Phase Equilibrium and Minor Element Distribution between Slag and Copper Matte under High Partial Pressures of SO_2

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ABSTRACT

As a fundamental study for the oxygen-blowing copper smelting, the phase equilibrium between slag, SiO_2-FeO_x, SiO_2-CaO-FeO_x and CaO-FeO_x, and copper matte was investigated at 1573 and 1523 K under the partial pressures of SO_2 with 10.1, 50.7 and 101.3 kPa, using a sulfur reservoir for controlling the partial pressure of S_2. An oxygen-sulfur potential diagram was constructed in relation to matte grade{mass %X in matte}, and it was clarified that the ratio of (p_{O_2}/p_{S_2}) was constant against p_{SO_2} when the matte grade was specified. The solubilities of copper and sulfur in the slag were also determined in relation to the matte grade. They were found to be independent of p_{SO_2} when the matte grade was specified and it was considered that this behavior was ascribable to the constancy of (p_{O_2}/p_{S_2}) against p_{SO_2}. The solubility of sulfur decreased gradually with increasing matte grade. The distribution ratio of some minor elements such as silver, lead, arsenic, antimony and bismuth between slag and copper matte was investigated. When the distribution ratio, $L_x^{s/m}$, is defined as (mass %X in slag) / {mass %X in matte}, $L_x^{s/m}$ is found to change considerably with matte grade. It is clarified that the distribution ratios of lead, arsenic, antimony and bismuth increase remarkably with p_{SO_2} and it is indicated that the proportion of these elements in the slag phase increases with increasing oxygen-enrichment. The results obtained were analyzed successfully by assuming a mutual reaction between a metallic species in the matte and an oxide species in the slag for arsenic, antimony and bismuth. The deviation from experimental results was shown for silver and lead which suggested the mutual reaction between the metallic species in the matte and sulfide species in the slag at the low matte grade for these elements.

I. INTRODUCTION

The use of oxygen or oxygen-enriched air as the blowing gas for copper smelting has the special advantage of fully utilizing the fuel value of the concentrates and producing a smaller amount of the combustion gas with higher strength of SO_2. Hence, the combination of intensive smelting reactors with the use of oxygen has provided a number of improved copper smelting processes such as INCO-Flash, Outokumpu-Flash and Mitsubishi-Continuous Processes.

Phase equilibrium studies for slag and copper matte phases under high partial pressure of SO_2 are of practical importance for thermodynamically discussing the above mentioned oxygen smelting processes. Although a series of experimental studies(1)~(5) were carried out in a restricted condition of p_{SO_2} at about 10.1 kPa which corresponds to the smelting with air blowing, there remain few data on the phase equilibrium under the high partial pressures of SO_2. Tavera and Davenport(6) studied for the fayalite slag and matte phases under the controlled partial pressures of SO_2 at 10.1-101.3 kPa, without controlling the partial pressures of sulfur and oxygen. As suggested by a potential diagram(7) for the Cu-Fe-S-O system at 1523-1573 K, the partial pressure of S_2 in the gas equilibrated with the slag and matte phases under high SO_2 pressure is considerably high at 10-1000 Pa. This condition is likely to need the controlling of p_{S_2} or p_{O_2} as well as p_{SO_2} in the equilibrium experiments, otherwise, the equilibrium is hardly attained due to the continued flushing of sulfur from the system.

The objective of the present work has been to extend the slag-matte studies from the air-blowing condition at about 10.1 kPa into the oxygen-smelting condition at p_{SO_2} with more than 10.1 kPa. The partial pressure of S_2 gas was controlled by means of the liquid sulfur reservoir through which a stream of the controlled SO_2 gas passed before entering into the matte/slag system. The phase equilibrium between the copper matte and slag with Q=%CaO/(%CaO+SiO_2)=0, 0.35 and 1 as well as the distribution ratios of Ag, Pb, As, Sb and Bi between both phases were investigated at 1523-1573 K under the controlled partial pressures of SO_2 at 10.1, 50.7 and 101.3 kPa.

II. EXPERIMENTAL

The mixture of Ar-SO_2-S_2 gas was used to control p_{SO_2} and p_{S_2}. Accordingly, p_{O_2} was also fixed at a given value, based on an equilibrium relationship for the reaction of $1/2S_2(g)+O_2(g)=SO_2(g)$. Although the mixture of CO_2-H_2-SO_2-Ar gas(1) was available for controlling p_{SO_2}, p_{S_2} and p_{O_2}, its use will be restricted to the system under considerably low p_{SO_2} and p_{S_2}.

The mixture of SO_2 and Ar gas with a flow rate of 2.2-3.0x10^{-6} m^3/s was passed through the reservoir with liquid sulfur which was kept at a given temperature. The gas after passing the reservoir was led to the slag / matte system at 1523-1573 K through a glass tube which was heated at 320-340 K to prevent the condensation of sulfur. Judging from the result of a thermodynamic calculation for the dissolution equilibrium between the polyatomic gas species of sulfur, it was considered that the evaporated sulfur could be completely dissociated into the diatomic gas after entering into the reaction system at 1523-1573 K. The relation between the partial pressure of S_2 at 1523-1573 K and the temperature of the reservoir was determined previously by measuring the weight of sulfur in a duplicated glass condenser immersed in an ice bath, which was condensed from a given amount of argon gas passing through the reservoir

FeS and Cu_2S for the matte components were made pyrometallurgically from the metals and sulfur with 99.9 mass % purity. The molten slags with Q=(%CaO/(%CaO+SiO_2))=0, 0.35 and 1 were synthesized in iron crucible. 8 g of the slag and an equal amount of the matte composed of FeS and Cu_2S were put in a MgO crucible with an inner diameter of 22 mm and a height of 60 mm. To make the equilibrium between the slag and matte phases in a limited time, the copper content (matte grade) in the starting matte was adjusted to be higher than that in the equilibrium state because P_{S_2} in the inlet gas was considerably high at 10-1000 Pa and the amount of sulfur required to sulfidize the iron oxide in the slag phase could be provided easily to the reaction system. It was found in the preliminary experiment that the equilibration was made in 144 ks when the copper content in the starting matte was about 3% higher than that in the equilibrated one. Hence, the sample was heated at 1523-1573 K for 162 ks in the present experiments. After that, it was cooled rapidly by flushing a large amount of argon gas onto a surface of the slag layer with a flow rate of more than 5×10^{-3} m^3/s to prevent the segregation of the slag components during the solidification.

An optical microscopic observation, an EPMA analysis and chemical analyses were made for the solidified matte and slag specimens. The copper content in the matte was determined by titration with EDTA. Sulfur was analyzed gravimetrically after precipitation as barium sulfate. Iron was titrated with potassium dichromate. Calcium and magnesium and the minor elements of silver, lead, arsenic, antimony and bismuth in the matte and slag phases as well as copper in the slag phase were determined by ICP.

As to the minor element distribution, preliminary experiments were conducted to find out the possibility of multiply adding the minor elements to the charge. Two combinations of silver and lead and arsenic, antimony and bismuth were tested and it was found for each combination that the multiple additions with 1.5 mass % of the charge gave no effect on the distribution ratio of each component. Hence, two series of experimental runs were made in this study. A total of about 0.19 g of silver and lead and about 0.44 g of Cu_3As, CuSb and bismuth were added into sample, respectively.

