Phase Relations and Activity of Arsenic in Cu-Fe-S-As System at 1473 K

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To analyze the arsenic behavior in the copper smelting process, the phase relations and the arsenic activity in the miscibility gap of Cu-Fe-S-As system with arsenic as a minor element have been determined at 1473 K by the quenching method and the double Knudsen cell-mass spectrometric method, respectively. The experiments have been conducted for the charges in the miscibility gap with mass%Fe/mass%Cu ratios of 0, 0.023, 0.059, 0.098 and 0.131 with varying arsenic content. The activity measurements indicate that the arsenic activities in both the metal and matte phases show extremely negative deviation from the ideal behavior. The Raoultian activity coefficients at infinite dilution in the metal and matte phases are found to be almost constant against the charges in the miscibility gap and they are 4.3×10^{-3} and 5.5×10^{-2} for the metal and matte phases, respectively. The vapor pressures of predominant As, As₂ and AsS species in the gas phase equilibrated with the immiscible solutions have been calculated on the basis of the determined activity coefficients and they are very small at less than 1 Pa even when the arsenic content in the metal phase is increased up to 10 mass%.

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1. Introduction

Due to the diminishing availability of high grade copper sulfide ores, the treatment of low grade and complex ores has become important in recent years. These ores generally contain large amounts of the group VA elements in the periodic table such as arsenic, antimony and bismuth, which make removal problems during the copper smelting processes. Elimination of these impurities is essential because they have a detrimental effect on the mechanical and electrical properties of the produced copper.

An understanding of their behavior in the copper smelting process requires knowledge of their thermodynamic properties in the related metallurgical substances, of which the matte is of practical importance. It is mainly composed of copper, iron and sulfur, having compositions in an area surrounded by the Cu₂S-FeS tie line and the line b c in Fig. 1. By further removing iron and sulfur in the matte, the compositions shift into a range of the miscibility gap surrounded by a b c d in Fig. 1 and then molten copper is finally produced.

As for arsenic, phase relations in the miscibility gap of the Cu-S-As ternary system have been reported by Asano and Wada,¹⁾ and Gerlach *et al.*²⁾ However, no data are available for the phase relations when arsenic is added in the miscibility gap of the Cu-Fe-S system. The arsenic activities in molten copper have been reported by Azakami and Yazawa,³⁾ Jones and Philipp,⁴⁾ Hino⁵⁾ and Bode *et al.*⁶⁾ Those in the Cu₂S-FeS mattes have been reported by Lau *et al.*,⁷⁾ Itagaki *et al.*,⁸⁾ Hino,⁵⁾ Roine and Jalkanen,⁹⁾ and Zhong and Lynch,¹⁰⁾ while those in the Cu₂S matte equilibrated with copper at 1423 K by Hino and Toguri.¹¹⁾ However, the arsenic activities in the Cu-Fe-S mattes existing in the miscibility gap, which contain arsenic as a minor element, are not available.

Thus, in the present study, the phase relations and arsenic activities in the miscibility gap of the Cu-Fe-S-As system were determined at 1473 K by the quenching method and the double Knudsen cell-mass spectrometric method, respectively.

2. Experimental

2.1 Determination of phase relations

The compositions of copper, iron and sulfur in the starting samples were fixed at the Points of A, B, C, D and E in Fig. 1 and the equilibrium relations between the molten metal (copper alloy) and matte phases were determined at 1473 K when the amount of arsenic added to the Cu-S and Cu-Fe-S systems was varied. The samples of about 6×10^{-3} kg were prepared by proportionally mixing the copper and iron sulfides, which were pyrometallurgically synthesized, as well as the copper and iron chips. The copper arsenide was also put in the sample to control composition. The sample was vacuum-sealed in quartz ampoule with an inner diameter of 8×10^{-3} m and then it was kept in a vertical tube furnace at

Fig. 1 A part of isothermal section in the Cu-Fe-S system at 1473 K.

