Phase Equilibrium and Minor Elements Distribution between SiO$_2$–CaO–FeO$_x$–MgO Slag and Copper Matte at 1573 K under High Partial Pressures of SO$_2$

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Phase equilibrium between copper matte and SiO$_2$–CaO–FeO$_x$–MgO slag with $Q=0.35$ ($Q=(\text{mass}\%\text{CaO}\div(\text{mass}\%\text{CaO}\text{+mass}\%\text{SiO}_2))$ was investigated at 1573 K under the SO$_2$ partial pressures of 10.1, 50.7 and 101.3 kPa as a fundamental study for thermodynamically discussing oxygen-smelting processes to produce copper. The copper and sulfur solubilities in the slag were found to be independent of $p_\text{SO}_2$ when the matte grade was specified, and it was considered that this behavior was ascribed to the constancy of $(p_\text{O}_2/p_\text{SO}_2)$ against $p_\text{SO}_2$ at a given matte grade. When the distribution ratio of a minor element, X, between the slag and matte phases was defined as $L_{\text{X,Slag}}=(\text{mass}\%\text{X in slag})/(\text{mass}\%\text{X in matte})$, $L_{\text{Ag,Slag}}$ for Ag, Sb and Bi at a given matte grade increased with increasing $p_\text{SO}_2$. This behavior was explained reasonably by assuming a mutual reaction between a metallic species in the matte and an oxidic species in the slag. The distribution ratio, $L_{\text{Ag,Slag}}$, at a given matte grade was almost constant against $p_\text{SO}_2$. This was considered to be ascribed to the sulfidic species of AgS$_{0.3}$ prevailing in the matte phase and the constancy of $(p_\text{O}_2/p_\text{SO}_2)$ against $p_\text{SO}_2$.

(Received March 4, 1997)

Keywords: copper smelting, oxygen blowing, copper matte, SiO$_2$–CaO–FeO$_x$–MgO slag, phase equilibrium, solubility, distribution ratio

I. Introduction

The combination of intensive smelting reactors with the use of oxygen or oxygen-enriched air has provided a number of improved copper smelting operations such as the INCO-Flash, Outokumpu-Flash and Mitsubishi-Continuous Processes. Phase equilibrium studies for the copper matte and the slag under high partial pressures of SO$_2$ are of practical importance for thermodynamically discussing the behaviors of the components such as the solubility of copper in the slag and the distributions of valuable and detrimental minor elements between the matte and slag phases in the oxygen smelting processes. However, there remain very few data on the phase equilibrium under the high partial pressures of SO$_2$ though a series of experimental studies$^{(0-5)}$ were carried out in a restricted condition of $p_\text{SO}_2$, at about 10.1 kPa which corresponds to the smelting with air blowing.

The present study was carried out at the oxygen-smelting conditions with $p_\text{SO}_2$ of 10.1, 50.7 and 101.3 kPa and controlled partial pressures of O$_2$ and S$_2$. The phase equilibrium and the distribution ratios of minor elements such as Ag, Pb, As, Sb and Bi between the copper matte and SiO$_2$–CaO–FeO$_x$–MgO slag phases were investigated at 1573 K. The slag composition generally has an effect on the phase equilibrium$^{(6)}$ and the value of $Q$, defined as $Q=(\text{mass}\%\text{CaO}/(\text{mass}\%\text{CaO}\text{+mass}\%\text{SiO}_2))$, was 0.35 in the present study, which is close to that of the slag in the copper smelting operations. The results obtained for the slag with $Q=1$ (calcium ferrite slag) are reported in separate papers$^{(7,8)}$.

II. Experimental

The experimental apparatus and procedure are same as in the previous studies$^{(9,10)}$. A mixture of Ar–SO$_2$–S$_2$ gas was used to control $p_\text{SO}_2$ and $p_\text{S}_2$. Accordingly, $p_\text{O}_2$ was also fixed at a given value. The sulfur partial pressure in the SO$_2$–Ar gas was controlled by controlling the temperature of a sulfur reservoir. In the preliminary experiment, the relationship between the partial pressure of S$_2$ at 1573 K and the temperature of the reservoir was determined by measuring the weight of sulfur condensed in a duplicated glass condenser immersed in an ice bath$^{(7)}$. The gas after passing the reservoir was led to the slag/matte system at 1573 K through a glass tube which was heated at 320–340 K to prevent the condensation of sulfur.

