1. Introduction

Phase diagrams for the CaO–SiO₂–FeOₓ–Al₂O₃ and CaO–SiO₂–FeOₓ–MgO systems are important thermodynamic data for the analysis of melting reaction in sintering process and smelting reaction of iron and copper ores, since recently the iron ore has been degraded and the gangue contents of Al₂O₃ and MgO are increasing. Furthermore, for the design of raw material of new sinter having low melting point and softening and reducing properties, the phase relationship is of fundamental importance.

The phase diagram for the CaO–SiO₂–FeO system in air and that for the CaO–SiO₂–Fe₂O₃ system equilibrated with iron were reported as well known phase diagrams. The authors have studied the effect of partial pressure of oxygen on the liquidus for the CaO–SiO₂–FeO–Fe₂O₃ system at 1573 K. It was shown that the liquid area enlarges with decreasing the oxygen partial pressure and the control of oxygen partial pressure is an important factor for the control of the quality of sinter.

However, the effect of gangue composition such as Al₂O₃ or MgO on the liquidus for the CaO–SiO₂–FeO system has not been made clear and very little studies on the phase diagrams are available. Yan et al. measured the effect of Al₂O₃ on the liquid area for the CaO–SiO₂–FeO system in air at 1573 K. The addition of 2 mass% Al₂O₃ has the effect to enlarge the liquid area and two separated liquid areas were combined to form one liquid area in air. Shigaki et al. observed the liquidus isotherms for the CaO–SiO₂–Fe₃O₄ system with \( P_{O_2} = 10^{-2} \) Pa at 1573 K and the effect of Al₂O₃ addition. The addition of 5 mass% Al₂O₃ enlarges the liquid area to CaO and SiO₂ corner on the ternary phase diagram.

Recently, Kongoli et al. developed the quantitative model calculations and reported the calculated liquid surface of the CaO–SiO₂–FeOₓ–Al₂O₃ or –MgO systems with various oxygen partial pressures at around 1573 K. Characteristics of sinter in ironmaking process depend on the formation of melts during sintering. The control of chemical composition of sinter is an important factor to form high quality sinter. Therefore, knowledge of phase relationship for the CaO–SiO₂–FeOₓ–Al₂O₃ or –MgO systems at various oxygen partial pressures is required.

In the present research, the phase diagrams for the CaO–SiO₂–FeOₓ–Al₂O₃ or –MgO systems at various low oxygen partial pressures are observed by using chemical equilibration technique and the design of chemical composition of sinter is discussed.

2. Experimental

2.1. Measurement of Phase Diagram

Experimental procedure was described in detail in the previous paper. A chemical equilibration technique was employed to measure the phase relationships for the CaO–SiO₂–FeOₓ–Al₂O₃ or –MgO systems. About eight grams of mixture of CaO, SiO₂, FeO, Fe₂O₃, Al₂O₃ and MgO powders melted in a platinum crucible (inner diameter 35 mm, height 40 mm) are equilibrated with an oxide pellet (2CaO·Fe₂O₃, Fe₂O₃, 2CaO·SiO₂, 3CaO·2SiO₂, CaO·SiO₂ and SiO₂) in CO–CO₂ or Ar–air atmosphere (flow rate: about 150 cm³/min). The platinum crucible con-
taining sample was put into a mullite tube (inner diameter 52 mm, outer diameter 60 mm, height 1000 mm) set in an electric furnace. The oxygen partial pressure of the system was controlled from 10^{-3} to 10^{-1} Pa by changing the CO/CO_2 ratio according to reaction (1). A high purity CO gas was purified by passing through columns of soda lime, H_2SO_4 and Mg(ClO_4)_2. A high purity CO_2 gas was purified by H_2SO_4 and Mg(ClO_4)_2. The oxygen partial pressure of 2.1 \times 10^2 Pa was controlled with mixing high purity argon gas and air. A sample melt was held for 20 h at 1573 K in an electric furnace.

