Distribution Equilibria of Arsenic and Antimony between Na₂CO₃–Na₂O–SiO₂ Melts and Liquid Copper*

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Following the previous report on phase equilibria between Na₂CO₃–Na₂O–SiO₂ melts and liquid copper, the distribution equilibria of arsenic and antimony have been investigated at 1523 K to investigate the optimum conditions for removal of these detrimental elements from copper by use of soda flux. The obtained results were explained by the terms of oxygen potential and soda-ratio in slag, and iso-bars of the distribution ratios were illustrated on the ternary diagram of (Na₂CO₃+Na₂O)-SiO₂-Cu₂O. The increase in oxygen potential or in basicity of slag results in high removability of these elements. Tri-valent arsenic or antimony is common in the slag with low soda ratio, but penta-valent becomes predominant as the basicity of slag or oxygen potential increases. Pentavalent is more stable for arsenic than for antimony, and bring about drastic variations in the distribution ratio. Sodium carbonate melt under high oxygen potential represents high removability of arsenic and antimony with rather small dissolution of copper. Basic sodium silicate slag has also high removability of these detrimental elements, but copper content in slag is too high under high oxygen potential. High distribution ratio of arsenic and antimony is also observed for Cu₂O slag containing 10 to 20% Na₂O.

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I. Introduction

Arsenic and antimony are well-known detrimental elements in copper metallurgy, and the behavior of these elements during copper smelting has been clarified thermodynamically and from the experimental data(1). It is revealed from both theoretical analysis and practical observations that the contents of these elements in the crude copper are sometimes tend to surpass the limits allowable for electrolytic refining. It has been known that the removal of arsenic and antimony from crude copper can be realized by use of basic soda flux(2-(5)), but the optimum conditions and the detailed mechanisms are not yet clarified although several basic studies have been reported recently(6)-(8).

Following the authors previous report(9) on phase equilibria between liquid copper and Na₂CO₃–Na₂O–SiO₂ melts, the distribution equilibria of arsenic and antimony are discussed in the present paper. The experimental procedures were the same as described in the previous report(9), and the equilibrium experiments were always carried out at 1523 K under a flow of Ar gas.

II. Distribution Thermodynamics

The slag-metal distribution of a minor element X having the valence of 2v is discussed on the basis of the following reaction:
The equilibrium constant $K$ is expressed in terms of the activities, $a$, and the oxygen partial pressure, $p_{O_2}$:

$$K = \frac{a_{XO}}{(a_X \cdot p_{O_2}^{1/2})}$$

where $p_{O_2}$ is defined by $P_{O_2}(Pa)/P^*_{O_2}$, and $P^*_{O_2}$ denotes the standard oxygen pressure of 101325 Pa O$_2$ in this paper. The distribution ratio of X between slag and liquid copper is described as follows:

$$L_{X/Cu}^{\%} = \frac{(\%)_X}{(\%)_X} = \frac{K(n_T)[y_X]p_{O_2}^{1/2}}{[n_T](y_{XO})},$$

where ( ) and [ ] denote the values in slag and metal phases, respectively, and $n_T$ is the total mole number of the constituents in 100 g of each phase. The activity coefficient of arsenic or antimony in liquid copper is $[y_{As}] = 0.004$ or $[y_{Sb}] = 0.03(10)$, respectively. Because of these extremely small values of $[y_X]$, arsenic and antimony in liquid copper are generally difficult to remove into slag. However, when the slag is the basic soda system, the activity coefficient, $y_{XO}$ of arsenic or antimony oxide which is of acidic character becomes extremely small. Thus, a considerable large value of $L_{X/Cu}$ is expected, and removal of arsenic and antimony is accomplished.

### III. Experimental Results and Discussions

#### 1. Distribution ratios between soda slag and liquid copper

The phase relations in the (Na$_2$CO$_3$ + Na$_2$O)–SiO$_2$–Cu$_2$O system equilibrating with liquid copper, reported previously, are reproduced in Fig. 1 together with iso-bars of the distribution ratio of arsenic which will be mentioned later. Figure 2 shows the distribution ratios of arsenic and antimony in liquid copper for the (Na$_2$CO$_3$ + Na$_2$O)–SiO$_2$–Cu$_2$O system at 1523 K.
arsenic and antimony between soda slag and metallic copper in relations to the oxygen potential and "soda-ratio". The soda-ratio is defined by eq. (4) as discussed in the previous report:

$$\text{soda-ratio} = \frac{n_{\text{Na}_2\text{X}}}{n_{\text{Na}_2\text{X}} + n_{\text{SiO}_2}}$$  \hspace{1cm} (4)

where $n$ is the mole number and X corresponds O and CO$_3$. The small regions shown by triangle abc and crescent shaped def found on the upper right of each figure correspond to the miscibility gaps abc and def in Fig. 1, and the distribution ratios in these regions will be discussed hereafter.

