Dephosphorization of Fe–C–P Alloy at 1623 K by Potassium Ferrite

Yasushi SASAKI, Kazunobu TAKETA and Kuniyoshi ISHII

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan.

1) Formerly at Graduate School of Engineering, Hokkaido University, Now at NHK Spring Co., Ltd., Yokohama, Japan.

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1. Introduction

It is quite common practice now to reduce phosphorus and sulfur in metals by pretreatment of hot metal. A recent strong demand to minimize the total amount of slags urges to develop high efficient dephosphorizing fluxes. The alkali oxide base fluxes are certainly the most suitable flux4–9) to meet these demands if the several difficulties of their unfriendly nature and high cost were solved. In the present study, dephosphorization of molten Fe–C–P alloy by potassium ferrite was chosen due to the following reasons;

1) Since calculated optical basicity of K2O has a larger value than that of Na2O, high efficient dephosphorization may be expected with K2O based flux than that with Na2O.9)

2) The vaporization of K2O may be reasonably suppressed due to the relatively low activity of K2O in the flux.

3) The flux itself possesses a high oxidizing potential since it contains Fe2O3.

4) Potassium ferrite can be easily produced from the low cost FeCl3 and KCl by applying the spray pyrolysis process which most of steelworks have.

5) Dephosphorized slags can be used for fertilizers because it contains the high content of potassium and phosphorus, which are major elements of fertilizer (P, K, N).

Concerning with the dephosphorization by potassium based fluxes, only one result with K2CO3 was reported9) and it was concluded that K2CO3 based flux is more efficient than that with Na2CO3. In the present study, the flux itself contains Fe2O3 so that the dephosphorization and decarburization reaction take place simultaneously. The decarburization reaction might have some effects on the dephosphorization reaction, therefore, it was also investigated.

2. Experimental Details

2.1. Apparatus

An alumina crucible (250 mm height, internal diameter 15 mm), which contained liquid Fe–C–P alloy (about 2×10−3 kg) was held in an alumina reaction tube (internal diameter 34 mm) and was heated by a resistance furnace. A 10 mm bore alumina tube was inserted coaxially just 10 mm below the open top of the alumina crucible. Another end of the inserted alumina tube was jointed with a glass tube with a branch which is fitted with a silicone rubber tube. Potassium ferrite granules were held in the silicone rubber tube by pinching the lower part of the connecting rubber tube. Appropriate amount of potassium ferrite granules (3.5×10−3 kg) were introduced to liquid iron through this glass and alumina tubes. All experiments were carried out at 1623 K where the temperature was measured by means of a thermocouple held in an alumina protection tube just below the bottom of the alumina crucible.

Purified Ar gas of 6.66×10−4 m3/s was delivered into the crucible through the alumina tube during the experiments. A mass flow controller was used to control the Ar flow rate. The increase in volume of gas due to the decarburization reaction was determined by recording the reading of a wet flow meter at the interval of 6 second. The phosphorus content in iron was analyzed by using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) and that in slag was by EDS (Energy Dispersed Spectroscopy).

2.2. Preparation of Materials

Potassium ferrite was prepared10) by mixing equimolar amount of K2CO3 and Fe2O3 powder together in an agate mortar in air and set in a Pt crucible. The mixture was heated at 1027 K for 28.8 ks, then analyzed by XRD method and was confirmed to be potassium ferrite. As the melting point of potassium ferrite is about 1923 K,11) to lower the melting point of potassium ferrite based flux, Fe2O3 was added to it. Namely, equimolar amount of potassium ferrite and Fe2O3 were ground together again and this mixture was heated at 1027 K for 10.8 ks. Since the weight decrease of mixture due to heating was about 2.0 mass%, the sublimation of K2O may be negligible. The expected melting point of this final product was about 1723 K11) and was used for all experiments. In the actual experiments, Fe2O3 is expected to be reduced to FeO and also formed Fe2O3 dissolved into the flux during experiments, thus, much lower melting point of flux can be expected. Fe–C–P alloy was prepared by inductively melting iron with an appropriate amount of carbon and Fe–P alloy in an alumina crucible. The content of phosphorus and carbon in iron were initially adjusted to 0.45 and 4.5 mass%, respectively.

2.3. Procedure

The crucible was charged with about 2×10−3 kg of Fe–C–P alloy and was brought to 1623 K under flowing argon and held about two hours to ensure thermal equilibrium. Potassium ferrite granules of 3.5×10−3 kg were then dropped on the surface of the molten Fe–C–P alloy through the alumina tube which took time about 60 s. The starting time for the reaction is that of dropping the ferrite granules. After a particular time, the crucible was pulled down to the lower part of the furnace. By this procedure, the temperature of crucible went down to 1273 K within 1 min and all melt can be solidified. Thus the reacting time may contain the error of 1 min at least. The cooled sample was surface ground and divided into small pieces for chemical analyses...
for the carbon and phosphorus concentrations.

3. Results

The typical change of phosphorus content in iron with time due to the dephosphorization reaction with K₂Fe₂O₄ at 1 623 K is shown in Fig. 1. The phosphorus content rapidly decreased from the initial content of about 0.4 mass% to about less than 0.05 mass% within 180 s, and after that the phosphorus content was almost constant. The rephosphorization was not observed even after 2.4 ks. The phosphorus content in slag was found to be about 5 to 15 mass% (as P₂O₅) depending on the collected positions. CO gas evolution started at a high rate just after the addition of K₂Fe₂O₄, then gradually decreased and almost ceased after 5 min. From the total evolution of produced CO gas, about 80% of carbon in metal was removed.

