Effect of Iron Oxide Dissolution on Thermochemical Property of Solid Solution between Ca_2SiO_4 and $Ca_3P_2O_8$ at 1 573 K

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The key to a better understanding of phosphorus removal from hot metal is to know the thermochemical properties of solid solution between Ca_2SiO_4 and $Ca_3P_2O_8$. Although the solid solutions would inevitably incorporate iron oxide in steelmaking slags, there is a still lack of knowledge about the solid solutions containing iron oxide. The present study focused on the effect of FeO dissolution on the activities of components in the $Ca_2SiO_4-Ca_3P_2O_8$ solid solution. The P_2O_5 activities were measured in the solid solution containing FeO at 1 573 K. Subsequently, the activities of Ca_2SiO_4 , $Ca_3P_2O_8$, and Fe_2SiO_4 were derived from the Gibbs-Duhem equation with the measured P_2O_5 activities and reported FeO activities. When iron oxide dissolved into the $Ca_2SiO_4-Ca_3P_2O_8$ solid solution, the $Ca_3P_2O_8$ activity decreased, while the Ca_2SiO_4 activity was insensitive. As a result, the dissolution of iron oxide into the solid solution caused a drastic decrease in the P_2O_5 activity.

KEY WORDS: P₂O₅ activity; iron oxide; di-calcium silicate; tri-calcium phosphate.

1. Introduction

Phosphorus is a typical harmful impurity in steel and is removed from hot metal by oxidation reaction in steelmaking processes. It has been reported that phosphorus oxide in slags is concentrated in solid solutions between di-calcium silicate, Ca₂SiO₄, and tri-calcium phosphate, Ca₃P₂O₈,^{1–9)} and the solid solutions have important roles in the dephosphorization reactions.¹⁰⁾ To understand phosphorus removal from hot metal, a number of investigations have been carried out to determine the thermochemical properties of the slags containing the Ca₂SiO₄–Ca₃P₂O₈ solid solutions.^{11–19)}

The part of the reported iso-thermal section of the CaO– SiO₂–P₂O₅ ternary phase diagram at 1 573 K^{20–22)} and the phase diagram of the Ca₂SiO₄–Ca₃P₂O₈ pseudo-binary system²³⁾ are given in **Fig. 1**. These diagrams show that the solid solutions between α -Ca₂SiO₄ and $\bar{\alpha}$ -Ca₃P₂O₈, denoted as <Ca₂SiO₄–Ca₃P₂O₈>_{SS}, coexists with some multiple oxides in the CaO–SiO₂ or CaO–P₂O₅ binary system at 1 573 K. In the preceding studies, the activities of P₂O₅ in the solid solutions coexisting with CaO, CaSiO₃, or Ca₃SiO₅ were determined at 1 573 K by equilibrating phosphorus-containing copper with oxides under a stream of Ar + H₂ + H₂O gas mixtures.^{11,12)} The P₂O₅ activity in the <Ca₂SiO₄–Ca₃P₂O₈>_{SS} + CaO two-phase region









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was found to be about seven digits lower than that in the <Ca₂SiO₄-Ca₃P₂O₈>_{SS} + CaSiO₃ two-phase region.¹¹ At higher temperatures, Zhong et al. measured the P2O5 activities in the solid solutions at 1 823 K and 1 873 K through a chemical equilibrating method, in which iron-phosphorus alloys were brought into the equilibrium with oxides in magnesia crucibles under fixed oxygen potentials.^{13–15)} In their study, it was also reported that the oxide phase was contaminated by 0.2-0.8% MgO and 0.3-2.1% FeO.13) Yu et al.24) investigated the crystallographical properties of <Ca₂SiO₄–Ca₃P₂O₈>_{SS} and discussed that the composition dependence of a lattice parameter was compatible with that of the P₂O₅ activity in the solid solutions based on the work by Zhong et al.¹⁴⁾ However, it would be better to consider the activities of Ca2SiO4 and Ca3P2O8 rather than P2O5 since the P2O5 activity changes drastically depending on the solid phases coexisting with <Ca₂SiO₄–Ca₃P₂O₈>_{SS} as mentioned previously.¹¹⁾

When added to the CaO–SiO₂–P₂O₅ ternary system, iron oxide would form quaternary liquid phase and also dissolve into <Ca₂SiO₄–Ca₃P₂O₈>_{SS} as seen in **Fig. 2**(a), which is the schematic phase diagram of the CaO–SiO₂–P₂O₅–FeO quaternary system at 1 573 K. The base of the tetrahedron in Fig. 2(a) corresponds to the CaO–SiO₂–P₂O₅ ternary phase diagram (same as Fig. 1(a)). In <Ca₂SiO₄–Ca₃P₂O₈>_{SS}, Fe²⁺ is considered to substitute for Ca²⁺,²⁵ and thus the solid solution containing FeO can be expressed as (Ca, Fe)₂SiO₄–(Ca, Fe)₃P₂O₈. In Fig. 2 and hereafter, the following abbreviations are used.

