Thermodynamic Considerations for Eliminating P and Si from Molten Copper by Na₂CO₃-Based Slag

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Thermodynamic properties of NaO_{0.5}-CO₂-XO_{v/2} slag (X: P or Si, *v*: valence of X) have been investigated by conducting the following measurements:

- (1) Solubility measurements of Na₃PO₄ (*s*) into sodium carbonate melts at 1423 to 1523 K under various partial pressures of CO₂ and oxygen.
- (2) Activity measurements of NaO_{0.5} under various partial pressures of CO₂.
- (3) Solubility measurements of CO₂ in the slags.

Based on the results, the equilibrium distribution ratios of P and Si between the slags and the molten copper have been estimated as a function of partial pressures of CO₂ and oxygen and the slag composition at 1523 K.

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I. Introduction

Considering the application of sodium carbonate slag to the production of high purity copper and to the more effective refining of crude copper, the authors have been studying on the elimination of As, Sb, Sn, Fe, Te, Se, Ni and Zn from molten copper by using Na₂CO₃ slag⁽¹⁾⁻⁽¹⁰⁾.

In the present study, thermodynamic properties of NaO_{0.5}-CO₂-XO_{v/2} slag (X: P or Si, *v*: valence of X) have been investigated to estimate the distribution ratios of P and Si between Na₂CO₃ slag and molten copper as a function of partial pressures of CO₂ and oxygen and the slag composition $N \{N = n_{\text{Na}} / (n_{\text{Na}} + n_{\text{X}}), n$: the number of moles}.

II. Principle for Calculating the Distribution Ratio

When an impurity element, X, exists as *v*-valent oxide in slag, the distribution reaction of X between slag and molten copper may be represented by:

The distribution ratio of X, L_X , which is defined by $(\% \text{X in the slag}) / [\% \text{X in metal}]$ can be evaluated from the following expression:

$$L_X = \frac{(\% \text{X})}{[\% \text{X}]} = \frac{K_{(1)} \cdot (n_T) \cdot [\gamma_X]}{[n_T] \cdot (\gamma_{\text{XO}_{v/2}})} \cdot p_{\text{O}_2}^{v/4} \quad (2)$$

where $K_{(1)}$ is the equilibrium constant of reaction (1), $[n_T]$ and (n_T) are the molar amount of 100 g metal and slag, respectively, γ_i is the Raoultian activity coefficient of component *i*, and p_{O_2} is the standardized oxygen partial pressure at the slag-metal interface. p_i is defined as $p_i = (P_i / \text{Pa}) / (P^\circ / \text{Pa})$, where P_i / Pa is the partial pressure of *i* and $P^\circ / \text{Pa} = 101325$. In eq. (2), the values of $K_{(1)}$ and $[\gamma_X]$ are available in the literature, however, the thermodynamic properties of slag, such as (n_T) and $(\gamma_{\text{XO}_{v/2}})$ should be determined experimentally.

Figure 1 shows the phase diagram of the Na₂O·P₂O₅-3Na₂O·P₂O₅ binary system⁽¹¹⁾. As one can see, PO_{2.5} reacts with NaO_{0.5} to form a solid compound Na₃PO₄ at $N = 0.75$ (melting point 1856 K). On the right side, the equilibrium phase relationship of the slag has not yet been clarified. Therefore, as a first step to evaluate the thermodynamic properties of the NaO_{0.5}-CO₂-PO_{2.5} slag system, solubility measurements of Na₃PO₄ (*s*) into sodium carbonate melt were conducted at 1423 and 1523 K.

Figure 2 shows the flow chart for calculating the distribution ratio of P. After establishing the equilibrium phase relationship of the slag, by measurement (1), activities of NaO_{0.5} were measured by EMF technique in the (solid-liquid) coexisting region and in the liquid region. Then, activities of PO_{2.5} were evaluated separately in both regions.

In case of Si, by combining the measurement (2) with activity measurements reported by Yamaguchi *et al.*⁽¹²⁾, activities of SiO₂ were calculated by using the Gibbs-Duhem integration method.

As the value (n_T) can be determined by measuring the CO₂ solubility, the distribution ratios of P and Si can be finally estimated as a function of partial pressures of CO₂ and O₂ and the slag composition *N*.

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Fig. 1 Phase diagram of the $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ - $3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ system⁽¹¹⁾.

