Dephosphorization of Molten Pig Iron Containing Chromium by Lithium Carbonate*

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Synopsis

The dephosphorization of molten pig iron containing 18 % chromium by the addition of Li_2CO_3 has been studied using a laboratory scale high frequency induction furnace. The degrees of dephosphorization, desulfurization, and denitrification obtained by adding 60~125 g/kg-metal of Li_2CO_3 to molten pig iron (0.03 % P, 0.03 % S, 0.02 % N) containing chromium in a graphite crucible were more than 80 %. The oxidation loss of chromium was less than 0.5 %. The degree of dephosphorization by the addition of Li_2CO_3 was 2.1 times as large as that by the addition of Na_2CO_3 when the same weight of flux was added to the melt. The slag basicity after treatment by Li_2CO_3 was higher than that by Na_2CO_3 . The degree of dephosphorization decreased remarkably with increasing temperature. It is preferable to treat the pig iron at a temperature below 1 480 °C. The carbon content of pig iron had a remarkable effect on the dephosphorization reaction. When the carbon content was low (3.5 %), the oxidation loss of chromium was very large and the degree of dephosphorization was lowered to about 20 %. By X-ray diffraction analysis, Li_4SiO_4 and LiCrO_2 were identified in the slag after treatment, and Li_3PO_4 in the phosphorus-enriched slag.

I. Introduction

It has been reported¹⁻⁵⁾ that phosphorus enhances the susceptibility to stress-corrosion cracking in austenitic stainless steels and that to hot cracking in austenitic single-phase stainless steels. However, industrial dephosphorization processes are still being developed. Many laboratory scale experiments have been made on the dephosphorization of molten steel or iron containing chromium by adding such fluxes as Na_2CO_3 ,¹⁾ Ca-CaF_2 ,⁷⁻⁹⁾ $\text{CaC}_2\text{-CaF}_2$,¹⁰⁻¹²⁾ CaO-FeCl_2 ,¹³⁾ CaC_2 ,¹⁴⁾ or Ca .¹⁵⁾ These studies can generally be classified into the following two; reducing dephosphorization and oxidizing dephosphorization methods. In the case of reducing dephosphorization method, it is necessary to complete the dephosphorization reaction in reducing or neutral atmosphere without oxidizing calcium in slag as a dephosphorizing agent. Furthermore if the slag after dephosphorization treatment is allowed to stand, phosphine, PH_3 , is formed by the following reaction (Eq. (1)).

Therefore it has been said¹²⁾ that the slag must be treated so as not to generate such a poison gas. On the other hand, the oxidizing dephosphorization method is free from such a problem and can be performed in the air, that is, it has the practical ease. However, from a study⁶⁾ on the oxidizing dephosphorization of molten steel containing chromium by the

addition of alkaline metal compounds (Na_2CO_3 flux and K_2CO_3 flux), it has been found the fact that the oxidation of chromium occurred predominantly, but not dephosphorization.

From the preliminary experiments, it has also been found that among alkaline metal compounds, Li_2CO_3 shows a marked effect on the refining of molten pig iron containing chromium. This paper concerns a subsequent fundamental research on the dephosphorization of molten pig iron containing chromium.

II. Experimentals

A schematic diagram of the furnace used and the experimental conditions adopted are shown in Fig. 1 and Table 1, respectively. Chromium pig iron saturated with carbon of 1.2 kg in weight was melted in a graphite crucible with a high frequency induction furnace. The carbon content of pig iron containing 17.0 % chromium was 6.1 % at 1 430 °C. In the molten bath, powdered Li_2CO_3 was added by 10~125 g/kg-metal as a dephosphorizing flux. Several parts of flux were added every 3 to 5 min. The metal samples were taken with a silica tube by suction at intervals of 5 to 10 min during the experimental run, and the slag sample was taken with a steel spoon at the end of runs. The experimental time was 40 min in most cases. In the experiment to study the effect of carbon content of pig iron on the dephosphorization, magnesia crucible was used as an inner crucible. Temperature of the metal bath was controlled by measuring the temperature of the outer crucible after correcting the difference in temperature between inner and outer crucibles. Most of the experiments were made by keeping the metal at $1\,430 \pm 10$ °C. In the case of examining the temperature dependency of the degree of dephosphorization, the metal was kept at 1 430, 1 460, 1 500 and 1 600 °C. Although most of the experiments were made in the air, the top blowing of CO_2 gas was additionally applied to some experiments. Change in the composition of slag with time was examined by adding the total amount of flux at once in the beginning to molten pig iron of 3 kg in weight. In this case, the slag samples were taken at intervals of 5 to 10 min during the run. As a flux, Na_2CO_3 was also used in order to compare the result obtained with that of Li_2CO_3 addition.

