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Trial on the Application of Capillary Phenomenon of Solid CaO to Desulfurization of Liquid Fe

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In order to carry out the de-sulfurization of liquid Fe, solid CaO is usually used as a flux, but some of solid CaO particles are not melted into molten slag, and all CaO are not always used for the refining. We have investigated how to use the solid CaO directly and efficiently for the above refining processes. Solid CaO particles have small capillary tubes from their surface to inside. When a molten slag is wetted with solid CaO, the molten slag containing some impurities such as CaS and P_2O_5 is expected to penetrate into those capillary tubes. Although chemical reactions in solid phase are generally believed to be very slow due to slow diffusion in solid phase, those impurities are absorbed in solid CaO rapidly by capillary force and they are removed from molten steels. We named this refining process as Capillary Refining. In the present paper, we have tried to apply capillary refining to de-sulfurization of liquid Fe and carbon-saturated liquid Fe by using molten CaO– Al_2O_3 and CaO– SiO_2 –MgO– Al_2O_3 slags.

KEY WORDS: refining; desulfurization; capillary; molten slag.

1. Introduction

Recycling of slag generated as a by-product from the iron and steelmaking processes has become a subject of great interest. Although much of the slag is recycled for civil engineering products, concrete, *etc.*, significant attempts are being made to reduce the amount of slag generated from the iron and steelmaking processes.^{1,2)} Reduction of the large amounts of slag produced in the iron and steelmaking industry is especially critical.³⁾ Increasing the efficiency of the chemical reaction of CaO, which is used as a refining additive for desulfurization and dephosphorization in hot metal processing, should result in a reduction in slag mass produced. Since the reaction between solid and liquid phases is controlled by the diffusion of reaction products in the solid phase from the phase interface, as occurs when solid CaO is used for desulfurization and dephosphorization, the reaction rate is generally slow. For this reason, a liquid flux containing CaO as one of the components has been used for the above processing. CaO is added to the flux to increase its basicity, which further improves its effectiveness for desulfurization and dephosphorization. However, this may lead to some CaO remaining in the solid phase, resulting in an increase in slag volume and a possible decrease in reaction efficiency. In addition, the use of CaF_2 for producing liquid flux of high basicity has been limited due to environmental issues.³⁾ A new approach is therefore required for desulfurization and dephosphoriza-

tion in hot metal processing using pure solid CaO. Tanaka *et al.* proposed a method involving the use of small capillary tubes in solid CaO, which has been named “capillary refining”.⁴⁾ Capillary refining applied to desulfurization in hot metal processing should result in a higher efficiency in solid CaO usage. In this work, we investigate the possibility of capillary refining for the desulfurization of liquid iron or carbon-saturated iron alloys. Fundamental experiments have been carried out to elucidate certain factors such as the microstructure of solid CaO and the selection of a molten slag that can coexist with solid CaO in the capillary refining application.

2. Principle of Capillary Refining

When a porous material is dipped into a liquid phase, the liquid penetrates spontaneously into its capillary tubes, known as capillary penetration. Impurities present in the liquid phase can also be expected to penetrate into the capillaries with the liquid phase. If the impurities react with the liquid phase or porous solid material, they can be removed from the liquid phase and become fixed on the surface of the porous structure. The burning of $CaCO_3$ results in the production of CaO with porous internal structure and many capillary tubes. If a liquid phase containing phosphorus and sulfur penetrates into those capillary tubes, highly effective desulfurization and dephosphorization could be achieved. In particular, capillary penetration occurs rapidly with a liq-

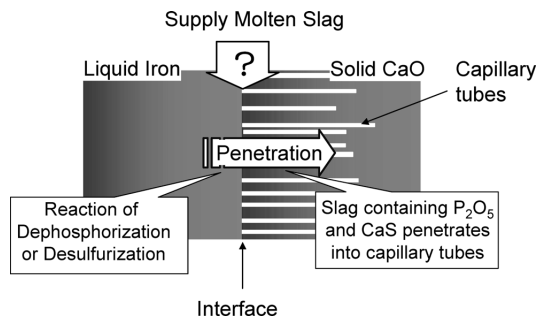


Fig. 1. Concept of capillary refining.

uid phase with low viscosity and high surface tension and so the reaction does not always depend on the diffusion of species into the solid phase.