The starting slags had the compositions of 39%SiO$_2$, 40%FeO and 21%CaO with $Q=0.35$ and were synthesized in an iron crucible. 8 g of the matte composed of FeS and Cu$_2$S and the slag were put in a MgO crucible with an inner diameter of 22 mm and a height of 60 mm. The amount of the slag was adjusted so that the iron content in the slag after equilibration might be almost constant at about 22%. The solubility of MgO in the equilibrated slag was considerably high at 10–15 mass%. Hence, the slag is designated as the SiO$_2$–CaO–FeO$_x$–MgO system in the present study. Two series of experimental runs were made to determine the distribution ratio of the minor elements. The total of about 0.19 g of

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silver and lead and about 0.44 g of Cu$_3$As, CuSb and bismuth were added into the sample, respectively. The sample was heated at 1573 K for 162 ks, that was long enough to reach the equilibrium, as confirmed in the previous study\(^7\). After that, it was cooled rapidly by flushing a large amount of argon gas onto a surface of the slag layer to prevent the segregation of the slag components during the solidification. The chemical analyses were made for the solidified matte and slag specimens, using the same methods\(^6\).

### III. Experimental Results

1. **Relation between matte grade and \(p_{SO_2}\) or \(p_{O_2}\)**

The slag 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 value of \(Q\) for the slag after equilibration was almost constant at 0.35 against the matte grade (mass% copper in the matte) because the maximum solubility of calcium in the matte was considerably small at 0.5 mass% and because the silica content in the slag did not change so much though a thin layer of 2MgO·SiO$_2$ was formed on a surface of the MgO crucible. The iron content in the slag was between 20 and 24%.

For the given \(p_{SO_2}\) the relation between the matte grade and \(p_{SO_2}\) as well as \(p_{O_2}\) which was calculated by using an equilibrium constant\(^6\) of the reaction, \(1/2S_2(g) + O_2(g) = SO_2(g)\), is shown in Fig. 1. It is noted in a general tendency that \(p_{SO_2}\) decreases with increasing matte grade while \(p_{O_2}\) increases and the decrement of \(p_{SO_2}\) and the increment of \(p_{O_2}\) are remarkable when the matte grade is over 75%Cu. At a given matte grade, \(p_{SO_2}\) and \(p_{O_2}\) increase with increasing \(p_{SO_2}\). A very similar relationship\(^7\) was found for the two-phase equilibria between the copper matte and CaO-FeO$_2$ slag phases. This may be ascribed to a similarity in the constituents of the matte phases between the present system with the SiO$_2$-CaO-FeO$_2$-MgO slag and that with the CaO-FeO$_2$ slag. Both mattes are considered to be fundamentally composed of Cu$_2$S, FeS and FeO$_2$\(^6\).

2. **Solubility of component in slag and matte**

As shown in Fig. 2, the copper content in the slag is almost constant around 0.12% in the range of matte grades between 10 and 60%Cu and increases remarkably in the range of higher matte grades. The solubility is likely to be independent of the partial pressure of SO$_2$ within the scatter of experimental points. The solubility of sulfur in the slag, as shown in Fig. 3, represents a maximum with about 1% at a matte grade of 0%Cu and decreases simply with increasing matte grade. The solubility of sulfur is also likely to be independent of \(p_{SO_2}\). The solubility of MgO in the slag was between 10 and 15% while the calcium and silica contents in the equilibrated matte were at most 0.5% and 0.7%, respectively, at the matte grade of 0%Cu.

