Thermodynamic Considerations for Elimination of Te and Se from Molten Copper by Using Na₂CO₃ Slag[†]

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In order to estimate the distribution ratios of Te and Se between sodium carbonate-based slag and molten copper, the following measurements have been conducted on the thermodynamic properties of the slags containing Te- or Se-oxide at 1423 to 1523 K.

(1) Electrochemical measurements of activity of NaO_{0.5} in NaO_{0.5}-CO₂-XO₂ slag (X: Te or Se) under various partial pressures of CO₂ over the composition range of $1 > N \geq 0.667$ ($N = n_{\text{Na}} / (n_{\text{Na}} + n_{\text{X}})$, n : the number of moles) by using β'' -alumina as a solid electrolyte.

(2) Distribution equilibrium measurements of X between the slag and molten copper, and

(3) Solubility measurements of CO₂ in the slags.

Finally, based on the results, the equilibrium distribution ratios of these elements between the slags and molten copper have been estimated as a function of partial pressures of CO₂ and oxygen and the slag composition at the temperatures of 1423 K and 1523 K. Higher distribution ratios for both elements are achieved under conditions of higher partial pressure of oxygen and lower partial pressure of CO₂.

Distribution experiments were also conducted for the slag of $N \cong 1$ in order to evaluate the effect of partial pressure of oxygen on the distribution ratios. The distribution ratios of Te and Se have two different dependences on the oxygen partial pressure. Under the relatively low oxygen partial pressure, the distribution ratios of both elements decrease with increasing oxygen partial pressure while, under the relatively high oxygen partial pressure the distribution ratios increase with increasing oxygen partial pressure. In both areas, higher distribution ratios are achieved under the condition of lower partial pressure of CO₂.

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I. Introduction

Considering the application of sodium carbonate slag to the production of high purity copper and the more effective refining of crude copper, the authors have been studying on the elimination of various impurities from molten copper by using sodium carbonate slags⁽¹⁾⁻⁽⁹⁾. In these studies it was demonstrated, based on thermodynamic considerations, that sodium carbonate is a suitable slag to remove As, Sb, Sn and Fe from molten copper.

Kojo *et al.*⁽¹⁰⁾ reported the equilibrium distribution ratios of Te and Se between molten copper and sodium carbonate slag at 1473 K for $P_{\text{CO}_2} = 0.1$ MPa. In their investigation, however, the effects of partial pressure of CO₂, slag composition and temperature on the distribution ratio were not evaluated.

The purpose of this research is to investigate the thermodynamic properties of sodium carbonate-based slags

containing Te- or Se-oxide and to estimate the equilibrium distribution ratios of these elements between the slags 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, X: Te or Se}.

II. Experimental Principle

In the case of oxidizing conditions, the distribution reaction of X between the slag and molten copper may be represented by:

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

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

where $K_{(1)}$ is the equilibrium constant of eq. (1), $[n_T]$ and (n_T) the molar amount of 100 g metal and slag, respectively, γ_i 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

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Fig. 1 Flow chart for calculating the distribution ratio.

$P^\circ/\text{Pa}=101325$).

In order to estimate the distribution ratio of Te or Se between molten copper and the sodium carbonate-based slag containing the oxide of Te or Se, the following measurements were conducted at the temperatures of 1423 to 1523 K:

(a) Electrochemical measurements of activity of NaO_{0.5} in NaO_{0.5}-CO₂-XO₂ slags under various partial pressures of CO₂,

(b) Activity measurements of XO₂ by slag/metal

equilibrium technique,

(c) Solubility measurements of CO₂ in the slags.

Figure 1 shows the flow chart to calculate the distribution ratio. Combination of the results of (a) and (b) enables us to calculate the activity of XO₂, from the activity of NaO_{0.5} by integrating the Gibbs-Duhem relation. As the value (n_T) can be determined by measuring the CO₂ solubility, the distribution ratios of X are finally estimated as a function of partial pressures of CO₂ and oxygen and the slag composition N .

