Effect of Partial Pressure of CO₂ on the Distribution Ratios of Sb and Cu between Na₂CO₃ Slag and Molten Copper at 1523 K

By Chikabumi Yamauchi*, Toshiharu Fujisawa*, Shigeaki Goto**
and Hiroyuki Fukuyama**

The distribution ratios of Sb and Cu $\{L_X^{S/Cu} = (\text{mass\% of X in slag}) / [\text{mass\% of X in copper}], X = \text{Sb or Cu}\}$ between Na₂CO₃ slag and molten copper have been determined for various partial pressures of CO₂ at 1523 K as a function of the oxygen partial pressure calculated from the oxygen content in molten copper by using appropriate thermodynamic data. The distribution ratios of Sb and Cu are both affected strongly by the partial pressure of CO₂. This effect for Sb can be evaluated by the equation

$$\log L_{\text{Sb}}^{S/Cu} = \log Q + 3 \log a_{\text{NaO}_{0.5}} + (5/4) \log P_{\text{O}_2} \quad (Q: \text{a constant determinable experimentally})$$

using activity data of NaO_{0.5} in Na₂O–CO₂–Sb₂O₃ melt under various partial pressures of CO₂ which have been measured electrochemically by the aid of β'' -alumina as a solid electrolyte. The distribution ratio of Cu increases with decreasing partial pressure of CO₂. This implies that the activity coefficient of CuO_{0.5} in Na₂CO₃ slag is lowered rapidly as the partial pressure of CO₂ is diminished.

Furthermore, a relation has been discussed between the oxygen partial pressure calculated from the oxygen content in the bulk of molten copper which can be determined experimentally and that at the slag-metal interface which regulates essentially the distribution ratios of Sb and Cu.

(Received December 21, 1988)

Keywords: distribution ratio, sodium carbonate slag, sodium carbonate flux, antimony, copper, oxygen partial pressure, partial pressure of carbon dioxide gas

I. Introduction

There has been a growing emphasis on using special slags in the fire refining of crude copper due to the diminishing availability of pure copper ore. From this viewpoint, the authors have reported in the previous paper⁽¹⁾⁽²⁾ on the distribution ratio of Sb between Na₂CO₃ slag and molten copper in argon atmosphere of 0.1 MPa with respect to temperature, oxygen partial pressure, and slag composition. However, considering the three phases equilibrium among gas, metal, and slag, the number of degrees of freedom of this system is equal to 4. Thus, this system can be thermodynamically fixed by specifying, *e.g.*, the partial pressure of CO₂ in addition to the temperature, the oxygen partial pressure, and the slag composition.

For this reason, the purpose of this work is to experimentally evaluate the effect of the partial pressure of CO₂ on the distribution ratios of Sb and Cu between Na₂CO₃ slag and molten copper at 1523 K.

II. Experimental

The experimental apparatus is shown schematically in Fig. 1. Gas mixtures of CO–CO₂ with three kinds of mixing ratios were diluted with argon gas to permit various partial pressures of CO₂ at a constant oxygen partial pressure. In this case, mass flow controllers which enabled us to measure a minimum flow rate of $1.67 \times 10^{-8} \text{ Nm}^3 \cdot \text{s}^{-1}$ ($1 \text{ mL} \cdot \text{min}^{-1}$) were used. An alumina crucible of 18 mm i.d. and 100 mm height was charged with about 20 g of high purity oxygen free copper and prescribed amounts of 50% Cu–50% Sb alloy, and Cu₂O, if necessary, and heated to 1523 K in a stream of the Ar–CO–CO₂ gas mixture described above in a SiC resistance furnace.

* Department of Metallurgy, Faculty of Engineering, Nagoya University, Nagoya 464, Japan.

** Graduate Student, Nagoya University, Nagoya.

Fig. 1 Experimental apparatus.

