The Dephosphorization of Hot Metal outside the Steelmaking Furnace*

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Synopsis
The preliminary dephosphorization method of hot metal outside the steelmaking furnace was investigated to obtain extra low phosphorus steels and to utilize the LD slag.

Hot metal with the phosphorus content of 0.09 - 0.16% was treated in a ladle with the dephosphorization agent consisting of LD slag and iron oxide or lime and iron oxide, and the phosphorus content of hot metal was reduced to 0.020 - 0.060% or 0.003 - 0.020%, respectively.

By refining the dephosphorized hot metal in LD converter, extra low phosphorus killed steels having the phosphorus content of lower than 0.005% were obtained.

By applying this dephosphorization method for the production of normal phosphorus steels, the amount of generated LD slag is decreased, and the LD slag can be utilized mainly as a dephosphorizing agent of hot metal again.

I. Introduction
Desulphurization and dephosphorization of steels have become very important metallurgical techniques in steelmaking process to produce high quality steels. The desulphurization technique of hot metal has made remarkable progress recently, and extra low sulphur commercial steels, which contain sulphur of lower than 0.005%, can easily be obtained. As the phosphorus content is controlled by the reaction in LD converter, the double slag technique has generally been applied to obtain low phosphorus killed steels. However, this technique is accompanied by the increase in operating time and the decrease of metal yield. In addition to the productivity problems, an enormous amount of LD slag, 100 kg slag from 1 t steel, is generated in the operation of LD converter.

In this paper, the preliminary dephosphorization method of hot metal is investigated to obtain extra low phosphorus steels and to utilize the LD slag.

II. Experimental Procedure
In order to investigate the dephosphorization behaviour of hot metal, the following experiments were performed.
1) Laboratory scale test; treatment of 4 kg hot metal in a crucible
2) 1 t scale test; treatment of 1 t hot metal in a ladle
3) Industrial scale test; treatment of 45 t hot metal in an industrial ladle

1. Experimental Apparatus and Method
Schematic diagram of the experimental apparatus used for the laboratory scale test is shown in Fig. 1. 4 kg pig iron was melted in an alumina crucible in the electric resistance furnace. After the iron was kept at 1300 °C, the dephosphorization agent was added onto the surface of hot metal and the iron was stirred mechanically by an impeller. The schematic profile of the experimental equipment used for the industrial scale test is shown in Fig. 2. As almost the same as in the case of laboratory scale test, 45 t hot metal was stirred mechanically after the addition of

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dephosphorization agent. But in the industrial scale test, a small amount of oxygen was injected into the metal during the stirring period to prevent the decrease of the hot metal temperature.

2. Dephosphorization Agent

For both the laboratory scale and industrial scale tests, two types of dephosphorization agent were used.

1) Type A agent; consisting of LD slag and iron oxide

Type A agent was applied to the dephosphorization of hot metal with low basicity slag (CaO/SiO₂: 0.5~1.0) solving the LD slag problem. Type B agent was applied to the dephosphorization of hot metal with high basicity slag (CaO/SiO₂: 1.5~3.0) aiming the high degree of dephosphorization. In some cases, fluorspar was added to type B agent to form the fluid slag. The experimental condition adopted for the industrial scale tests is shown in Table 1. The phosphorus content of the hot metal tested is 0.09~0.16%.

III. Experimental Results of Hot Metal Dephosphorization

1. Chemical Composition of Hot Metal during Dephosphorizing Treatment

In order to grasp the overall characteristics of the dephosphorization reaction, a typical change in the composition of hot metal during the treatment in the laboratory scale tests is shown in Figs. 3 and 4. These are the results obtained by the use of type A and type B dephosphorization agents, respectively. These figures well illustrate that the phosphorus content decreases as the silicon and manganese contents decrease and the decarburization is suppressed. By adding type A agent, the phosphorus content of hot metal was lowered to about 0.040%. In this case, the slag basicity after the treatment was about 0.8. On the other hand, by the addition of type B agent, the phosphorus content of hot metal was lowered to 0.003%. In this case, the slag basicity after the treatment was 2.1. In both cases, effective dephosphorization took place in the first 25 min.

