Rate of Transfer of Phosphorus between Metal and Slag*

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Synopsis

Rate of transfer of phosphorus from iron melt to slag and vice versa was measured at temperature from 1 570° to 1 680°C. The slags contained iron oxide and their basicity ranged from 0.57 to 1.76.

The rate of dephosphorization by slag increased with slag basicity, while the rate of rephosphorization from slag decreased. The rate of rephosphorization increased with temperature but the effect of temperature on the dephosphorization was not noticeable.

These results were interpreted as the mass-transfer-controlled reaction.

Mass transfer coefficients in the liquid iron phase were from 0.33×10^{-2} to 1.09×10^{-2} cm/sec and in the slag phase from 0.47×10^{-3} to 4.3×10^{-3} cm/sec, at the experimental temperature range.

I. Introduction

It is well known that phosphorus is harmful for the mechanical properties of steels and much effort has been made to manufacture steels of lower phosphorus content. Most of phosphorus in iron can be removed by slag during oxidizing period of steel-making. However, some quantity of phosphorus would be absorbed by molten steel from the slag in a ladle, when the deoxidizers are added after the converting process. If so, the dephosphorization in the converter becomes less effective.

Phosphorus equilibrium between liquid iron and slag has been studied by many investigators, while the kinetics of reactions involving phosphorus has been scarcely investigated. Thus, further studies must be made on the reaction kinetics between the metal and the slag to realize the more effective dephosphorization during steelmaking.

The present paper gives the result of an experimental study on the rate of dephosphorization and rephosphorization of molten steel at 1 570° to 1 680°C.

II. Experimental Procedure

After addition of the slag onto liquid iron contained in a magnesia crucible, samples were taken both from the iron and slag at an appropriate interval. The rate of dephosphorization or rephosphorization was determined from the change of phosphorus content in the samples. At the same time, the change of oxygen content of the metal was determined by the conventional analysis.

The furnace assembly used for the dephosphorization experiment is shown in Fig. 1. For some experiments on dephosphorization and for all experiments on rephosphorization, an electric-resistance heater was used instead of an induction heating coil shown in

Fig. 1.

The procedure of experiment on dephosphorization was as follows:

A 250 g of iron containing about 0.4%P was melted in a fused magnesia crucible (I.D. 40 mm) under argon gas atmosphere. After holding for a time at the experimental temperature of 1 570° to 1 680°C, a slag holder (iron crucible) containing 40 g slag was lowered to touch the liquid iron surface. The time, when the liquid slag in the holder flowed out, was taken as the beginning of the reaction. A graphite ring was fixed to the upper part of the crucible to heat the slag by the induction to the same temperature with liquid iron.

Temperature was measured by a PtRh(6%)-PtRh(30%) thermocouple inserted from the bottom of the reaction chamber.

Samples were taken by sucking up the metal into silica tubes and by sticking slag to cold iron rods inserted through a sampling hole at the upper cap of the reaction chamber.

The procedure of rephosphorization experiment was

Fig. 1. Experimental apparatus

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almost the same. However, the inner diameter of the crucible used was 30 mm and the weights of iron and slag were 180 and 20 g, respectively.

The slags have the basicity range from 0.57 to 1.76. Slags were made from iron oxide prepared by decomposition of $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$, CaO , SiO_2 and $3\text{CaO} \cdot \text{P}_2\text{O}_5$. Mixtures of powders were melted in iron crucibles. Therefore, the slag compositions were restricted to those of low melting point and low basicity. The chemical composition of the slags is shown in Table 1.

III. Experimental Results

1. Dephosphorization

Experimental conditions and results are summarized in Table 2, including the temperature, reaction time, phosphorus and oxygen contents of liquid iron before and after the reaction, and the chemical composition of final slags.

Magnesia in the final slags originated from the magnesia crucible and the concentration was nearly equal to its solubility. The concentration of iron oxide decreased considerably during the run but the concentrations of CaO and SiO_2 were almost unchanged. In spite of sampling losses, the quantity of slag seemed to be kept nearly constant probably due to the dissolution of magnesia. Therefore, the decrease of iron oxide would be compensated by the dissolution of magnesia into slag.