1473 K for 72 ks to attain equilibrium. It was then quenched in water to obtain the metal and matte portions. After separation, they were analyzed by the ICP method for the determination of arsenic content. Iron content was determined by the volumetric titration with $K_2Cr_2O_7$ while sulfur content gravimetrically as $BaSO_4$.

2.2 Measurement of arsenic activity

2.2.1 Principle of double Knudsen cell-mass spectrometry

A double Knudsen cell configuration coupled with a double-focusing magnetic field mass spectrometer made by Denshi Kagaku (model EMD-05H) was used in the present experiments. With this system, the arsenic activities were determined basing on the ratio of intensities of the arsenic vapor between the samples in which the arsenic activities are known and unknown. The intensity of the As_2 species was determined in the present study because it was mostly prevailing of all the arsenic species in the equilibrium vapor. Hence, the arsenic activity, a_{As} , is given by eq. (1).

$$a_{As(u)}^2 = p_{As_2(u)} / p_{As_2}^0 \quad (1)$$

$$a_{As(u)}^2 = [p_{As_2(u)} / p_{As_2(r)}] a_{As(r)}^2 \quad (2)$$

Rearranging eq. (1) leads to eq. (2) which redefines the arsenic activity in terms of the known (r) and unknown (u) arsenic activities.

The fundamental relationship between the measured ion intensity, $I_{As_2^+}$, and the partial pressure of As_2 , p_{As_2} , in the equilibrium vapor in the Knudsen cell is given by eq. (3).

$$p_{As_2} = K I_{As_2^+} T \quad (3)$$

where K is a constant which includes a relative ionization cross section and multiplier efficiency, and T is temperature of the sample. Substituting eq. (3) into eq. (2) leads to eq. (4).

$$a_{As(u)}^2 = C [I_{As_2(u)} / I_{As_2(r)}] a_{As(r)}^2 \quad (4)$$

The constant C , that compensates for the geometrical discrepancies between the two cells, can be determined for each particular pair of cells by performing a complimentary run using the same pure materials in both cells and copper used in the present study. Two kinds of Cu–As binary alloys were used as the reference in the present study, depending on the ion intensity under study, and the activity data reported by Hino⁵⁾ were employed in eq. (4).

2.2.2 Double Knudsen cell

The configuration of the double Knudsen cell is shown in Fig. 2. It is made of alumina with an inner diameter of 8.8×10^{-3} m and a height of 14×10^{-3} m. An orifice is made at the sidewall, whose size is varied from 3 to 5×10^{-4} m ϕ depending on the vapor pressure of the samples under study. A molybdenum heating element is wound around the cell holder on a refractory guide. The element is surrounded by a series of molybdenum radiation shields. Temperature is measured by a Pt/Pt–13Rh thermocouple inserted in the middle of the cell holder.

2.2.3 Procedure

In each experimental run, the reference and unknown samples of about 2.5×10^{-3} kg were put in a pair of the Knudsen

Fig. 2 Schematic diagram of the Knudsen cell-mass spectrometer assembly.

cells. The ratios of compositions between copper, iron and sulfur were fixed at the points of A, B, C, D and E in Fig. 1 and the arsenic content was varied in the sample. Their compositions were adjusted by proportionally mixing the copper and iron sulfides, which were pyrometallurgically synthesized, as well as the metallic copper and iron chips. Arsenic was put in the sample as the copper alloy.

Once the experimental temperature was attained, the cell containing the reference samples was aligned toward the ion source. As_2^+ signals were then monitored for at least 0.9 ks confirming a constant intensity height. The ionizing energy, which was employed to avoid fragmentation of the As_2 species, was 2.08×10^{-18} J (13 eV). The background intensity was recorded by turning the cell holder by about 90° . The net ion intensity was obtained as the difference between them. The same procedure was repeated for the unknown sample. The whole process was repeated at least three times and average intensity ratio between the unknown and reference samples was used to calculate the activities according to eq. (4).