Then, about 5 g of Na_2CO_3 slag was charged which had been dried, melted, and solidified in advance⁽¹⁾⁽²⁾. After the attainment of temperature to 1523 K again, one end of an alumina gas blowing tube of 1 mm i.d. was dipped into the copper melt, into which the Ar-CO-CO₂ gas mixture was blown at a flow rate of $8.33 \times 10^{-7} \text{ Nm}^3 \cdot \text{s}^{-1}$ over a constant period of time. After that, the gas blowing tube was withdrawn from the melt, which was then settled for a period of $1.8 \times 10^3 \text{ s}$ to allow separation of copper droplets from the slag phase. In the previous work⁽¹⁾⁽²⁾ sampling was made by employing a silica sampling tube for molten copper and dipping a stainless steel rod for liquid slag. It was, however, sometimes difficult to take sound samples. Therefore, in the present work, the melt was taken together with the crucible out of the furnace and quenched rapidly by jetting helium gas. For this reason, fine crucibles of 18 mm i.d. were used[†].

Oxygen contents in the quenched copper samples were determined by the argon fusion automatic coulometric method. The usual AAS techniques were employed for the analysis of Sb in the quenched slag samples.

[†] No segregation was recognized by analyzing antimony and oxygen of eight samples taken from 8 different parts of the quenched copper.

However, for the determination of antimony contents in the quenched copper samples the hydride-AAS techniques had to be applied because of their extremely low levels.

III. Experimental Results

The variations with time of the oxygen partial pressure calculated from oxygen content in molten copper and the distribution ratios of Sb and Cu $L_X^{S/\text{Cu}} \{L_X^{S/\text{Cu}} = (\text{mass\% of X in slag}) / [\text{mass\% of X in molten copper}], X = \text{Sb, or Cu}\}$ were first investigated by using an Ar-CO-CO₂ gas mixture with the partial pressures of CO₂ and O₂ of 0.0028 MPa and $4.30 \times 10^{-3} \text{ Pa}$, respectively, both of which were the lowest ones used in this study. The results obtained are shown in Fig. 2. The dash-dot-dash and dash-double dots-dash lines represent, respectively, the partial pressure of oxygen ($4.30 \times 10^{-3} \text{ Pa}$) in the gas mixture before blown into molten copper and that in the Na_2CO_3 slag calculated under the assumption that Na_2O dissociates stoichiometrically according to the reaction $\text{Na}_2\text{O(l)} = 2\text{Na(g)} + (1/2)\text{O}_2\text{(g)}$. The closed circles, squares, and triangles and open circles at the zero time represent the initial oxygen partial pressures calculated from the oxygen contents in molten copper before charging Na_2CO_3 slag. As is obvious from the figure, the oxygen partial pressures in copper melt reach in 28.8 ks at the latest a steady state value which lies between the oxygen partial pressures in the gas and slag phases, whether the initial oxygen partial pressures in copper melt are higher (●, ■ and ▲) than that in the gas phase or lower (○). Especially in the case of ● and ■ where the initial oxygen contents were higher than the oxygen contents which were required for Sb to entirely transfer from molten copper to Na_2CO_3 slag according to the reaction $2\text{Sb} + 5\text{O} = \text{Sb}_2\text{O}_5$, the steady state value was already reached in 7.2 ks. In this case, the distribution ratios of Sb and Cu reach also in 7.2 ks at the latest the respective constant values. Therefore, in the following experiments, a period of time of 14.4 ks was taken as the reaction time for the same experimental conditions as those in the case of ● and ■. For the reason mentioned later the ox-

Fig. 2 Change with time of P_{O_2} in molten copper and of distribution ratios of Sb and Cu between Na₂CO₃ slag and molten copper under partial pressures of CO₂ and O₂ of 0.0028 MPa and 4.3×10^{-3} Pa, respectively, in gas phase at 1523 K.

xygen partial pressure affecting the distribution ratios of Sb and Cu was calculated from oxygen content in copper melt in this study.

