Softening, Melting, and Permeation Phenomena of CaO–FeO–SiO₂ Oxide on a Coke Bed

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For the low carbon operation of blast furnace, it is necessary to maintain the gas permeability in the furnace at low coke rate. The pressure drop in the cohesive zone of the blast furnace is significantly high, and the gas permeability of the cohesive zone has an influence on the productivity of the iron-making process. The gas permeability increases as the thickness of the cohesive zone decreases. The present study aimed to decrease the thickness of the cohesive zone by achieving a higher softening temperature and a lower temperature for the dripping of the sinter ore. The softening, melting, and permeation processes of CaO–FeO–SiO₂ oxide on a coke bed was investigated. The change in the shape of the oxide tablet, the formation of the liquid droplet, and its permeation into the coke bed were observed with increasing temperature in several CO/CO₂ atmospheres. Softening of the oxide was observed at a temperature that was slightly above the solidus temperature. The deformation of the oxide tablets was strongly affected by the liquid phase ratio. Furthermore, there was no relationship between the temperature of permeation and the melting of the oxide tablet. The permeation of the oxide melt into the coke bed is dependent on the wettability between them.

KEY WORDS: sinter; cohesive zone; softening; melting; molten slag; molten iron; wettability; dripping zone; blast furnace.

1. Introduction

Much research has been conducted in order to reduce CO₂ emissions from blast furnaces.^{1,2)} Researchers have considered replacing coke and/or coal with gas containing CO and/or H₂, while decreasing the rate of consumption of the reducing agent. During such operations, the coke rate would be greatly reduced. The coke employed during the operation of a blast furnace functions both as a reducing agent and as a structural material to maintain the gas permeability in the furnace. Therefore, a decrease in the coke rate would result in a loss of pressure and reduce the productivity.

With the development of low coke operation technology, it is increasingly important to estimate and control the flow of solids and gases in the blast furnace.^{3–5)} During a low coke rate operation, the relative thickness of the coke slit at the cohesive zone decreases. The ore layer exhibits a solid-liquid coexistence at the cohesive zone, and the permeability decreases. The loss of pressure in the furnace is considerably owed to the softening of the ore in the cohesive zone;^{6,7)} for a lower coke rate operation, an improvement in the permeability of the cohesive zone is required. The loss of pressure in the whole furnace can be decreased by decreasing the thickness of the cohesive zone in the vertical direction.⁸⁾

The cohesive zone consists of a phase of coexisting solid-liquid as a result of the melting phenomenon of iron ore. Therefore, in order to reduce the thickness of the cohesive zone, it is required to increase the solid softening temperature and decrease the liquid dripping temperature.

A quantitative evaluation of the pressure loss owed to the melting of the ore has been conducted via a softening test under loading.^{6,7)} Since, the softening, melting, and dripping of ore are comprehensively evaluated during the softening test under loading, it was not possible to clarify each phenomenon and their causal relationships. In order to reduce the thickness of the cohesive zone, researchers have proposed to increase the liquid phase formation temperature of the ore.^{9,10)} However, the studies that have been conducted on the high temperature softening and low temperature dripping of iron ore are insufficient. It is important to clarify the effect of the ore composition, reduction ratio, and atmosphere on the softening, melting, and dripping temperatures in order to design the iron ore and to control both the burden charging and the blast gas.

The present study has aimed to increase the softening temperature and decrease the dripping temperature. The CaO–FeO–SiO₂ system was employed as the main component of the sinter ore. The oxide was heated under an atmosphere with a specific CO/CO₂ ratio. During heating, we measured the deformation and droplet formation temperatures, in addition to the temperature at which the permeation in the coke bed occurred, while observing the

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change in shape. The liquidus and solidus temperatures, in addition to the equilibrium phases were derived with the aid of a thermodynamic database.¹¹⁾ During the present study, the softening and melting temperatures were measured and compared with each other, and the non-equilibrium reactions of the system were discussed.