III. Electrochemical Measurements of Activity of NaO_{0.5}

1. Experimental method

Activities of NaO_{0.5} in the molten slags were determined by the EMF method using a β'' -alumina (manufactured by NGK Spark Plug Co., Ltd.) as a solid electrolyte under various partial pressures of CO₂ at $P_{O_2}=0.02$ MPa within the temperature range of 1423 to 1523 K. The experimental procedure was almost the same as reported before by Fujisawa *et al.*⁽¹⁾ The electrochemical cell used can be represented as:

The activity of NaO_{0.5} in the sample melt can be evaluated by the following equation⁽¹⁾:

$$\log a_{\text{NaO}_{0.5}}(l) = \frac{-5039 \cdot E}{T} + \log a_{\text{NaO}_{0.5}}(l)^* - \frac{1}{4} \log \left(\frac{P_{O_2}^*}{P_{O_2}} \right) \quad (3)$$

where E is the electromotive force, T the absolute temperature, and the superscript, *, denotes the values for the reference melt. The activity of sodium oxide in the reference melt, $a_{\text{NaO}_{0.5}}^*$, was reported in a previous paper⁽⁵⁾.

2. Preparation of sample melts

(1) NaO_{0.5}-CO₂-TeO₂ system

Chemical reagent grade Na₂CO₃ and TeO₂, dried at rd. 443 K for more than 1.2 Ms (14 d), were mixed in an appropriate composition and charged into a Pt-crucible. The sample was heated first to 673 K for 3.6 ks (1 h), and to 973 K for 7.2 ks (2 h) in order to prevent effervescent slopping by the CO₂ liberation. Then it was heated to the corresponding experimental temperature and the measurement was conducted.

(2) NaO_{0.5}-CO₂-SeO₂ system

Due to the very high vapor pressure of SeO₂, chemical reagent grade Na₂CO₃ and Na₂SeO₃ were used for the preparation of the sample melts of this system. After

being dried for more than 1.2 Ms (14 d), they were mixed in a needed composition, charged in an alumina crucible, and heated to the experimental temperature in order to start the measurements.

3. Experimental results

(1) Activities of NaO_{0.5}(l) in the NaO_{0.5}-CO₂-TeO₂ system

Figure 2(a) shows the activity of NaO_{0.5} in the NaO_{0.5}-CO₂-TeO₂ system over the composition range of $1 > N \geq 0.667$ under various partial pressures of CO₂ for $P_{O_2}=0.02$ MPa at 1523 K. The values for $N=1$ were calculated from the equilibrium relationship of the reaction,

$$\text{Na}(\text{CO}_3)_{0.5}(l) = \text{NaO}_{0.5}(l) + (1/2)\text{CO}_2(g): \Delta G_{(4)}^\circ/\text{J} = 155685 - 63.85T^{(12)} \quad (4)$$

where the activity of Na(CO₃)_{0.5} is equated to unity. The partial pressure of CO₂ has a significant influence on the activity of NaO_{0.5}. For a constant partial pressure of CO₂, the activity of NaO_{0.5} gradually decreases as N approaches 0.667. EMF measurement was also conducted at $N=0.571$, but the electromotive force did not reach a constant value and the run was stopped. By the chemical analyses, it was found that N was higher than the starting composition. This increment of the slag composition can be attributed to the relatively high vapor pressure of

Fig. 2 (a) Composition dependence of the activity of $\text{NaO}_{0.5}(l)$ at 1523 K, and (b) effect of temperature on the activity of $\text{NaO}_{0.5}(l)$ for $P_{\text{CO}_2} = 0.01$ MPa in $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ melts under $P_{\text{O}_2} = 0.02$ MPa.

$\text{TeO}_2^{(11)(12)}$ which enhances the vaporization losses of TeO_2 .

Figure 2(b) shows the effect of temperature on the activity of $\text{NaO}_{0.5}(l)$ in the $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ system for various slag compositions at $P_{\text{CO}_2} = 0.01$ MPa. The dashed line corresponds 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.

(2) Activities of $\text{NaO}_{0.5}(l)$ in the $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ system

The activity of $\text{NaO}_{0.5}$ in the $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ system at 1523 K is shown in Fig. 3(a). For a constant partial pressure of CO_2 , the activity of $\text{NaO}_{0.5}$ gradually decreases as N approaches to 0.824. Experiments were also conducted for $N = 0.667$ and 0.788 which showed similar behavior as that observed for the Te-oxide con-

taining system at $N = 0.571$. Therefore the runs were also stopped. By the chemical analyses it was found that N was higher than the starting composition. This increment of the slag composition can be also attributed to the relatively high vapor pressure of $\text{SeO}_2^{(11)(12)}$.