Figure 4 shows the amount of sulfur in the copper matte in relation to the matte grade. %S in the matte, which was calculated from %Fe and %Cu in the matte by assuming that Fe and Cu form FeS and Cu$_2$S in the matte phase, respectively, is also shown in this figure. Although %S observed in the experiments is close to the calculated one at higher matte grade, it deviates consider-
ably at the lower matte grades. When FeS is equilibrated with the slag, %S in the matte is about 10% less than the calculated value. This means that the sulfur in the matte should be oxidized to SO\(_2\) according to the reaction (1) or (2) and FeO or Fe\(_2\)O\(_4\) remains in the matte.

\[ \text{FeS}(l) + 3/2\text{O}_2(g) = \text{FeO}(l) + \text{SO}_2(g) \quad (1) \]
\[ \text{FeS}(l) + 5/3\text{O}_2(g) = 1/3\text{Fe}_2\text{O}_4(s) + \text{SO}_2(g) \quad (2) \]

Since the dissolved oxygen in the copper matte was not analyzed in the present study, the difference between 100% and the sum of (%Cu + %Fe + %S + %Ca + %SiO\(_2\)) in the matte was assumed to be the content of the dissolved oxygen in the matte. This estimation is same as that by Yazawa and Kameda\(^{100}\), which was proposed for the equilibrium between matte, slag and metallic iron. The estimated value is about 10% at the matte grade of 0%Cu.

3. Distribution ratio of minor element 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:

\[ L_{X}^{mm} = \frac{\text{mass} \% \ X \ \text{in slag}}{\text{mass} \% \ X \ \text{in matte}} \quad (3) \]

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

As shown in Fig. 5, the distribution ratio of silver, \( L_{\text{Ag}}^{mm} \), decreases with increasing matte grade up to about 70%Cu, and then increases remarkably in the range of higher matte grade. It is shown that the dependency of \( L_{\text{Ag}}^{mm} \) on the partial pressure of SO\(_2\) is very small. The distribution ratio of lead, \( L_{\text{Pb}}^{mm} \), as shown in Fig. 6 decreases slightly with increasing matte grade up to about 55%Cu and increases remarkably in the higher range. A clear dependency on \( p_{\text{SO}_2} \) is found for \( L_{\text{Pb}}^{mm} \) in that it increases with increasing \( p_{\text{SO}_2} \). While, as shown in Fig. 7, the distribution ratio of arsenic, \( L_{\text{As}}^{mm} \), is almost constant in the range of matte grade less than 70%Cu but decreases abruptly in the range of higher matte grade. The \( p_{\text{SO}_2} \) dependency is also observed clearly and \( L_{\text{As}}^{mm} \) increases with increasing \( p_{\text{SO}_2} \). The ratio \( L_{\text{As}}^{mm} \) in the range of low grade matte could not be determined at \( p_{\text{SO}_2} \) of 101.3 kPa due to the significant vaporization of arsenic in the specimen in this range and the contents of arsenic in the slag and matte phases were too small to be determined precisely by the chemical analysis. The distribution ratio of an-
timony, as shown in Fig. 8, increases gradually with increasing matte grade up to about 70% Cu and also decreases drastically in the range of higher grades. The dependency on $p_{SO_2}$ is notable in that $L_{Sb}^\text{SM}$ increases with increasing $p_{SO_2}$. On the other hand, as shown in Fig. 9, the distribution ratio of bismuth decreases very slightly with increasing matte grades and increases drastically in the range of higher grade above 65% Cu.

IV. Discussion

1. $\log p_{O_2}$-$\log p_{S_2}$ potential diagram

Based on the experimental results shown in the Fig. 1, a part of oxygen potential diagram was constructed for the slag with $Q=0.35$ at 1573 K and is illustrated in Fig. 10. The $p_{S_2}-\log p_{O_2}$ plots for each matte grade of 0, 50, 60 and 70% Cu are located approximately on straight lines with the slope of unity. This means that, for a given matte grade, the $(p_{S_2}/p_{O_2})$ ratio and accordingly the $(a_{FeO}/a_{FeS})$ ratio are constant against $p_{SO_2}$, as given by the following equations:

$$\text{FeO}(l) + \frac{1}{2} S_2(g) = \text{FeS}(l) + \frac{1}{2} O_2(g)$$ (4)

![Fig. 8 Distribution ratio of Sb between slag and matte against matte grade at 1573 K.](image)

Fig. 8 Distribution ratio of Sb between slag and matte against matte grade at 1573 K.

