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Application of Capillarity of Solid CaO to Dephosphorization of Hot Metals

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The penetration behavior of molten slag in solid CaO has been observed when liquid iron alloy containing phosphorus was oxidized by air or oxygen in CaO crucible. It was found from the present experiment that the phosphate was absorbed in the porosities of solid CaO accompanying the penetration of molten FeO slag when the carbon-saturated liquid iron alloy was oxidized at localized position. The phosphate is found to be fixed as $4\text{CaOP}_2\text{O}_5$ from X-ray diffraction. Since the penetration can be evaluated theoretically to proceed much faster than the penetration rate obtained from the experimental results, the oxidation process of liquid iron alloy is considered to be the rate-determining step for the total reaction rate of the dephosphorization process using the capillarity of solid CaO. The application of the capillary phenomena to the dephosphorization of hot metal by solid CaO may be one of the useful engineering processes although the adequate oxidation procedures have to be considered.

KEY WORDS: Fe-C-P alloy, penetration, molten slag, capillary phenomena, $4\text{CaOP}_2\text{O}_5$

1. Introduction

There have been a lot of research work to pursue high efficient dephosphorization procedures of hot metals so far in order to reduce the amount of molten slags in steelmaking processes by providing minimum amount of highly reactive dephosphorization fluxes. Although many investigations have been carried out on the dephosphorization of hot metals by solid CaO from the view points of thermodynamics and kinetics, the present authors have paid attention to the interfacial phenomena related to the dephosphorization of liquid iron alloys by solid CaO. One of the major interfacial phenomena between liquid and solid phases is a penetration of liquid into small porosity in solid, in other words, capillary phenomena. When solid surface is wetted with liquid, the liquid is absorbed in small capillary tubes quickly. Since molten FeO slag has been known to have good wettability with solid CaO, the penetration of molten FeO slag in solid CaO has been investigated in various field of iron and steel making processes such as sintering process¹⁾, damage of refractory blocks by molten slags^{2,3)} and so on. For example, Troemel et al.^{4,5)} began to study the physicochemical phenomena concerning the contacts among solid CaO, molten slags and hot metals in 1950s.

Thus, when the hot metal containing phosphorus is oxidized near the surface of solid CaO for the dephosphorization and then molten FeO base slag is formed, the

molten slag penetrates into small porosities of solid CaO as shown in Fig.1. In this process, we should understand the behavior of the phosphate accompanying the penetration of molten FeO slag into solid CaO.

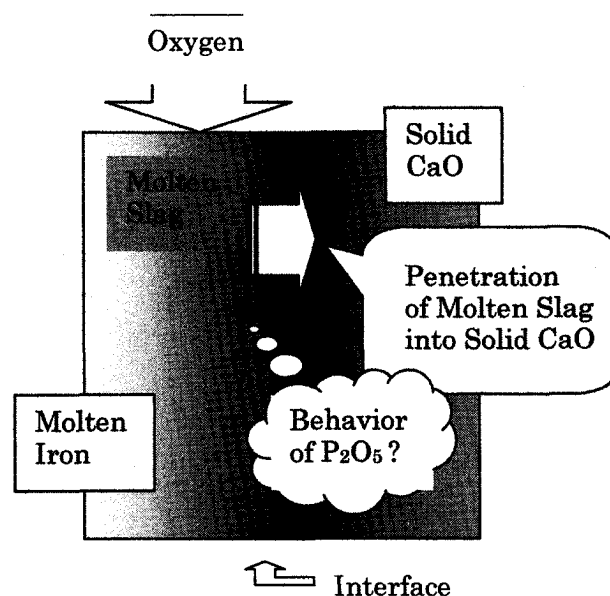


Fig.1 Concept of application of capillarity of solid CaO to dephosphorization of hot metal.

In the previous work⁶⁾ of the present authors, the penetration of molten FeO slag into CaO crucible was investigated for Fe-2%P alloy at 1873K, Fe-4%C-1%P and Fe-4%C-0.5%Si 1%P alloys at 1573K. It was found from these experiments that the phosphate was absorbed in the porosities of CaO crucible accompanying the penetration of molten FeO slag. Although the phosphorus concentration was reduced from initial 1mass% to 0.02mass% after the oxidation of Fe-4%C-1%P alloy, the final carbon concentration of the specimen was also reduced because molten FeO slag began to be formed after the carbon concentration in the iron alloy was decreased to a certain level. In order to oxidize a localized position of iron alloys without the reduction of the carbon content in iron alloys, additional experiments should be carried out because the carbon concentration in hot metals is usually kept to be about 4 mass% in steelmaking processes during the dephosphorization procedures.

