Penetration Behavior of Calcium Ferrite Melts into Hematite Substrate

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Effects of adding SiO_2 or Al_2O_3 on the penetration characteristics of calcium ferrite (CF) melts into hematite substrate with the different percentage of porosity were examined, and were discussed from the viewpoints of the relation to the solubility gap, $\Delta\text{Fe}_2\text{O}_3$ (mol%), viscosity and surface tension of the CF-based melts.

In case of dense hematite substrate with 5% porosity, the penetration depth of CF melts into hematite substrate was depressed by the addition of SiO_2 or Al_2O_3 , and the addition of SiO_2 was more effective than that of Al_2O_3 . Moreover, the penetration of CF-based melts along grain boundaries into hematite substrate did not take place, and melts/hematite interface moved down by dissolution of solid hematite into these melts. The penetration depth of CF-based melts into hematite substrate was mostly determined by $\Delta\text{Fe}_2\text{O}_3$ (mol%), which meant that the dissolution of hematite into melts was rate-determine.

In case of porous hematite substrate with 15% porosity, the penetration of CF-based melts along grain boundaries into hematite substrate occurred, and the penetration depth was 10 times deeper than the case of dense hematite substrate with 5% porosity for each slag. The penetration depth of CF melts was increased by the addition of SiO_2 due to the decrease of melting temperature in the calcium ferrite system. The penetration depth of CF melts with the addition of Al_2O_3 was very similar to that of CF melts. These melts penetrated into hematite substrate with crystallization (solid) due to the increase of the melting temperature in calcium ferrite system by the dissolution of hematite into the liquid phase. The penetration depth of CF-based melts into hematite substrate was dominated by the ratio between the surface tension and viscosity of melts taking the suspension-corrected into consideration.

KEY WORDS: calcium ferrite melts; hematite substrate; porosity; penetration behavior.

1. Introduction

In the current blast furnace process, the amount of iron ore sinter has been increased because of maintaining the stable operations and increasing its productivity.^{1,2)} The iron ore sinter is produced by liquid phase sintering, the formation and the flow of melts play important role to assist the agglomeration in the sintering process of fine ores for controlling the strength and the reducibility of iron ore sinter.³⁾ It is reported that the composition of the melts starts from that of mono-calcium ferrite ($\text{CaO} \cdot \text{Fe}_2\text{O}_3$), meaning the lowest temperature that the $\text{CaO}-\text{Fe}_2\text{O}_3$ system evolves melt.^{4,5)} Recently, as the usage of limonite ore has been increased,^{6,7)} so that it is important to determine the effects of ore porosity and gangue, such as SiO_2 or Al_2O_3 , on the behavior of melts formation and flow during the iron ore sintering, and also important to decrease the sintering temperature by the formation of melts with low melting temperature.^{8,9)}

In this study, the effects of ore porosity and melts com-

position (adding SiO_2 or Al_2O_3) on the penetration behavior of melts into iron ore have been examined, and discussed with the relation to solubility gap of Fe_2O_3 , viscosity and surface tension of the melts.

2. Samples and Experimental Procedures

We allowed the reaction couple to simulate melts-ore system for sintering reaction, which composed melts former on a hematite substrate as shown in **Fig. 1(a)**. The chemical compositions of the melts former used in these experiments are listed in **Table 1**. The melts former, CF ($\text{CaO} \cdot \text{Fe}_2\text{O}_3$), CF with Al_2O_3 (CF-3A and CF-5A) and SiO_2 (CF-3S and CF-5S) at different content of additive, 3 and 5 mass%, respectively, were synthesized by pre-melting a mixture of chemical reagents at desired ratios. The slag powders (under $44\ \mu\text{m}$) were shaped into tablet ($\phi 7\ \text{mm} \times 2.0\ \text{mm}$) and examined.

The hematite substrate ($\phi 24\ \text{mm} \times 8\ \text{mm}$) changed in porosity for representing dense ores or porous ones. The

Fig. 1. Schematic drawing of sample configuration (a) and apparatus (b) for experiment.

Table 1. Chemical composition of melts former (mass%).

	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
CF	26.0	74.0	–	–
CF-3A	25.2	71.8	3.0	–
CF-5A	24.7	70.3	5.0	–
CF-3S	25.2	71.8	–	3.0
CF-5S	24.7	70.3	–	5.0

dense substrate was prepared by pressing hematite powder reagent (under 10 μm), and then sintered them at 1300°C for 3 h to give 5% porosity. The porous one was prepared by pressing hematite powder reagent (under 10 μm) with 4 wt% wheat powder, and sintered them at 1300°C for 30 min after pre-sintering at 500°C for 30 min to give 15% porosity.