2. Softening, Melting, and Permeation Temperatures of CaO–FeO–SiO₂ Oxide

The thickness of the cohesive zone directly relates to the gas permeability, and consequently, it is desirable to be able to predict the position and thickness of the cohesive zone depending on the operation conditions of the blast furnace. In order to clarify the temperature of both the softening and the permeation into the coke bed, the variation in the shape of an oxide tablet consisting of a CaO–FeO–SiO₂ system was observed, and the softening, melting, and permeation temperatures were determined.

2.1. Measuring Procedure

Reagent grade Fe₂O₃, Fe, CaCO₃, and SiO₂ were employed to prepare the samples. The Fe powder and Fe₂O₃ were mixed to a stoichiometric ratio in advance, and the mixture was melted and quenched in order to form FeO. The CaO was prepared by heating CaCO₃ at a temperature of 1 400°C for 14 h. The oxides were mixed to the compositions shown in **Table 1**. An oxide mixture weighing 2 g was pressed in a die to produce a tablet with a diameter of 10 mm. The sample denoted as s1 was used as a standard

Table 1. Composition of sample.

Sample No.	CaO (mass%)	SiO ₂ (mass%)	FeO (mass%)
s1	38.2	31.8	30.0
s2	43.6	36.4	20.0
s3	49.1	40.9	10.0
s4	21.0	49.0	30.0
s5	35.0	35.0	30.0
s6	42.0	28.0	30.0
s7	49.0	21.0	30.0

sample, and the samples denoted as s2–3 and s4–7 were used to investigate the effect of the FeO concentration and the basicity (CaO/SiO₂), respectively. The coke of 1–2 mm in diameter was placed in a shallow alumina crucible and the oxide tablet was placed on the coke bed. The properties of the coke are shown in **Table 2**. As shown in **Fig. 1**, a horizontal electric resistance furnace with a mullite tube ($\phi 35$ mm ID) was used for the observation and measurements. The sample was placed in the center of the tube, and the changes in the appearance of the sample were observed using a camera placed near the end of the reaction tube. The temperature of the furnace was controlled by a proportional-integral-derivative (PID) controller connected to a thermocouple located near the sample. N₂ gas was introduced at a flow rate of 100 ml/min and the temperature was increased to 900°C at a heating rate of 10°C/min. The temperature was subsequently increased to 1 450°C at a rate of 5°C/min under a gas flow consisting of a mixture of CO/CO₂, and the temperature was subsequently maintained at 1 450°C for 1 800 s. The mixing ratio of CO/CO₂ was controlled at 4/6, 5/5, and 6/4 with the use of mass flow controllers. The softening, melting, and permeation temperatures were measured by observing the changes in the shape of the tablet.

2.2. Observation of Samples

In the present study, the softening, melting, and permeation processes were determined by observing the change in the shape of the samples. The shapes of the heated samples are shown in **Fig. 2**. The photographs denoted as a, b, c and d represent the initial sample, the softening and melting of the sample, and the sample following permeation, respectively. A liquid phase is formed in the heated tablet, and the shape of the surface of the sample changes at the softening temperature. The melting temperature was defined as the temperature at which the softened sample formed into a smooth droplet. The permeation temperature was defined as the temperature at which the liquid phase of the sample

Table 2. Property of coke.

mass%			
Fixed carbon	Volatile matter	Ash	Water
87.66	0.26	12.08	0.28

Fig. 1. Schematic diagram of the experimental apparatus.

gradually permeated into the coke bed after softening, or the temperature at which the droplet suddenly permeated into the coke bed after remaining on the coke bed for a period of time. If a temperature of 1 450°C was attained and the droplets did not permeate the coke bed, the permeation temperature was determined as 1 450°C regardless of the time taken for permeation. Following the tests, the permeated oxide and the reduced iron melt were either distributed in the coke bed or adhered to the crucible, and therefore, it was not possible to collect these samples for chemical analysis.

2.3. Observation of the Interface between the Oxide and Coke

In order to study the variation in the wettability of the molten oxide and coke, their interface was observed. Sample s1 was heated to a temperature of 1 450°C under an N₂ atmosphere, and it was quenched immediately after melting or following a period of 900 s or 3 600 s. Following melting, the sample exhibited low wettability during the experiment. Following a period of 900 s, the interface of the oxide and coke became wettable. The quenched sample was observed using field emission electron probe microanalysis (FE-EPMA).