Figure 2 shows the change of the phosphorus and oxygen contents in iron during runs with "slag D" (basicity=1.14) and Figure 3 shows those with other slags at 1 640°C. As shown in these results, the dephosphorizing reaction by the slags proceeded very fast, and within about 10 min, phosphorus in the metal reached constant values. The final contents were lower with the slags of higher basicity and higher iron oxide content at lower temperature. This agrees with the equilibrium distribution ratio of phosphorus

Table 1. Composition of slags (%)

	T. Fe	FeO	Fe_2O_3	CaO	SiO_2	P_2O_5	CaO/SiO ₂
A	32.7	35.0	10.0	35.3	20.7		1.70
B	38.7	41.7	11.9	28.1	21.3		1.32
C	18.0	19.3	5.6	40.2	35.2		1.14
D	25.8	28.0	7.5	34.9	30.6		1.14
E	35.0	42.1	5.8	18.1	28.5		0.64
F	36.8	40.5	7.6	29.8	16.9	5.3	1.76
G	39.2	42.7	8.6	25.6	17.2	5.9	1.49
H	37.4	43.3	5.4	25.7	18.6	7.0	1.38
I	53.7	61.0	9.0	12.0	11.6	7.4	1.03
J	30.4	35.0	4.5	27.1	26.4	7.0	1.03
K	30.7	34.3	5.8	23.3	29.5	7.1	0.79
L	19.5	22.7	2.9	25.8	43.8	5.1	0.59
M	23.6	27.3	3.4	24.1	41.3	3.9	0.58
N	21.0	20.5	7.2	25.0	43.8	3.6	0.57

Table 2. Changes of phosphorus and oxygen content of liquid iron and composition of final slags (Dephosphorization)

Slag	Run No.	Temp. (°C)	Time (min)	[%P]		[%O]		Final slag (%)				
				Init.	Final	Init.	Final	T. Fe	CaO	SiO_2	MgO	P_2O_5
A	H*33	1 570	12	0.352	0.027	0.029		22.8	38.3	22.2	3.5	4.9
	H 34	1 640	15	0.374	0.030	0.034	0.155	22.8	35.7	21.9	6.5	5.4
	H 35	1 680	12	0.417	0.046	0.029	0.166	20.1	37.9	22.2	6.9	6.2
	R*13	1 540	11	0.359	0.058	0.042	0.142	21.9	37.6	22.3	3.8	5.3
	R 14	1 595	11	0.412	0.053	0.039	0.154	21.7	37.4	22.3	5.0	4.8
B	H 41	1 570	14	0.330	0.027	0.032	0.139	31.0	28.0	21.2	6.4	4.4
	H 42	1 640	19	0.430	0.069	0.031	0.171	25.6	27.7	22.1	11.8	5.5
	H 43	1 680	20	0.439	0.058	0.031	0.188	26.8	27.6	22.1	10.9	5.4
C	H 24	1 570	11.5	0.407	0.180	0.026	0.064	11.9	39.1	34.2	9.0	3.3
	H 25	1 640	11	0.401	0.158	0.027	0.073	10.0	38.5	32.5	10.7	3.2
	H 26	1 680	11	0.444	0.223	0.025	0.083	9.0	38.0	31.5	12.9	3.7
	R 17	1 595	12.5	0.747	0.500	0.031		10.4	34.9	34.9	10.2	5.2
D	H 38	1 570	14	0.332	0.045	0.034	0.107	16.4	35.2	28.8	10.1	3.5
	H 39	1 640	14	0.361	0.064	0.028	0.115	16.0	35.0	29.1	10.9	3.8
	H 40	1 680	15	0.364	0.109	0.039	0.125	13.5	33.9	29.4	13.5	3.7
	R 11	1 540	14	0.388	0.109	0.070	0.113	18.1	33.0	28.0	10.1	3.8
	R 12	1 595	14	0.388	0.117	0.082	0.127	19.4	31.9	26.6	11.3	3.7
E	H 27	1 570	15.5	0.443	0.167	0.025	0.123	27.0	16.7	27.3	13.2	3.3
	H 28	1 640	14.5	0.413	0.223	0.025	0.135	24.3	16.5	27.9	18.2	3.4
	H 29	1 680	12.5	0.407	0.208		0.099	23.9	17.3	27.0	17.5	3.3
	R 9	1 540	12	0.351	0.180	0.078	0.133	29.0	16.1	26.2	15.6	2.4
	R 10	1 595	11.5	0.300	0.214	0.102	0.162	27.8	15.1	25.0	17.0	2.4

* H and R indicate the run in a H.F. induction furnace and in a SiC resistance furnace, respectively.

