Effect of Simultaneous Addition of Al₂O₃ and MgO on the Liquidus of the CaO–SiO₂–FeOₓ System with Various Oxygen Partial Pressures at 1 573 K

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(Received on August 28, 2009; accepted on October 29, 2009)

To investigate the effect of simultaneous addition of Al₂O₃ and MgO on the liquid phase area for the CaO–SiO₂–FeOₓ system, liquidus for the CaO–SiO₂–FeOₓ–2.5mass%Al₂O₃–2.5mass%MgO system were measured at 1 573 K with various oxygen partial pressures by using chemical equilibration technique. By the addition of Al₂O₃ and MgO to the CaO–SiO₂–FeOₓ system, the liquid phase area enlarges with the oxygen partial pressure of 1.8×10⁻³ Pa. The liquid phase area separates into two liquid phase areas with the oxygen partial pressure of 0.18 Pa. The liquid phase area shrinks at low SiO₂ region with the oxygen partial pressure of 2.1×10² Pa.

KEY WORDS: phase diagram; thermodynamics; CaO–SiO₂–FeOₓ system; simultaneous addition of Al₂O₃ and MgO; oxygen partial pressure; melting behavior.

1. Introduction

Recently iron ore has been degraded and the gangue contents such as Al₂O₃ and MgO are increasing. Furthermore, the amount of pisolite ore and fine ore as raw material for ironmaking are increasing. The contents of gangue and combined water affect both the productivity of sintering process and the quality of sinter. Phase diagrams for the CaO–SiO₂–FeOₓ–Al₂O₃–MgO system are important fundamental data for the analysis of melting and solidifying mechanisms of ore in sintering process and smelting reaction of iron and copper ores.

The phase diagram for the CaO–SiO₂–Fe₂O₃ system in air and that for the CaO–SiO₂–FeOₓ system equilibrated with iron are well known.1,2) In addition, several researchers have investigated the effect of Al₂O₃ or MgO addition on the liquidus area with various oxygen partial pressures.3–5) Phase diagrams for the CaO–SiO₂–Fe₂O₃–Al₂O₃–MgO system are important fundamental data for the analysis of melting and solidifying mechanisms of ore in sintering process and smelting reaction of iron and copper ores.

The phase diagram for the CaO–SiO₂–Fe₂O₃ system in air and that for the CaO–SiO₂–FeOₓ system equilibrated with iron are well known.2,1) In addition, several researchers have investigated the effect of Al₂O₃ or MgO addition on the liquidus area with various oxygen partial pressures.3–5) Phase diagrams for the CaO–SiO₂–Fe₂O₃–Al₂O₃–MgO system are important fundamental data for the analysis of melting and solidifying mechanisms of ore in sintering process and smelting reaction of iron and copper ores.

The results, it was clarified that the liquid phase area enlarges with decreasing the oxygen partial pressure, and tends to enlarge or shrink with addition of Al₂O₃ or MgO, respectively. Therefore, the control of oxygen partial pressure and composition of blend are important factors for the control of the quality of sinter.

Recently, Henao et al.9) observed the effect of Al₂O₃ or MgO addition on the liquidus saturated with iron oxide for the CaO–SiO₂–FeOₓ system at 1 573 K with various oxygen partial pressures by using optical microscopy and EPMA analysis. They reported that liquid phase area shrinks by Al₂O₃ or MgO addition and this shrinkage is more significant with MgO addition.

Actual sinter blends contain these gangue components simultaneously at various concentrations. In this study, the effect of simultaneous addition of Al₂O₃ and MgO on the liquidus for the CaO–SiO₂–FeOₓ system at 1 573 K with various oxygen partial pressures was investigated by using chemical equilibration technique.

2. Experimental

Experimental method was described in detail in previous papers.6–8) Chemical equilibration technique was employed to measure the phase relationship for the CaO–SiO₂–FeOₓ–Al₂O₃–MgO system. About 10 g of mixture of CaO, SiO₂, FeO, Fe₂O₃, Fe₃O₄, Al₂O₃, and MgO powders melted in a platinum crucible (inner diameter 35 mm, height 40 mm) were equilibrated with an oxide pellet (2CaO·Fe₂O₃, Fe₂O₃, 2FeO·SiO₂, 3CaO·2SiO₂, CaO·SiO₂, and SiO₂) in CO–CO₂ or Ar–air atmosphere. The platinum crucible containing sample was put into a mullite tube (inner diameter 52 mm, outer diameter 60 mm, height 1 000 mm) set in an electric furnace. The oxygen partial pressures of 0.18 and 1.8×10⁻³ Pa were controlled by changing the CO/CO₂ ratio according to reaction (1). A high purity CO gas was purified by passing through columns of soda lime and dehydrated by H₂SO₄ and Mg(ClO₄)₂. A high purity CO₂ gas
was dehydrated by H$_2$SO$_4$ and Mg(ClO$_4$)$_2$. The oxygen partial pressure of $2.1 \times 10^2$ Pa was controlled by mixing high purity argon gas and air, which were purified by passing through columns of soda lime and dehydrated by H$_2$SO$_4$ and Mg(ClO$_4$)$_2$. A sample melt was held for 20 h at 1 573 K in an electric furnace.