3. Influence of the Reduction of FeO in the CaO–FeO–SiO₂ Melt on the Melting Process

3.1. Influence of the FeO Concentration on the Melting Process of CaO–FeO–SiO₂

The softening, melting, and permeation temperatures of the CaO–FeO–SiO₂ mixture heated under a CO/CO₂=5/5 atmosphere are shown in Fig. 3. The ratio of CaO/SiO₂ was 1.2/1 and the FeO concentrations were 30, 20, and 10 mass%. The FeO concentration of the initial sample did not have an influence on the softening and melting temperatures. The softening and melting temperatures were approximately 1 300 and 1 400°C, respectively.

According to the phase diagram of the CaO–FeO–SiO₂ system, the initial liquid phase of the experimental samples consists of liquid Olivine phase equilibrated with 2CaO. SiO₂. Therefore, the liquid phase may have formed at a temperature greater than 1 221°C under equilibrium conditions; however, during the actual measurement, the liquid formed at a temperature greater than 1 300°C. The liquidus temperature of the samples (s1–3) is approximately 1 400°C. Mean-

Fig. 2. Appearances of sample at softening, melting and permeation temperatures.

while, when the temperature was maintained at 1 450°C for approximately 10 min, the molten oxide permeated into the coke bed.

The appearances of the samples (s1–3) at 1 350°C is shown in Fig. 4. For each sample, the temperature is greater than the softening temperature but below the melting point; however, a different shape is exhibited for each tablet. With a lower FeO concentration, the ratio of the solid phase is high, and the shape of the tablet is maintained. Since the liquid phase reduces the porosity of the sinter layer, the liquid phase ratio should be considered in order to evaluate the permeability of the cohesive layer.

3.2. Influence of the Atmosphere on the Melting Process

Figure 5 demonstrates the appearance of the s1 sample at a temperature of 1 350°C under atmospheres with CO/CO₂ ratios of 4/6 and 6/4. A droplet is formed under the atmosphere with a CO/CO₂ ratio of 4/6; however, the shape of the tablet is maintained when the ratio is 6/4. The ratio of the solid phase is greater in an atmosphere with a high CO/CO₂ ratio.

Figure 6 shows the softening, melting, and permeation temperatures of the s1 sample at atmospheric pressure with CO/CO₂ ratios of 4/6, 5/5, and 6/4. Both the softening and

Fig. 3. Influence of concentration of FeO on apparent softening and melting temperatures of oxide tablet.

Fig. 4. Influence of concentration of FeO on appearance of oxide tablet at 1 350°C.

Fig. 5. Appearance of sample in CO/CO₂ atmosphere at 1 350°C. CO/CO₂ = 4/6(a), 6/4(b).

Fig. 6. Influence of atmosphere on softening and melting temperature of oxide.

melting temperatures increase when the CO concentration in the gas phase is increased. We observed the influence of the atmosphere on the softening process of the oxide. Permeation was observed when the temperature was maintained at 1 450°C for over 10 min, and the time that elapsed prior to the permeation was not influenced by the atmosphere.

The equilibrium partial pressure of oxygen changes when the CO/CO₂ ratio of the atmosphere is varied. At temperatures greater than 900°C, the FeO exhibits a stable phase, iron oxide, under the atmospheres with CO/CO₂ ratios of 4/6 to 6/4. According to the present experimental results and the phase diagram for the CaO–FeO–SiO₂ system,¹²⁾ the softening and melting temperatures are not influenced by the FeO concentration of the initial oxide phase. Owing to the reduction by the coke, the FeO concentration decreased. However, the change in the FeO concentration would have little effect on the melting process.

3.3. Relationship between the Permeation and the Reaction of the Iron at the Interface of the Coke and Oxide

There is no direct relationship between the formation of the oxide droplet and its permeation into the coke bed. The wettability of the coke and the oxide melt significantly influences the permeation of the liquid. The molten oxide remained on the coke bed for a period of time prior to permeation. Therefore, it can be assumed that the wettability between the oxide and coke changed from a non-wetting to a wetting condition. In order to investigate the phenomena at the interface, the oxide was melted on a coke plate and subsequently quenched for observation.

