Activity of Silver in Molten Copper Sulfide Saturated with Copper

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A double Knudsen cell configuration combined with a mass spectrometer has been adopted to determine the activity of silver as a minor element in the equilibrium Cu-CuS immiscible liquids at 1373, 1423 and 1473 K to analyze the silver behavior in the copper smelting process. The phase relation and distribution ratio of silver between the molten copper and copper matte phases in the copper rich corner of the Cu-Ag-S system have also been determined experimentally at 1473 K by the quenching method and the boundaries of the miscibility gap were determined. Silver activities in the Cu-Ag binary system have been measured using both the double Knudsen cell and the conventional single cell methods in order to obtain the required reference activity value for activity measurements in the Cu-Ag-S system.

The activity measurements in both binary and ternary systems indicate that silver deviates positively from the ideal behavior with the Raoultian activity coefficient at infinite dilution of 3.3 and 9.9 at 1473 K in the copper rich and copper matte phases, respectively. It is found that the activity coefficients of silver at infinite dilution in the molten copper and in the copper rich phase saturated with matte are the same at 1473 K, giving $c_{Ag}^\infty = 0$. Assuming copper sulfide with minor amounts of silver to be a Cu$_7$S$_5$-$x$-Ag$_x$S$_5$ solution, activity coefficient of Ag$_{x}$S$_5$ at infinite dilution is estimated to be 0.81 at 1473 K. Although silver proves to have the highest vapor pressure among the components in the Cu-Ag-S ternary system, it is concluded that the removal of silver to the gas phase is not likely to occur during the converting process of copper matte.

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I. Introduction

Copper concentrates usually contain small amounts of impurity elements which are deleterious to the properties of the final copper product and should be eliminated in copper smelting process. During matte smelting stage, minor elements are distributed more or less into the matte phase and the removal of impurities is mostly left for the converting operation, either as volatiles in the gas phase or as oxides in the slag phase. Thus, knowledge of thermodynamic properties of minor elements in copper mattes, in particular, is important to analyze the behavior of the elements in a major part of the copper smelting and possibly to optimize the current elimination processes or develop new elimination methods. Thermodynamic activities of some minor elements in copper mattes have been estimated in a number of reports, however, very few direct measurements of thermodynamic properties are available.

Although silver is usually recovered as a valuable byproduct in the electric refining stage of copper smelting, directly measured activity values of silver in copper mattes are not available. Silver activity in molten copper have been reported by several researchers$^{(1)}$ while general agreement is not observed among the reports. In the present study, activity of silver in the miscibility gap of the Cu-Ag-S ternary system has been measured from 1373 K to 1473 K by the double Knudsen cell-mass spectrometric method. Measurement of silver activity in Cu-Ag binary system at the same temperature range is also discussed to serve as a reliable reference value in measurements of the ternary system. To estimate the composition of metallic copper and copper sulfide phases in the samples of activity measurement by the mass spectrometric method, the phase relation between two phases is required. This relation has been reported by Asano et al.$^{(1)}$ in the composition range below 7 mass%Ag in the copper phase and also by Gerlach et al.$^{(2)}$ in the region higher than 12 mass%Ag at 1473 K. However, the miscibility gaps suggested by those reports do not agree at the same temperature. Thus, the phase separation boundaries in the Cu-Ag-S ternary system has been verified in the present study at 1473 K by the quenching method in the composition range of up to 16 mass%Ag in the copper phase.

II. Principles of the Double Knudsen Cell-Mass Spectrometry

The applicability of the Knudsen effusion cell combined with the mass spectrometer to high-temperature thermodynamic studies is owed to the fundamental relationship between measured ion intensity in the mass spectrometer and the partial pressure of the species in the equilibrium vapor in the Knudsen cell according to eq. (1):

$$p_i = K_i I_i T$$  \hspace{1cm} (1)

where $p_i$ is partial pressure of the component $i$, $K_i$ is the proportionality constant related to the mass spectrometer, Knudsen cell and species, $I_i$ is the measured intensity of $i$ and $T$ is temperature of the sample in the Knudsen cell. To avoid the troublesome determination of the
proportionality constant $K$, in eq. (1), the so-called ion intensity ratio/Gibbs-Duhem integration method has been developed by Belton and Fruehan\(^{19}\). However, the method requires ion intensity measurements of all components over a wide compositional range which generally makes it inappropriate for multi-component systems and systems with a big difference in component volatilities.

