Effects of Coexisting Oxygen and Antimony in Molten Copper on Rate of Arsenic Elimination from the Copper Phase by the Use of Na₂CO₃ Slag[*1]

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The rate of As elimination from molten copper by the use of Na₂CO₃ slag was measured at 1523 K. The results obtained, under the experimental conditions of this study, show that As in molten copper is eliminated in a pentavalent form and that its elimination rate increases with increasing initial oxygen concentration in molten copper. Based on the results obtained in the present study, the overall rate of As elimination is probably controlled by mass transfer in molten copper. The mass-transfer coefficient of As in molten copper at 1523 K was determined to be $1.3(\pm0.4) \times 10^{-4}\,\mathrm{m\cdot s^{-1}}$ based on the material balances of As and oxygen in the molten copper and slag phases, and the equilibrium relationship of the As elimination reaction at the slag-metal interface. In addition, the behavior of the simultaneous elimination of As and Sb, which coexist as impurities in molten copper at 1523 K, were also investigated from a kinetic viewpoint. The results show that the elimination rate of As is much higher than that of Sb, and two types of elimination behaviors are observed depending on the initial oxygen concentration in molten copper. At relatively low initial oxygen concentrations, As is preferentially eliminated with an initial plateauing of Sb elimination. On the other hand, both elements are eliminated simultaneously at relatively high initial oxygen concentrations. These behaviors were examined from the viewpoint of the oxygen concentration at the slag-metal interface.

1. Introduction

Sodium carbonate slag treatment is expected to be one of the most promising methods for the fire refining of crude copper as well as for the production of high purity copper. Several research groups have therefore been conducting fundamental studies on this slag treatment. Using a thermodynamic approach, Yamauchi and coworkers have investigated the distribution ratios of various impurities between the Na₂CO₃ slag and the molten copper, L_X, {defined as (mass% of X in slag)/[mass% of X in molten copper]}, where the impurity element X = Sb,[1–6] As,[5,7] Sn,[8] Fe,[9,10] Te,[11] Se,[11] P,[12] Si,[12] Ni,[13] Zn,[13] S,[14] and have discussed the slag consumption of this refining process using a mathematical model.[15,16]

From a kinetic viewpoint, the Sb elimination rate from molten copper by injecting soda ash into molten copper has been measured by Kozlowski *et al.*[17] and Stapurewicz *et al.*[18] However, the kinetic mechanism of impurity elimination during this injection process is too complicated and has not yet been clarified. The reported kinetic information on the copper refining process by the use of Na₂CO₃ is not sufficient to apply this process on an industrial scale. Therefore, the authors have conducted the kinetic study to elucidate the rate and mechanism of Sb elimination from molten copper by the use of Na₂CO₃ slag. The rate of Sb elimination was measured at 1523 K with the Na₂CO₃ slag placed directly on molten copper, which makes the system simpler than the slag injection process.[19]

In the present study, As was selected as an impurity element, and its elimination rate and mechanism was investigated by a very similar kinetic analytical method as the one described in the previous paper.[19] It should be noted that all the previous studies[1–19] were conducted for the purpose of elucidating the elimination behavior of single impurity elements from molten copper. However, from the viewpoint of practical operations, multiple impurity elements coexist in crude copper and will simultaneously react with Na₂CO₃ slag. In this paper therefore, the behavior of simultaneous elimination of As and Sb from molten copper at 1523 K was also investigated from a kinetic viewpoint.

2. Experimental Details

2.1 Experimental conditions

The experimental conditions used in the study are summarized in Table 1. The concentration of a minor element X (X = As, Sb, O) in the bulk molten copper phase on a mass ppm scale is represented by [ppm X]. The subscripts "0" and "*f*" denote the values at time $t = 0$ (initial values) and at the end of each run (final values), respectively. Runs A-1 to A-4 were conducted in order to measure the rate of As single elimination, and runs AS-1 to AS-6 were conducted to measure the rates of simultaneous elimination of As and Sb. Run AS-1 was intentionally conducted under the condition of the initial oxygen concentration being 540 mass ppm, which is not sufficient to eliminate all As and Sb in the molten

Table 1   The initial and final compositions of molten copper obtained in each experiment.

Run*	Time, t/ks	Initial concentrations of oxygen, Sb & As in molten copper			Final concentrations of oxygen, Sb & As in molten copper		
		[ppm O]$_0$	[ppm Sb]$_0$	[ppm As]$_0$	[ppm O]$_f$	[ppm Sb]$_f$	[ppm As]$_f$
A-1	7.08	620	—	1010	130	—	32
A-2	2.40	1290	—	868	830	—	8
A-3	2.40	1340	—	1430	600	—	6
A-4	7.38	1440	—	1200	840	—	11
AS-1	21.60	540	1270	1380	170	11	9
AS-2	21.60	1030	1490	1530	300	12	8
AS-3	21.60	1230	1490	1600	510	7	8
AS-4	10.80	1530	1410	1490	830	17	8
AS-5	10.80	1980	1590	1530	920	16	8
AS-6	7.20	4050	1310	1390	3060	8	9
B-1	21.60	50	—	—	180	—	—

*All experiments (runs A-1 through B-1) were conducted in an Ar atmosphere at 1523 K.

copper as their oxides from a viewpoint of the material balances of the impurities and oxygen, for the purpose of further examination of the effects of oxygen concentration on the behavior of simultaneous elimination of these two impurity elements. In addition to the above experiments, run B-1 was also conducted under the condition of [ppm As]$_0$ = [ppm Sb]$_0$ = 0. Details of this experiment will be described in sub-section 3.2.1.

2.2   Measurements of elimination rates of impurities

The experimental procedure for runs A-1 to A-4 and AS-1 to AS-6 is the same as that for the measurement of the rate of Sb single elimination under the condition wherein the molten copper was not stirred externally.[19] An alumina crucible, with an inside diameter of 35 mm and a height of 150 mm, was charged with 400 g of a mixture of oxygen-free copper (99.99% pure), appropriate amounts of Cu$_2$O powder (98% pure), Cu–As and/or Cu–Sb alloys for the initial composition of the copper phase shown in Table 1. The sample in the crucible was heated to 1523 K. Argon gas was continuously flushed at a flow rate of 3.33×10^{-6} Nm^3·s^{-1} over the sample melt to prevent the oxygen dissolution onto the melt from the gas phase. In the case of run B-1, 400 g of oxygen-free copper (99.99% pure) was melted at the same temperature in the same atmosphere. After the sample in the crucible was melted, 25 g of Na$_2$CO$_3$ pellets were added into the melt. The start of the reaction ($t = 0$) was defined to be the time when the Na$_2$CO$_3$-addition was completed. Sampling of the metallic specimen was done at appropriate time intervals using a quartz tube. The obtained samples were subjected to As and Sb analysis by inductivity coupled plasma atomic emission spectrometry (ICP-AES) and oxygen analysis by inert gas fusion-infrared absorptiometry (IGF-IRA).