III. EXPERIMENTAL RESULTS

1. Phase Separation into Slag and Matte

The slag with Q (%CaO/(%CaO+SiO_2)) of 0 separated completely from the matte with the copper content between 0 and 80%, at the P_{SO_2} of 10.1, 50.7 kPa. While, at P_{SO_2}=101.3 kPa,the slag and the matte with copper content less than 25% dissolved each other. The starting slag had the composition of 35%SiO_2 and 65%FeO. After equilibration, the excess SiO_2 floated on the top of slag layer. This means that the equilibration with the copper matte was made under a condition of SiO_2 - saturation. The SiO_2 content in the equilibrated slag was between 32 and 37% and has a tendency to slightly decrease with decreasing matte grade. The MgO solubility in the slag was between 4 and 8% .

The slag with Q=0.35 separated completely from the matte with the copper content between 0 and 80% at P_{SO_2} of 10.1, 50.7 and 101.3 kPa. The starting slag had the composition of 39%SiO_2, 40%FeO and 21%CaO. Owing to the low solubility of calcium in the matte and because the amount of the matte changes from that of the starting matte, the iron content in the slag decreased and it was between 20 and 24%. The solubility of MgO in the slag was between 10 and 15%.

In the experiments for the slag with Q=1, the calcium content in the starting slag was almost constant at about 16.5%(23%CaO). Because the calcium content in the equilibrated matte was at most 2.4% when the matte grade is 52.5% Cu, the slag after equilibration had almost 10%Ca. It was found that the phase relation between the copper matte and the slag with Q=1 represented a quite different feature in which the mutual dissolution occurred when the matte grade was low. The phase separation initiated when the matte grades were higher than 50, 60 and 70 mass % Cu at P_{SO_2}=10.1, 50.7 and 101.3 kPa, respectively. It should be noted that the grade of matte after equilibration, at which the phase separation initiated, increased with increasing P_{SO_2}. The solubility of MgO in the CaO-FeO_X slag was found to be considerably small at about 3%.

2. Relation between Matte grade and P_{S_2} or P_{O_2}

For given P_{SO_2} of 10.1, 50.7 and 101.3 kPa, the relations between the matte grade and P_{S_2} as well as P_{O_2} which was calculated by using an equilibrium constant(7) of the reaction, $1/2S_2(g)+O_2(g)=SO_2(g)$, are shown in Fig. 1(a), (b) and (c) for the slags with Q of 0, 0.35 and 1, respectively. It is noted in a general tendency that P_{S_2} decreases with increasing matte grade while P_{O_2} increases and the decrement of P_{S_2} and the increment of P_{O_2} are remarkable when the matte grade is over 75% Cu . At a given matte grade, P_{O_2} and P_{S_2} increase with increasing P_{SO_2}. These relationships are very similar among the slag systems with Q of 0, 0.35 and 1. This may be ascribed to a similarity in the constituents of the matte phases equilibrating with these slags. The mattes are considered to be fundamentally composed of Cu_2S, FeS and FeO_X(1), and P_{S_2} over the matte phase will be almost same when the matte grade is specified.

3. Solubility of Copper and Sulfur in Slag

Solubility of copper in the slag was determined in relation to the matte grade as shown in Fig. 2(a), (b) and (c) for the slags with Q of 0, 0.35 and 1, respectively. The copper content in the slag with Q=0 increases with increasing matte grade and shows a maximum around 25-30% Cu in matte then decreases slightly in the region of matte grade between 30 to 60% Cu, and increases abruptly in the region of higher matte grade. The solubility is likely to be independent of the partial pressure of SO_2 within the scatter of experimental points. The present results under P_{SO_2} of 10.1 kPa agree well, as a whole, with those by Kaiura and co-workers(1), which was reported to have a maximum at about 35% Cu in matte.

The copper solubility with Q of 0.35 changes against the matte grade in a similar way as that in the slag with Q of 0 and also seems to be independent of P_{SO_2}. On the contrary, the slag with Q of 1 has the copper solubility which decreases with increasing matte grade up to about 73% Cu and increases abruptly in the region of higher matte grade. As shown in Fig. 2(c) with a dash-dot line, the data determined by Acuna and Yazawa(2) under P_{SO_2} of 10.1 kPa agree fairly well with the present results.

When the copper solubilities at a given matte grade in its higher region were compared among the slag systems with different Q, the system with Q of 0.35 represents the smallest solubility.

The solubilities of sulfur in the slags with Q of 0, 0.35 and 1 are shown in Fig. 3(a), (b) and (c), respectively, in relation to the matte grade. The solubility represents a general tendency to decrease simply with increasing matte grade and is likely to be independent of P_{SO_2}. Yazawa and co-workers(1),(2) determined the sulfur solubility in the slags with Q of 0 and 1 under P_{SO_2} of 10.1 kPa, as shown in Fig. 3(a) and (c) with dash-lines and dash-dot-lines, respectively. The tendency against the matte grade agrees well with the

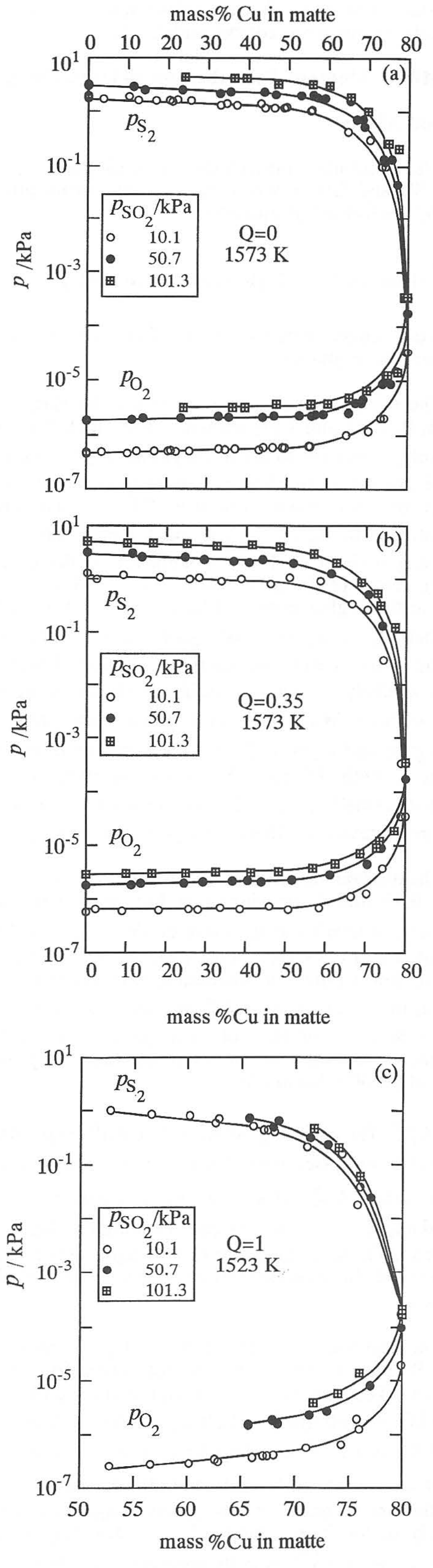

Fig. 1 Relation between oxygen or sulfur partial pressure and copper content in the matte under p_{SO_2} of 10.1, 50.7, 101.3 kPa, for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

