

# Effect of Iron Oxide Dissolution on Thermochemical Property of Solid Solution between $\text{Ca}_2\text{SiO}_4$ and $\text{Ca}_3\text{P}_2\text{O}_8$ 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  $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3\text{P}_2\text{O}_8$ . 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  $\text{FeO}$  dissolution on the activities of components in the  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$  solid solution. The  $\text{P}_2\text{O}_5$  activities were measured in the solid solution containing  $\text{FeO}$  at 1 573 K. Subsequently, the activities of  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Ca}_3\text{P}_2\text{O}_8$ , and  $\text{Fe}_2\text{SiO}_4$  were derived from the Gibbs-Duhem equation with the measured  $\text{P}_2\text{O}_5$  activities and reported  $\text{FeO}$  activities. When iron oxide dissolved into the  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$  solid solution, the  $\text{Ca}_3\text{P}_2\text{O}_8$  activity decreased, while the  $\text{Ca}_2\text{SiO}_4$  activity was insensitive. As a result, the dissolution of iron oxide into the solid solution caused a drastic decrease in the  $\text{P}_2\text{O}_5$  activity.

KEY WORDS:  $\text{P}_2\text{O}_5$  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,  $\text{Ca}_2\text{SiO}_4$ , and tri-calcium phosphate,  $\text{Ca}_3\text{P}_2\text{O}_8$ ,<sup>1–9)</sup> and the solid solutions have important roles in the dephosphorization reactions.<sup>10)</sup> 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  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$  solid solutions.<sup>11–19)</sup>

The part of the reported iso-thermal section of the  $\text{CaO}$ – $\text{SiO}_2$ – $\text{P}_2\text{O}_5$  ternary phase diagram at 1 573 K<sup>20–22)</sup> and the phase diagram of the  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$  pseudo-binary system<sup>23)</sup> are given in Fig. 1. These diagrams show that the solid solutions between  $\alpha$ - $\text{Ca}_2\text{SiO}_4$  and  $\bar{\alpha}$ - $\text{Ca}_3\text{P}_2\text{O}_8$ , denoted as  $\langle \text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}}$ , coexists with some multiple oxides in the  $\text{CaO}$ – $\text{SiO}_2$  or  $\text{CaO}$ – $\text{P}_2\text{O}_5$  binary system at 1 573 K. In the preceding studies, the activities of  $\text{P}_2\text{O}_5$  in the solid solutions coexisting with  $\text{CaO}$ ,  $\text{CaSiO}_3$ , or  $\text{Ca}_3\text{SiO}_5$  were determined at 1 573 K by equilibrating phosphorus-containing copper with oxides under a stream of  $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$  gas mixtures.<sup>11,12)</sup> The  $\text{P}_2\text{O}_5$  activity in the  $\langle \text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}} + \text{CaO}$  two-phase region

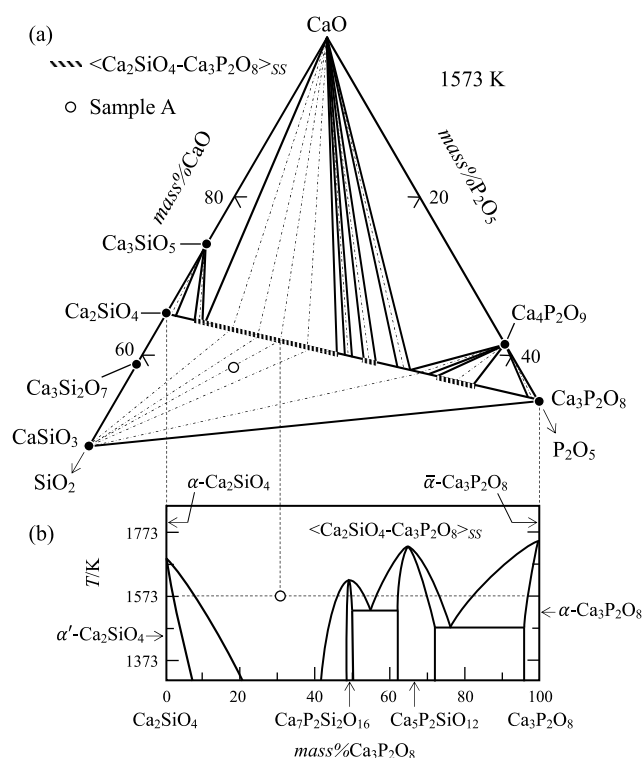


Fig. 1. (a) Iso-thermal section at 1 573 K of the  $\text{CaO}$ – $\text{SiO}_2$ – $\text{P}_2\text{O}_5$  ternary phase diagram.<sup>20–22)</sup> (b) Phase diagram of the  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$  pseudo-binary system.<sup>23)</sup>

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was found to be about seven digits lower than that in the  $\langle \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}} + \text{CaSiO}_3$  two-phase region.<sup>11)</sup> At higher temperatures, Zhong *et al.* measured the  $\text{P}_2\text{O}_5$  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.<sup>13–15)</sup> 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.<sup>13)</sup> Yu *et al.*<sup>24)</sup> investigated the crystallographical properties of  $\langle \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}}$  and discussed that the composition dependence of a lattice parameter was compatible with that of the  $\text{P}_2\text{O}_5$  activity in the solid solutions based on the work by Zhong *et al.*<sup>14)</sup> However, it would be better to consider the activities of  $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3\text{P}_2\text{O}_8$  rather than  $\text{P}_2\text{O}_5$  since the  $\text{P}_2\text{O}_5$  activity changes drastically depending on the solid phases coexisting with  $\langle \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}}$  as mentioned previously.<sup>11)</sup>

When added to the  $\text{CaO--SiO}_2\text{--P}_2\text{O}_5$  ternary system, iron oxide would form quaternary liquid phase and also dissolve into  $\langle \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}}$  as seen in Fig. 2(a), which is the schematic phase diagram of the  $\text{CaO--SiO}_2\text{--P}_2\text{O}_5\text{--FeO}$  quaternary system at 1 573 K. The base of the tetrahedron in Fig. 2(a) corresponds to the  $\text{CaO--SiO}_2\text{--P}_2\text{O}_5$  ternary phase diagram (same as Fig. 1(a)). In  $\langle \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8 \rangle_{\text{SS}}$ ,  $\text{Fe}^{2+}$  is considered to substitute for  $\text{Ca}^{2+}$ ,<sup>25)</sup> and thus the solid solution containing FeO can be expressed as  $(\text{Ca}, \text{Fe})_2\text{SiO}_4\text{--}(\text{Ca}, \text{Fe})_3\text{P}_2\text{O}_8$ . In Fig. 2 and hereafter, the following abbreviations are used.