Figure 1 shows the concept of capillary refining. Since capillary refining requires capillary penetration, the solid CaO must be wet with a liquid phase; however, solid CaO is generally not wet with liquid iron, especially not a carbon-saturated liquid iron. Therefore, a molten oxide phase should be placed between the solid CaO and liquid iron alloy to transport phosphorus and sulfur from the liquid iron alloy into the capillary tubes to be fixed on the solid CaO porous structure surface. Since the molten oxide phase is not only able to remove the sulfur and phosphorus but when it coexists with solid CaO, the activity of CaO in the molten oxide phase is maintained at a constant high value, giving it a high desulfurization capacity.

3. Experimental

3.1. Formation of Solid CaO

Capillary refining utilizes capillary penetration, and the porous CaO structure affects the efficiency of this process. Three kinds of solid CaO were used in the experiments: soft-burned CaO, hard-burned CaO and medium-burned CaO. The small pores in soft-burned CaO are produced from the removal of CO_2 gas after burning CaCO_3 . Soft-burned CaO is most often used in industrial processes. Hard-burned CaO is produced from burning CaCO_3 for a longer period of time at higher temperature than soft-burned CaO. Small pores in the CaO decrease in size and only relatively large pores remain. To produce CaO for this work, CaCO_3 was burned for: 1) 3 h at 950°C (soft-burned), 2) 5 h at 1250°C (hard-burned), and 3) 1 h at 1200°C in a graphite crucible. The solid CaO microstructure was studied by SEM.

3.2. Desulfurization Using Molten Calcium Aluminate

Desulfurization was carried out for a liquid iron alloy droplet placed on a thin molten calcium aluminate layer formed on solid CaO using the experimental furnace shown in **Fig. 2**. A graphite crucible used as heating element is placed in the center of the furnace. Molten calcium aluminate was formed by coating the surface of a CaO specimen ($10\text{ mm} \times 10\text{ mm} \times 10\text{ mm}$) placed in a CaO crucible with alumina powder, heating the specimen to 1500°C for approximately 100 min, and maintaining at that temperature for 90 min to produce calcium aluminate. Approximately 1–2 g carbon-saturated Fe–0.2 mass% S alloy was placed on

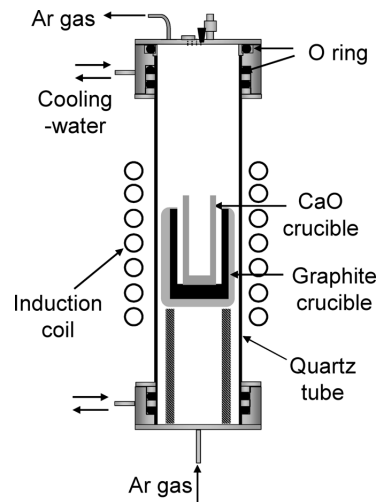


Fig. 2. Schematic diagram of the induction furnace.

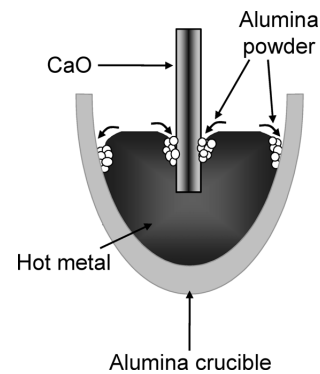


Fig. 3. Reaction of CaO with Al_2O_3 powders at the meniscus on liquid iron specimen.

the solid calcium aluminate-coated CaO at 1500°C for 30 min under Ar gas atmosphere, resulting in the desulfurization reaction. The specimen microstructure was examined using SEM, and the distribution of elements measured by EDX. The sulfur content in the iron alloys was analyzed by infrared absorption.

Desulfurization by capillary refining was carried out using a method in which calcium aluminate formation and desulfurization occur simultaneously. The furnace in **Fig. 2** and an alumina crucible instead of the CaO crucible were used, and the experiment was conducted at 1450°C under Ar atmosphere. The iron specimen (0.2 mass% S) was made by mixing carbon-saturated iron and FeS. Approximately 100 g of iron alloy was melted with alumina powder in an alumina crucible as shown in **Fig. 3**. The alumina powders were floated on the surface of liquid iron, and the CaO block ($5\text{ mm} \times 10\text{ mm} \times 50\text{ mm}$) was then dipped into the liquid iron alloy. The alumina powders gathered at the meniscus between the liquid iron alloy and the solid CaO block, and calcium aluminate formation and the accompanying desulfurization reaction occurred simultaneously. After immersion for 5 min, the CaO block was removed, and the microstructure and elemental distribution of the specimens studied by SEM and EDX.