3.   Results and Discussion

3.1   As single elimination
3.1.1   Time dependence of As and oxygen concentrations in molten copper

Figure 1 shows examples of the time dependence of As and oxygen concentrations in the molten copper at (a) relatively low (run A-1) and (b) high (run A-2) initial oxygen concentrations. In Fig. 1(b), the results of run A-2 are compared with previously reported data for the rate of Sb single elimination for a similar level of initial oxygen concentration.[19] The solid and the broken lines in Fig. 1 represent the mathematically determined curves of an equation of the form: log[ppm X] = $a/(t + b) + c$, where a, b, and c are constants, by fitting the experimental results. This regression equation was adopted as a function of the reaction time, t, for the following reasons. It is important to evaluate the change in the As concentration in molten copper accurately for the kinetic analysis (the analytical method II), which will be described in sub-section 3.1.3 (3). The change in the As concentration at the beginning stage, immediately after the Na$_2$CO$_3$-addition, is too drastic to be evaluated using (Δ[% As]/Δt), determined from the slopes of the straight lines that connects the neighboring two plots in Fig. 1. In the present study, by a trial and error analysis, the above-mentioned equation of the form was determined to be the regression curve to adequately represent the experimental results. In the analytical method II, the values of ($-d$[% As]/dt), at any time obtained by differentiating the regression equation with respect to t was applied for the determination of the rate constant of As elimination and the As concentration at the slag-metal interface.

Figure 1 shows that As is eliminated as the concentration of the coexisting oxygen decreases. It can also be observed that the final arsenic concentration in the molten copper nearly approaches zero. The rate of As elimination increases with increasing initial oxygen concentration. For a similar initial oxygen concentration, the elimination rate of As is much higher than that of Sb.

In the previous study on the rate of Sb single elimination,[19] it was clarified that the overall Sb elimination rate without external stirring of the molten copper phase could be controlled by mass transfer in the molten copper phase. Based on these reported results, the rate and the mechanism of As single elimination will be discussed on the assumption that its overall rate is controlled by the same step (mass transfer in the molten copper phase) in the following sub-sections.
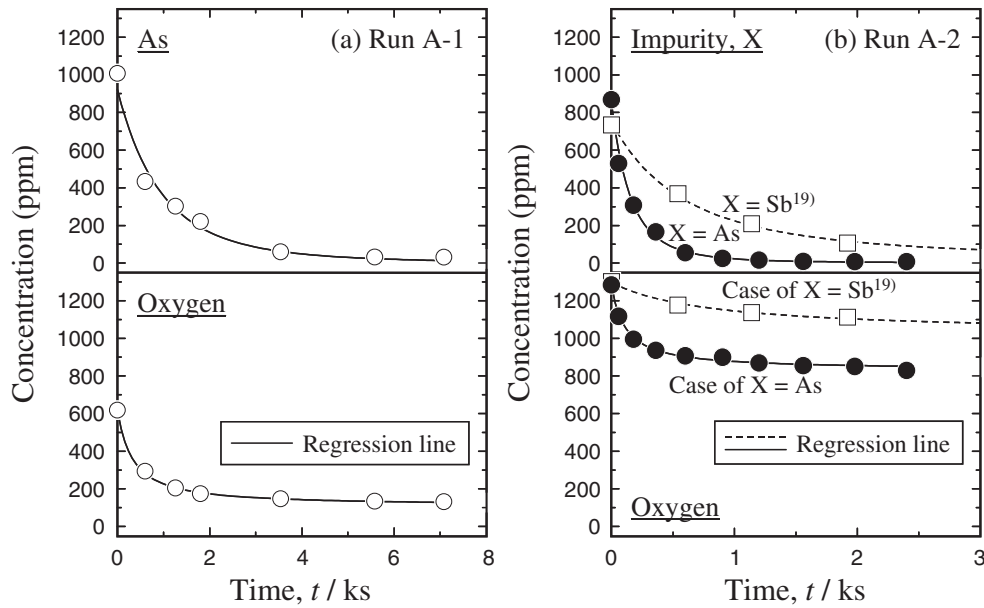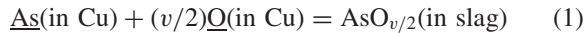
Fig. 1 Time dependence of As and oxygen concentrations in the bulk molten copper phase for the As single elimination experiments (runs (a) A-1 and (b) A-2) at 1523 K.

3.1.2 Elimination reaction of As at slag-metal interface

The elimination reaction of As at the slag-metal interface can be expressed as follows:

$$\underline{As}(\text{in Cu}) + (v/2)\underline{O}(\text{in Cu}) = AsO_{v/2}(\text{in slag}) \qquad (1)$$

where v corresponds to the valence of the As. Arsenic could change its valence in the Na$_2$CO$_3$ slag melt depending on the experimental conditions. In order to discuss the mechanism of As elimination, it is necessary to examine the value of v in reaction (1) under the experimental conditions of this study. Based on the results obtained, the value of v in reaction (1) was estimated as follows.

From the stoichiometry of reaction (1), the following relationship can be derived:

$$\Delta[n_O] = (v/2)\Delta[n_{As}] \qquad (2)$$

This relates the consumption of As in molten copper, $\Delta[n_{As}]$, and that of oxygen, $\Delta[n_O]$. If the values of $\Delta[n_O]$ are plotted as a function of $\Delta[n_{As}]$, a linear relationship with a slope of $(v/2)$ can be obtained. These relationships for runs A-1 and A-2 are plotted in Figs. 2(a) and (b), respectively. In both cases, the results follow a linear relationship, although there is some scatter. Using least squares regression analysis, the values of v were determined for these runs. The results from other runs were also analyzed by the same method.

The v values thus determined are plotted in Fig. 3 as a function of the initial copper composition, defined as the ratio of mole fraction of oxygen to that of As, $\{[X_O]_0/[X_{As}]_0\}$. The $\{[X_O]_0/[X_{As}]_0\}$ parameter was used as an index of the oxygen partial pressure at the slag-metal interface in this study. The interfacial oxygen partial pressure increases when this parameter increases. As shown in Fig. 3, the value of v in reaction (1) is 5 for all runs, which implies that As in molten copper is eliminated as As-oxide, AsO$_{2.5}$, to the Na$_2$CO$_3$ slag phase under the experimental conditions of this study.
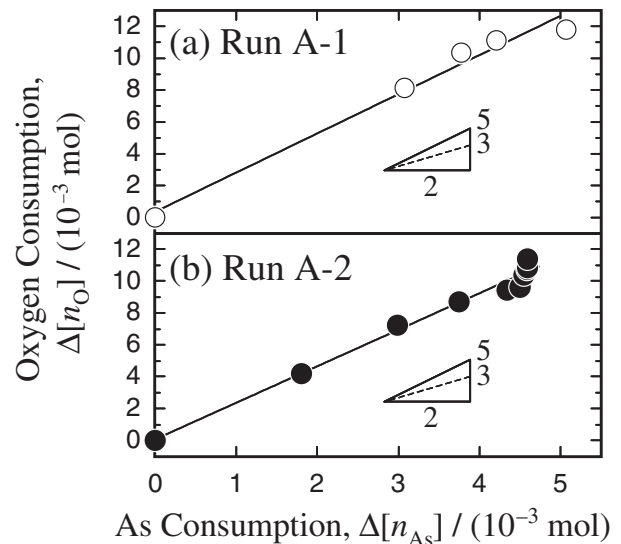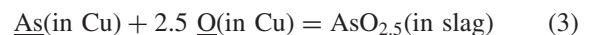

Fig. 2 The relationship between oxygen consumption and As consumption during As single elimination from molten copper for the experiments (runs (a) A-1 and (b) A-2) at 1523 K.

$$\underline{As}(\text{in Cu}) + 2.5\,\underline{O}(\text{in Cu}) = AsO_{2.5}(\text{in slag}) \qquad (3)$$

