



Activities of P_2O_5 in Solid Solutions between Di-calcium Silicate and Tri-calcium Phosphate at 1 573 K

Taihei SAITO,¹⁾ Toru NISHIMURA,²⁾ Keijiro SAITO³⁾ and Masakatsu HASEGAWA^{3)*}

1) Graduate Student, Kyoto University. Now at Nippon Steel Corp., 12 Nakamachi, Muroran, Hokkaido, 050-8550 Japan.

2) Graduate Student, Kyoto University. Now at Mitsubishi Materials Corp., 7-147 Shimoishito, Kitamoto, Saitama, 364-0028 Japan.

3) Department of Energy Science and Technology, Kyoto University, Yoshida-hon-machi, Sakyo-ku, Kyoto, 606-8501 Japan.

(Received on March 30, 2020; accepted on May 13, 2020)

The knowledge of P_2O_5 activities in solid solutions between Ca_2SiO_4 and $Ca_3P_2O_8$ is required for more effective dephosphorization. In the present study, firstly, the P_2O_5 activities in these solid solutions coexisting with CaO or $CaSiO_3$ at 1 573 K were measured by equilibrating molten copper with oxide phases under a stream of Ar + H₂ + H₂O gas mixtures. Subsequently, the sub-regular solution model was applied to Ca_2SiO_4 – $Ca_3P_2O_8$ solid solutions. The P_2O_5 activities calculated with the solution model agreed well with the present experimental results and the literature data. It was found that the P_2O_5 activity in Ca_2SiO_4 – $Ca_3P_2O_8$ solid solution coexisting with CaO was about 7 digits lower than that coexisting with $CaSiO_3$.

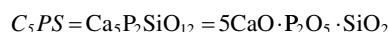
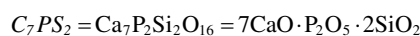
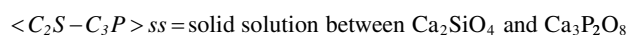
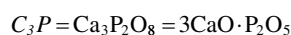
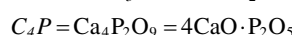
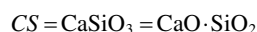
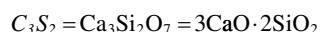
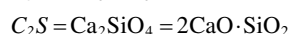
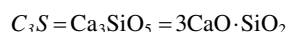
KEY WORDS: dephosphorization; activity; di-calcium silicate; tri-calcium phosphate; solid solution.

1. Introduction

The dephosphorization reaction in steelmaking processes can be formulated by

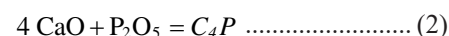


, where $[P]_{Fe}$ is phosphorus in liquid iron, $(FeO)_{slag}$ and $(P_2O_5)_{slag}$ represent FeO and P_2O_5 in slag, respectively, and $\{Fe\}$ indicates liquid iron. According to Le Chatelier's principle, the thermochemical conditions for effective dephosphorization are low P_2O_5 activity, high FeO activity, and low temperature. In order to decrease P_2O_5 activities in slags, CaO is added, and then P_2O_5 often is present in solid solutions between di-calcium silicate, Ca_2SiO_4 , and tri-calcium phosphate, $Ca_3P_2O_8$,¹⁾ as seen in **Fig. 1(a)**; the pseudo-binary phase diagram of Ca_2SiO_4 and $Ca_3P_2O_8$ reported by Fix *et al.*²⁾ Hereafter, the following abbreviations are used.

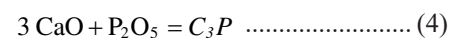


Based on this consideration, a number of investigations have been conducted to determine activities of P_2O_5 in dephosphorization slags.

Figure 1(b) gives the phase relationship in the region of CaO– $CaSiO_3$ – $Ca_3P_2O_8$ of the ternary system CaO– SiO_2 – P_2O_5 at 1 573 K.³⁾ The thermochemical data on the formations of C_4P and C_3P from CaO and P_2O_5 have been reported as



$$\begin{aligned} \log K(2) &= \log a_{C_4P} - 4 \log a_{CaO} - \log a_{P_2O_5} \quad \text{..... (3)} \\ &= 25.18 \quad \text{at } 1\,573\text{ K}^{4,5)} \end{aligned}$$



$$\begin{aligned} \log K(4) &= \log a_{C_3P} - 3 \log a_{CaO} - \log a_{P_2O_5} \quad \text{..... (5)} \\ &= 24.80 \quad \text{at } 1\,573\text{ K}^{4-6)} \end{aligned}$$

By using Eqs. (3) and (5), the P_2O_5 activities, $a_{P_2O_5}$, in the three-phase region of CaO + C_3PS + C_4P and the two-phase assemblage of C_4P + C_3P could be derived as follows, respectively.

$$\begin{aligned} &\text{region of } CaO + C_3PS + C_4P \\ \log a_{P_2O_5} &= -\log K(2) = -25.18 \quad \text{at } 1\,573\text{ K} \quad \text{..... (6)} \end{aligned}$$

$$\begin{aligned} &\text{region of } C_4P + C_3P \\ \log a_{P_2O_5} &= 3 \log K(2) - 4 \log K(4) = -23.66 \quad \text{at } 1\,573\text{ K} \\ &\quad \text{..... (7)} \end{aligned}$$