The distribution ratios of Sb obtained for the partial pressures of CO₂ ranging from 0.0028 to 0.095 MPa are plotted against $\log P_{O_2}$ in Fig. 3. The solid lines represent the linear relationships between $\log L_{Sb}^{S/Cu}$ and $\log P_{O_2}$ determined by the method of least squares for the respective partial pressures of CO₂. From this figure it is evident that the distribution ratio of Sb depends strongly on the partial pressure of CO₂. In Fig. 3, the results obtained in the argon atmosphere of 0.1 MPa by the authors⁽¹⁾⁽²⁾ and by Yazawa *et al.*⁽³⁾⁽⁴⁾, respectively, and those in CO₂ atmosphere of 0.1 MPa by Kojo⁽⁵⁾ are also shown in comparison

Fig. 3 Distribution ratio of Sb between Na₂CO₃ slag and molten copper under various partial pressures of CO₂ as a function of $\log P_{O_2}$ at 1523 K.

with the results obtained in the present work. The distribution ratio of Sb obtained in argon atmosphere of 0.1 MPa by the authors is by chance in good agreement with that obtained in an atmosphere containing a partial pressure of CO₂ of 0.0028 MPa in the present work, whereas the results obtained by Yazawa *et al.* are rather close to those obtained in an atmosphere containing a partial pressure of CO₂ of 0.095 MPa. The results obtained in the CO₂ atmosphere of 0.1 MPa by Kojo agree well with those obtained under the partial pressure of CO₂ of 0.095 MPa in the present work within experimental error. From the above-mentioned fact that the value of $L_{Sb}^{S/Cu}$ obtained in the atmosphere of Ar of 0.1 MPa by the authors is in good agreement with that obtained in the atmosphere containing the partial pressure of CO₂ of 0.0028 MPa in the present work, it may be concluded that even in the case of using the argon atmosphere of 0.1 MPa the partial pressure of CO₂ at the slag-metal interface reaches *ca.* 0.003 MPa at 1523 K due to the thermal decomposition of Na₂CO₃ slag. By the way, the authors have measured electrochemically the activity of NaO_{0.5} in Na₂O-Sb₂O₅ melt under an atmosphere of Ar(0.08 MPa)+O₂(0.02 MPa) at 1523 K⁽⁶⁾⁽⁷⁾. From the results obtained, the value of $\log a_{NaO_{0.5}}$ for the slag composition $[N = n_{Na_2O} / (n_{Na_2O} + n_{Sb_2O_5}) = 0.996]$ as mentioned later, n : number of

moles] can be calculated to be -0.833 . Substituting this value in eq. (2) which represents the equilibrium relationship of the reaction (1) where $a_{\text{Na}(\text{CO}_3)_{0.5}}$ is equated to unity

$$\log P_{\text{CO}_2} = -16261/T + 6.669 - 2 \log a_{\text{NaO}_{0.5}} \quad (2)$$

gives 0.00046 MPa to the partial pressure of CO_2 , the value of which is about one-sixth of 0.0028 MPa. The difference between them may be attributed to the fact that, when the atmosphere containing oxygen gas is used, the thermal decomposition of Na_2CO_3 due to the reaction $\text{Na}_2\text{CO}_3(\text{l}) \rightarrow 2\text{Na}(\text{g}) + \text{CO}_2(\text{g}) + (1/2)\text{O}_2(\text{g})$ is suppressed much more strongly than in the case of pure argon. It must be, therefore, kept in mind that, even if an atmosphere without CO_2 gas is used, the atmosphere, particularly adjacent to Na_2CO_3

melt, has a partial pressure of CO_2 depending on its oxygen partial pressure, which is reflected directly on the distribution ratio of Sb.

Figure 4 shows the distribution ratio of Cu, $L_{\text{Cu}}^{\text{S/Cu}}$, between Na_2CO_3 slag and molten copper under various partial pressures of CO_2 at 1523 K. The vertical axis can be also regarded as the logarithm of [(mass% of Cu in slag)/100], because the copper content in molten copper is *ca.* 100%. The solubility of copper in Na_2CO_3 slag increases as the partial pressure of CO_2 decreases and reaches around 10% for the partial pressure of CO_2 of 0.0028 MPa. This value is comparable to the solubility⁽⁷⁾⁽⁸⁾ ($\times$ in Fig. 4) of copper for a slag with a composition of $N=0.75$ under the partial pressure of CO_2 of 0.095 MPa at 1523 K. In order to examine the dependence of the solubility of copper on the partial pressure of CO_2 , the activity coefficient of $\text{CuO}_{0.5}$, $\gamma_{\text{CuO}_{0.5}}$, in Na_2CO_3 slag was calculated as follows:

$$\Delta G_3^\circ/J = -58800 + 19.55 T^{(9)} \quad (4)$$

This gives 9.88 to the equilibrium constant of the reaction (3) at 1523 K. Therefore, by taking the activity of Cu in molten copper as approximately unity in the equilibrium relationship of the reaction (3), the following equation can be obtained,

$$\gamma_{\text{CuO}_{0.5}} = \frac{9.88 \cdot P_{\text{O}_2}^{1/4}}{X_{\text{CuO}_{0.5}}} \quad (5)$$

where $X_{\text{CuO}_{0.5}}$ represents the molar fraction of $\text{CuO}_{0.5}$ in Na_2CO_3 slag, which is calculated here approximately on the assumption that the slag consists of Na_2CO_3 and $\text{CuO}_{0.5}$ only, because of the low level of Sb. Figure 5 shows the dependence of $\gamma_{\text{CuO}_{0.5}}$ calculated in this manner on P_{CO_2} . The vertical line put on each plot is given to show the extent of the error. The value of $\gamma_{\text{CuO}_{0.5}}$ is always larger than unity and falls off strongly with decreasing the partial pressure of CO_2 . This implies that the Na_2CO_3 - Cu_2O melt approaches an ideal solution as the partial pressure of CO_2 decreases. The value of $\gamma_{\text{CuO}_{0.5}}$ for the partial pressure of CO_2 of 0.095 MPa agrees with that obtained in the CO_2 atmosphere of 0.1 MPa at 1473 K by Kojo

Fig. 4 Distribution ratio of Cu between sodium oxide-base slag and molten copper under various partial pressures of CO_2 at 1523 K.

	N	$P_{\text{CO}_2}/\text{MPa}$
■	0.996	0.095
□	0.996	0.03
●	0.996	0.01
△	0.996	0.0028
×	0.75	0.095

Fig. 5 Effect of partial pressure of CO₂ on $\gamma_{\text{CuO}_{0.5}}$ in Na₂CO₃ slag at 1523 K.

et al.⁽¹⁰⁾ within the limits of experimental error.

In Fig. 4, furthermore, the distribution ratios of Cu obtained in the argon atmosphere of 0.1 MPa at 1523 K by Yazawa *et al.*⁽³⁾⁽⁴⁾ and in the CO₂ atmosphere of 0.1 MPa at the same temperature by Kojo⁽⁵⁾ are shown by the dash-dot-dash line and the dash-double dots-dash line, respectively. In spite of the different atmospheres, both are of the same order of magnitude and close to the values obtained under the partial pressure of CO₂ of 0.095 MPa in this work. As shown in Fig. 3, the value of $L_{\text{Sb}}^{\text{S/Cu}}$ obtained in the argon atmosphere of 0.1 MPa by Yazawa *et al.*⁽³⁾⁽⁴⁾ was also in the neighborhood of that for the partial pressure of CO₂ of 0.095 MPa in the present work. If, in the work of Yazawa *et al.*, the partial pressure of CO₂ was in the vicinity of 0.1 MPa for some reason, their distribution ratio of Cu can be understood. However, the reason is not clear yet. By the way, a plot of $\log L_{\text{Cu}}^{\text{S/Cu}}$ against $\log P_{\text{O}_2}$ for each partial pressure of CO₂ gives a straight line with a slope somewhat larger than that corresponding to CuO_{0.5}. However, the range of the oxygen partial

pressures used is too narrow to discuss this matter in detail.