 $CS = \text{CaSiO}_3 = \text{CaO} \cdot \text{SiO}_2$ $C2S = \text{Ca}_2 \text{SiO}_4 = 2\text{CaO} \cdot \text{SiO}_2$ $C3P = \text{Ca}_3 \text{P}_2 \text{O}_8 = 3\text{CaO} \cdot \text{P}_2 \text{O}_5$ $C4P = \text{Ca}_4 \text{P}_2 \text{O}_9 = 4\text{CaO} \cdot \text{P}_2 \text{O}_5$ $W2S = \text{Fe}_2 \text{SiO}_4 = 2\text{FeO} \cdot \text{SiO}_2$ $<C2S - C3P >_{SS} = \text{Ca}_2 \text{SiO}_4 - \text{Ca}_3 \text{P}_2 \text{O}_8 \text{ solid solution}$ $<C2S - C3P - W2S >_{SS}$ $= (\text{Ca}, \text{Fe})_2 \text{SiO}_4 - (\text{Ca}, \text{Fe})_3 \text{P}_2 \text{O}_8 \text{ solid solution}$ $= \text{Ca}_2 \text{SiO}_4 - \text{Ca}_3 \text{P}_2 \text{O}_8 - \text{Fe}_2 \text{SiO}_4 \text{ solid solution}$ $Liquid = \text{CaO} - \text{SiO}_2 - \text{P}_2 \text{O}_5 - \text{FeO} \text{ quaternary liquid}$

The phase relations around $\langle C2S-C3P-W2S \rangle_{SS}$ in the quaternary system are projected onto the CaO-(SiO₂+P₂O₅)-FeO pseudo-ternary field in Fig. 2(b).^{16–18,26)} Im *et al.*²⁶⁾ and Ito and Sano¹⁶⁾ measured the phosphorus distribution ratios between Liquid and molten iron when the slags were saturated with CS and C2S, respectively. Phalevani et al. conducted the study on the distribution of P2O5 between the solid solutions and Liquid, in which the dissolutions of the iron oxide into $\langle C2S-C3P \rangle_{SS}$ were also observed.¹⁹⁾ In the three-phase region of $\langle C2S-C3P-W2S \rangle_{SS}$ + CS + Liquid, Matsugi *et al.* measured the P₂O₅ activities at 1 548 K-1 598 K with an electrochemical technique involving stabilized zirconia electrolyte.¹⁷⁾ The measured P₂O₅ activities in this three-phase assemblage were about one digit lower than those in the $\langle C2S-C3P \rangle_{SS} + CS$ two-phase region reported by T. Saito et al., and it was attributed to the dissolution of iron oxide into the solid solution.¹¹⁾ The P₂O₅ activity in the solid solution coexisting with CS can be



Fig. 2. (a) Schematic phase diagram of the CaO–SiO₂–P₂O₅–FeO quaternary system at 1 573 K. (b) Phase diagram of the CaO–(SiO₂+P₂O₅)–FeO pseudo-ternary system at 1 573 K.

determined through Reaction (1).

$$P_2O_5 + 3C2S = C3P + 3CS \dots (1)$$

Since the dissolution of iron oxide affects both C2S and C3P activities in the solid solution, the effect of FeO on the P₂O₅ activity would be complex and not obvious.

Based on the considerations above, the purpose of this study was to clarify the effect of FeO dissolution on the activities of components in $\langle C2S-C3P-W2S \rangle_{SS}$. The P₂O₅ activities were measured in $\langle C2S-C3P-W2S \rangle_{SS}$ coexisting with *CS* by equilibrating molten copper alloys with oxides under a stream of Ar + H₂ + H₂O gas mixtures. The *C2S*, *C3P*, and *W2S* activities in the solid solutions were subsequently derived from the measured results.

2. Experimental Aspects

2.1. Principle of the Activity Measurements

In the present experiment, the Cu–Fe–P liquid alloys were brought into equilibrium with $\langle C2S-C3P-W2S \rangle_{SS} + CS$ under a stream of Ar + H₂ + H₂O gas mixture with a fixed partial pressure ratio of H₂/H₂O, p_{H_2} / p_{H_2O} , at 1 573 K. According to the Gibbs phase rule, the present experimental system contained the four phases ($\langle C2S-C3P-W2S \rangle_{SS}$, CS, Cu alloy, and gas) and the seven independent components (CaO, SiO₂, P₂O₅, FeO, Cu, H₂, and H₂O), and thus the number of degrees of freedom is five (= 7+2–4). Hence, when temperature, C3P and W2S concentrations in $\langle C2S-C3P-W2S \rangle_{SS}$, p_{H_2} , and p_{H_2O} were fixed, all the intensive properties were determined in this system.

