Effect of Lime Particle Size on Melting Behavior of Lime-containing Flux

Jian YANG, Mamoru KUWABARA, Takashi ASANO, Akihiro CHUMA and Jun DU

Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan.

(Received on May 17, 2007; accepted on August 16, 2007)

By use of an infrared-ray vacuum furnace, effect of CaO particle size on melting behavior of lime-containing flux is studied in the present work. Two kinds of CaO particles of the average diameters of $10\ \mu\text{m}$ and $75\ \mu\text{m}$ are used. Four kinds of lime-containing fluxes are employed, which are CaO–SiO₂, CaO–FeO, CaO–SiO₂–Al₂O₃ as ironmaking slag and CaO–SiO₂–FeO as steelmaking slag.

The relationships of reaction products, heating temperature and holding time are obtained for the fluxes of CaO–SiO₂ and CaO–FeO under the present experimental conditions. As for the flux melting, decreasing the lime particle size can shorten the holding time, but can not decrease the heating temperature. In the melting process of CaO–SiO₂, a layer of $2\text{CaO}\cdot\text{SiO}_2$ is observed on the periphery of CaO particle, which tends to inhibit the melting of CaO particles. Decreasing the CaO particle size can also effectively promote the dissolution of CaO particles into both kinds of slag of CaO–SiO₂–Al₂O₃ and CaO–SiO₂–FeO.

KEY WORDS: lime-containing flux; melting; dissolution of lime; slag formation; particle size of lime.

1. Introduction

Lime-containing flux is widely used as a reagent of desulfurization and dephosphorization in ironmaking and steelmaking process. However, since the melting point of CaO is as high as 2843 K,¹⁾ which is much higher than the ordinary temperature for ironmaking and steelmaking, lowering the melting point of flux is usually done by addition of gangue minerals of SiO₂ and Al₂O₃ to enhance the reaction rate between slag and molten metal. For further promoting the melting of lime-containing flux, fluorspar (CaF₂) is also commonly used as an additive. But owing to fluorine containing species released into atmosphere and dissolved into soil from the disposed slag, utilization of fluorspar is increasingly limited from the view point of environmental protection.

Many methods have been developed to promote the melting of lime-containing flux in place of using fluorspar (CaF₂). Shoji *et al.*²⁾ indicated that desulfurization could be improved by addition of aluminum into hot metal in the powdered lime injection process. Instead of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$ layer formed on the lime surface, which retarded sulfur transferring to its interior, the molten CaO–Al₂O₃–FeO layer was formed on the lime surface to enhance sulfur transfer. Ban-ya *et al.*³⁾ developed CaO–Al₂O₃–Fe_xO_y flux as a substitute for CaO–CaF₂–Fe_xO_y flux, which was commonly used for dephosphorization and desulfurization of hot metal. The most suitable composition for dephosphorization was (38–45)CaO–(12–5)Al₂O₃–50Fe_xO_y in weight percentage. Mukawa *et al.* obtained the optimum Na₂O content in Na₂O–CaO flux,⁴⁾ and the optimum Al₂O₃

content in CaO–Al₂O₃ flux⁵⁾ to gain the maximum rate of desulfurization of hot metal. Shimoda *et al.*⁶⁾ proposed that CaO–Al₂O₃–TiO₂ flux had the greatly promoting effect on desulfurization of hot metal, due to its low melting point and low viscosity. Furthermore, Lee *et al.*⁷⁾ developed a new flux of burnt lime(CaO) coated with di-calcium ferrite ($2\text{CaO}\cdot\text{FeO}$). It was claimed that this new kind of flux had a high resistance to hydration and a capacity of fast and complete dissolution into the steelmaking slag of BOF and EAF.