Since the slag was in the activated state, samples were ground in ethyl alcohol and then dried. Con-

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Fig. 1. A schematic diagram of furnace used.

Table 1. Experimental conditions.

Furnace	High frequency induction furnace						
Crucible	Graphite* or Magnesia						
Weight of metal	1.2 kg* or 3.0 kg						
Initial composition of metal (%)	C	Si	P	S	Cr	N	
	2, 3.5 or 6*	tr.~ 1.2	0.03	0.03	18	0.02	
Flux	Li ₂ CO ₃ * or Na ₂ CO ₃ (Chemical reagent, 1st grade)						
Amount of flux added	10~125 g/kg-metal						
Temperature of metal	1 430 °C*, 1 400~1 600 °C						
Atmosphere	In the air (without* or with the top blowing of CO ₂ gas)						

* Mainly used

tents of total lithium (T.Li) and Li₂CO₃ in slag were obtained by the atomic absorption method and by determining the amount of CO₂ gas using a Schrötter meter, respectively. Phosphorus content of pig iron containing chromium was determined by the molybdenum blue method.

III. Results

1. Refining Characteristics of Li₂CO₃

As shown in Fig. 2, phosphorus, sulfur and nitrogen in molten pig iron containing chromium were removed remarkably by the addition of Li₂CO₃. On the other hand, the oxidation loss of chromium was usually less than 0.5 %. As shown in Fig. 3, silicon was predominantly oxidized in the range above 0.5 % Si,

Fig. 2. Typical example of the change in composition of molten pig iron containing chromium after the addition of Li₂CO₃.

Fig. 3. Typical example of the change in composition of molten pig iron containing chromium after the addition of Li₂CO₃.

but silicon and phosphorus were simultaneously oxidized in the range below that. When the amount of Li₂CO₃ added was larger than 100 g/kg-metal, the degree of dephosphorization (*D_p*) for pig iron of high silicon content (about 1 % Si) was not smaller than that for pig iron of low silicon content. But, when the amount of Li₂CO₃ added was smaller than 60 g/kg-metal, *D_p* decreased with increasing content of silicon in pig iron. In this case, *D_p* was considered to be effected by the basicity of slag formed as mentioned later. The content of carbon in pig iron ([%C]) was kept at a constant value during the run because a graphite crucible was used. The effect of the added amount of Li₂CO₃ on *D_p* was remarkable when the added amount was in the range of 10~100 g/kg-metal, as shown in Fig. 4. In the runs *D*, *E* and *F* in the same figure, CO₂ gas, Na₂CO₃ and FeO were added besides the addition of Li₂CO₃ to compensate the shortage of oxidizing source. The value of *D_p* reached about 90 % when Li₂CO₃ of

Amount of flux (g/kg-metal)
and the top blown gas: [%Si]ini.
A: Li_2CO_3 100: 0.05
B: Li_2CO_3 100: 0.05
C: Li_2CO_3 62.4: 0.55
D: Li_2CO_3 10+ CO_2 23 (l/kg-metal): 0.10
E: Li_2CO_3 10+ Na_2CO_3 42: 0.06
F: Li_2CO_3 10+ FeO 42: 0.05

Fig. 4. Effect of the amount of flux added on the degree of dephosphorization.