$\text{CS} = \text{CaSiO}_3 = \text{CaO} \cdot \text{SiO}_2$

$\text{C2S} = \text{Ca}_2\text{SiO}_4 = 2\text{CaO} \cdot \text{SiO}_2$

$\text{C3P} = \text{Ca}_3\text{P}_2\text{O}_8 = 3\text{CaO} \cdot \text{P}_2\text{O}_5$

$\text{C4P} = \text{Ca}_4\text{P}_2\text{O}_9 = 4\text{CaO} \cdot \text{P}_2\text{O}_5$

$\text{W2S} = \text{Fe}_2\text{SiO}_4 = 2\text{FeO} \cdot \text{SiO}_2$

$\langle \text{C2S--C3P} \rangle_{\text{SS}} = \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$  solid solution

$\langle \text{C2S--C3P--W2S} \rangle_{\text{SS}}$

$= (\text{Ca}, \text{Fe})_2\text{SiO}_4\text{--}(\text{Ca}, \text{Fe})_3\text{P}_2\text{O}_8$  solid solution

$= \text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8\text{--Fe}_2\text{SiO}_4$  solid solution

$\text{Liquid} = \text{CaO--SiO}_2\text{--P}_2\text{O}_5\text{--FeO}$  quaternary liquid

The phase relations around  $\langle \text{C2S--C3P--W2S} \rangle_{\text{SS}}$  in the quaternary system are projected onto the  $\text{CaO--}(\text{SiO}_2 + \text{P}_2\text{O}_5)\text{--FeO}$  pseudo-ternary field in Fig. 2(b).<sup>16–18,26)</sup> Im *et al.*<sup>26)</sup> and Ito and Sano<sup>16)</sup> 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  $\text{P}_2\text{O}_5$  between the solid solutions and *Liquid*, in which the dissolutions of the iron oxide into  $\langle \text{C2S--C3P} \rangle_{\text{SS}}$  were also observed.<sup>19)</sup> In the three-phase region of  $\langle \text{C2S--C3P--W2S} \rangle_{\text{SS}} + \text{CS} + \text{Liquid}$ , Matsugi *et al.* measured the  $\text{P}_2\text{O}_5$  activities at 1 548 K–1 598 K with an electrochemical technique involving stabilized zirconia electrolyte.<sup>17)</sup> The measured  $\text{P}_2\text{O}_5$  activities in this three-phase assemblage were about one digit lower than those in the  $\langle \text{C2S--C3P} \rangle_{\text{SS}} + \text{CS}$  two-phase region reported by T. Saito *et al.*, and it was attributed to the dissolution of iron oxide into the solid solution.<sup>11)</sup> The  $\text{P}_2\text{O}_5$  activity in the solid solution coexisting with CS can be

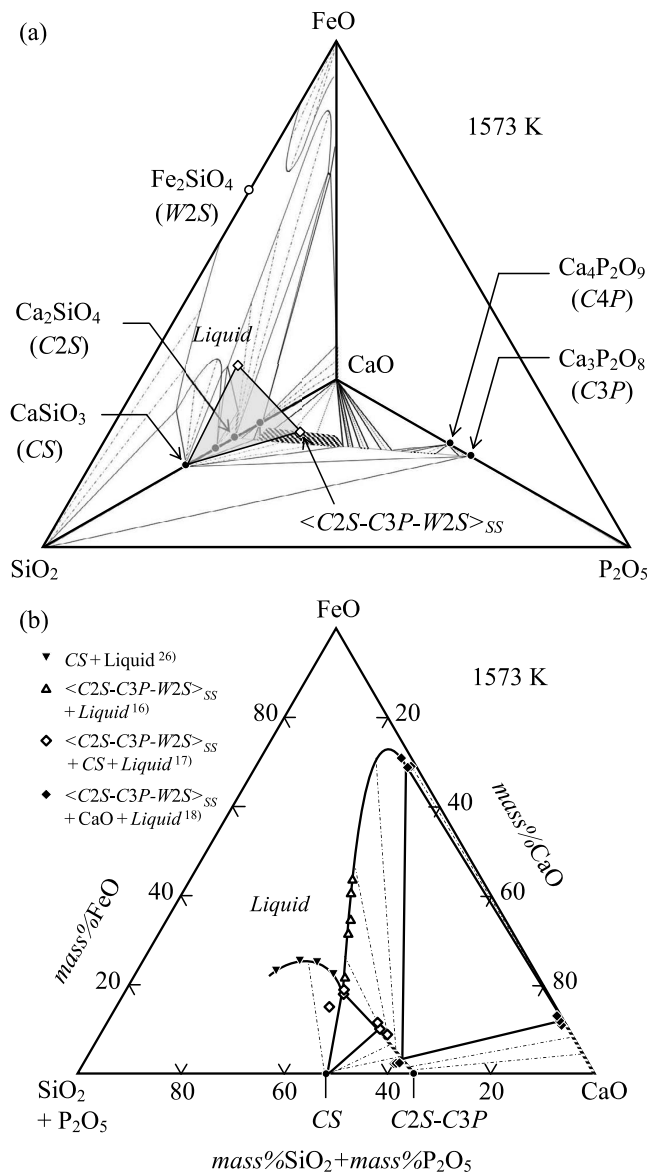
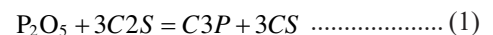


Fig. 2. (a) Schematic phase diagram of the  $\text{CaO--SiO}_2\text{--P}_2\text{O}_5\text{--FeO}$  quaternary system at 1 573 K. (b) Phase diagram of the  $\text{CaO--}(\text{SiO}_2 + \text{P}_2\text{O}_5)\text{--FeO}$  pseudo-ternary system at 1 573 K.

determined through Reaction (1).



$$\log a_{\text{P}_2\text{O}_5} = \log a_{\text{C3P}} - 3 \log a_{\text{C2S}} - \log K_1 \quad \text{..... (2)}$$

Since the dissolution of iron oxide affects both C2S and C3P activities in the solid solution, the effect of FeO on the  $\text{P}_2\text{O}_5$  activity would be complex and not obvious.