2. Effect of Slag Composition on Dephosphorization Reaction

1. Effect of Slag Basicity on Dephosphorization

Relation between the phosphorus content of hot metal after the treatment and the slag basicity is shown in Fig. 5. Figure 5 shows the results obtained by the use of two dephosphorization agents. It is obvious that the more the slag basicity increases, the lower the phosphorus content of hot metal after the treatment becomes. By the addition of type A dephosphorization agent, with the slag basicity of 0.5 to 1.0, the phosphorus content of hot metal can be lowered to 0.020~0.060%. Thus, the sufficient dephosphorization can be achieved by using low basicity slag. Such a dephosphorization reaction can not be expected during the refining in LD converter using such low basicity slag. By adding type B dephosphorization agent, with the slag basicity of 1.5~3.0, the phosphorus content of hot metal can be lowered to 0.003~0.020%. It was found that the extra low phosphorus hot metal having the phosphorus content of less than 0.005% can be easily obtained by the slag with the basicity of 2.0~3.0. These results show the effectiveness of this dephosphorization treatment.

2. Effect of Iron Oxide Content of Slag on Dephosphorization Reaction

Relation between the total iron content of slag and the degree of dephosphorization is shown in
From the experimental results, it was found that the higher the total iron content of slag is, the more the dephosphorization occurs. To get a higher degree of dephosphorization, the iron content of slag should be high when the slag basicity becomes more acidic.

3. Relation between Dephosphorization Efficiency and Chemical Composition of Hot Metal during Treatment

1. Relation between Decarburization and Dephosphorization

As shown in Fig. 7, the dephosphorization occurs as the decarburization proceeds, but the degree of decarburization is not so much. The effect of slag basicity on the relation between dephosphorization and decarburization is also shown in the figure. It is seen that the degree of dephosphorization increases with increasing slag basicity at the same degree of decarburization.

2. Relation between Silicon and Manganese Oxidation and Dephosphorization

As shown in Figs. 8 and 9, the dephosphorization occurs as the silicon and manganese oxidation proceed. To obtain a higher degree of dephosphorization, it is necessary to oxidize silicon completely. On the other hand, slag basicity affects the relation between dephosphorization and manganese oxidation. Namely, a higher degree of dephosphorization is obtained with little manganese oxidation when high basicity slag is used. And this phenomenon is considered to be due to the increase in the activity of manganese oxide in more basic slag.

3. Desulphurization during Treatment

Change in the sulphur content during the dephosphorization treatment is shown in Fig. 10. When the initial sulphur content is higher than 0.030%, only little desulphurization proceeds, and no desulphurization occurs if the initial sulphur content is very low. The desulphurization proceeds more effectively by the use of type B dephosphorization agent than type A agent, because of high slag basicity. Thus, the desulphurization does not proceed so much in this treatment. Therefore, to get low phosphorus and low sulphur steels, another desul-
A dephosphorization technique is needed in addition to this dephosphorization treatment. In this case, the order of these two treatments should be considered. It is preferable for the desulphurization to treat the melt when it contains silicon. In this respect, the desulphurization should be done before the dephosphorization. However, the resulphurization from the dephosphorizing agent must be taken into account. Then, the amount resulphurized by the dephosphorizing agent was calculated using the sulphur content of the agent and the sulphur distribution ratio between slag and metal of these experiments. And it was found that the amount resulphurized is lower than 0.001 % when type B dephosphorizing agent is used, but it increases up to 0.003~0.004 % when type A dephosphorizing agent is used, because the LD slag contains sulphur. Therefore, the desulphurization treatment may be carried out before the dephosphorization treatment by type B dephosphorizing agent, because almost no resulphurization would occur. But, the dephosphorization treatment by type A dephosphorizing agent should be carried out before the desulphurization treatment because of the resulphurization. In this case, it has been assumed that the degree of desulphurization would decrease, because almost no silicon is contained in the dephosphorized hot metal. However, as shown in Fig. 11, the desulphurization of dephosphorized hot metal using calcium carbide was almost the same as that of usual hot metal containing silicon. In any case, the removal of desulphurization slag and dephosphorization slag is very important to produce low sulphur and low phosphorus steels.

