

# Fundamental Study on New Zinc Distillation Process Utilizing Zinc Sulfide Reaction with Metallic Copper

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Phase relations of copper-zinc-sulfur ternary system have been investigated at temperatures of 1100 and 1200 K by equilibrating synthetic samples in evacuated sealed quartz tubes. Using the activities of copper and zinc in the copper-zinc binary system reported in literatures, the activities of the components in the copper-zinc-sulfur ternary system have been then calculated by applying the Gibbs-Duhem equations to the phase relation of metal-sulfide equilibrium. The reaction path of a new zinc distillation process, in which zinc sulfide is directly reduced to zinc vapor with metallic copper, and sulfur in zinc sulfide is fixed as copper sulfide, has been discussed in terms of the activities of the components in the copper-zinc-sulfur ternary system. [doi:10.2320/matertrans.48.1007]

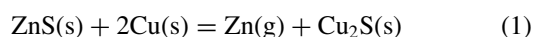
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## 1. Introduction

A new zinc distillation process with environmental consciousness has been proposed previously by the authors,<sup>1-4)</sup> in which zinc sulfide concentrate ore that is a raw material in conventional zinc extraction process is directly reduced to zinc vapor with metallic iron, and sulfur in ore is fixed as iron sulfide, that is, sulfur fixation with sulfur dioxide free. Roasting and sintering of zinc sulfide to zinc oxide calcine or sinter are not required. Utilization of an iron scrap as reducing agent, instead of high quality of coke that is usually expensive, leads to the reduction both of energy consumption and environmental burdens in the current zinc extraction process.

As well as an iron scrap, a copper scrap would be used as a reducing agent of zinc sulfide. With respect to a reduction and distillation process of zinc sulfide by metallic copper, Warner proposed a new process,<sup>5,6)</sup> in which zinc sulfide concentrate ore is melted first in a  $\text{Cu}_2\text{S-FeS}$  matte to make  $\text{Cu}_2\text{S-ZnS-FeS}$  matte (melting stage) and then zinc sulfide in the matte is reduced by molten copper to form zinc vapor (reduction stage). The  $\text{Cu}_2\text{S-FeS}$  matte is oxidized with air to produce molten copper, iron oxide slag and sulfur dioxide (oxidation stage). The Warner process has basically three stages as mentioned above and seems to have a problem at a point of energy efficiency due to the circulation of large amounts of high temperature molten matte and copper, while the process proposed by the present work has a single stage of direct zinc sulfide reduction at lower temperatures without sulfur dioxide generation, namely, sulfur fixation as copper sulfide, as expressed by eq. (1).



In order to discuss the process feasibility, the thermodynamics of copper-zinc-sulfur ternary system is of fundamental importance. Azuma *et al.*<sup>7)</sup> and Surapunt *et al.*<sup>8)</sup> investigated near  $\text{Cu-Cu}_2\text{S}$  in copper-zinc-sulfur ternary system at 1473 K. Their data are inappropriate for discussing the

process expressed by eq. (1) at lower temperatures around 1200 K where the condensed phases are solid-state, since their reports have dealt with molten copper matte.

The objective of the present work is to investigate the phase equilibria in the copper-zinc-sulfur ternary system at temperatures of 1100 and 1200 K, and also to discuss the zinc distillation process utilizing zinc sulfide reaction with metallic copper. First, the phase relations in the copper-zinc-sulfur ternary system were investigated by equilibrating synthetic samples in evacuated sealed quartz tubes. The activities of the components in the ternary system were then calculated by applying the Gibbs-Duhem equations to the phase relation of metal-sulfide equilibrium.

## 2. Experimental

The primary starting materials were copper powder (99.9 mass% purity), doubly distilled zinc (99.999 mass% purity), analytical reagent grade  $\text{ZnS}$  (99.99 mass% purity) and block sulfur (99.5 mass% purity). Copper sulfide  $\text{Cu}_2\text{S}$  was synthesized by reacting the stoichiometric mixture of copper and sulfur with molar ratio of 2 : 1 in an evacuated sealed quartz tube. The sample for the determination of the phase relations of  $\text{Cu-Zn-ZnS-Cu}_2\text{S}$  system in the copper-zinc-sulfur ternary system was prepared as follows: metallic copper, zinc,  $\text{ZnS}$  and  $\text{Cu}_2\text{S}$  were mixed at the desired compositions which were represented by open circles in Fig. 1. Then the sample was pressed to the 10 mm diam., 1.5 g briquette under about 400 MPa. The briquette sample was put in a quartz tube of 13 mm i.d., and the quartz tube was then evacuated to about 0.4 Pa and sealed. The quartz capsule was held to heat for a desired holding time at temperatures of 1100 and 1200 K, and then quenched in water. The composition of all phases in the samples was determined by electron probe X-ray microanalysis (EPMA) using atomic-number (Z), absorption and fluorescence corrections, that is, the ZAF method, and the phases were identified using X-ray diffraction (XRD).