Varied information can be obtained from Fig. 2. Arsenic and antimony are concentrated mainly in the liquid copper phase when both of oxygen potential and soda-ratio are low, but principally in the slag phase under the conditions of high oxygen potential and high basicity of the slag. The removal of arsenic from crude copper seems to be much easier than that of antimony because the distribution ratio of arsenic is one to two orders of magnitude higher. Even at a lower oxygen potential, the removal of these elements may be realized by the use of basic soda slag, but is rather difficult with acidic slag. As shown in Fig. 2, the distribution ratios for calcium ferrite or iron silicate slag are also similar to or somewhat lower than those for the slag with a soda-ratio of 0.33. The distribution ratios increase as the soda-ratio in the silicate slag increases, but those for carbonate melt as shown by the closed marks are not necessarily high in the region of lower oxygen potentials.

Based on eq. (3), the valence of arsenic and antimony dissolved in the slag are estimated from the slopes of the curves in Fig. 2. The increases in oxygen potential and soda-ratio tend to increase the valence of the dissolved species although tri-valent oxidic arsenic or antimony seems to be most common in the slag. Pentavalent is very stable for arsenic than antimony.

It is evident from Fig. 2 that the distribution ratios in general are not different in the region of soda-ratios between 0.33 and 0.4 or 0.5, but are different distinctly when penta-valent arsenic or antimony is participating under a higher oxygen potential. This may be attributed to the fact that the penta-valent oxide is more acidic than tri-valent. It is also suggested from the figure than the dependence of the distribution ratios on soda-ratio is larger for arsenic than for antimony, suggesting that oxides of arsenic are more acidic than those of antimony. It is interesting to note the general behavior that the dependence of the distribution ratio on oxygen potential, temperature or basicity of slag becomes drastic for higher valence of the dissolved species.

The curves in Fig. 2 become flatten under extremely high oxygen potential where a considerable amount of cuprous oxide is dissolved in the slag as shown in the previous report. On the other hand, under an extremely low oxygen potential, the curves tend also to be flat-
The distribution ratios between liquid copper and the sodium silicate slag containing less than 20% iron oxide are plotted in the region of low oxygen potentials. These distribution ratios were obtained in the presence of solid iron, and the experimental condition and the precise data will be given elsewhere. The distribution ratios were also determined by use of a graphite crucible under a current of CO gas \((\log p_{O_2} = -16.8)\), and the values of \(10^{-3}\) to \(10^{-4}\) were obtained for both arsenic and antimony. The experimental proofs are not necessarily sufficient, but the distribution ratios at low oxygen potential may be assumed to converge at a level of \(\log L = -4\) without any dependence on oxygen potential.

As shown in Fig. 6 of the previous report(9), the logarithmic concentration of copper in slag generally has a linear relation to the oxygen potential with the slope of 1/4, suggesting the monovalent oxidic dissolution in slag. Accordingly, the abscissa in Fig. 2 may be replaced by the content of copper in slag to represent the relation between the removability of arsenic or antimony and the loss of copper in slag. As shown in Fig. 3, the increase of the soda-ratio in slag may serve to increase the removability of arsenic or antimony with a low level of copper loss in slag. Plain sodium carbonate melt would be quite promising from this point of view. Figure 3 shows the variation in the valence of dissolved arsenic or antimony and the difference in the distribution ratios between arsenic and antimony as explained already for Fig. 2.

The logarithmic values of the distribution ratios of arsenic and antimony are plotted on ternary diagrams for the \((Na_2CO_3 + Na_2O) - SiO_2 - Cu_2O\) system as shown in Figs. 1 and 4, respectively. From the iso-bars for the distribution ratio, it is also observed that the effect of the concentrations of soda and cuprous oxide on the distribution ratio of arsenic is greater than on the case of antimony.

2. Distribution ratios in the systems including \(Cu_2O\) slag

It is well known that liquid copper separates cuprous oxide under a higher oxygen potential. As explained in the previous report(9), miscibility gaps are observed between cuprous oxide slag and sodium carbonate or silicate as shown in Fig. 1 and Fig. 4. Thus, the distribution ratios of arsenic and antimony were also determined for various systems containing cuprous oxide slag.

(1) Distribution ratios in \(Cu_2O - Na_2O\) and \(Cu_2O - SiO_2\) systems

In Fig. 5 the logarithmic values of the distribution ratios of arsenic and antimony are plotted against the content of \(SiO_2\) or \(Na_2O\) in the binary cuprous oxide slag. The values plotted at the extreme left on the ordinate correspond to the distribution ratios in the plain \(Cu_2O - Cu\) system, and \(L_{As/Cu} = 3\) for arsenic and...
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As the literature values, Heinrich et al. (11) and Tani et al. (12) reported $L_{\text{s,Cu}}$ = 4, while for $L_{\text{s,Sb}}$ the value of 8 by Mann et al. (13), 7 by Heinrich et al. (11), and 10 by Tani et al. (12) are available.

The addition of SiO$_2$ to the Cu$_2$O melt increases the distribution ratio slightly, but the distribution ratio remains nearly constant. On the other hand, a drastic increase in the distribution ratio is observed by the addition of basic Na$_2$O, especially for arsenic. Pentavalent arsenic is separated from the liquids as a stable compound of 3Na$_2$O·As$_2$O$_5$, which has extremely small solubility in the Cu$_2$O melt.