In the case of the Sb single elimination,[19] it was clarified that Sb is eliminated as Sb-oxide, SbO$_{2.5}$, for $\{[X_O]_0/[X_{Sb}]_0\}$ larger than 5 (relatively high interfacial oxygen partial pressure), while it is eliminated as SbO$_{1.5}$ for $\{[X_O]_0/[X_{Sb}]_0\}$ less than 5 (relatively low interfacial oxygen partial pressure). Fujisawa *et al.* have measured the redox equilibrium for As and Sb individually in Na$_2$CO$_3$-based slag under various oxidizing conditions.[5] According to their results, As exists in a pentavalent form in the slag, while Sb exists in a trivalent and a pentavalent forms at relatively low and high oxygen partial pressures, respectively. The results in the present and previous[19] kinetic studies support the Fujisawa
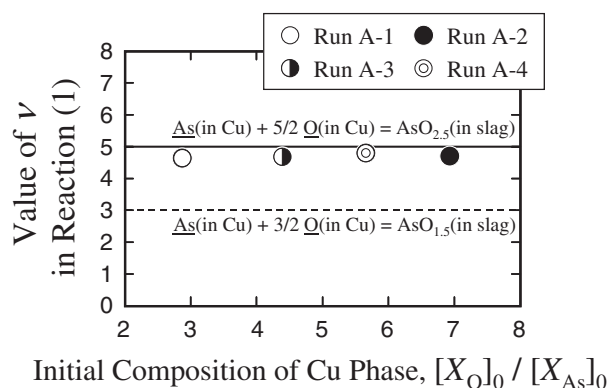
Fig. 3 Effects of the initial composition of the molten copper phase on the estimated value of v in reaction (1) at 1523 K.
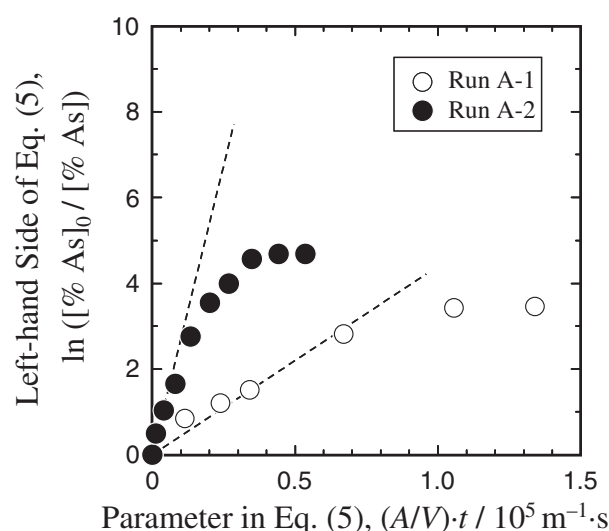

Fig. 4 Relationship between $\ln([\% \text{ As}]_0/[\% \text{ As}])$ and $(A/V) \cdot t$ during As single elimination from molten copper for the experiments (runs A-1 and A-2) at 1523 K.

et al.'s results on the redox equilibrium from a thermodynamic viewpoint.[5]

3.1.3 Kinetic analysis

(1) Rate equation

Based on the observation that the rate-controlling step of the As single elimination process could be mass transfer in the molten copper phase, the rate of As single elimination was analyzed by using the following mass-transfer rate equation for a minor element, X (X = As, O), in molten copper:

$$- d[\% \text{ X}]/dt = (A/V) \cdot k_{m,\text{X}} \cdot ([\% \text{ X}] - [\% \text{ X}]_\text{i}) \quad (4)$$

where $[\% \text{ X}]_\text{i}$ and $k_{m,\text{X}}$ are respectively the concentration of component X in the metallic phase at the slag-metal interface and its mass-transfer coefficient ($\text{m} \cdot \text{s}^{-1}$), t is the reaction time (s), A is the slag-metal interfacial area (m^2), and V is the volume of the metallic phase (m^3). Strictly speaking, the driving forces of the mass transfer of As and oxygen should be represented by the gradients of their chemical potentials. In this study, however, their concentrations were used instead of the chemical potential gradients in the kinetic analysis for simplicity, assuming that As and oxygen in molten copper phase obey Henry's law wherein the activity of a minor element is equal to their concentration on a mass% scale.

In the As elimination process using Na_2CO_3 slag, the concentrations of As and oxygen at the slag-metal interface ($[\% \text{ As}]_\text{i}$ and $[\% \text{ O}]_\text{i}$) are expected to change as reaction (3) progresses. Therefore, the mass-transfer rates of As and oxygen in the molten copper phase were analyzed by evaluating As and oxygen concentrations at the slag-metal interface. In this study, two methods, called "Analytical method I" and "Analytical method II" and described in subsections 3.1.3 (2) and (3), respectively, were adopted for evaluation of the interfacial concentrations of As and oxygen in molten copper and their mass-transfer coefficients. In both analyses, the cross-sectional area of the alumina crucible was A. The value of V, the volume of metallic phase, was approximated to be the volume of 400 g of pure liquid copper, which can be calculated using the reported value of copper density at 1523 K ($7.87 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$).[20]

(2) Analytical method I wherein As concentration at the slag-metal interface is neglected ($[\% \text{ As}]_\text{i} = 0$)

Since Na_2CO_3 slag has a relatively high removal capability

for As from molten copper,[7] the value of $[\% \text{ As}]_\text{i}$ at the beginning stage of the elimination process is expected to be much lower than the As concentration in the bulk molten copper phase, $[\% \text{ As}]$. Thus, using the following integral form of the mass-transfer rate equation for As in molten copper:

$$\ln([\% \text{ As}]_0/[\% \text{ As}]) = (A/V) \cdot k_{m,\text{As}} \cdot t \quad (5)$$

the values of $k_{m,\text{As}}$ were determined on the assumption that $[\% \text{ As}]_\text{i}$ can be neglected in eq. (4) for X = As (the analytical method I).

Equation (5) indicates that the value of $k_{m,\text{As}}$ for each run can be determined from the slope of the straight line obtained by plotting the left-hand side of eq. (5) as a function of $(A/V) \cdot t$. Figure 4 shows these relationships for the results of runs A-1 and A-2. In both cases, linear relationships can be observed at the beginning stage while the results display some deviation from linearity in later stages in each run. This may be because in the later stages, the As concentration in the bulk molten copper phase becomes so low that the effect of the interfacial As concentration on the kinetic behavior of the As single elimination cannot be neglected. Therefore, in the analytical method I, least squares regression analysis of the results at the beginning stage, wherein a linear relationship can be observed in the $\ln([\% \text{ As}]_0/[\% \text{ As}])$–$(A/V) \cdot t$ plot, was used to determine the values of $k_{m,\text{As}}$.

The values of $k_{m,\text{As}}$ for runs A-1 through A-4 determined by this method are plotted in Fig. 5 as a function of $\{[X_\text{O}]_0/[X_\text{As}]_0\}$. As seen in this figure, the values of $k_{m,\text{As}}$ increase with increasing $\{[X_\text{O}]_0/[X_\text{As}]_0\}$, although $k_{m,\text{As}}$ should be constant, independent of the initial copper composition. This suggests that the assumption of $[\% \text{ As}]_\text{i} = 0$ leads to a considerable error in the calculated value of $k_{m,\text{As}}$.