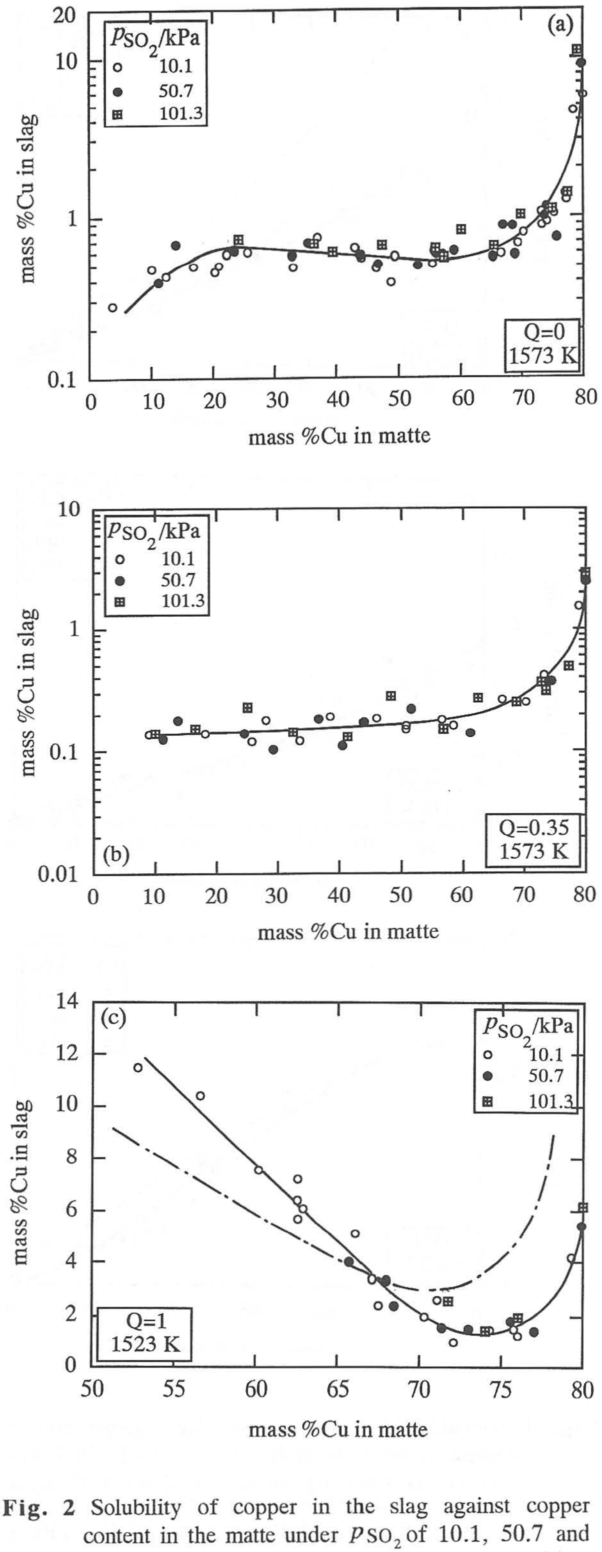

Fig. 2 Solubility of copper in the slag against copper content in the matte under p_{SO_2} of 10.1, 50.7 and 101.3 kPa for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K (—— - ——: Acuna *et al.*(2) under p_{SO_2} of 10.1 kPa at 1523 K).

present one. It is noted that the sulfur solubility at a given matte grade increases remarkably with Q=1.

4. Minor Element Distribution between Slag and Matte

The distribution ratio of the minor element X (X: Ag, Pb, As, Sb and Bi) between the slag and matte phases is defined by the following equation,

$$L_X^{s/m} = (\text{mass\% X in slag})/\{\text{mass\% X in matte}\} \qquad (1)$$

and was determined from the results of chemical analysis for the slag and matte phases.

The distribution ratios of silver for the slag systems with Q of 0, 0.35 and 1 are shown in Fig. 4(a), (b) and (c), respectively, in relation to the matte grade. $L_{Ag}^{s/m}$ for the slags with Q of 0 and 0.35 are almost constant against matte grade in the range of matte grade less than 60% Cu but increase considerably in the higher matte grade. On the contrary, $L_{Ag}^{s/m}$ for the slag with Q of 1 has a tendency to decrease with increasing matte grade up to about 75-77% Cu, and then increase in the higher matte grade. It is noted for each slag system that $L_{Ag}^{s/m}$ at a given matte grade does not change very much with P_{SO_2} within the scatter of the experimental data though it is likely to increase slightly with increasing partial pressure of SO_2. When $L_{Ag}^{s/m}$ at a given matte grade in its higher region and a given P_{SO_2} were compared among the slag systems with different Q, the system with Q of 0.35 represents the smallest $L_{Ag}^{s/m}$. This is considered to be ascribed to the largest activity coefficient of $AgO_{0.5}$ in the slag(8).

The distribution ratios of lead for the slag systems with Q of 0, 0.35 and 1 are shown in Fig. 5(a), (b) and (c), respectively, in relation to the matte grade. $L_{Pb}^{s/m}$ for the slag with Q of 0 and 0.35 are almost constant against the matte grade in its lower range but increase remarkably in the higher range. On the other hand, $L_{Pb}^{s/m}$ for the slag with Q of 1 represents the minimum value at a matte grade with about 73% Cu and increases remarkably in its higher range, approaching around 1 at the 80% Cu grade.

$L_{Pb}^{s/m}$ for each slag system is clearly dependent on P_{SO_2} and it increases with P_{SO_2} when a matte grade is specified. When $L_{Pb}^{s/m}$ at a given matte grade in its higher range and a given P_{SO_2} are compared among the slag systems with different Q, the system with Q of 0 represents the largest value owing to the smallest activity coefficient of PbO in the acidic slag.

The distribution of arsenic in the slag systems with Q of 0, 0.35 and 1 are shown in Fig. 6(a), (b) and (c), respectively. The content of arsenic in the slags under P_{SO_2} of 101.3 kPa was so small in the range of low matte grade less than 35% Cu that $L_{As}^{s/m}$ could not be determined in this range. $L_{As}^{s/m}$ for the slags with Q of 0 and 0.35 are almost constant against the matte grade in its lower range but decrease remarkably in the higher range. It is noteworthy that this abrupt decrease in $L_{As}^{s/m}$ is quite opposite to the behaviors of $L_{Ag}^{s/m}$ and $L_{Pb}^{s/m}$ which increase abruptly in the higher range. $L_{As}^{s/m}$ for the slag with Q of 1 is likely to represent the

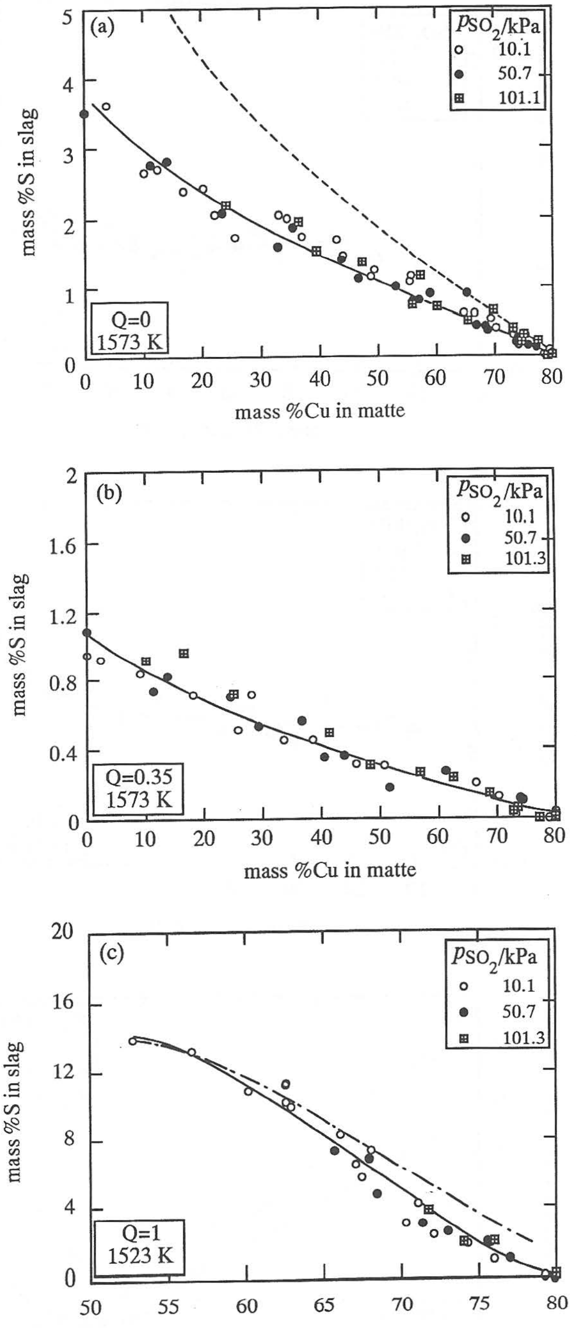

Fig. 3 Solubility of sulfur in the slag against copper content in the matte under P_{SO_2} of 10.1, 50.7 and 101.3 kPa for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K
(------ : Kaiura *et al.*(1) under P_{SO_2} of 10.1 kPa at 1573 K).
(—·— : Acuna *et al.*(2) under P_{SO_2} of 10.1 kPa at 1523 K).