* Corresponding author: E-mail: hasegawa.masakatsu.7r@kyoto-u.ac.jp



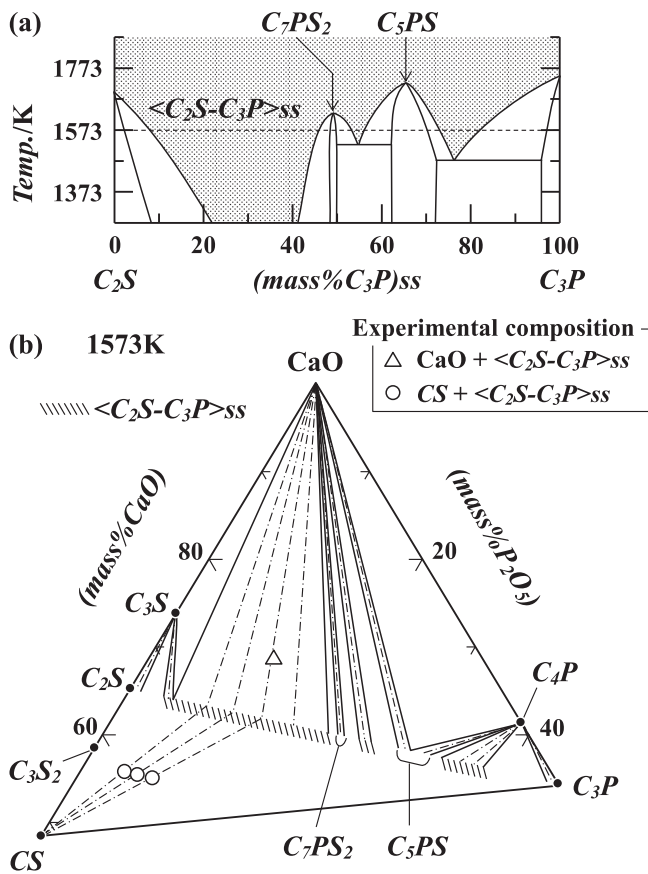


Fig. 1. (a) Phase diagram of the Ca_2SiO_4 – $\text{Ca}_3\text{P}_2\text{O}_8$ pseudo-binary system,²⁾ (b) Iso-thermal section of the CaO – SiO_2 – P_2O_5 ternary system at 1573 K.³⁾

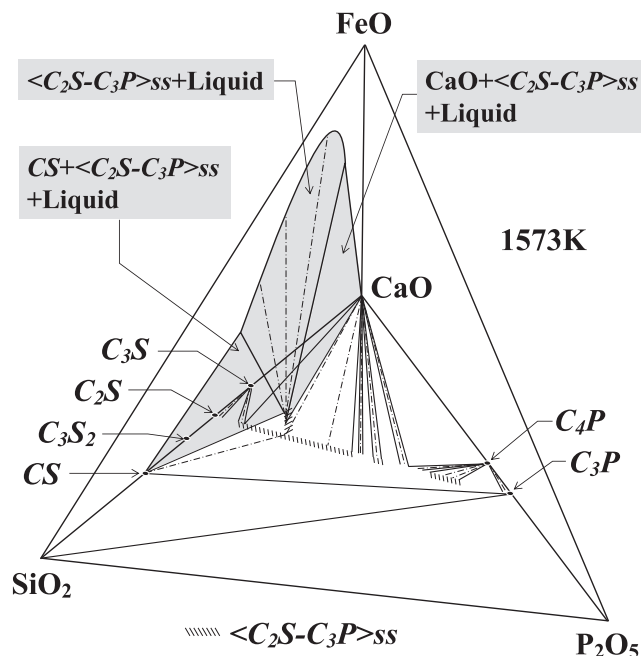


Fig. 2. Schematic diagram of phase relationship in the CaO – SiO_2 – P_2O_5 – FeO quaternary system at 1573 K.

Takeshita *et al.* measured $a_{\text{P}_2\text{O}_5}$ in the three-phase region of $\text{C}_3\text{S} + \text{C}_2\text{S} + \langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ through a gas equilibrium method, in which molten copper containing phosphorus was coexisted with oxides under a stream of $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ gas mixtures.⁷⁾ The result was given as

$$\text{region of } \text{C}_3\text{S} + \text{C}_2\text{S} + \langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}} \quad \text{..... (8)}$$

$$\log a_{\text{P}_2\text{O}_5} = -26.53 \quad \text{at } 1573 \text{ K}$$

At higher temperatures than 1573 K, Zhong *et al.* measured the P_2O_5 activities in $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ at 1823 K and 1873 K by equilibrating phosphorus-containing iron with solid solutions in oxygen partial pressures controlled by $\text{CO} + \text{CO}_2$ gas mixtures.^{8–10)}

Figure 2 is a schematic diagram of the phase relationship in the CaO – SiO_2 – P_2O_5 – FeO quaternary system at 1573 K. The base CaO – SiO_2 – P_2O_5 of this tetrahedron represents the phase diagram of the corresponding ternary system at 1573 K. It has been reported by Uchida *et al.* that there was the three-phase region of $\text{SiO}_2 + \text{CS} + \text{C}_3\text{P}$.^{11,12)} By combining Eq. (5) and the thermochemical data on the formation of CS given in Eq. (10), the P_2O_5 activity could be derived as follows.



$$\log K(9) = \log a_{\text{CS}} - \log a_{\text{CaO}} - \log a_{\text{SiO}_2} \quad \text{..... (10)}$$

$$= 2.92 \quad \text{at } 1573 \text{ K}^{13,14)}$$

region of $\text{SiO}_2 + \text{CS} + \text{C}_3\text{P}$

$$\log a_{\text{P}_2\text{O}_5} = \log a_{\text{C}_3\text{P}} - 3 \log a_{\text{CaO}} - \log K(4)$$

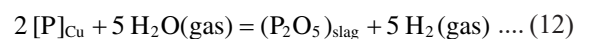
$$= -3[-\log K(9)] - \log K(4) = -16.04 \quad \text{at } 1573 \text{ K} \quad \text{..... (11)}$$

When iron oxide was added to the CaO – SiO_2 – P_2O_5 ternary slags, $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ could coexist with quaternary liquid phase, hereafter represented as “Liquid”. Matsugi *et al.* determined simultaneously the activities of P_2O_5 and FeO in the three-phase region of $\text{CS} + \langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}} + \text{Liquid}$ at 1573 K by employing electrochemical technique incorporating MgO -stabilized zirconia.¹⁵⁾ Pahlevani *et al.* calculated the P_2O_5 activities in the two-phase region of $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}} + \text{Liquid}$ at 1573 K by applying the regular solution model to Liquid.¹⁶⁾ For better understanding of dephosphorization reaction, the knowledge of P_2O_5 activities in $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ would be necessary, whereas there has been still lack of data measured at temperature of hot metal processing. In this study, firstly, the activities of P_2O_5 were measured in $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ at 1573 K to investigate the effects of coexisting solid phases, *i.e.*, CaO or CS , on the P_2O_5 activities. Subsequently, the parameters in the sub-regular solution model applied to $\langle \text{C}_2\text{S} - \text{C}_3\text{P} \rangle_{\text{ss}}$ were optimized by using the experimental data to discuss the thermochemical properties in the CaO – SiO_2 – P_2O_5 ternary system.