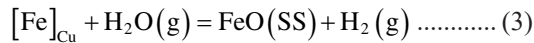
Based on the considerations above, the purpose of this study was to clarify the effect of FeO dissolution on the activities of components in  $\langle \text{C2S--C3P--W2S} \rangle_{\text{SS}}$ . The  $\text{P}_2\text{O}_5$  activities were measured in  $\langle \text{C2S--C3P--W2S} \rangle_{\text{SS}}$  coexisting with CS by equilibrating molten copper alloys with oxides under a stream of  $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$  gas mixtures. The C2S, C3P, and W2S activities in the solid solutions were subsequently derived from the measured results.

## 2. Experimental Aspects

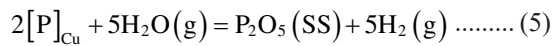
### 2.1. Principle of the Activity Measurements

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  $Ar + H_2 + H_2O$  gas mixture with a fixed partial pressure ratio of  $H_2/H_2O$ ,  $p_{H_2} / p_{H_2O}$ , 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,  $SiO_2$ ,  $P_2O_5$ , FeO, Cu,  $H_2$ , and  $H_2O$ ), 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

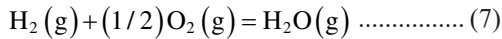


$$\log K_3 = \log a_{FeO} - \log h_{Fe} + \log(p_{H_2} / p_{H_2O}) \dots\dots\dots (4)$$

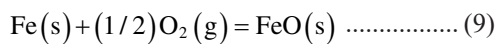


$$\log K_5 = \log a_{P_2O_5} - 2 \log h_P + 5 \log(p_{H_2} / p_{H_2O}) \dots\dots\dots (6)$$

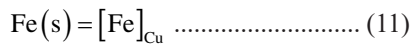
, where  $i(SS)$  and  $a_i$  represent the constituent oxide  $i$  in the solid solution and its Raoultian activity, respectively, and  $[j]_{Cu}$  and  $h_j$  are the component  $j$  in the liquid copper and its Henrian activity, respectively. The standard states of  $a_{FeO}$ ,  $a_{P_2O_5}$ , and  $h_j$  are taken to be pure solid non-stoichiometric FeO in equilibrium with metallic iron, pure hypothetical liquid  $P_2O_5$ , 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.



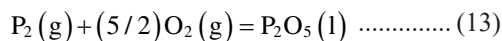
$$\log K_7 = 5.32 \quad \text{at } 1\,573\,K^{27)} \dots\dots\dots (8)$$



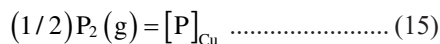
$$\log K_9 = 5.35 \quad \text{at } 1\,573\,K^{28)} \dots\dots\dots (10)$$



$$\log K_{11} = 0.68 \quad \text{at } 1\,573\,K^{29)} \dots\dots\dots (12)$$



$$\log K_{13} = 24.51 \quad \text{at } 1\,573\,K^{30)} \dots\dots\dots (14)$$



$$\log K_{15} = 4.12 \quad \text{at } 1\,573\,K^{31)} \dots\dots\dots (16)$$

$$\log K_3 = -\log K_7 + \log K_9 - \log K_{11} = -0.64 \quad \text{at } 1\,573\,K \dots\dots\dots (17)$$

$$\begin{aligned} \log K_5 &= -5 \log K_7 + \log K_{13} - 2 \log K_{15} \\ &= -10.34 \quad \text{at } 1\,573\,K \end{aligned} \dots\dots\dots (18)$$

, 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.

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

$$e_{Fe}^{Fe} = -0.0346 \quad 0 \leq [Fe]_{Cu} \leq 9.3 \quad \text{at } 1\,573\,K^{32-34)} \dots (20)$$

$$\log h_P = \log [P]_{Cu} + e_P^{Fe} [Fe]_{Cu} + e_P^P [P]_{Cu} \dots (21)$$

$$e_P^P = 0 \quad [P]_{Cu} < 1 \quad \text{at } 1\,573\,K^{31)} \dots\dots\dots (22)$$

, 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.<sup>35)</sup> 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.*<sup>10)</sup> 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  $\langle C2S-C3P-W2S \rangle_{SS} + CS$ .<sup>35)</sup> 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  $Ca_2SiO_4$ – $Fe_2SiO_4$ – $Ca_{1.5}PO_4$  ( $= C2S-W2S-(1/2)C3P$ ) triangle by using the following formulae.

$$X'_{Ca_{1.5}PO_4} = X_{PO_{2.5}} / (X_{SiO_2} + X_{PO_{2.5}}) \dots\dots\dots (23)$$

$$X'_{Fe_2SiO_4} = (X_{FeO} / 2) / (X_{SiO_2} + X_{PO_{2.5}}) \dots\dots\dots (24)$$

$$X'_{Ca_2SiO_4} = 1 - X'_{Ca_{1.5}PO_4} - X'_{Fe_2SiO_4} \dots\dots\dots (25)$$

, where  $X'_i$  or  $X_i$  represents the mole fraction of component  $i$  in the  $Ca_2SiO_4$ – $Fe_2SiO_4$ – $Ca_{1.5}PO_4$  or  $CaO$ – $SiO_2$ – $PO_{2.5}$ – $FeO$  system, respectively. Since  $SiO_4^{4-}$  were considered to be replaced by  $PO_4^{3-}$  in the solid solution,<sup>11,36,37)</sup> the compositions were expressed as the components with a single  $SiO_4^{4-}$  or  $PO_4^{3-}$  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.