In the double cell approach, a reference sample with the known activity of the component under study is examined together with an unknown sample in two Knudsen cells at the same time. Assuming vapor phase as an ideal gas,

$$a_{i(r)} = \frac{P_{i(r)}}{P^*} = a_{i(r)}\frac{P_{i(u)}}{P_{i(r)}}$$

The subscript $u$ and $r$ refers to the unknown and reference samples, respectively. Combining eqs. (1) and (2) yields eq. (3):

$$a_{i(u)} = C_a r_0(I_{i(u)})/I_{i(r)}.$$  

Equation (3) is the fundamental relationship for activity measurement by the double Knudsen cell-mass spectrometry. According to this equation, the activity of component $i$ at each composition can be directly obtained from the ratio of measured intensities of $i^+$ in the unknown sample to that in the reference sample. The constant $C_a$ that compensates for the geometrical discrepancies of the two cells, can be determined for each particular pair of cells by performing a complementary run using the same pure material in both cells.

III. Experimental

1. Quenching method

To establish the equilibrium phase relation between the metallic copper and copper matte phases, samples with about 6 g of total weight were prepared from high purity elemental Cu, Ag and S (99.99% purity or higher), putting in a quartz tube of 8 mm inner diameter and sealing with about 100 mm height under a vacuum of $10^{-4}$ Pa. The bulk composition of samples were such selected as to fall within the miscibility gap of Cu–Ag–S ternary system. The ampoules were inserted slowly in a vertical tube furnace allowing the vaporizing sulfur to react with the solids and kept at 1473 K overnight to attain equilibrium. The ampoules then quenched in water to obtain matte and metal portions. After separation, metal and matte samples were analyzed by the ICP method for the determination of silver content. Sulfur content was also determined gravimetrically as BaSO₄ in either phase.

2. Knudsen effusion-mass spectrometry

(1) Samples

Samples of about 2.5 g of total weight were prepared from the pure elements as described in the preceding section except that the ampoules were cooled in an inert gas. Each Knudsen cell containing a sample was weighed before and after the experimental run to examine the compositional change of samples due to vaporization.

(2) Double Knudsen cell

Knudsen cells made of alumina with an inner diameter of 8.8 mm and a height of 14.0 mm were employed. The orifice made at the side wall of the cell varied in size from 0.3–0.7 mm depending on the vapor pressure of the alloy under study. The configuration of the double Knudsen cell is shown in Fig. 1. The molybdenum cell holder containing two cells was heated by means of radiation from molibdenum heating element wound around the cell holder on a refractory guide. The heating element was surrounded by a series of molybdenum radiation shields.

Temperature was measured by a Pt/Pt–13Rh thermocouple inserted in the middle of the cell holder from the bottom while a separate thermocouple was set adjacent to the heating element for temperature control. The former thermocouple was calibrated by separate measuring of ion intensities of pure Ag and Cu over a wide temperature range covering the melting point of the metal and plotting $\ln (I/T)$ values against $1/T$. The intersection of interpolated straight lines corresponding to the solid and liquid phases was assigned to the true melting point of the corresponding pure metal.

