Activity of Phosphorus Pent-Oxide and Tri-Calcium Phosphate in $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ Solid Solution Saturated with CaO

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Equilibrium between molten iron and the $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution saturated with CaO was measured by the chemical equilibrium method with the oxygen partial pressure of 5.22×10^{-12} atm at 1823 K and 1.41×10^{-11} atm at 1873 K. The activity of P_2O_5 relative to hypothetical pure liquid P_2O_5 was determined from the analyzed content of P in molten iron and reported thermodynamic data. For the compositions in which the CaO phase was detected by XRD after reaction, the activity of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ was determined by the estimated activity of P_2O_5 and the activity of CaO which was unity due to its saturation. The activity coefficients of P_2O_5 and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ in solid solution and the phosphorus partition ratio between molten iron and the mixture of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and CaO were also estimated. Besides, the activity of $2\text{CaO}\cdot\text{SiO}_2$ and SiO_2 in the solid solution were also estimated by applying the Gibbs-Duhem equation.

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1. Introduction

Since phosphorus causes embrittlement for steel to decrease plasticity and toughness,¹⁻⁵⁾ usually it should be removed from molten iron and steel in the process of dephosphorization. As a cheap and efficient dephosphorization agent, CaO is commonly adopted. The excess CaO is added into slag in order to achieve better dephosphorization efficiency and thus the amount of slag and the consumption of CaO increase. Meanwhile due to CaO which remains unreacted or precipitates during solidification of dephosphorization slag, the slag is difficult to be reused. In consequence of the harm for environment and human, fluorite is strictly used although it can enhance the dissolution of CaO into slag.

During the reaction of solid CaO or $2\text{CaO}\cdot\text{SiO}_2$ with molten $\text{CaO}\cdot\text{SiO}_2\text{-FeO}\cdot\text{P}_2\text{O}_5$ slag, the formation of solid solution between di-calcium silicate and tri-calcium phosphate was confirmed by Suito and Inoue.^{6,7)} It was also confirmed that the di-calcium silicate forms a pseudo-binary solid solution with tri-calcium phosphate over a wide range of compositions at the range of steelmaking temperature.⁸⁾ For the purpose to utilize the solid solution in the process of dephosphorization, the conception of multi-phase flux was considered. The reaction mechanisms between solid CaO and the $\text{FeO}_x\text{-CaO}\cdot\text{SiO}_2\text{-P}_2\text{O}_5$ slag system were studied by Fukagai *et al.* and Hamano *et al.*,^{9,10)} and those between solid $2\text{CaO}\cdot\text{SiO}_2$ and the $\text{FeO}_x\text{-CaO}\cdot\text{SiO}_2\text{-P}_2\text{O}_5$ slag system were studied by Yang *et al.*¹¹⁻¹⁴⁾ Kitamura *et al.* also conducted the similar experiments to study the mass transfer of P_2O_5 between $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and the $\text{CaO}\cdot\text{SiO}_2\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3$ slag system.¹⁵⁾ The phase relationship of $\text{CaO}\cdot\text{SiO}_2\text{-FeO-}5\text{ mass\% P}_2\text{O}_5$ ($\sim 5\text{ mass\% Al}_2\text{O}_3$) slag system was studied by Gao *et al.* by applying the chemical equilibrium method.¹⁶⁻¹⁸⁾ The partition of P_2O_5 between $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and the $\text{CaO}\cdot\text{SiO}_2\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3$ or $\text{CaO}\cdot\text{SiO}_2\text{-P}_2\text{O}_5\text{-FeO}$ slag system was studied by applying the chemical equilibrium method to make equilibrium between $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution

and the slag by Pahlevani *et al.*,¹⁹⁾ meanwhile the activity of P_2O_5 in the solid solution was estimated by applying the regular solution model. Hasegawa *et al.* estimated the activity of P_2O_5 in the $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution by conducting the equilibrium experiments between molten Cu and the $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution at 1573 K and applying the established phase relationship.²⁰⁾ The free energy change of the formation of the solid solution between di-calcium silicate and tri-calcium phosphate was measured by Takeshita *et al.*²¹⁾