### IV. Refining of Dephosphorized Hot Metal in Converter

Dephosphorized hot metal was charged together with two 45 t hot metals and was refined by blowing oxygen in a 70 t LD converter. The flux consisting of 50~70 kg/t lime, 11~16 kg/t silica and 6~15 kg/t fluorspar was added to the converter after the hot metal was poured. In some cases of refining of dephosphorized hot metal which was obtained by type B dephosphorization agent, 4 kg/t Fe-Si was added as the exothermic agent instead of 6 kg silica to obtain the preferable end point temperature. The results of refining are shown in Fig. 12. Low phosphorus steels could be obtained as the phosphorus content of hot metal was low. When oxygen is blown into the dephosphorized hot metal treated by type A agent, the final phosphorus content decreased to 0.007 % or less, but when the dephosphorized hot metal treated by type B agent was refined, it decreased to 0.004 % or less. The phosphorus contents of the products were less than 0.010 % and 0.005 %, respectively, when rephosphorization at tapping was avoided by preventing the fall of converter slag into the ladle.

Phosphorus balance at the refining in LD converter is shown in Fig. 13. In this experiment, hot metal without treatment was blown in the converter before blowing the dephosphorized hot metal. The...
contamination of phosphorus from the slag having a high phosphorus content of previous heat which was adhered to the converter wall was found to be very high. The phosphorus from the adhered slag to the system was about 65%. Therefore, to obtain low phosphorus steels, it is preferable to blow dephosphorized hot metals continuously to prevent the contamination by the phosphorus rich slag.

V. Discussion

1. Phosphorus Distribution Ratio during Dephosphorization Treatment of Hot Metal

To discuss about the dephosphorizing capacity of slag in this dephosphorization treatment, it is very important to know whether the dephosphorization reaches to the equilibrium or not. As shown in Figs. 3 and 4, in the laboratory scale tests, the dephosphorization reached to the steady state as the treating time goes on, and the dephosphorization is considered to have reached almost to the equilibrium. In this case, the effect of slag basicity and total iron content in the slag on the phosphorus distribution ratio, \((P_2O_5)/[P]\), is shown in Fig. 14. The more the slag basicity and the more the total iron content in the slag are, the further the phosphorus distribution ratio increases within the range of the slag composition in this experiment. The results of the phosphorus distribution ratios are divided as the relation of the slag basicity and total iron contents of the slags into hyperbola. The results of industrial scale test are also shown in Fig. 14. It is seen that there are many heats which are considered not to have reached to the steady state within the time of treatment.

Then, the effect of slag basicity on the phosphorus distribution ratio of heats, where the dephosphorization is considered to have reached almost to the steady state, is shown in Fig. 15. It is found that the phosphorus distribution ratio increases gradually when the slag basicity is lower than 1, but it increases linearly if the slag basicity is higher than 1 and the effect of slag basicity on the phosphorus distribution ratio is very high. Extrapolating the curve of phosphorus distribution ratio linearly to the basicity of usual LD slag (CaO/SiO₂: 3.5~4.5), the phosphorus distribution ratio, \((P_2O_5)/[P]\), of this dephosphorization treatment would be 900~1200. The ratio is 5 to 10 times larger than that by blowing in a converter. It is the advantage of this dephosphorization treatment at low temperature.

2. Comparison of Experimental Results with the Equilibrium of Dephosphorization

To discuss whether the dephosphorization reached to the equilibrium or not, the experimental results, where the dephosphorization is considered to have reached almost to the steady state, are compared with the values calculated from the equilibrium equations.

The equilibrium equations used here are those of Balajiva et al. and Healy, which are the typical equilibrium equations at steelmaking temperature (Table 2). And those equations are used by extrapolating to the temperature of this dephosphorization treatment. Besides those equations, another famous equilibrium equations proposed by Winkler and Chipman and Herasymenko and Speight were used to compare with the experimental results. But from both theories, the effective component for dephosphorization such as CaO' and O₂ were not found in
the slag having the basicity of lower than about 1, even though sufficient dephosphorization took place.

Frohberg and Kapoor\(^7\) presented the equation for the calculation of the $O_2^-$ activity in slag. In this equation, the $O_2^-$ activity could be calculated even in such a low basicity slag. Then new calculating method of phosphorus distribution ratio using this equation was adopted as described below.

Comparison of the experimental results with the values obtained from Balajiva's equilibrium equation is shown in Fig. 16. The experimental results obtained by the slag having the basicity of higher than 1 are fairly close to the calculated equilibrium value. But the results obtained by the slag having the basicity of less than 1 are lower than the calculated equilibrium value. Therefore, it is considered that the Balajiva's equation can not be applied to the dephosphorization by low basicity slag.