On the other hand, much research work has been tried to clarify the mechanism of dissolution of lime into slag and develop the new methods to promote the dissolution. Schlitt *et al.*⁸⁾ found that the dissolution rate of lime into CaO–FeO–SiO₂ slag was markedly increased with increasing the FeO content in slag. It was also revealed⁹⁾ that the layer of $2\text{CaO}\cdot\text{SiO}_2$ was formed on the surface of CaO particles, and dissolution of CaO proceeded by migration of the molten slag through cracks on the layer of $2\text{CaO}\cdot\text{SiO}_2$. In the case of the higher Fe₂O₃ content, the layers of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$ compounds formed around the CaO crystal were not continuous but looked like particles, which promoted dissolution of CaO.¹⁰⁾ The diffusion of calcium through the slag boundary phase was revealed to be the rate-determining step for dissolution of solid lime into the liquid slag of CaO–SiO₂–Al₂O₃ or CaO–SiO₂–FeO.¹¹⁾ In addition, more porous lime was found to show higher reactivity in dissolution of lime into slag.¹²⁾ It was concluded^{13,14)} that the effect of the additives to Fe_tO–CaO–SiO₂ melt on increasing the dissolution rate of CaO was in the order of $\text{CaF}_2 > \text{CaCl}_2 > \text{B}_2\text{O}_3 > \text{Al}_2\text{O}_3$. Addition of CaF₂,

Fig. 1. Morphologies of all kinds of materials used in experiments.

MnO_x, FeO_x, and TiO₂ into Al₂O₃–CaO–SiO₂ slag increased the dissolution rate of lime into slag, while addition of SiO₂ had an opposite effect.¹⁵⁾

In the present work, by use of infrared-ray vacuum furnace, effect of lime particle size on melting behavior of lime-containing flux is studied. Four kinds of fluxes are employed, which are CaO–SiO₂, CaO–FeO, CaO–SiO₂–Al₂O₃ as ironmaking slag and CaO–SiO₂–FeO as steelmaking slag. The used two different sizes of CaO particles have the average diameters of 10 and 75 μm. For the different kinds of fluxes, the relationships of reaction products, heating temperature and holding time are obtained from analysis results of XRD patterns. The status of flux melting is observed with a scanning electron microscope (SEM) and is analyzed with an energy dispersive spectrometer (EDS).

2. Experimental Apparatus and Procedures

Figure 1 shows the morphologies of all kinds of materials before formation of pellets. Calcium oxide particles of the small size, which were the commercial reagent packed with Ar gas, were relatively uniform in diameter, having the average diameter of 10 μm with the purity of 99.9%. Calcium oxide particles of the large size were prepared as rapidly as possible by crushing the calcium oxide blocks of the commercial reagent and being sieved with sieve pores of 50 μm and 100 μm, having the average diameter of 75 μm and the purity of 99.9%. Silicon oxide powders were very fine in size with the average diameter of only 2.0 μm. α-hematite powders had greatly varied diameters and irregular shapes, having the average diameter of 15 μm and purity of 99.5%. The diameters of aluminium oxide powders were varied, ranging from 20 to 80 μm. The aluminum oxide particles were usually in clusters formed by many fine aluminum oxide powders and the aluminum oxide powders had the purity of 99.9%.

Slag 1 of CaO–SiO₂–Al₂O₃ was produced by melting the mixture of CaO, SiO₂ and Al₂O₃ powders at the mass ratio of 40:40:20 (mass%), which is closed to the common composition of slag used in blast furnace, in a dense Al₂O₃ crucible using an electric resistance furnace. Slag 2 of CaO–SiO₂–FeO was made by melting the mixture of CaO, SiO₂, FeO powders at the mass ratio of 40:40:20 (mass%),

Table 1. Chemical compositions and powder sizes of experimental samples together with used crucibles.

	Chemical composition (mass%)		Average Powder size (μm)	Crucible
Sample 1	CaO	37.0	10 or 75	C
	SiO ₂	63.0	2	
Sample 2	CaO	20.0	10 or 75	Al ₂ O ₃
	Fe ₂ O ₃	80.0	15	
Sample 3	CaO	10.0	10 or 75	C
	CaO-SiO ₂ -Al ₂ O ₃	90.0	30	
Sample 4	CaO	10.0	10 or 75	Al ₂ O ₃
	CaO-SiO ₂ -FeO	90.0	30	

Slag compositions:

Slag 1: CaO:SiO₂:Al₂O₃=40:40:20(mass%)(used in ironmaking)

Slag 2: CaO:SiO₂:FeO =40:40:20(mass%)(used in steelmaking)

which is near the common composition of slag used in steelmaking, also in a dense Al₂O₃ crucible using an electric resistance furnace. And then both kinds of slag were crushed in a mortar, having greatly varied diameters from 5 to 200 μm with the average diameter of about 30 μm.