(3) Analytical method II wherein changes in As concentration at slag-metal interface with reaction time are considered

It is difficult to experimentally determine the interfacial concentrations of minor elements in the copper refining process using Na_2CO_3 slag. Therefore, the authors have
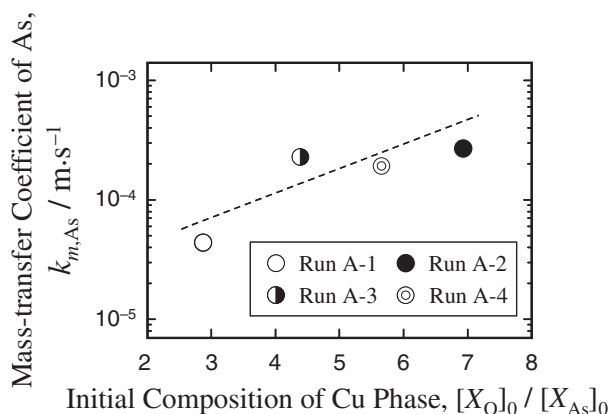
Fig. 5 Effects of the initial composition of the molten copper phase on the mass-transfer coefficient of As in copper at 1523 K determined by the analytical method I.

developed an analytical method to estimate the interfacial concentrations of Sb and oxygen during the Sb single elimination process from molten copper by the use of Na_2CO_3 slag and to determine the mass-transfer coefficients, $k_{m,Sb}$ and $k_{m,O}$, in molten copper.[19] In the present study, a similar method to above-mentioned one, the analytical method II, was applied to evaluate the interfacial concentrations of As and oxygen and to determine the value of $k_{m,As}$. The outline of the analytical method II is described as follows. For further details on this method, the reader should refer to the authors' previous paper.[19]

Based on the expectation that the As single elimination is controlled by mass transfer in the molten copper phase, reaction (3) at the slag-metal interface is assumed to be at equilibrium. The equilibrium constant for reaction (3), K_3, at the interface is given by:

$$K_3 = \frac{(a_{AsO_{2.5}})_i}{\{(f_{As})_i \cdot [\% \ As]_i\} \cdot \{(f_O)_i \cdot [\% \ O]_i\}^{2.5}}$$
$$\fallingdotseq \frac{a_{AsO_{2.5}}}{[\% \ As]_i \cdot \{(f_O)_i \cdot [\% \ O]_i\}^{2.5}} \tag{6}$$

where $a_{AsO_{2.5}}$ is the Raoultian activity of $AsO_{2.5}$ in the slag phase, f_X is the Henrian activity coefficient of the minor element X with respect to 1 mass% in the molten copper and values of the subscripts "i" denote the values at the slag-metal interface. In the analytical method II, the As concentration in molten copper at the slag-metal interface is so small that the interaction parameters related to the interfacial As concentration can be neglected. Thus, the As in the molten copper phase at the slag-metal interface obeys Henry's law, which means that the value of $(f_{As})_i$ is equal to unity. The Henrian activity coefficient of oxygen, $(f_O)_i$, can be expressed as a function of only the interfacial oxygen concentration by:

$$\log(f_O)_i = e_O^O[\% \ O]_i \tag{7}$$

where e_O^O is Wagner's first-order self-interaction parameter of oxygen in molten copper on a mass% scale. In addition, $(a_{AsO_{2.5}})_i$ was assumed to be equal to the activity in the bulk of the slag phase, $a_{AsO_{2.5}}$, in the present study.

A combination of eq. (6) and the relationships involving the material balance of As and oxygen in the molten copper

and the slag phases, and their mass-transfer rates for the copper phase yields:

$$\frac{2.5M_O}{M_{As}} \cdot \left\{ \left(\frac{k_{m,As}}{k_{m,O}} - 1 \right) \cdot [\% \ As] + [\% \ As]_0 \right.$$
$$\left. - \frac{k_{m,As}}{k_{m,O}} \cdot \frac{a_{AsO_{2.5}}}{K_3 \cdot \{(f_O)_i \cdot [\% \ O]_i\}^{2.5}} \right\}$$
$$+ [\% \ O]_i - [\% \ O]_0 = 0 \tag{8}$$

Here, M_X is the atomic weight of component X. According to this equation, if the ratio ($k_{m,As}/k_{m,O}$), the initial composition of molten copper ($[\% \ As]_0$ and $[\% \ O]_0$) and the value of $a_{AsO_{2.5}}$ at a specific time are known, the value of $[\% \ O]_i$ at that time can be calculated using the measured As concentration in the bulk copper phase, $[\% \ As]$, and the thermodynamic data of K_3 and e_O^O at 1523 K. The thermodynamic data were derived from previously reported values from the literature[21–25] which are tabulated in Table 2.

The activity of $AsO_{2.5}$, $a_{AsO_{2.5}}$, at a specific time was evaluated using the following equation:

$$a_{AsO_{2.5}} = \gamma_{AsO_{2.5}} \cdot X_{AsO_{2.5}} \fallingdotseq \gamma_{AsO_{2.5}}^{\circ} \cdot X_{AsO_{2.5}} \tag{9}$$

Since the $AsO_{2.5}$ concentration in the slag is dilute under the experimental conditions of this study, its Raoultian activity coefficient, $\gamma_{AsO_{2.5}}$, was assumed to be constant and equal to its value at an infinite dilution, $\gamma_{AsO_{2.5}}^{\circ}$. From the experimental data on the compositions of the molten copper and the slag phases, and the relationship expressed by eq. (9), the value of $\gamma_{AsO_{2.5}}^{\circ}$ for each run and the mole fraction of $AsO_{2.5}$ in the slag phase, $X_{AsO_{2.5}}$, were evaluated similarly to the case of the Sb single elimination process.[19]

On the other hand, the ratio ($k_{m,As}/k_{m,O}$) cannot be estimated based on the boundary-layer theory because there are no reports thus far on the diffusion coefficient of As in molten copper phase. Therefore, a method dissimilar to the kinetic analysis of the Sb single elimination that was adopted in the previous study[19] was used as the method of estimation for ($k_{m,As}/k_{m,O}$). In the case of the copper refining process using Na_2CO_3 slag, the As or Sb concentration in molten copper is reduced to a sufficiently low level that the effect of the As–O or the Sb–O interaction on the mass transfer of oxygen in the melt can be neglected. In the present study, by a trial-and-error technique, the mass-transfer rates of As and oxygen in the molten copper phase were analyzed on the assumption that the value of $k_{m,O}$ in this case is equal to that for the Sb single elimination process[19] expressed by:

$$k_{m,O} = 1.3(\pm 0.3) \times 10^{-4} \ m \cdot s^{-1} \quad (at \ 1523 \ K)^{[19]} \tag{10}$$

By substituting a provisional value for the ($k_{m,As}/k_{m,O}$) term in eq. (8), the interfacial concentrations of As and oxygen at a specific time, and the values of $k_{m,As}$ and $k_{m,O}$ for each run were estimated. This estimation was repeated to find the ($k_{m,As}/k_{m,O}$) value that allows the value of $k_{m,O}$ to become equal to $1.3(\pm 0.3) \times 10^{-4} \ m \cdot s^{-1}$, expressed by eq. (10).

Figure 6 shows an example of the time dependence of the oxygen concentration in molten copper at the slag-metal interface for run A-2, which was estimated under the condition and assumption that ($k_{m,As}/k_{m,O}$) was unity. In this figure, the time dependence of $[\% \ As]_i$ for the same run,

Table 2　Thermodynamic data used for the kinetic analysis in the present study.[21–25]

Thermodynamic data	Temp. range/K	Ref.
$As(s) + 5/4O_2(g) = AsO_{2.5}(s)$: $\Delta G^\circ/J = -462310 + 239.08(T/K)$	298–875	21)
$As(s) = As(l)$: $\Delta G^\circ/J = 23645 - 21.7(T/K)$	1089	22)
$As(l) = \underline{As}(\%$ in Cu): $\Delta G^\circ/J = RT \ln[(\gamma^\circ_{As(l)} \cdot M_{Cu})/(100 \cdot M_{As})] = -58210 - 42.15(T/K)$	1273–1423	23)
$1/2O_2(g) = \underline{O}(\%$ in Cu): $\Delta G^\circ/J = RT \ln[(\gamma^\circ_O \cdot M_{Cu})/(100 \cdot M_O)] = -76570 + 12.01(T/K)$	1373–1673	24, 25)
$\log \gamma^\circ_{As(l)} = -3040(T/K)^{-1} - 0.13$	1273–1423	23)
$\log \gamma^\circ_O = -3999(T/K)^{-1} + 2.028$	1373–1673	24, 25)
$\varepsilon^O_O = -31929(T/K)^{-1} + 14.157$ $(e^O_O = -0.1305^*)$	1373–1673 (1523)	24, 25)