IV. Discussion

1. Evaluation of the effect of the partial pressure of CO₂ on the distribution ratio of Sb

A theoretical expression for the distribution ratio of Sb between Na₂CO₃ slag and molten copper may be given by⁽¹⁾⁽²⁾

$$L_{\text{Sb}}^{\text{S/Cu}} = \frac{(\% \text{Sb})}{[\% \text{Sb}]} = \frac{K_7 \cdot M_{\text{Cu}} \cdot n_T \cdot \gamma_{\text{Sb}}}{100 \cdot \gamma_{\text{Na}_3\text{SbO}_4}} \cdot a_{\text{NaO}_{0.5}}^3 \cdot P_{\text{O}_2}^{5/4} \quad (6)$$

by taking into account the equilibrium constant, K_7 , of the reaction

where M_{Cu} is the molar mass of copper, n_T the molar amount of 100 g slag, γ_{Sb} and $\gamma_{\text{Na}_3\text{SbO}_4}$ the Raoultian activity coefficients of Sb in molten copper and Na₃SbO₄ in liquid slag, respectively, and $a_{\text{NaO}_{0.5}}$ the Raoultian activity of NaO_{0.5} in liquid slag. Taking the logarithm of eq. (6) yields

$$\log L_{\text{Sb}}^{\text{S/Cu}} = \log Q + 3 \log a_{\text{NaO}_{0.5}} + (5/4) \log P_{\text{O}_2} \quad (8)$$

where

$$Q = \frac{K_7 \cdot M_{\text{Cu}} \cdot n_T \cdot \gamma_{\text{Sb}}}{100 \cdot \gamma_{\text{Na}_3\text{SbO}_4}} \quad (9)$$

Since in the present work the contents of Sb in molten copper and in liquid slag are always adjusted to less than 0.5 mass% and around 1 mass%, respectively, the value of Q can be regarded as constant for a given temperature. Therefore, as seen from eq. (8), if the relationship between $a_{\text{NaO}_{0.5}}$ and P_{CO_2} is known, one can evaluate quantitatively the effect of the partial pressure of CO₂ on the distribution ratio of Sb.

The activity of NaO_{0.5} in Na₂O–CO₂–Sb₂O₅ melt was, therefore, measured electrochemically by using β'' -alumina (manufactured by NGK Spark Plug Co. Ltd.) as a solid electrolyte over the composition range of $N=0.7 \sim 1.0$ under various partial pressures of CO₂ at

Fig. 6 Estimation of activity of $\text{NaO}_{0.5}$ in Na_2CO_3 slag used under various partial pressures of CO_2 at 1523 K.

1423, 1473, and 1523 K⁽⁶⁾⁽⁷⁾. Figure 6 shows the results obtained only over the composition range of $N=0.913 \sim 1.0$ at 1523 K which is required to evaluate the effect of P_{CO_2} on $L_{\text{Sb}}^{\text{S/Cu}}$. The symbols of $\circ$ represent values measured experimentally, whereas the symbols of $\triangle$ values extra- or interpolated from the measured values. In addition, the values of $\circ$ at $N=1$ were calculated from eq. (2). As mentioned above, since in the present work the content of Sb after the distribution experiment is always adjusted to around 1 mass%, the corresponding value of N becomes *ca.* 0.996. The values of $a_{\text{NaO}_{0.5}}$ ($\bullet$ in Fig. 6) under various partial pressures of CO_2 at $N=0.996$ can be interpolated from the straight lines connecting the data points for $N=1$ and $N=0.96$.

The relationship between $a_{\text{NaO}_{0.5}}$ for the slag composition of $N=0.996$ and P_{CO_2} is now in our hands. Therefore, by determining the value of $\log Q$ from a relationship between $\log L_{\text{Sb}}^{\text{S/Cu}}$ and $\log P_{\text{O}_2}$ for any partial pressure of CO_2 , one can estimate the similar relationships for other partial pressures of CO_2 by the aid of eq. (8). The data for the partial pressure of CO_2 of 0.095 MPa shown in Fig. 3 was here selected to determine the value of $\log Q$. The relationships between $\log L_{\text{Sb}}^{\text{S/Cu}}$ and $\log P_{\text{O}_2}$ estimated for three other partial pressures of CO_2

Fig. 7 Evaluation of the effect of partial pressure of CO_2 on the distribution ratio of Sb between Na_2CO_3 slag and molten copper at 1523 K.

of 0.03, 0.01, and 0.0028 MPa are given by the dashed straight lines in Fig. 7. The estimated distribution ratios of Sb are in good agreement with those obtained experimentally. From this fact it may be concluded that the effect of the partial pressure of CO_2 on the distribution ratio of Sb between Na_2CO_3 slag and molten copper can be evaluated by eq. (8).