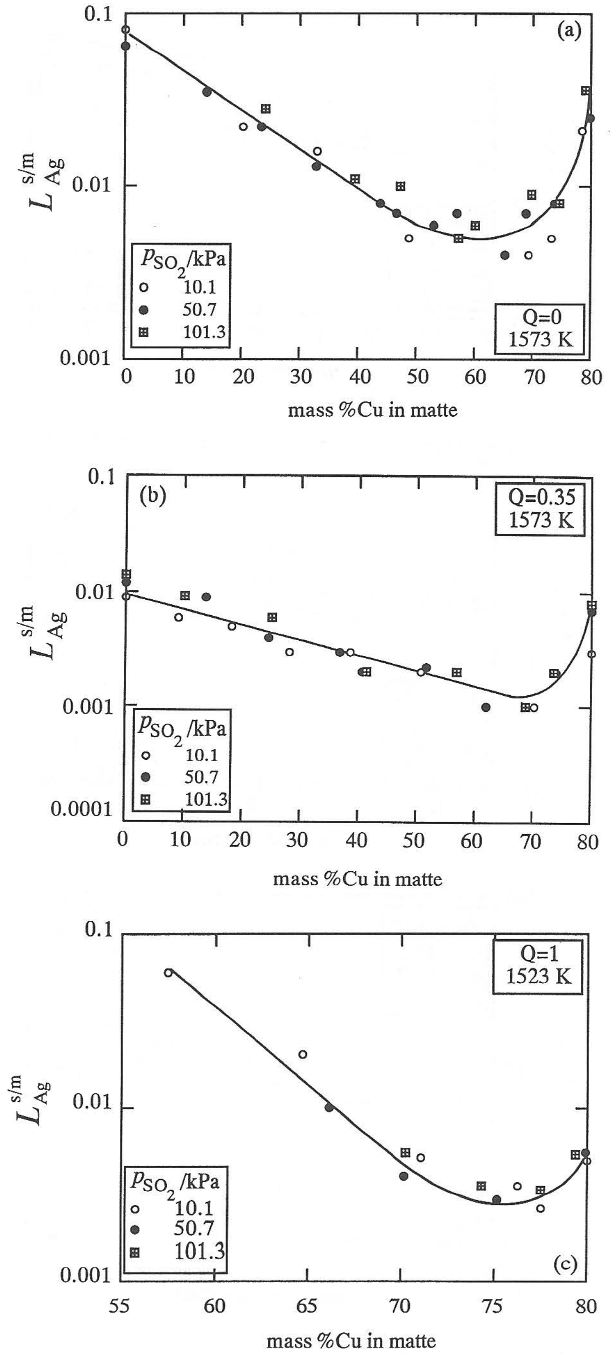

Fig. 4 Distribution ratio of Ag between slag and matte against matte grade for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

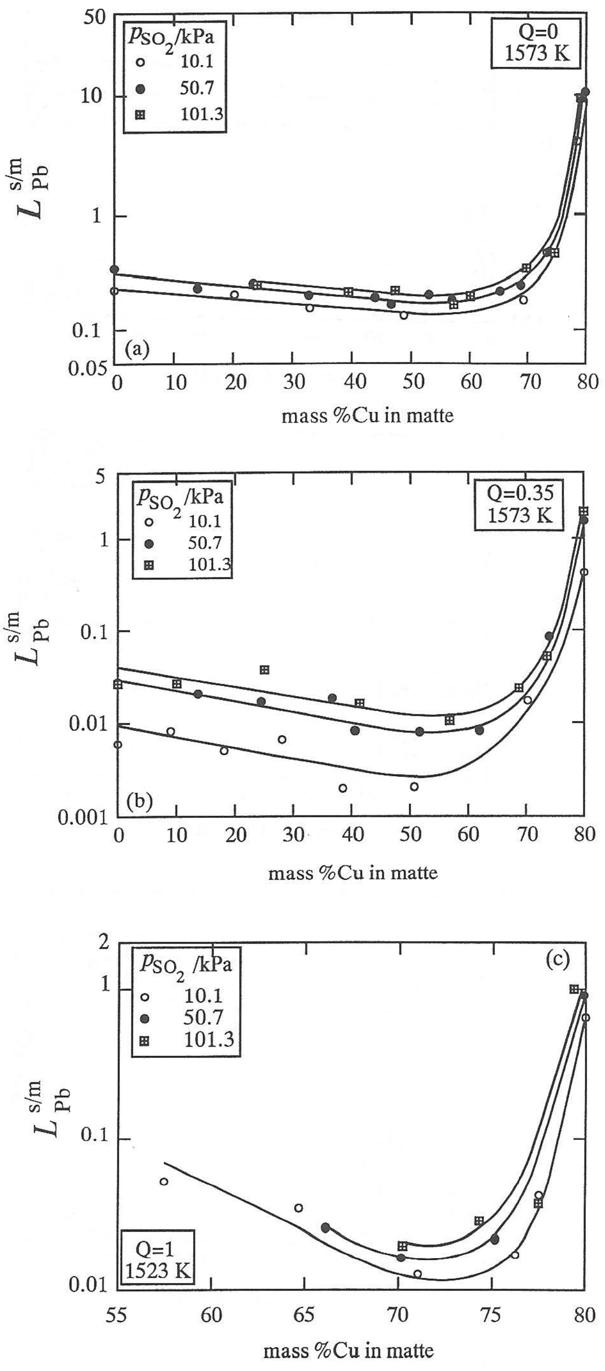

Fig. 5 Distribution ratio of Pb between slag and matte against matte grade for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