The sample configuration (a) and the experimental apparatus (b) used in this study are schematically shown in Fig. 1. A slag former tablet was placed on a hematite substrate, and put it in the furnace. After preheating at the temperature zone from 300–1000°C for 30 min, the sample was inserted into the temperature region at 1300°C, for different periods, 3, 5 or 10 min, then extracted from the furnace and cooled in air. The sample of the hematite substrate with solidified droplets were dissected perpendicular to the interface, and polished with 1 μm diamond paste. The cross sections of these samples were examined using an optical microscope, a scanning electron microscopy (SEM) and an electron probe micro analyzer (EPMA).

3. Results and Discussion

3.1. Measurement of Penetration Depth

The optical microscopic analysis of CF melts flow part into hematite substrate heated at 1300°C for 10 min are shown in Fig. 2((a) with 5% porosity and (b) with 15% porosity). It was found that the CF slag tablet was melted and spread, and penetrated into hematite substrate. Moreover, it was clearly found that the penetration depth into hematite substrate with 15% porosity was far deeper than that of hematite substrate with 5% porosity. The penetration depth of melts into a hematite substrate of each sample was measured as an interval from the initial interface to the deepest flow position of melts into substrate from the re-

sults of optical microscopic analysis shown by arrows in Fig. 2.

Figures 3 and 4 show the relationship between the heating period and the penetration depth of CF and CF with Al₂O₃ or SiO₂ melts into hematite substrate with 5% porosity and that with 15% porosity, respectively. From these figures, it was clear that the penetration depth of hematite sinter with 15% porosity was 10 times deeper than that with 5% porosity. Figure 3 shows that the penetration depth of CF melts into hematite substrate with 5% porosity was decreased by the addition of Al₂O₃ or SiO₂. Furthermore, the addition of SiO₂ was more effective than the addition of Al₂O₃ for decreasing the penetration depth of CF melts (CF > CF-3A $\approx$ CF-5A > CF-3S > CF-5S). On the other hand, Fig. 4 shows that the penetration depth of CF melts into hematite substrate with 15% porosity was found almost in reverse order with comparison to that with 5% porosity, in which the penetration depth of CF melts was increased by the addition of SiO₂ and that with the addition of Al₂O₃ was similar to that of CF melts (CF < CF-5A < CF-3A $\approx$ CF-5S < CF-3S).

3.2. Evaluation of Penetration Behavior of Slag Melts into Hematite Substrate

Figure 5(a) to 5(c) shows the EPMA mapping of Fe, Ca, Al and Si at the interface region of CF, CF-5A and CF-5S melts to the hematite substrate with 5% porosity after heated at 1300°C for 10 min, respectively. Other melts, CF-3A and CF-3S, showed similar behavior at the interface region. Note that these melts did not penetrate preferentially along or into grain boundaries of hematite substrate. In the case of CF-5A melts, as shown in Fig. 5(b), the reaction layer containing Al₂O₃ was present at the vicinity of the interface. According to the Fe₂O₃–CaO–Al₂O₃ ternary phase diagram,^{10–12} this reaction layer were solid solutions of ternary calcium ferrite (CaO·3(Fe_xAl_{1–x})₂O₃ system) formed of CaO·3Al₂O₃ and CaO·3Fe₂O₃. These results identified that the penetration of melts into hematite substrate along grain boundaries did not take place in the case of 5% porosity, and melts/hematite interface moved down by dissolution of solid hematite into CF melts. It, therefore, suggested that the penetration depth was controlled by the solubility gap of Fe₂O₃ for CF-based melts, $\Delta\text{Fe}_2\text{O}_3$ (mol%), which is the difference of the Fe₂O₃ concentration between the initial value and the saturation one that were determined by the Fe₂O₃–CaO,¹⁴ Fe₂O₃–CaO–Al₂O₃^{10–12} and Fe₂O₃–CaO–SiO₂¹³ phase diagrams.

Figures 6 and 7 show the relationship between the penetration depth and $\Delta\text{Fe}_2\text{O}_3$ (mol%) for the samples heated at 1300°C for 5 min and for 10 min, respectively. The penetration depth of all CF-based melts into hematite substrate with 5% porosity was monotonically increased with $\Delta\text{Fe}_2\text{O}_3$ (mol%), so that $\Delta\text{Fe}_2\text{O}_3$ (mol%) could be considered as the driving force of the dissolution of hematite into CF-based melts.

In the case of hematite substrate with 15% porosity, CF-based melts penetrated into hematite substrate along grain boundaries, and the penetration depth was 10 times deeper than the case of hematite substrate with 5% porosity for each slag.