100 g/kg-metal was added and about 80 % for the addition of 60 g/kg-metal. In the latter case, the initial content of silicon was 0.55 %. However, when the flux of 10 g/kg-metal was added, D_p remained 20 to 40 % in spite of supplying any oxidizing agent.

The dephosphorizing power of Li_2CO_3 was compared with that of Na_2CO_3 and is shown in Fig. 5. The value of D_p by the addition of Li_2CO_3 was 2.1 times as large as that by adding Na_2CO_3 when the same weight of flux was added, and was 1.5 times as large as that by the addition of Na_2CO_3 when the molar number of flux added was the same.

2. Change in Slag Composition during Dephosphorization Treatment

Figure 6 shows the change in slag composition with time after adding Li_2CO_3 in one portion. A rapid decrease in the content of Li_2CO_3 in slag ($(\% \text{Li}_2\text{CO}_3)$) and rapid increases in $(\% \text{Li}_2\text{O})$, $(\% \text{Cr}_2\text{O}_3)$, $(\% \text{SiO}_2)$ and $(\% \text{P})$ were observed just after the addition of Li_2CO_3 . Subsequently, slow decreases in the content of iron oxides formed (expressed as the total iron content (T.Fe)) and in $(\% \text{Li}_2\text{O})$ and slow increases in $(\% \text{SiO}_2)$, $(\% \text{Cr}_2\text{O}_3)$ and $(\% \text{P})$ occurred, but $(\% \text{Li}_2\text{CO}_3)$ did not show any change. Accordingly the oxidizing source was considered to be CO_2 gas generated by the decomposition of Li_2CO_3 and iron oxides formed just after the addition of flux. A rapid increase in $(\% \text{Cr}_2\text{O}_3)$ at the last stage of the run found in Fig. 6 is not considered to be normal behavior, but the reason is not clarified yet. Figure 7 shows the change in slag composition with time in the case that the initial content of silicon is high ($[\% \text{Si}]_{\text{ini.}} = 1.14$). In this case the dephosphorization did not occur because of low slag basicity. And, the content of SiO_2 was high, but the formation of chromium oxide was found to be suppressed as compared with the data of Fig. 6. In contrast with this, the con-

Fig. 5. Comparison of the dephosphorizing powers obtained by the addition of Li_2CO_3 and Na_2CO_3 .

Fig. 6. Typical example of the change in composition of slag during treatment.

Fig. 7. Typical example of the change in composition of slag during treatment.

tent of chromium oxide becomes high in the case of low initial content of silicon, and consequently the slag tended to lose the fluidity without the intermittent addition of Li_2CO_3 .

Typical composition of slag obtained after dephosphorization treatment is shown in Table 2. The phosphorus distribution ratio ($L_p \equiv (P)/[P]$) reached up to the value of 400 to 700. Not only in the case that $[\%Si]_{ini.}$ was low, but that the amount of Li_2CO_3 added was small, the tendency of increasing content of chromium oxide was observed. The latter was supposed to be resulted from the phenomenon that the metal surface did not perfectly covered with slag. The added Li_2CO_3 remained by 5 to 12 % in slag.

3. Temperature Dependence of Dephosphorization Reaction

As shown in Fig. 8, the degree of dephosphorization showed a remarkable temperature dependence on the dephosphorization treatment by Li_2CO_3 , that is, D_p decreased rapidly with increasing temperature. It was below 1 480 °C wherein a large degree of dephosphorization could be obtained. The range of temperature suitable for the dephosphorization treatment was considerably narrow, since in the case of 18 % chromium pig iron saturated with carbon the surface of metal bath began to solidify at some 1 380 °C.