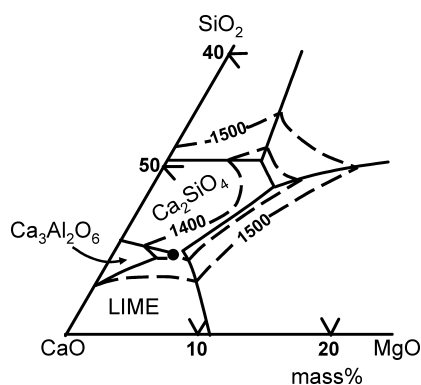


Fig. 4. Part of phase diagram in SiO_2 -CaO-MgO-35mass% Al_2O_3 system.

Table 1. Chemical composition of molten SiO_2 -CaO-MgO- Al_2O_3 slag equilibrated with solid CaO.

	SiO_2	CaO	MgO	Al_2O_3
mass%	7.4	52.7	4.9	35.0

3.3. Desulfurization Using Molten SiO_2 -CaO-MgO- Al_2O_3 Slag Equilibrated with Solid CaO

Iwase *et al.*⁶⁾ reported that the molten SiO_2 -CaO-MgO- Al_2O_3 slag is equilibrated with the solid CaO phase. Figure 4 shows part of the phase diagram in a quasi-ternary system of SiO_2 -CaO-MgO with 35 mass% Al_2O_3 . The point indicated with a circle in Fig. 4 shows the composition of molten slag coexisting with solid CaO at 1400–1450°C. This molten slag has been reported to have high sulfide capacity⁶⁾ and low viscosity,⁷⁾ which are suitable conditions for capillary refining.

An experiment was carried out to confirm the penetration of molten slag (chemical composition given in Table 1) into solid CaO. Molten slag was made by melting a mixture of SiO_2 , CaCO_3 , MgO and Al_2O_3 powders in a Pt crucible at 1600°C for 3 h to adjust the composition to the values in Table 1. The temperature was decreased to 1450°C, and part of the CaO block was dipped into molten slag for 60 s before being removed. The microstructure and distribution of elements in the specimens were studied by SEM and EDX.

A second desulfurization experiment was conducted using the molten SiO_2 -CaO-MgO with 35 mass% Al_2O_3 slag in the furnace in Fig. 2 at 1450°C under an Ar gas atmosphere. Slag powder (5 g, chemical composition in Table 1) was melted on the surface of carbon-saturated liquid iron with 0.1 mass% S (80 g) in a graphite crucible at 1450°C for 30 min. Part of a CaO block was dipped into the molten slag for 30 min before being removed. The microstructure and elemental distribution were investigated by SEM and EDX.

4. Experimental Results and Discussion

4.1. Structure of Three Types of Solid CaO

Figures 5–7 show SEM micrographs of the fracture surface of the three types of solid CaO used in this experiment. As shown in Fig. 5, CaO produced by burning CaCO_3 at 950°C for 3 h has 2–3 μm micropores at the CaO particle boundaries as well as micropores under 0.1 μm in

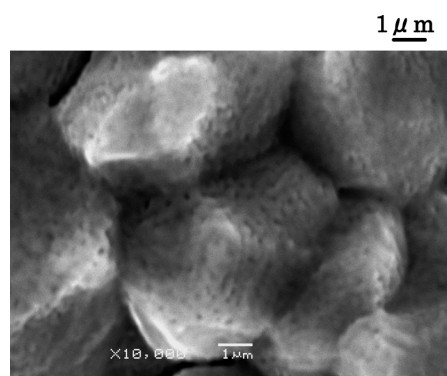


Fig. 5. Fracture surface of CaO after burning CaCO_3 at 950°C for 3 h.

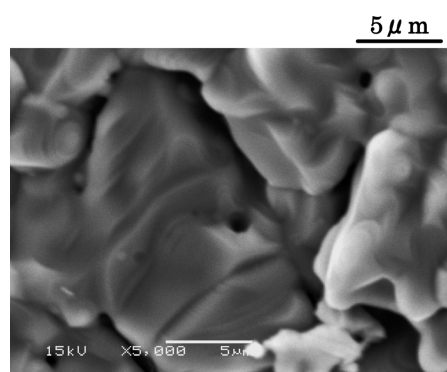


Fig. 6. Fracture surface of CaO after burning CaCO_3 at 1250°C for 5 h.