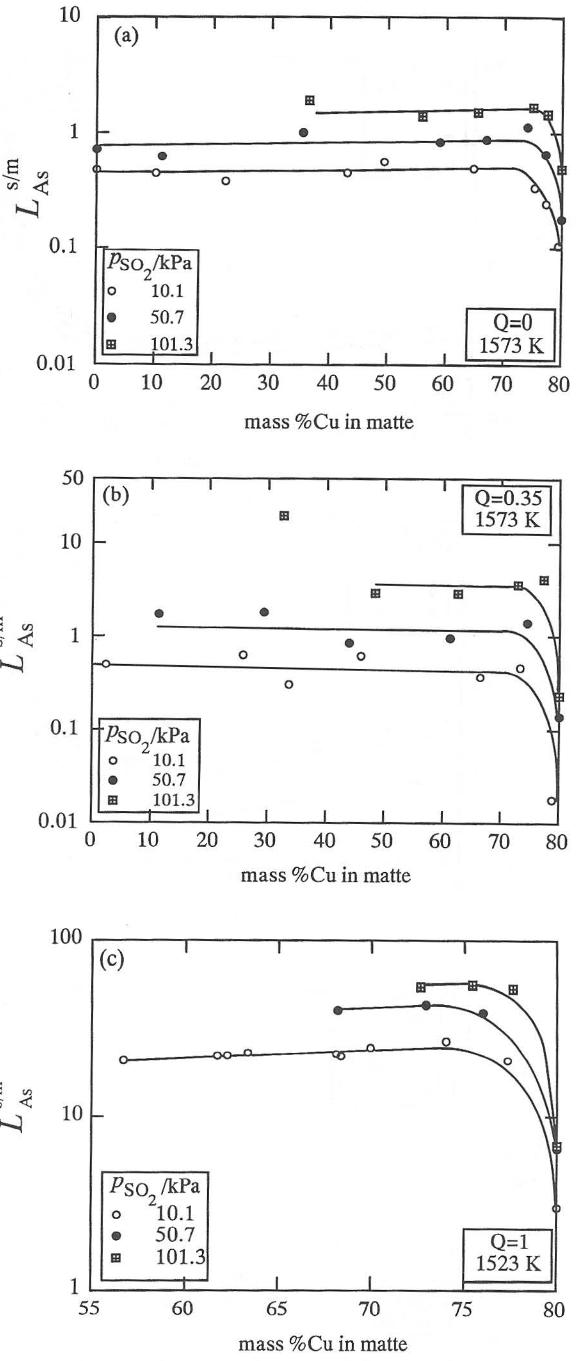

Fig. 6 Distribution ratio of As between slag and matte against matte grade for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

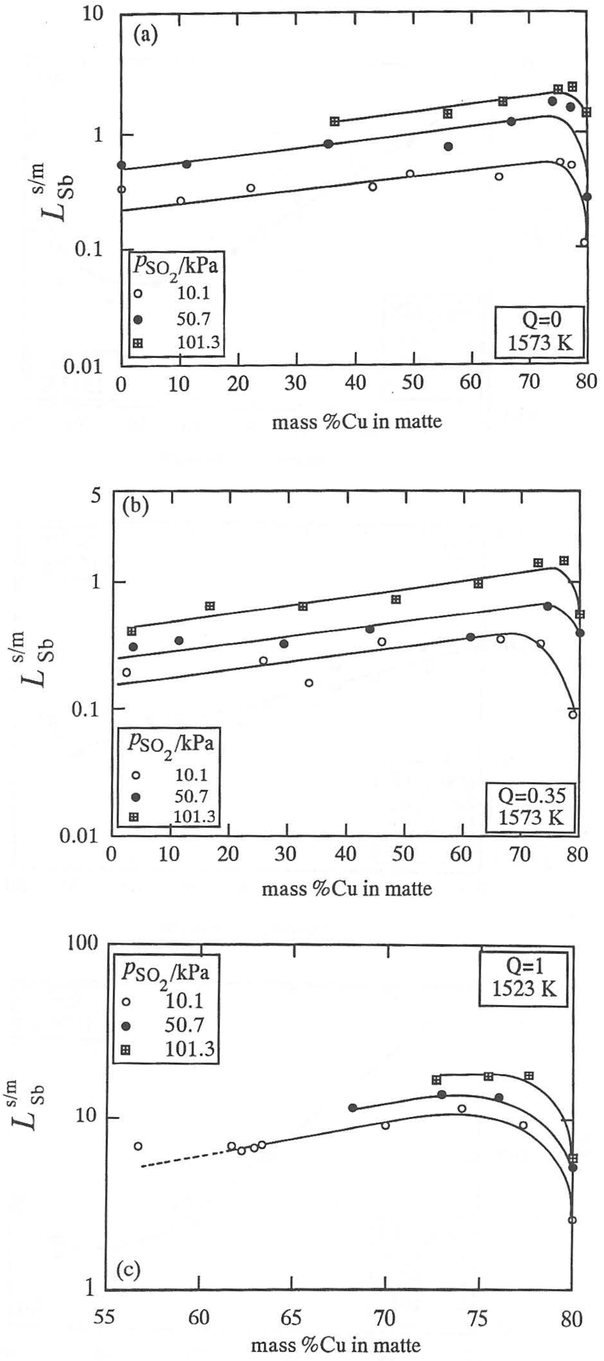

Fig. 7 Distribution ratio of Sb between slag and matte against matte grade for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

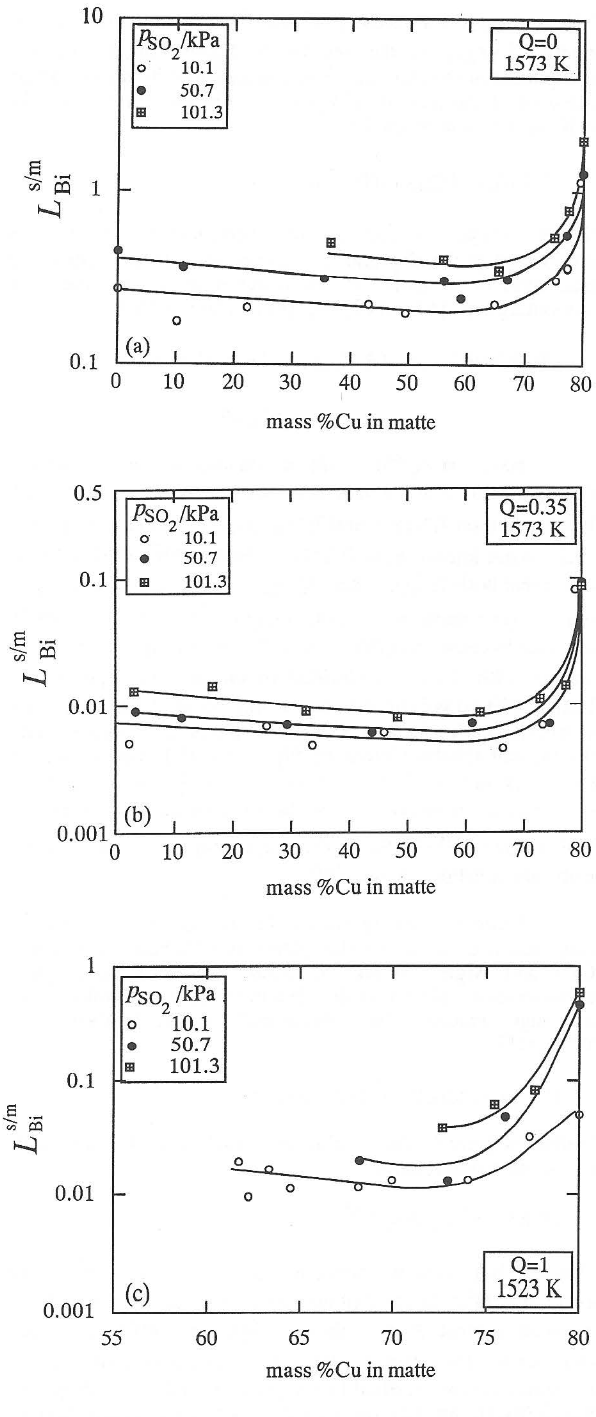

Fig. 8 Distribution ratio of Bi between slag and matte against matte grade for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K.

maximum at about 73-75% matte grade and then decreases remarkably in the range of higher matte grade.

The dependency on p_{SO_2} is also observed for the distribution of arsenic for each slag system and it is more remarkable than for $L^{s/m}_{Ag}$ and $L^{s/m}_{Pb}$. When $L^{s/m}_{As}$ at a given matte grade and a given p_{SO_2} are compared among the slag systems, it is found that $L^{s/m}_{As}$ increases with increasing Q, that is, as the basicity of the slag increases.