III. Solubility of Na_3PO_4 (s) into Sodium Carbonate Melt

1. Experimental procedure

Chemical reagent grade Na_3PO_4 was mixed with water to make a viscous paste and charged in an alumina crucible. The specimen was heated and sintered at 473 K for 7.2 ks (2 h) to ensure the water evaporation and then at 1523 K for 72 ks (20 h). After cooling, a small piece of sample was taken and analyzed by X-ray diffraction and Na_3PO_4 was identified. Then, a premelted mixture of sodium carbonate and Na_3PO_4 in the liquid slag region was charged in this crucible and heated at 1423 or 1523 K under various CO_2 - O_2 -(or CO)-Ar gas mixture to control the partial pressures of oxygen and CO_2 . Samples were taken from the upper melted part at given time intervals and were subjected to chemical analyses. The P and Na contents were analyzed by ICP spectrometric method and the CO_2 content by the B_2O_3 fusion coulometric method⁽¹³⁾.

2. Experimental results

Figure 3 shows the effect of partial pressure of CO_2 on the solubility of Na_3PO_4 into Na_2CO_3 at 1423 and 1523 K, expressed in terms of the saturated composition, N_{Sat} . Neither P_{CO_2} nor P_{O_2} has influence on N_{Sat} . The solubility values are also plotted in the $\text{NaO}_{0.5}$ - CO_2 - $\text{PO}_{2.5}$ ternary diagram and shown in Fig. 4. The experimental results

Fig. 2 Flow chart for calculating the distribution ratio of P.

Fig. 3 Effect of partial pressure of CO₂ on the solubility of Na₃PO₄ (s) into Na₂CO₃ melt.

Fig. 4 Solubility of Na₃PO₄ (s) into Na₂CO₃ melt.

are on the line connecting Na₂CO₃ and Na₃PO₄ (s). This implies that the dissolution reaction proceeds according to the following reaction:

and that phosphorus exits as PO₄³⁻ in the slag.

IV. Activity of NaO_{0.5} (l)

1. Experimental method

Activities of NaO_{0.5} in the slags were determined by EMF method using β"-alumina (manufactured by NGK Spark Plug Co., Ltd.) as a solid electrolyte under various partial pressures of CO₂ within the temperature range of 1423 to 1523 K. The experimental procedure was almost

the same as reported before⁽¹⁾. The electrochemical cell used can be represented as:

Reference		Sample
Pt, O ₂ (g, pO ₂ [*])	Na ⁺	CO ₂ (g, pCO ₂), O ₂ (g, pO ₂), Pt
NaO _{0.5} -SiO ₂ -FeO _{1.5}	β"-Al ₂ O ₃	NaO _{0.5} -CO ₂ -XO _{v/2}

Chemical reagent grade Na₂CO₃ and Na₃PO₄ or SiO₂, dried at 443 K for more than 1.2 Ms (14 d), were used for the preparation of the sample slag. The mixture in an appropriate composition was charged into a Pt-crucible and was heated first to 673 K for 7.2 ks (2 h) and then to 973 K for 7.2 ks (2 h) to prevent effervescent slopping by the CO₂ liberation. Then it was heated to the corresponding experimental temperature and the measurement was conducted.

2. Experimental results

(1) Activities of NaO_{0.5} (l) in the NaO_{0.5}-CO₂-PO_{2.5} system

Figure 5(a) shows the activity of NaO_{0.5} in the NaO_{0.5}-CO₂-PO_{2.5} system under various P_{CO₂} for P_{O₂}=0.02 MPa at 1523 K. The values at N=1 were calculated from the equilibrium relationship of the reaction,

$$\Delta G_{(4)}^\circ / \text{J} = 155685 - 63.85 \cdot T^{(14)} \quad (4)$$

where the activity of Na(CO₃)_{0.5} is equated to unity. The dot-dash-line corresponds to the solubility of Na₃PO₄ (s). The left side of the solubility line is the (solid-liquid) co-existing region, where a_{NaO_{0.5}} is constant for a fixed P_{CO₂}. The right side is the liquid region, where a_{NaO_{0.5}} increases with increasing N but tends to remain constant under constant P_{CO₂} for N=0.91~0.95. In both regions, the P_{CO₂} has a significant influence on a_{NaO_{0.5}}. In Fig. 5(b), the present results are compared with the experimental results on the binary system NaO_{0.5}-PO_{2.5}, reported by Yamaguchi *et al.*⁽¹⁵⁾ at 1523 K. A large change on the activity of NaO_{0.5} takes place at the composition of solid Na₃PO₄.