2. Experimental Aspects

2.1. Principle of Measurements

In order to determine the P_2O_5 activities in the heterogeneous slags, molten copper was brought into equilibrium with oxide mixtures under a stream of $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ gas mixtures. The reaction underlying the present study can be formulated as



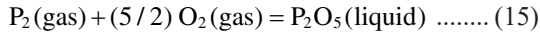
, where $[\text{P}]_{\text{Cu}}$ and $(\text{P}_2\text{O}_5)_{\text{slag}}$ denote phosphorus in liquid copper and P_2O_5 in slag, respectively. The Gibbs energy change

for the dissolution of gaseous phosphorus into liquid copper at 1 mass% solution was reported as

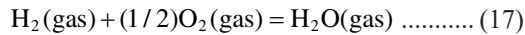
$$(1/2) \text{P}_2(\text{gas}) = [\text{P}]_{\text{Cu}} \dots\dots\dots (13)$$

$$\Delta G^\circ(13) / \text{J} \cdot \text{mol}^{-1} = -125\,000 + 0.54(T / \text{K})^{17} \dots (14)$$

The standard Gibbs energy changes for the following reactions were also available in the literature.



$$\Delta G^\circ(15) / \text{J} \cdot \text{mol}^{-1} = -1\,534\,500 + 506.3(T / \text{K})^4 \dots (16)$$



$$\Delta G^\circ(17) / \text{J} \cdot \text{mol}^{-1} = -246\,000 + 54.8(T / \text{K})^{18} \dots (18)$$

Hence, by combining Eqs. (14), (16) and (18), the equilibrium constant for reaction (12) at 1 573 K is given by

$$\begin{aligned} \log K(12) &= 5 \log(P_{\text{H}_2} / P_{\text{H}_2\text{O}}) + \log a_{\text{P}_2\text{O}_5} - 2 \log h_P \\ &= -10.34 \quad \text{at } 1\,573 \text{ K} \end{aligned} \dots (19)$$

In Eq. (19), the standard state of the P_2O_5 activity is taken to be pure hypothetical liquid P_2O_5 . At low phosphorus concentrations, the Henrian activity of phosphorus in liquid copper, h_P , would be equal to the phosphorus concentration in mass percent, $[\text{mass}\%P]_{\text{Cu}}$. Therefore, Eq. (19) can be rewritten by

$$\begin{aligned} \log a_{\text{P}_2\text{O}_5} &= -5 \log(P_{\text{H}_2} / P_{\text{H}_2\text{O}}) \\ &\quad + 2 \log[\text{mass}\%P]_{\text{Cu}} - 10.34 \quad \text{at } 1\,573 \text{ K} \end{aligned} \dots (20)$$

Equation (20) indicates that the values for $a_{\text{P}_2\text{O}_5}$ at 1 573 K can be determined by analyzing $[\text{mass}\%P]_{\text{Cu}}$ in liquid copper equilibrated with the heterogeneous slags under a stream of $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ gas mixtures in which $P_{\text{H}_2} / P_{\text{H}_2\text{O}}$ ratios are fixed.

2.2. Experimental Apparatus and Procedure

The preparation of CaO is based upon heating CaCO_3 at 1 273 K for 12 hours. C_3P and SiO_2 were obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K. C_2S and CS were obtained by mixing requisite portions of CaCO_3 and SiO_2 , and then heating at 1 573 K for 24 hours and 98 hours, respectively. The solid solutions, $\langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$, were prepared by mixing C_2S and C_3P , and heating at 1 573 K for 24 hours. The starting materials thus obtained were mixed to yield the bulk compositions listed in **Table 1**. In this table and hereafter, $(\text{mass}\% \text{C}_3\text{P})_{\text{ss}}$ represents the C_3P concentration in $\langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$. The oxide mixtures used in this study occurred at the two-phase regions of $\text{CaO} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$ and $\text{CS} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$, illustrated

in Fig. 1(b).

The experimental apparatus and associated gas trains, respectively, are schematically shown in **Figs. 3** and **4**. A SiC resistance furnace was equipped with a mullite reaction tube of 60-mm o.d., 50-mm i.d. and 1 000-mm in length. About 1-g of pure copper and about 0.6-g of the oxide mixtures were charged in alumina crucibles of 10-mm o.d., 8-mm i.d. and 30-mm in height. Seven crucibles were put into a nickel container of 38-mm o.d., 32-mm i.d. and 63-mm in height. This container was suspended from the furnace top via a nickel rod of 3-mm diameter and heated up to 1 573 K. Within the crucibles, copper was placed between the oxide mixtures, as shown in Fig. 3. The oxide mixtures, initially placed beneath the copper, did not rise up to the top of the molten copper surface. This arrangement was conducted to increase the contact area between oxide and copper. The oxide mixture on liquid copper was powdery and its thickness was about 2-mm; it would not prevent the contact between liquid copper and gas phase. In the experimental runs, the gas mixtures of $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ were introduced into the reaction tube at a flow rate of 200 mL/min.

Temperatures were measured with a Pt-PtRh13 thermocouple placed beside the nickel container, and controlled to ± 1 K by using a control thermocouple and a PID-type temperature regulator. The overall errors in temperature measurements and control were estimated to be less than ± 2 K.

The two-phase oxide of $\text{CaO} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$ was brought into equilibrium with $\text{Cu}-\text{P}$ alloys under a stream of the $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ gas mixture prepared by passing $\text{Ar} + 12\%\text{H}_2$ gas mixture through $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{C}_2\text{H}_2\text{O}_4$ mixture kept at 268 K within a thermostat bath. The equilibrium partial pressure of H_2O fixed by this two-phase mixture has been reported elsewhere;¹⁹⁾

$$\log(P_{\text{H}_2\text{O}} / \text{atm}) = 6.88 - 2\,810 / (T / \text{K}) \quad T < 293 \text{ K} \dots (21)$$

The water vapor pressures used in this study were much lower than those obtainable through the conventional technique. Thus, the $\text{Ar} + \text{H}_2$ gas mixture has to be rigidly moisture-free; the gas trains for $\text{Ar} + \text{H}_2$ gas mixture contained silica gel, phosphorus pentoxide and a cold trap kept below 223 K, as illustrated in Fig. 4.