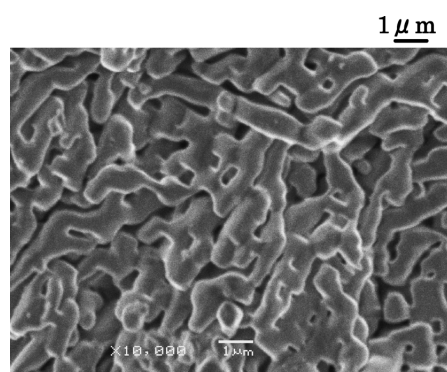


Fig. 7. Fracture surface of CaO after burning CaCO_3 at 1200°C for 1 h.

each CaO particle. Figure 6 shows the CaO microstructure produced by burning CaCO_3 at 1250°C for 5 h. The CaO has pores 5–10 μm in size as a result of the shrinkage of smaller pores during heating. This CaO can be classified as hard-burned CaO. As shown in Fig. 7, CaO made by burning CaCO_3 at 1200°C for 1 h in a graphite crucible has an interconnected microporous structure. This structure might occur from reacting some impurities in CaCO_3 with species contained in graphite, but we could not explain the detailed mechanism that forms this microstructure. This phenomenon should be studied in future in order to be able to control the microporous structure.

4.2. Desulfurization Using Molten Calcium Aluminate

A high rate of desulfurization (70–90%) was achieved when molten calcium aluminate slag was formed after coating the solid CaO surface with alumina powder. Figure 8

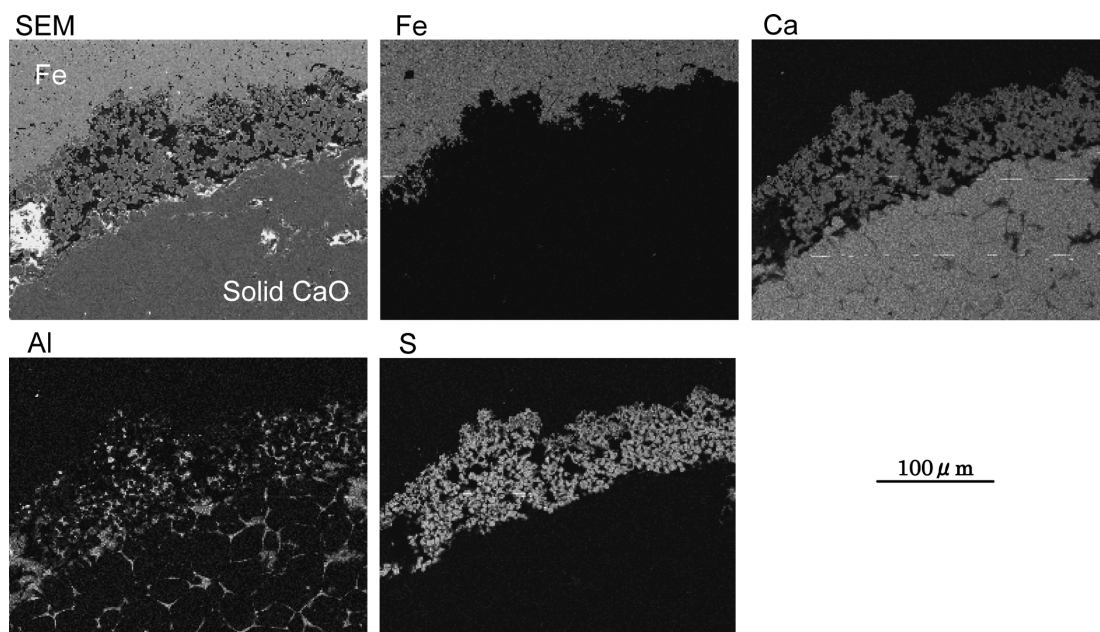


Fig. 8. SEM image and EDX mapping at the interface between CaO and liquid Fe after an experiment of desulfurization using molten calcium aluminate.

Table 2. EDX analysis of the chemical composition at interface layer between CaO and liquid Fe in Fig. 8.