Fig. 2. Changes of phosphorus and oxygen contents during runs (Slag D)

Fig. 3. Changes of phosphorus and oxygen contents in the iron under various slags at 1640°C

Fig. 4. Changes of phosphorus and oxygen contents in the iron in a high frequency induction furnace (H27, 33) and in a resistance furnace (R10, 14)

given by previous investigators.

The reaction rate of dephosphorization increased with increase of slag basicity as shown in Fig. 3, but the influence of temperature on the reaction rate was not clearly observed in Fig. 2.

The transfer of oxygen from the slag to the metal is also so fast as shown in Figs. 2 and 3. It was frequently observed that oxygen in iron decreased after reaching the maximum. This observation was presumably due to the decrease of the activity of iron oxide in slag with progress of the dephosphorizing

reaction and dissolution of MgO. This suggests that the rate of transfer of oxygen from the slag to the metal is higher than that of phosphorus.

In Fig. 4, the experimental results obtained in the resistance furnace are compared with those in the induction furnace to show the effect of agitation of liquid iron on the reaction rate. It seems that the reaction rate is low in a resistance furnace. However, this is probably due to the difference in the driving force for the reaction and if so, the rate constant (mass transfer coefficient) would be nearly the same as shown later.

2. Rephosphorization

Experimental conditions and chemical composition of final slags are shown in Table 3. In this case, the decrease of iron oxide in slag during the run was not so much as in the case of dephosphorization.

Figure 5 shows the changes of phosphorus and oxygen contents of liquid iron at about 1600°C with various slags and Figure 6 shows the effect of temperature with "slag H" (basicity=1.38). From these results, it is found that the rephosphorizing reaction proceeds also very fast and the phosphorus content in the metal becomes constant after about 20 min. The final content is lower with more basic slag and at lower temperature, corresponding to the distribution ratio of phosphorus between the metal and the slag. The reaction rate of rephosphorization was large in the case of acid slag at high temperature. The concentration of initial oxygen in the metal seemed to have little effect on the reaction rate.

IV. Discussion

1. Distribution of Phosphorus between Iron and Slag

It is necessary for the study of reaction kinetics to know the driving force for the reaction. There are many studies on the equilibrium distribution of phosphorus between iron melt and slag, but the reliable expression of the equilibrium is not yet obtained, because of the experimental difficulties. The simple equation derived by Turkdogan and Pearson¹⁾ was found to be inadequate, because values of the equilibrium constant defined by $N_{P_2O_5}/a_P^2 \cdot a_O^5$ calculated from their equation were lower by about two order than those calculated from the final phosphorus and oxygen contents in the present experiments. This suggests that the equation given by Turkdogan and Pearson cannot be applied to the wide range of slag composition.

Recently, Healy²⁾ presented another simple equation for the phosphorus distribution from the viewpoint of ionic theory of slag as follows:

$$\log L_P \left(= \frac{(\%P)}{[\%P]} \right) = \frac{22350}{T} + 0.08(\%CaO) + 2.5 \log (\%T.Fe) - 16.0 \quad \dots \dots \dots (1)$$

As shown in Fig. 7, values of L_P calculated from Eq. (1) are in a good accordance with the present experiments. Thus, Eq. (1) was employed in the

Table. 3. Changes of phosphorus and oxygen content of liquid iron and composition of final slags (Rephosphorization)