On the other hand, in the case of the two-phase oxide mixtures of $\text{CS} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$, the $\text{Ar} + \text{H}_2 + \text{H}_2\text{O}$ gas mixture was prepared by passing $\text{Ar} + 12\%\text{H}_2$ gas mixture through $\text{LiCl} \cdot 2\text{H}_2\text{O}$ -saturated water kept at 313 K. The equilibrium H_2O partial pressure of $\text{LiCl} \cdot 2\text{H}_2\text{O}$ -saturated water has been also reported elsewhere;¹⁹⁾

$$\log(P_{\text{H}_2\text{O}} / \text{atm}) = 5.94 - 2\,510 / (T / \text{K}) \quad T > 291.5 \text{ K} \dots (22)$$

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

Region	Bulk composition (mass%)			$(\text{mass}\% \text{C}_3\text{P})_{\text{ss}}$	P_{H_2} (atm)	$P_{\text{H}_2\text{O}}$ (atm)	$[\text{mass}\%P]_{\text{Cu}}$	$\log a_{\text{P}_2\text{O}_5}$
	CaO	SiO_2	P_2O_5					
$\text{CaO} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$	68.75	19.64	11.60	31	1.20×10^{-1}	2.23×10^{-4}	0.064 ± 0.004	-26.43 ± 0.05
	55.72	40.16	4.12	18	1.20×10^{-1}	8.53×10^{-3}	0.015 ± 0.002	-19.73 ± 0.10
$\text{CS} + \langle \text{C}_2\text{S}-\text{C}_3\text{P} \rangle_{\text{ss}}$	55.39	39.12	5.49	24	1.20×10^{-1}	8.53×10^{-3}	0.017 ± 0.002	-19.62 ± 0.09
	550.1	37.90	7.09	31	1.20×10^{-1}	8.53×10^{-3}	0.021 ± 0.004	-19.44 ± 0.15

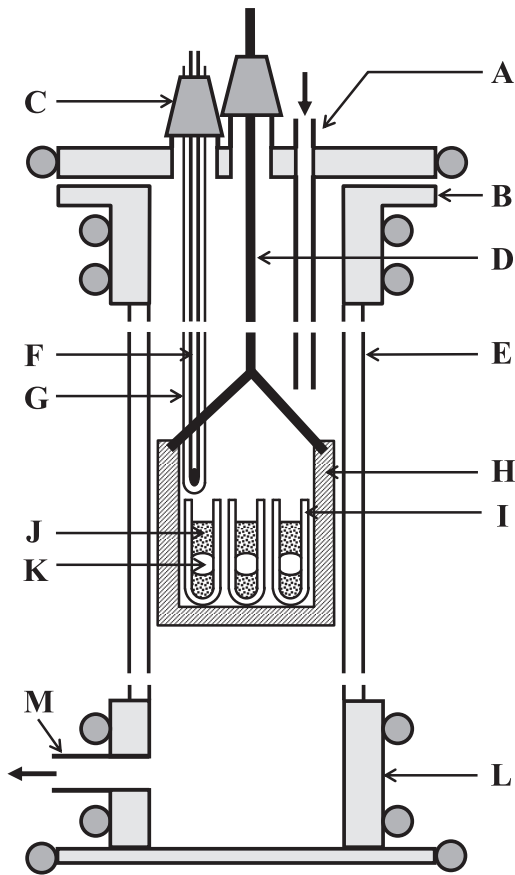


Fig. 3. Experimental apparatus. (A) Gas inlet, (B) Water-cooled brass flange, (C) Rubber stopper, (D) Nickel rod, (E) Mullite reaction tube, (F) Pt-PtRh13 thermocouple, (G) Alumina sheath, (H) Nickel container, (I) Alumina crucible, (J) Oxide mixture, (K) {Cu-P} liquid alloy, (L) Water-cooled brass flange, (M) Gas outlet.

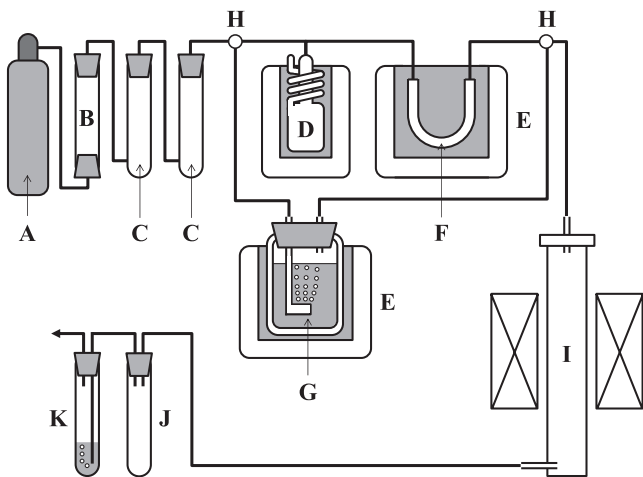


Fig. 4. Gas trains. (A) Ar + H₂ gas cylinder, (B) Silica-gel, (C) Phosphorus pentoxide, (D) Cold trap, (E) Thermostat bath, (F) C₂H₂O₄·2H₂O + C₂H₂O₄ mixture, (G) LiCl·2H₂O-saturated water, (H) Two-way stopcock, (I) Furnace assembly, (J) Empty tube, (K) Di-n-butyl-phthalate bleeder.

The experimental conditions are summarized in Table 1.

After the furnace was kept at the experimental temperature for 22 hours, the nickel container was lowered onto the bottom of the water-cooled brass flange inside the furnace tube. The oxide mixtures were then removed from the alumina crucibles, ground and subsequently charged again

into the crucibles for repeated durations. These procedures were repeated at an interval of 22 hours. In this study, these procedures were essential, because neither metal nor oxide phases could be agitated during experimental runs. Any unexpected reactions could not be observed between the oxide mixtures and alumina crucibles.

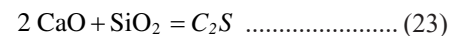
For analyzing phosphorus contents in copper, samples were dissolved in HCl + HNO₃ solution. In order to separate copper and phosphorus, ammonium phosphor-molybdate was precipitated from the solution by addition of ammonium molybdate. After being filtered, the precipitate was dissolved in NaOH solution, and subsequently phosphorus was analyzed with an inductive-coupled plasma spectrometer.

3. Experimental Results and Discussion

3.1. Activity Measurements

Figure 5 gives a typical relation between phosphorus content in liquid copper coexisting with oxide mixture of CS + <C₂S–C₃P>_{ss} of (mass% C₃P)_{ss} = 31 and duration at 1573 K. Although there were experimental variations, the equilibrium value for [mass%P]_{Cu} could be obtained if the experiment was continued for 120 hours and more. Taking the mass balance of phosphorus between oxide and metallic phases into account, the change of C₃P concentration in <C₂S–C₃P>_{ss} could be estimated to be less than 0.3-mass%.