ΔG° is the standard Gibbs free energy change for each reaction, ε^O_O and e^O_O are the self-interaction parameters of oxygen in molten copper, γ°_X and M_X are the Raoultian activity coefficient in molten copper at infinite dilution and atomic weight of component X, respectively.
*The value of e^O_O was determined using the reported value of ε^O_O.
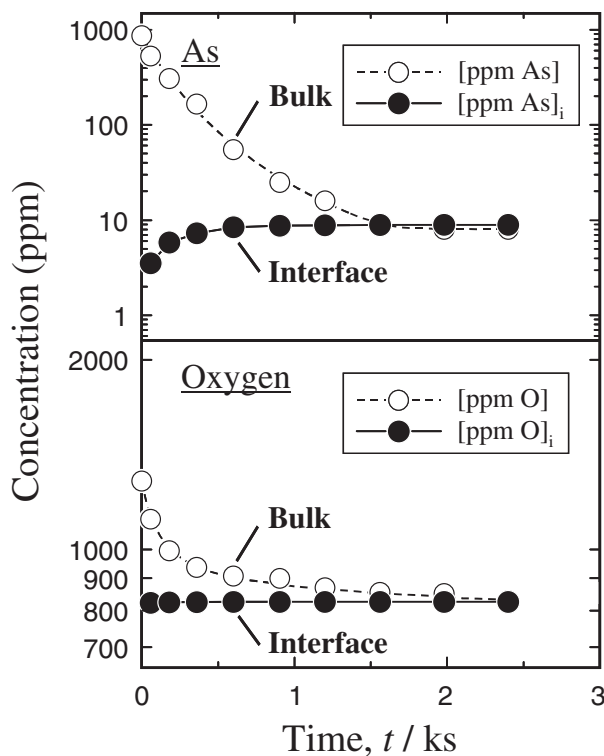

Fig. 6　Time dependence of As and oxygen concentrations in molten copper at the slag-metal interface and in the bulk molten copper phase during As single elimination from molten copper for run A-2 at 1523 K determined by the analytical method II for $k_{m,As}/k_{m,O} = 1$.
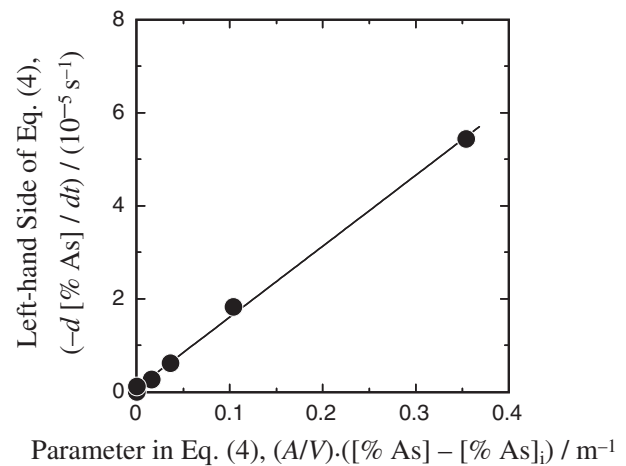

Fig. 7　Relationship between $(-d[\% \text{ As}]/dt)$ and $(A/V) \cdot ([\% \text{ As}] - [\% \text{ As}]_i)$ during As single elimination from molten copper for run A-2 at 1523 K for $k_{m,As}/k_{m,O} = 1$.

obtained from eq. (6) using the estimated values of $[\% \text{ O}]_i$ and $a_{AsO_{2.5}}$ at a specific time, are also plotted and compared with the experimental results of their concentrations in the molten copper bulk phase. Figure 6 indicates that the interfacial As concentration approaches the bulk concentration as the As single elimination progresses. It was clarified that the change in the interfacial As concentration can not be neglected in comparison to the bulk concentration because the As concentration in the bulk molten copper phase is reduced drastically at the beginning of the run.

　　The value of $k_{m,As}$ was estimated from eq. (4) for X = As, using the values of $[\% \text{ As}]_i$ obtained for a specific time.

Figure 7 shows the relationship between the values of $(A/V) \cdot ([\% \text{ As}] - [\% \text{ As}]_i)$ and the left-hand side of eq. (4) for X = As, $(-d[\% \text{ As}]/dt)$, at given times, which can be calculated from the regression formula for $[\% \text{ As}]$ vs t. Figure 7 shows the results for run A-2 in the case of $(k_{m,As}/k_{m,O})$ being unity. The value of $k_{m,As}$ was determined from the slope of the resulting straight line, and the value of $k_{m,O}$ was determined from this value of $k_{m,As}$ and the assumed value of $(k_{m,As}/k_{m,O})$.

　　The values of $k_{m,As}$ and $k_{m,O}$ estimated by this method when $(k_{m,As}/k_{m,O})$ is 0.2, 1 and 5 are plotted in Figs. 8(a) to (c) as a function of $\{[X_O]_0/[X_{As}]_0\}$. Unlike the results shown in Fig. 5, the values of $k_{m,As}$ and $k_{m,O}$ in this figure are constant, independent of the initial composition of the molten copper, although there is some scatter as seen in Fig. 8. This indicates that the overall rate of As elimination can be controlled by mass transfer in molten copper. The data also show that the analytical method II is superior for the estimation of $k_{m,As}$. From the results in Figs. 8(a) to (c), the value of $k_{m,O}$ obtained based on the assumption of $(k_{m,As}/k_{m,O})$ being unity is in agreement with that for Sb single elimination[19] represented by the horizontal broken
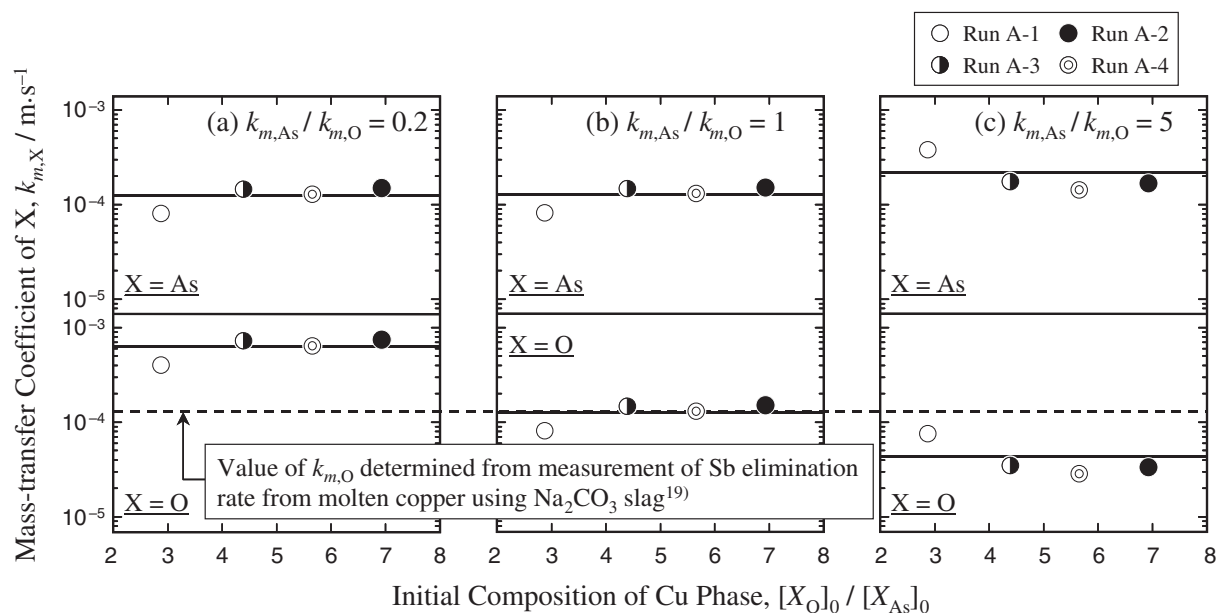
Fig. 8   Effects of the initial composition of the molten copper phase on the mass-transfer coefficients of As and oxygen in copper at 1523 K determined by the analytical method II for $k_{m,As}/k_{m,O}$ = (a) 0.2, (b) 1 and (c) 5.