The underlying reactions can be expressed by

$$\log K_3 = \log a_{\rm FeO} - \log h_{\rm Fe} + \log (p_{\rm H_2} / p_{\rm H_2O}) \dots \dots (4)$$

$$2[P]_{Cu} + 5H_2O(g) = P_2O_5(SS) + 5H_2(g) \dots \dots \dots (5)$$

$$\log K_5 = \log a_{\rm P_2O_5} - 2\log h_{\rm P} + 5\log(p_{\rm H_2} / p_{\rm H_2O}).....(6)$$

, where *i*(SS) and a_i represent the constituent oxide *i* in the solid solution and its Raoultian activity, respectively, and $[j]_{Cu}$ and h_j are the component *j* in the liquid copper and its Henrian activity, respectively. The standard states of a_{FeO} , a_{P2O_5} , and h_j are taken to be pure solid non-stoichiometric FeO in equilibrium with metallic iron, pure hypothetical liquid P₂O₅, and solute *j* in liquid copper at 1 mass% solution, respectively. The values for K_3 and K_5 can be obtained by combining the following reactions.

$$H_2(g) + (1/2)O_2(g) = H_2O(g)$$
(7)

$$\log K_7 = 5.32$$
 at 1 573 K²⁷(8)

$$Fe(s)+(1/2)O_2(g) = FeO(s)$$
(9)

$$\log K_9 = 5.35$$
 at 1 573 K²⁸⁾(10)

$$\operatorname{Fe}(s) = [\operatorname{Fe}]_{C_{11}}$$
(11)

$$\log K_{11} = 0.68$$
 at 1 573 K²⁹(12)

$$P_2(g) + (5/2)O_2(g) = P_2O_5(1)$$
(13)

$$\log K_{13} = 24.51$$
 at 1 573 K³⁰(14)

$$(1/2)P_2(g) = [P]_{C_u}$$
(15)

$$\log K_{15} = 4.12$$
 at 1 573 K³¹(16)

 $\log K_3 = -\log K_7 + \log K_9 - \log K_{11} = -0.64 \text{ at } 1573 \text{ K}$(17)

$$\log K_5 = -5 \log K_7 + \log K_{13} - 2 \log K_{15}$$

$$= -10.34 \text{ at } 1573 \text{ K}$$
(18)

, where K_i is the equilibrium constant of reaction *i* and the symbol "log" represents the common logarithm. By using

the interaction parameters, e_j^k , the activities of Fe and P at 1 573 K can be expressed as follows.

$$\log h_{\rm Fe} = \log \left[\% {\rm Fe}\right]_{\rm Cu} + e_{\rm Fe}^{\rm Fe} \left[\% {\rm Fe}\right]_{\rm Cu} + e_{\rm Fe}^{\rm P} \left[\% {\rm P}\right]_{\rm Cu} \dots (19)$$

$$e_{\text{Fe}}^{\text{Fe}} = -0.0346$$
 $0 \le \left[\%\text{Fe}\right]_{\text{Cu}} \le 9.3$ at 1 573 K³²⁻³⁴ ... (20)

$$\log h_{\rm P} = \log \left[\% \mathbf{P} \right]_{\rm Cu} + e_{\rm p}^{\rm Fe} \left[\% \mathrm{Fe} \right]_{\rm Cu} + e_{\rm P}^{\rm P} \left[\% \mathbf{P} \right]_{\rm Cu} \dots (21)$$

$$e_{\rm P}^{\rm P} = 0$$
 [%P]_{Cu} <1 at 1573 K³¹(22)

, where $[\% j]_{Cu}$ denotes the mass% concentration of the solute *j*. When $[\% P]_{Cu}$ is small, the last term of Eq. (19) is negligible. Therefore, if the value for e_p^{Fe} is available, Eqs. (6), (18), (21), and (22) indicate that $a_{P_2O_5}$ at 1 573 K can be determined by analyzing the compositions of the liquid copper alloys equilibrated with the quaternary oxides under fixed p_{H_2} / p_{H_2O} .

2.2. Materials and Procedure

The details of the procedure have already been reported in the previous study.³⁵⁾ Hence, only a brief description is given in this paper. The preparations of oxides used in this study are summarized in **Table 1** and the compositions of the oxide samples are listed in **Table 2**. The composition of $\langle C2S-C3P \rangle_{SS}$ in Sample A plotted in Fig. 1 was the same as that in the preceding study by T. Saito *et al.*¹⁰⁾ for comparison. The compositions of Samples B to D were identical to those in the previous work, in which the FeO activities were measured in $\langle C2S-C3P-W2S \rangle_{SS} + CS.^{35}$) The reported FeO activities at 1 573 K are given in the last column of Table 2. **Figure 3** gives the compositions of the solid solutions plotted on the Ca₂SiO₄–Fe₂SiO₄–Ca_{1.5}PO₄ (= *C2S-W2S*-(1/2)*C3P*) triangle by using the following formulae.

$$X'_{\text{Ca}_2\text{SiO}_4} = 1 - X'_{\text{Ca}_{1.5}\text{PO}_4} - X'_{\text{Fe}_2\text{SiO}_4}$$
(25)

, where X'_i or X_i represents the mole fraction of component *i* in the Ca₂SiO₄–Fe₂SiO₄–Ca_{1.5}PO₄ or CaO–SiO₂–PO_{2.5}–FeO system, respectively. Since SiO₄^{4–} were considered to be replaced by PO₄^{3–} in the solid solution, ^{11,36,37)} the compositions were expressed as the components with a single SiO₄^{4–} or PO₄^{3–} in this figure. The mole ratios of P/(Si+P) (= $X'_{Ca_{1.5}PO_4}$) in the solid solutions were almost constant, while the Fe/(Ca+Fe) ratios varied from 0 to 0.052. The oxide mixtures were pressed in a steel die to form crucibles of 15 mm o.d., 8 mm i.d., and 8 mm in height.