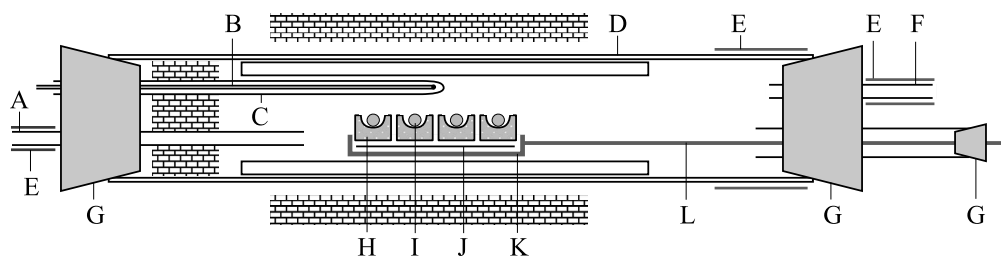
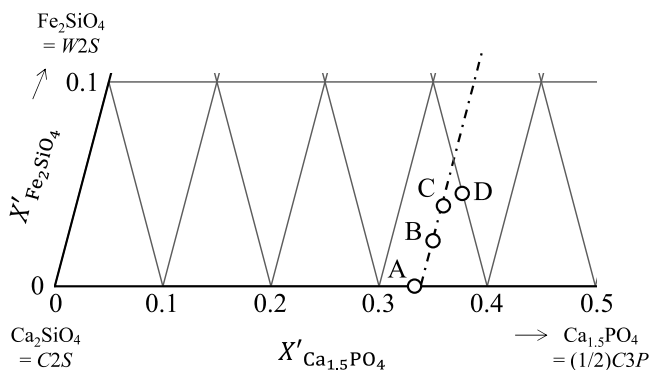
The experimental apparatus is shown in **Fig. 4**. Copper shavings (Nakalai Tesque Inc., Kyoto, Japan), powdery iron (Nakalai Tesque Inc. Kyoto, Japan), and copper phosphide (14.8 mass%P, Hirano Seizaemon Co. Ltd., Tokyo, Japan) were charged in the crucibles made from the oxide samples and held in a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

**Table 1.** Starting materials and preparations of oxide samples.

| Material                         | Preparation                                                                                                 |
|----------------------------------|-------------------------------------------------------------------------------------------------------------|
| CaCO <sub>3</sub>                | Obtained from Nacalai Tesque, Inc., Kyoto, Japan.                                                           |
| SiO <sub>2</sub>                 | Obtained from FUJIFILM Wako Pure Chemical Co., Osaka, Japan, and dried at 413 K.                            |
| Fe                               | Obtained from Nacalai Tesque, Inc., Kyoto, Japan.                                                           |
| Fe <sub>3</sub> O <sub>4</sub>   | Obtained from Nacalai Tesque, Inc., Kyoto, Japan.                                                           |
| C3P                              | Obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K.                                       |
| CS                               | CaCO <sub>3</sub> + SiO <sub>2</sub> mixture (1:1) was fired in air at 1 573 K for 300 h.                   |
| C2S                              | CaCO <sub>3</sub> + SiO <sub>2</sub> mixture (2:1) was fired in air at 1 573 K for 24 h.                    |
| W2S                              | Fe + Fe <sub>3</sub> O <sub>4</sub> + SiO <sub>2</sub> mixture (1:1:2) was fired in Ar at 1 373 K for 80 h. |
| <C2S-C3P> <sub>SS</sub> + CS     | C2S + C3P mixture was fired in air at 1 573 K for 24 h and mixed with CS.                                   |
| <C2S-C3P-W2S> <sub>SS</sub> + 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 2.** Compositions of samples and the FeO activities at 1 573 K.

| Sample | Bulk composition |       |       |                  | Composition in Solid Solution |       |       |                  |                   |          |             | $a_{\text{FeO}}^{(35)}$ |
|--------|------------------|-------|-------|------------------|-------------------------------|-------|-------|------------------|-------------------|----------|-------------|-------------------------|
|        | (mole fraction)  |       |       |                  | (mole fraction)               |       |       |                  | (mole ratio)      |          |             |                         |
|        | Name             | CaO   | FeO   | SiO <sub>2</sub> | PO <sub>2.5</sub>             | CaO   | FeO   | SiO <sub>2</sub> | PO <sub>2.5</sub> | P/(Si+P) | Fe/(Ca+Fe)  |                         |
| A      | 0.610            | 0     | 0.302 | 0.088            | 0.647                         | 0     | 0.235 | 0.117            | 0.333             | 0        | 0           |                         |
| B      | 0.599            | 0.011 | 0.302 | 0.088            | 0.624                         | 0.016 | 0.238 | 0.122            | 0.339             | 0.026    | 0.058±0.006 |                         |
| C      | 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+H<sub>2</sub>+H<sub>2</sub>O 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.**Fig. 3.** Compositions of the solid solutions in Samples A to D.

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

$$\log(p_{\text{H}_2\text{O}} / \text{atm}) = 19.732 - 2900 / (T / \text{K}) - 4.65 \log(T / \text{K})$$

(distilled water, 273 K < *T* < 373 K)<sup>(27)</sup> ..... (26)

$$\log(p_{\text{H}_2\text{O}} / \text{atm}) = 5.94 - 2510 / (T / \text{K})$$

(LiCl-saturated water, *T* > 291.5 K)<sup>(38)</sup> ... (27)

The experimental conditions for  $p_{\text{H}_2} / p_{\text{H}_2\text{O}}$  are given in **Table 3**. After durations, the quenched alloy samples were dissolved in HCl + HNO<sub>3</sub> 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 extraction<sup>(39)</sup> was adopted, in which phosphorus in the solution was converted to phosphomolybdate, [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>, and extracted in diethyl ether. Phosphorus was quantified indirectly from the molybdenum originating in [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>.

The initial compositions of the alloy samples are listed in

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

| Sample Name | $\frac{p_{H_2}}{p_{H_2O}}$ | Holding Time/<br>hour | [%Fe] <sub>Cu</sub> | [%P] <sub>Cu</sub> |             |                 | log $h_p$  |
|-------------|----------------------------|-----------------------|---------------------|--------------------|-------------|-----------------|------------|
|             |                            |                       |                     | Initial            | Equilibrium | average         |            |
| A           | 13.52                      | 47                    | 0                   | 0                  | 0.0166      | 0.0159±0.0028   | −1.80±0.08 |
|             |                            | 91                    |                     | 0                  | 0.0203      |                 |            |
|             |                            | 123                   |                     | 0                  | 0.0132      |                 |            |
|             |                            | 142                   |                     | 0                  | 0.0137      |                 |            |
|             | 25.51                      | 40                    | 0                   | 0                  | 0.0688      | 0.0765±0.0077   | −1.12±0.04 |
|             |                            | 40                    |                     | 0.34               | 0.0842      |                 |            |
|             | 9.57                       | 52                    | 3.12                | 0                  | 0.00450     | 0.00421±0.00060 | −2.99±0.06 |
|             |                            | 52                    |                     | 0.066              | 0.00321     |                 |            |
|             |                            | 77                    |                     | 0                  | 0.00432     |                 |            |
|             |                            | 77                    |                     | 0.066              | 0.00480     |                 |            |
| B           | 13.52                      | 49                    | 5.18                | 0                  | 0.0344      | 0.0383±0.0051   | −2.43±0.06 |
|             |                            | 49                    |                     | 0.11               | 0.0350      |                 |            |
|             |                            | 105                   |                     | 0                  | 0.0471      |                 |            |
|             |                            | 105                   |                     | 0.11               | 0.0368      |                 |            |
|             | 15.71                      | 24                    | 7.71                | 0.50               | 0.122       | 0.118±0.007     | −2.44±0.03 |
|             |                            | 90                    |                     | 0.50               | 0.113       |                 |            |
|             |                            | 114                   |                     | 0                  | 0.127       |                 |            |
|             |                            | 114                   |                     | 0.50               | 0.110       |                 |            |
| C           | 7.83                       | 23                    | 6.61                | 0.052              | 0.0183      | 0.0179±0.0026   | −3.04±0.06 |
|             |                            | 66                    |                     | 0                  | 0.0145      |                 |            |
|             |                            | 66                    |                     | 0.052              | 0.0209      |                 |            |
| D           | 6.43                       | 49                    | 7.87                | 0.11               | 0.0167      | 0.0174±0.0010   | −3.30±0.03 |
|             |                            | 95                    |                     | 0                  | 0.0167      |                 |            |
|             |                            | 95                    |                     | 0.11               | 0.0188      |                 |            |

