Simultaneous Dephosphorization and Desulfurization of Carbon-saturated Iron by Sodium Carbonate-Sodium Sulfate Flux*

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Synopsis

The effect of temperature, silicon and manganese in carbon-saturated iron (0.1% P, 0.05% S) on the dephosphorization and desulfurization was studied by the use of $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux. The degree of dephosphorization and desulfurization considerably decreased and the evaporation of sodium increased with increasing temperature. As the flux was consumed for the oxidation of silicon, the degree was found to markedly decrease, whereas manganese in metal was found to gradually decrease. The reversion of phosphorus and sulfur was observed after the end of the flux addition.

The behavior of dephosphorization and desulfurization obtained with $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux was compared with that with Na_2CO_3 flux or $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux. The degree of dephosphorization for the three fluxes was almost the same, but remarkable evaporation of phosphorus was observed for $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux according to the acceleration of CO formation by the reduction of iron oxide with carbon in metal. The phosphorus evaporation was also observed for $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux, but its extent decreased with increasing content of P_2O_5 and SiO_2 in the flux.

I. Introduction

In recent years, the growing concern for the dephosphorization process has arisen, because of the degradation of raw materials with respect to phosphorus and the increasing importance of phosphorus control in steel. Today, in Japan, LD slag is not fully utilized yet, although it is partially returned to blast furnaces and utilized in the field of the civil engineering and construction. Under these circumstances, the necessity for the dephosphorization of hot metal has been recognized and particularly the studies on the external dephosphorization by soda ash have been reported.¹⁻⁵⁾

In 1965, Oelsen⁶⁾ carried out experiments on the dephosphorization and desulfurization of carbon-saturated iron melt containing high phosphorus (1~2%). The mixture of Na_2CO_3 and Na_2SO_4 which has a strong oxidizing power was used in the temperature range between 1200°C and 1300°C. However, the degree of dephosphorization and desulfurization as a function of time was not thoroughly determined and the reversion of phosphorus and sulfur and the evaporation of phosphorus were not discussed in his work. In the previous paper,⁷⁾ the present authors carried out a fundamental work on the dephosphorization and desulfurization of carbon-saturated iron melt containing 0.2 to 1.0% phosphorus by using the $\text{Na}_2\text{CO}_3\text{--Na}_2\text{SO}_4$ flux. The aim of the present investigation was to study the simultaneous dephosphorization and desulfurization of carbon-saturated iron melt by using $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux. The effect of temperature, silicon, manganese and

chromium on the dephosphorization and desulfurization was also studied. The dephosphorization and desulfurization with Na_2CO_3 flux and $\text{Na}_2\text{CO}_3\text{--Fe}_2\text{O}_3$ flux were compared with those with $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux. The difference among these fluxes was discussed from the viewpoint of the reversion of phosphorus and sulfur to metal and the phosphorus evaporation.

II. Experimental

1. Apparatus

The schematic diagram of the experimental apparatus is illustrated in Fig. 1. An induction furnace (15 kW, 8 100 Hz) was used for melting. A graphite crucible (50 mm I.D., 70 mm depth) was placed inside a graphite protection crucible with a graphite lid to keep CO atmosphere and uniform temperature. An alumina thermocouple sheath was inserted into the wall of the protection crucible. When the temperature measured at this position by a Pt-Pt/13%Rh thermocouple was compared with that measured simultaneously by another thermocouple immersed in the melt, no difference was observed between them under stirring condition. The temperature could be kept within the limits of $\pm 5^\circ\text{C}$ in the range of 1250°~1350°C for about 30 min. A graphite sampler and

Fig. 1. Schematic diagram of experimental apparatus.

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a graphite stirring rod were used.

2. Materials

Electrolytic iron of 400 g (0.005% C, 0.005% S, 0.004% P, 0.005% Si and 0.005% Mn) was melted in a graphite crucible and then the alloying elements were added to obtain a required composition. The initial concentrations of phosphorus and sulfur were chosen in most cases to be 0.1% and 0.05%, respectively. Commercial grade Fe-26.1% P alloy, Fe-75.5% Si alloy, Fe-61.8% Cr alloy and reagent grade FeS and manganese were used for the alloying additions. The reagent grade Na_2CO_3 , Na_2SO_4 , Fe_2O_3 and SiO_2 were used for flux materials. These chemicals were sufficiently dried at 120°C and pressed in a cylindrical shape with 13 mm in diameter. The $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux was chosen, because it was found in the previous work⁷⁾ that at this composition of Na_2CO_3 - Na_2SO_4 system, the degree of dephosphorization and desulfurization and iron yield were excellent and further the evaporation loss of sulfur and sodium was comparatively small.