The components of samples are shown in Table 1. Sample 1 contained CaO and SiO₂ of a mass ratio of 37:63 (mass%), which was the eutectic composition having the melting point of 1709 K.¹⁾ Sample 2 consisted of CaO and Fe₂O₃ of a mass ratio of 20:80 (mass%), which was near the eutectic composition having the melting point of 1473 K.¹⁶⁾ In Sample 3, Slag 1 of CaO–SiO₂–Al₂O₃ and CaO were mixed at a mass ratio of 90:10 (mass%). In Sample 4, Slag 2 of CaO–SiO₂–FeO and CaO were mixed at a mass ratio of 90:10 (mass%). After mixing, the above four kinds of samples were respectively formed into pellets, having the diameter of 3 mm and the length of 2 mm, by use of a cold isostatic press (CIP) under a pressure of 150 MPa for 1 h.

Figure 2 is a schematic diagram of the infrared vacuum furnace. On the each side of the furnace, a infrared lamp was placed at the first focal spot of a golden ellipsoidal reflecting mirror, while the heating sample was located at the

Fig. 2. Schematic illustration of infrared ray vacuum furnace.

Fig. 3. Decrease in temperature with time after cutting down the electric power supply of the furnace.

second focal spot. In this way, the sample could be heated up to a high temperature in a short time mainly by heat radiation mechanism. The pellets of the mass of 0.34 ± 0.01 g were placed in an alumina or graphite sample crucible. Since the pellet mass was rather small, the heat transfer in the pellets should not be the rate-controlling step. Furthermore, in order to ensure the pellets to be uniformly heated, the sample crucible was placed inside a larger graphite crucible that had good conductivity. The temperature was measured by a thermocouple with its front edge attached to the side wall of the protection graphite crucible. From the above heating principle, the temperature measured by the thermocouple should be close to the temperature in the pellets. But the specific difference needs to be studied in the future. The pellets, crucibles and thermocouple were sealed in a transparent quartz tube, in which 1×10^{-7} atm of vacuum degree could be retained by a vacuum pump. Infrared ray was focused to heat the pellet from two infrared ray generators located on the two lateral sides. Increasing and decreasing in temperature were adjusted by temperature controlling program.

The pellets were heated at the temperature increasing rate of 300 K/min. After holding for a certain time at the prescribed temperature, they were cooled to the room temperature as quickly as possible by shutting down the electric power supply. The decrease in temperature with time after turning off the electric power supply of the furnace is shown in Fig. 3. For all of the initial temperatures of 1 673, 1 580 and 1 533 K, it took about only 70 s to decrease to 1 100 K, having the initial temperature decreasing rate of larger than 370 K/min. And below 1 100 K, all of the sam-

Fig. 4. XRD patterns of CaO-SiO₂ pellet after heating at different temperatures for various times. (CaO average diameter of 75 μm)

ples used in the present experiments have not any new phase transformation. It is therefore deduced that the phases of samples after cooling to the room temperature are close to the phases held at the experimental temperatures. Then the components of the reaction products after heating were determined by use of X-ray diffraction (XRD). Cross-section of the cooled pellets were observed using SEM. The microscopic compositions at various positions on the pellet surface were determined by EDS analysis.

3. Experimental Results and Discussion

3.1. Melting of CaO-SiO₂ Flux

From the CaO-SiO₂ binary phase diagram, Sample 1 of CaO-SiO₂ at the mass ratio of 37 : 63 (mass%) has the eutectic composition of the melting point of 1 709 K. Therefore, for CaO of the average particle diameter of 75 μm, samples were heated at 1 703 K for 1 200 s, at 1 723 K for 600 s and 1 200 s, at 1 743 K for 120 s and 300 s, at 1 773 K for 120 s, respectively. The cooled samples were analyzed with XRD and the results are shown in Fig. 4.

It is seen that after heating at the temperature of 1 703 K below the melting point, the pellets mainly contained CaO and SiO₂. Some 2CaO·SiO₂ was also formed during the heating. With increasing the heating temperature and holding time, the intensities of CaO peak and SiO₂ peak decreased. The peaks of CaO disappeared at 1 743 K for 120 s, and the peaks of SiO₂ disappeared at 1 743 K for 300 s.

From above XRD results, the relationships of reaction products, heating temperature and holding time can be summarized as in Fig. 5. It clearly shows that in the reaction products after heating, CaO and SiO₂ disappeared in turn, while 2CaO·SiO₂ and 3CaO·SiO₂ appeared in turn with increasing the heating temperature and holding time. The solid line in the figure represents the boundary line of pellet meltdown determined by SEM observation of pellets

after heating, which will be explained later.