For deeper understanding of the multi-phase flux, it is necessary to clarify the thermodynamic properties of the $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution. About the activity and activity coefficient of P_2O_5 in solid solution, the regular solution model and the phase relationship were adopted for estimating the values although it has been measured so far. In experiments conducted by Pahlevani *et al.*, although the activity of P_2O_5 in molten slag and the $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution was equal because of the equilibrium between them, the alleged $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution was the enrichment phase of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution which included up to 10 mass% of other components and the activity of P_2O_5 in slag was estimated by applying the regular solution model. In experiments conducted by Hasegawa *et al.*, molten Cu was adopted rather than molten Fe for a low experimental temperature of 1573 K, and for estimating the activity of P_2O_5 the regular solution model was adopted. Besides, for the free energy change from $\alpha'\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ phase to $\alpha\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ phase at 1743 K, some simplified assumptions were applied during deducing the activity of P_2O_5 due to the limited literature data. Meanwhile for some compositions the activity of P_2O_5 was deduced by the measured activity of P_2O_5 of other compositions by applying the previously established phase relationship. In order to eliminate the deviation of the regular solution model and the phase relationship, the equilibrium between molten iron and the mixture of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and CaO was meas-

ured to obtain the activity of P₂O₅ at 1823 and 1873 K directly in our current research. The activity of 3CaO·P₂O₅ was also estimated for the compositions where the CaO phase was detected by XRD after reaction. Furthermore, the activity of 2CaO·SiO₂ in the solid solution was estimated by applying the Gibbs-Duhem equation at 1823 and 1873 K, respectively, and based on the estimated activity of 2CaO·SiO₂ the activity of SiO₂ in the solid solution was also calculated.

2. Experimental

The chemical equilibrium method which is commonly adopted to measure the thermodynamic data was adopted for the current research. The molten iron was equilibrated with the mixture of 2CaO·SiO₂-3CaO·P₂O₅ solid solution and CaO. The electrolytic iron was used whose content of P was less than 0.0003 mass%. The mixture of 2CaO·SiO₂-3CaO·P₂O₅ solid solution and CaO was made by sintering the mixture with various ratios of reagent grade SiO₂, CaHPO₄·2H₂O and CaO obtained by the calcination of reagent grade CaCO₃. The mixture was heated in air at 1873 K in a Pt crucible for 24 h, quenched by Ar stream and then ground into fine powder. These steps were repeated twice to obtain the powder of the mixture of solid solution and CaO. The formation of target phases was confirmed by XRD. For all compositions, SiO₂ or CaHPO₄·2H₂O phase was not detected but the solid solution was detected, and CaO phase was detected for some compositions as shown in Fig. 1. About 1.5 g of powder was charged into a steel dies to be pressed into a cylindrical tablet (diameter: 18 mm, thickness: 3 mm) at 50 MPa.

The vertical-resistance furnace with an Al₂O₃ tube (outer diameter: 60 mm, inner diameter: 50 mm, length: 1000 mm) was applied for the experiment. Before each experiment, temperature was measured by a B-type thermocouple from the top of the tube and the suitable hot zone with temperature of 1823 K ± 1 K or 1873 K ± 1 K was determined. Temperature during the experiment was monitored by a thermocouple placed at the bottom of an MgO crucible. The side thermocouple measured the temperature for PID controller. The partial pressure of oxygen was controlled by the mixture of CO and CO₂ gases according to reaction (1). The CO/CO₂ ratio was 110/1 with the total flow rate of 366 mL/min, in which condition the partial pressure of oxygen was calculated to be 5.22×10^{-12} atm at 1823 K or 1.41×10^{-11} atm at 1873 K.

Before charging the sample, air in the tube was replaced by Ar gas, and then the atmosphere was shifted to CO-CO₂ gas. About 10 g electrolytic iron was equilibrated with the synthesized tablet in an MgO crucible at 1823 or 1873 K. According to the preliminary experiments conducted with tablets in the same composition for different reaction time, the concentration of P in Fe barely changed as the reaction time was longer than 12 h. Finally the equilibrium duration was determined to be 24 h for the whole experiments in order to ensure equilibrium for various compositions of tablets.

Fig. 1 XRD pattern of 80 mass%2CaO·SiO₂-20 mass%3CaO·P₂O₅ solid solution plus 24 mass% CaO.

Table 1 The initial conditions of experiments.