2. Relation between the oxygen partial pressure in the bulk of molten copper and that at the Na_2CO_3 slag-molten copper interface.

In Fig. 2 it is shown that, when the partial pressure of CO_2 in gas phase was as low as 0.0028 MPa, the oxygen partial pressure in the bulk of molten copper reached in a certain period of time no equilibrium value among gas, molten copper, and slag phase but a stationary state one which lay between the oxygen partial pressures in gas and slag phases, whether the initial oxygen partial pressures in molten copper was higher than that in the gas phase or lower. If such is the case, there will be a fear that the oxygen partial pressure in the bulk of molten copper differs from that at the Na_2CO_3 slag-molten copper interface (this interface will be expressed hereinafter by the slag-metal interface) which directly affects the

distribution ratios of Sb and Cu. Nevertheless, in Figs. 3, 4 and 7, the distribution ratio of Sb and Cu were plotted against the oxygen partial pressure in the bulk of molten copper. Therefore, the relation between the oxygen partial pressure in the bulk of molten copper and that at the slag-metal interface ought to be clarified.

Figure 8 shows the dependence of the difference between the oxygen partial pressure in molten copper, $P_{O_2}(\text{Cu})$, after the distribution experiment and that in the gas phase, $P_{O_2}(\text{gas}) = 4.30 \times 10^{-3}$ Pa, on the partial pressure of CO₂ in gas phase. This difference rapidly diminishes with the increase of P_{CO_2} . From this fact it seems reasonable to make the following two assumptions for Na₂CO₃ slag phase.

(i) The thermal decomposition of Na₂CO₃ proceeds in two steps, i.e.,

and the rate of the reaction (10) is much faster than that of the reaction (11).

(ii) Under the assumption of (i), by equating P_{Na} to $4P_{\text{O}_2}$, one can calculate the oxygen partial pressures in pure Na₂CO₃ slag for various partial pressures of CO₂ at 1523 K by using appropriate thermodynamic data for the reactions (10) and (11).

The values of P_{O_2} calculated are 24.7, 14.8,

Fig. 8 Dependence of the difference between the oxygen partial pressure in molten copper ($P_{\text{O}_2}(\text{Cu})$) and that in gas phase ($P_{\text{O}_2}(\text{gas}) = 4.30 \times 10^{-3}$ Pa) on the partial pressure of CO₂ in gas phase.

9.55, and 6.03 Pa for the partial pressures of CO₂ of 0.0028, 0.01, 0.03, and 0.095 MPa, respectively. These values of P_{O_2} are always higher than the oxygen partial pressure in molten copper. That is, the Na₂CO₃ slag has an oxidizing ability for molten copper. On the contrary, the Ar-CO-CO₂ gas mixture has a reducing ability for molten copper^{††}. It is, therefore, reasonable to consider that the stationary state value of P_{O_2} attained in progress of the distribution reaction shown in Fig. 2 resulted from a balance between the rates of the oxidation reaction

and the reduction reaction

This situation is illustrated schematically in Fig. 9, where the points A and C represent the equilibrium oxygen partial pressures of the reaction (11) or (12) and (13) or (14),

Fig. 9 Schematic view illustrative of the oxygen partial pressure which Na₂CO₃ slag gives during CO-CO₂ gas bubbling (The oxygen partial pressure in gas phase is always fixed at a constant value of 4.30×10^{-3} Pa).

^{††} When the initial oxygen partial pressure in molten copper is lower than that in the gas mixture as in the case of ○ in Fig. 2, then, the gas mixture also has an oxidizing ability for molten copper. However, after the oxidation of molten copper by both the slag and the gas mixture proceeds to the extent that the oxygen partial pressure in molten copper exceeds that in the gas mixture, the gas mixture has a reducing ability for molten copper.

respectively, for a given partial pressure of CO_2 in gas phase, and $\overline{AB}$ and $\overline{CD}$ the respective reaction rate curves. When both the reaction rates are equal to each other, i.e., $\overline{EF} = \overline{EG}$, a stationary state is realized^{†††}.