The compositions of the unknown sample were fixed in a miscibility gap with the metal (copper alloy) and matte phases. To determine the compositions of these phases equilibrated at 1473 K, rapidly cooled specimens are required for the chemical analysis. However, the rapid cooling was structurally not possible for the present mass spectrometer assembly. Hence, the compositions were evaluated from the data on the equilibrium phase relations determined in the separate experiments of the present study.

3. Results

The composition of the charges, the mole fraction of the components in the coexisting metal and matte phases, the mole fraction of the reference Cu–As binary alloy, the intensity ratio of As_2 and the calculated arsenic activity taking the liquid standard state are summarized in Table 1 for given ratios of mass%Fe/mass%Cu in the charge.

3.1 Phase relations

The equilibrium compositions of the immiscible metal and matte phases and the conjugate lines in the Cu–Fe–S system at 1473 K are shown in Fig. 1. As far as the composition of the matte phase is concerned, the present result is in a good agreement with the literature data reported by Nagamori *et al.*¹²⁾

Table 1 Compositions of samples, measured ion intensity ratios and activity of arsenic in Cu–Fe–S–As system at 1473 K.

Charge composition (mass%)					Metal phase				Matte phase				Reference		
%Fe/%Cu	%Cu	%Fe	%S	%As	N_{Cu}	N_{Fe}	N_S	N_{As}	N_{Cu}	N_{Fe}	N_S	N_{As}	(Cu–As) N_{As}	$I_{(u)}/I_{(r)}$	$a_{As(u)}$
0	89.45	10.55	—	—	0.974	—	0.026	—	0.666	—	0.334	—	—	—	—
0	89.30	10.50	0.20	—	0.972	—	0.023	0.005	0.664	—	0.335	0.001	—	—	—
0	88.10	10.40	1.50	—	0.960	—	0.025	0.015	0.665	—	0.333	0.002	—	—	—
0	87.70	10.35	1.95	—	0.945	—	0.025	0.030	0.665	—	0.332	0.003	0.059	0.242	2.10×10^{-4}
0	86.70	10.20	3.10	—	0.932	—	0.025	0.043	0.675	—	0.320	0.005	0.059	0.420	3.65×10^{-4}
0	85.70	10.10	4.20	—	0.925	—	0.023	0.052	0.669	—	0.324	0.007	0.059	0.623	5.41×10^{-4}
0	85.45	10.05	4.50	—	0.915	—	0.020	0.065	0.668	—	0.324	0.008	0.100	0.367	9.00×10^{-4}
0	84.91	10.00	5.09	—	0.870	—	0.021	0.109	0.673	—	0.314	0.013	0.100	0.787	2.13×10^{-3}
0	84.43	10.00	5.57	—	0.857	—	0.020	0.123	0.677	—	0.308	0.015	0.100	1.187	2.92×10^{-3}
0.023	87.95	2.00	10.05	—	0.964	0.010	0.026	—	0.624	0.034	0.342	—	—	—	—
0.023	86.21	1.99	9.85	1.95	0.936	0.008	0.027	0.029	0.634	0.024	0.340	0.002	0.059	0.192	1.84×10^{-4}
0.023	84.40	1.95	9.65	4.00	0.911	0.008	0.022	0.059	0.632	0.028	0.334	0.006	0.059	0.564	4.89×10^{-4}
0.023	83.72	1.93	9.59	4.76	0.890	0.010	0.020	0.080	0.646	0.020	0.326	0.008	0.059	1.174	1.02×10^{-3}
0.023	83.01	1.92	9.50	5.57	0.881	0.009	0.024	0.086	0.640	0.029	0.322	0.009	0.059	1.829	1.59×10^{-3}
0.059	84.85	5.01	10.14	—	0.942	0.033	0.025	—	0.597	0.048	0.355	—	—	—	—
0.059	83.06	4.90	9.95	2.09	0.925	0.022	0.022	0.031	0.582	0.071	0.344	0.003	0.059	0.187	1.87×10^{-4}
0.059	81.60	4.86	9.80	3.74	0.902	0.024	0.019	0.055	0.593	0.066	0.335	0.006	0.059	0.575	5.00×10^{-4}
0.059	80.77	4.79	9.70	4.74	0.874	0.026	0.020	0.080	0.617	0.054	0.321	0.008	0.059	1.151	1.00×10^{-3}
0.059	80.03	4.74	9.58	5.65	0.870	0.026	0.017	0.087	0.597	0.064	0.331	0.008	0.059	1.392	1.21×10^{-3}
0.098	81.70	8.04	10.26	—	0.919	0.055	0.026	—	0.526	0.102	0.372	—	—	—	—
0.098	80.00	7.83	10.10	2.07	0.904	0.044	0.020	0.032	0.523	0.116	0.358	0.003	0.059	0.187	1.80×10^{-4}
0.098	78.49	7.67	9.90	3.94	0.868	0.049	0.024	0.059	0.518	0.122	0.353	0.007	0.059	0.656	5.51×10^{-4}
0.098	77.83	7.60	9.80	4.77	0.846	0.050	0.022	0.082	0.524	0.118	0.350	0.008	0.059	1.188	1.07×10^{-3}
0.098	77.14	7.53	9.71	5.62	0.840	0.052	0.020	0.088	0.526	0.115	0.349	0.010	0.059	1.355	1.19×10^{-3}
0.131	77.83	10.17	12.00	—	0.903	0.069	0.028	—	0.503	0.124	0.373	—	—	—	—
0.131	76.29	9.97	11.75	1.99	0.866	0.072	0.028	0.034	0.491	0.138	0.368	0.003	0.059	0.248	2.24×10^{-4}
0.131	74.74	9.80	11.55	3.91	0.840	0.072	0.026	0.062	0.504	0.133	0.356	0.007	0.059	0.932	8.10×10^{-4}
0.131	74.07	9.72	11.42	4.79	0.826	0.072	0.022	0.080	0.516	0.129	0.347	0.008	0.059	1.369	1.19×10^{-3}
0.131	73.39	9.63	11.30	5.68	0.815	0.076	0.024	0.085	0.511	0.129	0.350	0.010	0.059	1.496	1.30×10^{-3}