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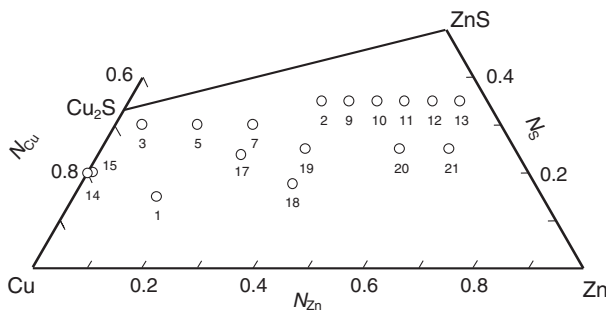


Fig. 1 Starting sample compositions in schematic diagram of Cu-Zn-S ternary system. ○: compositions of starting samples.

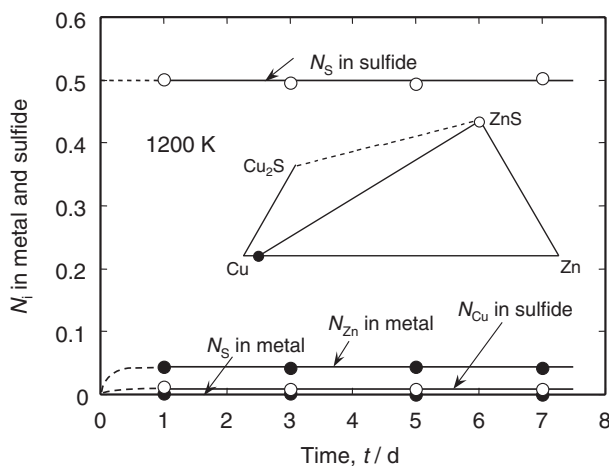


Fig. 2 Relation between the sample composition and time at 1200 K for sample No. 2.

### 3. Results

#### 3.1 Determination of holding time for equilibrium

The relation between the sample composition and holding time at the temperature 1200 K is shown in Fig. 2 as an example, where the sample number 2 corresponds to the number in Fig. 1. The sample was two-condensed-phase combination, namely, the metal phase (Cu s.s.) coexisted with the sulfide phase (ZnS s.s.) where s.s. denotes a solid solution. The sample appears to be attained to equilibrium within one day. However, a microscope observed segregation for the one- and three-days holding samples. Thus, the sample was heated for five days at 1200 K in order to establish the equilibrium. Similarly, at 1100 K the sample was heated for seven days followed by quenching in water.

#### 3.2 Phase relations in copper-zinc-sulfur ternary system

The results of EPMA of the equilibrated samples are shown in Tables 1 and 2. The phases identified by XRD are listed in Tables 3 and 4. From these results, the phase diagrams of the Cu-Zn-ZnS-Cu<sub>2</sub>S system at 1100 and 1200 K are illustrated in Fig. 3(a) and (b), where open circles (○) and triangles (△) denote the compositions in the two-condensed-phase and three-condensed-phase combinations, respectively. The solid lines connecting the open circles are tie lines which represent the conjugate solutions. At the temperature of 1200 K the dotted areas surrounded by the triangles indicate the three-condensed-phase fields of Cu<sub>2</sub>S + ZnS + Cu s.s. and ZnS + Cu s.s. + liquid Zn. At 1100 K the phase relation is relatively complicated compared to that at 1200 K, since  $\beta$ - and  $\gamma$ -solid solutions are stable at lower

Table 1 Results of electron probe X-ray microanalysis (EPMA) of the equilibrated samples at 1100 K.

No.	Cu s.s.			Cu <sub>2</sub> S s.s.			ZnS s.s.			$\beta$			$\gamma$			Zn(l)		
	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$
14	0.9946*	0.0034	0.0020	0.6617*	0.0022	0.3361	—	—	—	—	—	—	—	—	—	—	—	—
15	0.9919*	0.0067	0.0014	0.6670*	0.0019	0.3312	—	—	—	—	—	—	—	—	—	—	—	—
3, 5	0.9790*	0.0195	0.0015	0.6555*	0.0067	0.3378	0.0195	0.4805*	0.5001	—	—	—	—	—	—	—	—	—
2	0.9694*	0.0293	0.0014	—	—	—	0.0166	0.4809*	0.5025	—	—	—	—	—	—	—	—	—
19	0.7654*	0.2336	0.0010	—	—	—	0.0173	0.4812*	0.5015	—	—	—	—	—	—	—	—	—
10	0.6951*	0.3039	0.0010	—	—	—	0.0095	0.4891*	0.5014	—	—	—	—	—	—	—	—	—
11	—	—	—	—	—	—	0.0066	0.4915*	0.5020	0.5162*	0.4826	0.0012	—	—	—	—	—	—
20	—	—	—	—	—	—	0.0083	0.4888*	0.5030	0.4567	0.5424*	0.0009	0.4156	0.5838*	0.0006	—	—	—
21	—	—	—	—	—	—	0.0041	0.4930*	0.5029	—	—	—	—	—	—	0.2558	0.7440*	0.0002
13	—	—	—	—	—	—	0.0032	0.4905*	0.5063	—	—	—	—	—	—	0.1833	0.8157*	0.0010

where  $N_i$ : mole fraction, \*: balance.

Table 2 Results of electron probe X-ray microanalysis (EPMA) of the equilibrated samples at 1200 K.