Slag	Run No.	Temp. (°C)	Time (min)	[%P]		[%O]		Final slag (%)				
				Init.	Final	Init.	Final	T. Fe	CaO	SiO ₂	MgO	P ₂ O ₅
F	G 20	1 575	20	0.010	0.056	0.034	0.171	34.2				3.9
	G 19	1 595	"	0.009	0.062	0.029	0.171	32.6				4.0
G	E 7	1 595	"	0.010	0.064	0.072	0.180	34.7	25.2	16.9	8.1	4.5
H	G 1	1 570	"	0.007	0.049	0.057	0.148	34.7	23.0	16.7	9.4	5.5
	G 3	1 640	"	0.007	0.078	0.057	0.189	33.8	23.7	17.2	9.7	5.2
I	E 21	1 615	"	0.007	0.141	0.061	0.174	50.9	11.9	11.5	7.5	3.6
J	G 4	1 570	"	0.006	0.081	0.075	0.135	29.7	23.5	27.5	10.2	4.6
	G 5	1 600	"	0.008	0.087	0.097	0.177					3.7
	G 6	1 650	"	0.008	0.115	0.103	0.197					3.8
K	E 5	1 595	"	0.006	0.099	0.076	0.162	26.9	18.5	23.4	18.3	4.7
	E 17	1 595	"	0.007	0.097	0.153	0.162	28.6	15.1	21.5	19.8	4.4
L	E 2	1 600	"	0.006	0.108	0.086	0.115	17.8	19.1	32.4	23.6	1.6
M	E 20	1 610	"	0.007	0.171	0.046	0.105	19.2	17.7	30.3	25.6	1.4
N	G 8	1 600	"	0.008	0.071	0.082	0.145	23.6	16.7	29.2	21.9	1.4

Fig. 5. Changes of phosphorus and oxygen contents during runs at about 1600°C

Fig. 6. Changes of phosphorus and oxygen contents during runs (Slag H)

followings to examine the reaction rate of phosphorus between iron and slag, although other slag components than lime and iron oxide are neglected in the equation.

Fig. 7. Distribution ratio of phosphorus plotted against equilibrium values

2. Rate of Transfer of Phosphorus between Iron and Slag

Transfer of phosphorus across the metal-slag interface would proceed with electrochemical reactions as follows:

The amount of transferred phosphorus must satisfy the following relation to keep the electro-neutrality of the system.

$$5\Delta n_{\text{P}} = 2\Delta n_{\text{O}} + 2\Delta n_{\text{Fe}^{2+}} + 3\Delta n_{\text{Fe}^{3+}} \dots\dots\dots(2)$$

where Δn is number of transferred ions.

This was examined with the experimental results of rephosphorization. The increase of phosphorus in the metal was nearly equal to the sum of the increase of oxygen in metal and iron in slag as shown in Fig. 8.

Fig. 8. Mass balance for Run E 5 (rephosphorization)

When many reactions proceed simultaneously, it is usually difficult to determine the rate-controlling step. Aratani and Sanbongi³⁾ proposed that the chemical reaction at the interface was the rate-controlling step in the dephosphorizing reaction by slag, but the chemical equation was not given in their report.

Generally speaking, the rate of chemical reaction at high temperature is higher than that of mass transfer of reaction species to and from the reaction site. Thus, the present results were analyzed on the assumption that the reaction was controlled by the mass transfer step. As described in the above, the oxygen content of liquid iron frequently decreased after reaching the maximum during the run. This indicates that the rate of transfer of oxygen is high comparing with that of phosphorus.

When the transfer of phosphorus in the slag controls the reaction rate, the rate equation can be expressed by

$$\frac{d[\%P]}{dt} = \frac{A}{W_m} \rho_s k_s \{(\%P) - L_P[\%P]\} \quad \dots\dots\dots(3)$$

When the rate-controlling step is in the metal phase,

$$\frac{d[\%P]}{dt} = \frac{A}{W_m} \rho_m k_m \left\{ \frac{(\%P)}{L_P} - [\%P] \right\} \quad \dots\dots\dots(4)$$

where, A : the interfacial area
 W_m : the weight of metal
 ρ_s, ρ_m : densities of slag and metal
 k_s, k_m : mass transfer coefficients in slag and metal.

Strictly speaking, the mass flux of one component in multicomponent system like the present slag should be affected by the concentration differences of other components and thus, must be described by the equation containing these terms. However, it is difficult to express quantitatively such an effect because of the lack of necessary data. Therefore, in the present paper, the rate equation was expressed as Eq. (3) by applying the film theory with binary diffusion.