For CaO of the average diameter of $10\text{ }\mu\text{m}$, samples 1 were heated at 1703 K for 1200 s, at 1723 K for 600 s, at 1723 K for 1200 s and at 1743 K for 120 s. The similar changes in the compositions of pellets after heating were found as shown in Fig. 6. But the peaks of SiO_2 disappeared at 1743 K for 120 s. The holding time is shorter than 300 s for CaO of the average diameter of $75\text{ }\mu\text{m}$. In addition, the peaks of $3\text{CaO}\cdot\text{SiO}_2$ appeared from 1703 K holding for 1200 s, the heating temperature was lower than 1723 K for CaO of the average diameter of $75\text{ }\mu\text{m}$. These results can be clearly summarized in Fig. 7, which shows the relationships of reaction products, heating temperature and holding time for CaO of the average diameter of $10\text{ }\mu\text{m}$.

Figure 8 gives results of SEM images and EDS analyses for $\text{CaO}(75\text{ }\mu\text{m})\text{-SiO}_2$ pellet after heating at 1703 K for 1200 s, at 1743 K for 120 s and 300 s. After heating at 1703 K for 1200 s, the individual CaO particle still remained in the pellet as shown in diagram (a). EDS analysis shows that CaO was mainly contained at the center of the particle. A product layer was observed around the periphery

of the CaO particle from the SEM image. EDS analysis indicates that it had the component close to $2\text{CaO}\cdot\text{SiO}_2$, which theoretically contains CaO of 65.1 mass%. It is obvious that the pellet was not melting at this temperature. The $2\text{CaO}\cdot\text{SiO}_2$ layer retarded the mutual mass transfer of the

Fig. 6. XRD patterns of CaO-SiO_2 pellet after heating at different temperatures for various times. (CaO average diameter of $10\text{ }\mu\text{m}$)

Fig. 5. Relationships of reaction products, heating temperature and holding time after heating CaO-SiO_2 pellet at different temperatures for various times. (CaO average diameter of $75\text{ }\mu\text{m}$)

Fig. 7. Relationships of reaction products, heating temperature and holding time after heating CaO-SiO_2 pellet at different temperatures for various times. (CaO average diameter of $10\text{ }\mu\text{m}$)

EDS analysis results (mass%)

	①	②	③	④	⑤
CaO	96.5	63.0	8.8	80.1	40.6
SiO_2	3.5	37.0	91.2	19.9	59.4

Fig. 8. SEM images and EDS analyses of $\text{CaO}(75\text{ }\mu\text{m})\text{-SiO}_2$ pellet after heating.

(a) 1703K holding for 1200 s

(b) 1743K holding for 120 s

EDS analysis results (mass%)

	CaO	SiO ₂
①	1.46	98.54
②	75.05	24.95
③	38.05	61.95

Fig. 9. SEM images and EDS analyses of CaO(10 μm)-SiO₂ pellet after heating.

CaO and SiO₂ phases.

After heating at 1743 K for 120 s, the pellet displayed different microstructures at different regions on the pellet surface. The region with the smaller particles at the point ③ in diagram (b) contained mainly SiO₂, while the region with the larger particles at the point ④ contained mainly CaO. The pellet was obviously not fully melting. After heating at 1743 K for 300 s, the uniform appearance on the pellet surface was observed, and the EDS analysis results indicate that its component is the same as the initially mixing ratio of CaO and SiO₂ in the pellets. Therefore, it is confirmed that the pellet was melted down at 1743 K for 300 s. The boundary line of pellet meltdown is shown as the solid line in Fig. 5.

Figure 9 shows the results of SEM images and EDS analyses of CaO(10 μm)-SiO₂ pellet after heating at 1703 K for 1200 s and at 1743 K for 120 s. At 1703 K holding for 1200 s, different morphologies appeared at different regions on the pellet surface. At the point ①, the dominant component was SiO₂. On the other hand, at the point ②, the primary component was CaO. Thus the pellet was not fully melting under this condition. At 1743 K holding for 120 s, uniform appearance on the pellet surface indicates that the pellet was meltdown. The EDS analysis result shows that it had the same components as the initially mixing ratio of CaO and SiO₂. Therefore, the meltdown of pellet was confirmed.