As the partial pressure of CO_2 in the gas phase is raised, the equilibrium oxygen partial pressure for the reaction (11) or (12) is lowered as $A \rightarrow A'$, because the activity of Na_2O in Na_2CO_3 slag is reduced. Accordingly, the rate curve of the oxidation reaction of (11) or (12) is shifted to the lower side of the oxygen partial pressure as $\overline{AB} \rightarrow \overline{A'B'}$. On the other hand, the reduction reaction rate by the gas mixture increases proportionately with increasing partial pressure of CO_2 in the gas phase as $\overline{CD} \rightarrow \overline{CD'}$, whereas the point C remains unchanged as it is owing to the fixed ratio of P_{CO_2} to P_{CO} in the gas mixtures. Therefore, the raising of the partial pressure of CO_2 in gas phase results in a rapid access of the oxygen partial pressure at the stationary state to that in molten copper ($E \rightarrow E'$). This situation is consistent well with the results shown in Fig. 8.

The following two rate determining steps can be considered for the oxidation reaction of molten copper by Na_2CO_3 slag, i.e., (a) the dissociation reaction of Na_2O represented by

at the slag-metal interface and (b) the mass transfer of dissolved oxygen from the slag-metal interface to the bulk of molten copper represented by

where $\underline{\text{O}}^*$ and $\underline{\text{O}}$ are dissolved oxygen in molten copper at the slag-metal interface and that in the bulk of molten copper, respectively. Figure 10(a) and 10(b) show schematic views of the distribution of the oxygen partial pressure among the slag-metal-gas phases at the sta-

Fig. 10 Schematic diagram of the distribution of the oxygen partial pressure among the slag-metal-gas phases at the stationary state for the CO_2 partial pressure of 0.0028 MPa.

tionary state in the respective cases for the CO_2 partial pressure of 0.0028 MPa. When the dissociation reaction of Na_2O is the rate determining step, the oxygen partial pressure corresponding to the concentration of $\underline{\text{O}}^*$ at the slag-metal interface should agree with that corresponding to the concentration of $\underline{\text{O}}$ in the bulk of molten copper, because the mass transfer rate of dissolved oxygen in molten copper at the slag-metal interface is so fast that the dissociation reaction rate of Na_2O can be neglected, whereas the oxygen partial pressures should differ from each other for the case of the mass transfer of dissolved oxygen being rate determining step. If the distribution reaction of Sb and Cu are controlled by the case (b), their distribution ratios should have respectively a constant value which is independent of the oxygen partial pressure in the bulk of molten copper, as the result of being deter-

^{†††} For the reduction of dissolved oxygen in molten copper there are two more reactions, i.e., $2\text{Sb(in l-Cu)} + 5\text{O(in l-Cu)} = \text{Sb}_2\text{O}_5(\text{in slag})$ and $2\text{Cu(in l-Cu)} + \underline{\text{O}}(\text{in l-Cu}) = \text{Cu}_2\text{O}(\text{in slag})$, in addition to the reaction (13). However, both the reaction rates should become zero at the stationary state. Therefore, these reaction rate curves were omitted from the figure for simplicity.

mined by the oxygen partial pressure in molten copper at the slag-metal interface which is equal to that in Na₂CO₃ slag. This assumption is, however, in conflict with the results shown in Figs. (3) and (4). Furthermore, by using the mass transfer coefficient of 0.02 cm·s⁻¹ for dissolved oxygen in molten copper which can be calculated by the aid of the method developed by Hirasawa *et al.*⁽¹¹⁾⁽¹²⁾, the oxygen partial pressure at the slag-metal interface can be calculated to be 7.42×10^{-2} Pa by balancing the mass transfer rate of dissolved oxygen from the slag-metal interface to the bulk of molten copper with the reduction rate by the gas mixture. This value is extremely low in comparison with the oxygen partial pressure (2.8×10 Pa) in Na₂CO₃ slag. This fact also makes a denial of the case (b). For the above reasons, it is reasonable to consider that the distribution of the oxygen partial pressure among the slag-metal-gas phases at the stationary state is given as in Fig. 10(a). In this case, the oxygen partial pressure at the slag-metal interface can be regarded as being equal to that in the bulk of molten copper.