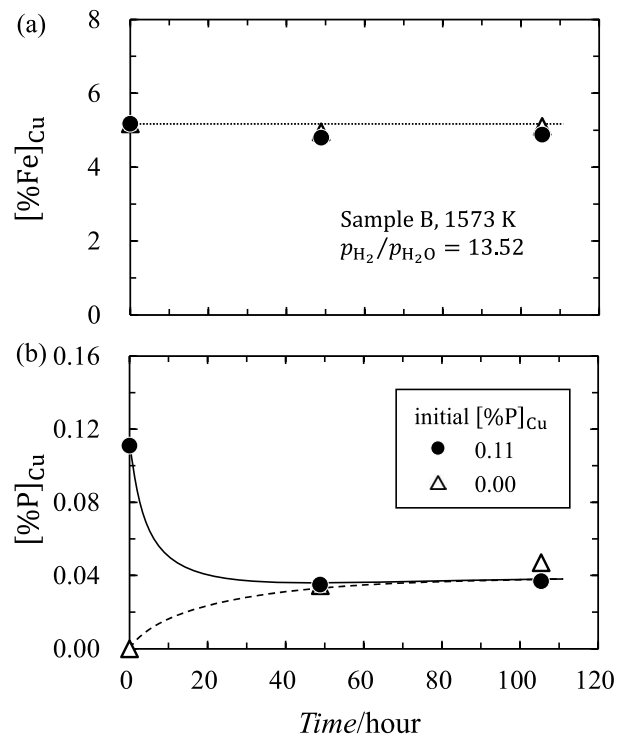
Table 3. The concentrations of phosphorus in initial metals were set to zero or high values, while those of iron were the equilibrium values calculated from Eqs. (4), (17), and (19) with the FeO activities given in Table 2.<sup>35)</sup> Phosphorus contents in alloys without initial P would increase 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 P<sub>2</sub>O<sub>5</sub>

Figure 5 shows typical changes in [%Fe]<sub>Cu</sub> and [%P]<sub>Cu</sub> over duration time for Sample B at  $p_{H_2}/p_{H_2O}=13.52$ . Figure 5(a) indicates that [%Fe]<sub>Cu</sub> remained unchanged and Reaction (3) proceeded toward neither right nor left hand. From Fig. 5(b), the equilibrium value for [%P]<sub>Cu</sub> was determined as  $0.0383\pm0.0051$ . 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.

$$2\log[\%P]_{Cu} - 5\log(p_{H_2}/p_{H_2O}) = -2e_p^{Fe}[\%Fe]_{Cu} + \log a_{P_2O_5} - \log K_5 \quad (28)$$

The  $P_2O_5$  activity is constant when the composition of the oxide phase is fixed, and hence Eq. (28) implies that the relationship between  $[2\log[\%P]_{Cu} - 5\log(p_{H_2}/p_{H_2O})]$  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.*<sup>40)</sup>

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  $\log(p_{H_2}/p_{H_2O})$  should be linear with a slope of  $5/2$  and an intercept of  $[(1/2)\log a_{P_2O_5} - (1/2)\log K_5]$ .

$$\log h_p = (5/2)\log(p_{H_2}/p_{H_2O}) + (1/2)\log a_{P_2O_5} - (1/2)\log K_5 \quad (29)$$

Figure 7 shows such relationships. The result of the previous study by T. Saito *et al.*<sup>11)</sup> 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 data<sup>11)</sup> and linear relations with slopes close to  $5/2$  can be observed for Samples A and B. Therefore, the  $P_2O_5$  activities at 1 573 K can be determined from their intercepts as follows.

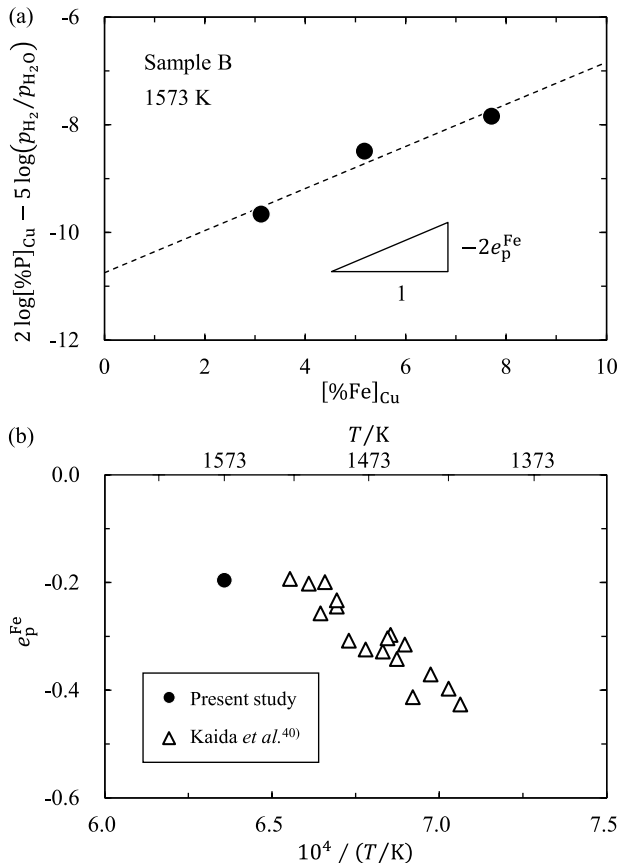


Fig. 6. (a) Relationship between  $[2\log[\%P]_{Cu} - 5\log(p_{H_2}/p_{H_2O})]$  and  $[\%Fe]_{Cu}$  for Sample B. (b) Interaction parameter,  $e_p^{Fe}$ , as a function of reciprocal temperature.

