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Trial of capillary refining by porous CaO with molten slag

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Abstract

The authors have investigated how to use solid CaO directly and efficiently for the desulphurisation or dephosphorisation of liquid Fe. Solid CaO particles have small capillary tubes from their surface to inside. If a molten slag is generated between solid CaO and liquid Fe, 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 the solid phase are generally believed to be very slow due to slow diffusion in the solid phase, those impurities are rapidly absorbed in solid CaO by capillary force and they are removed from liquid Fe. We named this refining process capillary refining. In this paper, our trial is described to apply capillary refining to desulphurisation of liquid Fe and carbon-saturated liquid Fe by using molten $CaO-Al_2O_3$ and $CaO-SiO_2$ based slags.

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, such as concrete, significant attempts are being made to reduce the amount of slag generated from the iron and steelmaking processes. Here, the increase of the efficiency for the chemical reaction with CaO, which is used as a refining additive for desulphurisation and dephosphorisation in steelmaking processing, should result in a reduction in slag mass produced. Since the reaction with solid phases is controlled by the diffusion of reaction products in the solid phase, as occurs when solid CaO is used for desulphurisation and dephosphorisation, 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 usually added to the flux to increase its basicity, which further improves its effectiveness for desulphurisation and dephosphorisation. 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 a liquid flux of high basicity has been limited due to environmental issues. To cope with the above problems, the authors proposed a new approach involving the use of small

capillary tubes in solid CaO, which has been named “Capillary Refining”.^{1,2} Capillary refining applied to desulphurisation and dephosphorisation in steelmaking processing should result in a higher efficiency in solid CaO usage.

In this paper, the concept of capillary refining is explained and the possibility of capillary refining is discussed for the desulphurisation of liquid iron or carbon-saturated iron alloys. Fundamental experimental results are shown to elucidate certain factors such as the microstructure of solid CaO and the selection of a molten slag that can co-exist with solid CaO in the capillary refining application.

Fundamental principle of capillary refining

When a porous material is dipped into a liquid phase and the material is wetted by the liquid, 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 in the liquid phase react with the 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 or Ca(OH)_2 etc. results in the production of CaO with porous internal structure and many capillary tubes. If a liquid phase containing phosphorus and sulphur penetrates into those capillary tubes, highly effective desulphurisation and dephosphorisation could be achieved. In particular, capillary penetration occurs rapidly with a liquid 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 fundamental concept of capillary refining. Since capillary refining requires capillary penetration, the solid CaO must be wetted by a liquid phase;

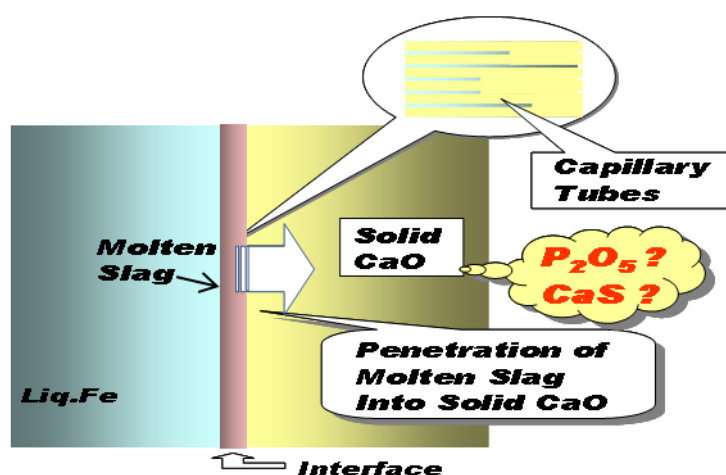


Figure 1 : Concept of Capillary Refining

however, solid CaO is generally not wetted by 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 sulphur 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 sulphur and phosphorus but when it co-exists with solid CaO, the activity of CaO in the molten oxide phase is maintained at a constant high value, giving it a high desulphurisation or dephosphorisation capacity. In addition, the gradient of concentrations of sulphur or phosphorus is expected to exist from the interface with liquid Fe toward the centre of porous CaO to prevent the reactions from reaching a final equilibrium state and to keep stationary reactions of De-P and De-S.