$$CO(g) + \frac{1}{2} O_2(g) = CO_2(g)$$

$$\Delta G^\circ_T = -281 000 + 85.23 T J/mol^{(1)}$$  \hspace{1cm} (1)

After equilibration, a platinum crucible was taken out from the furnace and sample melts in the crucible were quenched in an argon flow. The compositions of Fe$^{2+}$ and Fe$^{3+}$ were analyzed by titration. Calcium, aluminum and magnesium contents were determined by ICP spectroscopy and SiO$_2$ contents were measured by gravimetry.

3. Results and Discussion

3.1. Liquids for the CaO–SiO$_2$–FeO–$x$–2.5mass% Al$_2$O$_3$–2.5mass%MgO System

The final compositions of samples for the CaO–SiO$_2$–FeO–Al$_2$O$_3$–MgO system are shown in Tables 1, 2 and 3 with the oxygen partial pressures of $1.8 \times 10^{-2}$, 0.18 and $2.1 \times 10^2$ Pa at 1 573 K, respectively. Although initial contents of Al$_2$O$_3$ and MgO of each sample were about 2.5 mass%, final contents of Al$_2$O$_3$ and MgO varied from 2 to 4 mass%. The liquids for the CaO–SiO$_2$–FeO–Al$_2$O$_3$–MgO system at 1 573 K with the various oxygen partial pressures are shown in Figs. 1, 2 and 3. Since Al$_2$O$_3$ and MgO content in the sample is small as 2 to 4 mass%, all data were normalized as the CaO–SiO$_2$–FeO ternary system as shown in Figs. 1 to 3. In these figures, solid circles are the observed compositions of liquid phases saturated with the oxide pellets, bold curves show liquidus.

Table 1. Experimental results for the CaO–SiO$_2$–FeO–2.5 mass% Al$_2$O$_3$–2.5mass%MgO system with $P_{O_2}=1.8 \times 10^{-2}$ Pa at 1 573 K.

| Sample | Composition of sample (mass%) | $f^{3+}/f^{2+}$ |
|--------|--------------------------------|-----------------|
| 104    | CaO 14.9 SiO$_2$ 11.1 FeO 18.9 Fe$_2$O$_3$ 8.9 Al$_2$O$_3$ 3.9 MgO 5.9 | 1.53            |
| 105    | CaO 14.3 SiO$_2$ 11.4 FeO 18.8 Fe$_2$O$_3$ 8.9 Al$_2$O$_3$ 4.0 MgO 5.0 | 1.50            |
| 106    | CaO 14.0 SiO$_2$ 11.5 FeO 18.7 Fe$_2$O$_3$ 9.0 Al$_2$O$_3$ 4.1 MgO 5.1 | 1.47            |

Table 2. Experimental results for the CaO–SiO$_2$–FeO–2.5 mass% Al$_2$O$_3$–2.5mass%MgO system with $P_{O_2}=0.18$ Pa at 1 573 K.

| Sample | Composition of sample (mass%) | $f^{3+}/f^{2+}$ |
|--------|--------------------------------|-----------------|
| 201    | CaO 15.4 SiO$_2$ 14.4 FeO 19.5 Fe$_2$O$_3$ 9.3 Al$_2$O$_3$ 4.6 MgO 5.7 | 1.62            |
| 202    | CaO 15.2 SiO$_2$ 14.2 FeO 19.6 Fe$_2$O$_3$ 9.4 Al$_2$O$_3$ 4.7 MgO 5.8 | 1.60            |
| 203    | CaO 15.0 SiO$_2$ 14.0 FeO 19.7 Fe$_2$O$_3$ 9.5 Al$_2$O$_3$ 4.8 MgO 5.9 | 1.58            |

Fig. 1. Liquids for the CaO–SiO$_2$–FeO–2.5mass%Al$_2$O$_3–2.5$ mass%MgO system with $P_{O_2}=1.8 \times 10^{-2}$ Pa at 1 573 K.

Fig. 2. Liquids for the CaO–SiO$_2$–FeO–2.5mass%Al$_2$O$_3–2.5$ mass%MgO system with $P_{O_2}=0.18$ Pa at 1 573 K.
Figure 4 shows the comparison of liquidus with various oxygen partial pressures of 1.8 × 10^{-3}, 0.18 and 2.1 × 10^{-2} Pa at 1 573 K. As the oxygen partial pressure decreases, the liquid phase area shrinks and separates two regions, and then enlarges and moves to the region of low CaO content. The liquid phase area on the SiO$_2$–FeO$_x$ binary system does not exist with high oxygen partial pressures of 2.1 × 10^{-2} and 0.18 Pa, while it appears with oxygen partial pressure of 1.8 × 10^{-3} Pa.