	Ca	Al	S	Fe
at%	49.2	5.2	44.5	1.1

Table 3. EDX analysis of the chemical composition at network structures that appeared in Al EDX mapping of Fig. 8.

	Ca	Al	S
at%	63.4	33.8	2.7

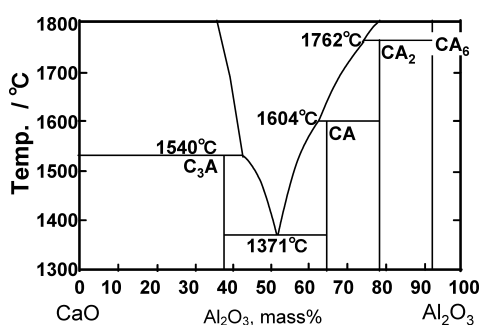


Fig. 9. Phase diagram in CaO–Al₂O₃ binary system.

shows the microstructure of the cross-section at the interface between the solid CaO and liquid iron. As shown in Fig. 8, a layer 50–100 μm thick existed where Al and S were concentrated at the interface between solid CaO and liquid iron. The chemical composition of this layer given in Table 2 shows that it contains calcium aluminate and CaS because the sulfur content is approximately 45%. The chemical composition of the network structures that appeared from the EDX mapping of Al in Fig. 8 is given in Table 3. As shown in this table, sulfur does not exist in the solid CaO network structure and the Ca content is higher than the Al content. From the CaO–Al₂O₃ binary system phase diagram in Fig. 9, the molten calcium aluminate phase with low

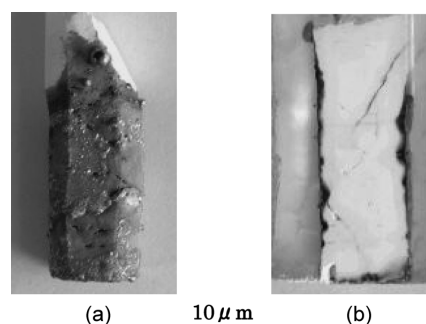


Fig. 10. (a) External appearance and (b) cross-section of soft burned CaO after desulfurization using molten calcium aluminate.

melting point is formed at around 1 500°C with a composition of approximately Ca : Al = 1 : 1. As molten slag penetrates into the solid CaO porous structure, the CaO content in the slag is expected to increase. When the CaO content in the molten calcium aluminate increases, 3CaOAl₂O₃ with high melting point is precipitated in the capillary tubes. Since the melting point of this 3CaOAl₂O₃ is 1 540°C, the calcium aluminate in the solid CaO capillary tubes solidifies or forms a solid–liquid phase, which disturbs further molten slag penetration. In particular, before desulfurization, calcium aluminate may have already formed on the CaO surface when penetration of the molten slag occurred. To allow sulfur to penetrate into the solid CaO, it is desirable that molten calcium aluminate penetration occurs simultaneously with desulfurization.

Figure 10 shows an example of the external appearance and cross-section of a soft-burned CaO block used in the experiment in which molten calcium aluminate penetration and desulfurization occur simultaneously. The external block color changed where the block was dipped into the liquid iron alloy. In cross-section, a black section approximately 1 mm thick was visible inside the solid CaO near the interface between the CaO and liquid iron. Figure 11 shows the SEM image and EDX mapping at the interface