$$\log a_{P_2O_5} = -19.60 \pm 0.13 \quad \text{for Sample A} \quad (30)$$

$$\log a_{P_2O_5} = -21.09 \pm 0.20 \quad \text{for Sample B} \quad (31)$$

$$\log a_{P_2O_5} = -20.89 \pm 0.13 \quad \text{for Sample C} \quad (32)$$

$$\log a_{P_2O_5} = -20.97 \pm 0.05 \quad \text{for Sample D} \quad (33)$$

The error ranges represent the standard deviations from all experimental points. Figure 8 shows the  $P_2O_5$  activity as a function of the Fe/(Ca+Fe) mole ratio in the solid solution coexisting with CS. The  $P_2O_5$  activity decreased drastically when the iron oxide dissolved into  $\langle C2S-C3P \rangle_{SS}$ , 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.*<sup>17)</sup> in the  $\langle C2S-C3P-W2S \rangle_{SS} + CS + \text{Liquid}$  three-phase region.

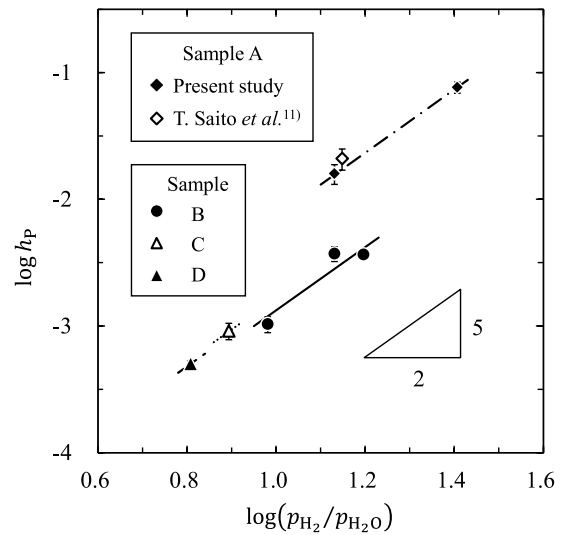


Fig. 7. Relation between  $\log h_p$  and  $\log p_{H_2}/p_{H_2O}$  at 1 573 K.

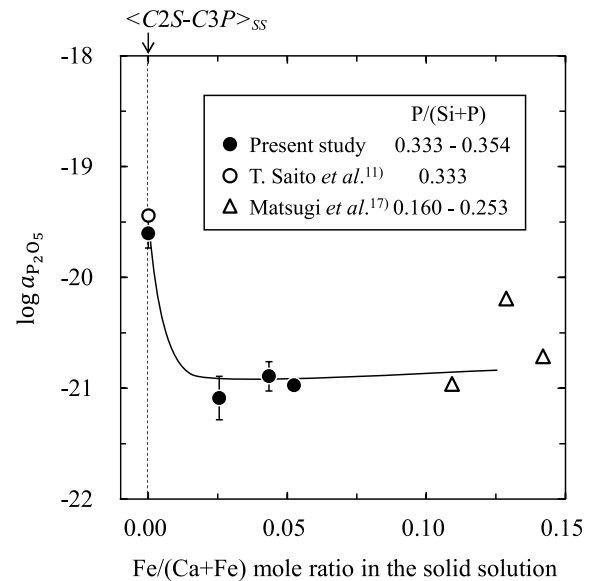


Fig. 8. Relationship between the  $P_2O_5$  activity and Fe/(Ca+Fe) mole ratio in  $\langle C2S-C3P-W2S \rangle_{SS}$  coexisting with CS at 1 573 K.

### 3.2. Calculation of the Activities of CaO, SiO<sub>2</sub>, C2S, C3P, and W2S

As already mentioned, it would be better to consider the activities of C2S, C3P, and W2S rather than P<sub>2</sub>O<sub>5</sub> to understand the thermochemical properties of <C2S-C3P-W2S><sub>SS</sub> since the P<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> and FeO activities as follows. The Gibbs-Duhem equation for the CaO-SiO<sub>2</sub>-PO<sub>2.5</sub>-FeO quaternary system under constant temperature and pressure is given by

$$X_{\text{CaO}} d\log a_{\text{CaO}} + X_{\text{SiO}_2} d\log a_{\text{SiO}_2} + X_{\text{PO}_{2.5}} d\log a_{\text{PO}_{2.5}} + X_{\text{FeO}} d\log a_{\text{FeO}} = 0 \quad (34)$$

The standard states of  $a_{\text{CaO}}$  and  $a_{\text{SiO}_2}$  are taken to be pure solid CaO and SiO<sub>2</sub>, respectively. The activities of PO<sub>2.5</sub> and FeO are expressed as

$$a_{\text{PO}_{2.5}} = (a_{\text{P}_2\text{O}_5})^{0.5} \quad (35)$$

$$d\log a_{\text{PO}_{2.5}} = 0.5 d\log a_{\text{P}_2\text{O}_5} \quad (36)$$

$$a_{\text{FeO}} = \gamma_{\text{FeO}} \cdot X_{\text{FeO}} \quad (37)$$

$$\begin{aligned} d\log a_{\text{FeO}} &= d\log \gamma_{\text{FeO}} + d\log X_{\text{FeO}} \\ &= d\log \gamma_{\text{FeO}} + \frac{\log e}{X_{\text{FeO}}} dX_{\text{FeO}} \end{aligned} \quad (38)$$

, where  $\gamma_{\text{FeO}}$  is the activity coefficient of FeO. In the present experiments, pure solid CS coexisted with <C2S-C3P-W2S><sub>SS</sub>. Hence, the following formulae are obtained.

$$\text{CaO}(\text{SS}) + \text{SiO}_2(\text{SS}) = \text{CS}(\text{s}) \quad (39)$$