As shown in the Fig. 7(a), (b) and (c), the distribution ratios of antimony represent the behaviors against the matte grade and the partial pressure of SO2 which are very similar to those for $L^{s/m}_{As}$. $L^{s/m}_{Sb}$ decreases remarkably with increasing matte grade in it higher range.

The distribution ratios of bismuth for the slag systems with Q of 0, 0.35 and 1 are shown in Fig. 8 (a), (b) and (c), respectively. Although bismuth, along with arsenic and antimony, belongs to the Vb group in the periodic table, $L^{s/m}_{Bi}$ behaves quite oppositely against the matte grade, that is, it increases abruptly with increasing matte grade in its higher range. This behavior is very similar to that of $L^{s/m}_{Pb}$, as shown in Fig. 5, but the dependency on p_{SO_2} is more remarkable than for $L^{s/m}_{Pb}$.

IV. DISCUSSION

1. log p_{O_2} - log p_{S_2} Potential Diagram

The relation between p_{S_2} and p_{O_2} in the slag/matte equilibria is given by the following equations.

$$FeO(l)+1/2S_2(g)=FeS(l)+1/2O_2(g) \qquad (2)$$

$$\log p_{O_2}=\log p_{S_2}+2\log K_2+2\log(a_{FeO}/a_{FeS}) \qquad (3)$$

where K_2 is the equilibrium constant for the reaction (2), and a_{FeO} and a_{FeS} are activities of FeO and FeS, respectively. In a case that, at a given matte grade, the activity ratio (a_{FeO}/a_{FeS}) is constant against p_{SO_2}, the log p_{O_2} - log p_{S_2} plots for the given matte will present a straight line with a slope of unity, that is, log(p_{O_2}/p_{S_2}) will be constant.

Based on the experimental results shown in Fig. 1 (a), (b) and (c), log p_{O_2} - log p_{S_2} potential diagrams are illustrated in Fig. 9 (a), (b) and (c) for the slag systems with Q of 0, 0.35 and 1, respectively. It is noteworthy for each slag system that log p_{O_2} - log p_{S_2} plots are located approximately on a straight line with a slope of unity for each matte. This indicates that (a_{FeO}/a_{FeS}) and (p_{O_2}/p_{S_2}) are constant against p_{SO_2} at each matte grade. This result has important meaning in the following discussion on the dissolutions of copper and sulfur in the slag.

2. Solubility of Copper and Sulfur in Slag

The solubility of copper in the slag, (%Cu), is given by the sum of an oxidic part, $(\%Cu)_O$, and a sulfidic part, $(\%Cu)_S$, as follows.(9),(10)

$$(\%Cu)=(\%Cu)_S+(\%Cu)_O \qquad (4)$$

From the following reaction,

$$CuS_{0.5}(l)+1/4O_2(g)=CuO_{0.5}(l)+1/4S_2(g) \qquad (5),$$

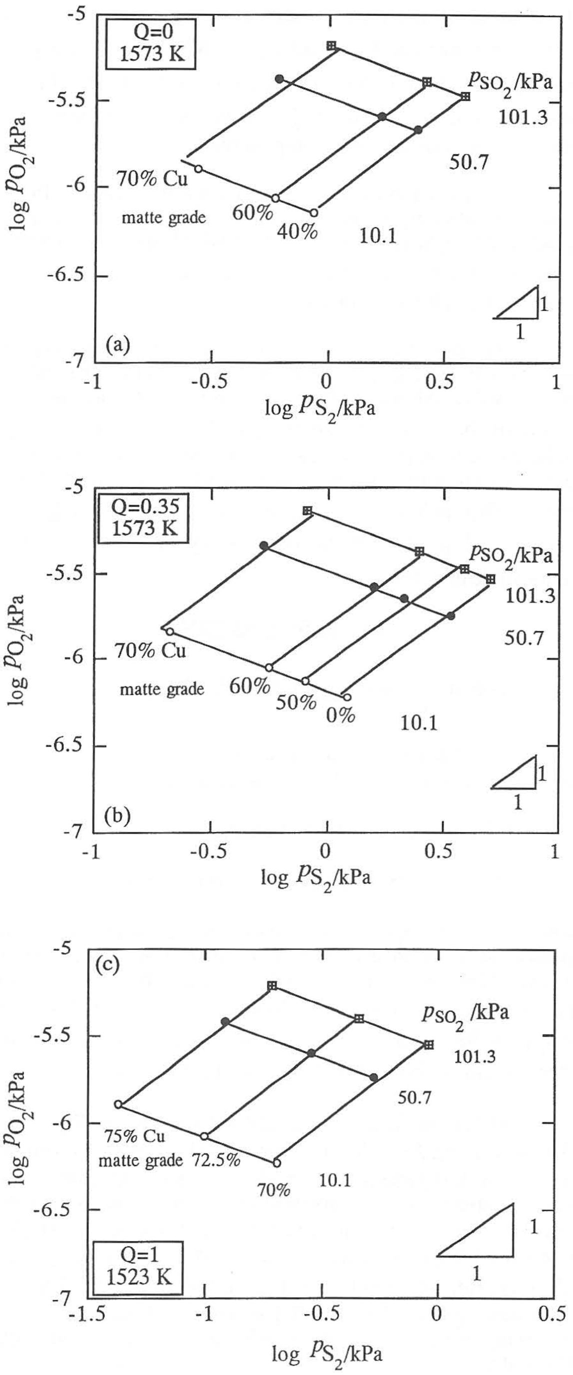

Fig. 9 Sulfur-oxygen potential diagram for different matte grades in relation to p_{SO_2} for the slag with Q=0 (a) and Q=0.35 (b) at 1573 K, and with Q=1 (c) at 1523 K.

the oxidic part is given by

$$(\%Cu)_O = a_{CuS_{0.5}}(A/\gamma_{CuO_{0.5}})(p_{O_2}/p_{S_2})^{\nu/4} \qquad (6)$$

Where $a_{CuS_{0.5}}$ is activity of the $CuS_{0.5}$ component in the matte, $\gamma_{CuO_{0.5}}$ is the activity coefficient of the $CuO_{0.5}$ component in the slag and A is constant to which equilibrium constant of the reaction (5) pertains. On the other hand, the sulfidic part is expressed as

$$(\%Cu)_S = a_{CuS_{0.5}}(B/\gamma_{CuS_{0.5}}) \qquad (7)$$

Where $\gamma_{CuS_{0.5}}$ is the activity coefficient of the $CuS_{0.5}$ component in the slag and B is a constant which contains the total number of moles of the components in the slag. By combining eqs. (6) and (7), eq. (4) can be rewritten as

$$(\%Cu) = a_{CuS_{0.5}}[(A/\gamma_{CuO_{0.5}})(p_{O_2}/p_{S_2})^{\nu/4} + (B/\gamma_{CuS_{0.5}})] \qquad (8)$$

Based on eq.(8), it can be considered how (%Cu) will change with p_{SO_2} when the matte grade is specified. Information on $\gamma_{CuO_{0.5}}$ and $\gamma_{CuS_{0.5}}$ in eq. (8) is very limited and it is not known how $\gamma_{CuO_{0.5}}$ changes with p_{SO_2}. In the event that both $\gamma_{CuO_{0.5}}$ and $\gamma_{CuS_{0.5}}$ in the slag equilibrating with a given matte are constant against p_{SO_2}, (%Cu) will be constant because the $(p_{O_2}/p_{S_2})^{1/4}$ term in eq. (8) does not change with p_{SO_2} as clarified in the present experiments. Hence, (%Cu) will be dependent only on $a_{CuS_{0.5}}$, in other word, the grade of matte. This prediction is in accordance with the present results shown in Fig. 2(a), (b) and (c) in that (%Cu) is independent of p_{SO_2} when the matte grade is specified. Conversely, it is predicted from the present results that $\gamma_{CuO_{0.5}}$ and $\gamma_{CuS_{0.5}}$in the slag equilibrating with a given matte are constant against p_{SO_2}.

