Formation Rate of Calcium Ferrite Melt Focusing on SiO_2 and Al_2O_3 Component

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The effect of the particle size of hematite on the formation rate of calcium ferrite melt and the dissolution rate of solid hematite into molten calcium ferrite were investigated. Without regard to the particle size of hematite, the addition of SiO_2 was more effective than the addition of Al_2O_3 for increasing the melting rate and reducing the melt formation temperature in calcium ferrite system. On the other hand, the addition of Al_2O_3 was more effective than the addition of SiO_2 for increasing the dissolution rate of solid hematite into the generated molten ternary calcium ferrite. The amount of dissolved hematite into molten calcium ferrite increased linearly with increasing the immersion time. The dissolution rate of solid hematite into molten calcium ferrite was mostly determined by $\Delta(\text{mol}\%\text{Fe}_2\text{O}_3)$ that was considered to be the driving force of the dissolution and the effect of the revolution speed on the amount of dissolved hematite can be negligible. Therefore, the dissolution reaction of solid hematite at the reaction interface was the rate-controlling step under the condition of this study.

KEY WORDS: calcium ferrite; particle size; melt formation rate; dissolution rate; iron ore sintering.

1. Introduction

As the iron ore sinter is the main blast furnace burden, the input energy curtailment in ironmaking process become possible by manufacturing iron ore sinter at low temperature or for a short time. Since iron ore sinter is sintering through liquid phase, if the liquid phase can be made to generate for a short time and at low temperature, it will become possible cutting down the energy in the sintering process. By the way, it is reported¹⁾ that the composition of primary melt in sintering process is similar to monocalcium ferrite ($\text{CaO} \cdot \text{Fe}_2\text{O}_3$) and the lowest temperature of melt formation in the $\text{CaO}-\text{Fe}_2\text{O}_3$ system²⁾ is 1 205°C. Therefore, if the formation temperature of the primary melt can be reduced from this temperature, it will become possible to cut down the energy in the sintering process. Then, in the previous study,³⁾ the effects of SiO_2 and Al_2O_3 addition on the formation rate of calcium ferrite melt were investigated.

By the way, iron ores that is constituent element of pseudo particles have wide particle distribution from several 10 μm to several mm. Therefore, it is considered that the particle size of iron ore also affects on the melt formation rate of calcium ferrite. Moreover, it is considered that the amount of melt in sintering process is determined by the dissolution rate of hematite into molten calcium ferrite. Then, in this study, the effects of particle size of iron ore on the formation rate of calcium ferrite melt and the dissolution rates of hematite into molten calcium ferrite were investigated.

2. Formation Rate of Calcium Ferrite Melt

2.1. Sample and Experimental Method

The reagent grade powders of Fe_2O_3 and CaCO_3 were mixed to be the composition of $\text{CaO} \cdot \text{Fe}_2\text{O}_3(\text{CF})$ and $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3(\text{CF}_2)$, and the reagent grade powders of SiO_2 and Al_2O_3 were added to these mixtures to be the composition shown in **Table 1**. In order to investigate the effect of particle size of hematite on the formation rate of calcium ferrite melts, hematite that was sintered at 1 370°C was crushed to be under 45 μm , 45–75 μm , 75–125 μm and 125–250 μm , respectively. These powders were shaped into triangular pyramid and this shaped sample was used for experiment. The experiment was conducted according to the coal ash melting examination method (JIS M 8801-10). The experimental apparatus used in this study is schematically shown in **Fig. 1**. The experiment was carried out as follows. At first, the isothermal zone of the electric furnace was set up so that it might become 1 300°C and a sample was set on the hematite substrate (16.0 mm diameter, 3.5 mm height and about 5% porosity) and then it was kept for a short time in the place at 1 000°C. Next, the sample was inserted into the place at 1 300°C. The melting process of sample was recorded by digital camcorder and the temperature of sample was measured by Pt–Rh (13 mass%) thermocouple simultaneously. The relationship between the sample height and time was examined by using the picture of digital camcorder. Moreover, the JIS (M-8801) method that was defined as shown in **Fig. 2** was referred to the judgment of the melting state of a sample. That is, the temperature when the tip of a sample became rounded shape was defined as soft-

Table 1. Chemical composition of samples as mixed (mass%).