3. Procedure

After carbon-saturated iron melt (430 g) with a given composition was melted at 1 250°C, the flux was added to the melt every one minute. Even after the end of the flux addition, the stirring was continued so as to examine the reversion of phosphorus and sulfur and the evaporation of phosphorus. The sample of metal (4~5 g) was taken by the graphite sampler at a given time. Preliminary experiments indicated that when the total amount of the flux was added to the melt at one time, a part of the flux was scattered out of the crucible. In addition, enormous amount of evaporation loss of sodium was observed as a result of the reaction of the flux with carbon in iron melt and graphite. Thus, an attempt was made to add pelletized flux intermittently. Soon after the flux melts down, it reacts with iron melt so vigorously, evolving white fume and yellow flame. After 40~50 sec of the flux addition, the evolution of the fume and flame was reduced. For this reason, in the experiment with 0.1% initial phosphorus, 4 g of the flux was added to the melt every one minute. This way of flux addition made the results of the dephosphorization and desulfurization satisfactorily reproducible for each measurement.

4. Analysis

Details of the methods of the chemical analysis for phosphorus and sulfur in metal and for phosphorus, total sulfur, SO_4^{2-} , CO_3^{2-} , sodium, total iron and Fe^{2+} in slag are already described elsewhere.⁷⁾ Silicon and manganese in metal were determined by the absorptiometry of silicomolybdate blue (JIS-G-1212) and by that of permanganic acid after oxidizing manganese by KIO_4 (JIS-G-1213), respectively. Chromium was determined by the volumetric determination after oxidizing it with KMnO_4 (JIS-G-1217).

III. Results and Discussion

1. Effect of Flux Addition, Amount of Flux and Temperature

By varying the interval and the amount of $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux addition and temperature, the behavior of phosphorus and sulfur in metal was studied. These results are shown in Fig. 2. To study the effect of the flux addition on the dephosphorization and desulfurization at 1 350°C, 20 g of the flux was added at one minute intervals in 2 g portion (Run No. 32) or in 4 g portion (Run No. 62). The time of the flux addition is indicated by arrows in Fig. 2 which shows that the rate and degree of dephosphorization and desulfurization are greater for the addition in 4 g portion (Run No. 62).

In Run No. 101, 20 g of the total flux was added at 1 250°C in 4 g portion at one minute intervals. These results were compared with those obtained with 10 g of the total flux which was added in 2 g portion (Run No. 21). The degree of dephosphorization was greater with increasing total weight of flux, but there was very little or no difference in the degree of desulfurization. This can be explained as follows: The dephosphorization and desulfurization power will be decreased much faster, if the flux weight added at one time is small. In such a case, the reversion of phosphorus and sulfur occurs before the next addition as discussed later in Section II. 3.

The effect of temperature was studied at 1 250°C (Run No. 101) and 1 350°C (Run No. 62). The maximum degree of dephosphorization at 1 250°C and 1 350°C were 97% and 57%, respectively. As

Fig. 2. Variation of P and S in metal with time—Effect of flux weight, flux addition and temperature.

can be seen from Fig. 2, both the degree and the rate of dephosphorization increase with decreasing temperature despite the fact that dephosphorization reaction by Na_2CO_3 becomes favorable with rising temperature.⁷⁾ The reason that the dephosphorization becomes less favorable with increasing temperature can be explained by the fact that the reactions between Na_2CO_3 and carbon in melt and free carbon as the dephosphorization product⁷⁾ become more violent with increasing temperature. As shown in Fig. 2, the phosphorus reversion to metal was observed in all experiments and a more extensive reversion can occur after the end of the flux addition. It is, however, apparent from Fig. 2 that as the temperature increases the rate of phosphorus reversion gradually decreases and the phosphorus content in slag approaches to constant values as a result of the phosphorus evaporation. The maximum degree of desulfurization at 1 250°C (Run No. 101) and 1 350°C (Run No. 62) are 90% and 85%, respectively. It is of particular significance that the sulfur reversion occurs after the end of the phosphorus reversion. Particularly, the sulfur reversion in the experiment at 1 350°C (Run No. 62) is more pronounced. Further considerations of the phosphorus evaporation and the sulfur reversion are given in Section III. 5. Although the curves for Run Nos. 32 and 21 end at 10 min, it is expected that the sulfur reversion will proceed after 10 min.