Images of the interface between the molten oxide and coke are shown in Figs. 7–9. The s1 sample was melted on a coke plate at 1 450°C. Figures 7, 8, and 9 show the sample immediately after melting, and following periods of 900 s and 3 600 s, respectively.

In Fig. 7, the oxide and coke can be observed at upper and lower side, respectively. Fe, Si, Ca, and O can be detected on the upper surface of the oxide, however, an area of oxide with high Fe, Ca, and O concentrations can be observed on both the left and bottom surfaces of the oxide. On the bottom surface, it can be confirmed that irregular shaped Fe and Ca–O phases coexist. Some of the iron in the oxide in the vicinity of the coke is reduced to metallic iron. It is assumed that the iron exhibits a solid phase since it has an irregular

shape and the temperature is below the melting point of iron.

The upper and lower parts of Fig. 8 represent the oxide and the coke phase, respectively. Following a period of 900 s, the oxide forms a droplet on the coke but has yet to permeate the coke. Small metallic iron particles are concentrated at the interface. Moreover, a Fe–Si–O rich phase can be observed in the coke layer following a period of 3 600 s (Fig. 9). Therefore, liquid Olivine can permeate the coke. The iron particles at the interface are larger than those observed at 900 s. The particles exhibit a spherical shape, and therefore include the liquid iron phase.

4. Influence of the Basicity of the CaO–FeO–SiO₂ System on the Melting Process

The softening, melting, and permeation temperatures of the CaO/SiO₂ = 7/3 (s4), 6/4 (s5), 1.2/1 (s1), 5/5 (s7), 3/7 (s7) samples are shown in Fig. 10. The samples were heated under an atmosphere of CO/CO₂ = 5/5. The s1 sample exhibited the highest softening temperature, and this decreases as the basicity increases and decreases. Following the formation of a droplet, the oxides of the s1, s4, s5, and s6 sample permeate the coke. Meanwhile, the samples with high (s7) basicities permeate at the same time as the softening occurs, and a residue remains on the coke.

We observed the permeation process following softening, and the permeation following the formation of the droplet. Here, there is no clear correlation between the permeation and the melting of the oxide.

5. Discussion

5.1. Derivation of the Liquid Ratio of the Oxide Phase

The liquid ratios of the oxides consisting of CaO/SiO₂ = 1.2/1 and FeO = 30, 20, 10 (mass%) were simulated by a thermodynamic database with varying temperatures.¹¹⁾ For each temperature, the oxygen partial pressure was determined under an atmosphere of CO/CO₂ = 1/1. The results are shown in Fig. 11.

The relationship between the temperature and the liquid ratio of the CaO–FeO–SiO₂ oxide is shown in Fig. 11. The FeO concentration was set as 30, 20, and 10 mass%. The open and solid circles denote the softening and melting temperatures measured during the present experiment, respectively.

Using the same method as above, the liquid ratios of the oxide with FeO = 30 (mass%) were calculated with varying CaO/SiO₂ ratios. For each temperature, the oxygen partial pressure was determined under an atmosphere of CO/CO₂ = 1/1. The calculation results are shown Fig. 12. The open and solid circles denote the softening and melting temperatures measured during the present experiment, respectively. The sample in which the initiation of the softening and permeation processes simultaneously occurred is represented by an open square.

5.2. Relationship between Solidus Temperature and Softening Temperature

The liquidus temperature of the oxide consisting of FeO = 30 (mass%) is 1 221°C under equilibrium conditions, and that of FeO = 20 and 10 (mass%) is 1 207°C, as

Fig. 7. Distribution of concentration of element near interface of molten oxide and coke at 1450°C.

Fig. 9. Distribution of concentration of element near interface of molten oxide and coke kept for 3600 s at 1450°C.

Fig. 8. Distribution of concentration of element near interface of molten oxide and coke kept for 900 s at 1450°C.

Fig. 11. Influence of concentration of FeO on liquid ratio of CaO-SiO₂-FeO oxide.