line. From Fig. 8, the value of $k_{m,As}$ obtained by the analytical method II in the case of ($k_{m,As}/k_{m,O}$) being unity is:

$$k_{m,As} = 1.3(\pm 0.4) \times 10^{-4} \, \text{m·s}^{-1} \quad \text{(at 1523 K)} \quad (11)$$

This was determined to be the mass-transfer coefficient of As in molten copper under the experimental conditions of this study. The error term in eq. (11) was evaluated based on the following two factors. The first was by least squares regression analysis, *i.e.* the deviation of the plots from the regression line in Fig. 7, and the other was from the scatter among the plots of $k_{m,As}$ in Fig. 8(b).

## 3.2   Simultaneous elimination of As and Sb
3.2.1   Time dependence of As and Sb concentrations in molten copper

Figures 9(a) to (f) show the time dependence of As and Sb concentrations in the bulk molten copper phase as the initial oxygen concentration was changed from 540 to 4050 mass ppm at a constant initial concentration of about 1500 mass ppm individually for As and Sb.

Figures 9(a) to (f) show that the elimination rate for As is much higher than that for Sb. The results obtained from runs AS-1 to AS-3 show that As is preferentially eliminated with the initial plateauing of Sb elimination at the beginning stage of each run. The time period of this initial plateau of Sb elimination is lengthened with decreasing initial oxygen concentration. This interesting phenomenon of the stagnation of Sb elimination was not observed for the Sb single elimination process at relatively low initial oxygen concentrations.[19] This phenomenon will be further discussed in sub-section 3.2.2.

Another interesting phenomenon was observed in Fig. 9(a). The horizontal broken line shown in Fig. 9(a) represents the residual As concentration calculated on the assumption that all the oxygen (540 mass ppm) initially dissolved in molten copper is consumed for the As

elimination according to reaction (3). From the viewpoint of material balance of oxygen and impurities, it was expected that in the beginning stage, where As is preferentially eliminated with stagnation of Sb elimination, residual Sb and As in the molten copper cannot be further eliminated to the slag phase as oxides. However, it can be seen from Fig. 9(a) that the As concentration continually decreases to nearly zero without stopping. In addition to As, Sb in the molten copper was also eliminated. The reason for this reduction in the concentrations of these two impurities despite the lack of oxygen in the molten copper is discussed based on the results reported by Yamauchi *et al.*[2,3] According to their results, the oxygen partial pressure between the $NaO_{0.5}$–CO_2–$SbO_{2.5}$ slag and the molten copper at equilibrium lies between the oxygen partial pressure thermodynamically determined according to the thermal decomposition reaction of Na_2CO_3 slag [reaction (12)] and the dissolution reaction of O_2 gas into molten copper [reaction (13)]:

$$2NaO_{0.5}(l) = 2Na(g) + 1/2O_2\,(g) \quad (12)$$

$$1/2O_2(g) = \underline{O} \,(\text{in Cu}) \quad (13)$$
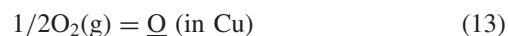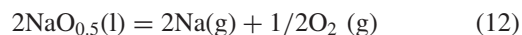
and that in the CO–CO_2–Ar gas atmosphere. From a thermodynamic viewpoint, reactions (12) and (13) are expected to be enhanced at relatively low initial oxygen concentrations, which corresponds to relatively low oxygen partial pressures at the slag-metal interface. Considering this fact, the dissociated O_2 gas by reactions (12) and (13) might contribute to the elimination of As and Sb after the consumption of the oxygen initially dissolved in the molten copper for the As preferential elimination in run AS-1.

In order to confirm this, the dissolution of O_2 gas, dissociated by the thermal decomposition reaction of Na_2CO_3 slag, into oxygen-free copper melt was examined by conducting run B-1. Figure 10 shows the time dependence of oxygen concentration in the oxygen-free copper melt, together with the results of run AS-1. The results for run B-1
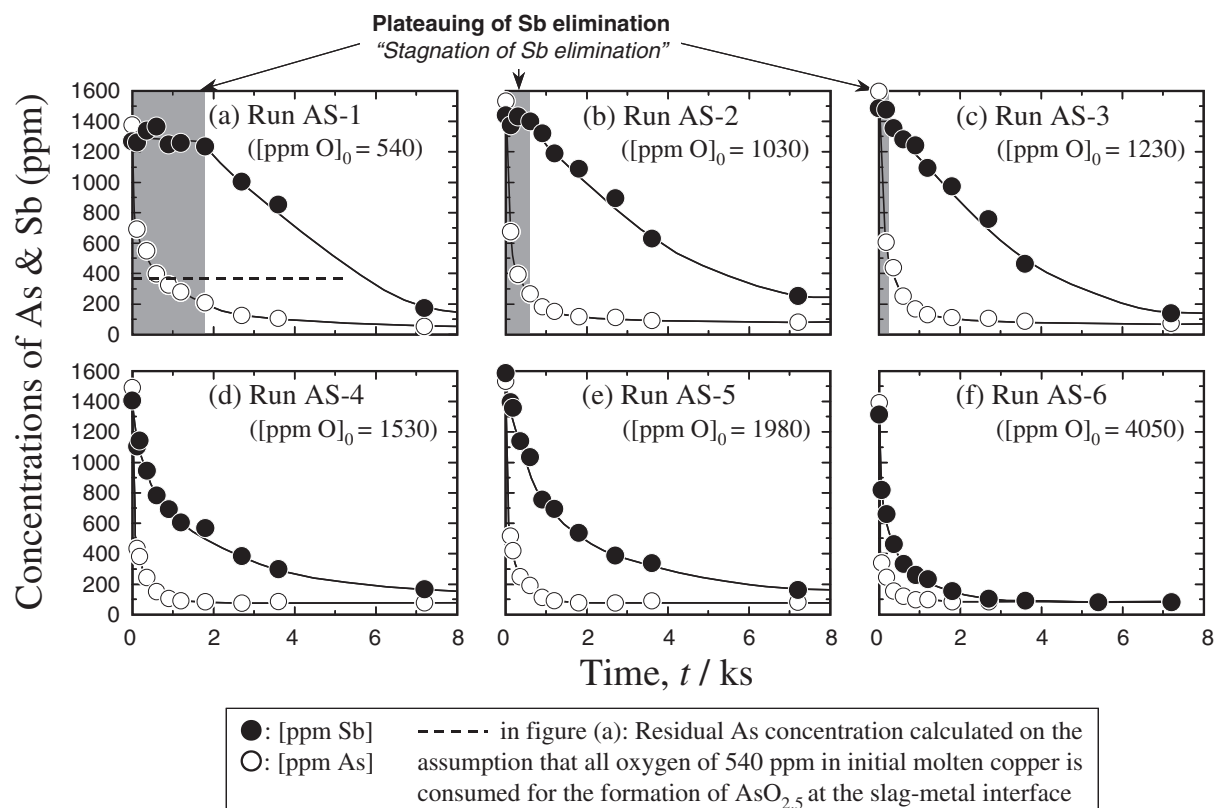
Fig. 9   Time dependence of As and Sb concentrations in the bulk molten copper phase for simultaneous elimination of these two impurities (runs (a) AS-1, (b) AS-2, (c) AS-3, (d) AS-4, (e) AS-5 and (f) AS-6) at 1523 K.
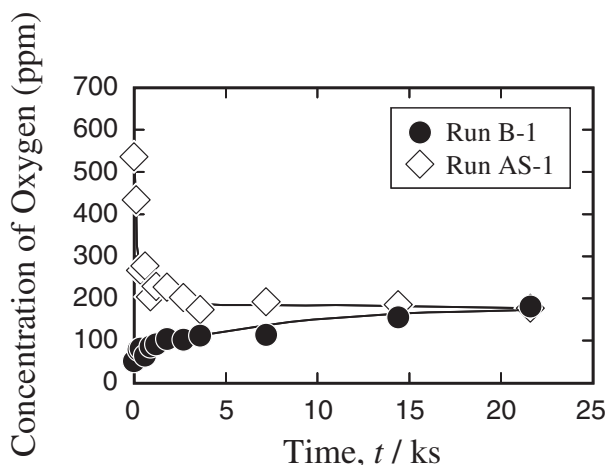