(3) Procedure

A double-focusing magnetic field mass spectrometer made by the Denshi Kagaku (model EMG-05H) was employed. In each experimental run, a reference and an unknown sample was put in a pair of Knudsen cells. Pure silver and a Cu–10 at%Ag alloy served as reference samples for determination of activities in the Cu–Ag binary and Cu–Ag–S ternary systems, respectively. Once the experimental temperature attained, the cell containing the reference sample was aligned toward the ion source. $^{106}$Ag⁺ signals were then monitored for at least 20 minutes confirming a constant intensity height upon recording employing an ionizing energy of $2.7 \times 10^{-18}$ J (17 eV). The background intensity was recorded by turning the cell holder for about 90°. The net ion intensity corresponding to the parent silver atoms in the Knudsen cell was obtained as the difference between intensities corresponding to the consecutive aligned and misaligned positions. The same procedure was repeated for the unknown sample. The whole process repeated for at least
three times and the average intensity ratio between the unknown and reference samples was used to calculate activities according to eq. (3). For the Cu–Ag binary alloys, the intensity of $^{64}$Cu$^+$ was also measured at the same ionization energy for silver.

IV. Results

1. Phase relation between Cu rich and Cu$_2$S matte phases

The equilibrium compositions of the copper and copper sulfide phases at 1473 K in the copper rich corner of the Cu–Ag–S ternary system is illustrated in Fig. 2 together with the phase boundaries of the miscibility gap. The phase relation is described by the tie lines which connect compositions of the two equilibrium phases. By the addition of silver to the Cu–Cu$_2$S two phase equilibrium, sulfur solubility slightly decreases and the composition of metal phase changes along the line drawn from Cu$_2$S saturated copper in the Cu–Cu$_2$S pseudo-binary toward Ag apex in the Cu–Ag–S ternary system. A lower sulfur content in matte phase is obtained in the present study compared to that by Asano et al.$^{(11)}$ which is shown by the dotted line in Fig. 2, while almost the same boundary line is observed in the copper phase. On the other hand, the present results agree well with the miscibility gap reported by Gerlach et al.$^{(12)}$ in both phases.

2. Silver activity

For adopting a Cu–Ag alloy as the reference sample in the activity measurement in Cu–Ag–S system, silver activity in Cu–Ag binary system was first measured at 1373, 1423 and 1473 K which is shown in Fig. 3. Copper activity calculated from silver activity at 1473 K by applying the Gibbs-Duhem integration, is also illustrated in the figure. Positive deviation from the ideal behavior is observed for both elements in the binary system. The activity values show small temperature dependency in the temperature range of 1373–1473 K.

The equilibrium compositions of the copper and copper sulfide phases and the relevant silver activities determined by the double Knudsen cell method are illustrated in Fig. 4 for 1473 K. The composition of both phases are estimated from the bulk composition of the sample based on the phase relation shown in Fig. 2. Silver activity in the molten copper and copper sulfide phases at 1373, 1423 and 1473 K as well as in the Cu–Ag binary alloys at 1473 K are plotted against silver content of the corresponding phases in Fig. 5. In this figure, it is assumed that the phase relation between copper and copper sulfide phases at 1473 K evaluated in the present study, is not affected by a decrease of 100 K in temperature as will be discussed later. The figure shows that activities exhibit positive deviation from ideal behavior and the magnitude of the deviation increases with increasing sulfur content, from copper rich phase to copper sulfide phase, while the addition of about 2 at.%S to the sulfur-free copper alloy gives no evident effect on the silver activity at 1473 K.
reported by Asano et al.\(^{(11)}\), even though the equilibrium composition of the two phases, especially sulfur content in the copper sulfide phase, shows disagreement as discussed earlier. Gerlach et al.\(^{(12)}\) also reported the phase relation between the copper rich and copper matte phases in the Cu–Ag–S ternary system at the same temperature in the composition region higher than 12 mass%Ag in the copper phase that is beyond the range of the activity measurement of the present study. The point corresponding to the lowest silver content reported by Gerlach et al.\(^{(12)}\) is shown by the square symbol in Fig. 6. This point deviates from the straight line when extrapolated to the higher silver contents. However, the line of silver distribution defined by the results of the present study is matched at higher silver content with the distribution curve obtained from the data reported by Gerlach et al.\(^{(12)}\).

