The amount of Ca$_2$Fe$_2$O$_5$ increased as the reaction time increases (Table 3). Thus, Ca$_2$Fe$_2$O$_5$ may be possibly formed from ‘FeO’ and CaO directly.

\[
2\text{‘FeO’} + 2\text{CaO} + 1/2 \text{O}_2 \rightarrow 3\text{Ca}_2\text{Fe}_2\text{O}_5
\]

Fukuyama et al.\textsuperscript{7} studied kinetics of Ca$_2$Fe$_2$O$_5$ formation process by using a diffusion couple method at 1273 K. They also confirmed that Ca$_2$Fe$_2$O$_5$ was formed at the interface between ‘FeO’ and CaO plates, but no intermediate calcium ferrites are indentified.
4.4 Calcium Ferrite Formation Rates

Figure 13 shows the formation rates of Ca$_2$Fe$_2$O$_5$ with each iron oxide under various $p$O$_2$. Since phase quantification of XRD result needs some assumptions that all phases need to be identified and considered as a crystalline phase, the formation rates obtained from the TGA results are more reliable than that from the XRD. Therefore, the formation rates of Ca$_2$Fe$_2$O$_5$ in the 10 CO, 20 CO, 30 CO, 40 CO, 50 CO and 60 CO were estimated by using the weight changes of the TGA results. In the 0 CO, however, there was no weight change during the formation of Ca$_2$Fe$_2$O$_5$. It means that it is impossible to estimate the formation rate using the TGA result. Therefore, the quantitative phase analysis result from the XRD was used to evaluate the formation rate only in the 0 CO. In every case, Ca$_2$Fe$_2$O$_5$ was formed as a final phase by the reaction between CaO and each iron oxide of Fe$_2$O$_3$, Fe$_3$O$_4$, or ‘FeO’. However, the intermediate calcium ferrite phases were different in all three cases. These differences in reaction mechanisms may cause the formation rate differences of Ca$_2$Fe$_2$O$_5$. As already mentioned, it is very difficult to precisely decide the time when the calcium ferrite formation reaction starts since some amount of calcium ferrite formation will start before the temperature reaches 1 273 K. There are inflection points in TGA curves during calcinations interval as shown in Figs. 7, 9 and 11 those are not observed for pure CaCO$_3$ calcinations process. Thus, these inflection points may correspond to the starting point of calcium ferrite formation. However, it is very difficult to confirm the existence of small amount of calcium ferrite by XRD. Thus, in the present study, the completion point of calcinations was nominally defined as starting point of calcium ferrite formation rate determination in each experiment. Even so, the fundamental features shown in Fig. 13 do not change essentially.

The conversion rate was estimated on the basis of Eq. (7) with TGA results of each experiment (10 CO, 20 CO, 30 CO, 50 CO and 60 CO).

\[
\text{conversion rate} = \frac{\alpha_t - \alpha_0}{\alpha_{100} - \alpha_0} \quad \text{...............(7)}
\]

where 
\[\alpha_t = \text{sample weight difference at time } t\]
\[\alpha_0 = \text{initial sample weight before Ca}_2\text{Fe}_2\text{O}_5 \text{ formation}\]
\[\alpha_{100} = \text{theoretical sample weight of 100% Ca}_2\text{Fe}_2\text{O}_5 \text{ formation}\]

It is found that the formation rate of Ca$_2$Fe$_2$O$_5$ was different depending on the types of reactant iron oxide (from Fe$_2$O$_3$ in 0 CO; from Fe$_3$O$_4$ in 10, 20 and 30 CO; from ‘FeO’ in 50 and 60 CO). The following order of reactant iron oxide can be found for the formation rate of Ca$_2$Fe$_2$O$_5$.