and Chang *et al.*¹³⁾ though the conjugate lines reported by Chang *et al.*¹³⁾ considerably shift to the iron side of the metal phase. The sulfur content in the metal phase is in a good agreement with that reported by Chang *et al.*,¹³⁾ while smaller than the value reported by Nagamori *et al.*¹²⁾

The phase relations in the Cu–S–As ternary system at 1473 K are shown in Fig. 3. It is found that the slope of the conjugate lines increases with increasing arsenic content in the charge. The sulfur content in the matte phase decreases with increasing arsenic content in the charge, while that in the metal phase is almost constant at $N_S = 0.020$ – 0.026 . The miscibility gap reported by Asano and Wada¹⁾ is shown with the broken lines in Fig. 3, which is very close to the present result.

The phase relations in the Cu–Fe–S–As system with mass%Fe/mass%Cu of 0.131 in the charge are shown in Fig. 4. The composition plots for the metal and matte phases are located on the approximately smooth lines, respectively. This suggests that all the conjugate lines in Fig. 4 are on a given cross section in the compositional Cu–Fe–S–As tetrahedron, which makes a contact to the bottom Cu–Fe–S plane. As in the Cu–S–As system, the slope of the conjugate line increases with increasing arsenic content in the charge, while the sulfur content in the metal phase is almost constant. The similar phase relations were found for other Cu–Fe–S–As sys-

Fig. 3 Phase relations between the matte and metal phase within the miscibility gap of Cu–S–As ternary system with the charge composition of %S/%Cu = 0.118 at 1473 K.

tems with different charge compositions.