No.	Temp./K	Compositions of tablets/mass%					
		CaO	SiO ₂	P ₂ O ₅	2CaO·SiO ₂	3CaO·P ₂ O ₅	Extra CaO
1-1	1823	71.8	21.2	7.0	80.0	20.0	24.0
1-2	1823	70.2	15.9	13.9	60.0	40.0	24.0
1-3	1823	68.5	10.6	20.9	40.0	60.0	24.0
1-4	1823	66.9	5.3	27.8	20.0	80.0	24.0
1-5	1823	66.0	2.7	31.3	10.0	90.0	24.0
2-1	1873	71.8	21.2	7.0	80.0	20.0	24.0
2-2	1873	70.2	15.9	13.9	60.0	40.0	24.0
2-3	1873	68.5	10.6	20.9	40.0	60.0	24.0
2-4	1873	66.9	5.3	27.8	20.0	80.0	24.0
2-5	1873	66.0	2.7	31.3	10.0	90.0	24.0
3-1	1823	65.9	25.7	8.4	80.0	20.0	8.0
3-2	1823	63.9	19.3	16.8	60.0	40.0	8.0
3-3	1823	61.9	12.8	25.3	40.0	60.0	8.0
3-4	1823	59.9	6.4	33.7	20.0	80.0	8.0
3-5	1823	58.9	3.2	37.9	10.0	90.0	8.0
4-1	1873	65.9	25.7	8.4	80.0	20.0	8.0
4-2	1873	63.9	19.3	16.8	60.0	40.0	8.0
4-3	1873	61.9	12.8	25.3	40.0	60.0	8.0
4-4	1873	59.9	6.4	33.7	20.0	80.0	8.0
4-5	1873	58.9	3.2	37.9	10.0	90.0	8.0

When the equilibrium was established, the sample was quenched by Ar stream at the outside of the furnace. The molybdenum-blue spectrophotometric solvent extraction method or the phosphomolybdate blue spectrophotometric method was adopted for analyzing the content of P in iron. The content of P₂O₅ in the tablet was analyzed by the phosphomolybdate blue spectrophotometric method. The content of SiO₂ in the tablet was analyzed by the gravimetry. The contents of CaO, FeO and MgO in the tablet were analyzed by ICP-OES. The formation of phases in the tablet was confirmed by XRD. Table 1 shows the initial conditions for experiments and the initial compositions of tablets were projected onto the CaO-SiO₂-P₂O₅ ternary phase diagram as shown in Fig. 2. In Table 1, the 2CaO·SiO₂ and 3CaO·P₂O₅ compositions were the mass percent in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution and the extra CaO composition was the

Fig. 2 Projection of initial compositions of tablets onto the CaO-SiO₂-P₂O₅ ternary phase diagram near the CaO corner. The open circle presented the compositions which turned into molten slag after reaction. The boundary and tie lines in the phase diagram were determined at 1773 K by Gutt.²³⁾

Table 2 The compositions of tablets and the content of P in molten iron after reaction.

No.	Compositions of tablets/mass%						P in Fe/mass%
	P ₂ O ₅	SiO ₂	CaO	MgO	FeO	Total	
1-1	6.94	21.23	67.98	0.49	0.38	97.0	0.00479
1-2	13.8	15.37	66.30	0.77	0.42	96.7	0.00917
1-3	20.6	10.68	65.37	0.37	0.39	97.4	0.0153
1-4	28.2	5.187	63.69	0.33	0.47	97.9	0.015
1-5	31.7	2.469	63.45	0.25	0.36	98.2	0.016
2-1	6.98	20.64	68.63	0.65	0.75	97.7	0.00553
2-2	13.8	16.49	67.95	0.53	0.86	99.6	0.0093
2-3	20.6	9.878	65.87	0.74	0.94	98.0	0.0150
3-1	8.73	25.05	62.17	0.28	0.84	97.1	0.0028
3-2	17.2	18.74	58.44	0.23	0.91	95.5	0.0035
3-3	26.5	13.63	58.27	0.39	0.63	99.4	0.00836
3-4	34.7	6.517	56.53	0.27	0.34	98.4	0.0214
3-5	38.0	3.357	57.80	0.30	1.38	100.8	0.0491
4-1	8.58	25.60	60.19	0.39	1.28	96.0	0.0036
4-2	17.2	17.41	57.71	0.36	2.13	94.8	0.00666
4-3	26.5	12.78	59.13	0.67	0.25	99.3	0.0267
4-5	38.6	3.262	56.85	0.43	0.29	99.4	0.0734

Table 3 The normalized compositions after reaction and the calculated thermodynamic data.