The experimental apparatus is shown in **Fig. 4**. Copper shavings (Nakalai Tesque Inc., Kyoto, Japan), powdery iron (Nakalai Tesque Inc. Kyoto, Japan), and copper phosphide (14.8 mass%P, Hirano Seizaemon Co. Ltd., Tokyo, Japan) were charged in the crucibles made from the oxide samples and held in a mullite reaction tube at 1 573 K. The Ar + H₂ + H₂O gas mixtures were introduced into the reaction tube to fix p_{H_2} / p_{H_2O} . The gas mixture was prepared by passing the Ar + 12%H₂ gas mixture through either distilled

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Material	Preparation
CaCO ₃	Obtained from Nacalai Tesque, Inc., Kyoto, Japan.
SiO_2	Obtained from FUJIFILM Wako Pure Chemical Co., Osaka, Japan, and dried at 413 K.
Fe	Obtained from Nacalai Tesque, Inc., Kyoto, Japan.
Fe ₃ O ₄	Obtained from Nacalai Tesque, Inc., Kyoto, Japan.
C3P	Obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K.
CS	CaCO ₃ + SiO ₂ mixture (1:1) was fired in air at 1 573 K for 300 h.
C2S	CaCO ₃ + SiO ₂ mixture (2:1) was fired in air at 1 573 K for 24 h.
W2S	$Fe + Fe_3O_4 + SiO_2 mixture (1:1:2)$ was fired in Ar at 1 373 K for 80 h.
$_{SS}+CS$	C2S + C3P mixture was fired in air at 1 573 K for 24 h and mixed with CS.
$_{SS}+CS$	C2S + C3P + W2S + CS mixture was fired in Ar at 1 423 K for 12 h and at 1 573 K for 24 h.

Table 1. Starting materials and preparations of oxide samples.

 Table 2.
 Compositions of samples and the FeO activities at 1 573 K.

Sample -	Bulk composition				Composition in Solid Solution						
	(mole fraction)				(mole fraction)				(mole ratio)		
Name	CaO	FeO	SiO_2	PO _{2.5}	CaO	FeO	SiO_2	PO _{2.5}	P/(Si+P)	Fe/(Ca+Fe)	<u>-</u>
А	0.610	0	0.302	0.088	0.647	0	0.235	0.117	0.333	0	0
В	0.599	0.011	0.302	0.088	0.624	0.016	0.238	0.122	0.339	0.026	0.058 ± 0.006
С	0.588	0.022	0.303	0.088	0.616	0.028	0.235	0.121	0.341	0.043	0.117 ± 0.005
D	0.577	0.033	0.303	0.088	0.603	0.033	0.235	0.129	0.354	0.052	0.154 ± 0.013



Fig. 4. Experimental apparatus. (A) Ar+H₂+H₂O gas inlet, (B) Pt-PtRh13 thermocouple, (C) Alumina sheath, (D) Mullite reaction tube, (E) Ribbon Heater, (F) Gas outlet, (G) Rubber stopper (H) Crucible of oxide sample, (I) Cu–Fe–P liquid alloy, (J) Pt plate, (K) Alumina pedestal, (L) Mo rod.



water kept at 278 K–289 K or LiCl-saturated water kept at 303 K–311 K in a thermostat bath. The water vapor pressure in equilibrium with distilled water or LiCl-saturated water can be calculated as

 $\log(p_{\rm H_{2}O} / \text{atm}) = 19.732 - 2900 / (T / K) - 4.65 \log(T / K)$

(distilled water, 273 K < T < 373 K)²⁷⁾

$$\log(p_{\rm H_{2O}} / \text{atm}) = 5.94 - 2510 / (T / K)$$

(LiCl-saturated water, $T > 291.5 \text{ K}$)³⁸⁾ ... (27)

The experimental conditions for $p_{\rm H_2}/p_{\rm H_20}$ are given in **Table 3**. After durations, the quenched alloy samples were dissolved in HCl + HNO₃ solutions and submitted to ICP-OES to determine the iron and phosphorus concentrations. For analyzing phosphorus in copper alloys, an indirect spectrometric method involving solvent extraction³⁹⁾ was adopted, in which phosphorus in the solution was converted to phosphomolybdate, $[PMo_{12}O_{40}]^{3-}$, and extracted in diethyl ether. Phosphorus was quantified indirectly from the molybdenum originating in $[PMo_{12}O_{40}]^{3-}$.