Fig. 10   Time dependence of oxygen concentration in the bulk molten copper phase for runs B-1 and AS-1 at 1523 K.

show that the oxygen concentration increases and approaches ~200 mass ppm, which is the same level as the final oxygen concentration in run AS-1, as the dissolution reaction of O_2 gas into molten copper progresses by reactions (12) and (13).

From the results shown in Figs. 9(a) and 10, it is clarified that for relatively low initial oxygen concentration, As and Sb in molten copper react not only with the oxygen initially dissolved in the molten copper but also with the oxygen generated according to reactions (12) and (13) so that they are transferred into the slag phase as oxides. In other words, it is necessary to raise the oxygen concentration in the molten

copper in order not only to enhance the elimination rates of As and Sb but also to prevent the evaporation loss of the Na_2CO_3 slag.

3.2.2   Effects of interfacial oxygen in molten copper

The results obtained in the previous[19] and the present studies on the single elimination of Sb or As individually suggest that the behavior of the simultaneous elimination of these two elements is affected by the interfacial oxygen concentration. Therefore, by using the mass-transfer rate equation [eq. (4)] for X = O, the change in the oxygen concentration at the slag-metal interface with the progress of the As and Sb elimination was evaluated in order to analyze the rates of simultaneous elimination. In this study, it is assumed that the kinetic mechanism of the simultaneous elimination of As and Sb is the same as that for the single elimination each of As or Sb, *i.e.* the rate-controlling step for the overall elimination rate, the values of mass-transfer coefficients in molten copper etc. Based on this assumption, $[ppm\ O]_i$ at a specific time was determined from eq. (4) using the value of $k_{m,O}$ obtained [eq. (10)] and the results of the oxygen concentration in the bulk molten copper phase at that time.

Figure 11 shows the time dependence of the values of $[ppm\ O]_i$ determined for the time period from 0 to 2.0 ks in runs AS-2 to AS-6, together with the concentrations of Sb, As and oxygen in the bulk molten copper phase for each run [Figs. 11(b) to (f)]. In this figure, the reported results for the Sb single elimination[19] for a lower initial oxygen concentration than in run AS-2 are plotted [Fig. 11(a)]. The results obtained in run AS-1, which includes the effects of the
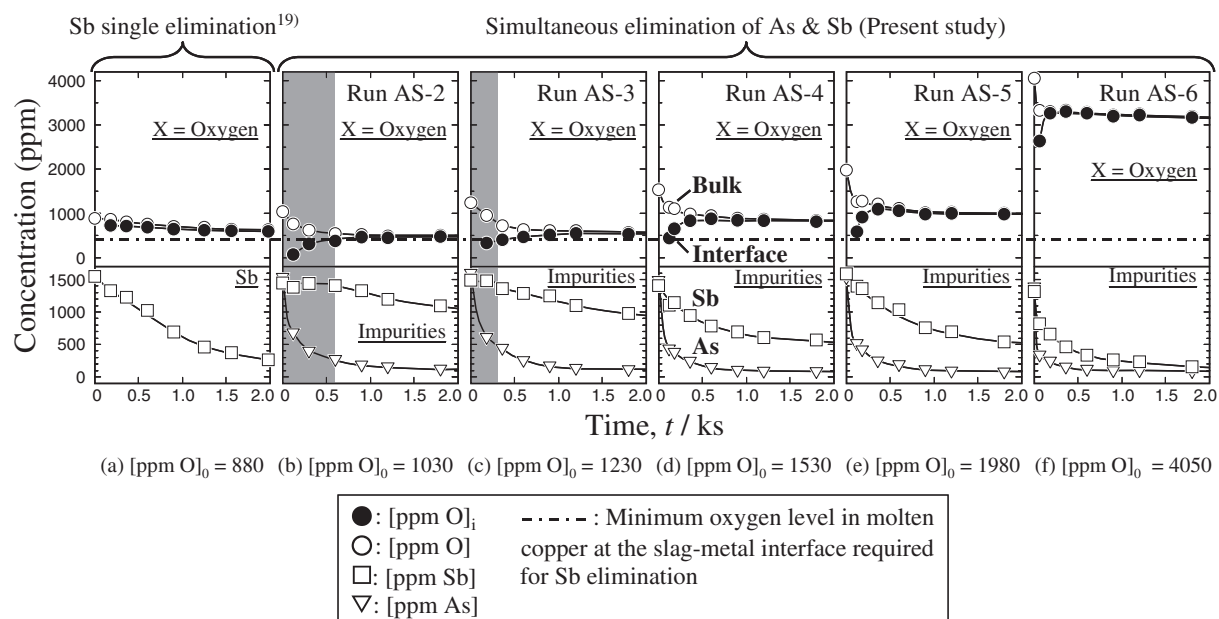
Fig. 11 Time dependence of oxygen concentration in molten copper at the slag-metal interface and composition of the bulk molten copper phase for (a) Sb single elimination[19] and (b–f) simultaneous elimination of As and Sb (runs (b) AS-2, (c) AS-3, (d) AS-4, (e) AS-5 and (f) AS-6) at 1523 K.

dissociated O_2 gas by the thermal decomposition reaction of the Na_2CO_3 slag, is too complicated to be analyzed using the above method, and is therefore omitted from Fig. 11.