The experimental results are summarized in Table 1, and Fig. 6 shows the P₂O₅ activities at 1573 K plotted against (mass% C₃P)_{ss}. The P₂O₅ activity in the two-phase region of CS + <C₂S–C₃P>_{ss} increased with an increase in (mass% C₃P)_{ss}. In this two-phase region, the reactions expressed by Eqs. (4), (9) and (23) achieved the equilibrium states.



$$\log K(23) = \log a_{\text{C}_2\text{S}} - 2 \log a_{\text{CaO}} - \log a_{\text{SiO}_2} \quad \dots\dots\dots (24)$$

$$= 4.78 \quad \text{at } 1573 \text{ K}^{13,14}$$

By combining Eqs. (5), (10) and (24), we obtained

$$\log a_{\text{P}_2\text{O}_5} = \log a_{\text{C}_3\text{P}} - 3 \log a_{\text{C}_2\text{S}} - 19.22 \quad \text{at } 1573 \text{ K} \dots\dots\dots (25)$$

Equation (25) indicated that the P₂O₅ activity in <C₂S–C₃P>_{ss} coexisting with CS increased as (mass% C₃P)_{ss} increased at a constant temperature, due to an increase in the C₃P activity and a decrease in the C₂S activity. Therefore, the relationship between *a*_{P₂O₅} and (mass% C₃P)_{ss} illustrated in Fig. 6 was thermodynamically consistent with Eq. (25).

Figure 6 also shows that *a*_{P₂O₅} in the two-phase region of CaO + <C₂S–C₃P>_{ss} is about 7 digits lower than that in the two-phase region of CS + <C₂S–C₃P>_{ss} at the same C₃P content in <C₂S–C₃P>_{ss}. The thermodynamic consistency of this behavior was discussed based on the comparisons of the CaO and SiO₂ activities in the CaO–SiO₂–P₂O₅ ternary system derived by using the present experimental results with those in the CaO–SiO₂ binary system, described as follows.

The P₂O₅ activities measured in this study are given in cells (b) and (h) of Table 2. Considering the experimental conditions, the activities of CaO and CS are unity in cells (a) and (j), respectively. Therefore, by inserting the activities of

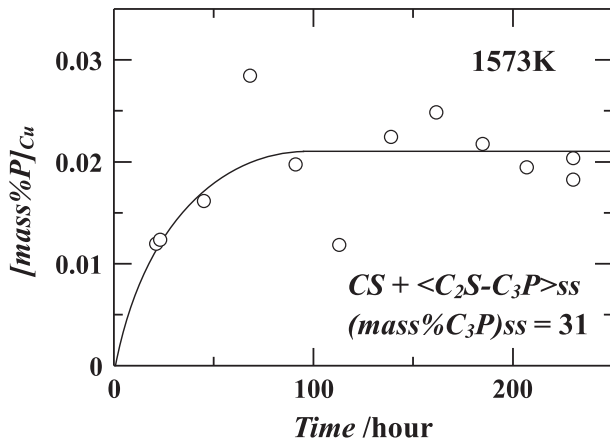


Fig. 5. Typical relation between phosphorus content in liquid copper and duration at 1573 K.

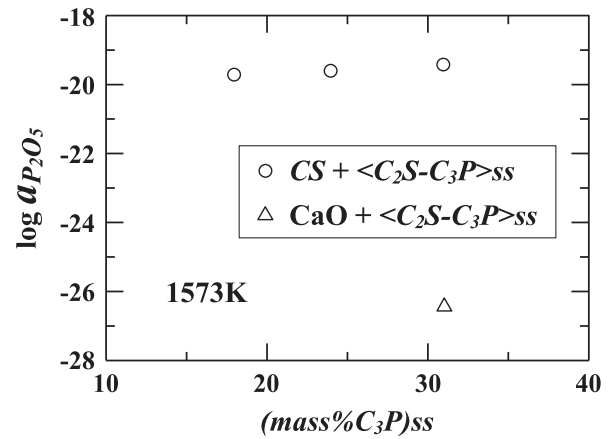


Fig. 6. Relation between logarithmic value for P_2O_5 activity and C_3P content in $<C_2S-C_3P>_{ss}$ at 1573 K.

Table 2. Calculation results of activities in the CaO–SiO₂–P₂O₅ ternary system at 1573 K.

Region	(mass%C ₃ P) _{ss}	log a_{CaO}	log $a_{P_2O_5}$	log a_{SiO_2}	log a_{CS}	log a_{C_3P}	log a_{C_2S}
CaO + $<C_2S-C_3P>_{ss}$	31	(a) 0	(b) -26.43	(c) -5.25	(d) -	(e) -1.63	(f) -0.47
CS + $<C_2S-C_3P>_{ss}$	31	(g) -2.33	(h) -19.44	(i) -0.59	(j) 0	(k) -1.63	(l) -0.47

CaO and P_2O_5 into Eq. (5), we can obtain

$$\begin{aligned} \log a_{C_3P}(\text{cell } e) &= \log K(4) + 3 \log a_{CaO}(\text{cell } a) \\ &+ \log a_{P_2O_5}(\text{cell } b) \quad \dots (26) \\ &= 24.80 + 3 \times 0 + (-26.43) = -1.63 \end{aligned}$$

Now, it can be assumed that the C_3P activity remains constant in $<C_2S-C_3P>_{ss}$ of $(\text{mass}\%C_3P)_{ss} = 31$, whether $<C_2S-C_3P>_{ss}$ coexists with CaO or CS.

$$\log a_{C_3P}(\text{cell } k) = \log a_{C_3P}(\text{cell } e) = -1.63 \quad \dots (27)$$

Then, the followings are obtainable from Eqs. (5), (10), (24) and (27).