To prevent the phosphorus evaporation and the phosphorus reversion, which are the serious drawbacks of soda ash flux, it is absolutely necessary and important to add the flux effectively so as to make the slag-metal reaction rapidly. By using the flux premelted homogeneously before use, the dephosphorization and desulfurization experiments were carried out to be compared with those by using the flux mixed mechanically, but there was no difference between them. It is considered that higher temperatures such as 1 350~1 450°C should be necessary for the practical application to the dephosphorization of hot metal, but the present experiment was carried out at 1 250°C, since the vaporization loss of the flux was found to be smaller. The effect of silicon, silica, manganese and chromium on the dephosphorization and desulfurization was studied by adding 20 g of the flux every one minute by 4 g. These results will be presented in subsequent sections.

2. Effect of Silicon and Silica

The effect of silicon and silica in the flux on the dephosphorization and desulfurization was studied at 1 250°C. The results are shown in Fig. 3. The flux of 20 g was added to carbon-saturated iron melt containing 0.5% initial silicon (Run No. 34). The initial dephosphorization rate is smaller and the degree of dephosphorization is lower (54%) compared with the corresponding results obtained without silicon (Run No. 101). The desulfurization degree was about 80% which was slightly less than that without silicon. It can be seen from Fig. 3 that silicon is completely oxidized to SiO_2 as the concentration of silicon ap-

Fig. 3. Variation of P and S in metal with time—Effect of Si and SiO_2 .

proaches to zero in 8 min. The reasons that the degree of dephosphorization and desulfurization decreases in the experiment with silicon (Run No. 34) may be explained as such that the flux is also consumed by the oxidation of silicon and the activity of Na_2O is lowered by silica formed in slag. The above results indicate that the desiliconization reaction is extremely important in the dephosphorization of hot metal by soda ash flux.

Considering that silica remains in slag after the desiliconization treatment, the effect of silica on the dephosphorization and desulfurization was investigated. $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux (20 g) was mixed with 5 g of silica, which was nearly equal to the amount produced when 0.5% of silicon in carbon-saturated iron melt (430 g) was completely oxidized. This flux was added to carbon-saturated iron melt (Run No. 63). The results are also shown in Fig. 3. The degree of dephosphorization and desulfurization were 67% and 77%, respectively, and these figures were lower than the corresponding ones obtained without silica present in the flux (Run No. 101). However, the dephosphorization is better than that with silicon in metal (Run No. 34). This is because the flux is not necessarily consumed by the oxidation of silicon. The important characteristics found in the curves for Run Nos. 34 and 63 shown in Fig. 3 are the reversion of phosphorus and sulfur to metal. The phosphorus reversion in the curve for Run No. 63 does not approach constant, but gradually increases. It can be expected that the curve for Run No. 34 will have the same trend as that for Run No. 63, although the experiment was not continued after 8 min. The sulfur

reversion was not observed in Run No. 63. These behavior will be discussed in Section III. 5.

3. Effect of Manganese and Chromium

Figure 4 shows the effect of manganese and chromium in carbon-saturated iron melt on the dephosphorization and desulfurization at 1250°C. The variations of manganese and chromium with time are shown in Fig. 5. In Run No. 103 where 20 g of the flux was added to carbon-saturated iron melt containing 0.5% initial manganese, the degree of dephosphorization and desulfurization was found to be almost the same as that in Run No. 101 performed without containing manganese. The manganese content is gradually reduced from 0.47% to 0.38% in 20 min, a decrement of 19%. The reason that man-

ganese decreases even after the end of flux addition is considered due to the following reaction:

The reactant Na₂S in Eq. (1) is the product according to the reactions between Na₂SO₄ and carbon and phosphorus.⁷⁾ Assuming that Na₂S, MnS and manganese are in their standard states, the reaction given by Eq. (1) will proceed thermodynamically to the right when the vapor pressure of sodium exceeds 6.8×10⁻² atm. Therefore, the decrease of manganese content in melt is explained by Eq. (1) in addition to the oxidation of manganese by flux. The reason that manganese is not oxidized as marked as phosphorus appears to be attributed to relatively high activities of MnO and MnS in slag.

In Run No. 102 where 20 g of the flux was added to carbon-saturated iron melt containing 8% initial chromium, the maximum degree of dephosphorization is 82%, which is slightly lower than that obtained in Run No. 101. On the other hand, there is little or no difference in the degree of desulfurization between the two experiments as shown in Fig. 4. During the flux addition, chromium is oxidized from 7.9% to 7.2%, but after the end of the flux addition, its concentration increases to the initial value by reduction. In Run Nos. 101, 102 and 103, considerable phosphorus reversion to metal was observed after the end of the flux addition, and the sulfur reversion tends to occur as the phosphorus concentration reaches a plateau.