The distribution ratios of arsenic between the matte and metal phases, defined as $L_{As}^{m/c} = \{\text{mass\%As in matte}\} / [\text{mass\%As in metal}]$, were calculated from the data in Table 1 and are shown in Fig. 5, in relation to the mole fraction of arsenic in the metal phase. It is found that $L_{As}^{m/c}$ is likely to be independent of the charges with A–E within scattering of the

Fig. 4 Phase relations between the matte and metal phases within the miscibility gap of Cu-Fe-S-As quaternary system with the charge composition of %Fe/%Cu = 0.131 at 1473 K.

Fig. 5 Distribution ratio of arsenic between matte and metal phases in the Cu-S-As and Cu-Fe-S-As systems at 1473 K.

data, as illustrated with the broken line, and tends to slightly increase with increasing arsenic content.

3.2 Activity and activity coefficient of arsenic

The activity of arsenic in the Cu-S-As system at 1473 K is shown in Fig. 6, in relation to the atomic fraction of arsenic in the matte or metal phase. For comparison, the data at 1423 K reported by Hino and Toguri¹¹⁾ are illustrated with the broken lines in Fig. 6. Arsenic activity in the metal phase shows an extremely large negative deviation from ideality, while that in the matte phase is much larger than in the metal phase for the same arsenic concentration in each phase even though it still shows a considerably large negative deviation from Raoult's law. The present results are found to be in an excellent agreement with those by Hino and Toguri¹¹⁾ when the temperature difference between both experiments is not taken into account. When the present activity value at 1473 K is converted to that at 1423 K using the regular solution model, it is about 5% more negative than the value at 1473 K. This may enlarge the discrepancy between the present and reported values. Nevertheless, it can be noted that the agreement between both results is still satisfactory.

The activity of arsenic in the Cu-Fe-S-As system with mass%Fe/mass%Cu of 0.131 in the charge at 1473 K is shown

Fig. 6 Activity of arsenic in the miscibility gap of Cu-S-As ternary system at 1473 K.

Fig. 7 Activity of arsenic in the miscibility gap of Cu-Fe-S-As quaternary system with the charge composition of %Fe/%Cu = 0.131 at 1473 K.

Fig. 8 Activity coefficient of arsenic in the matte phase at the miscibility gap of Cu-S-As and Cu-Fe-S-As systems at 1473 K.

in Fig. 7. It is found that the arsenic activities in both phases are very similar to those in the Cu-S-As ternary system, showing large negative deviations from the Raoult's law. The relationship between the arsenic activity and the mole fraction of arsenic in the matte or metal phase for other Cu-Fe-S-As systems with different mass%Fe/mass%Cu in the charge resembles to that shown in Fig. 7.

Fig. 9 Activity coefficient of arsenic in the metal phase at the miscibility gap of Cu-S-As and Cu-Fe-S-As systems at 1473 K.

The Raoultian activity coefficients of arsenic, $\{\gamma_{\text{As}}\}$, in the matte phase at the miscibility gap of the Cu-S-As and Cu-Fe-S-As systems with different charge compositions at 1473 K are shown in Fig. 8, in relation to the mole fraction of arsenic in the matte phase. It is found that $\{\gamma_{\text{As}}\}$ is likely to be independent of the charges with A-E and $\log\{\gamma_{\text{As}}\}$ almost proportionally increases with N_{As} in the matte phase within scattering of the data. By the least square treatment, $\ln\{\gamma_{\text{As}}\}$ can be expressed as

$$\ln\{\gamma_{\text{As}}\} = -2.90 + 92.1\{N_{\text{As}}\} \quad (5)$$

with $\{\gamma_{\text{As}}^0\}$ at infinite dilution of 5.5×10^{-2} .