During the period from n -th to $(n+1)$ -th sampling, the following mass balance relation should hold:

$$W_{mn}[\%P]_n + W_{sn}(\%P)_n = W_{m(n+1)}[\%P]_{n+1} + W_{s(n+1)}(\%P)_{n+1} \quad \dots\dots\dots(5)$$

$$\begin{aligned} (\%Fe)_n - (\%Fe) &= \frac{5M_{Fe}W_{mn}}{2M_PW_{sn}} \{[\%P]_n - [\%P]\} \\ &- \frac{M_{Fe}W_{mn}}{M_OW_{sn}} \{[\%O]_n - [\%O]\} \quad \dots\dots\dots(6) \end{aligned}$$

where, W_s : the weight of slag

M : the atomic weight.

Substituting $(\%P)$ from Eq. (5) into Eqs. (3) and (4) and expressing as the sum of integrals, one has

$$\sum_n \int_{[\%P]_n}^{[\%P]_{n+1}} [W_{mn}/\{(W_{mn}/W_{sn})[\%P]_n + (\%P)_n - (L_P + W_{mn}/W_{sn})[\%P]\}] \cdot d[\%P] = A \cdot \rho_s k_s \cdot t \quad \dots\dots\dots(7)$$

$$\sum_n \int_{[\%P]_n}^{[\%P]_{n+1}} [W_{mn}L_P/\{(W_{mn}/W_{sn})[\%P]_n + (\%P)_n - (L_P + W_{mn}/W_{sn})[\%P]\}] \cdot d[\%P] = A \cdot \rho_m k_m \cdot t \quad \dots\dots\dots(8)$$

The present results were analyzed by using above Eqs. (7) and (8). The distribution ratio L_P and the mass transfer coefficients k_s and k_m were determined from the numerical calculation by a computer so as to hold the linear relation between the sum of integrals and time.

In the calculation, the following assumptions were used:

(1) In the case of dephosphorization, the reaction is controlled by the transfer of phosphorus from the metal-slag interface to the bulk slag, because the effect of agitation of the liquid metal on the reaction rate was small.

(2) In the case of rephosphorization, the reaction was assumed to be controlled by the transfer of phosphorus from the metal-slag interface to the bulk metal.

In the case of dephosphorization, the amount of slag W_s was kept constant during a run, while the amount of metal W_m decreased by sampling. Distribution ratio of phosphorus L_P varied during a run according to Eq. (9), which is a more simplified form of Eq. (1):

$$L_P = a(\%T.Fe)^{2.5} \quad \dots\dots\dots(9)$$

where a was constant and regarded as a parameter instead of L_P in the calculation. Values of $(\%P)$ and $(\%T.Fe)$ were calculated by Eqs. (5) and (6). Density of slag was assumed to be constant. Examples of the result of calculations on dephosphorization are shown in Fig. 9 (a).

In the case of rephosphorization, the assumption of (2) was found to be adequate from the independency of k_m on L_P and from the lower value of the activation energy as shown later. The distribution ratio, L_P was assumed to be constant during the run, because the change of the slag composition was little. The change of metal and slag quantities caused by sampling was taken into account in the calculation. Examples of the result of calculations on rephosphorization are shown in Fig. 9 (b).

Values of calculated mass transfer coefficients k_s and k_m are given in Tables 4 and 5. Also, values of distribution ratio L_P are given in the same tables in comparison with those obtained experimentally, which

are in good accordance with each other. Values of k_s are from 0.47×10^{-3} to 4.3×10^{-3} cm/sec and k_m from 0.33×10^{-2} to 1.09×10^{-2} cm/sec. Values of k_m are nearly equal to those obtained by Klein *et al.*⁵⁾ for the rate of oxidation of Si, Al and Mn in liquid iron

by slag in a Tamman furnace ($k_m = 0.2 \sim 1.4 \times 10^{-2}$ cm/sec).

Solid curves in Figs. 2 to 6 of the phosphorus content in the metal are based upon the calculated values of k_s , k_m and L_P , but well agree with the experimental results.