4. Comparison with the Results Obtained by Na2CO3 Flux and Na2CO3-Fe2O3 Flux

To compare the dephosphorization and desulfurization by 2Na₂CO₃·Na₂SO₄ (Run No. 101) with that by Na₂CO₃ (Run No. 125) or 2Na₂CO₃·Fe₂O₃ (Run No. 66), experiments were made at 1250°C with the three fluxes (20 g). These results are illustrated in Fig. 6. The flux for Run No. 66 is of 2Na₂CO₃·Fe₂O₃ composition and is molten at 1250°C. As can be seen from Fig. 6, the dephosphorization- and desulfurization-curves (Run Nos. 125, 66 and 101) are almost the same to each other. On the other hand, the extent of phosphorus reversion in Run No. 66 is lower than that in other experiments, Run Nos. 101 and 125. The reversion of phosphorus and sulfur and the evaporation of phosphorus will be discussed in more detail in the following Section III. 5. Only the behavior of dephosphorization will be discussed here.

Oelsen⁶⁾ explained the dephosphorization mechanism by considering Na₂SO₄ as an oxidizer and Na₂CO₃ as a stabilizer, but as mentioned in the previous report,⁷⁾ the dephosphorization could occur either by using Na₂SO₄ flux or by using Na₂CO₃ flux. These dephosphorization reactions are expressed as

Fig. 4. Variation of P and S in metal with time—Effect of Mn and Cr.

Fig. 5. Variation of Mn and Cr in metal with time.

Fig. 6. Variation of P and S in metal with time.

$\Delta G^{\circ} = 37\,540 + 24.18T^{8-10} \quad (\text{cal})$

In the experiment⁷⁾ using carbon-saturated iron melt containing 1% initial phosphorus, the dephosphorization degree by 2Na₂CO₃·Na₂SO₄ flux was found to be greater than that by Na₂CO₃ flux. This is explained by the fact that the unreacted Na₂CO₃ flux reacts with free carbon produced by the reaction between Na₂CO₃ and phosphorus as given by Eq. (3). In the experiment with 0.2% initial phosphorus and 0.05% initial sulfur, the degree of dephosphorization by Na₂SO₄ flux was lower than that by Na₂CO₃ flux. The degree of dephosphorization by Na₂CO₃ flux was almost the same as that by 2Na₂CO₃·Na₂SO₄ flux. These are also observed in the present investigation. The final slag volume observed after these experiments was much smaller for Na₂CO₃ flux than for 2Na₂CO₃·Na₂SO₄ flux. This is because the sodium evaporation loss is much greater in the former experiment. Phosphorus content in slag decreases as a result of the phosphorus evaporation. Then the extent of phosphorus reversion will be reduced in the experiment with Na₂CO₃ flux. Therefore, the equally high degree of dephosphorization was obtained in both experiments. In the experiment using 2Na₂CO₃·Fe₂O₃ flux, when the initial phosphorus content is small, the extensive phosphorus evaporation loss resulting from CO gas formed by the reduction of iron oxide was observed during the flux addition. Details of this evaporation loss will be described in the following section. The extent of phosphorus reversion is reduced because low P₂O₅ content in slag causes the phosphorus evaporation during the flux addition.

Fig. 7. Variation of P in metal for reduction of 3Na₂O·P₂O₅ with carbon at 1 250°C.

Therefore, the same degree of dephosphorization was obtained in both Na₂CO₃ flux and 2Na₂CO₃·Fe₂O₃ flux, in spite of the smaller quantity of Na₂CO₃ in 2Na₂CO₃·Fe₂O₃ flux. However, the effect of oxidation by Fe₂O₃ on the dephosphorization is not certain from the present work.

Then, to examine the effect of oxidation by Fe₂O₃ and the reaction mechanism for the dephosphorization by 2Na₂CO₃·Fe₂O₃ flux, 2Na₂CO₃·Fe₂O₃ was melted in a platinum crucible to obtain Na₂O–Fe₂O₃ flux. The dephosphorization and desulfurization experiments were undertaken by this flux at 1 250°C (Run No. 106). Decomposition of Na₂CO₃ amounted to 62% and the amount of addition of this flux was 17.8 g. The dephosphorization curve for Run No. 106 for carbon-saturated iron melt containing 0.1% initial phosphorus and 0.14% initial sulfur is also shown in Fig. 6. Na₂O–Fe₂O₃ flux shows lower degree of dephosphorization than 2Na₂CO₃·Fe₂O₃ flux, although the difference is not great. This is probably due to the fact that the contribution of Na₂CO₃ to the dephosphorization reaction given by Eq. (3) decreases as Na₂CO₃ decomposes. It is not certain, however, how much the oxidizing effect of Fe₂O₃ contributes to the dephosphorization degree, since Na₂CO₃ could not be completely decomposed in the present experiment.