$$\begin{aligned} \log a_{CaO}(\text{cell } g) &= [\log a_{C_3P}(\text{cell } k) - \log K(4) - \log a_{P_2O_5}(\text{cell } h)] / 3 \quad \dots (28) \\ &= [(-1.63) - 24.80 - (-19.44)] / 3 = -2.33 \end{aligned}$$

$$\begin{aligned} \log a_{SiO_2}(\text{cell } i) &= \log a_{CS}(\text{cell } j) - \log a_{CaO}(\text{cell } g) - \log K(9) \quad \dots (29) \\ &= 0 - (-2.33) - 2.92 = -0.59 \end{aligned}$$

$$\begin{aligned} \log a_{C_2S}(\text{cell } l) &= 2 \log a_{CaO}(\text{cell } g) + \log a_{SiO_2}(\text{cell } i) + \log K(23) \quad \dots (30) \\ &= 2 \times (-2.33) + (-0.59) + 4.78 = -0.47 \end{aligned}$$

It can be assumed again that the C_2S activity is constant in $<C_2S-C_3P>_{ss}$ of $(\text{mass}\%C_3P)_{ss} = 31$.

$$\log a_{C_2S}(\text{cell } f) = \log a_{C_2S}(\text{cell } l) = -0.47 \quad \dots (31)$$

By using Eqs. (24) and (31), we have

$$\begin{aligned} \log a_{SiO_2}(\text{cell } c) &= \log a_{C_2S}(\text{cell } f) - 2 \log a_{CaO}(\text{cell } a) - \log K(23) \quad \dots (32) \\ &= (-0.47) - 2 \times 0 - 4.78 = -5.25 \end{aligned}$$

On the other hand, the CaO and SiO₂ activities in the CaO–SiO₂ binary system can be calculated by using the thermodynamic data,^{13,14)} and are illustrated in Fig. 7. As seen in this figure, the ranges of the CaO and SiO₂ activities coexisting with CS at 1573 K are as follows.

$$-2.92 \leq \log a_{CaO} \leq -2.07 \quad \dots (33)$$

$$-0.85 \leq \log a_{SiO_2} \leq 0 \quad \dots (34)$$

Equations (28) and (29) were consistent with Eqs. (33) and (34), respectively.

As shown in Fig. 1(b), $(\text{mass}\%C_3P)_{ss}$ in the three-phase coexistence of CaO + C_3S + $<C_2S-C_3P>_{ss}$ is lower than 31, and the SiO₂ activity in this three-phase region is equal to that in the two-phase region of CaO + C_3S ; $\log a_{SiO_2} = -4.81$ at 1573 K, seen in Fig. 7, while Table 2 gives $\log a_{SiO_2} = -5.25$ in $<C_2S-C_3P>_{ss}$ of $(\text{mass}\%C_3P)_{ss} = 31$ coexisting with CaO. Considering Eq. (24), this result was consistent with the thermochemical consideration that, in the case of coexisting with CaO, the SiO₂ activity decreased as the concentration and activity of C_2S decreased in $<C_2S-C_3P>_{ss}$. As already mentioned above, the CaO and SiO₂ activities in Table 2 were derived by using the P_2O_5 activities measured in this study. Therefore, it could be concluded that the present experimental data were not inconsistent with the phase relationship of the CaO–SiO₂–P₂O₅ ternary system.

3.2. Solution Model Applied to $<C_2S-C_3P>_{ss}$

Figure 8(a) shows that $<C_2S-C_3P>_{ss}$ forms between α - C_2S and $\bar{\alpha}$ - C_3P , and it is acceptable that electrically neutral molecules of “(1/2)Ca₃P₂O₈” replace with those of “Ca₂SiO₄” in solid solutions, as illustrated in Fig. 9. Based on this simple assumption, the present authors suggested the regular solution model applied to $<C_2S-C_3P>_{ss}$.²⁰⁾ In this study, the solution model was modified by using the present experimental data.

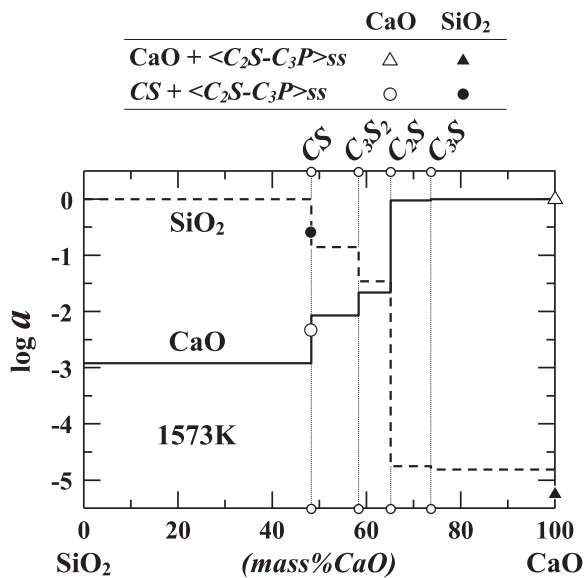


Fig. 7. Activities of CaO and SiO₂ in the CaO–SiO₂ binary system at 1 573 K.

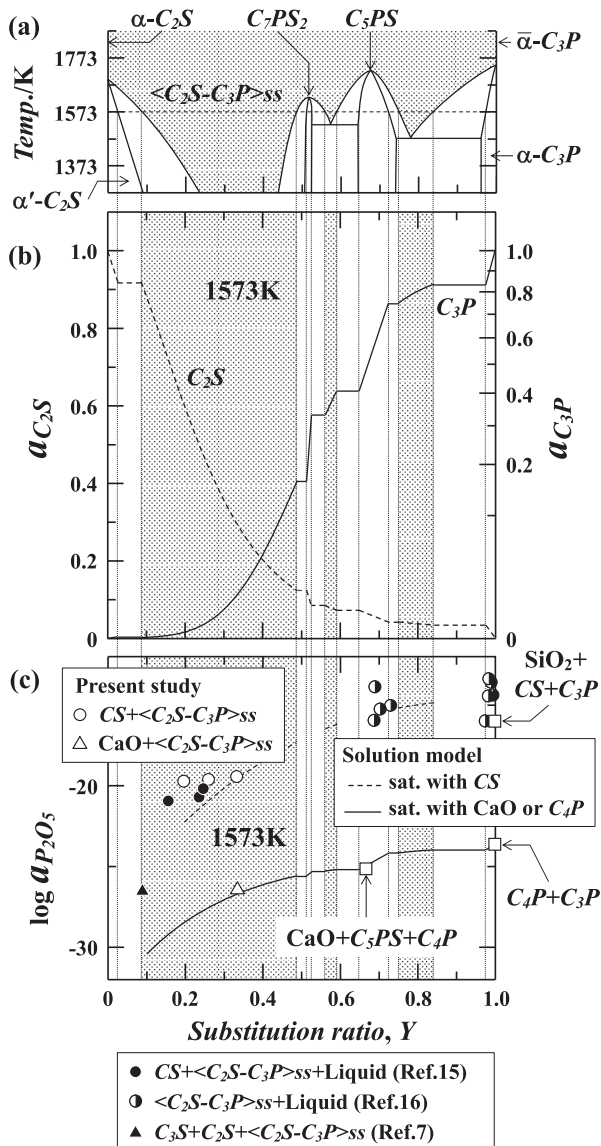


Fig. 8. (a) Phase diagram of the Ca₂SiO₄–Ca₃P₂O₈ pseudo-binary system, (b) Activity curves of C₂S and C₃P calculated at 1 573 K, (c) Logarithmic values for P₂O₅ activities plotted against substitution ratio at 1 573 K.