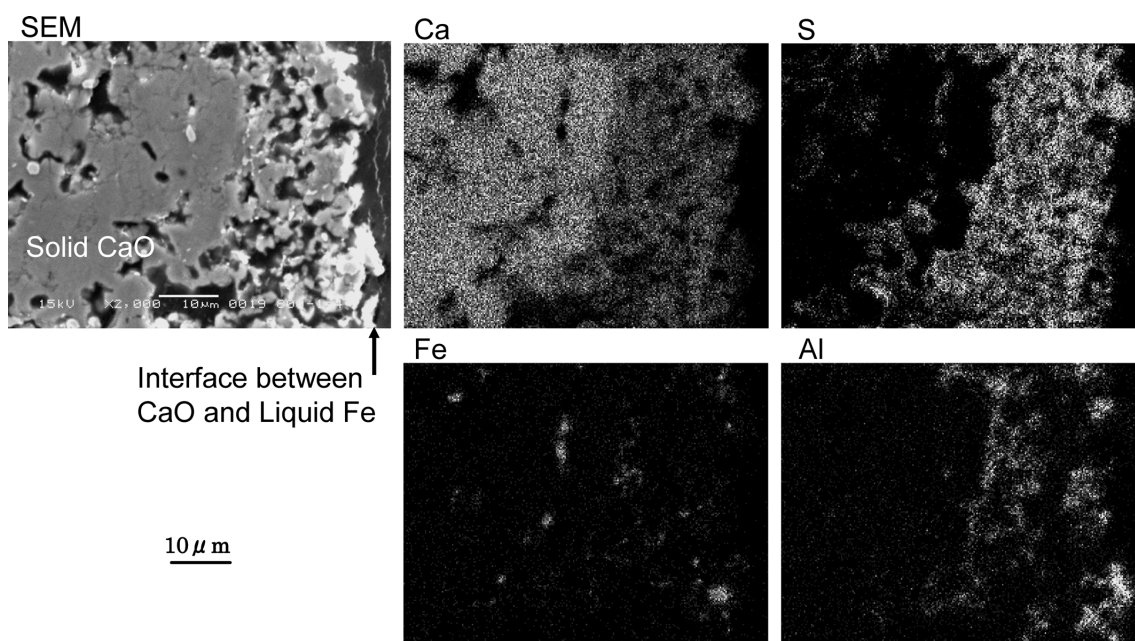


Fig. 11. SEM image and EDX mapping at the interface between CaO and liquid Fe in soft burned CaO after desulfurization using molten calcium aluminate.

Table 4. EDX analysis of the chemical composition at interface layer between CaO and liquid Fe in Fig. 11.

	Ca	Al	S	Fe
at%	47.6	5.2	39.7	7.5

between the solid CaO and liquid Fe. The right hand side in Fig. 11 shows the interface and a 20–50 μm thick layer in which Al and S were concentrated (chemical composition in Table 4). The sulfur content is approximately 40% indicating that this layer consists mainly of CaS while the amount of calcium aluminate is low because the Al content is only 5.2%. Thus, molten calcium aluminate promotes the desulfurization reaction under current experimental conditions, but molten slag penetration into the solid CaO was not accompanied by sulfur because the amount of calcium aluminate formed was small. Even if a large amount of calcium aluminate is formed that could penetrate into the solid CaO, part of the molten calcium aluminate solidifies to $3\text{CaOAl}_2\text{O}_3$, which may prevent further penetration as described above. To ensure slag penetration, molten slag equilibrated directly with a pure solid CaO phase should be used.

4.3. Desulfurization Using Molten $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ Slag Equilibrated with Solid CaO

As shown in Fig. 9, molten calcium aluminate can coexist with pure solid CaO in a $\text{CaO-Al}_2\text{O}_3$ binary system. To test another candidate molten slag that can be equilibrated with pure solid CaO below 1500°C, we investigated molten $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ slag, which Iwase *et al.* reported to have high sulfide capacity.

Figure 12 shows the external appearance of the solid CaO block used for desulfurization with molten $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ slag. Arrows in Fig. 12(a) soft-burned CaO, Fig. 12(b) hard-burned CaO and Fig. 12(c) medium-burned CaO indicate the surface position where the CaO block was immersed into the molten slag. It can be con-

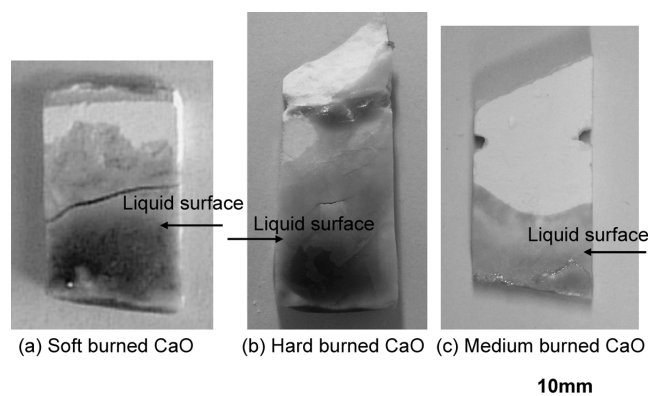


Fig. 12. External appearance of solid CaO after immersion test with molten $\text{SiO}_2\text{-CaO-MgO-35mass}\%\text{Al}_2\text{O}_3$ slag.