‘FeO’ $>$ Fe$_3$O$_4$ $>$ Fe$_2$O$_3$

The external surfaces of produced Ca$_2$Fe$_2$O$_5$ from each iron oxide after 2 h are shown in Fig. 14. The apparent grain or particle size of calcium ferrite formed from Fe$_2$O$_3$, Fe$_3$O$_4$ and ‘FeO’ are about less than 1 $\mu$m, 1–3 $\mu$m, and 5–7 $\mu$m, respectively. Namely, the apparent grain or particle size increases with Fe$_2$O$_3$, Fe$_3$O$_4$ and ‘FeO’ in order. This tendency agrees well with the rate of Ca$_2$Fe$_2$O$_5$ formation as shown in Fig. 13. Since the Ca$_2$Fe$_2$O$_5$ formation occurs as a sintering process or a solid state diffusion process, the types of reactant iron oxide may be considered as one of the important factors in calcium ferrite formation mechanism. By the existence of large amount of cation defects in wüstite, the diffusion process in wüstite phase can be enhanced. This non-stoichiometric nature of wüstite may also explain the fastest formation rate of Ca$_2$Fe$_2$O$_5$.

Intriguingly, Ca$_2$Fe$_2$O$_5$ formation from Fe$_3$O$_4$, rates decrease with the increase of $p$O$_2$. However, in the case of ‘FeO’, the formation rate does not depend on $p$O$_2$. As al-

**Table 3. Quantitative phase analysis of samples under CO–40%CO$_2$.**

|          | Ca$_2$Fe$_2$O$_5$ | FeO  | CaO  | $\chi^2$ |
|----------|------------------|------|------|----------|
| 10 min   | 69.9%            | 15.8%| 14.3%| 2.24     |
| 30 min   | 91.9%            | 4.6% | 3.4% | 2.54     |

**Fig. 13.** Formation rate of Ca$_2$Fe$_2$O$_5$ under various $p$O$_2$. The formation rates from Fe$_3$O$_4$ and ‘FeO’ are estimated by using the TGA results of each experiment, while the formation rate from Fe$_2$O$_3$ is estimated by using the quantitative phase analysis result of XRD in 0 CO.

**Fig. 14.** SEM images of external surfaces under (a) pure CO$_2$, (b) CO–90%CO$_2$ and (c) CO–40%CO$_2$. 

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ready mentioned, \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) formation from ‘FeO’ and \( \text{Fe}_2\text{O}_4 \) requires extra oxygen from the atmosphere. Namely, the extra oxygen can be supplied by the \( \text{CO}_2 \) dissociation reaction at the iron oxide surface. It has been well known that the rate constants of the \( \text{CO}_2 \) dissociation rate on iron oxides are closely described by the equation

\[
k_d = k_d(a_o)^{-n}
\]

where \( a_o \) is the \( \text{CO}_2/\text{CO} \) ratio in equilibrium with the oxides and \( n \) is the constant with value from 0.66 to 1.0.\(^9\)\(^,\)\(^10\) Namely, \( \text{CO}_2 \) dissociation rate increases with decrease of \( p\text{O}_2 \). Thus, the supply rate of extra oxygen can be fast and sufficient enough to form \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) under the very low \( p\text{O}_2 \) where ‘FeO’ is stable. However, the oxygen supply rates may rather be slow under relatively high \( p\text{O}_2 \) where \( \text{Fe}_2\text{O}_4 \) is stable so that \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) formation rate can be influenced by \( p\text{O}_2 \).

5. Conclusions

TGA and XRD have been used to study the formation of dicalcium ferrite and intermediate phases by the reactions between different iron oxides and \( \text{CaO} \) under controlled atmospheres. For the present conditions, the following conclusions may be drawn.

(1) \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) can be formed even under the low \( p\text{O}_2 \) range where ‘FeO’ and \( \text{Fe}_2\text{O}_4 \) are stable.

(2) Extra oxygen is employed from the atmosphere for the \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) formation reactions when starting from \( \text{Fe}_2\text{O}_3 \) and ‘FeO’.

(3) Intermediate calcium ferrite phases of \( \text{Ca}_4\text{Fe}_2\text{O}_7 \) and \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) are formed prior to the \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) formation when using \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_4 \) as starting materials, respectively.

(4) \( \text{Ca}_4\text{Fe}_2\text{O}_7 \) formation rates are different depending on the reactant iron oxide phases, and the formation rates increase with \( \text{Fe}_2\text{O}_3, \text{Fe}_2\text{O}_4 \) and ‘FeO’ in order.

(5) \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) formation from \( \text{Fe}_2\text{O}_4 \) rates decrease with increase of \( p\text{O}_2 \). However, in the case of ‘FeO’, the formation rates do not depend on \( p\text{O}_2 \).

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