Figure 6 shows the effect of temperature on a_{NaO_{0.5}} in the NaO_{0.5}-CO₂-PO_{2.5} system for various slag composition at P_{CO₂}=0.01 MPa. The dashed line corresponds to the values calculated from the equilibrium relation of eq. (4) for a_{Na(CO₃)_{0.5}}=1. With increasing temperature, a_{NaO_{0.5}} increases.

(2) Activities of NaO_{0.5}(l) in the NaO_{0.5}-CO₂-SiO₂ system

Figure 7(a) shows the activity of NaO_{0.5} in the NaO_{0.5}-CO₂-SiO₂ system under various P_{CO₂} for P_{O₂}=0.02 MPa at 1523 K. The values at N=1 were calculated from the equilibrium relationship of reaction (4). Experiments were also conducted for N<0.90, but severe corrosion was observed on the solid electrolyte and the measurement was quit. The results reported by Yamaguchi *et al.*⁽¹²⁾, using β-alumina, are also plotted in the figure. P_{CO₂} has a great influence on a_{NaO_{0.5}} for N>0.67. Figure 7(b) shows the effect of the temperature on a_{NaO_{0.5}} for

Fig. 5 Composition dependence of the activity of NaO_{0.5} (l) at 1523 K (a) in the NaO_{0.5}-CO₂-PO_{2.5} system, and (b) in combination with the results reported by Yamaguchi *et al.*⁽¹⁵⁾ for the NaO_{0.5}-PO_{2.5} binary system.

Fig. 6 Effect of temperature on the activity of NaO_{0.5} (l) in the NaO_{0.5}-CO₂-PO_{2.5} system for $P_{\text{CO}_2} = 0.01$ MPa and $P_{\text{O}_2} = 0.02$ MPa.

$N = 0.92$. The dashed lines correspond to the values calculated from the equilibrium relation of eq. (4) for $a_{\text{Na}(\text{CO}_3)_{0.5}} = 1$. With increasing temperature, $a_{\text{NaO}_{0.5}}$ also increases.

V. CO₂ Solubility

After the EMF measurements, the CO₂ as well as the other components in the slag were chemically analyzed to determine the slag composition.

The solubility values of CO₂ for the respective slag system were plotted on the NaO_{0.5}-CO₂-PO_{2.5} (or SiO₂) ternary diagram, respectively.

Figure 8 shows the experimental results of the solubility of CO₂ in the NaO_{0.5}-PO_{2.5} system for $P_{\text{CO}_2} = 0.08$ MPa at 1523 K. The dashed line corresponds to the solubility

data reported by Kawahara *et al.*⁽¹⁶⁾ for $P_{\text{CO}_2} = 0.1$ MPa at 1423 K. The experimental points of the present work are distributed along the straight line connecting Na₂CO₃ with Na₃PO₄ (s). The above results indicate that the CO₂ solubility in NaO_{0.5}-PO_{2.5} melts is mainly determined by the following reaction:

Figure 9 shows the experimental results of the solubility of CO₂ in the NaO_{0.5}-SiO₂ system for $P_{\text{CO}_2} = 0.08$ MPa at 1523 K. The small point on the line connecting Na₂CO₃ with SiO₂ corresponds to the starting composition. The large black filled point corresponds to the melt composition after the equilibrium. The dashed line represents the solubility data reported by Kawahara *et al.*⁽¹⁶⁾ for $P_{\text{CO}_2} = 0.1$ MPa at 1423 K. As the results of the both experimental works locate in the triangular area Na₂CO₃-Na₂SiO₃-Na₄SiO₄, the CO₂ solubility in NaO_{0.5}-SiO₂ melts is mainly determined by a combination of the following reactions:

VI. Activities of PO_{2.5} (l) and SiO₂ (s)

1. Activity of PO_{2.5} (l)

Since the activity of Na₃PO₄ is always unity in the (solid-liquid) region, then the activity of PO_{2.5} can be calculated from the measured activities of NaO_{0.5} via the following equilibrium relation:

Fig. 7 (a) Composition dependence of the activity of NaO_{0.5} (l) at 1523 K, and (b) effect of temperature on the activity of NaO_{0.5} (l) at $N=0.92$ in the NaO_{0.5}-CO₂-SiO₂ system under various P_{CO_2} for $P_{\text{O}_2}=0.02$ MPa.