Formation of solid porous CaO

Capillary refining utilises capillary penetration, and the porous CaO structure affects the efficiency of this process. Three kinds of solid CaO have been used in our experiments: soft-burned CaO and medium-burned CaO from CaCO_3 as well as CaO from Ca(OH)_2 . The small pores in soft-burned CaO are produced from the removal of CO_2 gas after calcining CaCO_3 . Soft-burned CaO is most often used in industrial processes. Hard-burned CaO is also used in industrial processes and it is produced from calcining CaCO_3 for a longer period of time at higher temperature than soft-burned CaO, resulting in a decrease in small pores in the CaO leaving only relatively large pores. To produce CaO for our work, CaCO_3 was calcined for 3 h at 950°C (soft-burned), and 1 h at 1200°C in a graphite crucible (medium-burned). In addition, we have tried to make porous CaO by burning Ca(OH)_2 fine powders mixed with starch.

The solid CaO microstructure was studied using SEM. Figure 2 shows SEM micrographs of the fracture surface of the three types of solid CaO used in our experiments. As shown in Fig. 2(a), CaO produced by burning CaCO_3 at 950°C for 3 h has 2–3 μm micro-pores at the CaO particle boundaries as well as micro-pores under 0.1 μm in each CaO particle. As shown in Fig. 2(b), 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 the reaction of some impurities in CaCO_3 with species contained in graphite although we could not explain the detailed mechanism that forms this microstructure. Figure 2(c) shows the microstructure of porous CaO made by burning Ca(OH)_2 mixed with starch. At low temperature, the starch vaporises to leave pores. In this work, we have mainly used porous CaO obtained in (b) and (c) conditions.

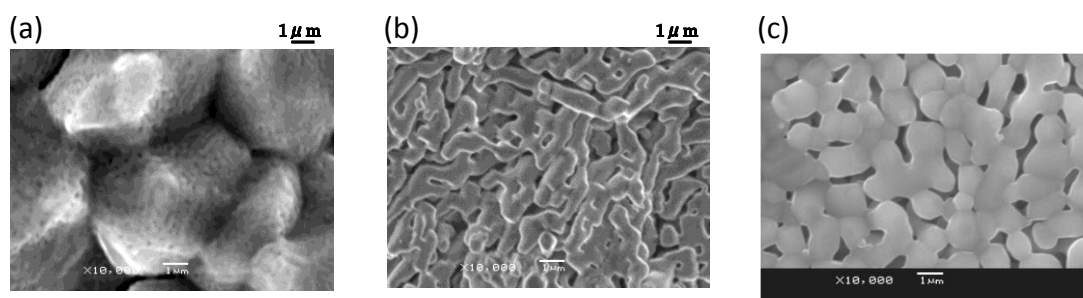


Figure 2 : Microstructures of soft-burned CaO (a), medium-burned CaO (b) and CaO made by burning $\text{Ca}(\text{OH})_2$ (c)

Capillary refining for De-S by CaO-SiO₂ based flux

In an experiment on the application of capillary refining to desulphurise liquid iron alloys, we used molten CaO-SiO₂-MgO-35wt% Al₂O₃ slag, which is equilibrated with solid CaO at around 1723 K as shown in Fig. 3 and has been reported as having high sulphide capacity by Hayakawa *et al.*³ and low viscosity by Nakamoto *et al.*⁴. In the present work, we have conducted the desulphurisation of carbon-saturated liquid Fe by capillary refining as follows: The iron specimen saturated with carbon containing sulphur was melted in a graphite crucible. After CaO-SiO₂-MgO-35% Al₂O₃ slag was melted on the surface of the liquid iron, a solid CaO block with porous structure was connected to the molten slag for a period to absorb the molten slag containing S into the capillary pores in solid CaO. The solid CaO containing molten slag with CaS was then removed from the molten slag, and the cross-section of the CaO specimen was observed with an electron probe micro-analyser.