Comparison of these experimental results with the values calculated from Healy's equilibrium equation is shown in Fig. 17. Results of the laboratory scale test show a linear relationship which is parallel to the theoretical line. However the phosphorus distribution ratio of this experiment is much lower than that of the equilibrium value. Calculating from Healy's equation, the phosphorus distribution ratio at such low temperatures (about 1 300 °C) as in this experiment is 400 times larger than that at high temperatures (for example 1 650 °C) like blowing in LD converter. The value is much larger than that obtained by dividing the extrapolated phosphorus distribution ratio in this dephosphorization treatment of hot metal by that of the refining in LD converter.

Recently, Iwasaki et al.\(^8\) investigated the phosphorus distribution ratios in an equilibrium state, which can be applied to the dephosphorization of hot metal, and reported that the obtained values are much different from those obtained by extrapolating Healy's equation to 1 300 °C. Comparison of these experimental results with Iwasaki's phosphorus distribution ratios is shown in Fig. 18. The order of these experimental results is nearly equal to Iwasaki's results. Therefore, the dephosphorization in this experiment, which seems to have reached to the steady state, is considered almost to have reached to the equilibrium, and it is concluded that Healy's equation might not be extrapolated to this hot metal dephosphorization treatment at about 1 300 °C.

Next, the calculation method of phosphorus distribution ratio by using the activity of $O_2^-$ in slag is shown below. The following equation is used.

$$P + \frac{5}{2} Fe^{3+} + 4O_2^- = PO_4^{3-} + \frac{5}{2} Fe$$

The equilibrium constant $K$ of this reaction is represented by Eq. (2).

$$K = \frac{a_{PO_4^-}}{a_P \cdot a_{O_2^-} \cdot a_{Fe^{3+}}}$$

Here,

$$a_{Fe^{3+}} = a_{Fe^{2+}}$$

Therefore,

$$\frac{a_{PO_4^-}}{a_P} = K \frac{a_{Fe^{3+}} a_{O_2^-}}{a_{Fe^{2+}}}$$

It is assumed that $a_{PO_4^-} / a_P$ is in proportion to $(\% P_2O_5)/[\% P]$.

Then, the ratio of $a_{PO_4^-} / a_P$ can be given by Eq. (4).

$$\frac{a_{PO_4^-}}{a_P} = \alpha \frac{(\% P_2O_5)}{[\% P]}$$

Fig. 17. Comparison of experimental results with Healy's equilibrium calculation.

Fig. 18. Comparison of phosphorus distribution ratio of this experiment with equilibrium phosphorus distribution ratio (by Iwasaki et al.\(^8\)).
where, $a$: constant. Substituting Eq. (4) to Eq. (3), Eqs. (5) and (6) are obtained.

$$\frac{(% P_2O_5)}{[% P]} = K' a_{FeO}^{2/3} a^{3/2}_{O_2}$$

$$\log \frac{(% P_2O_5)}{[% P]} = \log K' + \log a^{2/3}_{FeO} a^{3/2}_{O_2}$$

where, $K' = K/a$.

Here, $a_{FeO}$ is obtained from the iso-activity curve given by Turkdogan and Pearson and $a_{O_2}$ is calculated from the equation derived from Frohberg and Kapoor. The relation of Eq. (6) is shown in Fig. 19. The results of laboratory scale test seem to show a rough tendency to this relation. It is difficult to discuss about the equilibrium of these experimental results by using Eq. (6), but it was found that the comparatively good agreement can be achieved by using the calculated $O_2^{-}$ activity in slag, even in the case of low basicity slag. Therefore, it is considered that the $O_2^{-}$ ion exists even in the low basicity slag and the $O_2^{-}$ ion contributed this dephosphorization reaction.