Figures 9, 10 and 11 show the results of EPMA analyses

Fig. 2. Optical microscopic analysis of slag melt flow part (porosity of hematite substrate; (a)=5%, (b)=15%).

Fig. 3. Relationship between heating time and penetration depth (porosity=5%).

Fig. 4. Relationship between heating time and penetration depth (porosity=15%).

Fig. 5. Mapping analysis of interface between slag and hematite substrate with porosity of 5% heated at 1300°C for 10 min.

Fig. 6. Relationship between solubility gap, $\Delta \text{Fe}_2\text{O}_3$, and penetration depth heated at 1300°C for 5 min (porosity=5%).

Fig. 7. Relationship between solubility gap, $\Delta \text{Fe}_2\text{O}_3$, and penetration depth heated at 1300°C for 10 min (porosity=5%).

at the different depth (A) to (C) as shown in Fig. 8 of CF, CF-5A and CF-5S melts to the hematite substrate with 15% porosity after heated at 1300°C for 5 min. Other melts, CF-3A and CF-3S, showed similar penetration behavior into hematite substrate. The chemical compositions of slag pointed by ①–④ in Figs. 9, 10 and 11 are shown in Tables 2, 3 and 4. As shown in these figures, the penetration depth of slag melts into hematite sinter along grain boundaries was clearly seen for each type of melts for the hematite substrate with 15% porosity. In the case of CF-5A slag with 15% porosity shown in Fig. 10, the reaction layer containing Al_2O_3 , namely ternary calcium ferrite ($\text{CaO} \cdot 3(\text{Fe}_x\text{Al}_{1-x})_2\text{O}_3$ system), was present at the vicinity of the interface, as in the case of Fig. 5(b), and CF melts without Al_2O_3 penetrated into hematite substrate. It was found from Tables 2 and 3 that the concentration of Fe_2O_3 was increased with increasing the penetration depth in the case of CF and CF-5A slag. Consequently, it is predicted from the phase diagrams,¹⁴⁾ that the Fe_2O_3 -saturated liquid phase with solid phase penetrated into hematite substrate in the case of CF and CF-5A slag. On the other hand, it was seen from Fig. 11, Table 4 and the phase diagrams¹³⁾ that the liquid along with SiO_2 penetrated into hematite substrate which did not saturated with any solid phase in the case of CF-5S slag.

The penetration depth of liquid phase into substrate can be correlated with the surface tension of melts and inversely proportional to the viscosity.¹⁵⁾ It has been reported that the square value of the penetration depth of glass melts into alumina substrate was proportional to the ratio between the surface tension and the viscosity of glass melts, γ/η .¹⁶⁾

Consequently, the penetration depth of CF-based slag melts into hematite sinter with 15% porosity was correlated from the viewpoints of the relation to the viscosity and the surface tension of melts, namely the value of γ/η .

The viscosity of suspension liquid for CF and CF with Al_2O_3 , namely of liquid phase with solid, was calculated by the Eq. (1).^{17,18)}

$$\eta_r = \frac{\eta}{\eta_0} \dots\dots\dots(1)$$

where η_r , η and η_0 are the viscosity of relative value, of suspension and of liquid phase (disperse phase). The values

Fig. 8. Schematic illustration of mapping analysis points in samples.

Fig. 9. Mapping analysis of interface and penetration layer between CF slag and hematite substrate with porosity of 15% heated at 1300°C for 5 min. ((A), (B), (C) correspond to analysis points in sample shown in Fig. 8.)

Fig. 10. Mapping analysis of interface and penetration layer between CF-5Al₂O₃ slag and hematite substrate with porosity of 15% heated at 1300°C for 5 min. ((A), (B), (C) correspond to analysis points in sample shown in Fig. 8.)

Fig. 11. Mapping analysis of interface and penetration layer between CF-5SiO₂ slag and hematite substrate with porosity of 15% heated at 1300°C for 5 min. ((A), (B), (C) correspond to analysis points in sample shown in Fig. 8.)

Table 2. Chemical compositions of melts pointed by ①–④ in Fig. 9 (mass%).

①	17CaO·83Fe ₂ O ₃
②	15CaO·85Fe ₂ O ₃
③	14CaO·86Fe ₂ O ₃
④	11CaO·89Fe ₂ O ₃

Table 3. Chemical compositions of melts pointed by ①–④ in Fig. 10 (mass%).