After equilibration, a platinum crucible was taken out from an electric furnace and sample melts in a platinum crucible were quenched in an argon flow. The compositions of CaO, Fe^{2+} and Fe^{3+} were analyzed by titration. Aluminum and magnesium contents were determined by ICP spectrometry and SiO_2 contents were done by gravimetry.

Reagent grade powders of CaO, SiO_2, Al_2O_3, MgO and Fe_2O_3 chemicals were used to form the melts. FeO powder was prepared by melting reagent grade of iron and Fe_2O_3 powders in an iron crucible and quenched in water bath. X-ray diffraction was conducted to confirm the formation of FeO.

Pellets of 2CaO·Fe_2O_3, Fe_2O_3, 2CaO·SiO_2, 3CaO·2SiO_2 and CaO·SiO_2 were prepared by pressing and sintering a mixture of powder of reagent grade oxides. Oxide melts were separated from a pellet of saturating oxide by platinum plate to prevent the contamination of a pellet oxide into melts when the sample was quenched. In some experiments, since an oxide pellet such as 2CaO·SiO_2 becomes powder during cooling, a platinum dish with an oxide pellet was taken out from a platinum crucible at first to prevent the contamination, and then a platinum crucible with molten sample was taken out from a furnace.

In some experiments, the mixture of powder of chemicals without solid phase of pellet was melted in a controlled atmosphere and the melting behavior was observed.

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\Delta G^\ddagger = -281,000 + 85.233T \quad \text{J/mol}^7
\]

3. Results and Discussion

3.1. Liquidus for the CaO–SiO_2–FeO–Fe_2O_3–Al_2O_3 System

The compositions of samples for the CaO–SiO_2–FeO–Fe_2O_3–Al_2O_3 system are shown in Tables 1, 2 and 3 with the oxygen partial pressure of 1.8 \times 10^{-3}, 1.8 \times 10^{-1} and 2.1 \times 10^2 Pa at 1573 K, respectively. The isothermal phase relationships for the CaO–SiO_2–FeO–Fe_2O_3–Al_2O_3 system at 1573 K with the oxygen partial pressure of 1.8 \times 10^{-3}, 1.8 \times 10^{-1} and 2.1 \times 10^2 Pa are shown in Figs. 1, 2 and 3. Since the slag system of the present study is essentially the CaO–SiO_2–FeO–Fe_2O_3 system, the phase diagrams should be shown on the quaternary system. However, since the number of experimental data points are not enough to show on the quaternary system and the variation of Al_2O_3 composition is small as about 4 to 5 mass%, the phase diagram in the present study is shown as the CaO–SiO_2–(FeO+

Fe_2O_3) ternary system.

Figure 4 shows the comparison of liquidus with the oxygen partial pressure of 2.1 \times 10^2, 1.8 \times 10^{-1} and 1.8 \times 10^{-3} Pa at 1573 K. The liquid area at high (FeO+Fe_2O_3) content shrinks and it moves to the CaO rich side with increasing the oxygen partial pressure. The liquid phase of
the SiO$_2$–(FeO/H$_2$O/Fe$_2$O$_3$) system exists at low oxygen partial pressure. However, it disappears at high oxygen partial pressure of 2.1$\times$10$^2$ Pa. At high CaO content area, the liquid area enlarges with increasing the oxygen partial pressure.

### 3.2. Relationship between the (Fe$^{3+}$)/(Fe$^{2+}$) Ratio and Oxygen Partial Pressure

The relationship between the (Fe$^{3+}$)/(Fe$^{2+}$) ratios on 2CaO·SiO$_2$ liquidus and the slag composition (mass%CaO)/(mass%SiO$_2$) ratio with different oxygen partial pressure of 2.1$\times$10$^2$, 1.8$\times$10$^1$ and 1.8$\times$10$^{-3}$ Pa at 1 573 K is shown in Fig. 5 for the CaO–SiO$_2$–FeO–5mass%Al$_2$O$_3$ system. The (Fe$^{3+}$)/(Fe$^{2+}$) ratios increase with increasing (mass%CaO)/(mass%SiO$_2$) ratio at each oxygen partial pressure.