5. Phosphorus Reversion and Evaporation, and Sulfur Reversion

In the dephosphorization curve obtained for soda ash flux under the present experimental conditions, the phosphorus reversion occurs to a large extent after the end of the flux addition. To recognize the extent of phosphorus reversion, 3Na₂O·P₂O₅ (m.p. 1 583°C)¹¹⁾ was added to carbon-saturated iron melt at 1 250°C. The results are demonstrated in Fig. 7, where phosphorus in metal is plotted against time. It is apparent that phosphorus in iron melt increases linearly with time according to the following equation:

The reactants and products in Eq. (4) being in their standard states, the reaction will proceed to the right above 1 462°C as thermodynamic calculation indicates. Actually, however, as the partial pressure of CO and sodium are no longer unity, the reaction is thermodynamically calculated to proceed to the right at lower temperatures (1 241°C at $P_{CO}=P_{Na}=10^{-1}$ atm). In fact, P_2O_5 is not present as $3Na_2O \cdot P_2O_5(s)$, but dissolved in molten slag, so the following equation should be considered for the phosphorus reversion:

From the plot of the standard free energies of formation of $P_2O_5(l)$ and CO against temperature shown in Fig. 8, the reaction expressed by Eq. (5) is calculated to proceed to the right above 610°C provided that the reactants and products are in their standard states. However, the activity of P_2O_5 is extremely lowered by the presence of Na_2O in molten slag. One may see from the standard free energies of formation of $Na_2CO_3(l)$ and $P_2O_5(l)$ shown in Fig. 8 that, if other components are in their standard states, the activity of P_2O_5 must be lowered below 9.7×10^{-24} so that the dephosphorization by Eq. (3) can occur.

Fig. 8. Free energies of formation of CO, $P_2O_5(l)$, $Na_2O(l)$ and $Na_2CO_3(l)$.

It follows from similar free energy calculations that the partial pressure of CO must be reduced to 8.1×10^{-2} so that the phosphorus reversion by Eq. (5) can occur when the activity of P_2O_5 is 9.7×10^{-24} and carbon and phosphorus are in their standard states. The activity of P_2O_5 increases with increasing evaporation loss of sodium formed by the reduction of Na_2O with carbon. One may see from Fig. 8 that the phosphorus reversion occurs when the activity of P_2O_5 exceeds 2.7×10^{-18} .

The reason that phosphorus content in metal approaches to a constant value after the phosphorus reversion can be explained by the occurrence of the phosphorus evaporation expressed by

An experiment was carried out to study the phosphorus evaporation. $2Na_2CO_3 \cdot Na_2SO_4$ flux or $2Na_2CO_3 \cdot Fe_2O_3$ flux each 20 g was added every one minute in 4 g portion to carbon-saturated iron melt containing 0.1% or 1% initial phosphorus.

One minute or 16 min after the end of the flux addition, the graphite crucible containing the sample was quenched and the total phosphorus content in slag was determined. The phosphorus content evaporated was calculated from the total phosphorus content and the initial and final phosphorus content in metal. The fraction of the phosphorus lost by evaporation against the initial phosphorus content $\Delta P_2/P_{initial}$ is now defined as the degree of phosphorus evaporation. The results obtained are summarized in Table 1 and Fig. 9, in which the degree of phosphorus evaporation is plotted against time as a function of the initial phosphorus concentration.

In the experiment where $2Na_2CO_3 \cdot Na_2SO_4$ flux was added to the melt with 0.1% initial phosphorus, the degree of phosphorus evaporation was found to be about 9% at 1 min after the end of the flux addition (*i.e.*, experimental time 5 min). As noted in Section II. 3, when the flux was added to carbon-saturated iron melt with 0.1% phosphorus every one minute in 4 g portion, the excess sodium fume is evolved until 40~50 sec after the addition and then it becomes quiet until the next addition, *i.e.*, for 10~20 sec.

Table 1. Mass balance of P on dephosphorization by $2Na_2CO_3 \cdot Na_2SO_4$ flux and $2Na_2CO_3 \cdot Fe_2O_3$ flux at 1 250°C.