V. Conclusion

The distribution ratios of Sb and Cu between Na₂CO₃ slag and molten copper at 1523 K were determined with respect to the oxygen partial pressures in molten copper for various partial pressures of CO₂ in gas phase. In order to estimate the dependence of the distribution ratio of Sb on the partial pressure of CO₂, the activities of NaO_{0.5} in Na₂O-CO₂-Sb₂O₅ melts under various partial pressures of CO₂ were measured electrochemically by using β"-alumina as a solid electrolyte. The results obtained are summarized as follows.

(1) The distribution ratio of Sb {(mass% of Sb in slag)/[mass% of Sb in metal]} decreases with increasing the partial pressure of CO₂ in gas phase. This effect can be evaluated quantitatively by eq. 8 using the rela-

tionship between $a_{\text{NaO}_{0.5}}$ in Na₂O-CO₂-Sb₂O₅ melt and P_{CO_2} .

(2) The distribution ratio of Cu also diminishes with enhancing the partial pressure of CO₂. This implies that the activity of CuO_{0.5} in Na₂CO₃ slag is lowered rapidly as the partial pressure of CO₂ is raised.

(3) Under a given condition with respect to temperature, partial pressure of CO₂, and slag composition, the distribution ratios of Sb and Cu are determined essentially by the oxygen partial pressure at the slag-metal interface. However, there is no procedure to measure it. Therefore, their distribution ratios were arranged by using the oxygen partial pressure calculated from oxygen content in copper melt. A consideration was presented in which the oxygen partial pressure at the slag-metal interface can be regarded as equal to that in the bulk of molten copper.

REFERENCES

- (1) Ch. Yamauchi, K. Otsuki, T. Fujisawa and H. Sakao: J. Japan Inst. Metals, **52** (1988), 561.
- (2) Ch. Yamauchi, K. Otsuki, T. Fujisawa and H. Sakao: Trans. JIM, **29** (1988), 727.
- (3) A. Yazawa: *Proceedings of the Second International Symposium on Metallurgical Slags and Fluxes*, Lake Tahoe, Nevada, U.S.A., (1984), TMS-AIME, p. 701.
- (4) Y. Takeda, G. Rivberos, Y. J. Park and A. Yazawa: J. Min. Metall. Inst. Japan, **102** (1986), 375.
- (5) I. V. Kojo: Acta Polytechnica Scandinavica, Chemical Technology and Metallurgy Series No. 161, Helsinki University of Technology, (1985), 1.
- (6) T. Fujisawa, T. Kuno, H. Fukuyama, S. Takai and Ch. Yamauchi: Submitted to J. Japan Inst. Metals.
- (7) T. Fujisawa, T. Kuno, H. Fukuyama and Ch. Yamauchi: Submitted to Trans. JIM.
- (8) Ch. Yamauchi, T. Fujisawa, Sh. Goto, H. Fukuyama and K. Matsuda: Submitted to J. Japan Inst. Metals.
- (9) *Kohza-Gendai-no-Kinzoku-Gaku, Seiren-Hen 2, Hitetsu-Kinzoku-Seiren*, ed. by Japan Inst. Metals, (1980), 315-321.
- (10) I. V. Kojo, P. Taskinen and K. Lilius: Erzmetall, **37** (1984), 21.
- (11) M. Hirasawa, K. Mori, M. Sano, A. Hatanaka, Y. Shimatani and Y. Okazaki: Tetsu-to-Hagané, **73** (1987), 1343.
- (12) M. Hirasawa, K. Mori, M. Sano, Y. Shimatani and Y. Okazaki: Tetsu-to-Hagané, **73** (1987), 1350.