Sample	Fe ₂ O ₃	CaO	Al ₂ O ₃	SiO ₂
CF	74.0	26.0	-	-
CF-5A	70.5	24.7	4.8	-
CF-10A	67.3	23.6	9.1	-
CF-5S	70.5	24.7	-	4.8
CF-10S	67.3	23.6	-	9.1

Fig. 1. Schematic view of experimental apparatus for measuring of melt formation rate.

Fig. 2. Schematic view of melting process.

Fig. 3. Relationship between overall view of melting process and variation of time.

ening point, melting point was defined when the ratio of width and height was set to 3 : 1 and melt down point was defined when the sample height became one third of the melting point.

2.2. Results and Discussion

As an example of experiment results, **Fig. 3** shows the relationship between the shape change and time in the melting process of samples when the particle size of hematite was under 45 μm . From this figure, it was found that the time to reach the softening and the melting points of SiO₂ and Al₂O₃ added CF sample was shorter than that of pure CF sample. Moreover, when the time to reach the softening and the melting point of SiO₂ added sample was compared with that of Al₂O₃ added sample, it was found that the time

Fig. 4. Relationship between overall view of melting process and variation of time.

Fig. 5. Effect of particle size of Fe₂O₃ on melting process using pure CF sample.

Fig. 6. Effect of particle size of Fe₂O₃ on melting process using CF-5A sample.

of SiO₂ added sample was shorter than that of Al₂O₃ added sample. **Figure 4** shows the melting process of samples added 9.1 mass% Al₂O₃. As shown in this figure, this sample was not able to measure the sample height accurately because the tip of this sample was bended rapidly during experiment.

Figures 5 and **6** show the effect of particle size of hematite on the softening and melting process for the CF and 4.8 mass% Al₂O₃ added sample, respectively. From these figures, it was found that the time to reach the softening and the melting point of samples became shorter as the particle size of hematite became smaller. Although the results of SiO₂ added samples were not shown here, almost the same tendency was obtained. Therefore, it was found that the formation rate of calcium ferrite melt was influenced by the particle size of hematite.

Figures 7 and **8** show the effects of Al₂O₃ and SiO₂ addition on the softening and melting process, and these figures show the results of hematite particle size under 45 μm and

Fig. 7. Effect of adding SiO_2 and Al_2O_3 as additives on melting process using hematite particle size under $45\ \mu\text{m}$.

Fig. 8. Effect of adding SiO_2 and Al_2O_3 as additives on melting process using hematite particle size $125\text{--}250\ \mu\text{m}$.

$125\text{--}250\ \mu\text{m}$, respectively. From these figures, it was found that the time to reach the softening and the melting point of Al_2O_3 and SiO_2 added samples is shorter than that of pure CF sample without regard to the particle size of hematite. Moreover, when the time to reach the softening and the melting point of SiO_2 added sample was compared with that of Al_2O_3 added sample, it was found that the time of SiO_2 added sample was shorter than that of Al_2O_3 added sample. Although the results of samples having other particle sizes of hematite were not shown here, almost the same tendency was obtained. Consequently, the formation rate of calcium ferrite melt increased in the order of samples $\text{CF} < \text{CF-5A} < \text{CF-5S} < \text{CF-10S}$.

Based on the above experimental results, the apparent melting rates of samples in CF system were estimated by approximation of the straight line from the softening point to the melting point.

Figure 9 shows the relationship between the apparent melting rates and mean diameter (harmony average) of hematite particle. As shown in this figure, the effects of particle sizes of hematite on the apparent melting rate were small even if the chemical compositions of calcium ferrite were changed.

However, as compared with the same particle size of hematite, the apparent melting rate of SiO_2 added samples was larger than that of Al_2O_3 added samples. By the way, from the results of previous study,³⁾ it has shown that the softening and melting temperatures decreased with increasing the amount of added SiO_2 and Al_2O_3 . Furthermore, it has shown that the effect of SiO_2 addition on the reducing

Fig. 9. Relationship between apparent melting rate and mean diameter of Fe_2O_3 particle.

Fig. 10. Effect of surface tension on the apparent melting rate.

the softening and melting temperatures was larger than that of Al_2O_3 addition. Therefore, it was also found in this study that the SiO_2 addition was more effective than Al_2O_3 addition for increasing the melting rate and reducing the melt formation temperature of sample in calcium ferrite system without regard to the particle size of hematite.