No.	Flux	Time (min)	W_p^* initial (g)	W_p^* final (g)	$\frac{\Delta P_2}{P_{initial}} \times 100$ (%)	T. Fe (as oxide) (%)
26	$2Na_2CO_3 \cdot Na_2SO_4$	5	3.938	3.895	1.1	1.75
28	$2Na_2CO_3 \cdot Na_2SO_4$	20	3.969	3.878	2.3	—
107	$2Na_2CO_3 \cdot Fe_2O_3$	5	3.939	3.872	1.7	0.90
115	$2Na_2CO_3 \cdot Fe_2O_3$	20	4.515	4.377	3.0	0.50
128	$2Na_2CO_3 \cdot Na_2SO_4$	5	0.441	0.401	9.1	—
121	$2Na_2CO_3 \cdot Na_2SO_4$	20	0.431	0.268	38	—
122	$2Na_2CO_3 \cdot Fe_2O_3$	5	0.450	0.250	44	1.05
123	$2Na_2CO_3 \cdot Fe_2O_3$	20	0.421	0.184	56	0.78

W_p^* : Total weight of P in metal and slag.

Fig. 9. Variation of phosphorus evaporation (%) and T. Fe concentration with time.

From this observation, it is evident that the phosphorus evaporation occurs even during the flux addition, because the atmosphere becomes reducing. On the other hand, the degree of phosphorus evaporation was 38% at 16 min after the end of the flux addition, *i.e.*, experimental time of 20 min. Thus, out of total amount of phosphorus initially transferred from metal to slag, about one third each returned back into the metal (*i.e.*, phosphorus reversion), evaporated out of the slag, and remained in the slag.

In the experiment where $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux was added to carbon-saturated iron melt with 0.1% initial phosphorus, the degree of phosphorus evaporation was 44% and 56% at 5 min and 20 min, respectively. For this flux, about one half of the amount of phosphorus transferred from metal to slag evaporated during the flux addition. After the end of the flux addition, the phosphorus evaporation did not occur much. From the behavior of the total iron content in slag shown in Fig. 9, the phosphorus evaporation can be explained as follows: The total iron concentration in flux is initially 30%, but it decreases to less than 1% until the end of the flux addition. It is evident that CO produced by the reduction of iron oxide and Na_2O influences the phosphorus evaporation to a great extent.¹⁴⁾

Since CO gas formed by the reduction of iron oxide and Na_2O disturbs the physical contact between slag and metal, phosphorus produced by the reduction of P_2O_5 in slag cannot be transferred into metal and is vaporized as P_2 . According to the observation during the experiment with $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux, the reaction proceeds with the violent white fume and yellow flame until 20~30 sec after the flux addition, but after that, it proceeds quietly until the next addition. It is supposed that the phosphorus reversion and phosphorus evaporation are taking place.

The phosphorus evaporation appears to be sluggish in the experiment where $2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ flux or $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux was added to carbon-saturated iron melt with 1% initial phosphorus. This is at-

Fig. 10. Schematic diagram of dephosphorization, desulfurization, reversion of P and S, and phosphorus evaporation for low SiO_2 concentration (curves I, II, III) and high SiO_2 concentration (curves I', II', III').

tributed to the fact that the sodium evaporation is reduced with the increase of the phosphorus content in slag. As a result, the phosphorus evaporation is decreased with the increase of the P_2O_5 content in slag. In the experiment with 1% initial phosphorus, the white fume as a sodium vapor was hardly observed. In the two experiments with $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux and with 0.1% and 1% initial phosphorus, the iron oxide in slag was reduced almost completely before the end of the flux addition (5 min). The weight of the vaporized phosphorus is considered constant, since the volume of CO produced by the reduction of iron oxide is constant in the two experiments. However, Table 1 shows that the weight of the vaporized phosphorus becomes smaller when P_2O_5 content is high, since the sodium evaporation loss is suppressed as described above for the experiment with 1% phosphorus.

The curves for the dephosphorization and desulfurization by soda ash flux are schematically demonstrated in Fig. 10. Based on the experimental results of the phosphorus evaporation, the curves in Fig. 10 can be explained as follows:

The curve I–II–III represents the variations of phosphorus and sulfur with time when SiO_2 content is low.