In Fig. 7, the solid line is the meltdown boundary line for CaO of the average particle size of 10 μm, while the dashed line gives the meltdown boundary line for CaO of the average particle size of 75 μm. From Figs. 5 and 7, it is known that only 2CaO·SiO₂ and 3CaO·SiO₂ remained in the pellet after its melting. When the average diameter of CaO particles was decreased from 75 to 10 μm, the meltdown temperature did not change, but the holding time was shortened from 300 to 120 s. As a result, the melting of CaO-SiO₂ flux can be promoted by decreasing CaO particle size. This is because the interface area between CaO and SiO₂ particles is increased by decreasing CaO particle size.

By observing the lime-containing flux heated on Pt-filament directly through a microscope, Kimura *et al.*⁹⁾ found the layer of 2CaO·SiO₂ is formed on the surface of CaO particles, which hindered dissolution of CaO into slag. In the present studies, formation of the layer of 2CaO·SiO₂ around the CaO particles was also observed and 2CaO·SiO₂ has a rather high decomposition temperature of 2403 K.¹⁾ As the melting point of CaO-SiO₂ flux at the present mass ratio is 1709 K, the reason why the meltdown of pellet did not take place until 1743 K even if the average diameter of CaO particle was decreased to 10 μm can be attributed to the formation of 2CaO·SiO₂ layer on the surface of CaO particles.

3.2. Melting of CaO-Fe₂O₃ Flux

In our preliminary experiment, it is confirmed that after Sample 2 of CaO and Fe₂O₃ of the mass ratio of 20:80 (mass%) was heated at above 1373 K, the remaining product was FeO rather than Fe₂O₃ at the present vacuum degree of 1×10^{-7} atm. However, thermodynamic calculation indicates that Fe₂O₃ should be stable phase at this vacuum degree. The possible reason for the present experimental result is that the oxygen partial pressure was greatly decreased because the oxygen in the atmosphere reacted with the graphite crucible at the elevated temperature in vacuum. The mass ratio of CaO to FeO can be converted to be 21.7:78.3 (mass%) from the composition of Sample 2. From the binary phase diagram of CaO and FeO, the remaining product after heating Sample 2 at above 1373 K has the eutectic composition and its melting point is about 1423 K.¹⁾ Therefore, Sample 2 was heated at 1373, 1423, 1443 and 1473 K, and was held for 120, 300, 600, 1200 s at each temperature.

Then the cooled samples were analyzed with XRD and the results are given in Fig. 10. For CaO particles of the average diameters of 10 μm and 75 μm, no difference in the compositions of the remaining products was detected. After heating at 1373 K and after heating at 1423 K for less than 600 s, the remaining products were CaO and FeO. After

heating at 1423 K for more than 600 s, and after heating at 1443 and 1473 K, the remaining products were CaO, FeO and $\text{CaO} \cdot 2\text{FeO}$. With increasing the heating temperature and holding time, $\text{CaO} \cdot 2\text{FeO}$ was generated.

The cooled samples were further observed and analyzed with SEM-EDS and the results are shown in Fig. 11 for CaO particles of the average diameter of 75 μm . After heating at 1443 K for 300 s, some particles were not melting, and they contained much CaO as shown for the point ② in diagram (a). After heating at 1443 K for 600 s, the uniform appearance was observed on the pellet surface. From EDS analysis, no region contained ultra high CaO could be detected, thus the sample was melting. But the CaO content was not uniform at the different points on the pellet surface. This means that the diffusion of CaO in the melt did not complete. From above observations and analyses, it is verified that sample 2 with the average diameter of CaO particles of 75 μm became melting from heating at 1443 K for 600 s. The boundary line of pellet meltdown is shown as the dashed line in Fig. 10.

For the average diameter of CaO particles of 10 μm , re-

Fig. 10. Relationships of reaction products, heating temperature and holding time after heating CaO-FeO flux at different temperatures for various times.

sults of SEM images and EDS line analyses are presented in Fig. 12. After heating at 1423 K for 1200 s, the individual particle made its appearance. EDS line analysis shows that much CaO was detected across the particle. After heating at 1443 K for 300 s, the uniform appearance was observed on the pellet surface. EDS line analysis indicates that homogeneous distribution of the Fe and Ca contents were detected on the pellet surface. It is confirmed that sample 2 with CaO particles of the average diameter of 10 μm became melting from heating at 1443 K for 300 s. The boundary line of pellet meltdown for CaO particles of the average diameter of 10 μm is shown as the solid line in Fig. 10. The comparison between the solid and the dashed line clearly shows that with decreasing the CaO particle size, the melting temperature of CaO-FeO flux does not change, but the holding time can be shortened.