firmed that the molten slag penetrated rapidly into the CaO block above the slag surface level to a depth of 5 mm over 60 s. Figure 13 shows the SEM image of a cross-section of solid CaO after the penetration of molten slag. In Fig. 13(a), the molten slag was found at the boundaries between CaO particles in the soft-burned CaO. In Fig. 13(b) for hard-burned CaO, the molten slag which appears black in color penetrated into the boundary layer between the CaO particles resulting in a gray color. Since CaO growth and pore shrinkage was promoted in hard-burned CaO, we could not see many interfaces between the molten slag and CaO particles. In Fig. 13(c) for medium-burned CaO, some interconnected pores remained in the CaO, but a large volume of molten slag penetrated into the solid CaO. Since it is necessary to use the pore surface as much as possible for the reaction, hard-burned CaO, which does not have much surface area, is not adequate for capillary refining.

The formation of CO gas accompanying the desulfurization reaction indicated in Eq. (1) was observed immediately after melting the $\text{SiO}_2\text{-CaO-NgO-Al}_2\text{O}_3$ slag.



In Eq. (1), S and C are sulfur and carbon in the liquid iron alloy, and CaO, CaS and CO(g) are CaO and CaS in the molten slag and CO gas, respectively.

The formation of CO gas gradually decreased 5–10 min after melting of the SiO₂–CaO–MgO–Al₂O₃ slag, and finally the formation rate became constant. This occurs because of desulfurization when the CaO block was immersed into molten slag and the concentration of CaO in molten slag was changed to the composition that coexisted with pure solid CaO. **Figure 14** shows an example of the external appearance and cross-section of soft-burned CaO after desulfurization. The bottom section of the CaO block, which appears rounded in shape in Fig. 14, was dipped into the molten slag. Arrows in Fig. 14 indicate the surface position of the molten slag when the block was immersed in the slag. It can be confirmed that the molten slag penetrated up to the position above the molten slag surface. The cross-section shows the penetration of molten slag into the whole solid CaO portion. **Figure 15** shows the SEM image and EDX mapping at the molten slag penetration front into the soft-burned CaO. The slag penetrated into the CaO up to

the position indicated by the white curves in Fig. 15, which is further confirmed by the EDX mapping of Al, Mg and Si. Furthermore, sulfur also exists in the same area, indicating

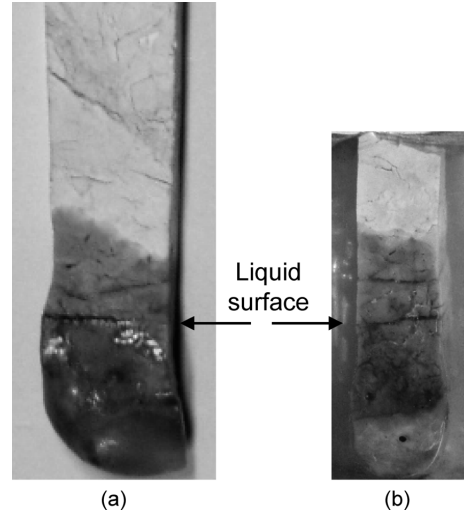


Fig. 14. (a) External appearance and (b) cross-section of soft burned CaO after desulfurization using molten SiO₂–CaO–MgO–Al₂O₃ molten slag.

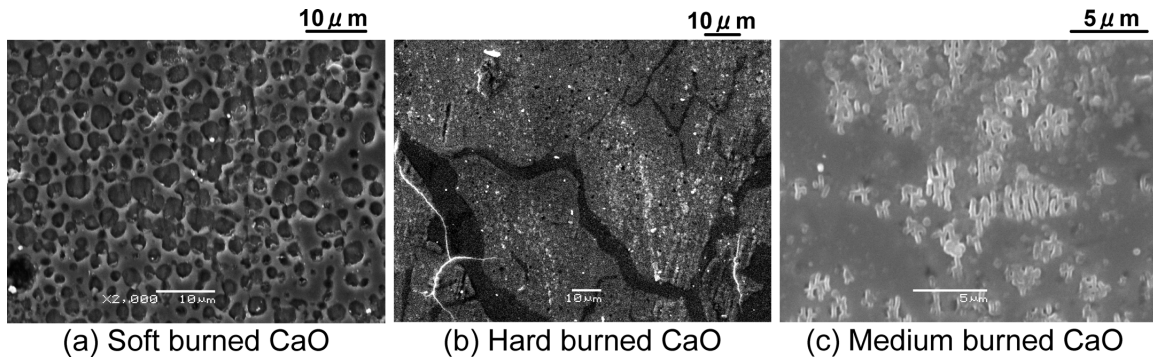


Fig. 13. SEM images of cross-section of solid CaO after immersion test with molten SiO₂–CaO–MgO–35mass%Al₂O₃ slag.