![Fig. 9 Distribution ratio of Bi between slag and matte against matte grade at 1573 K.](image)

Fig. 9 Distribution ratio of Bi between slag and matte against matte grade at 1573 K.

$$\log p_{O_2} = \log p_{S_2} + 2 \log K_4 + 2 \log \left(\frac{a_{FeO}}{a_{FeS}}\right)$$ (5)

where $K_4$ is the equilibrium constant for the reaction (4), and $a_{FeO}$ and $a_{FeS}$ are the activities of FeO and FeS, respectively.

2. Solubility of copper and sulfur in slag

The solubility of copper in the slag, (\% Cu), is considered to be given by the sum of an oxidative part and a sulfidic part, and based on reaction (6),

$$\text{CuS}_{2}(l) + \frac{1}{4} O_2(g) = \text{CuO}_{2.5}(l) + \frac{1}{4} S_2(g)$$ (6)

the solubility of copper in the slag can be written as follows\textsuperscript{10-12}:

$$\% \text{Cu} = a_{Cu_{S_{2.5}}} \left[ \frac{A}{\gamma_{CuO_{2.5}}(p_{O_2}/p_{S_2})^{1/4}} + \frac{B}{\gamma_{CuS_{2.5}}} \right]$$ (7)

where $a_{Cu_{S_{2.5}}}$ is the activity of the CuS\textsubscript{2.5} component in the matte, $\gamma_{CuO_{2.5}}$ and $\gamma_{CuS_{2.5}}$ are the Raoultian activity coefficients of the CuO\textsubscript{2.5} and CuS\textsubscript{2.5} components in the slag, respectively. A is a constant to which the equilibrium constant of reaction (6) pertains and B is a constant which contains the total number of moles of the components in the slag. Provided that $\gamma_{CuO_{2.5}}$ and $\gamma_{CuS_{2.5}}$ 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. (7) does not change with $p_{SO_2}$ as clarified in the present experiments. Hence, (\% Cu) will be dependent only on $a_{Cu_{S_{2.5}}}$, i.e., the grade of matte. This prediction is in accordance with the present experimental results shown in Fig. 2.

The sulfur solubility in the slag is dependent on $(p_{S_2}/p_{O_2})^{1/2}$ as reported by Richardson and Withers\textsuperscript{13}. Because this ratio is constant against $p_{SO_2}$ when the matte grade is specified, the solubility of sulfur does not change with $p_{SO_2}$ in accordance with the present results shown in Fig. 3.

3. Minor element distribution between slag and matte

It was suggested in the previous study\textsuperscript{8} that the following reactions were suitable for the thermodynamic analy-
sis of the minor element distribution between the slag and matte phases when the metallic, sulfidic and oxidic dissolutions of the minor element X in the slag and matte phases are taken into consideration.

\[
\langle X \rangle + v/4O_2(g) = \{XO_{v/2}\}, \quad \left(\frac{a_{XO_{v/2}}}{a_X}\right) = Ks P_{O_2}^{v/4} \tag{8}
\]

\[
\langle X \rangle + v/4S_2(g) = \{XS_{v/2}\}, \quad \left(\frac{a_{XS_{v/2}}}{a_X}\right) = Ks P_{S_2}^{v/4} \tag{9}
\]

where \( v \) is valency and the slag and the matte are designated as \( \langle \) and \( \{ \) , respectively.

The metallic species are incorporated in eqs. (8) and (9). Their stability in the matte phase can be predicted also from the result of the following calculation based on eq. (10).

\[
\langle X \rangle + v/4S_2(g) = \{XS_{v/2}\}. \tag{10}
\]

The activity ratios of the metallic species to the sulfidic species in the matte phase, \( \left(\frac{a_X}{a_{XS_{v/2}}}\right) \), for Ag, Pb, As, Sb and Bi were calculated in relation to the matte grade by using the free energy change\(^{10}\) of reaction (10) and \( P_{S_2} \) which was determined in the present study. The calculated result showed that the activity ratios for As, Sb and Bi were much higher than unity in the whole range of matte grade from 0 to 80% Cu. This result suggests that, for As, Sb and Bi, the metallic species are much more stable in the matte phase than the sulfidic species.