Reaction between Fe$^{3+}$ and Fe$^{2+}$ ions in molten slags is assumed to be expressed by Eq. (2), the equilibrium constant of reaction (2) is expressed by Eq. (3). If it is assumed that the activity of oxide ion does not change so much on the 2CaO·SiO$_2$ liquidus and the ratio of the activity coefficients of Fe$^{3+}$ and Fe$^{2+}$ ions are constant with changing molten slag composition, log (Fe$^{3+}$)/(Fe$^{2+}$) has a linear relationship with log $P_{O_2}$. The slope of line is estimated to be 0.25 according to Eq. (3). The values of the (Fe$^{3+}$)/(Fe$^{2+}$) ratio at (mass%CaO)/(mass%SiO$_2$)=1.5 were observed from the data shown in Fig. 5 and the relationship between

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**Fig. 1.** Liquidus for the CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$ system with $P_{O_2}=1.8\times10^{-3}$ Pa at 1 573 K.

**Fig. 2.** Liquidus for the CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$ system with $P_{O_2}=1.8\times10^{-1}$ Pa at 1 573 K.

**Fig. 3.** Liquidus for the CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$ system with $P_{O_2}=2.1\times10^2$ Pa at 1 573 K.

**Fig. 4.** Effect of oxygen partial pressure on the liquidus of the CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$ system at 1 573 K.

**Fig. 5.** Relationship between the (Fe$^{3+}$)/(Fe$^{2+}$) ratio and (mass%CaO)/(mass%SiO$_2$) on 2CaO·SiO$_2$ liquidus at 1 573 K for the CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$ system.
the (Fe\(^{3+}\))/(Fe\(^{2+}\)) ratio and the oxygen partial pressure is obtained as shown in Fig. 6. This shows a good linear relationship and its slope is calculated to be 0.22 that is in good agreement with the estimated value, 0.25, from Eq. (3).

### 3.3. Liquids for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\)–MgO System

The compositions of samples for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\)–MgO system are shown in Tables 4, 5 and 6 with the oxygen partial pressure of 1.8×10\(^{-3}\), 1.8×10\(^{-1}\) and 2.1×10\(^{2}\) Pa at 1573 K, respectively. The isothermal phase relationships for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\)–MgO system at 1573 K with the oxygen partial pressure of 1.8×10\(^{-3}\), 1.8×10\(^{-1}\) and 2.1×10\(^{2}\) Pa are shown in Figs. 7, 8 and 9.

The phase diagram in the present study is shown as the CaO–SiO\(_2\)–(FeO–Fe\(_2\)O\(_3\)) ternary system as mentioned previously.

At the oxygen partial pressure of 2.1×10\(^{2}\) Pa, the melting behavior of samples without solid phase was observed. The compositions of samples with homogeneous liquid phase were shown as open circle in Fig. 9. Those of heterogeneous phase in which the solid phase remains in liquid phase were shown as open square.

Figure 10 shows the comparison of liquids with the oxygen partial pressure of 2.1×10\(^{2}\), 1.8×10\(^{-1}\) and 1.8×10\(^{-3}\) Pa at 1573 K. The liquid area at high (FeO+Fe\(_2\)O\(_3\)) content shrinks and it moves to the CaO and SiO\(_2\) rich side with increasing the oxygen partial pressure. One liquid area separates to two parts of liquid areas and the liquid area shrinks with increasing the oxygen partial pressure.

### 3.4. Effect of Al\(_2\)O\(_3\) and MgO Addition on Liquids for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\) System

In comparison with the liquids for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\) system,\(^3\) the effects of Al\(_2\)O\(_3\) and MgO addition on liquids for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\) system are shown in Figs. 11 to 13 with the oxygen partial pressure of 1.8×10\(^{-3}\), 1.8×10\(^{-1}\) and 2.1×10\(^{2}\) Pa, respectively.