①	16CaO·78Fe ₂ O ₃ ·6Al ₂ O ₃
②	16CaO·83Fe ₂ O ₃ ·1Al ₂ O ₃
③	13CaO·87Fe ₂ O ₃
④	12CaO·88Fe ₂ O ₃

Table 4. Chemical compositions of melts pointed by ①–④ in Fig. 11 (mass%).

①	16CaO·84Fe ₂ O ₃
②	23CaO·72Fe ₂ O ₃ ·5SiO ₂
③	24CaO·72Fe ₂ O ₃ ·4SiO ₂
④	23CaO·74Fe ₂ O ₃ ·3SiO ₂

of viscosity of liquid phase (η_0) were obtained by extrapolating the temperature dependence of the viscosity measured previously^{19,20} to the temperature of 1300°C. The values of viscosity of relative value (η_r) were calculated by the Eq. (2) of Einstein–Roscoe.^{17,18)}

$$\eta_r = (1 - a\phi)^{-n} \dots \dots \dots (2)$$

where a and n are constant, and ϕ is a volume fraction of solid in liquid phase. The values of $a=1.35$ and $n=2.5$ given for spherical solid particles^{17,18)} were used in this study. The values of ϕ were calculated based on the phase diagrams,^{10–14)} and the chemical compositions of the deepest position of the penetration layer for each melts. Moreover, the surface tension of just as liquid phase for each melts were obtained by extrapolating the temperature dependence of the surface tension measured previously¹⁹⁾ to the temperature of 1300°C. In the case of CF with SiO₂ melts, the viscosity and the surface tension were obtained by extrapolating the temperature dependence of the surface tension and that of the viscosity measured previously^{19,20)} for the chemical compositions of liquid phase at the deepest position of the penetration layer for each melts. **Table 5** shows the values of γ/η with each values of ϕ , η and γ . The viscosities of CF and CF with Al₂O₃ slag are larger than that of CF with SiO₂ slag due to containing of solid phase. Therefore, the values of γ/η for CF with SiO₂ melts indicates one-order larger, compared with those for CF and CF with Al₂O₃ melts.

As shown in **Fig. 12**, the square values penetration depth (L^2) was directly proportional to the value of γ/η , and increased with the value of γ/η . It suggested that the penetration behavior depth of CF-based melts into hematite substrate with 15% porosity was controlled by capillary force, represented as the ratio between the surface tension and the viscosity of melts.

Table 5. Volume fraction of solid ϕ , viscosity η , surface tension γ and the value of γ/η of melts.

	ϕ	η (Pa·s)	γ (mN/m)	γ/η
CF	0.353	0.115	677	2.56
CF-3A	0.353	0.159	677	2.56
CF-5A	0.294	0.112	677	3.61
CF-3S	0	0.044	672	11.7
CF-5S	0	0.053	671	11.0

Fig. 12. Relationship between γ/η and penetration depth (L^2) heated at 1300°C for 5 min (porosity=15%).

4. Conclusions

Effects of adding SiO₂ or Al₂O₃ on the penetration characteristics of calcium ferrite (CF) melts into hematite sinter with the different percentage of porosity were examined, and were discussed from the viewpoints of the relation to the solubility gap, $\Delta\text{Fe}_2\text{O}_3$ (mol%), viscosity and surface tension of the CF-based melts. The results obtained are as follows:

(1) The penetration depth of CF melts into dense hematite substrate with 5% porosity was depressed by the addition of SiO₂ or Al₂O₃, and the addition of SiO₂ was more effective than that of Al₂O₃.

(2) The penetration of CF-based melts along grain boundaries into dense hematite substrate with 5% porosity did not take place, and melts/hematite interface moved down by dissolution of solid hematite into these melts.

(3) The penetration depth of CF-based melts into dense hematite substrate with 5% porosity was mostly determined by $\Delta\text{Fe}_2\text{O}_3$ (mol%), which meant that the dissolution of hematite into CF-based melts was rate-determine.

(4) The penetration depth of CF melts into porous hematite substrate with 15% porosity was accelerated by the addition of SiO₂ because of reducing the melting temperature in calcium ferrite system. The penetration depth of CF melts with Al₂O₃ was almost the same as that of CF melts. These melts penetrated into hematite substrate with crystallization due to the increase of the melting temperature in calcium ferrite system by the dissolution of hematite into the melts.

(5) The penetration of CF-based melts along grain boundaries into porous hematite substrate with 15% porosity occurred, and the penetration depth was 10 times deeper than the case of dense hematite substrate with 5% porosity for each slag.

(6) The penetration depth of CF-based melts into hematite substrate with 15% porosity was dominated by the ratio between the surface tension and viscosity of melts tak-

ing the suspension-corrected into consideration.

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