[Region I] The dephosphorization according to Eqs. (2) and (3) occurs in this region. Fe_2O_3 in $2\text{Na}_2\text{CO}_3 \cdot \text{Fe}_2\text{O}_3$ flux does not influence the dephosphorization, but CO gas produced by the reduction of iron oxide promotes the phosphorus evaporation. Further the phosphorus reversion occurs in this region. The reasons for the phosphorus evaporation

and reversion are considered to be mainly due to carbon in melt. It is not certain, however, from the present work whether the reduction is due to carbon formed by Eq. (3), which gives free carbon when the original carbon content is high enough.

[Region II] The activity of P_2O_5 is extremely lowered during dephosphorization as explained in Fig. 8. However, after the end of the flux addition the atmosphere becomes reducing and the activity of P_2O_5 increases gradually due to the sodium loss by evaporation. Accordingly, the reversion and evaporation of phosphorus occur after Eqs. (5) and (6), respectively. With $2Na_2CO_3 \cdot Fe_2O_3$ flux, as the phosphorus evaporation already occurred in region [I], the extent of reversion and evaporation of phosphorus becomes small in region [II]. The phosphorus evaporation occurs because the physical contact between iron melt and P_2 gas formed after Eq. (6) is disturbed by CO gas produced by the following reactions;

[Region III] Approaching to the end of the evaporation and reversion of phosphorus, the activity of Na_2S increases because Na_2S content increases in slag. Na_2S is produced as the product of desulfurization and the reaction between Na_2SO_4 and phosphorus [Eq. (2)] and that between Na_2SO_4 and carbon, *i.e.*,

The sulfur reversion may be considered as follows;

The reaction for Eq. (7) proceeds to the right at $1\,250^\circ\text{C}$, if the vapor pressure of sodium is less than 1.8×10^{-2} atm and Na_2S , FeS and iron are in their standard states. This is experimentally confirmed by Topkaya and Lu¹⁵⁾ for Fe-S-C alloy.

When SiO_2 content is high in slag (curve I-II'-III'), the progress of reaction, $Na_2O(l) + C = 2Na(g) + CO$, becomes delayed as a consequence of lowering activity of Na_2O . This makes the phosphorus evaporation difficult to occur. The phosphorus reversion as expressed by Eq. (5) occurs, but when SiO_2 content is high, the phosphorus reversion is retarded to some extent because the activity of P_2O_5 remains in low value to suppress the sodium vaporization. With the decrease of the sodium- and phosphorus-vaporization, the content of Na_2O and P_2O_5 increases in slag. Thus the sulfur reversion as given by Eqs. (7) and (8) does not occur as the activity of Na_2S is not increased.

6. Comparison with Previous Works and Problems Associated with Practical Application

When the present experimental results obtained for Na_2CO_3 - Na_2SO_4 flux are compared with those obtained for soda ash flux^{1-6,16-18)} the effect of temperature and silicon on the dephosphorization and desulfurization and the behavior of silicon and manganese were almost the same as those found in the previous works.^{1-6,16-18)}

Phosphorus content in carbon-saturated iron melt used in Oelsen's⁶⁾ experiment is higher (1~2%P) than that in the present work. Also, the phosphorus- and sulfur-reversion and the phosphorus evaporation are not referred to in Oelsen's work.⁶⁾ Oelsen introduced the following for the dephosphorization reaction:

considering that Na_2SO_4 is used to oxidize phosphorus and Na_2CO_3 is used to be combined with P_2O_5 . Na_2CO_3/Na_2SO_4 molar ratio of 6 was concluded to be the best flux composition for the simultaneous dephosphorization and desulfurization. However, the present authors⁷⁾ reported that the dephosphorization by Na_2CO_3 or Na_2SO_4 proceeds according to Eq. (2) or Eq. (3) which is different from what was proposed by Oelsen.⁶⁾ It was demonstrated by Oelsen that the degree of dephosphorization by Na_2CO_3 - Fe_2O_3 flux at $1\,200^\circ\text{C}$ is lower than that by Na_2CO_3 - Na_2SO_4 flux, since solid iron (2.75%C) is formed in slag by the reduction of Fe_2O_3 . On the other hand, in the present work for Na_2CO_3 - Fe_2O_3 flux, the degree of dephosphorization and desulfurization was nearly the same as that for Na_2CO_3 - Na_2SO_4 flux. Further, the extent of phosphorus reversion for Na_2CO_3 - Fe_2O_3 flux was small as a consequence of the considerable evaporation of phosphorus.