No.	3CaO·P ₂ O ₅ /mol%	Extra CaO /mass%	(mass% P) [mass% P]	$a_{P_2O_5}$	$a_{3CaO \cdot P_2O_5}$
1-1	12.2	20.9	6.58×10^2	8.28×10^{-25}	9.49×10^{-6}
1-2	27.4	22.0	6.88×10^2	3.05×10^{-24}	3.49×10^{-5}
1-3	44.9	21.7	6.08×10^2	8.54×10^{-24}	9.79×10^{-5}
1-4	69.7	21.2	8.5×10^2	8.2×10^{-24}	9.4×10^{-5}
1-5	84.5	21.8	8.9×10^2	9.3×10^{-24}	1.1×10^{-4}
2-1	12.5	22.7	5.73×10^2	1.08×10^{-24}	4.77×10^{-6}
2-2	26.2	21.2	6.6×10^2	3.1×10^{-24}	1.4×10^{-5}
2-3	46.9	23.9	6.22×10^2	8.06×10^{-24}	3.55×10^{-5}
3-1	12.9	5.3	1.4×10^3	2.8×10^{-25}	3.2×10^{-6}
3-2	28.0	3.3	2.3×10^3	4.4×10^{-25}	5.1×10^{-6}
3-3	45.1	1.4	1.41×10^3	2.53×10^{-24}	2.90×10^{-5}
3-4	69.3	3.3	7.24×10^2	1.68×10^{-23}	1.93×10^{-4}
3-5	82.7	6.6	3.41×10^2	9.12×10^{-23}	1.04×10^{-3}
4-1	12.4	2.4	1.1×10^3	4.6×10^{-25}	2.0×10^{-6}
4-2	29.5	5.2	1.22×10^3	1.57×10^{-24}	6.93×10^{-6}
4-3	46.7	3.9	4.40×10^2	2.58×10^{-23}	1.14×10^{-4}
4-5	83.4	5.1	2.32×10^2	2.05×10^{-22}	—

mass percent of CaO in the mixture of the solid solution and CaO.

3. Results and Discussion

The tablet contained a certain amount of FeO and MgO after reaction. Although the initial compositions of all 2CaO·SiO₂-3CaO·P₂O₅ solid solution plus 8 or 24 mass% CaO tablets were solid phase at 1873 K, the tablets for Nos. 2-4, 2-5 and 4-4 in Table 1 turned into slag phase after reaction as shown in Fig. 2 by open circles. The phase relationship for these compositions was not clear in the previous study²³⁾ and thus these three compositions are not discussed in the following. Table 2 presents the contents of P in molten iron and the compositions of tablets after reaction.

Since molten iron coexisted, iron oxide in the tablet was assumed to be FeO. Because of the analytical accuracy, the significant digits for the concentration of P in Fe in Table 2 and the thermodynamic data in Table 3 are different.

The MgO phase was barely detected in the XRD patterns of the tablets after reaction while the CaO phase was detected for some samples. Figure 3 shows an example of XRD pattern and Fig. 4 shows the projections of the compositions of tablets after reaction onto the CaO-SiO₂-P₂O₅ ternary phase diagram.

3.1 Contents of FeO and MgO in the mixture of 2CaO·SiO₂-3CaO·P₂O₅ solid solution and CaO after reaction

Figure 5 shows the relationship between the P₂O₅ content

Fig. 3 XRD pattern of 80 mass% $2\text{CaO}\cdot\text{SiO}_2$ -20 mass% $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution plus 24 mass% CaO after reaction.

Fig. 5 Contents of FeO and MgO in tablets after reaction.

Fig. 4 Projection of the compositions of tablets after reaction onto the $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$ ternary phase diagram near the CaO corner. The compositions in which CaO phase was detected by XRD were marked as solid circles while the composition without CaO phase was marked as an open circle.

and the FeO or MgO content in tablets after reaction. There was no obvious change in the content of FeO or MgO with the increase of P_2O_5 content. Since the tablet was contaminated with more or less MgO crucible particles and iron particles when the tablet was separated from the surface of solidified iron at the inside of the MgO crucible, contents of FeO and MgO were larger for some samples. Except the irregular points, both of the contents of FeO and MgO were smaller than 1 mass%.