If the reaction rate is controlled by both mass transfers in slag and metal, rate equations for dephosphorization and rephosphorization are, respectively

$$\frac{d[\%P]}{dt} = \frac{A}{W_m} \frac{1}{(1/\rho_s k_s^\circ + L_P/\rho_m k_m^\circ)} \times \{(\%P) - L_P[\%P]\} \dots\dots\dots(10)$$

$$\frac{d[\%P]}{dt} = \frac{A}{W_m} \frac{1}{(1/\rho_m k_m^\circ + 1/L_P \rho_s k_s^\circ)} \times \left\{ \frac{(\%P)}{L_P} - [\%P] \right\} \dots\dots\dots(11)$$

Because the term of the driving force for mass transfer in Eqs. (3) and (10) is same and also in Eqs. (4) and (11), the mass transfer coefficients must be equal with each other. Therefore, if the terms of mass transfer coefficient in Eqs. (3) and (4) are equal to $1/\rho_s k_s^\circ$ and $1/\rho_m k_m^\circ$ in Eqs. (10) and (11), then the reaction was controlled by a single step. Values of $1/\rho_s k_s$ obtained from Eq. (3) were plotted against L_P and $1/\rho_m k_m$ from Eq. (4) against $1/L_P$ in Fig. 10.

In the case of dephosphorization (the upper part of Fig. 10), an increasing tendency of $1/\rho_s k_s$ with L_P is observed. This suggests that the resistance in the metal phase ($L_P/\rho_m k_m^\circ$) has an influence on the transfer of phosphorus and cannot be neglected, in particular at higher value of L_P . In the case of rephosphorization (the lower part of Fig. 10), values of $1/\rho_m k_m$ seem to be nearly constant. This shows that the resistance in the slag phase may be negligibly

Fig. 9. Relation between integral value and reaction time calculated from Eqs. (7) and (8)

Table 4. Distribution ratio and mass-transfer-coefficient of phosphorus

Slag	Run No.	Temp. (°C)	L_P		k_s (cm/sec)
			Exp.	Calc.	
A	H 33	1 570	74.0	69.3	0.00068
	H 34	1 640	60.4	69.0	0.0012
	H 35	1 680	49.1	46.0	0.0015
	R 13	1 540	37.9	36.8	0.00061
	R 14	1 595	39.7	38.3	0.00076
B	H 41	1 570	62.0	55.4	0.00047
	H 42	1 640	33.4	30.2	0.0016
	H 43	1 680	38.5	28.1	0.0018
C	H 24	1 570	7.6	7.4	0.0024
	H 25	1 640	8.9	7.3	0.0026
	H 26	1 680	5.8	5.6	0.0043
	R 17	1 595	7.9	7.2	0.0015
D	H 38	1 570	36.9	34.0	0.00089
	H 39	1 640	28.3	26.1	0.0014
	H 40	1 680	13.9	12.9	0.0024
	R 11	1 540	20.8	14.5	0.00078
	R 12	1 595	18.9	10.8	0.0012
E	H 27	1 570	8.9	8.8	0.0013
	H 28	1 640	7.1	5.4	0.0016
	H 29	1 680	5.7	5.7	0.0032
	R 9	1 540	6.9	4.8	0.0013
	R 10	1 595	3.3	2.8	0.0016

Table 5. Distribution ratio and mass-transfer-coefficient of phosphorus

Slag	Run No.	Temp. (°C)	L_P		k_m (cm/sec)
			Exp.	Calc.	
F	G 20	1 575	30.0	33.6	0.0051
	G 19	1 600	28.2	31.6	0.0075
G	E 7	1 595	31.0	32.2	0.0069
H	G 1	1 570	49.7	54.1	0.0072
	G 3	1 640	29.5	30.7	0.0077
I	E 21	1 615	11.2	14.1	0.0058
J	G 4	1 570	24.7	29.1	0.0075
	G 5	1 600	18.8	26.0	0.0068
	G 6	1 650	14.3	18.0	0.0085
K	E 5	1 595	20.7	23.6	0.0096
	E 17	1 595	19.6	22.6	0.0109
L	E 2	1 600	6.4	10.0	0.0089
M	E 20	1 610	3.7	3.6	0.0060
N	G 8	1 600	8.8	10.6	0.0033

Fig. 10. Relation between mass-transfer-coefficient and distribution ratio

small.