Fig. 8 Solubility of CO₂ in NaO_{0.5}-PO_{2.5} melts for $P_{\text{CO}_2}=0.08$ MPa at 1523 K.

Fig. 9 Solubility of CO₂ in NaO_{0.5}-SiO₂ melts for $P_{\text{CO}_2}=0.08$ MPa at 1523 K.

$$a_{\text{PO}_{2.5}} = \frac{a_{\text{Na}_3\text{PO}_4}}{K_{(8)} \cdot a_{\text{NaO}_{0.5}}^3} = \frac{1}{K_{(8)} \cdot a_{\text{NaO}_{0.5}}^3} \quad (9)$$

where $K_{(8)}$ is the equilibrium constant of reaction (8).

The activity of PO_{2.5} in the liquid region was calculated from the activity of NaO_{0.5} by using the Gibbs-Duhem integration method. Under the condition of a constant P_{CO_2} , the Gibbs-Duhem relation for the NaO_{0.5}-CO₂-PO_{2.5} system is given as:

$$n_{\text{NaO}_{0.5}} d \ln a_{\text{NaO}_{0.5}} + n_{\text{PO}_{2.5}} d \ln a_{\text{PO}_{2.5}} = 0 \quad (10)$$

Substituting N into this equation and integrating gives:

$$(\ln a_{\text{PO}_{2.5}})_{N=N} = (\ln a_{\text{PO}_{2.5}})_{N=N_{\text{Sat.}}} - \int_{N=N_{\text{Sat.}}}^{N=N} \frac{N}{N-1} d \ln a_{\text{NaO}_{0.5}} \quad (11)$$

To calculate the activity of PO_{2.5}(l), the liquidus composition, $N_{\text{Sat.}}$, was used as the starting point for the integration.

The calculated activities of PO_{2.5}(l) at 1523 K are shown in Fig. 10(a). The black points correspond to the initial values of the integration. The activity of PO_{2.5} (l) keeps constant for a constant P_{CO_2} in the (solid-liquid)

Fig. 10 (a) Activity of PO_{2.5} in the NaO_{0.5}-CO₂-PO_{2.5} system, and (b) in combination with the estimated one based on data reported by Yamaguchi *et al.*⁽¹⁵⁾ for the NaO_{0.5}-PO_{2.5} binary system at 1523 K.

coexisting region. In the liquid region, with increasing N and decreasing P_{CO_2} , the activity of PO_{2.5} (l) decreases but remains constant for constant P_{CO_2} at $N=0.91 \sim 0.95$. The activity of PO_{2.5} in $N < 0.75$ is also calculated based on the activity of NaO_{0.5}, reported by Yamaguchi *et al.*⁽¹⁵⁾, which is shown in Fig. 10(b). The black point corresponds to the initial value of the integration. A large change on the activity of PO_{2.5} takes place at the composition of solid Na₃PO₄.

2. Activity of SiO₂ (s)

Combining the activities of NaO_{0.5} obtained in the present work with the ones reported by Yamaguchi *et al.*⁽¹²⁾, the activities of SiO₂ (s) were calculated by using the Gibbs-Duhem integration method as same as the activities of PO_{2.5} (l) in the liquid phase. The calculated activities of SiO₂ (s) at 1523 K are shown in Fig. 11. The dashed line corresponds to the calculated results based on the data of Yamaguchi *et al.*⁽¹²⁾. The black point corresponds to the liquidus composition⁽¹²⁾ used as the initial value of the integration. For $N > 0.667$, with increasing N and decreasing P_{CO_2} the activity of SiO₂ (s) decreases.

VII. Distribution Ratios of P and Si

The distribution ratios of P and Si between the sodium carbonate-based slag and molten copper can be estimated, based on the above mentioned method, as a function of partial pressures of oxygen and CO₂ and the slag composition N .