Fig. 12. Influence of CaO/SiO₂ ratio on liquid ratio of CaO-SiO₂-FeO oxide.

shown in Fig. 11. For the oxides with FeO concentrations of 30% and <20%, the initial liquid phases are equilibrated with Olivine and 2CaO.SiO₂, and Olivine and 3CaO.SiO₂, respectively. There are different compositions determined for the initial liquid and the equilibrated solid phases. For the sample with 30% FeO, the liquid ratio increases rapidly when the solidus temperature is attained. Furthermore, for the sample with less than 20% FeO, the equilibrium solid phase/liquid phase changes from Olivine/3CaO.SiO₂ to

3CaO.SiO₂, 3CaO.SiO₂/2CaO.SiO₂, and 2CaO.SiO₂ in that order, and the liquid ratio gradually increases. The actual

Fig. 10. Influence of CaO/SiO₂ on softening and melting temperature of oxide.

measured softening temperature was approximately 1 300°C for all the samples under an atmosphere of CO/CO₂ = 1/1. In the present experiment, the softening temperature is not affected by the FeO concentration; therefore, the formation of the liquid phase occurs under non-equilibrium conditions.

The experimental results showed that the softening temperature increased from 1 270 to 1 320°C when the CO/CO₂ ratio of the atmosphere was changed. The results also demonstrate that the softening temperature decreases as the oxygen partial pressure of the atmosphere increases. Meanwhile, the solidus temperature derived by FACTSage with varying CO/CO₂ ratios of 4/6, 5/5, and 6/4 are 1 219, 1 221, and 1 222°C, respectively. It is possible that the oxygen partial pressure of the atmosphere influences the reaction rate of the liquid formation under non-equilibrium conditions.

As shown in Fig. 12, for the various basicities, the softening temperature was 20–70°C higher than the calculated solidus temperature for the s1 and s4–7 samples. The initial liquid phase at the solidus temperature consists of Olivine or a CaO–FeO melt, and the equilibrated solid phase consists of SiO₂, CaO·SiO₂, 2CaO·SiO₂, or 3CaO·SiO₂. These equilibrium phases are determined by the basicity, however, the relative difference between the solidus and softening temperatures does not show significant change.

The measured softening temperature is higher than the calculated solidus temperature; this can be explained as follows: 1) The softening and solidus temperatures differ from each other, and therefore the oxide softens at a certain liquid ratio value. 2) The reaction forming the liquid phase takes time to reach equilibrium.

It is clear from the comparison above that a non-equilibrium melting reaction occurred, and a non-equilibrium liquid phase may have initially formed, as indicated by literature.^{9,10} The softening and liquidus temperatures are relatively similar under an atmosphere with a higher oxygen partial pressure, therefore, it is possible that equilibrium can be achieved at a faster rate under an atmosphere with a high oxygen partial pressure.

5.3. Relationship between the Melting and Permeation Temperatures

The melting temperatures of the s1 and s6 samples (at which the oxide becomes a droplet) are lower than their liquidus temperatures; the melting temperatures were determined to be the temperatures at which the liquid ratios were

90% and 70%, respectively. Accordingly, the oxide would become a droplet at a temperature below the liquidus temperature, and it may permeate into the coke bed before the liquidus temperature is attained.

The droplet of the s1 sample remained on the coke bed for a period of time and subsequently permeated into the coke bed. However, when the samples with high and low basicities were softened, the liquid permeated immediately, and a residue remained on the coke bed. A relationship between the melting and permeation temperatures was not observed; the permeation depends on the wettability of the oxide melt and the coke.

During heating, the initial liquid phases of the s4, s1 and s7 samples consist of liquid with compositions close to that of Olivine saturated with SiO₂ and CaO·SiO₂, Olivine saturated with 2CaO·SiO₂, and CaO–FeO saturated with 2CaO·SiO₂, respectively. The wettability of the above samples with the coke were good, poor, and good, respectively. The oxide melt with a high FeO concentration tends to exhibit good wettability; the reduction of the FeO by the coke may affect the wettability between the oxide and the coke.