3.3. Melting of $(\text{CaO-SiO}_2\text{-Al}_2\text{O}_3)\text{-CaO}$ Flux

From the ternary phase diagram of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$,¹⁾ Slag 1 containing CaO, SiO_2 and Al_2O_3 of the mass percentage ratio of 40:40:20 (mass%) has the melting point of 1573 K. It is commonly used in the ironmaking process. After 10 mass% CaO is mixed with Slag 1, its melting point will rise to 1753 K. Both of Slag 1 and 90 mass% Slag 1+10 mass% CaO belong to the region of primary crystal of Gehlenite. Therefore, Samples 3 of 90% Slag 1+10% CaO were heated at 1793 K for 120, 300, 600, and 1200 s, respectively.

As Slag 1 in Sample 3 has a much lower melting point than the experimental temperature, Sample 3 was fully melting from its appearance observed with SEM. No difference could be detected for the different holding times at 1793 K.

In terms of the XRD patterns, Slag 1 was preliminarily examined. No elemental substance of CaO was detected. Therefore, the detected elemental substance of CaO for Samples 3 after heating was caused by the additionally added CaO particles. Although the elemental substance of CaO was detected by XRD patterns for Samples 3, they

	①	②	③	④	⑤	⑥
CaO	19.4	45.9	8.7	14.4	6.8	8.8
Fe_2O_3	80.6	54.1	91.3	85.6	93.2	91.2

Fig. 11. SEM images and EDS analyses of CaO(75 μm)-FeO pellet after heating.

(a) 1423K holding for 1200s

(b) 1443K holding for 300s

— Ca — Fe

 Fig. 12. SEM images and EDS line analyses of CaO(10 μm)-FeO pellet after heating.

was fully melting from their appearance observed with SEM. This is because the slight amount fine CaO particles are very difficult to be distinguished by SEM.

Figure 13 shows changes in intensities of CaO peaks in XRD pattern with the holding time for CaO particles of the average diameters of 75 and 10 μm . After heating at 1793 K for 120 s, almost the same intensities of CaO peaks were detected for Samples 3 with the different CaO particle sizes. With increasing the holding time, the intensity of CaO peak decreased very fast for CaO particles of the average diameter of 10 μm . After 600 s, the CaO peak disappeared, indicating that the additionally added CaO particles were completely melted down with the slag. But until holding for 1200 s, the CaO peak could be detected for CaO particles of the average diameter of 75 μm . It is therefore concluded that with decreasing CaO particle size, the dissolution rate of CaO particles into molten slag of 40%CaO–40%SiO₂–20%Al₂O₃ is greatly increased.

3.4. Melting of (CaO–SiO₂–FeO)–CaO Flux

From the ternary phase diagram of CaO–SiO₂–FeO,¹⁾ Slag 2 containing CaO, SiO₂ and FeO of 40:40:20 (mass%) has the melting point of 1593 K, which is in the region of primary crystal of CaO·SiO₂. It is usually employed in the steelmaking process. After 10 mass% CaO is additionally mixed with the slag, its melting point increases to 1773 K and it is in the region of primary crystal of 2CaO·SiO₂. Therefore, Samples 4 of 90% Slag 2+10%

 Fig. 13. Changes in intensities of CaO peaks in XRD patterns with time for (CaO–SiO₂–Al₂O₃)–CaO flux with different diameters of CaO particles.

CaO were heated at 1793 K for 120, 300, 600 and 1200 s.

Since the experimental temperature is much higher than the melting temperature of Slag 2, the Samples 4 appeared melting from the SEM observation. No difference in appearance could be detected for the different holding times.

The preliminary XRD analysis was also conducted for Slag 2, no elemental substance of CaO could be detected. Therefore, the CaO peak detected for Samples 4 after heating is originated from the additionally added CaO particles.