Figure 3(b) shows the temperature dependence of the $a_{\text{NaO}_{0.5}}$ for $P_{\text{CO}_2} = 0.01$ MPa.

IV. CO_2 Solubility

After the EMF measurements, the CO_2 as well as other components in the melt were chemically analyzed in order to determine the slag composition. The Na and Te (or Se) contents were analyzed by ICP spectrometric and atomic absorption spectrometric methods. The CO_2 contents in the samples were analyzed by B_2O_3 fusion

Fig. 3 (a) Composition dependence of the activity of $\text{NaO}_{0.5}(l)$ at 1523 K, and (b) effect of temperature on the activity of $\text{NaO}_{0.5}(l)$ for $P_{\text{CO}_2} = 0.01$ MPa in $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ melts under $P_{\text{O}_2} = 0.02$ MPa.

coulometric method⁽⁴⁾⁽¹³⁾.

The solubility values of CO₂ on the respective slag system were plotted on the NaO_{0.5}-CO₂-TeO₂ (or SeO₂) ternary diagram as shown in Figs. 4 and 5, respectively, for $P_{\text{CO}_2}=0.08$ MPa at 1523 K. The small points on the line connecting Na₂CO₃ with TeO₂ correspond to the starting compositions. The large black filled points correspond to the melt compositions after the experiments. The experimental points are distributed along a straight line connecting Na₂CO₃ with Na₂TeO₃ or Na₂SeO₃, respectively. These results indicate that the CO₂ solubility in NaO_{0.5}-TeO₂ melts is determined by the following reaction:

Fig. 4 Solubility of CO₂ in NaO_{0.5}-TeO₂ melts for $P_{\text{CO}_2}=0.08$ MPa at 1523 K.

Fig. 5 Solubility of CO₂ in NaO_{0.5}-SeO₂ melts for $P_{\text{CO}_2}=0.08$ MPa at 1523 K.

and in NaO_{0.5}-SeO₂ melts:

V. Activities of TeO₂(l) and SeO₂(s)

The activities of TeO₂(l) and SeO₂(s) in NaO_{0.5}-CO₂-XO₂ melts can be calculated from the activity of NaO_{0.5}(l) by using the Gibbs-Duhem relation. Under the condition of a constant P_{CO_2} , the Gibbs-Duhem relation for the NaO_{0.5}-CO₂-XO₂ system is given as⁽¹⁾:

$$N d \ln a_{\text{NaO}_{0.5}} + (1-N) d \ln a_{\text{XO}_2} = 0 \quad (7)$$

and the integration gives

$$(\ln a_{\text{XO}_2})_{N=N} - (\ln a_{\text{XO}_2})_{N=N_1} = \int_{N=N_1}^{N=N} \frac{N}{1-N} d \ln a_{\text{NaO}_{0.5}}. \quad (8)$$

In order to calculate the activity of XO₂, the initial values for the integration of eq. (8) were needed. To determine the initial values, distribution equilibrium experiments for Te (or Se) were conducted by equilibrating the respective slag with molten copper. The experimental procedure was almost the same as reported in the previous paper⁽²⁾.

From the equilibrium relationship of eq. (1), the activity of XO₂ (l or s) can be expressed in the following way:

$$a_{\text{XO}_2} = K_{(1)} \cdot \gamma_{\text{X}} \cdot X_{\text{X}} \cdot p_{\text{O}_2} \quad (9)$$

where X_{X} is the molar fraction of Te or Se in molten copper. The Raoultian activity coefficients of Te and Se in molten copper, γ_{X} , were evaluated by using the regular solution approximation from the results reported by Hino *et al.*⁽¹⁴⁾ on the activities of Te and Se in the binary systems Cu-Te at 1423 and 1473 K and Cu-Se at 1473 K.