The relationship between the apparent melting rates and the surface tension of calcium ferrite melt⁴⁾ was shown in Fig. 10. From this figure, it was found that the apparent melting rate became large as the surface tension of sample became small without regard to the particle size of hematite. Therefore, the surface tension of calcium ferrite melt affects greatly on the softening and melting process of calcium ferrite.

3. Dissolution Rate of Solid Hematite into Molten Calcium Ferrite

3.1. Sample and Experimental Method

The experimental apparatus used in this study is schematically shown in Fig. 11. The calcium ferrite samples were prepared by mixing the reagent grade powders of Fe_2O_3 , CaCO_3 , Al_2O_3 and SiO_2 . The chemical compositions of calcium ferrite samples were shown in Table 1. A solid hematite rod was prepared by sintering the reagent grade powders of Fe_2O_3 at 1350°C for 1.5 h. A sintering hematite rod was about 5 g in weight, about 2.3 cm in height, about 0.8 cm in diameter and 3–5% in porosity.

The experiment was carried out as follows. At first, a calcium ferrite sample of about 45 g was charged in a magnesia crucible and was set in a SiC electric resistance furnace. A sintering hematite rod was set to a speed variable motor

Fig. 11. Schematic view of experimental apparatus for measuring of dissolving rate.

through an alumina tube and was located to a position just above the calcium ferrite sample. Next, the calcium ferrite sample was heated to 1300°C and melted in air atmosphere. The revolution speed of the sintering hematite rod was set to a selected value and the rod was submerged in the molten calcium ferrite. The submerged depth was fixed at 1.5 cm for each run. The submerged time was 2, 4, 6 and 8 min and revolution speed of the sintering hematite rod was 0, 20 and 40 rpm, respectively.

After a given period of time, the rod was removed from the system and was quenched. The calcium ferrite melt that was adhering to the hematite rod was dissolution with 46% HF solution and the weight of the hematite rod was measured. The amount of dissolution Fe_2O_3 was determined by weighting the hematite rod before and after the experiment.

3.2. Results and Discussion

Figures 12 and 13 show the relationship between the amount of dissolved hematite and the immersion time for the pure CF and CF-5A sample, respectively. The amount of dissolved hematite into molten calcium ferrite increased linearly with increasing the immersion time and it had little concerned with the composition of molten calcium ferrite. The amount of dissolved hematite also increased a little with increasing the revolution speed but its amount was very small. Therefore, the effect of the revolution speed on the amount of dissolved hematite can be negligible. Although the results of CF-5S and CF-10A sample were not shown here, almost the same tendency was obtained as mentioned above. In the case of CF-10S sample, the experiment could not be carried out because the magnesia crucible charged CF-10S sample was broken down during the heating up to 1300°C. At present, the reason for breaking down the crucible charged CF-10S sample has not been clarified.

Figure 14 shows the effect of the composition of molten calcium ferrite on the amount of dissolved hematite when the revolution speed of hematite rod is 40 rpm. Although the results of samples having other revolution speed of hematite rod were not shown here, almost the same tendency was obtained. In the all the revolution speed, the amount

Fig. 12. Relationship between immersion time and dissolved Fe_2O_3 using pure CF sample.

Fig. 13. Relationship between immersion time and dissolved Fe_2O_3 using CF-5A sample.

Fig. 14. Effect of the composition of calcium ferrite melts on the amount of dissolved Fe_2O_3 at 40 rpm.

of dissolved hematite increased as increasing the immersion time in the order of samples $\text{CF-5S} < \text{CF-5A} < \text{CF} < \text{CF-10A}$. By the way, as mentioned above Chapter 2, the formation rate of calcium ferrite melt increased in the order of samples $\text{CF} < \text{CF-5A} < \text{CF-5S} < \text{CF-10S}$. Consequently, the adding SiO_2 as the additive oxide is more effective than the adding A_2O_3 as the additive oxide for the formation rate of calcium ferrite melt that is generated by the reaction between Fe_2O_3 and CaO . On the other hand, the adding A_2O_3 is more effective than the adding SiO_2 for the dissolution rate of hematite that is dissolved into melt by the reaction between a solid hematite and a molten ternary calcium ferrite.

The dissolution rate of hematite into molten calcium ferrite ($\Delta W/t$: kg/s) can be estimated by the slope of the straight line in Fig. 14 and the dissolution rate can be re-

Fig. 15. Relationship between $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$ and dissolution rate.