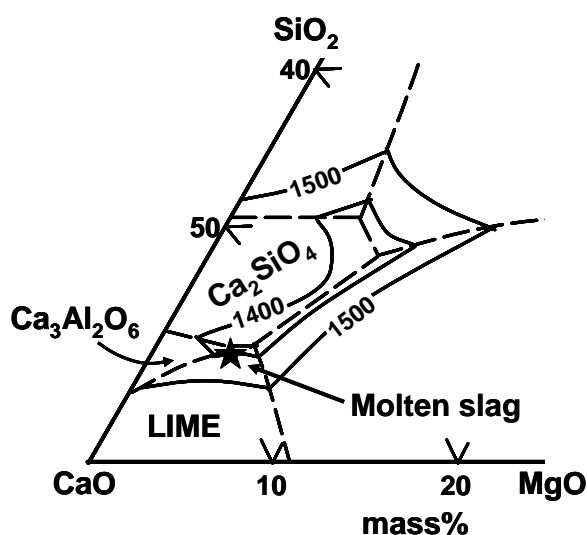


Figure 3 : Phase diagram⁴ of CaO-SiO₂-MgO-35%Al₂O₃.

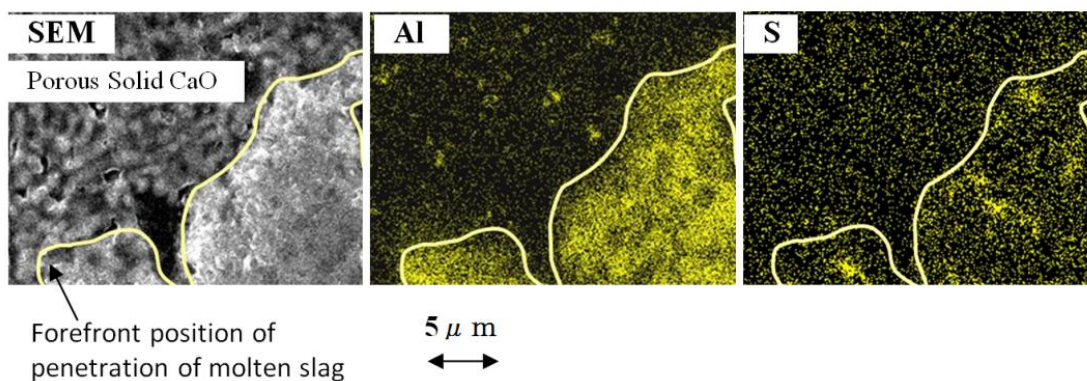


Figure 4 : Experimental results for the penetration of molten slag containing CaS into solid CaO with porous microstructure.

Figure 4 shows an example of the experimental results for the application of capillary refining with porous CaO in Fig. 2(b) to the De-S of carbon-saturated liquid Fe at 1723 K.² It is found from Fig. 4 that molten slag with CaS reached the forefront position of the penetration area in solid CaO after the molten slag penetrated a few mm into the porous solid CaO block. Thus, we can carry out capillary refining for the De-S of carbon-saturated liquid Fe using solid CaO with adequate porous structure.

Capillary refining for De-S by CaO-Al₂O₃ flux

In this section, we describe our trials on capillary refining for desulphurisation of liquid Fe by using CaO-Al₂O₃ based flux. As shown in CaO-Al₂O₃ binary phase diagram in Fig. 5, solid CaO is equilibrated with CaO-Al₂O₃ liquid phase above 1540°C.