The activity coefficient of the dissolved oxygen in molten copper, γ_{O} , was defined as follows:

$$p_{\text{O}_2}^{1/2} = \left(\frac{P_{\text{O}_2}}{P^0} \right)^{1/2} = \gamma_{\text{O}} \cdot X_{\text{O}} \quad (10)$$

where P^0 is the standard state (101325 Pa) and X_{O} is the molar fraction of the dissolved oxygen in molten copper. The oxygen partial pressure was calculated from the chemically analyzed oxygen and Te (or Se) contents in molten copper by using eq. (10). The thermodynamic data used in the calculations were tabulated in Table 1. Tables 2 and 3 show the experimental results obtained from the distribution experiments conducted for the determination of the initial values for the integration of eq. (8), for Te and Se, respectively. The arithmetic mean of the calculated oxides activities, of each oxide, was used as the initial value of the integration. The CuO_{0.5} content in the slag is considered to be low enough to neglect the effect on the a_{XO_2} .

The calculated activities of TeO₂(l) and SeO₂(s) for 1523 K are shown in Figs. 6 and 7, respectively, together with the experimentally obtained points. The black points correspond to experiments performed to deter-

Table 1 Thermodynamic data used in the calculations.

Reaction	$\Delta G^0/\text{J}$	Temperature, T/K	Ref. No.
$\text{Te}(l) + \text{O}_2(g) = \text{TeO}_2(l)$	$-315470 + 176.15T$	1006–1267	(11)
$\text{Se}(l) + \text{O}_2(g) = \text{SeO}_2(s)$	$-229870 + 189.74T$	493–601	(11)
$1/2\text{O}_2(g)$ =O (mass% in Cu)	$-76576.6 + 12.01T$	1373–1673	(16)(17)
Activity coefficient			
$\log \gamma_{\text{O}}^{\circ}$	$-3999/T + 2.03$	1373–1673	(16)(17)
$\gamma_{\text{Te}}^{\circ}$	$\begin{cases} 2.9 \times 10^{-2} \\ 3.3 \times 10^{-2} \end{cases}$	$\begin{cases} 1423 \\ 1473 \end{cases}$	$\begin{cases} (14) \\ (14) \end{cases}$
$\gamma_{\text{Se}}^{\circ}$	2.0×10^{-3}	1473	(14)
Interaction parameter			
$\varepsilon_{\text{O}}^{\circ}$	$-31929/T + 14.157$	1373–1673	(16)(17)
$\varepsilon_{\text{O}}^{\text{Te}}$	$-115370/T + 67.7$	1373–1473	(18)
$\varepsilon_{\text{O}}^{\text{Se}}$	$-52583/T + 24.20$	1373–1473	(19)(20)

Table 2 Activity of $\text{TeO}_2(l)$ in $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ melts.

P_{CO_2} /MPa	Molar fraction				N	$X_{\text{Te}} \times 10^2$ (in Cu)	P_{O_2}/Pa	$\log a_{\text{TeO}_2}$
	$\text{NaO}_{0.5}$	TeO_2	CO_2	$\text{CuO}_{0.5}$				
0.08	0.654	0.029	0.305	0.012	0.958	2.74	0.376	-6.94
0.08	0.655	0.033	0.299	0.013	0.953	2.47	0.415	-6.92
0.08	0.668	0.032	0.296	0.003	0.953	3.38	0.427	-6.80
0.08	0.649	0.044	0.294	0.010	0.937	2.04	0.641	-6.79
0.01	0.664	0.040	0.287	0.008	0.943	0.79	0.208	-7.56
0.01	0.653	0.040	0.293	0.014	0.942	0.46	0.300	-7.59
0.01	0.654	0.041	0.291	0.014	0.940	0.42	0.362	-7.54
0.01	0.659	0.043	0.284	0.014	0.939	0.37	0.413	-7.53

Table 3 Activity of $\text{SeO}_2(s)$ in $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ melts.