4 Effect of [%C] on Dephosphorization Reaction

The effects of [%C] on D_p and on the oxidation loss of chromium are shown in Fig. 9. When [%C] was about 3.5, the oxidation of chromium was vigorous and the slag lost the fluidity soon after the addition of Li_2CO_3 . In the case that [%C] was about 2, the dephosphorization did not occur at all but the loss of chromium became still larger. As shown in Table 2, the content of chromium oxide is remarkably high when [%C] is equal to 3.54 as compared with the values in the cases of the saturated carbon content and of adding Li_2CO_3 of nearly the same amount. Low value of $\{(\%Li_2CO_3) + (\%Li_2O)\}$ may be resulted from an increase in the slag volume due to the vigorous oxidation of chromium. Large ratio of $(\%Li_2CO_3)/(\%Li_2O)$ may suggest that the decomposition of Li_2CO_3 did not sufficiently proceed. The experiments for the metals unsaturated with carbon and saturated with carbon were made by using magnesia and graphite crucibles, respectively. Therefore the difference in the results of the two is considered to be caused not only by the difference in [%C] but by the difference in crucible materials. That is, the walls of graphite crucible may reduce the slag (es-

pecially, iron and chromium oxides) and supply the heat to the slag.

5. X-ray Analysis of Slags after Treatment

By the X-ray diffraction analysis of the slag after dephosphorization treatment, Li_4SiO_4 and Li_2O were identified as strong peaks, and $Li_2OH \cdot H_2O$, $LiCrO_2$ and Li_2CO_3 were identified as weak peaks as shown in Fig. 10. However, any compound containing phosphorus was not found. $LiOH \cdot H_2O$ seemed to be formed by moistening of Li_2O during the preparation of slag sample. On the other hand, a strong peak of Li_3PO_4 and weak peaks of $LiOH \cdot H_2O$, Li_2O and Li_2CO_3 were observed for the slag cooled after keeping 150 g of Li_2CO_3 and 100 g of Fe-25%P alloy in a graphite crucible for 16 min at 1 400 °C, as shown in Fig. 11. The formation reactions of these compounds which are identified by the X-ray analysis may be expressed as follows:

Fig. 8. Temperature dependence of D_p .

Fig. 9. Effect of [%C] on D_p and chromium loss.

Table 2. Composition of slag after treatment. ([%C]=satu., 1 430 °C)

[%Si] _{ini.}	Amount of Li_2CO_3 added	Composition of slag (%)						(P)/[P]
		(Li_2CO_3)	(Li_2O)	(SiO_2)	(Cr_2O_3)	(Fe_tO)	(P)	
0.17	125 g/kg-metal	10.49	45.04	5.63	21.44	5.61	0.72	720
0.76	125 g/kg-metal	10.21	34.35	29.84	0.64	1.65	0.22	72
0.04	100 g/kg-metal	5.74	58.20	5.26	8.79	20.56	1.27	420*
0.10	10 g/kg-metal	5.79	25.02	15.30	45.35	5.70	0.76	33
0.29	50 g/kg-metal	11.82	30.08	16.11	41.11	2.35	0.34	110
0.07	100 g/kg-metal	11.62	13.69	0.57	57.52	11.86	0.04	0.48**

* 1 460 °C
** [%C]=3.54

Fig. 10. X-ray diffraction pattern of the slag after the treatment.

Fig. 11. X-ray diffraction pattern of the phosphorus-enriched slag.

It is presumed from the above result that chromium oxide behaves as an acidic oxide in the slag and phosphorus is stabilized as lithium phosphate.

IV. Discussion

1. Relation between L_p and Slag Composition

The phosphorus distribution ratio increased with increasing basicity of slag as shown in Fig. 12, where the data for pig iron saturated with carbon shown in Table 2 were used again. Since $[\% \text{Si}]$ after the treatment is below 0.08 % in all cases, the influence of $[\% \text{Si}]$ on L_p is considered to be eliminated. Here, the basicity of slag was defined as a ratio of the molar fraction ($N_{\text{Li}_2\text{O}}$) of Li_2O stoichiometrically calculated from $(\% \text{T.Li})$ to the molar fraction of SiO_2 . Since $(\% \text{Cr}_2\text{O}_3)$ is considerably high in the slag formed in the current experiments, Cr_2O_3 should also be considered as a component affecting the basicity of slag.