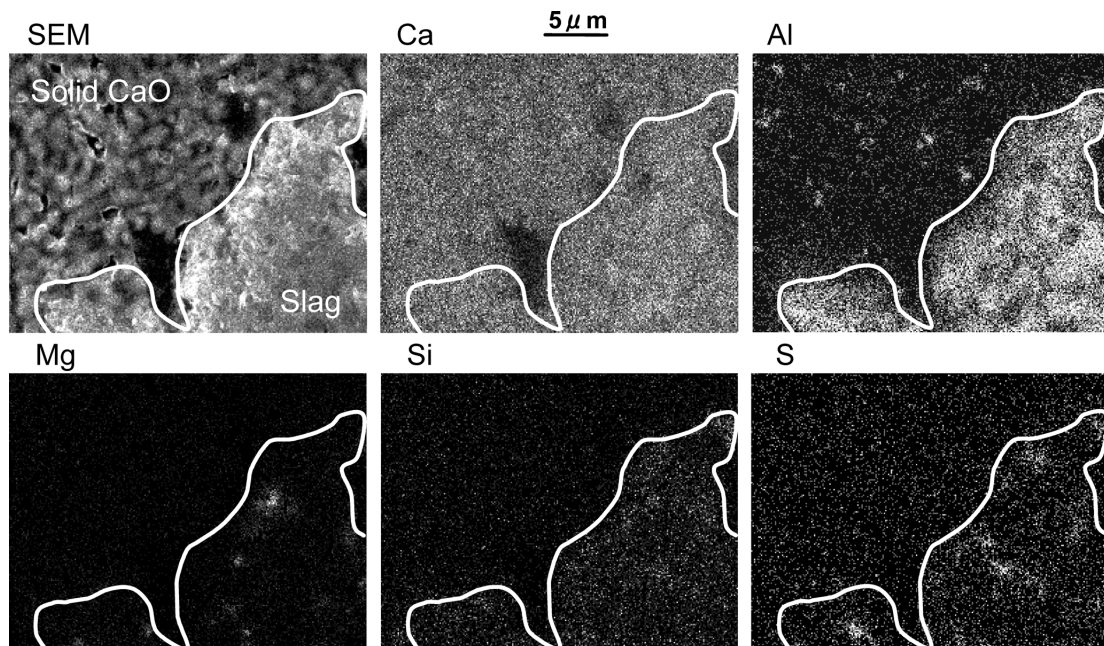


Fig. 15. SEM image and EDX mapping at the molten SiO₂–CaO–MgO–Al₂O₃ slag penetration front in solid CaO after desulfurization.

that sulfur was transported with the molten slag up to the front. Thus, it was possible to carry out capillary refining for desulfurization even under 1500°C using molten SiO₂-CaO-MgO-Al₂O₃ slag equilibrated with a pure solid CaO phase.

5. Conclusion

The authors carried out fundamental experiments to investigate the possibility of capillary refining for the desulfurization of liquid iron and carbon-saturated iron alloys with solid CaO. The results obtained were as follows:

(1) Molten slag penetration into solid CaO was disturbed by the formation of a solid calcium aluminate compound in the capillary tubes of solid CaO when molten calcium aluminate slag in the CaO-Al₂O₃ binary system under 1500°C was used in capillary refining. Thus, molten slag equilibrated with a pure solid CaO phase should be used for the penetration of molten slag with sulfur into solid CaO.

(2) Molten SiO₂-CaO-MgO-35mass%Al₂O₃ slag penetrated rapidly into solid CaO.

(3) In the desulfurization experiment using molten SiO₂-CaO-MgO-35mass%Al₂O₃ slag equilibrated with a pure solid CaO phase, the molten slag with sulfur penetrated into the solid CaO at 1450°C. It was possible to carry out capillary refining for the desulfurization of liquid iron alloys using solid CaO.

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