The substitution ratio of Ca₂SiO₄ for (1/2)Ca₃P₂O₈, Y , was defined as

$$Y = n_{(1/2)Ca_3P_2O_8} / (n_{Ca_2SiO_4} + n_{(1/2)Ca_3P_2O_8}) \quad (35)$$

$$= 2n_{Ca_3P_2O_8} / (n_{Ca_2SiO_4} + 2n_{Ca_3P_2O_8})$$

, where n_i represents the number of moles of chemical species i in solid solutions. In order to calculate the C₂S and C₃P activities, the sub-regular solution model was applied to <C₂S–C₃P>ss, formulated as follows.

$$RT \ln a_{C_3P} = 2RT \ln a_{(1/2)Ca_3P_2O_8}$$

$$= \Delta G^\circ_i(C_3P) + 2RT \ln Y + 2A(1-Y)^3 + 2B(1-Y)^2 \quad (36)$$

$$RT \ln a_{C_2S} = \Delta G^\circ_i(C_2S) + RT \ln(1-Y) - AY^3 + \left(\frac{3}{2}A + B\right)Y^2 \quad (37)$$

In Eqs. (36) and (37), R is the gas constant, $\Delta G^\circ_i(i)$ represents the Gibbs energy change of the phase transformation of i , and the parameters A and B are independent of composition and temperature. The standard states of C₂S and C₃P are taken to be the most stable forms at 1 573 K, i.e., α' -C₂S and α -C₃P, respectively. Equations (36) and (37) satisfy Gibbs-Duhem equation.

The thermal data on C₂S, heat capacity and heat of the phase transformation, were available.²¹⁾ By extrapolating the value for heat capacity of α -C₂S, $\Delta G^\circ_i(C_2S)$ could be calculated as

$$\Delta G^\circ_i(C_2S) / J \cdot mol^{-1} = 1132 \quad \text{at } 1573 \text{ K} \quad (38)$$

On the other hand, the heat of the phase transformation between α -C₃P and $\bar{\alpha}$ -C₃P has been reported to be zero.²¹⁾

$$\Delta G^\circ_i(C_3P) / J \cdot mol^{-1} = 0 \quad \text{at } 1573 \text{ K} \quad (39)$$

Namely, Eqs. (36) and (37) could be rewritten as Eqs. (40) and (41), respectively.

$$\log a_{C_3P} = 2 \log Y + 2a(1-Y)^3 + 2b(1-Y)^2 \quad (40)$$

$$\log a_{C_2S} = 3.76 \times 10^{-2} + \log(1-Y) - aY^3 + \left(\frac{3}{2}a + b\right)Y^2 \quad (41)$$

$$a = A / (R \times 1573 \times \ln 10) \quad (42)$$

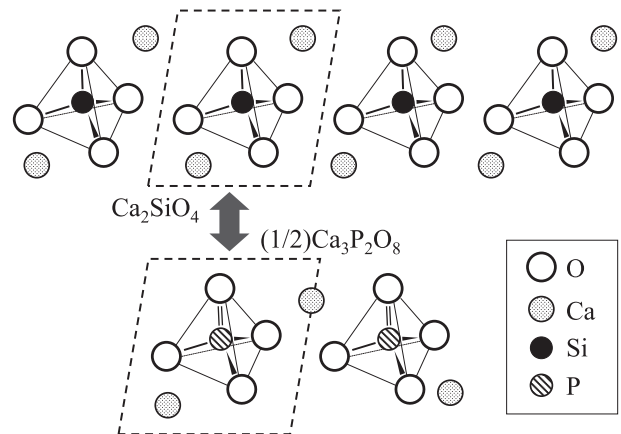


Fig. 9. Schematic illustration of solid solution between Ca₂SiO₄ and Ca₃P₂O₈.

$$b = B / (R \times 1573 \times \ln 10) \dots\dots\dots (43)$$

By combining Eqs. (5) and (40), the P_2O_5 activity in $<C_2S-C_3P>_{ss}$ coexisting with CaO could be given as

$$\begin{aligned} \log a_{P_2O_5} &= \log a_{C_3P} - \log K(4) \\ &= 2 \log Y + 2a(1-Y)^3 + 2b(1-Y)^2 - 24.80 \end{aligned} \dots\dots (44)$$

From Eqs. (5), (10), (24), (40) and (41), the P_2O_5 activity in $<C_2S-C_3P>_{ss}$ coexisting with CS could be also formulated as

$$\begin{aligned} \log a_{P_2O_5} &= \log a_{C_3P} - 3[\log K(9) - \log K(23) + \log a_{C_2S}] - \log K(4) \\ &= -19.22 + [2 \log Y + 2a(1-Y)^3 + 2b(1-Y)^2] \\ &\quad - 3 \left[3.76 \times 10^{-2} + \log(1-Y) - aY^3 + \left(\frac{3}{2}a + b \right) Y^2 \right] \end{aligned} \dots\dots\dots (45)$$

The optimization of the values for the parameters a and b was conducted by comparing the P_2O_5 activities measured with those calculated from Eqs. (44) and (45). Then, we obtained

$$a = -4.98 \dots\dots\dots (46)$$

$$b = 2.26 \dots\dots\dots (47)$$

Figure 8(b) shows the C_3P and C_2S activities calculated as functions of Y , deviated negatively from Raoult's law. These behaviors corresponded to the chemical affinity between C_3P and C_2S in solid solutions.