The Raoultian activity coefficients of arsenic, $[\gamma_{\text{As}}]$, in the metal phase at the miscibility gap of the Cu-S-As and Cu-Fe-S-As systems with different charge compositions at 1473 K are shown in Fig. 9, in relation to the mole fraction of arsenic in the metal phase. $[\gamma_{\text{As}}]$ is also likely to be independent of the charges with A-E and $\log[\gamma_{\text{As}}]$ almost proportionally increases with $[N_{\text{As}}]$, which can be expressed as

$$\ln[\gamma_{\text{As}}] = -5.46 + 14.6[N_{\text{As}}] \quad (6)$$

with $[\gamma_{\text{As}}^0]$ at infinite dilution of 4.3×10^{-3} .

4. Discussions

4.1 Distribution ratio of arsenic

The distribution ratio of arsenic between the matte and metal phases, as shown in Fig. 5, is almost independent of the mass%Fe/mass%Cu in the charge and this result will be thermodynamically analyzed on the basis of eq. (7), which is established for the phase equilibrium between the matte and metal phases.

$$\{\gamma_{\text{As}}\}N_{\text{As}} = [\gamma_{\text{As}}]N_{\text{As}} \quad (7)$$

By rearranging eq. (7) and converting the mole fraction to the mass% basis, the following equation is obtained.

$$L_{\text{As}}^{m/c} = \frac{\{\text{mass\%As}\}}{[\text{mass\%As}]} = \frac{(n_{\text{T}}/[n_{\text{T}}])([\gamma_{\text{As}}]/\{\gamma_{\text{As}}\})}{1} \quad (8)$$

where $\{n_{\text{T}}\}$ and $[n_{\text{T}}]$ are the mole amount of 0.1 kg in the matte and metal phases, respectively.

$\{\gamma_{\text{As}}\}$ and $[\gamma_{\text{As}}]$ in eq. (8), as respectively shown in Figs. 8 and 9, are almost independent of the mass%Fe/mass%Cu in the charge. Hence, for $L_{\text{As}}^{m/c}$ to be independent of the charge, $\{n_{\text{T}}\}/[n_{\text{T}}]$ in eq. (8) is also to be independent. $\{n_{\text{T}}\}/[n_{\text{T}}]$, which were calculated from the compositions in the equilibrium matte and metal phases in Table 1, are found to be between 1.18 and 1.22, that almost satisfies the condition required for the nondependency of $L_{\text{As}}^{m/c}$ on the charge composition. This observed coordination among the $L_{\text{As}}^{m/c}$, γ_{As} and compositions between/in the equilibrium matte and metal phases, in terms of their nondependency on the mass%Fe/mass%Cu in the charge, may suggest a validity of the present experimental results.

4.2 Influence of iron on arsenic activity

One of the authors⁸⁾ clarified that the copper and iron activities have a serious effect on the arsenic activity in the matte with compositions close to those on a tie line connecting Cu_2S and FeS in the Cu-Fe-S system, due to a strong chemical affinity of arsenic with copper and iron, and that the activity coefficient of arsenic in the matte remarkably decreases with increasing copper or iron activity. According to Nagamori *et al.*,¹²⁾ the copper activity in the miscibility gap of the Cu-Fe-S system at 1473 K shows a very large value of about 0.96, while the iron activity increases almost proportionally from 0 at mass%Fe/mass%Cu of 0 in the charge to about 0.5 at the mass%Fe/mass%Cu of 0.131. Hence, it is of interest to know how the iron activity, under the condition of very large copper activity, has an effect on the arsenic activity in the miscibility gap of the Cu-Fe-S-As system. The present experimental results, as shown in Fig. 8, strongly indicate that the influence of iron on the arsenic activity is very small. This means that the effect to the arsenic activity is not intensified by iron when the copper activity significantly prevails to that of iron.