Equation (8), which represents 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 As, Sb and Bi. Provisionally, it was also used for Ag and Pb. By rearranging eq. (8) and converting the mole fractions of X and XO\(_{v/2}\) to the mass% basis, the following equation is obtained:

\[
L_k^{as} = K_s (n_t) / (\gamma_{X}/\gamma_{XO_{v/2}}) \tag{11}
\]

where \( \gamma_X \) and \( \gamma_{XO_{v/2}} \) are activity coefficients of X in the matte and XO\(_{v/2}\) in the slag, and \( n_t \) and \( n_t \) are the mole amounts of the 100 g matte and the slag, respectively.

If, at a given matte grade, the activity coefficients of minor elements in the slag and matte phases do not change with increasing \( P_{S_2} \), the relation between the distribution ratio and \( p_{O_2} \) given by eq. (11) would suggest the valency of \( v \) in reaction (8). This is because the total numbers of moles in the slag and matte can be given at constant values, respectively, and the equilibrium constant of \( K_s \) for reaction (8) is constant at a given temperature.

The distribution ratios of the minor elements which were obtained in the present study are plotted against \( p_{O_2} \) in Fig. 11. As shown in Fig. 11(a), (b) and (c) for As, Sb and Bi, respectively, the slopes of the log \( L_k^{as} - \log p_{O_2} \) plots are approximately 3/4. This indicates that \( v \) are 3 (trivalent) for these elements. On the other hand, as shown in Fig. 11(d), the log \( L_k^{as} - \log p_{O_2} \) plots for Pb represent nearly straight lines but their slopes are considerably different between the matte grades. The slopes in the range of low matte grades are considerably larger than 1/2 and this may be ascribed to the dissolution mechanism of Pb in the slag, to which the sulfidic dissolution pertains in addition to the oxidic dissolution, as discussed later. From the above discussion, the valency, \( v \), were supposed to be 1 for Ag, 2 for Pb, and 3 for As, Sb

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**Fig. 11** Distribution ratios of (a) As, (b) Sb, (c) Bi and (d) Pb in relation to \( p_{O_2} \) at 1573 K.
and Bi.

The dependency of the oxygen partial pressure, matte grade and activity coefficient of the minor elements on the distribution ratios of these elements between the calcium ferrite slag and the copper matte phases was discussed in the previous study\(^{(10)}\). A similar treatment will be possible for the present slag with \(Q = 0.35\). The distribution ratio of the minor elements was defined as:

\[
L_X^m = \alpha \left( \frac{n_x}{\gamma_X} \right) \left( \frac{p_{SO_2}}{n_t} \right) \tag{12}
\]

with \(\alpha\) given as \(K_a/\langle \gamma_X \rangle\). The values of \(\{\gamma_X\}\) were reported for Pb by Kaiura et al.\(^{(10)}\) and those for As, Sb and Bi by one of the authors\(^{(14)}\). The value of \(\{\gamma_X\}\) for Ag can be known from the data by Sinha et al.\(^{(15)}\). It was supposed that \(\alpha \) was constant against the matte grade. Once \(\alpha\) was determined for the given matte grade of 72.5%Cu, it was put in eq. (12) to reproduce \(L_X^m\) for other matte grades.