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

$$d\log a_{\text{SiO}_2} = -d\log a_{\text{CaO}} \quad (41)$$

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

$$\begin{aligned} d\log a_{\text{CaO}} &= \frac{0.5X_{\text{PO}_{2.5}}}{X_{\text{SiO}_2} - X_{\text{CaO}}} d\log a_{\text{P}_2\text{O}_5} + \frac{\log e}{X_{\text{SiO}_2} - X_{\text{CaO}}} dX_{\text{FeO}} \\ &+ \frac{X_{\text{FeO}}}{X_{\text{SiO}_2} - X_{\text{CaO}}} d\log \gamma_{\text{FeO}} \end{aligned} \quad (42)$$

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

$$\begin{aligned} \log a_{\text{CaO}} - \log a_{\text{CaO}}(\text{A}) &= \int_{\text{A}} \frac{0.5X_{\text{PO}_{2.5}}}{X_{\text{SiO}_2} - X_{\text{CaO}}} d\log a_{\text{P}_2\text{O}_5} \\ &+ \int_{\text{A}} \frac{\log e}{X_{\text{SiO}_2} - X_{\text{CaO}}} dX_{\text{FeO}} + \int_{\text{A}} \frac{X_{\text{FeO}}}{X_{\text{SiO}_2} - X_{\text{CaO}}} d\log \gamma_{\text{FeO}} \end{aligned} \quad (43)$$

**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 SiO<sub>2</sub>, C2S, C3P, and W2S are obtainable from Eqs. (40), (45), (47), and (49), respectively.

$$2\text{CaO}(\text{SS}) + \text{SiO}_2(\text{SS}) = \text{C2S}(\text{SS}) \quad (44)$$

$$\log K_{44} = \log a_{\text{C2S}} - 2\log a_{\text{CaO}} - \log a_{\text{SiO}_2} = 4.78 \text{ at } 1573 \text{ K}^{41,42}) \quad (45)$$

$$3\text{CaO}(\text{SS}) + \text{P}_2\text{O}_5(\text{SS}) = \text{C3P}(\text{SS}) \quad (46)$$

$$\begin{aligned} \log K_{46} &= \log a_{\text{C3P}} - 3\log a_{\text{CaO}} - \log a_{\text{P}_2\text{O}_5} \\ &= 24.81 \text{ at } 1573 \text{ K}^{30,41,42}) \end{aligned} \quad (47)$$

$$2\text{FeO}(\text{SS}) + \text{SiO}_2(\text{SS}) = \text{W2S}(\text{SS}) \quad (48)$$

$$\begin{aligned} \log K_{48} &= \log a_{\text{W2S}} - 2\log a_{\text{FeO}} - \log a_{\text{SiO}_2} \\ &= 0.52 \text{ at } 1573 \text{ K}^{27}) \end{aligned} \quad (49)$$

The standard states of  $a_{\text{C2S}}$  and  $a_{\text{C3P}}$  are taken to be pure solid  $\alpha$ -C2S and  $\alpha$ -C3P, respectively, while that of  $a_{\text{W2S}}$  is taken as pure solid W2S called fayalite, which has the same orthorhombic crystal structure as  $\gamma$ -C2S.<sup>45)</sup> If the standard state of  $a_{\text{W2S}}$  was taken to be hypothetical unstable solid W2S with the same hexagonal structure as  $\alpha$ -C2S, the value for  $a_{\text{W2S}}$  would become much lower. The calculated results are shown in Table 4, and **Fig. 9(a)** shows  $\log a_{\text{C2S}}$ ,  $\log a_{\text{C3P}}$ , and  $\log a_{\text{W2S}}$  plotted against the Fe/(Ca+Fe) mole ratio in the solid solution. The C3P activity decreased when the iron oxide dissolved into <C2S-C3P><sub>SS</sub>, 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<sub>2</sub>O<sub>5</sub> activities in <C2S-C3P-W2S><sub>SS</sub> coexisting with CS are determined by Eq. (2), it can be concluded that the decrease in the P<sub>2</sub>O<sub>5</sub> 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 | $\frac{0.5X_{\text{PO}_{2.5}}}{X_{\text{SiO}_2} - X_{\text{CaO}}}$ | $\log a_{\text{P}_2\text{O}_5}$ | $\frac{\log e}{X_{\text{SiO}_2} - X_{\text{CaO}}}$ | $X_{\text{FeO}}$ | $\frac{X_{\text{FeO}}}{X_{\text{SiO}_2} - X_{\text{CaO}}}$ | $\log \gamma_{\text{FeO}}$ | $\log a_{\text{CaO}}$ | $\log a_{\text{SiO}_2}$ | $\log a_{\text{C2S}}$ | $\log a_{\text{C3P}}$ | $\log a_{\text{W2S}}$ |
|-------------|--------------------------------------------------------------------|---------------------------------|----------------------------------------------------|------------------|------------------------------------------------------------|----------------------------|-----------------------|-------------------------|-----------------------|-----------------------|-----------------------|
| A           | -0.143                                                             | -19.60                          | -1.06                                              | 0                | 0                                                          | 0.559*                     | -2.33 <sup>11)</sup>  | -0.59                   | -0.47                 | -1.78                 | -                     |
| B           | -0.158                                                             | -21.09                          | -1.13                                              | 0.016            | -0.041                                                     | 0.559                      | -2.12                 | -0.80                   | -0.26                 | -2.65                 | -2.75                 |
| C           | -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.

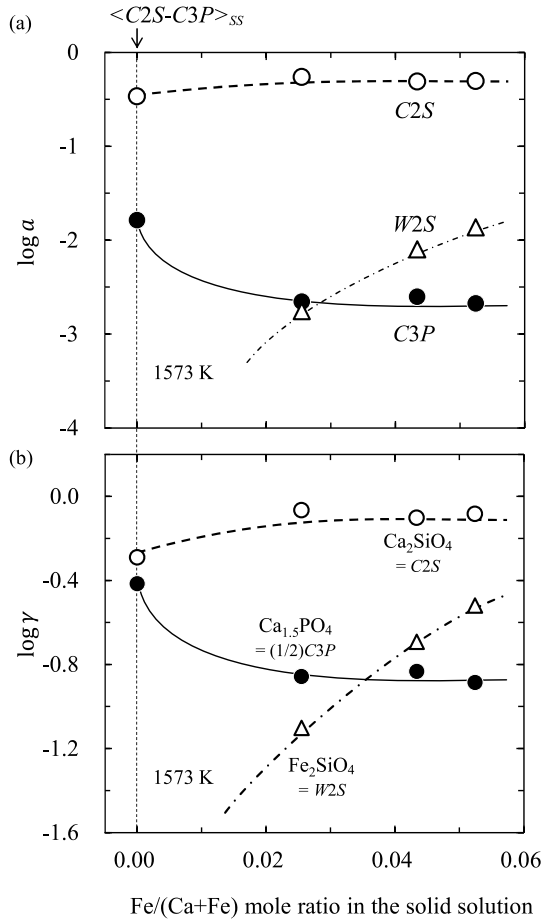


Fig. 9. (a)Activities and (b) activity coefficients of  $C2S$ ,  $C3P$ , and  $W2S$  plotted against the  $Fe/(Ca+Fe)$  mole ratio in  $<C2S-C3P-W2S>_{ss}$  at 1573 K.