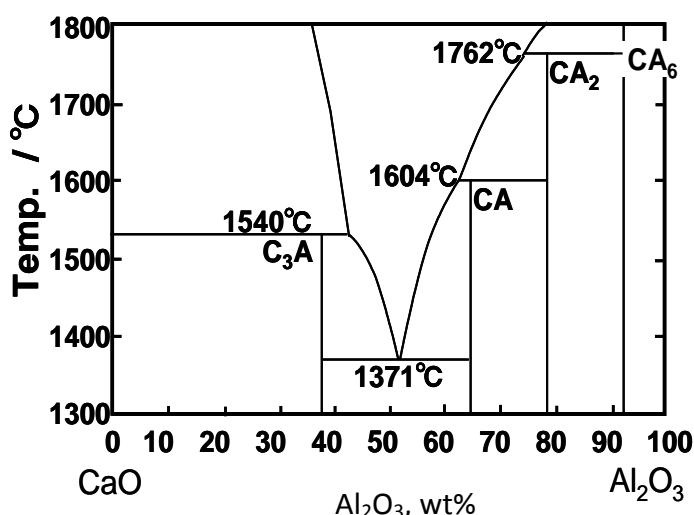


Figure 5 : Phase Diagram of CaO –Al₂O₃ Binary System.

Thus, the capillary refining by using $\text{CaO-Al}_2\text{O}_3$ flux cannot be applied below this temperature because a $2\text{CaO} \cdot \text{Al}_2\text{O}_3 (\text{C}_3\text{A})$ layer will form to clog the pores in solid CaO when solid CaO is attached with liquid $\text{CaO-Al}_2\text{O}_3$ flux. The capillary refining for desulphurisation of liquid Fe by using a $\text{CaO-Al}_2\text{O}_3$ based flux has been carried out in the following three ways:

Method 1

To immerse a porous CaO block into liquid Fe , on which Al_2O_3 powders float as shown in Fig. 6, to make a $\text{CaO-Al}_2\text{O}_3$ liquid phase when those powders contact with the CaO block at the meniscus.

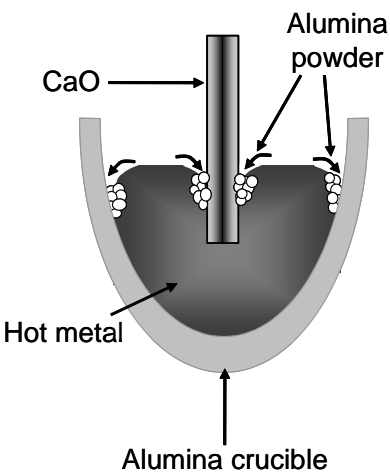


Figure 6 : Procedure for making $\text{CaO-Al}_2\text{O}_3$ flux by immersing porous CaO with Al_2O_3 powders floating on Liquid Fe .

Method 2

To immerse a porous CaO block coated with Al_2O_3 powders into liquid Fe as shown in Fig. 7.