Figure 8(c) illustrates the P_2O_5 activities at 1573 K in the two-phase regions of $CaO + <C_2S-C_3P>_{ss}$, $C_4P + <C_2S-C_3P>_{ss}$ and $CS + <C_2S-C_3P>_{ss}$ calculated from Eqs. (44), (49), and (45), respectively.

$$3C_4P + P_2O_5 = 4C_3P \dots\dots\dots (48)$$

$$\begin{aligned} \log a_{P_2O_5} &= 4 \log a_{C_3P} - 4 \log K(4) + 3 \log K(2) \\ &= 4 \left[2 \log Y - 9.96 \times (1-Y)^3 + 4.51 \times (1-Y)^2 \right] \dots\dots (49) \\ &\quad - 23.66 \end{aligned}$$

Although the P_2O_5 activities were estimated too low in the region of $Y < 0.2$, the values for $a_{P_2O_5}$ calculated with the solution model were in good agreement with those in $CaO + <C_2S-C_3P>_{ss}$ and $CS + <C_2S-C_3P>_{ss}$ measured in the present study and those in $C_4P + C_3P$, $CaO + C_3PS + C_4P$ and $SiO_2 + CS + C_3P$ derived with the literature data⁴⁻⁶⁾ (With respect to detailed calculation methods, see *introduction*).

Figure 8(c) also shows the P_2O_5 activities in the three-phase region of $CS + <C_2S-C_3P>_{ss} + \text{Liquid}$ ¹⁵⁾ and the two-phase coexistence of $<C_2S-C_3P>_{ss} + \text{Liquid}$.¹⁶⁾ It could be concluded here that the values for $a_{P_2O_5}$ in $CS + <C_2S-C_3P>_{ss} + \text{Liquid}$ were slightly lower than those in $CS + <C_2S-C_3P>_{ss}$ due to dissolution of iron oxide into $<C_2S-C_3P>_{ss}$ (See Fig. 2). Considering the chemical affinity between CaO and P_2O_5 , it would be expected that the

P_2O_5 activity decreased with an increase in slag basicity. As seen in Fig. 8(c), the values for $a_{P_2O_5}$ in $<C_2S-C_3P>_{ss} + \text{Liquid}$ reported in the literature¹⁶⁾ were much higher than those in $CaO + <C_2S-C_3P>_{ss}$ and were almost equal to those in $CS + <C_2S-C_3P>_{ss}$ calculated in this study; these results were acceptable. However, the detailed effect of slag basicity on $a_{P_2O_5}$ in liquid phase saturated with $<C_2S-C_3P>_{ss}$ would be our important future subject.

4. Conclusion

For better understanding phosphorus removal from hot metal, the present study was aimed at measuring the P_2O_5 activities in solid solutions between Ca_2SiO_4 and $Ca_3P_2O_8$ coexisting with CaO or $CaSiO_3$ at 1573 K. It was clarified that the P_2O_5 activity in the two-phase region of $CaO + Ca_2SiO_4-Ca_3P_2O_8$ solid solution was about 7 digits lower than that in the two-phase region of $CaSiO_3 + Ca_2SiO_4-Ca_3P_2O_8$ solid solution. The values for the activities of components determined in this study were consistent with the phase relationship in the $CaO-SiO_2-P_2O_5$ ternary system. The P_2O_5 activities calculated with the solution model applied to $Ca_2SiO_4-Ca_3P_2O_8$ solid solution were in good agreement with the present experimental results and the literature data.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 15K06524.

REFERENCES

- 1) H. Suito, Y. Hayashida and Y. Takahashi: *Tetsu-to-Hagane*, **63** (1977), 1252.
- 2) W. Fix, H. Heymann and R. Heinke: *J. Am. Ceram. Soc.*, **52** (1969), 346.
- 3) M. Matsu-sue, M. Hasegawa, K. Fushi-tani and M. Iwase: *Steel Res. Int.*, **78** (2007), 465.
- 4) E. T. Turkdogan and J. Pearson: *J. Iron Steel Inst.*, **175** (1953), 393.
- 5) M. Iwase, H. Fujiwara, E. Ichise, H. Kitaguchi and K. Ashida: *Iron Steelmak.*, **16** (1989), No. 4, 45.
- 6) H. Yama-zoye, E. Ichise, H. Fujiwara and M. Iwase: *Trans. Iron Steel Soc. AIME*, **13** (1992), 41.
- 7) H. Takeshita, M. Hasegawa, Y. Kashiwaya and M. Iwase: *Steel Res. Int.*, **81** (2010), 100.
- 8) M. Zhong, H. Matsuura and F. Tsukihashi: *Mater. Trans.*, **56** (2015), 1192.
- 9) M. Zhong, H. Matsuura and F. Tsukihashi: *ISIJ Int.*, **55** (2015), 2283.
- 10) M. Zhong, H. Matsuura and F. Tsukihashi: *Metall. Mater. Trans. B*, **47** (2016), 1745.
- 11) Y. Uchida, N. Sasaki and Y. Miki: *ISIJ Int.*, **58** (2018), 869.
- 12) C. Watanabe and Y. Uchida: *CAMP-ISIJ*, **33** (2020), 1527 (in Japanese).
- 13) O. Kubaschewski, C. B. Alcock and P. J. Spencer: *Materials Thermochemistry*, 6th ed., Pergamon Press, Oxford, (1993), 257.
- 14) S. Seetharaman, ed.: *Treatise of Process Metallurgy*, Vol. 1: *Process Fundamentals*, Elsevier, Oxford, (2014), 539.
- 15) R. Matsugi, K. Miwa and M. Hasegawa: *ISIJ Int.*, **57** (2017), 1718.
- 16) F. Pahlevani, S. Kitamura, H. Shibata and N. Maruoka: *ISIJ Int.*, **50** (2010), 822.
- 17) M. Iwase, E. Ichise and N. Yamada: *Steel Res.*, **56** (1985), 319.
- 18) O. Kubaschewski and C. B. Alcock: *Metallurgical Thermochemistry*, 5th ed., Pergamon Press, Oxford, (1979), 380.
- 19) H. Takeshita, M. Hasegawa and M. Iwase: *High Temp. Mater. Process.*, **27** (2008), 19.
- 20) M. Hasegawa, Y. Kashiwaya and M. Iwase: *High Temp. Mater. Process.*, **31** (2012), 421.
- 21) I. Barin: *Thermochemical Data for Pure Substances*, VCH Verlagsgesellschaft mbH, Weinheim, (1989), 327.