3.2 Equilibrium content of P in molten iron and phosphorus partition ratio between molten iron and the mixture of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and CaO

Figure 6 shows the relationship between the equilibrium content of P in molten iron and the content of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ in the solid solution. The $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution was considered to be the binary system of di-calcium silicate and tri-calcium phosphate. The normalized contents of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ in the solid solution were calculated

from the analyzed SiO_2 and P_2O_5 contents, respectively. As a whole, the content of P in molten iron increased with the increase of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. For a constant composition of the solid solution, the content of P barely changed with the change of temperature or extra CaO content. The phosphorus partition ratio between molten iron and the mixture of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and CaO is shown in Fig. 7 and Table 3. The phosphorus partition ratio decreased with the increase of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. For a constant composition of the solid solution, there is no obvious change in the phosphorus partition ratio with the change of temperature and extra CaO content because of the limited accuracy of chemical analyses, though the phosphorus partition ratio decreases with the increase of extra CaO content in principle.

3.3 Activity and activity coefficient of P_2O_5 in $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution initially adding 8 and 24 mass% CaO

The equilibrium between molten iron and the mixture of

Fig. 6 Equilibrium content of P in molten iron after reaction.

Fig. 7 Phosphorus partition ratio between molten iron and the mixture of 2CaO·SiO₂-3CaO·P₂O₅ solid solution and CaO.

Table 4 The reference data about interaction coefficients of solutes in molten iron.

e_i^j		j		
		P	C	O
i	P	0.054 ²⁶⁾	0.126 ²⁷⁾	0.13 ²⁸⁾
	C	0.051 ²⁷⁾	0.243 ²⁵⁾	-0.32 ²⁵⁾
	O	0.07 ²⁸⁾	-0.421 ²⁵⁾	-0.17 ²⁹⁾

2CaO·SiO₂-3CaO·P₂O₅ solid solution and CaO is expressed in term of phosphorus as reaction (2).

Since the partial pressure of oxygen was controlled by the mixture of CO and CO₂, contents of C and O in molten iron were calculated by eqs. (3) and (4) and the reported interaction coefficients shown in Table 4.

Fig. 8 The relationship between the activity of P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO and the 3CaO·P₂O₅ content in the solid solution. Fig. 9 The relationship between the activity coefficient of P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO and the 3CaO·P₂O₅ content in the solid solution.

The activity of P₂O₅ was calculated by eq. (2) from the analyzed content of P and the reported thermodynamic data. The mole percent of P₂O₅ in the solid solution was calculated by the normalized content of 3CaO·P₂O₅ in Table 3 and the values of the activity of P₂O₅ were listed in Table 3. The activity of P₂O₅ is relative to hypothetical pure liquid P₂O₅. Figures 8 and 9 show the change in the activity and the activity coefficient of P₂O₅ with the content of 3CaO·P₂O₅ in the solid solution. The activity and the activity coefficient of P₂O₅ increased with the increase of 3CaO·P₂O₅ content in the solid solution. For a constant composition of the solid solution, the activity and the activity coefficient of P₂O₅ barely changed with the change of temperature and extra CaO content. Comparing with the values of P₂O₅ activity estimated by Hasegawa *et al.* at 1573 K, the current values were larger. The activity of P₂O₅ was in the range from 2.8×10^{-25} to 2.05×10^{-22} , and the activity coefficient of P₂O₅ was in the range from 5.2×10^{-24} to 9.44×10^{-22} .

3.4 Activity and activity coefficient of 3CaO·P₂O₅ in 2CaO·SiO₂-3CaO·P₂O₅ solid solution

For the compositions in which the CaO phase was detected

Fig. 10 The relationship between the activity of 3CaO·P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution and the 3CaO·P₂O₅ content.