The initial compositions of the alloy samples are listed in

Sample	$p_{ m H_2}$	Holding Time/	[0/E-1		1 7			
Name	$p_{ m H_2O}$	hour	[%Fe] _{Cu}	Initial	Equilibrium	average	logn	
A		47		0	0.0166			
	12.52	91	0	0	0.0203	0.0150 + 0.0028	-1.80 ± 0.08	
	13.52	123	0	0	0.0132	0.0159±0.0028		
		142		0	0.0137			
	25.51	40	0	0	0.0688	0.0765 + 0.0077	1 12 1 0 0 4	
	25.51	40	0	0.34	0.0842	0.0765±0.0077	-1.12 ± 0.04	
		52		0	0.00450		-2.99±0.06	
	0.57	52	2.12	0.066	0.00321	0.00.401 + 0.000/0		
В	9.57	77	3.12	0	0.00432	0.00421 ± 0.00060		
		77		0.066	0.00480			
		49		0	0.0344		-2.43 ± 0.06	
	12.52	49	5 10	0.11	0.0350	0.0292 + 0.0051		
	13.52	105	5.18	0	0.0471	0.0383 ± 0.0031		
		105		0.11	0.0368			
		24		0.50	0.122		-2.44±0.03	
	16.71	90	1	0.50	0.113	0.110 + 0.007		
	15./1	114	7.71	0	0.127	0.118±0.007		
		114		0.50	0.110			
С		23		0.052	0.0183		-3.04 ± 0.06	
	7.83	66	6.61	0	0.0145	0.0179 ± 0.0026		
		66		0.052	0.0209			
D		49		0.11	0.0167		-3.30 ± 0.03	
	6.43	95	7.87	0	0.0167	0.0174 ± 0.0010		
		95		0.11	0.0188			

Table 3. Experimental conditions and results at 1 573 K.

Table 3. The concentrations of phosphorus in initial metals were set to zero or high values, while those of iron were the equilibrium values calculated from Eqs. (4), (17), and (19) with the FeO activities given in Table 2.³⁵⁾ Phosphorus contents in alloys without initial P would increase while those with initial high-P would decrease, which corresponds to Reaction (5) proceeding toward left or right hand, respectively. When the phosphorus concentrations in such alloys agreed with each other within the experimental uncertainties, Reaction (5) was confirmed to reach the equilibrium state.

3. Experimental Results and Discussion

3.1. The Activity Measurements of P2O5

Figure 5 shows typical changes in $[\%Fe]_{Cu}$ and $[\%P]_{Cu}$ over duration time for Sample B at $p_{H_2} / p_{H_2O} = 13.52$. Figure 5(a) indicates that $[\%Fe]_{Cu}$ remained unchanged and Reaction (3) proceeded toward neither right nor left hand. From Fig. 5(b), the equilibrium value for $[\%P]_{Cu}$ was determined as 0.0383 ± 0.0051 . The experimental results for all the conditions are summarized in Table 3.

Combining Eqs. (6), (21), and (22), we have



Fig. 5. Iron and phosphorus concentrations in the Cu–Fe–P alloys plotted against the holding time.

$$2 \log [\%P]_{Cu} - 5 \log (p_{H_2} / p_{H_2O})$$

= $-2e_p^{Fe} [\%Fe]_{Cu} + \log a_{P_2O_5} - \log K_5$ (28)

The P₂O₅ activity is constant when the composition of the oxide phase is fixed, and hence Eq. (28) implies that the relationship between $[2\log[%P]_{Cu}-5\log(p_{H_2}/p_{H_2}o)]$ and $[%Fe]_{Cu}$ should be linear with a slope of $-2e_p^{Fe}$. Such plots for Sample B are shown in **Fig. 6**(a). The slope of a regression line in this figure gives $e_p^{Fe} = -0.195$ at 1 573 K. Figure 6(b) shows e_p^{Fe} plotted against reciprocal temperature. It can be seen that the present value for e_p^{Fe} is well consistent with the literature data at lower temperatures by Kaida *et al.*⁴⁰

By using derived e_p^{Fe} , the phosphorus activities in the copper alloys are calculated from Eq. (21) and given in Table 3. Equation (29) obtainable by rewriting Eq. (6) indicates that plots of $\log h_p$ against $\log(p_{\text{H}_2} / p_{\text{H}_2\text{O}})$ should be linear with a slope of 5/2 and an intercept of $[(1/2\log a_{\text{P}_2\text{O}_5} - (1/2)\log K_5]]$.

$$\log h_{\rm P} = (5/2) \log(p_{\rm H_2} / p_{\rm H_2O}) + (1/2) \log a_{\rm P_2O_5} - (1/2) \log K_5$$
.....(29)

Figure 7 shows such relationships. The result of the previous study by T. Saito *et al.*¹¹⁾ using $\langle C2S-C3P \rangle_{SS}$ of the same composition as Sample A is also plotted in this figure. The present results for Sample A are consistent with the literature data¹¹⁾ and linear relations with slopes close to 5/2 can be observed for Samples A and B. Therefore, the P₂O₅ activities at 1 573 K can be determined from their intercepts as follows.