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.

$$\log \gamma_{Ca_2SiO_4} = \log a_{C2S} - \log X'_{Ca_2SiO_4} \quad (50)$$

$$\log \gamma_{Ca_{1.5}PO_4} = (1/2) \log a_{C3P} - \log X'_{Ca_{1.5}PO_4} \quad (51)$$

$$\begin{aligned} \log \gamma_{Fe_2SiO_4} &= \log a_{W2S} - \log X'_{Fe_2SiO_4} \\ &= \log K_{48} + \log a_{SiO_2} + 2 \log a_{FeO} - \log (X_{FeO}/2) + \log (X_{SiO_2} + X_{PO_4}) \\ &= \log K_{48} + \log a_{SiO_2} + 2 \log \gamma_{FeO} + \log (2X_{FeO}) + \log (X_{SiO_2} + X_{PO_4}) \end{aligned} \quad (52)$$

Figure 9(b) shows the  $\log \gamma_{Ca_2SiO_4}$ ,  $\log \gamma_{Ca_{1.5}PO_4}$ , 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  $\log \gamma_{Ca_{1.5}PO_4}$  and this change in the activity coefficient may be explained by the following assumption:  $Fe^{2+}$  replacing  $Ca^{2+}$  has a chemical affinity for  $PO_4^{3-}$  and they form clusters in the solid solution, making the local compositions around  $PO_4^{3-}$  less variable.

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

The standard Gibbs energy change in the formation reac-

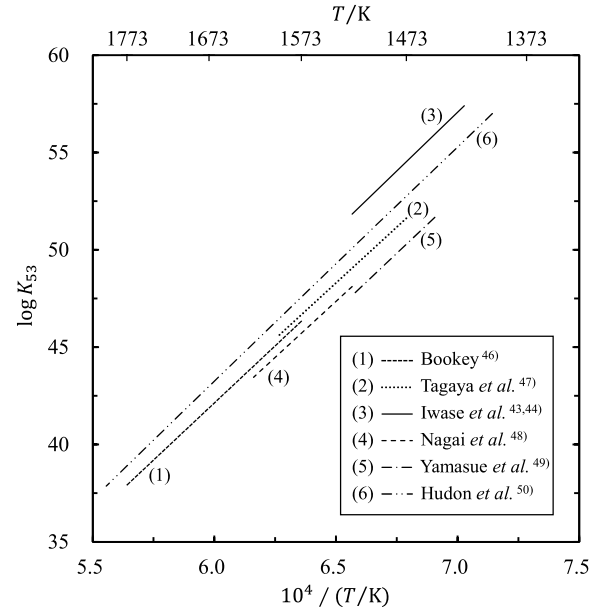
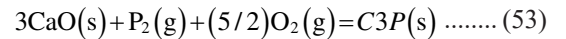


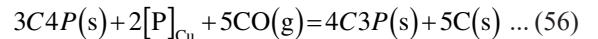
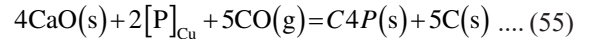
Fig. 10. The equilibrium constant of the reaction:  $3CaO + P_2 + (5/2)O_2 = Ca_3P_2O_8$ .

tion of  $C3P$ , Reaction (53), has been reported by several researchers.<sup>43–50</sup> However, there are significant discrepancies in their results as shown in Fig. 10.



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

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.<sup>43,44</sup>



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



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

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

Yamasue *et al.*<sup>49</sup> 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  $<C2S-C3P-W2S>_{ss}$  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.

$$\begin{aligned} \log a_{P_2O_5} &= 2 \log h_P - 5 \log (p_{H_2} / p_{H_2O}) \\ &\quad - 5 \log K_7 + \log K_{13} - 2 \log K_{15} \end{aligned} \quad (60)$$

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  $<C2S-C3P>_{ss}$  would not change. On the other hand, the  $C3P$

activities, which represent the thermodynamic properties of the solid solutions, can be expressed as

$$\begin{aligned}\log a_{C3P} &= 3\log a_{CaO} + \log a_{P_2O_5} + \log K_{46} \\ &= 3\log a_{CaO} - \log K_{13} + \log a_{P_2O_5} + \log K_{53} \text{ (Iwase)} \\ &= 3\log a_{CaO} + 2\log h_P - 5\log(p_{H_2} / p_{H_2O}) - 2(\log K_{15} - \log K_{15}) \\ &\quad - 5\log K_7 + (3/4)\log K_{55} + (1/4)\log K_{56} + 5\log K_{57} \\ &\quad \dots\dots\dots (61)\end{aligned}$$

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.*<sup>43,44)</sup> 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  $P_2O_5$  activities were measured in the  $(Ca, Fe)_2SiO_4$ – $(Ca, Fe)_3P_2O_8$  solid solutions coexisting with  $CaSiO_3$  at 1 573 K.

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

$$\log a_{P_2O_5} = -21.09 \pm 0.20 \text{ for } P/Si = 0.339/0.661, Fe/Ca = 0.026/0.974$$

$$\log a_{P_2O_5} = -20.89 \pm 0.13 \text{ for } P/Si = 0.341/0.659, Fe/Ca = 0.043/0.957$$

$$\log a_{P_2O_5} = -20.97 \pm 0.05 \text{ for } P/Si = 0.354/0.646, Fe/Ca = 0.052/0.942$$

, where  $P/Si$  and  $Fe/Ca$  represent the mole ratios of the elements in the solid solutions. The  $P_2O_5$  activity decreased drastically when iron oxide dissolved into the  $Ca_2SiO_4$ – $Ca_3P_2O_8$  solid solution, which was attributed to the decrease in the activity of  $Ca_3P_2O_8$  in the solid solution.

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