Formation of Calcium Ferrites under Controlled Oxygen Potentials at 1 273 K

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Solid state calcium ferrite formation reactions between different kinds of iron oxides and CaO under various pO_2 at 1 273 K have been investigated. The calcium ferrite formation rates are evaluated by using thermogravimetric method. The phase identification and quantification of calcium ferrites in the experiment have been carried out by using X-ray diffraction method (the Rietveld method). It has been found that intermediate calcium ferrite phases of $CaFe_2O_4$ and $CaFe_3O_5$ are formed prior to the $Ca_2Fe_2O_5$ formation when Fe_2O_3 and Fe_3O_4 are used as a starting iron oxide, respectively. When starting from wüstite, intermediate calcium ferrite phases are not formed. The rates of $Ca_2Fe_2O_5$ formation are found to be different depending on the starting reactant iron oxide phases. The $Ca_2Fe_2O_5$ formation rate from wüstite is faster than that from Fe_3O_4 , and that from Fe_3O_4 is faster than that from Fe_2O_3 . It is also found that the $Ca_2Fe_2O_5$ formation rate starting from Fe_3O_4 decreases with pO_2 , but that starting from wüstite is independent from pO_2 .

KEY WORDS: dicalcium ferrite; monocalcium ferrite; oxygen potential; TGA; sinter ore.

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⁾

Most of the studies on sinter ore have been carried out focusing on the last two steps. However, due to both the relatively low sintering temperature (1 523–1 573 K) and insufficient sintering time (10–15 min) which may be unable to melt all phases present in sinter, the first solid state sintering step should have some effects on the later stages and

Fig. 1. Schematic reaction flow of sintering process.

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 1273 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 pO_2 at 1273 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 pO_2

To investigate the solid state calcium ferrite formation process from iron oxides (Fe_2O_3 , Fe_3O_4 and wüstite) and CaO under various pO_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, pO_2 required to stabilize each iron oxide changes with temperature as shown in Fig. 2.⁵⁾ To solve these two problems, $CaCO_3$ and Fe_2O_3 have been used as starting materials in the present study.

The $CaCO_3$ decomposition reaction is given by

$$\Delta G^\circ = 161\,300 - 137.2T \quad J/mol^{(6)}$$

Based on the thermodynamic evaluation, the decomposi-

Fig. 2. The phase diagram of Fe- O_2 .⁵⁾

tion of $CaCO_3$ theoretically starts at 1114, 1168 and 1176 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 1173 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 1073 K in all cases. Under the present TGA experimental condition, the reduction of wüstite with CO -40% CO_2 and Fe_3O_4 with CO -90% CO_2 were found to be almost completed before reaching at 1073 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_3O_4 and Fe_2O_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_2O_3 and 1.1125 g of $CaCO_3$. Reductions of Fe_2O_3 to Fe_3O_4 , and Fe_3O_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 $Ca_2Fe_2O_5$ from Fe_2O_3 , Fe_3O_4 and 'FeO' causes 0%, 2.01% (+0.030 g) and 6.25% (+0.089 g) weight increase, respec-

Fig. 3. Thermogravimetric analysis result of $CaCO_3$ calcinations under CO -40% CO_2 ($pO_2 = 3.30 \times 10^{-15}$).

Fig. 4. Theoretical weight changes of materials through the reactions under (a) pure CO_2 , (b) CO -90% CO_2 and (c) CO -40% CO_2 .

Fig. 5. Thermogravimetric analysis result of calcium ferrite formation with 1 μm average particle diameter of starting iron oxide under $\text{CO-40\%CO}_2$ ($p_{\text{O}_2} = 3.30 \times 10^{-15}$).

tively.