1. Distribution ratio of P

The distribution reaction of P between slag and molten copper can be represented as:

Fig. 11 Activity of SiO₂ in the NaO_{0.5}-CO₂-SiO₂ system at 1523 K.

and the distribution ratio can be written as:

$$L_P = \frac{(\%P)}{[\%P]} = \frac{K_{(12)} \cdot (n_T) \cdot f_P \cdot M_P}{\gamma_{\text{PO}_{2.5}}} \cdot p_{\text{O}_2}^{5/4} \quad (13)$$

where $K_{(12)}$, f_P , and M_P are the equilibrium constant of reaction (12), the Henrian activity coefficient of P in mass% scale and the atomic weight of P, respectively.

The distribution ratios were calculated by considering that the equilibrium content of P in molten copper is low enough to assume $f_P = 1$.

Figures 12 shows the dependence of the distribution ratio of P on the slag composition N at 1523 K for (a) $P_{\text{CO}_2} = 0.08$ and (b) 0.01 MPa. The distribution ratios present considerably large values and increase with increasing P_{O_2} and decreasing P_{CO_2} and have a maximum value at $N = 0.91$. Figure 13 shows the present results together with the estimated distribution ratios based on the data reported by Yamaguchi *et al.*⁽¹⁵⁾. Higher values

Fig. 12 Distribution ratio of P between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-PO}_{2.5}$ slag at 1523 K for (a) $P_{\text{CO}_2}=0.08$ MPa and (b) $P_{\text{CO}_2}=0.01$ MPa.

Fig. 13 Distribution ratio of P between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-PO}_{2.5}$ and $\text{NaO}_{0.5}\text{-PO}_{2.5}$ slag for $P_{\text{CO}_2}=0.01$ MPa at 1523 K.

Fig. 14 Distribution ratio of Si between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-SiO}_2$ slag for $P_{\text{O}_2}=0.1$ Pa at 1523 K.

are achieved for $N > 0.75$.

2. Distribution ratio of Si

The estimated distribution ratios of Si between $\text{NaO}_{0.5}\text{-CO}_2\text{-SiO}_2$ slag and molten copper are shown in Figs. 14 and 15. The thermodynamic data used in the calculations are tabulated in Table 1. The distribution ratios of Si show considerably large values and increase with decreasing P_{CO_2} and increasing P_{O_2} and have a maximum value at $N=0.87$.

VIII. Concluding Remarks

Thermodynamic properties of $\text{NaO}_{0.5}\text{-CO}_2\text{-XO}_{v/2}$ (X: P or Si, v : valence of X) slag have been investigated for the application of sodium carbonate slag to the elimination of P and Si from molten copper by conducting the following experiments at 1423 to 1523 K.

- (1) Solubility measurements of Na_3PO_4 (s) into

Na_2CO_3 melt under various partial pressures of CO_2 and oxygen. Neither P_{CO_2} nor P_{O_2} has an influence on the saturated composition of the slag.

Table 1 Thermodynamic data used in the calculations.

Reaction	$\Delta G^\circ / \text{J}$	Temperature / K	Reference
$\text{Si}(s) + \text{O}_2(g) = \text{SiO}_2(s)$	$-901640 + 171.46T$	298–1685	(14)
Activity coefficient			
$\log \gamma_{\text{O}}^\circ = -3999/T + 2.03$		1373–1673	(19) (20)
$\log \gamma_{\text{Si}(l)}^\circ = -3.6$		1523	(21)
Interaction parameter			
$\epsilon_{\text{O}}^\circ = -31929/T + 14.57$		1373–1673	(19) (20)
$\epsilon_{\text{O}}^{\text{Si}} = -62$		1523	(21)

Fig. 15 Distribution ratio of Si between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-SiO}_2$ slag for $P_{\text{CO}_2}=0.01\text{ MPa}$ at 1523 K.

(2) Electrochemical measurements of activity of $\text{NaO}_{0.5}$ in $\text{NaO}_{0.5}\text{-CO}_2\text{-XO}_{v/2}$ slag under various partial pressures of CO_2 . In both slag systems, the P_{CO_2} has a significant influence on the activity of $\text{NaO}_{0.5}$.

(3) Solubility measurements of CO_2 in the slags.

From the results obtained, the distribution ratios of P and Si between the slag and molten copper were estimated as a function of partial pressures of CO_2 and oxygen and the slag composition. The distribution ratios of both elements present considerably large values and increase with increasing oxygen partial pressure and decreasing partial pressure of CO_2 .

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