The purpose of the present work is to observe the behavior of the phosphate accompanying the penetration of molten FeO slag into solid CaO when the carbon-saturated iron alloy containing phosphorus is oxidized for the dephosphorization in CaO crucible.

2. Experimental

Figure 2 shows the experimental apparatus for the dephosphorization of iron alloys, in which the high frequency heating furnace was used. The iron specimen (about 50g) containing carbon and phosphorus is melted in graphite crucible (the inner diameter = 40mm) at a given temperature to keep the specimen to be saturated with carbon. Fe-carbon saturated -1%P was used in the present work. The CaO crucible (the inner diameter = 20mm, the outer diameter=25mm) with a hole at the bottom is immersed in the liquid iron alloy in the above apparatus, and then only the alloy flown inside the CaO crucible was oxidized by blowing oxygen gas onto the surface of the iron alloy through a pipe located above the specimen. After the specimen is oxidized for a given time, the CaO crucible was cooled in air. Then the section of the CaO crucible was observed by EPMA to investigate the penetration of molten slag containing FeO and phosphate into CaO crucible.

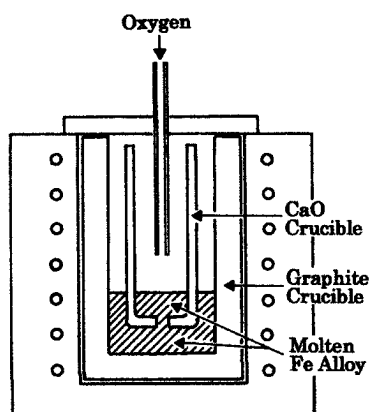


Fig. 2 Experimental apparatus.

3. Results and Discussion

Figure 3(a) shows the SEM image of the penetration layer in solid CaO. As shown in Figs.3(b) and (c), molten FeO slag penetrates in solid CaO phase with phosphates. From these results, it is confirmed that the phosphate is absorbed in the porosities of solid CaO with the penetration of molten FeO slag when the carbon-saturated iron alloy is oxidized at localized position. Thus, the capillary phenomena of solid CaO can be applied to the dephosphorization of hot metals in engineering processes by carrying out adequate local oxidation of the hot metals.

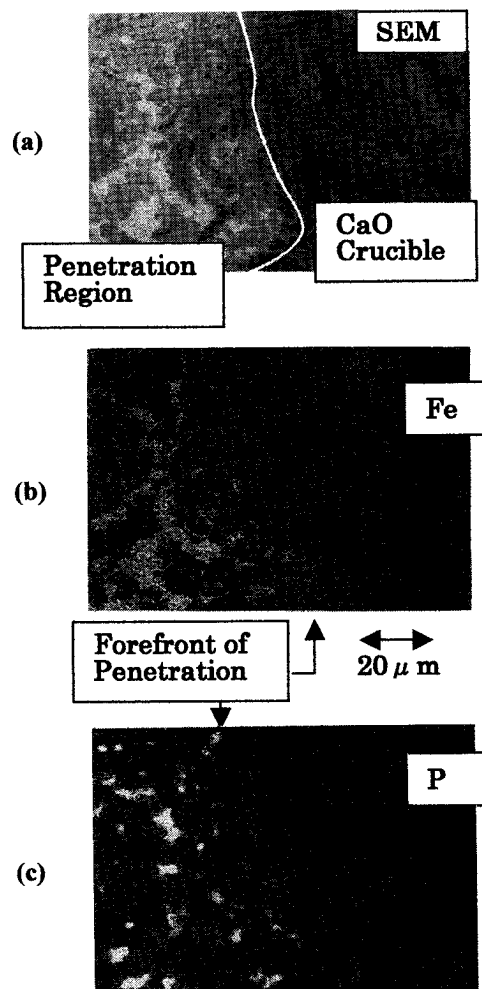


Fig.3 SEM image and characteristic X-ray images of Fe and Ca at the penetration layer in solid CaO for dephosphorization of Fe-C-P alloy locally oxidized at 1573K.

Figure 4 shows SEM image for a part of penetration region in solid CaO obtained in the localized oxidation of the above carbon-saturated iron alloy. This figure also indicates the X-ray intensity of Fe, Ca and P analyzed at each point numbered by "1"~"3". As shown in these figures, the calcium phosphate is formed in the point "2" in the molten slag, which consists mainly of CaO and iron oxide shown in the point "1". The point "3" indicates solid CaO phase. The phosphate is found to be fixed as $4\text{CaOP}_2\text{O}_5$ from X-ray diffraction.