To minimize the calcium ferrite formation reaction at less than 1273 K, the particle size of iron oxides is very critical. If the particle size of iron oxides is small (less than 1 μm), iron oxides can react with the produced CaO rapidly and most amount of iron oxides are converted to calcium ferrite phases before the temperature reaches to 1273 K, since CaCO_3 starts to decompose at around 1073 K. **Figure 5** shows the TGA result of calcium ferrite formation with 1 μm average particle diameter of starting iron oxide under $\text{CO-40\%CO}_2$. The initial two weight decreases of 0.030 g and 0.059 g indicate the reduction of Fe_2O_3 and Fe_3O_4 , respectively. After two steps of weight decrease, there was considerable amount of weight decrease (-0.40 g) which corresponding to the combination of weight decrease of CaCO_3 calcinations (-0.49 g) and weight increase of calcium ferrites formation ($+0.089$ g). It was well agreed with the theoretical calculation result. The presence of $\text{Ca}_2\text{Fe}_2\text{O}_5$ in the final product was also confirmed by using XRD. This result suggests that the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ was completed before the decomposition of CaCO_3 .

The effect of calcium ferrite formation before reaching at 1273 K can be decreased by using larger size of particles. When the appropriate size of particles is used, the rate of calcium ferrite formation can be minimized and the evaluation of kinetics of calcium ferrite formation becomes available. In the present study, particles of 3.5 μm average diameter are used as starting iron oxides to minimize the undesired calcium ferrite formation without the difficulty of kinetics evaluation.

3. Experimental Details

3.1. Sample Preparation

The reagent grade powder of Fe_2O_3 was pressed at 20 MPa and sintered at 1373 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 CaCO_3 . The determination of average particle diameter of starting iron oxides was carried out using commercial particle size analyzer. Mixture of Fe_2O_3 and CaCO_3 was prepared to be the composition of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$). Cylindri-

Fig. 6. Schematic diagram of experimental apparatus. (1) Magnetic suspension balance, (2) separable furnace, (3) alumina crucible, (4) silica tube, (5) Pt wire, (6) K-type thermocouple, (7) glycerol bubbler, (8) gas outlet, (9) gas inlet, (10) deoxidizing unit, (11) drying unit, (12) CO_2 absorption unit and (13) water cooling).

cal tablets 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 1273 K with heating rate of 10 K/min under various p_{O_2} adjusted by CO_2/CO ratio. The sample was held for 2 h at 1273 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 CaSO_4 as a desiccant. Additionally, Ar and CO_2 gases were passed through the deoxidizing unit filled with magnesium chips at 723 K, while CO gas was passed through the CO_2 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 p_{O_2} of 0, 10, 20, 30, 50 and 60 vol% CO with CO_2 balance were designated to 0 CO ($p_{\text{O}_2} = 5.91 \times 10^{-6}$), 10 CO ($p_{\text{O}_2} = 6.02 \times 10^{-13}$), 20 CO ($p_{\text{O}_2} = 1.19 \times 10^{-13}$), 30 CO ($p_{\text{O}_2} = 4.05 \times 10^{-14}$), 50 CO ($p_{\text{O}_2} = 7.44 \times 10^{-15}$) and 60 CO ($p_{\text{O}_2} = 3.30 \times 10^{-15}$), respectively. As already mentioned, under reductive condition, initial hematite (Fe_2O_3) in mixtures will be reduced to magnetite (Fe_3O_4) or wüstite ('FeO') before calcinations start depending on the p_{O_2} 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 CaCO_3 decomposition. Its definition

can be discussed in the Sec. 4.4. For the calcium ferrite formation from CaO and Fe_2O_3 , 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 CaCO_3 decomposition to estimate the calcium ferrite phase formation rate. In the case of the calcium ferrite formation from CaO and 'FeO' or Fe_3O_4 , 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, χ^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 Fe_2O_3 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 Fe_2O_3 . After calcinations resulting to 43.98% weight decrease of CaCO_3 (−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 $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_2O_4 and CaO phases. The phase Fe_2O_3 was detected at 5 and 30 min. From the XRD and quantitative phase analysis results, the amount of $\text{Ca}_2\text{Fe}_2\text{O}_5$ increased as the reaction time increases, while the amounts of CaFe_2O_4 and CaO decreased (Table 1). This result suggests that the reaction of Fe_2O_3 and CaO forms CaFe_2O_4 initially, followed by it reacts with CaO to form $\text{Ca}_2\text{Fe}_2\text{O}_5$.