3. Effect of Slag Composition on the Rate of Transfer

As described before, the rate of transfer of phosphorus from the metal to the slag increased with the slag basicity and that from the slag to the metal decreased. However, any meaningful relation was not found between the mass transfer coefficient and the slag basicity.

Viscosity of the slags used in the experiments is nearly the same according to the report of Kozakevitch.⁴⁾ Diffusion coefficient of phosphorus in the slag has never been measured, but perhaps it would not change so much with slag composition. So, the change of mass transfer coefficient k_s with slag composition may be little as seen in Table 4.

From the present results, it may be concluded that the main factor influencing the rate of phosphorus transfer is the difference of the driving force of the diffusion and not that of diffusion coefficient.

4. Effect of Temperature on the Reaction Rate

The mass transfer coefficients k_s and k_m increased with temperature as shown in Fig. 11. Apparent activation energies were estimated about 40 and 10 kcal/mol, respectively.

In spite of the increase of the mass transfer coefficient, the reaction rate of dephosphorization did not increase with temperature. This is due to the decrease of the driving force, that is, the decrease of distribution ratio of phosphorus with temperature. On the contrary, in the case of rephosphorization the distribution ratio (driving force) changed with temperature favorably for the proceeding of the reaction. Thus the effect of temperature on the reaction rate was observed clearly.

5. Rate of Transfer of Oxygen from Slag to Metal

Oxygen transfers from the slag to the metal simul-

Fig. 11. Effect of temperature on the mass-transfer-coefficients

taneously with phosphorus as shown in Figs. 2 to 6 and this oxygen transfer may have some influences on the rate of the phosphorus reactions. To examine this effect, the rate of transfer of oxygen was measured with the metal and the slag containing no phosphorus under the same experimental condition as the rephosphorization experiment.

From the result, it was found that the rate of transfer of oxygen was controlled by the transfer in the metal phase as in the rephosphorization process.

The rate equation is expressed by

$$\frac{d[\%O]}{dt} = \frac{A}{W_m} \rho_m k_o ([\%O]_e - [\%O]) \quad \dots\dots (12)$$

where, k_o is the mass transfer coefficient and $[\%O]_e$ is the equilibrium value. For the estimation of mass transfer coefficient, the final oxygen content, $[\%O]_f$ was used instead of $[\%O]_e$. From the linear relation between logarithms of $([\%O]_f - [\%O])$ and time in Fig. 12, the mass transfer coefficient was obtained as 0.9×10^{-2} cm/sec at 1595°C. In Fig. 12, some results on the change of oxygen content of the iron during rephosphorization are also shown. Calculated mass transfer coefficients of oxygen were from 0.9×10^{-2} to 1.5×10^{-2} cm/sec, nearly the same with the value obtained in the experiment without phosphorus transfer. This fact would indicate that the oxygen transfers faster than phosphorus and has little influence on the rate of phosphorus transfer.

V. Conclusion

The rates of dephosphorization and rephosphorization of iron melt were obtained from the change of the phosphorus contents of the metal and the slag contained in the magnesia crucible. Experiments were made on the slags of basicity from 0.57 to 1.76 at temperature from 1570° to 1680°C.

The reaction proceeded so fast that the phosphorus content in iron reached a constant value within about 20 min. It was lower with more basic slag and at

Fig. 12. Relation between $([\%O]_f - [\%O])$ and $A \cdot t/V$

lower temperature.

The rate of dephosphorization was higher with the

more basic slag, while the rate of rephosphorization was lower. The effect of temperature was negligible for the dephosphorization, whereas the rate of rephosphorization increased with temperature.

These results were interpreted by the model of mass-transfer-controlled reaction. It was found that the rate-controlling step was in both slag and metal phases for the dephosphorization and only in the metal phase for the rephosphorization. Mass transfer coefficient k_s was from 0.47×10^{-3} to 4.3×10^{-3} cm/sec and k_m was from 0.33×10^{-2} to 1.09×10^{-2} cm/sec.

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