At the oxygen partial pressure of 1.8×10\(^{-3}\) Pa, the shapes of liquids for the CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\), CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\)–Al\(_2\)O\(_3\), and CaO–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\)–MgO systems are approximately the same. However, the liquid phase area enlarges with Al\(_2\)O\(_3\) addition, but it shrinks with MgO addition at high iron oxide region as shown in Fig. 11. At the oxygen partial pressure of 1.8×10\(^{-1}\) Pa, the liquid phase area enlarges extremely with Al\(_2\)O\(_3\) addition. On the other hand, the liquid phase area separates into two liquid areas with MgO addition at high iron oxide region as shown in Fig. 12. At the oxygen partial pressure of 2.1×10\(^{2}\) Pa,
the liquid phase area also separates into two liquid areas with MgO addition at high iron oxide region. It is concluded that the change of oxygen partial pressure considerably affects the liquid area.

Kongoli et al.\textsuperscript{6} recently reported the calculated phase diagram for the CaO–SiO$_2$–FeO–Fe$_2$O$_3$–3mass%Al$_2$O$_3$ or –1mass%MgO system with oxygen partial pressure of 10$^{-3}$ Pa at 1 573 K. Their calculated phase diagrams are
compared with the results of the present study as shown in Figs. 14 and 15. Their calculated liquidus of SiO₂ or 2CaO·SiO₂ saturation for the CaO–SiO₂–FeO–Fe₂O₃–3mass%Al₂O₃ system is in very good agreement with the observed phase diagram in the present study, although there is the small difference of alumina contents.

For the CaO–SiO₂–FeO–Fe₂O₃–MgO system, the separation into two liquid phases was observed in the calculated phase diagram of Kongoli et al. However, the observed phase diagram in the present study shows one liquid area, although the MgO content of about 5 mass% observed in the present results is larger than that of 1 mass% for the calculated phase diagram. The reason of the difference is not
clear.

**Figure 16** shows the fraction of liquid phase in the solid–liquid two phase region at high iron oxide as a function of iron oxide content at the mass% ratio of CaO/SiO$_2$ = 1. The fraction of liquid phase increases with decreasing oxygen partial pressure at constant iron oxide contents. This indicates that the liquid forms at lower oxygen partial pressure.

The change of liquid area with adding Al$_2$O$_3$ or MgO and changing the oxygen partial pressure was observed as shown in Figs. 11, 12 and 13. For the practical sintering operation, the region of high iron oxide content is important to control the melting and sintering behavior. At high iron oxide region, the liquidus lines move from iron oxide side to CaO side by adding Al$_2$O$_3$. Therefore, the consideration of selection of ore and flux composition is important to control the melting and sintering behavior.

4. Conclusions

The phase diagrams for the CaO–SiO$_2$–FeO$_x$–Al$_2$O$_3$, or –MgO systems at 1573 K with oxygen partial pressure of $2.1 \times 10^2$, $1.8 \times 10^{-1}$ and $1.8 \times 10^{-2}$ Pa were investigated by chemical equilibration technique. The effects of Al$_2$O$_3$ or MgO addition on the liquid area of the system were observed. The liquid area enlarges by the addition of Al$_2$O$_3$ and shrinks by the addition of MgO. The (Fe$^{3+}$)/(Fe$^{2+}$) ratio in the melts increased with increasing (mass%CaO)/(mass%SiO$_2$) ratio at constant oxygen partial pressure.

REFERENCES

1) E. M. Levin, C. R. Robbins and H. F. McMurdie: Phase Diagrams for Ceramists, Vol. 1, The American Ceramic Society, Inc., Columbus, Ohio, (1964), 204 (Fig. 656), 228 (Fig. 586).