The activity coefficient of arsenic in the metal phase with arsenic, sulfur and iron as minor elements is given by eq. (9) as a function of interaction parameters when the second and higher order terms are neglected.

$$\ln[\gamma_{\text{As}}]_{\text{Cu-Fe-S}} = \ln[\gamma_{\text{As}}^0]_{\text{Cu}} + \varepsilon_{\text{As}}^{\text{As}}[N_{\text{As}}] + \varepsilon_{\text{As}}^{\text{S}}[N_{\text{S}}] + \varepsilon_{\text{As}}^{\text{Fe}}[N_{\text{Fe}}] \quad (9)$$

Because $[N_{\text{S}}]$ at the miscibility gap in the Cu-Fe-S system is almost constant against mass%Fe/mass%Cu in the charge, as shown in Fig. 1 and Table 1, the limiting activity coefficient of arsenic, $[\gamma_{\text{As}}^0]_{\text{Cu-Fe-S}}$, can be given by eq. (10).

$$\ln[\gamma_{\text{As}}^0]_{\text{Cu-Fe-S}} = \ln[\gamma_{\text{As}}^0]_{\text{Cu-S}} + \varepsilon_{\text{As}}^{\text{Fe}}[N_{\text{Fe}}] \quad (10)$$

The present study, as shown in Fig. 9, clarified that $[\gamma_{\text{As}}^0]_{\text{Cu-Fe-S}}$ is likely to be independent of the mass%Fe/mass%Cu, in other word mass%Fe, in the charge. This suggests that the interaction parameter of $\varepsilon_{\text{As}}^{\text{Fe}}$ in eq. (10) is very small.

The quasichemical model¹⁴⁾ for the A-B-C ternary solution with C as a solute atom suggests that $\log\gamma_{\text{Cu(A+B)}}^0$ at given N_{B} negatively deviates from the corresponding value on a tie line, which linearly connects between $\log\gamma_{\text{C(A)}}^0$ and $\log\gamma_{\text{C(B)}}^0$, when these are negative. It is also suggested by this model that the slope of the $\log\gamma_{\text{Cu(A+B)}}^0$ vs N_{B} plots in the dilute range of B becomes steeper with increasing differ-

ence between $\log \gamma_{C(A)}^0$ and $\log \gamma_{C(B)}^0$ when $\log \gamma_{C(B)}^0$ is more negative than $\log \gamma_{C(A)}^0$. This suggestion may be available for the present discussion when the Cu–Fe–S–As quaternary system in the metal phase is simplified to the Cu–Fe–As ternary due to the considerably small N_S at about 0.02. $\gamma_{Cu(As)}^0$ and $\gamma_{Fe(As)}^0$ at 1473 K, which were evaluated from the data by Hino and Toguri,¹¹⁾ and Hino and Azakami,¹⁵⁾ are 3×10^{-3} and 8×10^{-3} , respectively. Hence, according to the prediction based on the quasichemical model, ε_{As}^{Fe} is to have a negative value in the low concentration range of iron. Nevertheless, the present study showed that ε_{As}^{Fe} is zero within scattering of the data. This may suggest that the difference between $\gamma_{Cu(As)}^0$ and $\gamma_{Fe(As)}^0$ is too small to seriously affect ε_{As}^{Fe} in eq. (10).

4.3 Partial pressure of arsenic component

It has been experienced in the practical operations of copper smelting that elimination of arsenic by means of volatilization is very hardly attained in the copper-making stage of the converting process or in the reducing smelting to make the speiss phase which is mainly composed of copper, iron, arsenic and antimony. Hence, partial pressures of the arsenic components in the metal and matte phases of the miscibility gap are of practical concern in the copper smelting.

Based on the activity coefficient of arsenic in the metal and matte phases derived in the present study and the equilibrium constants^{16,17)} for the related reactions as listed in Table 2, partial pressures of the predominant arsenic gas species of As_2 , As and AsS were calculated and are shown in Figs. 10 and 11. The partial pressure of AsO is shown with broken lines, which was evaluated for a condition that a slag phase with the FeO activity of 0.35, which corresponds to the iron silicate slag with saturated silica is to be equilibrated with the matte and metal phases.