In the practical application to the dephosphorization and desulfurization of hot metal, the following aspects must be taken into consideration. In the present work, marked reversion of phosphorus and sulfur was observed with increasing temperature after the end of the flux addition. To prevent the reversion of phosphorus to metal, addition of MgO to the flux melt is known effective¹⁹⁾ to reduce the fluidity by solidifying the flux. However, this method is not preferable for recycling the flux, since the flux after the treatment becomes insoluble in water. It seems to be possible to prevent the phosphorus reversion by blowing oxygen into melt.³⁾ The presence of silicon in melt retards to a large extent the degree of dephosphorization and desulfurization, and makes cyclic utilization of the used flux unfavorable because the flux after desiliconization becomes less water soluble. When Na_2CO_3 - Na_2SO_4 flux is used, however, the flux after desiliconization may become water soluble by the fluxing effect of Na_2S and Na_2O produced after the treatment. In this flux, the sulfur reversion is promoted by Na_2S as pointed out in Section III. 5. When Na_2CO_3 flux is used, it is necessary

to increase the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio in the final slag to obtain the water soluble slag and good dephosphorization and desulfurization.^{3,20)} Thus, to increase the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio, one must increase the amount of flux or decrease the silicon content of metal by performing desiliconization before the dephosphorization and desulfurization. If silicon is left in the melt (*e.g.*, $<0.2\%\text{Si}$) owing to inadequate desiliconization, the sulfur reversion is prevented as a result of the decrease of the sodium evaporation loss, with the degree of dephosphorization and desulfurization decreased due to the consumption of flux for the oxidation of silicon remained in the melt. The phosphorus evaporation loss will also be decreased, but the extent of the decrease of the phosphorus reversion is not large judging from the present experimental results.

When $\text{Na}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ flux is added to the melt after completely removing the desiliconization slag, considerable evaporation of sodium and phosphorus occurs in addition to the dephosphorization and desulfurization. By collecting sodium and phosphorus vaporized out of the furnace, the vaporized substances can again be utilized as a flux *via* wet purifying treatment. The sulfur reversion must be prevented in the use of this flux, as the amount of Na_2S remained in the slag increases with increasing sodium- and phosphorus-evaporation. More consideration is hoped to be given in the future to the external dephosphorization and desulfurization by soda ash flux.

IV. Summary

The simultaneous dephosphorization and desulfurization of carbon-saturated iron melt were studied by using $2\text{Na}_2\text{CO}_3\cdot\text{Na}_2\text{SO}_4$, $2\text{Na}_2\text{CO}_3\cdot\text{Fe}_2\text{O}_3$ and Na_2CO_3 fluxes. The results obtained are summarized as follows:

(1) Remarkable dephosphorization and desulfurization were observed by using $2\text{Na}_2\text{CO}_3\cdot\text{Na}_2\text{SO}_4$ flux, but after the end of the flux addition, the reversion of phosphorus and sulfur was also observed under the present experimental conditions. The degree of dephosphorization and desulfurization was found to increase with decreasing temperature. The extent of the reversion of phosphorus and sulfur was reduced with decreasing temperature. The extent of sulfur reversion and the phosphorus evaporation were also reduced with increasing content of P_2O_5 and SiO_2 in slag.

(2) The degree of dephosphorization and desulfurization decreased when silicon was initially present in carbon-saturated iron melt and also SiO_2 was present in the resulting slag.

(3) The effect of manganese in iron melt on the dephosphorization and desulfurization was found to be little and its concentration did not change much with time.

(4) When $2\text{Na}_2\text{CO}_3\cdot\text{Fe}_2\text{O}_3$ flux was added to carbon-saturated iron melt containing 0.1% phosphorus, phosphorus- and sodium-evaporation were markedly observed even during the flux addition.

Consequently, it was found that the extent of the phosphorus reversion by this flux is less than that by $2\text{Na}_2\text{CO}_3\cdot\text{Na}_2\text{SO}_4$ flux.

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Appendix

The standard free energies of formation ΔG° used in the present paper are summarized below:

$$\Delta G^\circ = -290\,740 + 29.04T^{12,13} \quad (\text{cal})$$

$$\Delta G^\circ = -380\,480 - 119.8T^{9,12} \quad (\text{cal})$$

ΔG° for $\text{Na}_2\text{SO}_4(l)$, $\text{Na}_2\text{CO}_3(l)$, $\text{Na}_2\text{S}(l)$, $\text{MnS}(l)$, $\text{Na}_2\text{O}(l)$ and $\text{P}_2\text{O}_5(l)$ were quoted from Ref. 8) and ΔG° for CO , CO_2 , $\text{FeS}(l)$ and $\text{FeO}(l)$ were quoted from Ref. 10). The standard free energy of solution of various elements in liquid iron was obtained from Ref. 10).