The phase relation data determined in the present study at 1473 K, was applied to estimate the compositions of the copper and copper sulfide phases in the activity measurement by the mass spectrometry in the temperature range of 1373–1473 K. It is then assumed that the phase relation does not change noticeably with a decrease of 100 K in the experimental temperature. This assumption was based on the fact that the phase boundaries of the miscibility gap in the Cu–Cu2S pseudo-binary system show fairly weak dependency on the temperature within the temperature range of 1373–1473 K. It is further confirmed by the report of Bryukvin et al.\(^{(10)}\) who emphasize that the configuration of the miscibility gap in the Cu–Ag–S system is determined by the effect of the Cu–Cu2S and Ag–Ag2S pseudo-binary systems and the effect of temperature in the range of 1273–1573 K is noticeable only at the Ag–Ag2S side. Schlitt and Richards\(^{(15)}\) also have reported that the distribution ratio of silver in the metal-matte system was found to be independent of temperature within 1423 to 1523 K.

2. Silver activity in Cu–Ag system

For activity measurements of silver in Cu–Ag–S ternary system, a Cu–10 at%Ag alloy is adopted as the reference sample which requires a reasonable activity value for silver. Although silver activities in the molten Cu–Ag alloys have been reported by several authors\(^{(19)}\) in the temperature range of 1273–1473 K, good agreement is not observed among the reported values. The mass spectrometric method seems to be superior to the other techniques of activity measurements for low silver Cu–Ag alloys. In the present study, the activity of silver in the Cu–Ag system was measured by both the double Knudsen cell and conventional single cell methods. The results at 1473 K are shown in Fig. 7, and the activity values in the literature\(^{(7)}\) measured by the mass spectrometric method are also included for comparison. Silver activities obtained in the present study by both methods agree with that reported by Golonka et al.\(^{(8)}\) for low silver concentrations. At higher silver contents, activity values determined by the double Knudsen cell method exhibit lower values, while those determined by the single Knudsen
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Fig. 7 Comparison of activities in the Cu–Ag liquid alloys measured by the double and single Knudsen cell methods in the present study with those in the literature.

cell agree with all other data. Almost all of the reported activity data shown in Fig. 7, have been determined by the same conventional single Knudsen cell based on measuring $I_{Cu}/I_{Ag}$ ratios at different compositions and integration over a wide compositional range according to the Belton-Frulehan method. With a big difference between Cu and Ag volatilities, this method may result in considerable errors especially at high silver compositions which also affect to some extent the measured activity values at low silver compositions due to integration. On the other hand, in the double Knudsen cell approach adopted in the present study, an individual silver activity can be independently determined by a single measurement of ratio of silver intensity in the alloy under study to that in the reference sample. The present authors believe that the activity measured by the double Knudsen cell method is more reliable, and accordingly, it was adopted as a reference.

The activity coefficient of silver in the Cu–Ag system are plotted against $N_{Ag}$ in Fig. 8 at different temperatures. The straight lines are fitted by the least squares method in the composition region of 0–10 at% Ag giving eqs. (4) to (6).

\[
\ln \gamma_{Ag(Cu)} = 1.19 - 2.97 N_{Ag} \quad \text{(at 1473 K)} \tag{4}
\]

\[
\ln \gamma_{Ag(Cu)} = 1.28 - 3.63 N_{Ag} \quad \text{(at 1423 K)} \tag{5}
\]

\[
\ln \gamma_{Ag(Cu)} = 1.39 - 4.37 N_{Ag} \quad \text{(at 1373 K)} \tag{6}
\]

At infinite dilution, activity coefficient of silver in molten copper is expressed by eq. (7):

\[
\ln \gamma_{Ag(Cu)} = \ln \gamma_{Ag(Cu)}^{\infty} + \varepsilon_{Ag}^{0} N_{Ag} \tag{7}
\]

Activity coefficient of silver at infinite dilution, $\gamma_{Ag}^{\infty}$, and self interaction coefficient of silver, $\varepsilon_{Ag}^{0}$, may be estimated based on eqs. (4) to (6) from eq. (7) which gives 4.0, 3.6 and 3.3 for the activity coefficient of silver at infinite dilution in the molten copper at 1373, 1423, and 1473 K, respectively. These values suggest eq. (8) for the temperature dependency of $\gamma_{Ag}$ in molten copper:

\[
\ln \gamma_{Ag(Cu)}^{\infty} = \frac{4050}{T - 1.56} \quad (1373–1473 \text{ K}) \tag{8}
\]