(2) Distribution ratios among carbonate, Cu$_2$O slag, and liquid copper

The distribution equilibria among three liquid phases in the region abc in Figs. 1 and 4 were determined, and the obtained distribution ratios of arsenic and antimony between each of the two phases are illustrated in Fig. 6 in relation to the soda-ratio in the carbonate melt. As suggested from Fig. 2, pentavalent arsenic and antimony are expected in such highly basic melts under high oxygen potential. Usual metal oxide can hardly be dissolved in the carbonate melt, but as shown in the top...
Fig. 6 Logarithmic distribution ratios of As and Sb between sodium carbonate salt and Cu$_2$O-base slag (top figure), between sodium carbonate salt and metallic copper (middle figure) and between Cu$_2$O-base slag and metallic copper (bottom figure) against soda-ratio in sodium carbonate salt at 1523 K.

Fig. 7 Logarithmic distribution ratios of As and Sb between sodium silicate slag and Cu$_2$O-base slag (top figure), between sodium silicate slag and metallic copper (middle figure) and between Cu$_2$O-base slag and metallic copper (bottom figure) against soda-ratio in sodium silicate slag at 1523 K.

In Fig. 6, arsenic and antimony oxides are more concentrated in the carbonate melt than in the oxide slag. Extremely high distribution ratios shown in the middle and bottom figures suggest that complete elimination of arsenic and antimony from liquid copper is expected from the three liquid equilibria.

3. Summation of removability of arsenic and antimony by soda slag

The iso-bars of the distribution ratios of arsenic and antimony were also determined taking into account the data obtained in the region of miscibility gaps. The results are shown in Figs. 1 and 4, and the axis connecting between SiO$_2$ and (Na$_2$CO$_3$+Na$_2$O) corresponds approximately to the iso-bar of log $L$ = -3 to -4 in both figures.

The effects of the soda-ratio on the distribution ratios are rearranged in Fig. 8 at log $p_{O_2}$ = -5 and -8. The top figure shows the fractions of the remaining CO$_2$ in the melt. At a lower oxygen potential of log $p_{O_2}$ = -8, the distribution ratios increase sharply with increasing soda-ratio from 0.5 to 0.7, but decrease again when the value of soda-ratio is beyond 0.75. Thus, the sodium silicate slag with soda-ratio 0.75 will be the best for the
removal of arsenic and antimony at a lower oxygen potential, although the copper content in the slag is more than 10% at log \( p_{O_2} = -8 \).

At a higher oxygen potential of log \( p_{O_2} = -5 \), the distribution ratios of arsenic and antimony increase with increasing soda-ratio, and represent maximum values in the sodium carbonate melt. On the other hand, the copper content in the silicate slag is extremely high at a higher oxygen potential, but becomes minimum in the carbonate melt. Accordingly, the sodium carbonate melt will be most effective in removing arsenic and antimony at a higher oxygen potential with a rather low copper loss.

As shown in Fig. 3, the solubility of oxide in the liquid carbonate is generally very small. The dissolution of the trivalent oxide of arsenic or antimony is also low in carbonate even these oxides are acidic slightly, but that of the penta-valent oxide of high acidity is sharply increasing with oxygen potential as shown in Fig. 2. The difference observed in Fig. 8 between log \( p_{O_2} \) of \(-8\) and \(-5\) may be explained in terms of the copper content in slag relating to the slag basicity and acidity and the valence of the solute oxide. The high removability of arsenic and antimony is observed when they are not in the trivalent state, and the high oxygen potential, low temperature and high basicity of the solvent are deemed favorable for the stabilization of the penta-valent species.

As another possibility to get high removability of arsenic and antimony, the \( Cu_2O \) slag containing \( Na_2O \), the melt in the region a or f in Fig. 1 may be considered. A small amount of the required soda flux is also thought to be for this \( Cu_2O \) slag, although a considerable amount of cuprous oxide must be recycled.

IV. Summary

The distribution ratios of arsenic and antimony between sodium carbonate or silicate slag and liquid copper were determined at \( 1523 \text{ } K \) under varying oxygen potentials. The obtained distribution ratios were explained in terms of the oxygen potential and the soda-ratio, and iso-bars of the distribution ratios are illustrated in the ternary diagram of \( (Na_2CO_3+Na_2O)-SiO_2-Cu_2O \). Increasing the oxygen potential and basicity results in increasing the stability of higher valence dissolved species and the removability of arsenic and antimony from crude copper. The penta-valent of arsenic is more stable than that of antimony, the distribution ratio and its dependence on oxygen potential and basicity are higher for arsenic than antimony. From the experimental values of distribution ratios, the following three conditions are considered to be essential to achieve high removability of arsenic and antimony:

1. Basic sodium silicate slag under medium oxygen potential.
2. Sodium carbonate melt at high oxygen potential.
3. \( Cu_2O \) slag containing 10 to 20% \( Na_2O \).
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