As shown in Fig. 10, the partial pressures of AsS, As and As_2 , which the metal phase with 1 mass%As presents, are extremely small at the values with the orders of 10^{-2} and 10^{-3} Pa and almost constant against the iron content of the metal phase. It is noteworthy that they are one or two order of magnitude smaller than that of S_2 , which was calculated using the data reported by Nagamori *et al.*¹²⁾ The partial pressure of AsO increases with increasing iron content but AsS is still prevailing among the arsenic gas species.

The partial pressures calculated for the miscibility gap with the charge of mass%Fe/mass%Cu with 0.131, as shown in Fig. 11, remarkably increase with increasing arsenic content in the metal phase. It is found that As_2 is prevailing in the range of higher arsenic content and even prevails over S_2 . Nevertheless, the partial pressure of As_2 at 10 mass%As in the metal still presents a small value of about 1 Pa, suggest-

ing a difficulty in eliminating arsenic from the miscibility gap system by means of volatilization.

5. Conclusions

The phase relations in the miscibility gap of the Cu–Fe–S–As system with arsenic as a minor element were investigated at 1473 K by the quenching method. The double Knudsen cell-mass spectrometric method was successfully applied to determine the arsenic activities in the metal and matte phases of the miscibility gap at 1473 K. The phase relations and arsenic activities were determined for the charge compositions in the miscibility gap with mass%Fe/mass%Cu ratios of 0, 0.023, 0.059, 0.098 and 0.131 with varying arsenic content. The main results of the present study are summarized in the following.

(1) The distribution ratio of arsenic defined as {mass%As in matte}/[mass%As in metal] is found to be less than unity and slightly increases with increasing arsenic content in the metal phase but to be almost independent of the charge compositions in the miscibility gap.

(2) The arsenic activities show large negative deviations

Fig. 10 Partial pressures at 1473 K against mole fraction of iron in metal equilibrating with matte when arsenic content in the matte is 1 mass% (p_{AsO} is derived in a condition that slag with $a_{FeO} = 0.35$ is equilibrated).

Fig. 11 Partial pressures at 1473 K against mass%As in the metal phase of miscibility gap with charge of %Fe/%Cu = 0.131 (p_{AsO} : equilibrating with slag of $a_{FeO} = 0.35$).

Table 2 Equilibrium constants at 1473 K.

Reaction	log K	Reference
$As(l) = As(g)$	-3.481	7)
$2As(l) = As_2(g)$	0.830	7)
$2As(l) + S_2(g) = 2AsS(g)$	0.698	16)
$2As(l) + O_2(g) = 2AsO(g)$	4.299	17)

from the ideal behavior in both molten metal and matte phases.

(3) The activity coefficients of arsenic in both molten metal and matte phases are almost constant at a given arsenic content against the charge compositions in the miscibility gap.

(4) The activity coefficients of arsenic in the metal and matte phases in its dilute concentration change almost linearly with the arsenic mole fractions and the following relationships are obtained, respectively.

$$\ln[\gamma_{\text{As}}]_{\text{metal}} = -5.46 + 14.6[N_{\text{As}}]$$

$$\ln\{\gamma_{\text{As}}\}_{\text{matte}} = -2.90 + 92.1\{N_{\text{As}}\}$$

with γ_{As}^0 at infinite dilution of $[\gamma_{\text{As}}^0]_{\text{metal}} = 4.3 \times 10^{-3}$ and $\{\gamma_{\text{As}}^0\}_{\text{matte}} = 5.5 \times 10^{-2}$.

(5) The vapor pressures of predominant As, As₂, and AsS species in the gas phase equilibrated with the immiscible solutions in the Cu–Fe–S–As system, which were calculated on the basis of the obtained arsenic activity coefficients, are very small at less than 1 Pa even when the arsenic content in the metal phase is increased up to 10 mass%. This suggests that elimination of arsenic by means of volatilization is very hardly attained once the metal phase appears in the copper smelting process.

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