Fig. 11 The relationship between the activity coefficient of 3CaO·P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution and the 3CaO·P₂O₅ content.

as shown in Fig. 4 as solid circles, the activity of 3CaO·P₂O₅ was calculated by the estimated activity of P₂O₅ and the activity of CaO which was unity by eqs. (5) and (6). The values of the activity of 3CaO·P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution were listed in Table 3. Figures 10 and 11 show the change in the activity and the activity coefficient of 3CaO·P₂O₅ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution with the 3CaO·P₂O₅ content. The activity and the activity coefficient of 3CaO·P₂O₅ increased with the increase of 3CaO·P₂O₅ content in the solid solution. For a constant composition, the activity and the activity coefficient of 3CaO·P₂O₅ barely changed with the change of temperature and extra CaO content. Comparing with the 3CaO·P₂O₅ activity calculated from the activities of P₂O₅ and CaO estimated by Hasegawa *et al.*⁽²⁰⁾ at 1573 K by eqs. (5) and (6), the presents results were larger by approximately one to two orders of magnitude, which temperature dependence is thermodynamically feasible. The activity of 3CaO·P₂O₅ was in the range from 2.0×10^{-6} to 1.04×10^{-3} and the activity coefficient of 3CaO·P₂O₅ was in the range from 1.6×10^{-5} to 1.26×10^{-3} .

Fig. 12 The estimated activity of 2CaO·SiO₂ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution by applying the Gibbs-Duhem equation for the 2CaO·SiO₂-3CaO·P₂O₅ pseudo-binary system.

Fig. 13 The estimated activity of SiO₂ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO.

$$\Delta G_5^\circ = -2198000 + 504T \text{ J/mol}^{(30)} \quad (5)$$

$$\Delta G_6^\circ = -1655480 + 571.0T \text{ J/mol}^{(24)} \quad (6)$$

3.5 Activity of 2CaO·SiO₂ and SiO₂ in 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO

By applying the Gibbs-Duhem equation for the 2CaO·SiO₂-3CaO·P₂O₅ pseudo-binary system composed of two species, namely 2CaO·SiO₂ and 3CaO·P₂O₅, the activity of 2CaO·SiO₂ in the solid solution was calculated with the estimated activity coefficient of 3CaO·P₂O₅ as shown in Fig. 12. The relationship between the logarithmic activity coefficient of 3CaO·P₂O₅ and the mole fraction of 3CaO·P₂O₅ in the solid solution was expressed by a linear function by the least square method at the compositional range from 0.122 to 0.845 at 1823 K and from 0.124 to 0.469 at 1873 K, respectively. Temperature dependency of the estimated 2CaO·SiO₂ activity was not obvious within the experimental error range. Moreover, the activity of SiO₂ in the 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO was calculated by the estimated activity of 2CaO·SiO₂ and eq. (7) as shown in Fig. 13. Temperature dependency of the activity of SiO₂

was also little. The activity of SiO_2 in the solid solution saturated with CaO decreased monotonically from 1.0×10^{-4} to 6.9×10^{-7} with the increase of the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ content up to 84.5 mol% at 1823 K.

4. Conclusions

By applying the chemical equilibrium method, equilibrium between molten iron and the mixture of $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution and CaO was measured at 1823 K with the oxygen partial pressure of 5.22×10^{-12} atm and 1873 K with the oxygen partial pressure of 1.41×10^{-11} atm. The activity of P_2O_5 relative to the hypothetical pure liquid P_2O_5 in the $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution initially containing 8 and 24 mass% CaO increased with the increase of the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ content in the solid solution in the range from 2.8×10^{-25} to 2.05×10^{-22} and the activity coefficient of P_2O_5 was in the range from 5.2×10^{-24} to 9.44×10^{-22} within the $3\text{CaO} \cdot \text{P}_2\text{O}_5$ content in the solid solution from 12.2 to 84.5 mol% $3\text{CaO} \cdot \text{P}_2\text{O}_5$. For the compositions in which the CaO phase was detected by XRD after reaction, the activity of $3\text{CaO} \cdot \text{P}_2\text{O}_5$ in the $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution was in the range from 2.0×10^{-6} to 1.04×10^{-3} and the activity coefficient of $3\text{CaO} \cdot \text{P}_2\text{O}_5$ was in the range from 1.6×10^{-5} to 1.26×10^{-3} . The activity of $2\text{CaO} \cdot \text{SiO}_2$ calculated by applying the Gibbs-Duhem equation and that of SiO_2 in the solid solution calculated with the condition of CaO saturation decreased with the increase of $3\text{CaO} \cdot \text{P}_2\text{O}_5$ content in the solid solution at 1823 and 1873 K.

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