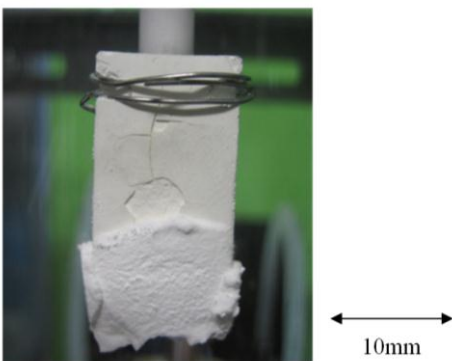


Figure 7 : Appearance of Porous CaO block coated with Al_2O_3 powders

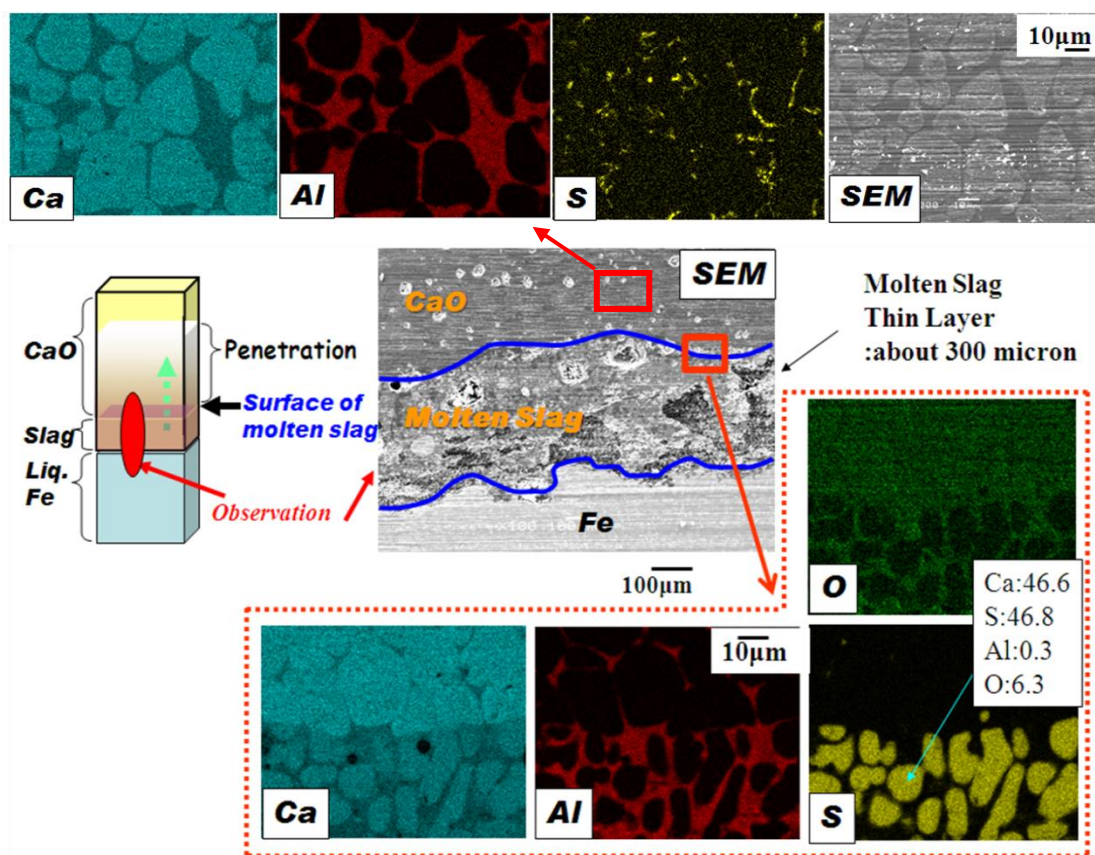


Figure 8 : An example of capillary refining by using CaO-Al₂O₃ flux in method 3

Method 3

To immerse porous CaO into liquid Fe, in which Al is added in advance to deoxidise the steel and to make Al₂O₃.

Figure 8 shows one example on the capillary refining for desulphurisation by using CaO-Al₂O₃ flux in method 3. These EDX results indicate the distribution of Ca, Al, S and O in a thin molten oxide layer formed between solid CaO and liquid Fe. This thin layer was formed by CaO with Al₂O₃ generated by the deoxidising reaction. The upper section in Fig. 8 show that molten slag with sulphur penetrates into the pores in porous CaO. As shown in these figures, even a thin layer of molten flux around CaO works for desulphurisation, and pores in porous solid CaO also contribute to desulphurisation by absorbing sulphur. On the other hand, the efficiency of desulphurisation from liquid Fe by this technique has not been measured yet in this fundamental experiment, which focused on the microscopic interfacial phenomena.

Conclusions

The authors carried out some fundamental experiments to investigate the possibility of capillary refining for the desulphurisation of liquid iron with solid porous CaO. In the desulphurisation experiment using molten $\text{SiO}_2\text{-CaO-MgO-35wt\% Al}_2\text{O}_3$ slag equilibrated with a pure solid CaO phase, the molten slag containing sulphur penetrated into the solid CaO. The CaO- Al_2O_3 based flux can be used to do the capillary refining for the desulphurisation of liquid iron beyond 1540°C. Thus, it was possible to carry out capillary refining for the desulphurisation of liquid iron alloys using solid porous CaO, although we have not determined yet which porous CaO in Fig. 2 is the most adequate type for the capillary refining. The authors have already reported the application of the capillary refining for dephosphorisation of liquid Fe in Ref.¹

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