The contact angle of an oxide melt on a carbonaceous material associated with blast furnace slag has been reported.⁹ The contact angle of the CaO–SiO₂–Al₂O₃–MgO melt on carbonaceous material varies significantly from 40 to 160° depending on the presence of ash in the coke and the concentration of FeO in the oxide. At 1 500°C, the contact angle of the CaO–SiO₂–Al₂O₃–MgO–FeO melt decreases from 125 to 105° in approximately 300 s.¹³ The contact angle decreases as a result of the reduction of the FeO. Owing to the reduction of SiO₂, the contact angle of the CaO–SiO₂–Al₂O₃–MgO–Fe₂O₃ melt decreases from 120 to 60°.¹⁴ As described above, it is reported that the contact angle of an oxide melt on coke widely varies, and a non-wet system will transform into a wet system as the reaction progresses at the interface.

For the liquid with a composition close to that of Olivine saturated 2CaO·SiO₂, the wettability was poor initially, and then it wet to coke after a few tens of minutes. Metallic iron particles were formed at the interface of the oxide and coke, as observed using FE-EPMA. Initially, an iron phase was present along the interface; this may prevent physical contact between the oxide and the coke. Subsequently, following permeation, spherically shaped iron particles were observed on the surface of the coke bed. From the shape of the iron particle, it is assumed that the iron was in the form of a liquid. Since the solid and liquid iron in the oxide melts exhibit different wettability values,¹⁵ the formation of the liquid iron would increase the wettability, and subsequently, the oxide melt would start to permeate into the coke bed.

5.4. Increasing the Softening Temperature and Decreasing the Permeation Temperature of Sinter Ore

During heating, both the softening and solidus temperatures, and the melting and liquidus temperatures of the oxide are different. As described above, in order to increase the gas permeability of the sinter layer in the cohesive zone, it is effective to increase the softening temperature and to prevent an increase in the liquid ratio. In the present experiment, for the CaO–FeO–SiO₂ system, the formation of an

initial liquid phase saturated with $2\text{CaO}\cdot\text{SiO}_2$ results in an increase in the softening temperature, and an increase in the reduction ratio of FeO is effective in preventing a rapid increase in the liquid ratio.

The permeation of the oxide into the coke bed depends on the wettability between them, and not on the melting temperature. By observing the permeation process, we can determine that the following factors will promote low temperature dripping and consequently ensure permeation: 1) Introduce a wetting condition and consequently promote dripping from a low temperature but allow the remaining residue to have a high melting point. 2) Melt the whole oxide and introduce dripping immediately. It is necessary to determine which dripping method is the most advantageous; this would be confirmed by particular methods, such as the softening test under loading. If method 1) is performed, the basicity needs to be controlled as the FeO concentration in the initial liquid phase increases; this will subsequently increase the reactivity between the coke and the melt. If method 2) is performed, the basicity of the C/S should be controlled to be within a range of 1.2 to 1.5. This will initially form a non-wettable liquid phase, and subsequently the reactivity between the liquid and coke should increase. The reactivity of the coke could be improved by controlling the texture of the surface and/or crystalline. Moreover, the wettability of liquid changes depending on size, shape and surface structure of the coke. In order to estimate amount of the hold-up in the coke bed, it is necessary to consider the contact phenomena of moving droplet on non-smooth surface.

6. Conclusions

The softening, melting, and permeation processes of $\text{CaO}\text{--}\text{FeO}\text{--}\text{SiO}_2$ oxide on a coke bed of 1–2 mm in diameter was investigated. We observed the change in the shape of the oxide tablet, the formation of the liquid droplet, and the permeation into the coke bed with increasing temperature under a CO/CO_2 atmosphere; the following conclusions were drawn:

(1) The measured softening temperature was 20–70°C higher than the calculated solidus temperature. Since the reaction occurs between a solid and a solid at a heating rate of 5°C/min, the formation of the liquid phase occurs in non-equilibrium conditions.

(2) The deformation of the oxide tablets following softening is strongly affected by the liquid phase ratio.

(3) There is no direct relationship between the formation of the oxide droplet and its permeation into the coke bed within the experimental condition.

(4) The permeation of the droplet depends on the wettability of the oxide melt and the coke, and it is affected by the initial composition of the oxide.

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