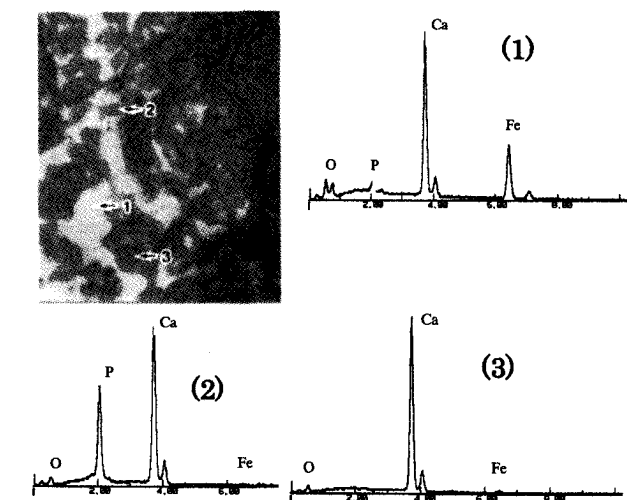


Fig.4 Characteristic X-ray analysis of Fe, Ca and P in the molten slag penetrated into solid CaO.

From the above investigation, the phosphate is absorbed in almost the same rate as the penetration of molten FeO slag in solid CaO. The average rate of the penetration obtained from the present experiments is about 0.4mm/60sec, but this rate is dependent upon the physical properties of CaO crucible, for example, capillary radius, porosity ratio, sintering conditions etc. as well as the oxidation rates to form molten FeO slag in the total processes of dephosphorization by using the capillary phenomena. The penetration rate of molten FeO slag in solid CaO was evaluated as follows: The penetration distance L of liquid in the capillary with radius r in Fig.5 is proportional to $1/2$ power of time t as shown in Eq.(1)³⁾.

$$L = (r \gamma t / 2 \eta)^{1/2} \quad \dots(1)$$

where γ and η : surface tension and viscosity of liquid.

In this evaluation, the porous solid CaO is regarded as a bundle of many capillary tubes and a capillary rise rate in a particular direction is assumed to be represented by that of a single capillary tube in the particular direction. Kaneki et al.⁸⁾ reported that Eq.(1) can be applied well to explain the penetration of liquid in porous materials under the above approximation.

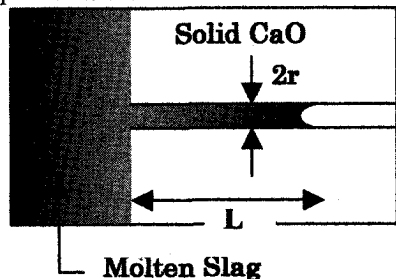


Fig.5 Schematic diagram for the penetration distance L of liquid into a capillary with radius r .

The value of γ/η was evaluated to be 1~10 from Ref.7) for molten FeO-CaO slags. Figure 6 shows the calculated results of the penetration distance L for $r=1 \times 10^{-5}m$ and $1 \times 10^{-6}m$. As shown in this figure, the

penetration proceeds at the rate of 5~20mm/60sec even for $r=1 \times 10^{-6}m$, and this rate is faster than the average penetration rate (0.4mm/60sec) obtained in the present experiments described above. Therefore, the oxidation process of liquid iron alloy is considered to be the rate-determining step for the total reaction rate of the dephosphorization process using the penetration of molten slag in solid CaO in the present experiments.

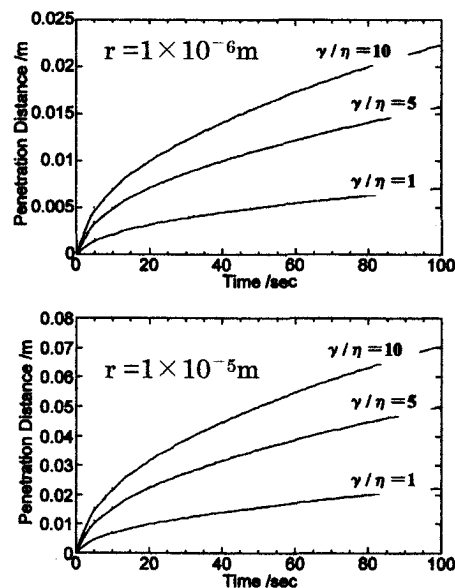


Fig.6 Calculated results of change in the penetration distance L with time t for various γ/η .

4. Concluding Remarks

It is found from the present experiments on the dephosphorization of the carbon-saturated iron alloys by solid CaO that the phosphate is absorbed in the porosities of solid CaO accompanying the penetration of molten FeO slag. Generally speaking, the chemical reaction with solid phase is usually avoided due to the low diffusion rate of species in the solid phase. When the penetration of liquid phase in solid is, however, used, the reaction rate can be revised to be enough fast to be applied to engineering processes. The application of the capillary phenomena to the dephosphorization of hot metals by solid CaO may be one of the useful steelmaking processes although the adequate oxidation procedures have to be considered.

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