P_{CO_2} /MPa	Molar fraction				N	$X_{\text{Se}} \times 10^3$ (in Cu)	P_{O_2}/Pa	$\log a_{\text{SeO}_2}$
	$\text{NaO}_{0.5}$	SeO_2	CO_2	$\text{CuO}_{0.5}$				
0.01	0.644	0.009	0.318	0.028	0.986	3.9	0.543	-12.32
0.01	0.647	0.009	0.312	0.025	0.986	4.9	0.586	-12.18
0.01	0.640	0.010	0.315	0.035	0.985	4.1	0.523	-12.30
0.01	0.649	0.010	0.311	0.030	0.984	5.1	0.531	-12.31
0.01	0.647	0.011	0.313	0.029	0.983	6.0	0.440	-12.22
0.01	0.642	0.011	0.315	0.032	0.983	5.1	0.418	-12.31
0.01	0.648	0.012	0.311	0.029	0.981	6.7	0.393	-12.22
0.01	0.647	0.013	0.312	0.028	0.980	7.3	0.389	-12.18
0.01	0.640	0.013	0.312	0.035	0.980	7.0	0.373	-12.22

mine the initial values for the Gibbs-Duhem Integration. With increasing N and decreasing CO_2 partial pressure, the activity of TeO_2 decreases. a_{SeO_2} was calculated only for $P_{\text{CO}_2}=0.01$ MPa, because of the lack of values for γ_{Se} in non-dilute compositions of the Cu-Se alloy.

VI. Distribution Ratios of Te and Se between Na_2CO_3 -based Slag and Molten Copper

The distribution ratios of Te and Se between sodium carbonate-based slags and molten copper can be esti-

Fig. 6 Activity of $\text{TeO}_2(l)$ in the $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ system at 1523 K. Fig. 7 Activity of $\text{SeO}_2(s)$ in the $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ system at 1523 K.

mated based on the above mentioned method as a function of partial pressures of oxygen and CO_2 and the slag composition N .

1. Distribution ratio of Te

The estimated distribution ratios of Te between $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ slag and molten copper for $P_{\text{CO}_2}=0.08$ and 0.01 MPa at 1523 K together with the experimental results, are shown in Fig. 8. The discontinuity of the lines corresponds to a miscibility gap in the Cu-Te binary system⁽¹⁵⁾. The Te distribution ratio increases with increasing partial pressure of oxygen and decreasing partial pressure of CO_2 and has the highest values for N close to unity.

Using the calculated activities of TeO_2 , it is also possible to estimate the content of Te in molten copper

Fig. 8 Distribution ratio of Te between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ slag for (a) $P_{\text{CO}_2} = 0.08 \text{ MPa}$ and (b) 0.01 MPa at 1523 K.

Fig. 9 Te content in molten copper equilibrated with $\text{NaO}_{0.5}\text{-CO}_2\text{-TeO}_2$ slag for (a) $P_{\text{CO}_2} = 0.08$ and (b) 0.01 MPa at 1523 K.

equilibrated with the slag. Figure 9 shows the equilibrium Te content in molten copper for $P_{\text{CO}_2} = 0.08$ and 0.01 MPa at 1523 K, together with the experimentally obtained results. The lower Te content in molten copper is achieved at lower CO_2 partial pressure, higher oxygen partial pressure and the N value close to unity.

2. Distribution ratio of Se

The estimated distribution ratios of Se between $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ slag and molten copper for $P_{\text{CO}_2} = 0.01 \text{ MPa}$ at 1523 K are shown in Fig. 10, together with the experimental results. The Se distribution ratio increases with increasing partial pressure of oxygen and has a maximum value at $N = 0.94$.

The estimated Se content in molten copper equilibrated with the slag for $P_{\text{CO}_2} = 0.01 \text{ MPa}$ at 1523 K is shown in Fig. 11 as a function of slag composition, together with the experimentally obtained results. The lower content of Se in molten copper is achieved under higher oxygen partial pressure and N values close to unity.

VII. Distribution Equilibrium Experiments for $N \cong 1$

Distribution experiments were also conducted for the slag of $N \cong 1$ in order to evaluate the effect of partial pressure of oxygen on the distribution ratios of Te and Se. Figures 12 and 13 show the relationships between the dis-

Fig. 10 Distribution ratio of Se between molten copper and $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ slag for $P_{\text{CO}_2}=0.01$ MPa at 1523 K.

Fig. 11 Se content in molten copper equilibrated with $\text{NaO}_{0.5}\text{-CO}_2\text{-SeO}_2$ slag for $P_{\text{CO}_2}=0.01$ MPa at 1523 K.

tribution ratio of Te (and Se) and oxygen partial pressure for $N \approx 1$. The distribution ratio has two different dependences on the oxygen partial pressure. Under the relatively low oxygen partial pressure, the distribution ratio of both elements decreases with increasing oxygen partial pressure (Reduction side). Under the relatively high oxygen partial pressure, on the other hand, the distribution ratio increases with increasing oxygen partial pressure (Oxidation side).