Fig. 12. Effect of the slag basicity on L_p .

Therefore, the basicity defined by expressing the molar fraction of acidic oxides as $(N_{\text{SiO}_2} + 1/2 N_{\text{Cr}_2\text{O}_3})$ was calculated and is also shown in Fig. 12. The scatter is somewhat small as compared with that obtained by considering SiO_2 as the only acidic oxide. Therefore, chromium oxide should be regarded as a component lowering the slag basicity. As for the dephosphorization treatment of pig iron containing chromium, $(\% \text{SiO}_2)$ and $(\% \text{Cr}_2\text{O}_3)$ after treatment become high when the initial content of silicon is high or low. It may be difficult to keep the slag basicity high, as compared with the case of treating pig iron containing no chromium. In addition to the harmful effect mentioned above, a serious problem that the slag loses the fluidity also arises when chromium oxide in slag is high.

2. Comparison of Dephosphorizing Powers of Li_2CO_3 and Na_2CO_3

The phosphorus distribution ratio obtained by the similar dephosphorization treatment using Na_2CO_3 instead of Li_2CO_3 is also shown in Fig. 12 as a function of slag basicity. When Na_2CO_3 is added, the slag basicity becomes much smaller than that by the addition of Li_2CO_3 . This behavior is considered to cause a small degree of dephosphorization by Na_2CO_3 . In order to clarify the reason, the compositions of slags after treatment by the additions of Li_2CO_3 and Na_2CO_3 are shown in Fig. 13 for pig iron of high and low silicon contents. The characteristic of the slag by the addition of Na_2CO_3 is that $(\% \text{T.X}_2\text{O})$ is low (where X shows alkaline metals), and $(\% \text{Cr}_2\text{O}_3)$ and $(\% \text{Fe}_t\text{O})$ are high. Since the amount of flux added is constant and $(\% \text{SiO}_2)$ in slag after treatment corresponds the content of silicon in pig iron, the amount of slag formed is considered to be constant. In the case of Na_2CO_3 addition, it is supposed that the vaporization loss of sodium is large and chromium and iron are easily oxidized by Na_2CO_3 . Equations for the decomposition of alkaline metal compounds and the equilibrium oxygen potentials for the reactions of pure substances are shown in Table 3. From this table, it can be seen that Na_2O easily decomposes into gaseous sodium. On the other hand, it is shown that Li_2O is difficult to decompose into gaseous lithium, although Li_2CO_3 easily decomposes into Li_2O . Thermal stability of Li_2O as a basic oxide seems to be superior to that of Na_2O . If it is assumed that

Fig. 13. Comparison of the slag compositions after the treatment.

Table 3. Equilibrium oxygen potential of reactions at 1430 °C.⁽¹⁶⁾

P _{O₂} (atm)	Chemical equations
4.9×10 ⁻⁸	Na ₂ O (l)=2Na (g)+1/2O ₂
6.6×10 ⁻¹⁰	Li ₂ CO ₃ (l)=Li ₂ O (s)+CO (g)+1/2O ₂ (g)
2.1×10 ⁻¹¹	Na ₂ CO ₃ (l)=2Na (g)+CO (g)+O ₂ (g)
2.5×10 ⁻¹³	Li ₂ CO ₃ (l)=Li ₂ O (s)+C (s)+O ₂ (g)
9.3×10 ⁻¹⁵	Na ₂ CO ₃ (l)=Na ₂ O (l)+CO (g)+1/2O ₂ (g)
9.5×10 ⁻¹⁶	Na ₂ CO ₃ (l)=Na ₂ O (l)+C (s)+O ₂ (g)
2.0×10 ⁻¹⁶	Li ₂ CO ₃ (l)=2Li (g)+CO (g)+O ₂ (g)
6.4×10 ⁻²³	Li ₂ O (s)=2Li (g)+1/2O ₂ (g)

the activity coefficients of iron and chromium oxides in Li₂CO₃ slag are nearly equal to those in Na₂CO₃ slag, the reason why the contents of iron and chromium oxides become high in the Na₂CO₃ slag can be explained by considering the high oxygen potential supplied by flux added. Such an inference that the oxygen potential of the system was influenced by the decomposition reaction is also supported by the data shown in Table 3 in a certain extent.