3. Activity of silver in Cu–Ag–S system

Activity coefficient of silver in the copper matte phase as well as in the molten copper are required to analyze the behavior of silver in the copper smelting process. The activity coefficient of silver in the copper rich and copper sulfide phases in the Cu–Ag–S system are plotted against silver content in the corresponding phases together with that in the molten copper at 1473 K in Fig. 9. The activity coefficients of silver at 1473 K are expressed as a function of silver content by eqs. (9) and (10):

\[
\ln \gamma_{Ag(Cu \text{ phase})} = 1.19 - 2.87 N_{Ag} \quad \text{(9)}
\]

\[
\ln \gamma_{Ag(matte \text{ phase})} = 2.29 - 8.20 N_{Ag} \quad \text{(10)}
\]

With the activity data obtained in the present work at
Table 1 Thermodynamic properties of silver in the Cu–Ag–S system at 1473 K obtained in the present study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{Ag(Cu)}$</td>
<td>3.3</td>
</tr>
<tr>
<td>$\gamma_{Ag(Cu-rich)}$</td>
<td>3.3</td>
</tr>
<tr>
<td>$\gamma_{Ag(matte)}$</td>
<td>9.9</td>
</tr>
<tr>
<td>$e_{Ag}^{S}$</td>
<td>-3.0</td>
</tr>
<tr>
<td>$e_{Ag}^{S}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Other temperatures, activity coefficients of silver in the copper-rich and copper sulfide matte phases are suggested in eqs. (11) and (12) as a function of temperature for the temperature range of 1373–1473 K and its vicinity.

\[
\ln \gamma_{Ag(Cu\ phase)} = \frac{3030}{T} - 0.87 \quad (1373–1473 \ K) \quad (11)
\]

\[
\ln \gamma_{Ag(matte\ phase)} = \frac{2830}{T} + 0.37 \quad (1373–1473 \ K). \quad (12)
\]

The activity coefficient of silver at dilute solution in the molten copper-rich phase can be evaluated by eq. (13):

\[
\ln \gamma_{Ag(Cu\ phase)}^{0} = \ln \gamma_{Ag(Cu)}^{0} + e_{Ag} \nu_{S}.
\]

(13)

It is interesting to note that the activity coefficient of silver in the matte-saturated copper exhibits the same trend with that in the sulfur-free copper at the 1473 K as shown in Fig. 9, even though the former phase contains almost 2 at.%S at the same temperature. Considering eqs. (4) and (9) with (13), it implies that $e_{Ag}^{S}$ = 0 at infinite dilution of silver in the matte-saturated copper phase at 1473 K, provided that $e_{Ag}^{S}$ is constant in the composition range of 0–2 at.%S in copper. Kaushal and Kapoor[18] have determined $e_{Ag}^{S}$ values in the molten copper at the temperature range of 1273 to 1373 K. Their reported values may be expressed by a linear relationship with the reciprocal temperature as in eq. (14):

\[
e_{Ag}^{S} = -13.04 + 18540 / T.
\]

(14)

If the values are extrapolated to 1473 K by eq. (14), a negative value for $e_{Ag}^{S}$ is obtained. However, thermodynamically it is more reasonable to suggest that $e_{Ag}^{S}$ approaches zero with increase in temperature[17].

The thermodynamic values estimated in the present study are summarized in Table 1.