On the oxidation side, the distribution reaction of Te (or Se) between Na_2CO_3 slag and molten copper may be expressed in the following way, considering the molecular form of X in the slag:

For this reaction, the distribution ratio of X can be expressed as,

pressed as,

$$\log L_X = \log \frac{K_{(11)} \cdot (n_T) \cdot \gamma_X}{[n_T] \cdot \gamma_{\text{Na}_2\text{XO}_3}} + 2 \log a_{\text{Na}(\text{CO}_3)_{0.5}} + \log p_{\text{O}_2} - \log p_{\text{CO}_2}. \quad (12)$$

At $N \approx 1$, the sodium carbonate activity can be equated to unity, and for a fixed temperature and partial pressure of CO_2 , the above equation can be reduced to:

$$\log L_X = \log p_{\text{O}_2} + \text{const.} \quad (13)$$

The experimental results fit in with expectations based on eq. (13), showing a slope of +1. This implies that Te and Se have a valence of +4 in the slags in oxidizing conditions; $\log (P_{\text{O}_2}/\text{Pa}) > -1.5$ and -0.5 , respectively, at 1523 K.

On the reduction side, X may be eliminated as a sodium compound (Na_2X), then the distribution reaction of X can be expressed as,

and the distribution ratio becomes,

$$\log L_X = \log \frac{K_{(14)} \cdot (n_T) \cdot \gamma_X}{[n_T] \cdot \gamma_{\text{Na}_2\text{X}}} + 2 \log a_{\text{Na}(\text{CO}_3)_{0.5}} - (1/2) \log p_{\text{O}_2} - \log p_{\text{CO}_2}. \quad (15)$$

As the sodium carbonate activity can be also equated to unity at $N \approx 1$, the above equation can be reduced to:

$$\log L_X = -(1/2) \log p_{\text{O}_2} + \text{const.} \quad (16)$$

for a fixed temperature and partial pressure of CO_2 .

The experimental results fit in with the above equation, indicating the formation of Na_2X in the slag.

Figures 12 and 13 also show the effect of partial pressure of CO_2 on the distribution ratio of Te and Se. With decreasing partial pressure of CO_2 , the distribution ratios of Te and Se increase in both sides. The results obtained

Fig. 12 Effect of partial pressure of oxygen on the distribution ratio of Te for $N \approx 1$.

Fig. 13 Effect of partial pressure of oxygen on the distribution ratio of Se for $N \cong 1$.

by Kojo *et al.*⁽¹⁰⁾ are also plotted in these figures. Their data are consistent with the present values.

VIII. Concluding Remarks

In order to estimate the distribution ratio of Te or Se between molten copper and the sodium carbonate-based slag containing the oxide of Te or Se, the following measurements were conducted at the temperatures of 1423 to 1523 K:

(a) Electrochemical measurements of activity of NaO_{0.5} in NaO_{0.5}-CO₂-XO₂ (X: Te or Se) slags under various partial pressures of CO₂,

(b) Activity measurements of XO₂ by slag/metal equilibrium technique,

(c) Solubility measurements of CO₂ in the slags.

From the results obtained, the distribution ratios of Te and Se between the slags and molten copper were estimated. The distribution ratio of Te increases with increasing partial pressure of oxygen and decreasing partial pressure of CO₂ and has the highest values for N close to 1 ($N = n_{\text{Na}} / (n_{\text{Na}} + n_{\text{X}})$, n : the number of moles). The distribution ratio of Se increases with increasing partial pressure of oxygen and has a maximum value at $N = 0.94$.

Distribution experiments were also conducted for $N \cong 1$ in order to evaluate the effect of partial pressure of oxygen on the distribution ratios of Te and Se. The relationship between the distribution ratio of X and the oxygen partial pressure has two different dependences. Under the relatively high oxygen partial pressure (oxida-

tion side) Te and Se react with Na₂CO₃ as,

while under the relatively low oxygen partial pressure (reduction side) Te and Se tend to form an intermetallic compound with sodium in the slag as,

In both areas, higher values of distribution ratios are achieved under condition of lower partial pressures of CO₂.

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