Fig. 16. Effect of revolution speed on mass transfer coefficient k_f .

placed to decrease in the radius of the solid hematite rod by Eq. (1). Furthermore, the liquid phase mass transfer coefficient, k_f (m/s) was calculated based on the results using Eq. (2) which was derived by Matsushima *et al.*⁵⁾:

$$-\frac{dr}{dt} = r_0 - \sqrt{r_0^2 - \frac{\Delta W/t}{\pi h \rho_{\text{Fe}_2\text{O}_3}}} \quad \text{.....(1)}$$

$$-\frac{dr}{dt} = k_f \frac{\rho_{\text{CF}}}{\rho_{\text{Fe}_2\text{O}_3}} \times \frac{\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)}{100} \quad \text{.....(2)}$$

where r_0 and h (cm) are the initial radius and the length of the solid hematite rod in molten calcium ferrite, $\rho_{\text{Fe}_2\text{O}_3}$ and ρ_{CF} are the density of solid hematite and molten calcium ferrite (kg/m^3), $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$ is the difference of the Fe_2O_3 concentration between the initial value and the saturation, where the saturated composition was determined by reading the liquidus on the $\text{Fe}_2\text{O}_3\text{--CaO--Al}_2\text{O}_3$ ⁶⁻⁸⁾ and $\text{Fe}_2\text{O}_3\text{--CaO--SiO}_2$ ternary phase diagrams.⁹⁾

Figure 15 shows the relationship between the dissolution rate and $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$. This figure indicated that the linear relationship was obtained between the dissolution rate of hematite and $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$.

Therefore, the dissolution rate of solid hematite into molten calcium ferrite was mostly determined by $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$, which was considered to be the driving force of the dissolution of solid hematite.

Figure 16 shows the relationship between the mass transfer coefficient of liquid phase and revolution speed of solid hematite rod. From this figure, it was found that the effects of the revolution speed of solid hematite rod on the mass

transfer coefficient were very small and the effects of the composition of molten calcium ferrite were very large. Generally, the dissolution rate of solid into melt is controlled by dissolution reaction of solute at reaction interface, diffusion of solute in melt, or combination of them. From the results mentioned above, since the effects of the revolution speed of solid hematite rod on the mass transfer coefficient were very small, it is thought that the dissolution reaction of solute at the reaction interface is the rate-controlling step under the condition of this experiment.

Consequently, it was found that the adding SiO_2 was more effective than the adding Al_2O_3 for increasing the formation rate of calcium ferrite melt which was generated by the reaction between Fe_2O_3 and CaO . On the other hand, it was also found the adding Al_2O_3 was more effective than the adding SiO_2 for increasing the dissolution rate of solid hematite into the generated molten ternary calcium ferrite.

4. Conclusions

As a fundamental study for clarifying the reaction phenomena of iron ore sintering process, the effect of the particle size of hematite on the formation rate of calcium ferrite melt and the dissolution rate of solid hematite into molten calcium ferrite were investigated. The results obtained are follows:

(1) The time to reach the softening and the melting point of samples became shorter as the particle size of hematite became smaller. Without regard to the particle size of hematite, the adding SiO_2 was more effective than the adding Al_2O_3 for increasing the melting rate and reducing the liquid formation temperature of sample in calcium ferrite system.

(2) The apparent melting rate became large as the surface tension of sample became small. Therefore, the surface tension of calcium ferrite melts affects greatly on the softening and melting process of calcium ferrites.

(3) The amount of dissolved hematite into molten calcium ferrite increased linearly with increasing the immersion time. The effect of the revolution speed on the amount of dissolved hematite can be negligible.

(4) The dissolution rate of solid hematite into molten calcium ferrite was mostly determined by $\Delta(\text{mol}\% \text{Fe}_2\text{O}_3)$, which was considered to be the driving force of the dissolution and the dissolution reaction of solute at the reaction interface was the rate-controlling step under the condition of this experiment.

(5) The adding SiO_2 as the additive oxide was more effective than the adding Al_2O_3 as the additive oxide for increasing the formation rate of calcium ferrite melt which was generated by the reaction between Fe_2O_3 and CaO . On the other hand, the adding Al_2O_3 was more effective than the adding SiO_2 for increasing the dissolution rate of solid hematite into the generated molten ternary calcium ferrite.

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