Since phosphorus is removed by the oxidation in the present treatment, the value of *L_p*, of course, should be affected by the oxygen potential of the system. As already mentioned, Na₂CO₃ is considered to supply higher oxygen potential to the system than that by the addition of Li₂CO₃. The values of *L_p* for Na₂CO₃ slag shown in Fig. 12 may be somewhat smaller if the oxygen potential of the Na₂CO₃ added system is the same to that of the Li₂CO₃ added system.

3. Temperature Dependence of Dephosphorization Reaction

The degree of dephosphorization obtained in the present experiments showed a remarkable temperature dependence. If it is assumed that the dephosphorization reaction at the end of experimental run is nearly in the equilibrium state, the enthalpy change of the dephosphorization reaction can be calculated from the temperature dependence of *D_p*. When all of phosphorus removed from metal is converted into slag, the following equation is obtained.

$$L_p = (W_M/W_S) \cdot D_p / (100 - D_p) \dots \dots \dots (6)$$

where, *W_M*, *W_S*: the weights of metal and slag, respectively.

By the use of the data on the temperature dependence of *D_p* shown in Fig. 8 and Eq. (6), the temperature dependence of *L_p* was calculated and the result obtained is shown in Fig. 14, where *W_S/W_M* was assumed

Fig. 14. Temperature dependence of *L_p*.

to be constant. The value of ΔH° obtained from Fig. 14 was -211 kcal/mol(P) . Since no thermochemical data was reported for Li₃PO₄, the thermochemical data for Na₃PO₄ were used for the comparison of the ΔH° value. The value of ΔH° obtained is relatively close to the enthalpy changes of the dephosphorization reactions expressed by Eqs. (7) and (8), but not by Eq. (9).

where, $\underline{P}$, $\underline{O}$: the metal components.
From the result obtained, it is found that Na₂CO₃ or Li₂CO₃ does not serve as an oxidizing agent at least at the last stage of experimental run.

V. Conclusions

The dephosphorization of molten pig iron containing 18 % chromium by the addition of Li₂CO₃ was studied using a laboratory scale high frequency induction furnace. The results obtained are summarized as follows:

- (1) The degrees of dephosphorization, desulfurization and denitrification obtained by adding 60~125 g/kg-metal of Li₂CO₃ to molten pig iron containing chromium in a graphite crucible were more than 80 %. On the other hand, the oxidation loss of chromium was less than about 0.5 %. Silicon was predominantly oxidized in the range above 0.5 % Si, but silicon and phosphorus were simultaneously oxidized in the range below that.
- (2) The degree of dephosphorization by the addition of Li₂CO₃ was 2.1 times as large as that by adding Na₂CO₃ when the weight of flux added was the same, and 1.5 times when the molar number of flux added was the same. In the case of Li₂CO₃ addition the basicity of slag after treatment was high,

which was considered to be the reason why a large degree of dephosphorization was obtained.

(3) The dephosphorization reaction showed a remarkable temperature dependence. That is, the degree of dephosphorization decreased rapidly with increasing temperature. It was below about 1480 °C that the temperature giving a large degree of dephosphorization was.

(4) The value of [%C] had a remarkable effect on D_p . Vigorous oxidation of chromium was observed in the case of low carbon content. Consequently, the slag lost the fluidity and D_p decreased to about 20 % at [%C]=3.5.

(5) By X-ray diffraction analysis, Li_4SiO_4 and LiCrO_2 were identified in the slag after treatment, and Li_3PO_4 in the phosphorus-enriched slag. From the above facts, it is presumed that chromium oxide behaves as an acidic oxide in the slag and phosphorus is stabilized as lithium phosphate.

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