From the standpoint of the molecular theory of the slag, sulfur exists in the slag phase as FeS($FeS_{1.5}$), $CuS_{0.5}$, CaS and MgS. When the ionic model is taken into consideration, sulfur may dissolve in the slag according to the exchange reaction first suggested by Richardson and Withers(12).

$$(O^{2-})+1/2S_2(g)=(S^{2-})+1/2O_2(g) \qquad (9)$$

Within the limit of dilute solution of sulfur, reaction (9) leads to the following relation.

$$(\%S)=C(p_{O_2}/p_{S_2})^{1/2} \qquad (10)$$

Where C is a constant which contains the activity of O^{2-}. In the event that $a_{O^{2-}}$ in the slag equilibrating with a given matte is constant against p_{SO_2}, the solubility of sulfur does not change with p_{SO_2} because the sulfur-oxygen pressure ratio is constant, as was clarified in the present study. As shown in Fig. 3 (a), (b) and (c), the present experimental results for the behavior of sulfur solubility against p_{SO_2} are accordant with this prediction.

3. Minor Element Distribution between Slag and Matte

Eq. (11), which is representing a mutual reaction between the metallic species in the matte and the oxide species in the slag, was selected for the thermodynamic analysis of the distribution ratios of silver, lead, arsenic, antimony and bismuth.

$$\{X\}+\nu/4\,O_2(g)=(XO_{\nu/2}) \tag{11}$$

$$K_{11}=(a_{XO_{\nu/2}})/\{a_X\}p_{O_2}^{\nu/4} \tag{12}$$

where ν is valency and K_{11} equilibrium constant of eq. (11). The slag and the matte are designated as ( ) and { }, respectively. By rearranging eq.(12) and the converting the mole fraction of X and $XO_{\nu/2}$ to the mass % basis, the following equation is obtained,

$$L_X^{s/m}=K_{11}(n_t)\{\gamma_X\}p_{O_2}^{\nu/4}/(\gamma_{XO_{\nu/2}})\{n_t\} \tag{13}$$

where $\{\gamma_X\}$ and $(\gamma_{XO_{\nu/2}})$are activity coefficient of X in the matte and $XO_{\nu/2}$ in the slag, and $\{n_t\}$ and (n_t) are mole amounts of 100 g matte and slag, respectively. The valency, ν, is considered to be 1 and 2 for silver and lead , respectively, and 3 for arsenic, antimony and bismuth

$\{\gamma_X\}$ were reported for lead by Kaiura *et al.*(1) and for arsenic, antimony and bismuth by one of the authors(13) which is reproduced in Fig. 10. $\{\gamma_X\}$ for silver can be known from the data by Sinha *et al.*(11). However, useful data are lacking for $(\gamma_{XO_{\nu/2}})$ in slag. Furthermore, due to the wide extrapolation of the low temperature data, the equilibrium constant , K_{11}, for the reaction (11) at high temperature are not accurate for arsenic, antimony and bismuth. Consequently, to make the quantitative analysis feasible, a parameter, α, which is composed of these unknown quantities was derived preliminary for a given matte grade by using the experimentally determined $L_X^{s/m}$ and p_{O_2} as well as $\{\gamma_X\}$.

$$L_X^{s/m}=\alpha[(n_t)\{\gamma_X\}p_{O_2}^{\nu/4}/\{n_t\}] \tag{14}$$

with α given as $K_{11}/(\gamma_{XO_{\nu/2}})$.

Once α was determined for a given matte grade, it was put in eq. (14) to reproduce $L_X^{s/m}$ for other matte grades by assuming that α is constant against matte grade.

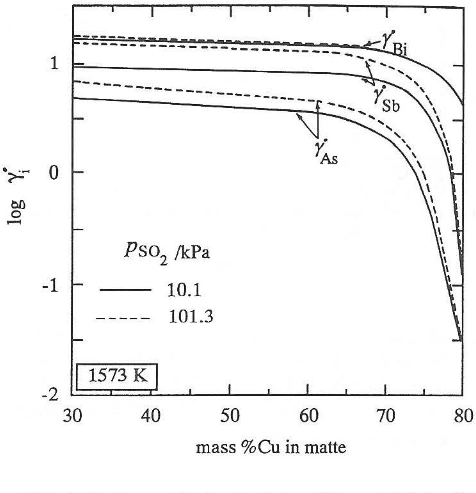

Fig. 10 Activity coefficient of As, Sb and Bi in the copper matte under p_{SO_2} of 10.1 and 101.3 kPa at 1573 K according to [13].

The calculated results for $L_{As}^{s/m}$ and $L_{Bi}^{s/m}$ for the slag systems with Q of 0, 0.35 and 1 are shown in Fig. 11 and Fig. 12 (a), (b) and (c), respectively. Fairy good agreements are found in the dependency on the matte grade between the calculated and observed $L_X^{s/m}$ under each p_{SO_2}. In that, $L_{As}^{s/m}$ decreases remarkably in the range of high matte grade while $L_{Bi}^{s/m}$ increases drastically. These tendencies are ascribed to p_{O_2} and $\{\gamma_X\}$ in eq. (13). As shown in Fig. 1 (a), (b) and (c), p_{O_2} increases drastically in the region of high matte grade. On the other hand $\{\gamma_{As}\}$ in the matte decreases remarkably while $\{\gamma_{Bi}\}$ is almost constant, as is shown in Fig. 10. According to eq. (13), $L_X^{s/m}$ is proportional to $p_{O_2}^{\nu/4}$ and $\{\gamma_X\}$. Consequently, $L_{As}^{s/m}$ decreases with matte grade owing to the balance between $\{\gamma_X\}$ and $p_{O_2}^{\nu/4}$ in which the contribution of $\{\gamma_X\}$ is prevailing in the region of high matte grade. While, $L_{Bi}^{s/m}$ increases with matte grade due to the predominant contribution of $p_{O_2}^{\nu/4}$. These results confirm the assumption of mutual reaction between a metallic species in the matte and an oxide species in the slag for arsenic and bismuth.

The same thermodynamic analysis was made also for silver, and lead and antimony. $L_{Sb}^{s/m}$ could be analyzed successfully as in the case of $L_{As}^{s/m}$ and $L_{Bi}^{s/m}$. However, for $L_{Ag}^{s/m}$ and $L_{Pb}^{s/m}$, it was impossible to get an agreement between the calculated and observed values for the slag with Q of 1 in the region of lower matte grade where the dissolution of sulfur in the slag is considerable, as shown in Fig. 3(c). Hence, it is considered that the sulfidic dissolution in the slag must be taken into account for silver and lead, in addition to the oxidic dissolution.

V. CONCLUSION

Phase equilibria between the copper matte and the slag of SiO_2-FeO_x or SiO_2-CaO-FeO_x or CaO-FeO_x were investigated at 1573 K and 1523 K under high partial pressures of SO_2 as a fundamental study for thermodynamically discussing some oxygen-smelting processes to produce copper. The partial pressures of S_2 and O_2 over the slag/matte and mutual dissolutions of copper and sulfur content in the slag were determined at 1573 K and 1523 K at p_{SO_2}=10.1, 50.7 and 101.3 kPa, in relation to the matte grade. The copper and sulfur solubilities in the slag were found to be independent of p_{SO_2} when the matte grade was specified, and it was clarified thermodynamically that this behavior was ascribed to the constancy of (p_{O_2}/p_{S_2}) against p_{SO_2} at a given matte. It was found that the solubility of sulfur in the slag decreased with increasing matte grade, while the slag with Q of 1 represented the minimum copper solubility at a matte grade with about 72.5 mass % Cu. The copper content in the slag with Q of 0.35 and 1 represents almost constant values in the region of matte grade between 10 and 60%Cu.