4. Vapor pressure of components

The composition of the copper phase saturated with the matte in the miscibility gap of the Cu–Ag–S ternary system changes along the line drawn from Cu$_2$S-saturated copper in the two phase region of the Cu–S binary system toward the silver corner of the ternary system by the addition of silver. This line is too close to a line of constant Cu/S in the compositional range of the present study. Then, the matte-saturated-copper phase in the ternary system may be regarded as a Cu(2 at.%S)–Ag pseudo-binary system. By applying the Gibbs-Duhem integration, activity of copper and S$_2$ pressure are calculated from silver activity along the line of the miscibility gap boundary at 1473 K. Activity of copper is assumed to be 0.98 at 1473 K in the Cu–Cu$_2$S two-phase region at the starting point of integration, while $1.10 \times 10^{-1}$ Pa[18] is adopted for $p_{S_2}$ at the same condition. The vapor pressure of silver, copper and S$_2$ is related to the silver content of the matte phase by the phase relation between the copper rich and copper matte phases and the relationships are plotted in Fig. 10. It is evident from the calculated results that silver vapor holds the highest partial pressure over a Cu–Ag–S melt at the experimental temperature. However, it is considered from a vapor pressure of lower than 10 Pa at dilute concentrations that remarkable vaporization of silver from the copper-saturated matte can not be expected.

5. Activity coefficient of Ag$_{0.5}$ in copper matte phase

Silver is assumed to form a sulfide species in a copper matte. At dilute concentrations of silver in the copper matte, two silver atoms are not expected to adjoin each other because of the repulsion between same cations and the attractive force between silver and sulfur atoms. Thus, silver sulfide may be represented by Ag$_{0.5}$ rather than Ag$_2$S. The formation of Ag$_{0.5}$S is expressed by reaction (15):

\[
Ag(1) + 1/4S_2(g) = Ag_{0.5}S(0)
\]

\[
\Delta G^0 = -52140 + 24.287T.
\]

(15)

The Gibbs energy, $\Delta G^0$, for the reaction (15) was estimated from the table of thermodynamic properties compiled by Knacke et al.[19] Combining $p_{S_2}$ in Fig. 10 and $a_{Ag}$ with $\Delta G^0$ of reaction (15) at 1473 K, activity of Ag$_{0.5}$ was calculated and plotted against Ag$_{0.5}$ content of the copper matte phase as in Fig. 11. Measured activities of silver in the metallic form in the matte phase are also illustrated in the figure for comparison. In the calculation, the matte phase is assumed to be a Cu$_{0.5}$Ag$_{0.5}$–Ag$_{0.5}$S$_2$ pseudo-binary. The activity of Ag$_{0.5}$ shows negative deviation from the ideal behavior while that of metallic silver exhibits an extremely positive deviation in the matte phase.

The logarithmic activity coefficient of Ag$_{0.5}$ at 1473 K is plotted against Ag$_{0.5}$ content of the Cu$_{0.5}$Ag$_{0.5}$–Ag$_{0.5}$S$_2$ pseudo-binary in Fig. 12. The activity coefficient of Ag$_{0.5}$ displays a linear relationship with Ag$_{0.5}$ content of the matte phase in the low silver content region. A value
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(2) Silver activity deviates positively from the ideal behavior in the molten copper, matte saturated copper and copper matte phases, and the highest degree of deviation is observed in the copper matte phase.

(3) It was found that activities of silver in the copper rich phase including 2 at%$S$ are the same with those in the molten copper at 1473 K which gives that $e_A^S$ equals to zero.

(4) The following relationships were obtained for activity coefficients of silver in the immiscible liquid phases of Cu–Ag–S ternary system at 1473 K:

\[
\ln \gamma_{Ag(Cu-rich\ phase)} = 1.19 - 2.87N_{Ag}
\]
\[
\ln \gamma_{Ag(matte\ phase)} = 2.29 - 8.20N_{Ag}
\]

(5) Activity of Ag$_{S_{0.5}}$ in the copper sulfide phase was calculated from measured silver activity and $\gamma_{Ag(S)}$ was estimated to be 0.81 at 1473 K when the matte phase is assumed to be a Cu$_{S_{0.5}}$–Ag$_{S_{0.5}}$ pseudo-binary solution.

(6) Silver is the most volatile component in the Cu–Ag–S ternary system at dilute concentrations in the copper matte at 1473 K, however, volatilization of silver in the converting operation of copper matte is not likely to occur due to its vapor pressure being less than 10 Pa.

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