### 3. Optimum Iron Oxide Content in Slag to Get High Phosphorus Distribution Ratio

Iron oxide and CaO in slag are the effective components for the dephosphorization and the phosphorus distribution ratio is increased with increasing contents of both components. However, the content of CaO in slag decreases linearly with increasing total iron content, when the amount of added CaO is fixed. Therefore, it is considered that the optimum content of iron oxide exists to get the highest phosphorus distribution ratio. In Section V. 2, the results calculated from Healy’s equation showed fairly good linear relationship which is parallel to the theoretical line. Then, to get the optimum slag composition for dephosphorization, the relation between $(\% P)/(% P)$ and the total iron content were calculated from the equation which was obtained by modifying the constant of Healy’s equation from $-16.0$ to $-17.5$ to fit the experimental results, and by using the linear relationship between the CaO and total iron contents in this experiment. The result obtained is shown in Fig. 20. As shown in Fig. 20, there are the optimum content of iron oxide to get the highest phosphorus distribution ratio, and it is observed that the lower the slag basicity is, the higher the total iron content is needed to get the high phosphorus distribution ratio. Figure 6 showed that the effective dephosphorization occurred when the total iron content is higher than the optimum total iron content shown in Fig. 20. It is considered that this phenomenon is due to the increase of slag volume, even if the phosphorus distribution ratio is little lowered with higher total iron content than the optimum content.

### 4. Comparison of Oxygen Potential of Slag with That of Metal in Dephosphorization Treatment of Hot Metal

In order to know the difference in the oxygen potentials between slag and metal in this dephosphorization treatment of hot metal, $a_{FeO}$ of the slag after treatment was compared with $a_{FeO}$ equilibrated with carbon in the melt under 1 atmospheric pressure of $P_{CO}$. $a_{FeO}$ of the slag was obtained from the iso-activity diagram of (FeO) at 1600 °C presented by Turkdogan and Pearson. Essentially, the iso-activity diagram at 1300 °C should be used. But the diagram presented by Bodsworth does not cover all the slag composition of this experiment, and $a_{FeO}$ at 1600 °C is not so much different from that at 1300 °C. Then the iso-activity diagram at 1600 °C presented by Turkdogan was used here. The result is shown in Fig. 21. It is seen that the oxygen potential of the slag is about a hundred times higher than that of the metal. Consequently, the decarburization in this dephosphorization treatment is extremely suppressed. It is considered that the suppression of decarburization is due to the fact that iron oxide was mainly used as an oxidizing agent and very little oxygen was injected compared with that in LD converter and bath temperature was low. In other words, the dephosphorization of hot metal proceeds with the suitable slag for dephosphorization containing a large amount of iron oxide, while the slag is reduced very slowly by carbon in the melt.
5. Recycle of LD Slag by Dephosphorization Treatment of Hot Metal

Slag balance in the process to get normal phosphorus steels using dephosphorized hot metal is calculated under the condition of the industrial operation. One example of the results is shown in Fig. 22. It was found that the amount of LD slag can be decreased, because very small amount of flux is needed, and the generated LD slag can mainly be used as the dephosphorization agent again and some of them can be returned to blast furnace. Then all LD slag can be converted to the dephosphorization slag with low basicity and blast furnace slag. As shown in Fig. 23, this slag from the hot metal treatment does not contain free lime, if the slag basicity is lower than 2, and it can be used effectively as a material for pavement and so on.

VI. Conclusion

Dephosphorization method of hot metal in a ladle was investigated to obtain extra low phosphorus steels and to find a utilization method of LD slag. The results are summarized as follows:

(1) By the dephosphorization treatment of hot metal with low basicity slag (CaO/SiO₂: 0.5~1.0) using dephosphorization agent consisting of LD slag and iron oxide, the phosphorus content of hot metal can be reduced to 0.020~0.060 %. By refining the dephosphorized hot metal in LD converter, low phosphorus killed steels with the phosphorus content of lower than 0.010 % can easily be obtained. And by applying this dephosphorization method for the production of normal phosphorus steels, the recycle of LD slag becomes possible, and the LD slag can be converted to the dephosphorization slag without free lime and blast furnace slag.

(2) By the dephosphorization treatment of hot metal with high basicity slag (CaO/SiO₂: 1.5~3.0) using dephosphorization agent consisting of lime and iron oxide, the phosphorus content of hot metal can be reduced to 0.003~0.020 %. By refining the dephosphorized hot metal in LD converter, extra low phosphorus killed steel with phosphorus content of lower than 0.005 % can be obtained.

(3) In this dephosphorization treatment of hot metal, it is considered that the decarburization reaction was far from the equilibrium, but the dephosphorization reaction has almost reached to the equilibrium state.

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