Fig. 6. (a) Relationship between $[2\log[\%P]_{Cu}-5\log(p_{H_2} / p_{H_2O})]$ and $[\%Fe]_{Cu}$ for Sample B. (b) Interaction parameter, e_p^{Fe} , as a function of reciprocal temperature.

- $\log a_{P_2O_5} = -19.60 \pm 0.13$ for Sample A (30)
- $\log a_{P_2O_5} = -21.09 \pm 0.20$ for Sample B(31)

The error ranges represent the standard deviations from all experimental points. **Figure 8** shows the P₂O₅ activity as a function of the Fe/(Ca+Fe) mole ratio in the solid solution coexisting with CS. The P₂O₅ activity decreased drastically when the iron oxide dissolved into $<C2S-C3P>_{SS}$, and it was almost constant when the Fe/(Ca+Fe) mole ratio was larger than 0.026. Furthermore, the present results were not inconsistent with those measured by Matsugi *et al.*¹⁷⁾ in the $<C2S-C3P-W2S>_{SS} + CS + Liquid$ three-phase region.



Fig. 7. Relation between $\log p_{\text{H}_2}$ and $\log p_{\text{H}_2} / p_{\text{H}_2\text{O}}$ at 1 573 K.



Fig. 8. Relationship between the P₂O₅ activity and Fe/(Ca+Fe) mole ratio in <C2S-C3P-W2S>_{SS} coexisting with CS at 1 573 K.

3.2. Calculation of the Activities of CaO, SiO₂, C2S, C3P, and W2S

As already mentioned, it would be better to consider the activities of *C2S*, *C3P*, and *W2S* rather than P_2O_5 to understand the thermochemical properties of $\langle C2S-C3P-W2S \rangle_{SS}$ since the P_2O_5 activities change drastically depending on the solid phases coexisting with the solid solutions. In this section, the *C2S*, *C3P*, and *W2S* activities were derived from the measured P_2O_5 and FeO activities as follows. The Gibbs-Duhem equation for the CaO–SiO₂–PO_{2.5}–FeO quaternary system under constant temperature and pressure is given by

$$X_{\text{CaO}} \text{dlog} a_{\text{CaO}} + X_{\text{SiO}_2} \text{dlog} a_{\text{SiO}_2} + X_{\text{PO}_2\varsigma} \text{dlog} a_{\text{PO}_2\varsigma} + X_{\text{FeO}} \text{dlog} a_{\text{FeO}} = \mathbf{0}$$
(34)

The standard states of a_{CaO} and a_{SiO_2} are taken to be pure solid CaO and SiO₂, respectively. The activities of PO_{2.5} and FeO are expressed as

$$a_{\rm PO_{2.5}} = (a_{\rm P_2O_5})^{0.5}$$
(35)

$$dloga_{PO_{2.5}} = 0.5 dloga_{P_2O_5}$$
(36)

$$a_{\rm FeO} = \gamma_{\rm FeO} \cdot X_{\rm FeO} \dots (37)$$

$$dlog a_{FeO} = dlog \gamma_{FeO} + dlog X_{FeO}$$

$$= \mathrm{dlog}\gamma_{\mathrm{FeO}} + \frac{\mathrm{log}e}{X_{\mathrm{FeO}}} dX_{\mathrm{FeO}} \quad \dots \dots \dots \dots \dots (38)$$

, where γ_{FeO} is the activity coefficient of FeO. In the present experiments, pure solid *CS* coexisted with $\langle C2S-C3P-W2S \rangle_{SS}$. Hence, the following formulae are obtained.

 $\log K_{39} = -\log a_{\text{CaO}} - \log a_{\text{SiO}_2} = 2.92 \text{ at } 1573 \text{ K}^{41,42} \dots (40)$

 $dlog a_{SiO_2} = -dlog a_{CaO} \dots (41)$

Inserting Eqs. (36), (38), and (41) into Eq. (34), we have

$$d\log a_{CaO} = \frac{0.5X_{PO_{25}}}{X_{SiO_2} - X_{CaO}} d\log a_{P_2O_5} + \frac{\log e}{X_{SiO_2} - X_{CaO}} dX_{FeO} + \frac{X_{FeO}}{X_{SiO_2} - X_{CaO}} d\log \gamma_{FeO}$$
.....(42)

The CaO activity in Sample A was determined in the literature, $\log a_{CaO}(A) = -2.33$.¹¹⁾ Thus, the integration of Eq. (42) from the composition of Sample A gives the activities of CaO in the other compositions.

$$\log a_{CaO} - \log a_{CaO} (A) = \int_{A} \frac{0.5 X_{PO_{2.5}}}{X_{SiO_{2}} - X_{CaO}} d\log a_{P_{2}O_{5}} \dots (43)$$
$$+ \int_{A} \frac{\log e}{X_{SiO_{2}} - X_{CaO}} dX_{FeO} + \int_{A} \frac{X_{FeO}}{X_{SiO_{2}} - X_{CaO}} d\log \gamma_{FeO}$$

Table 4 summarizes the values for each term in Eq. (43) and calculated results for the CaO activities in Samples B to D. The activity coefficient of FeO in Sample A was assumed to be the same as that in Sample B since the FeO contents are very low. Moreover, the activities of SiO₂, *C2S*, *C3P*, and *W2S* are obtainable from Eqs. (40), (45), (47), and (49), respectively.