Figure 14 presents changes in intensities of CaO peaks in XRD patterns with holding time for CaO particles of the average diameter of 75 μm and 10 μm . After heating at 1793 K for 120 s, almost the same intensities of CaO peaks were detected for the different CaO particle sizes. With in-

Fig. 14. Changes in intensities of CaO peaks in XRD patterns with time for (CaO-SiO₂-FeO)-CaO flux with different diameters of CaO particles.

creasing the holding time, the CaO peaks decreased rapidly. After holding for 300 s, the CaO peak could not be detected for CaO particles of the average diameter of 10 μm. After holding for 600 s, the CaO peak disappeared for CaO particles of the average diameter of 75 μm. Again, with decreasing CaO particle size, the dissolution of CaO particles into the slag of 40%CaO-40%SiO₂-20%FeO is greatly enhanced.

4. Conclusions

Effect of the CaO particle size on the melting behavior of lime-containing flux is studied by use of infrared-ray vacuum furnace in the present work. Two kinds of CaO particles of the average diameters of 10 and 75 μm are used. Four kinds of lime-containing fluxes are employed, which are CaO-SiO₂, CaO-FeO, CaO-SiO₂-Al₂O₃ as ironmaking slag and CaO-SiO₂-FeO as steelmaking slag. The following conclusions can be drawn:

(1) For CaO-SiO₂ flux, after its melting, 2CaO·SiO₂ and 3CaO·SiO₂ are generated and the elemental substances of CaO and SiO₂ can not be detected. The formation of 2CaO·SiO₂ on the surface of CaO particles tends to hinder the melting of CaO particles. Relationships of reaction products, heating temperature and holding time are obtained for CaO-SiO₂ flux under the present experimental conditions. In terms of the flux melting, decreasing CaO

particle size can shorten the holding time, but can not decrease the heating temperature.

(2) For CaO-FeO flux, the relationships of reaction products, heating temperature and holding time are obtained under the present experimental conditions. With decreasing the CaO particle size, although the melting temperature of CaO-FeO flux can not be decreased, the holding time can be shortened.

(3) Decreasing the CaO particle size can effectively promote the dissolution of CaO particles into both kinds of slag of CaO-SiO₂-Al₂O₃ and CaO-SiO₂-FeO.

Acknowledgement

This study was supported in part by JFE 21st Century Foundation, Grants-in-Aid for Scientific Research in 2006-2007.

REFERENCES

- 1) Hand Book of Iron and Steel (I), ed. by ISIJ, Maruzen, Tokyo, (1981), 47.
- 2) T. Shoji, T. Mitsuo, Y. Hatta, H. Ono, H. Mori and T. Kai: *Tetsu-to-Hagané*, **68** (1982), 609.
- 3) S. Ban-ya, M. Hino, R. Nagabayashi and O. Terayama: *Tetsu-to-Hagané*, **75** (1989), 66.
- 4) S. Mukawa and Y. Mizukami: *Tetsu-to-Hagané*, **82** (1996), 659.
- 5) S. Mukawa: *Tetsu-to-Hagané*, **90** (2004), 408.
- 6) I. Shimoda, T. Sato, T. Nakasuga, K. Nakashima and K. Mori: *Tetsu-to-Hagané*, **90** (2004), 401.
- 7) M. Lee and P. Barr: *Steel Res.*, **73** (2002), 123.
- 8) W. J. Schlitt and G. W. Healy: *Am. Ceram. Soc. Bull.*, **50** (1971), 954.
- 9) H. Kimura, T. Yanagase, F. Noguchi and Y. Ueda: *J. Jpn. Inst. Met.*, **38** (1974), 226.
- 10) F. Noguchi, Y. Ueda and T. Yanagase: *J. Jpn. Inst. Met.*, **41** (1977), 883.
- 11) M. Matsushima, S. Yadoomaru, K. Mori and Y. Kawai: *Trans. Iron Steel Inst. Jpn.*, **17** (1977), 442.
- 12) C. A. Natalie and J. W. Evans: *Ironmaking Steelmaking*, **6** (1979), 101.
- 13) T. Hamano, M. Horibe and K. Ito: *ISIJ Int.*, **44** (2004), 263.
- 14) T. Hamano, S. Fukagai and F. Tsukihashi: *ISIJ Int.*, **46** (2006), 490.
- 15) S. H. Amini, M. P. Brungs, S. Jahanshahi and O. Ostrovski: *Metall. Mater. Trans. B*, **37B** (2006), 773.
- 16) E. M. Levin, C. R. Robbins and H. F. McMurdie: *Phase Diagrams for Ceramists*, The American Ceramic Society, Columbus, USA, (1964), 49.