The calculated results are shown in Figs. 12-16 for As, Sb, Bi, Pb and Ag, respectively, in relation to the matte grade, together with the experimental ones. As shown in Figs. 12, 13 and 14, there is fairly good agreement in the dependency on the matte grade between the calculated and observed \(L_X^m\) for As, Sb and Bi under each \(p_{SO_2}\). In that, \(L_{As}^m\) and \(L_{Sb}^m\) decrease remarkably in the range of high matte grades while \(L_{Bi}^m\) increases drastically. These tendencies are ascribed to \(p_{SO_2}\) and \(\{\gamma_X\}\) in eq. (12). As clarified in the present study, \(p_{SO_2}\) increases drastically in the region of high matte grade. It was reported by one of the authors\(^{(14)}\) that \(\{\gamma_{As}\}\) and \(\{\gamma_{Sb}\}\) in the matte decrease remarkably while \(\{\gamma_{Bi}\}\) is almost constant in the range of high matte grades. Therefore, \(L_{As}^m\) and \(L_{Sb}^m\) decrease with the matte grade owing to the balance between \(\{\gamma_X\}\) and \(p_{SO_2}^{1/4}\) in the region of high matte grades in which the contribution of \(\{\gamma_X\}\) is prevailing over \(p_{SO_2}^{1/4}\). Conversely, \(L_{Bi}^m\) increases with the matte grade due to the predominant contribution of \(p_{SO_2}^{1/4}\). These results suggest that the assumption of a mutual reaction between a metallic species in the matte and an oxide species in the slag is reasonable for As, Sb and Bi, respectively.

On the other hand, for the distribution ratios of Pb and Ag, as shown in Figs. 15 and 16, fairly large discrepancies are found between the calculated and observed ones in the range of low matte grades though the dependency on the matte grade is accordant in the range of high matte grades. This discrepancy is considered to be ascribed partly to the stability of sulfide species in the slag phase in the range of low matte grades.

Thus, it is suggested that the sulfidic dissolution must be taken into consideration when the behavior of Pb or Ag is thermodynamically discussed. Hence, the sulfidic fraction of Ag in the slag as well as the oxidic fraction is discussed in this section. A similar discussion is possible for Pb. The oxidic and sulfidic fractions of Ag in the slag
were calculated at 1573 K and \( p_{SO_2} = 10.1 \text{ kPa} \), based on reaction (13). The oxidic dissolution of Ag in the slag, \((\% \text{Ag})_o\), is given by eq. (14). The sulfidic dissolution can be obtained by subtracting \((\% \text{Ag})_o\) from \((\% \text{Ag})\) which was determined experimentally:

\[
(AgS_{0.5}) + \frac{1}{4} O_2(g) = (AgO_{0.5}) + \frac{1}{4} S_2(g),
\]

\[
(\% \text{Ag}) = \left[ \frac{(\% \text{Ag})_{n_i}}{\left( \frac{K_{13} (\% \text{AgO}_{0.5})_{n_i}}{n_i} \right)} \right] \times \left( \frac{p_{O_2}}{p_{SO_2}} \right)^{1/4}
\]

By using the values of \((\% \text{AgO}_{0.5})\) estimated from the data reported by Takeda et al. and \((\% \text{Ag}_{n_i})\) estimated from the data by Sinha et al., the oxidic and sulfidic dissolution of Ag in the slag were calculated and are shown in Fig. 17. As a general tendency, the proportion of the sulfidic dissolution is very high in the range of matte grades less than 70% Cu and decreases drastically with the matte grade in a very high range. The solubility of sulfur in the slag increases with decreasing matte grade, as shown in Fig. 3, and this tendency is accordant with that of \((\% \text{Ag})_s\) as shown in Fig. 17.

V. Conclusion

The copper smelting processes using oxygen or oxygen-enriched air as blowing gas have advantages that they can increase production output, reduction in energy input and production of high grade \( SO_2 \) gas for making sulfuric acid. On the other hand, a disadvantage is pointed out for these processes that volatile and detrimental elements such as As, Sb, Bi and Pb tend to increase their fractional distribution in the matte phase, due to the decrease of their fractional distribution in the gas phase because the gas volume is decreased when oxygen or oxygen-enriched air is used. Nevertheless, as clarified in the present study, the distribution ratios of these minor elements between the slag and matte phases increase with \( p_{SO_2} \). Hence, it can be expected that the fractional distribution of these elements in the matte phase is suppressed by the increase of their fractional distribution in the slag phase. Furthermore, it is of practical importance that the fractional distributions of valuable Cu and Ag in the matte phase are not affected by \( p_{SO_2} \), that is, their loss in the slag phase does not increase with increasing \( p_{SO_2} \), as clarified in the present study.

REFERENCES