 $\log K_{44} = \log a_{C2S} - 2\log a_{CaO} - \log a_{SiO_2} = 4.78 \text{ at } 1573 \text{ K}^{41,42}$

$$3CaO(SS) + P_2O_5(SS) = C3P(SS)$$
(46)

$$\log K_{46} = \log a_{C3P} - 3\log a_{CaO} - \log a_{P_2O_5} \qquad \dots \dots \dots (47)$$
$$= 24.81 \text{ at } 1573 \text{ K}^{30,41,42}$$

$$\log K_{48} = \log a_{W2S} - 2\log a_{FeO} - \log a_{SiO_2}$$

$$= 0.52 \quad \text{at} 1573 \text{ K}^{27)} \quad \dots \dots \dots (49)$$

The standard states of a_{C2S} and a_{C3P} are taken to be pure solid α' -C2S and α -C3P, respectively, while that of a_{W2S} is taken as pure solid W2S called fayalite, which has the same orthorhombic crystal structure as γ -C2S.⁴⁵⁾ If the standard state of a_{W2S} was taken to be hypothetical unstable solid W2S with the same hexagonal structure as α -C2S, the value for a_{W2S} would become much lower. The calculated results are shown in Table 4, and **Fig. 9**(a) shows $\log_{a_{C2S}}$, $\log_{a_{C3P}}$, and $\log a_{W2S}$ plotted against the Fe/(Ca+Fe) mole ratio in the solid solution. The C3P activity decreased when the iron oxide dissolved into $\langle C2S-C3P \rangle_{SS}$, while the W2S activity increased with an increase in the Fe/(Ca+Fe) ratio. The C2S activity was insensitive to the change in the Fe/(Ca+Fe) ratio. As the P_2O_5 activities in $\langle C2S-C3P-W2S \rangle_{SS}$ coexisting with CS are determined by Eq. (2), it can be concluded that the decrease in the P₂O₅ activity seen in Fig. 8 is due to the decrease in the C3P activity in the solid solution. Since the C2S-based solid solutions can easily incorporate a variety of components, it should be aware that the activities may be affected significantly by trace components in the solid solutions.

Table 4. Calculated results for the activities at 1 573 K by the Gibbs-Duhem integrations.

Sample Name	$\frac{0.5 X_{\rm PO_{2.5}}}{X_{\rm SiO_2} - X_{\rm CaO}}$	$\log a_{\mathrm{P_2O_5}}$	$\frac{\log e}{X_{\rm SiO_2} - X_{\rm CaO}}$	$X_{\rm FeO}$	$\frac{X_{\rm FeO}}{X_{\rm SiO_2}-X_{\rm CaO}}$	$\log \gamma_{\rm FeO}$	log <i>a</i> _{CaO}	$\log a_{SiO_2}$	$\log a_{C2S}$	log <i>a</i> _{C3P}	log <i>aw2s</i>
А	-0.143	-19.60	-1.06	0	0	0.559^{*}	-2.3311)	-0.59	-0.47	-1.78	_
В	-0.158	-21.09	-1.13	0.016	-0.041	0.559	-2.12	-0.80	-0.26	-2.65	-2.75
С	-0.159	-20.89	-1.14	0.028	-0.073	0.621	-2.17	-0.75	-0.31	-2.60	-2.10
D	-0.175	-20.97	-1.18	0.033	-0.090	0.669	-2.17	-0.75	-0.30	-2.67	-1.86

* The activity coefficient of FeO in Sample A is assumed to be the same as that in Sample B since the FeO contents are low.





Fig. 9. (a)Activities and (b) activity coefficients of C2S, C3P, and W2S plotted against the Fe/(Ca+Fe) mole ratio in <C2S-C3P-W2S>_{SS} at 1 573 K.

In order to understand the interactions among the components in the solid solution, the activity coefficients of Ca_2SiO_4 (*C2S*), Fe_2SiO_4 (*W2S*), and $Ca_{1.5}PO_4$ ((1/2)*C3P*) were calculated as follows.