3.2. Effect of Simultaneous Addition of Al$_2$O$_3$ and MgO on Liquidus for the CaO–SiO$_2$–FeO$_x$ System

Figures 5, 6 and 7 show the effect of simultaneous addition of Al$_2$O$_3$ and MgO on liquidus for the CaO–SiO$_2$–FeO$_x$ system in comparison with the liquidus for the CaO–SiO$_2$–FeO$_x$ system with the oxygen partial pressure of 1.8 × 10^{-3}, 0.18 and 2.1 × 10^{-2} Pa, respectively.

The shapes of liquidus for the CaO–SiO$_2$–FeO$_x$, CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$, CaO–SiO$_2$–FeO$_x$–5mass%MgO, CaO–SiO$_2$–FeO$_x$–5mass%Al$_2$O$_3$–5mass%MgO and CaO–SiO$_2$–FeO$_x$–2.5mass%Al$_2$O$_3$–2.5mass%MgO system are approximately same at 1.8 × 10^{-3} Pa. The liquid phase area enlarges with simultaneous addition of Al$_2$O$_3$ and MgO.

The liquid phase area separates into two liquid phase region at 0.18 Pa, and the shape is the same as that for the 5% MgO addition.

At the oxygen partial pressure of 2.1 × 10^{-2} Pa, the liquid phase area shrinks at low SiO$_2$ region by MgO addition. On the other hand, the liquid phase area at other region is almost same as CaO–SiO$_2$–FeO$_x$ system since the effects of Al$_2$O$_3$ and MgO addition, which enlarges and shrinks the liquid phase area, respectively, were cancelled.
The addition of Al$_2$O$_3$ or MgO mainly affects two kinds of liquidus, one of which is saturated by 2CaO·SiO$_2$ and the other by FeO$_x$. On the contrary, other liquidus are not affected much as shown in Figs. 5 to 7. In the case of the liquidus saturated by 2CaO·SiO$_2$, the solid-liquid coexisting area tends to enlarge by the addition of MgO, and shrink by Al$_2$O$_3$ addition. This tendency is not changed by changing the partial pressure of oxygen. Since the dissolution of 2CaO·SiO$_2$ increases the basicity (CaO/SiO$_2$ ratio) of molten oxide, 2CaO·SiO$_2$ can be regarded as basic oxide. Therefore, aforementioned effect of oxide addition is considered as the fact that Al$_2$O$_3$ acts as acidic oxide in the 2CaO·SiO$_2$ saturating region while MgO acts as basic oxide.

The change of FeO$_x$ saturating region is not obvious in the case of Al$_2$O$_3$ addition at investigated oxygen partial pressure range. On the other hand, MgO addition tends to enlarge the solid-liquid coexisting region, especially at higher partial pressure of oxygen. Stable iron oxide phase is Fe$_2$O$_3$ at experimental oxygen partial pressure range at 1573 K. Therefore, the solubility of Fe$_2$O$_3$ to molten oxide determines the FeO$_x$ saturating region. The fraction of ferric oxide ion increases with increasing oxygen partial pressure as shown in Fig. 8, showing the relationship between Fe$^{3+}$/Fe$^{2+}$ ratio and (mass%CaO)/(mass%CaO+mass%SiO$_2$) ratio measured on FeO$_x$ saturated liquidus. Therefore, it is considered that FeO$_x$ saturating region is enlarged by the MgO addition because MgO acts as acidic oxide at high FeO$_x$ content region, resulting the increase in activity of Fe$_2$O$_3$. Since basic property of Al$_2$O$_3$ is similar to that of Fe$_2$O$_3$, the effect of Al$_2$O$_3$ addition on the change of FeO$_x$ saturated region is not obviously measured.

4. Conclusions

The phase diagrams for the CaO–SiO$_2$–FeO$_x$–2.5mass%Al$_2$O$_3$–2.5mass%MgO system at 1573 K with various oxygen partial pressures were investigated by chemical equilibrium technique. By the simultaneous addition of Al$_2$O$_3$ and MgO, the liquid phase area for the CaO–SiO$_2$–FeO$_x$ system at 1573 K enlarges with the oxygen partial pressure of 1.8×10$^{-3}$ Pa. The liquid area separates into two areas and the liquid region on the SiO$_2$–FeO$_3$ binary system disappears with the oxygen partial pressure of 0.18 Pa. The liquid phase area shrinks at low SiO$_2$ region, while the effects of Al$_2$O$_3$ and MgO addition are cancelled at other region with the oxygen partial pressure of 2.1×10$^2$ Pa.

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