In all cases of the simultaneous elimination of Sb and As, the interfacial oxygen concentrations are relatively low at the beginning of the run, and then increase with impurity elimination and finally approach the bulk concentrations. The final interfacial oxygen concentration, which is equal to the final bulk concentration, decreases with decreasing initial oxygen concentration. Since the distribution ratio of As is much larger than that for Sb for the same experimental conditions reported by Fukuyama *et al.*,[6,7] As is preferentially eliminated at the slag-metal interface in the instant when Na_2CO_3 slag is placed upon molten copper containing Sb and As. Therefore, the interfacial oxygen concentration at $t = 0$ is expected to be the value thermodynamically determined by the equilibrium relationship of reaction (3). At an initial oxygen concentration lower than 1230 mass ppm, the interfacial oxygen concentration is too low to eliminate Sb, which coexists with As, at $t = 0$. With progress of the preferential elimination of As, the interfacial oxygen concentration increases due to the transfer of oxygen from the bulk molten copper to the slag-metal interface. For an initial oxygen concentration higher than 1530 mass ppm, even when $t = 0$ where As is preferentially eliminated, there is still sufficient oxygen in the molten copper at the slag-metal interface to allow for simultaneous Sb elimination. When the interfacial oxygen concentration exceeds a critical value represented by the horizontal dot-dash line in Fig. 11, Sb elimination begins. It can be seen from Figs. 11(b) to (f) that the critical interfacial oxygen concentration is around 400 mass ppm under the present experimental conditions. In the case of As not coexisting with Sb in molten copper, Sb can be smoothly eliminated in spite of the initial oxygen

concentration lower than 1230 mass ppm, because the interfacial oxygen concentration at $t = 0$ shows a higher value than the critical concentration, as shown in Fig. 11(a). Based on the results obtained, the concentrations of minor elements at the slag-metal interface, such as the interfacial oxygen concentration, were clarified to affect not only the equilibrium state but also the kinetic behavior of the impurity elimination from molten copper by the use of Na_2CO_3 slag.

4. Conclusions

In order to elucidate the elimination behavior of impurity elements in molten copper by using Na_2CO_3 slag, from a kinetic viewpoint, the rate of As single elimination and simultaneous elimination of As and Sb were measured in an Ar atmosphere at 1523 K. The following results were obtained under the present experimental conditions:

(1) The rate of impurity elimination in this process is greatly affected by a change in the concentrations of the impurity elements and oxygen at the slag-metal interface as the elimination reaction progresses.

(2) In the As single elimination process, As is eliminated from the molten copper into the Na_2CO_3 slag as a pentavalent form ($AsO_{2.5}$), independent of the initial oxygen concentration in the molten copper, and its elimination rate increases with increasing initial oxygen concentration in the molten copper.

(3) From the experimental results for the As single elimination process, its overall rate is considered to be controlled by mass transfer in the molten copper. Based on this assumption, the interfacial concentration of As and oxygen were evaluated using the material balances of As and oxygen in the slag and the molten copper phases and the equilibrium relationship of the Sb elimination reaction at the slag-metal interface. Thus,

the mass-transfer coefficient of As in the molten copper phase at 1523 K was obtained to be:

$$k_{m,\mathrm{As}} = 1.3(\pm 0.4) \times 10^{-4}\,\mathrm{m\cdot s^{-1}}$$

(4) For the simultaneous elimination of As and Sb, the elimination rate of As is much higher than that of Sb. Two types of elimination behavior were observed depending on the initial oxygen concentration in the molten copper (strictly speaking, depending on the oxygen concentration at the slag-metal interface). At relatively low initial oxygen concentrations, As is preferentially eliminated with stagnation of the Sb elimination, whereas both elements are simultaneously eliminated at relatively high initial oxygen concentrations. The interfacial oxygen concentration is too low to eliminate Sb, which coexists with As, at $t = 0$. A lack of oxygen potential at the slag-metal interface due to preferential As elimination gives rise to the initial plateauing of Sb elimination. The oxygen potential at the slag-metal interface, which corresponds to around 400 mass ppm of oxygen concentration, is considered to be required for the elimination of Sb coexisting with As in molten copper.

(5) A lack of oxygen in the molten copper in the process leads to the plateauing of Sb elimination and thermal decomposition of Na_2CO_3 slag. Therefore, it is necessary to raise the oxygen concentration in molten copper in order not only to enhance the elimination rates of impurity elements but also to prevent evaporation loss of the Na_2CO_3 slag.

REFERENCES

1) C. Yamauchi, K. Ohtsuki, T. Fujisawa and H. Sakao: Trans. JIM **29** (1988) 727–734.
2) C. Yamauchi, T. Fujisawa, S. Goto and H. Fukuyama: Maters. Trans., JIM **30** (1989) 175–183.
3) C. Yamauchi, T. Fujisawa, S. Goto, H. Fukuyama and K. Matsuda: J. Japan Inst. Metals **53** (1989) 407–414.
4) T. Fujisawa, T. Kuno, H. Fukuyama, S. Takai and C. Yamauchi: J. Japan Inst. Metals **53** (1989) 558–564.
5) T. Fujisawa, H. Fukuyama, T. Kato, Y. Ikitsu and C. Yamauchi: Maters. Trans., JIM **33** (1992) 683–690.
6) H. Fukuyama, T. Fujisawa and C. Yamauchi: J. Japan Inst. Metals **57** (1993) 521–526.
7) H. Fukuyama, M. Tonsho, T. Fujisawa and C. Yamauchi: Metall. Rev. MMIJ **10-2** (1993) 72–86.
8) T. Fujisawa, H. Fukuyama, J. Shimotori and C. Yamauchi: Maters. Trans., JIM **35** (1994) 414–422.
9) H. Fukuyama, E. Wada, T. Fujisawa and C. Yamauchi: Maters. Trans., JIM **35** (1994) 603–610.
10) H. Fukuyama, E. Wada, T. Fujisawa and C. Yamauchi: Maters. Trans., JIM **36** (1995) 518–523.
11) G. R. Alvear, T. Kanai, H. Fukuyama, T. Fujisawa and C. Yamauchi: Maters. Trans., JIM **35** (1994) 508–515.
12) G. R. Alvear, K. Mizuno, H. Fukuyama, T. Fujisawa and C. Yamauchi: Maters. Trans., JIM **36** (1995) 48–55.
13) G. R. Alvear, K. Suzuki, H. Fukuyama, T. Fujisawa and C. Yamauchi: Maters. Trans., JIM **36** (1995) 524–532.
14) G. R. Alvear, I. Muto, M. S. Bafghi, T. Fujisawa and C. Yamauchi: Shigen-to-Sozai **114** (1998) 726–732.
15) H. Fukuyama, T. Fujisawa and C. Yamauchi: *Metallurgical Processes for the Early Twenty-First Century, Vol. 1. Basic Principles*, ed. by H. Y. Sohn, (TMS, Warrendale, PA, 1994) pp. 443–452.
16) G. R. Alvear, A. Tanaka, H. Fukuyama, T. Fujisawa and C. Yamauchi: Shigen-to-Sozai **115** (1999) 89–96.
17) M. A. Kozlowski and G. A. Irons: Can. Metall. Quart. **29** (1990) 51–65.
18) T. T. Stapurewicz and N. J. Themelis: Metall. Trans. B **21B** (1990) 967–975.
19) M. Tanahashi, Z. Su, K. Takeda, H. Y. Sohn and C. Yamauchi: Metall. Mater. Trans. B **34B** (2003) 869–879.
20) The Japan Inst. Metals: *Kinzoku Databook, Edition 3*, (Maruzen Co. Ltd., Tokyo, 1993) p. 16.
21) T. Azakami and Y. Awakura: *Kinzoku Kagaku Nyumon Series 3, Kinzoku Seiren Kogaku (Extractive Metallurgy)*, (The Japan Inst. Metals, Sendai, 1999) p. 177.
22) K. Itagaki and T. Nishimura: Metall. Rev. MMIJ **3-2** (1986) 29–48.
23) D. C. Lynch: *Arsenic Metall. Fundam. Appl.*, (U.S.A., 1988) pp. 3–33.
24) T. Oishi and K. Ono: Bull. Japan Inst. Metals **25** (1986) 291–299.
25) S. H. Sadat-Darbandi: Ph. D. Dissertation, (T. U. Berlin, Berlin, 1977) pp. 1–107.