 $\log \gamma_{\rm Fe_2SiO_4} = \log a_{W2S} - \log X'_{\rm Fe_2SiO_4}$

$$= \log K_{48} + \log a_{\text{SiO}_2} + 2\log a_{\text{FeO}} - \log(X_{\text{FeO}} / 2) + \log(X_{\text{SiO}_2} + X_{\text{PO}_4})$$

$$= \log K_{48} + \log a_{\text{SiO}_2} + 2\log \gamma_{\text{FeO}} + \log(2X_{\text{FeO}}) + \log(X_{\text{SiO}_2} + X_{\text{PO}_4})$$

.....(52)

Figure 9(b) shows the log $\gamma_{Ca_1,5PO_4}$, and log $\gamma_{Fe_2SiO_4}$ plotted against the Fe/(Ca+Fe) mole ratio in the solid solution. The value for log $\gamma_{Fe_2SiO_4}$ increases with an increase in the Fe/(Ca+Fe) ratio, which is due to the change in X_{FeO} as indicated by Eq. (52). The decrease in a_{C3P} can be attributed to the change in log $\gamma_{Ca_1,5PO_4}$ and this change in the activity coefficient may be explained by the following assumption: Fe²⁺ replacing Ca²⁺ has a chemical affinity for PO₄³⁻ and they form clusters in the solid solution, making the local compositions around PO₄³⁻ less variable.

3.3. Effects of Inaccuracy in the Thermochemical Data on the Activity Values

The standard Gibbs energy change in the formation reac-



Fig. 10. The equilibrium constant of the reaction: $3CaO + P_2 + (5/2)O_2 = Ca_3P_2O_8$.

tion of C3P, Reaction (53), has been reported by several researchers.^{43–50)} However, there are significant discrepancies in their results as shown in **Fig. 10**.

$$3CaO(s) + P_2(g) + (5/2)O_2(g) = C3P(s)$$
 (53)

$$\log K_{53} = -\Delta G_{53}^{\circ} / 2.30 RT \dots (54)$$

For example, Iwase *et al.*, whose results were adopted in Eq. (47), equilibrated the following reactions by using copper alloys as reference metals similar to the present study.^{43,44)}

$$4\text{CaO}(s) + 2[P]_{C_0} + 5\text{CO}(g) = C4P(s) + 5\text{C}(s) \dots (55)$$

$$3C4P(s)+2[P]_{Cu}+5CO(g)=4C3P(s)+5C(s)...(56)$$

To derive K_{46} and K_{53} , Reactions (55) and (56) were combined with Reactions (13), (15), and (57) as follows.

$$C(s)+(1/2)O_2(g)=CO(g)$$
(57)

$$\log K_{53} (\text{Iwase}) = 2\log K_{15} + (3/4)\log K_{55} + (1/4)\log K_{56} + 5\log K_{57}$$
 (58)

$$\log K_{46} = -\log K_{13} + \log K_{53} (\text{Iwase}) = 24.81 \text{ at } 1573 \text{ K} \dots (59)$$

Yamasue *et al.*⁴⁹⁾ have pointed out that the discrepancies in $\log K_{53}$ may be attributed to the inaccuracy of $\log K_{15}$. Thus, the effects of the inaccuracies in $\log K_{15}$ and $\log K_{53}$ on the values for activities in $\langle C2S-C3P-W2S \rangle_{SS}$ are discussed in this section.

From Eq. (60) obtained by rewriting Eqs. (6) and (18), it can be found that the P_2O_5 activities are affected by the inaccuracy of log K_{15} as well.

It should be noted here that all the points in Fig. 8 would be affected by $\log K_{15}$ equally and the present conclusion that $a_{P_2O_5}$ decreases with the dissolution of FeO into $\langle C2S - C3P \rangle_{SS}$ would not change. On the other hand, the C3P activities, which represent the thermodynamic properties of the solid solutions, can be expressed as

Equation (61) implies that the effects of the inaccuracy of $\log K_{15}$ on $\log a_{P_2O_5}$ and $\log K_{53}$ (Iwase) would be canceled out in calculating the C3P activities. By adopting the data for K_{53} from Iwase *et al.*^{43,44} using copper alloys as reference metals similar to the present study, more reliable values can be obtained for the C3P activities. Remeasurements and evaluations for Reactions (15) and (53) would be our important future work.

4. Conclusions

The P₂O₅ activities were measured in the (Ca, Fe)₂SiO₄-(Ca, Fe)₃P₂O₈ solid solutions coexisting with CaSiO₃ at 1 573 K.

 $\log a_{P_2O_5} = -19.60 \pm 0.13$ for P/Si = 0.333/0.667, Fe/Ca = 0/1

 $\log a_{P_2O_5} = -21.09 \pm 0.20$ for P/Si=0.339/0.661, Fe/Ca=0.026/0.974 $\log a_{P_{2}O_{5}} = -20.89 \pm 0.13$ for P/Si = 0.341/0.659, Fe/Ca = 0.043/0.957 $\log a_{P_2O_5} = -20.97 \pm 0.05$ for P/Si=0.354/0.646, Fe/Ca=0.052/0.942

, where P/Si and Fe/Ca represent the mole ratios of the elements in the solid solutions. The P2O5 activity decreased drastically when iron oxide dissolved into the Ca2SiO4-Ca₃P₂O₈ solid solution, which was attributed to the decrease in the activity of $Ca_3P_2O_8$ in the solid solution.

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