Distribution ratios of silver, lead, arsenic, antimony and bismuth between the above slags and the matte were also investigated at 1573 and 1523 K under partial pressures of SO_2 at 10.1, 50.7 and 101.3 kPa. When the distribution ratio, $L_X^{s/m}$, was defined as (mass% X in slag)/{mass % X in matte}, $L_{As}^{s/m}$ and $L_{Sb}^{s/m}$ were found to decrease drastically in the range of high matte grade while $L_{Bi}^{s/m}$ increased remarkably in this range. $L_{Ag}^{s/m}$ and $L_{Pb}^{s/m}$ decreased gradually with increasing matte grade up to about 75-77 mass% Cu and increase abruptly in the range of higher matte grade. It was

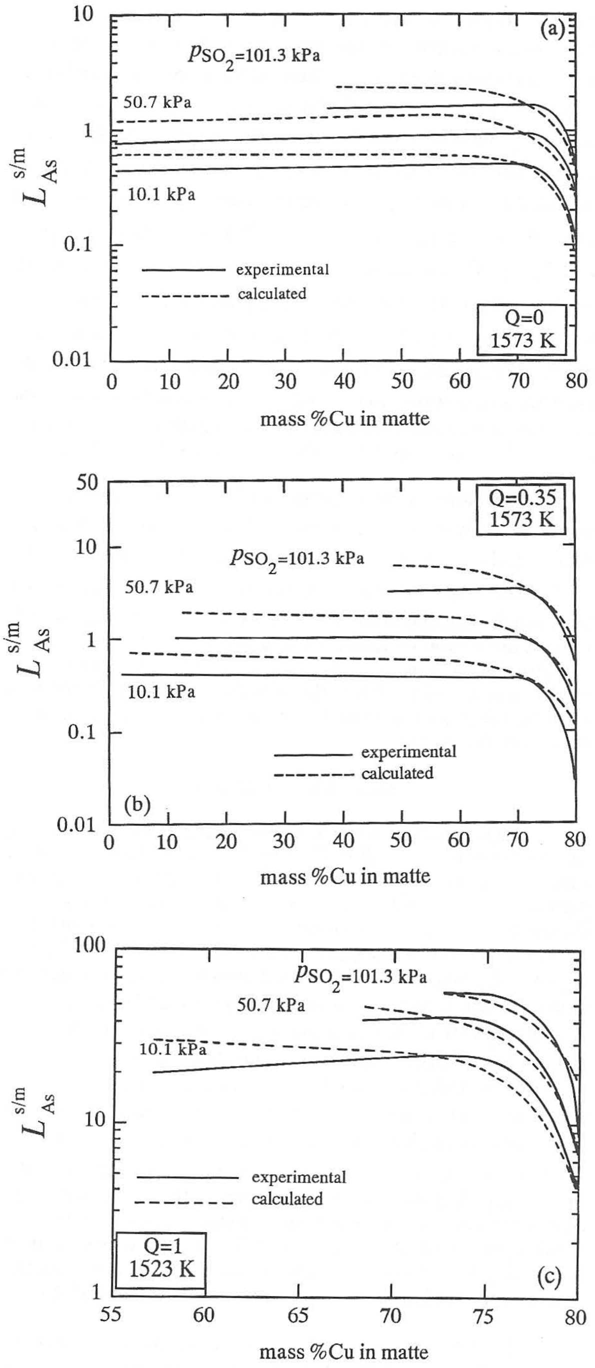

Fig. 11 Calculated distribution ratio (----) of As between slag and matte for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K, under p_{SO_2} of 10.1, 50.7 and 101.3 kPa, in comparison with the experimental results (——).

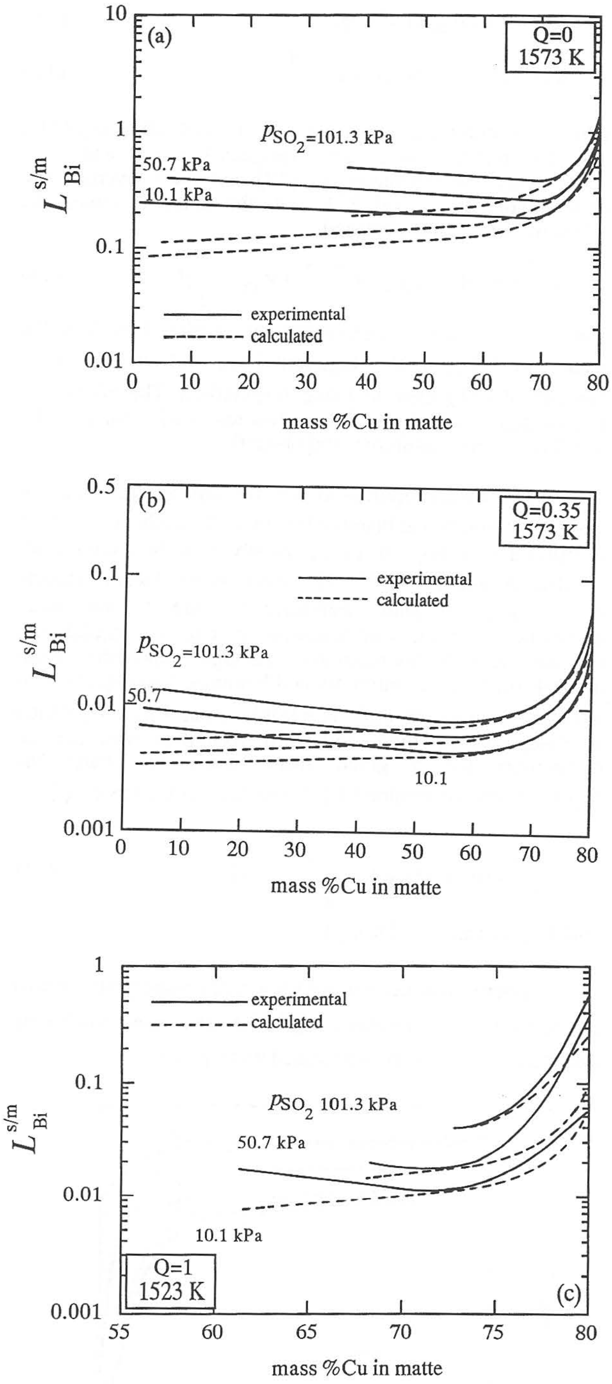

Fig. 12 Calculated distribution ratio (----) of Bi between slag and matte for the slag with Q of 0 (a) and 0.35 (b) at 1573 K, and with Q of 1 (c) at 1523 K, under p_{SO_2} of 10.1, 50.7 and 101.3 kPa, in comparison with the experimental results (——).

clarified that the distribution ratios of lead, arsenic, antimony and bismuth increased with P_{SO_2}. This result suggests that the use of oxygen or oxygen-enriched air for the blowing gas gives an effect to the distribution of these elements between the slag and matte phases and their proportion in the slag increased with increasing oxygen-enrichment.

The dependencies of $L_{As}^{s/m}$, $L_{Sb}^{s/m}$ and $L_{Bi}^{s/m}$ on matte grade were explained reasonably by assuming a mutual reaction between a metallic species in the matte and an oxidic species in the slag. Because of higher sulfidic fraction of silver and lead at lower matte grade in the slag, the sulfidic species of $AgS_{0.5}$ and PbS are expected to prevail in the range of low matte grade.

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