Scarlett *et al.*²⁾ studied the formation of SFCA and its inter-

Fig. 7. Thermogravimetric analysis result of calcium ferrite formation under pure CO_2 ($p\text{O}_2 = 5.91 \times 10^{-6}$). The open circles are the points where sampled for XRD analysis.

mediate phases using *in situ* XRD under vacuum condition. They reported that $\text{Ca}_2\text{Fe}_2\text{O}_5$ was the first appearing calcium ferrite phase from the reaction between Fe_2O_3 and CaO with some substitution of Al and Si. And then, CaFe_2O_4 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 Al_2O_3 or SiO_2 and $p\text{O}_2$ on the stability of intermediate calcium ferrite formation.

4.2. Calcium Ferrite Formation from Fe_3O_4 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 Fe_2O_3 to Fe_3O_4 is occurred as expected. In the following weight decrease step corresponding to the calcinations of CaCO_3 , 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 CaCO_3 , there was weight increase corresponding to the $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation. From the basis of this TGA result, it is suggested that extra oxygen from ambient atmosphere

Fig. 8. XRD patterns of samples under pure CO_2 at 5 min, 30 min, 1 h and 2 h after completion of calcination.

Table 1. Quantitative phase analysis of samples under pure CO_2 .

	$\text{Ca}_2\text{Fe}_2\text{O}_5$	CaFe_2O_4	CaO	Fe_2O_3	χ^2
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

Fig. 9. Thermogravimetric analysis result of calcium ferrite formation under CO-90%CO₂ ($p_{O_2}=6.02 \times 10^{-13}$). The open circles are the points where sampled for XRD analysis.

Fig. 10. XRD patterns of samples under CO-90%CO₂ at 30 min and 2 h after completion of calcination.

Table 2. Quantitative phase analysis of samples under CO-90%CO₂.

	Ca ₂ Fe ₂ O ₅	CaFe ₃ O ₅	CaO	Fe ₃ O ₄	χ^2
30 min	56.6%	27.1%	14.1%	2.2%	2.66
2 hours	88.7%	6.1%	4.3%	0.9%	2.42

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 Ca₂Fe₂O₅, CaFe₃O₅, CaO and Fe₃O₄. The amount of Ca₂Fe₂O₅ increased as the reaction time increases, but the amounts of CaFe₃O₅, CaO and Fe₃O₄ decreased after 2 h of reaction time as shown in Table 2. This result simply suggests that the reaction of Fe₃O₄ and CaO forms CaFe₃O₅ initially, after that it reacts with CaO to form the Ca₂Fe₂O₅.

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 cor-

Fig. 11. Thermogravimetric analysis result of calcium ferrite formation under CO-40%CO₂ ($p_{O_2}=3.30 \times 10^{-15}$). The open circles are the points where sampled for XRD analysis.

Fig. 12. XRD patterns of samples under CO-40%CO₂ at 10 and 30 min after completion of calcinations.

respond to the reduction of Fe₂O₃ to Fe₃O₄ and the reduction of Fe₃O₄ to 'FeO' just as predicted. In the following weight decrease step corresponding to the calcinations of CaCO₃, 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 CaCO₃, there was considerable weight increase corresponding to the Ca₂Fe₂O₅ 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 Ca₂Fe₂O₅, CaO and 'FeO'. Differing from the case of Fe₂O₃ or Fe₃O₄, the intermediate calcium ferrites were not detected. The amount of Ca₂Fe₂O₅ increased as the reaction time increases (Table 3). Thus, Ca₂Fe₂O₅ may be possibly formed from 'FeO' and CaO directly.