Compared with the dephosphorization reaction time and that of the decarburization, both reactions seemed to cease almost at the same time. The carbon content of melt gradually decreased with time due to the decarburization reaction, and finally reached to that on the liquidus line (about 1 mass% at 1 623 K). Then Fe alloy will be solidified and the decarburization reaction rate will be significantly decreased or essentially ceased. In obvious meaning, the carburization reaction would occur mainly at the liquid state but not solid state. Namely, the dephosphorization reaction can proceed under the condition of well-mixing of molten Fe–C–P alloy and flux due to the CO evolution.

4. Discussion

4.1. Free Energy of Formation of P₂O₅

The dephosphorization and decarburization reactions in the present study can be expressed by

\[ C + O^* = CO \] .............................(1)

\[ 2P + 5O^* = P₂O₅ \] .............................(2)

\[ mK₂O + nP₂O₅ = mK₂O \cdot nP₂O₅ \] .............................(3)

where C and P is dissolved C and P in the melt and O* may be dissolved oxygen or adsorbed oxygen at the interface. The free energies of formation change of CO and P₂O₅ with temperature known as the Ellingham diagram may be readily calculated from the available thermodynamic data and with varying the activity of P₂O₅ (aP₂O₅) and carbon content are shown in Fig. 2. In the calculation, the effect of carbon on the activity of phosphorus was neglected, since the interaction coefficient (e_p^C) is about −0.005 (at 1 873 K for the carbon saturated condition). Although the experimental temperature and the carbon concentration are not 1 873 K and that of the carbon saturation, but the slight change of the value of e_p^C will not essentially alter the calculated results.

The free energy of formation was presented in the unit of kJ per 1 mol of O₂. At the initial condition of the dissolved carbon of 4.5 mass% and phosphorus 0.5 mass%, the reaction of CO production is found to be more preferential than that of P₂O₅, at 1 623 K. Under these conditions, the dephosphorization reaction of (2) cannot occur, and only the decarburization reaction of (1) will be dominant.

In the previous discussion, aP₂O₅ is assumed to be unity. However, produced P₂O₅ will actually react with K₂O and form some potassium phosphates (reaction (3)) and so aP₂O₅ can be less than unity. The free energy change of formation of CO and P₂O₅ with varying aP₂O₅ and carbon content are also shown in Fig. 2. From this calculation, the P₂O₅ formation found to be more preferential than CO formation, if aP₂O₅ goes down to the order of 10⁻²⁰. In other words, if aP₂O₅ is lower than 10⁻²⁰, the dephosphorization reaction can continue even with the melt of high carbon content.

4.2. Estimation of aP₂O₅ in K₂O–P₂O₅ System

Unfortunately, as far as the authors concern, aP₂O₅ in the K₂O–P₂O₅ or the K₂O–P₂O₅–FeO system are not reported. However, the activities of Na₂O in the Na₂O–P₂O₅ system have been investigated and all results were well agreed within experimental scatters. Compared with the activity of Na₂O in the Na₂O–SiO₂ system and the activity of K₂O (aK₂O) in the K₂O–SiO₂ system, they show qualitatively the similar variation with composition, although the value of aK₂O is about 1 order smaller than that of Na₂O. Therefore, as a first approximation in the present study, aP₂O₅ in the K₂O–P₂O₅ system was assumed to be the same to that in the Na₂O–P₂O₅ system. The reported activities of Na₂O (aNa₂O) in the Na₂O–P₂O₅ system as a function of Na₂O mol fraction (N_{Na₂O}) at 1 473 K are shown as a single

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The high Na$_2$O concentration range which shown as a broken line in Fig. 5. The error of $\alpha_{P_{2}O_{5}}$ evaluation due to this assumption can be negligible especially for the low P$_2$O$_5$ concentration range which shown as a broken line in Fig. 5. The $\alpha_{P_{2}O_{5}}$ can be calculated from the variation of the activity of Na$_2$O by applying the Gibbs–Duhem equation. To carry out the integration of the area, $N_{Na_2O}/N_{P_{2}O_5}$ is assumed to be zero at log $a_{Na_2O}$ of -25. The obtained $\alpha_{P_{2}O_{5}}$ was converted to that at 1 623 K by assuming the melts as the regular solution and the result is shown in Fig. 4. The standard state of $\alpha_{P_{2}O_{5}}$ is pure liquid P$_2$O$_5$. It can be seen that the $\alpha_{P_{2}O_{5}}$ is less than the order of 10$^{-20}$ in the range of P$_2$O$_5$ concentration of less than 20 mol% (about 40 mass% P$_2$O$_5$). Thus, almost the same order of less than 10$^{-20}$ may be expected for the $\alpha_{P_{2}O_{5}}$ in the K$_2$O–P$_2$O$_5$ system. It means that the proceeding of the dephosphorization reaction of Fe–C–P melts with potassium ferrite flux in the high carbon melts can be expected just as observed in the present experiment. In this estimation, the effect of FeO content in the dephosphorized slags was neglected, while $\alpha_{P_{2}O_{5}}$ may become smaller with FeO. However, its fundamental aspect of the present estimation did not change by the existence of FeO.

The estimated significantly low $\alpha_{P_{2}O_{5}}$ of less than 10$^{-20}$ in the K$_2$O–P$_2$O$_5$ system will be one of the reasons why the dephosphorization reaction by K$_2$Fe$_2$O$_4$ flux can proceed in the melts with high carbon concentration. Further work is certainly needed to provide the quantitative information of the dephosphorization with K$_2$Fe$_2$O$_4$ flux, nevertheless, it can be said based on the estimated results that potassium ferrite will be the promised dephosphorizing flux constituent for the hot metal treatment.

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