Fukuyama *et al.*⁷⁾ studied kinetics of Ca₂Fe₂O₅ formation process by using a diffusion couple method at 1273 K. They also confirmed that Ca₂Fe₂O₅ 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 $\text{Ca}_2\text{Fe}_2\text{O}_5$ with each iron oxide under various $p\text{O}_2$. 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 $\text{Ca}_2\text{Fe}_2\text{O}_5$ 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 $\text{Ca}_2\text{Fe}_2\text{O}_5$. 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, $\text{Ca}_2\text{Fe}_2\text{O}_5$ was formed as a final phase by the reaction between CaO and each iron oxide of Fe_2O_3 , Fe_3O_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 $\text{Ca}_2\text{Fe}_2\text{O}_5$. As already men-

Table 3. Quantitative phase analysis of samples under CO–40%CO₂.

	$\text{Ca}_2\text{Fe}_2\text{O}_5$	FeO	CaO	χ^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 $\text{Ca}_2\text{Fe}_2\text{O}_5$ under various $p\text{O}_2$. The formation rates from Fe_3O_4 and 'FeO' are estimated by using the TGA results of each experiment, while the formation rate from Fe_2O_3 is estimated by using the quantitative phase analysis result of XRD in 0 CO.

tioned, 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 to 1273 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).

$$\text{conversion rate} = \frac{\alpha_t - \alpha_0}{\alpha_{100} - \alpha_0} \dots\dots\dots(7)$$

where

α_t =sample weight difference at time t

α_0 =initial sample weight before $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation

α_{100} =theoretical sample weight of 100% $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation

It is found that the formation rate of $\text{Ca}_2\text{Fe}_2\text{O}_5$ was different depending on the types of reactant iron oxide (from Fe_2O_3 in 0 CO; from Fe_3O_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 $\text{Ca}_2\text{Fe}_2\text{O}_5$.

The external surfaces of produced $\text{Ca}_2\text{Fe}_2\text{O}_5$ from each iron oxide after 2 h are shown in Fig. 14. The apparent grain or particle size of calcium ferrite formed from Fe_2O_3 , Fe_3O_4 and 'FeO' are about less than 1 μm , 1–3 μm , and 5–7 μm , respectively. Namely, the apparent grain or particle size increases with Fe_2O_3 , Fe_3O_4 and 'FeO' in order. This tendency agrees well with the rate of $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation as shown in Fig. 13. Since the $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation occurs as a sintering process or a solid state diffusion process,^{7,8)} 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 $\text{Ca}_2\text{Fe}_2\text{O}_5$.

Intriguingly, $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation from Fe_3O_4 , rates decrease with the increase of $p\text{O}_2$. However, in the case of 'FeO', the formation rate does not depend on $p\text{O}_2$. As al-

Fig. 14. SEM images of external surfaces under (a) pure CO₂, (b) CO–90%CO₂ and (c) CO–40%CO₂.

ready mentioned, $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation from 'FeO' and Fe_3O_4 requires extra oxygen from the atmosphere. Namely, the extra oxygen can be supplied by the CO_2 dissociation reaction at the iron oxide surface. It has been well known that the rate constants of the CO_2 dissociation rate on iron oxides are closely described by the equation

$$k_d = k_0(a_o)^{-n} \dots\dots\dots(8)$$

where a_o is the CO_2/CO ratio in equilibrium with the oxides and n is the constant with value from 0.66 to 1.0.^{9,10)} Namely, 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 Fe_3O_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 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 Fe_3O_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 Fe_3O_4 and 'FeO'.

(3) Intermediate calcium ferrite phases of CaFe_2O_4 and CaFe_3O_5 are formed prior to the $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation when using Fe_2O_3 and Fe_3O_4 as starting materials, respectively.

(4) $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation rates are different depending on the reactant iron oxide phases, and the formation rates increase with Fe_2O_3 , Fe_3O_4 and 'FeO' in order.

(5) $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation from Fe_3O_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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