No.	Cu s.s.			Cu <sub>2</sub> S s.s.			ZnS s.s.			Zn(l)		
	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$	$N_{Cu}$	$N_{Zn}$	$N_S$
14	0.9963*	0.0029	0.0008	0.6615*	0.0008	0.3376	—	—	—	—	—	—
15	0.9901*	0.0093	0.0006	0.6692*	0.0011	0.3296	—	—	—	—	—	—
3, 5, 7	0.9608*	0.0382	0.0011	0.6520*	0.0126	0.3353	0.0159	0.4774*	0.5068	—	—	—
1	0.9557*	0.0431	0.0012	—	—	—	0.0209	0.4854	0.4937*	—	—	—
2	0.9555*	0.0435	0.0010	—	—	—	0.0120	0.4829	0.5052*	—	—	—
17	0.9356*	0.0633	0.0012	—	—	—	0.0121	0.4854*	0.5026	—	—	—
9	0.9039*	0.0949	0.0012	—	—	—	0.0120	0.4846*	0.5034	—	—	—
10, 18	0.7056*	0.2932	0.0012	—	—	—	0.0099	0.4851*	0.5050	0.6734*	0.3258	0.0008
11	—	—	—	—	—	—	0.0042	0.4963*	0.4995	0.5612	0.4380*	0.0008
12	—	—	—	—	—	—	0.0027	0.4929*	0.5044	0.3871	0.6121*	0.0008
13	—	—	—	—	—	—	0.0016	0.4962*	0.5021	0.1699	0.8293*	0.0008

where  $N_i$ : mole fraction, \*: balance.

Table 3 Phases of the quenched sample after equilibrium at 1100 K, identified by X-ray diffraction (XRD).

Sample No.	Phase present
14, 15	Cu <sub>2</sub> S + Cu s.s.
3, 5	Cu <sub>2</sub> S + ZnS + Cu s.s.
2, 19, 10	ZnS + Cu s.s.
11	ZnS + $\beta$
20	ZnS + $\beta$ + $\gamma$
21, 13	ZnS + Zn(l)

Table 4 Phases of the quenched sample after equilibrium at 1200 K, identified by X-ray diffraction (XRD).

Sample No.	Phase present
14, 15	Cu <sub>2</sub> S + Cu s.s.
3, 5, 7	Cu <sub>2</sub> S + ZnS + Cu s.s.
1, 2, 17, 9	ZnS + Cu s.s.
10, 18	ZnS + Cu s.s. + Zn(l)
11, 12, 13	ZnS + Zn(l)

temperatures.<sup>9)</sup> The system has four kinds of three-condensed-phase combination of Cu<sub>2</sub>S + ZnS + Cu s.s., ZnS + Cu s.s. +  $\beta$ , ZnS +  $\beta$  +  $\gamma$  and ZnS +  $\gamma$  + liquid Zn.

The phase boundaries in the copper-zinc binary phase diagram<sup>9)</sup> at 1100 and 1200 K are shown with the crosses (×) in Fig. 3(a) and (b). These metal compositions are compatible with the present result at 1200 K. Since the sulfur content in the Cu-Zn metal is as small as 0.1 mol%, the solid solubility of the sulfide in the Cu-Zn metal is considered to be significantly small.

The important observations are as follows: Sulfide phases lie on the Cu<sub>2</sub>S-ZnS pseudo-binary system as shown in Fig. 3, and the sulfur solubility in metal coexisting with the sulfide is about 0.1 mol% sulfur and is negligibly small both at 1100 and 1200 K. The mutual solid solubility between Cu<sub>2</sub>S and ZnS is small both at 1100 and 1200 K, however, at 1200 K it is larger than that at 1100 K as shown in Fig. 3(a) and (b).

### 3.3 Partial pressures of sulfur and activities in copper-zinc-sulfur ternary system

In the case of a metal being equilibrated with sulfide, by applying the Gibbs-Duhem equations to the phase relation between the metal and sulfide phases in the copper-zinc-sulfur ternary system, the following two equations are given:

$$N_{\text{Cu}} d \log a_{\text{Cu}} + N_{\text{Zn}} d \log a_{\text{Zn}} + N_{\text{S}} d \log (P_{\text{S}_2}/10^5 \text{ Pa})^{1/2} = 0 \quad (2)$$

$$N'_{\text{Cu}} d \log a_{\text{Cu}} + N'_{\text{Zn}} d \log a_{\text{Zn}} + N'_{\text{S}} d \log (P_{\text{S}_2}/10^5 \text{ Pa})^{1/2} = 0 \quad (3)$$

where  $a_{\text{Cu}}$  and  $a_{\text{Zn}}$  are the activities of copper and zinc in the condensed phase, respectively.  $P_{\text{S}_2}$  is the partial pressure of sulfur.  $N_i$  and  $N'_i$  denote the mole fraction in metal and sulfide, respectively.

When the metal is equilibrated with sulfide, the activities of components of both phases have identical values. Equation (4) is derived from eqs. (2) and (3), and then the partial pressure of sulfur  $P_{\text{S}_2}$  can be calculated.

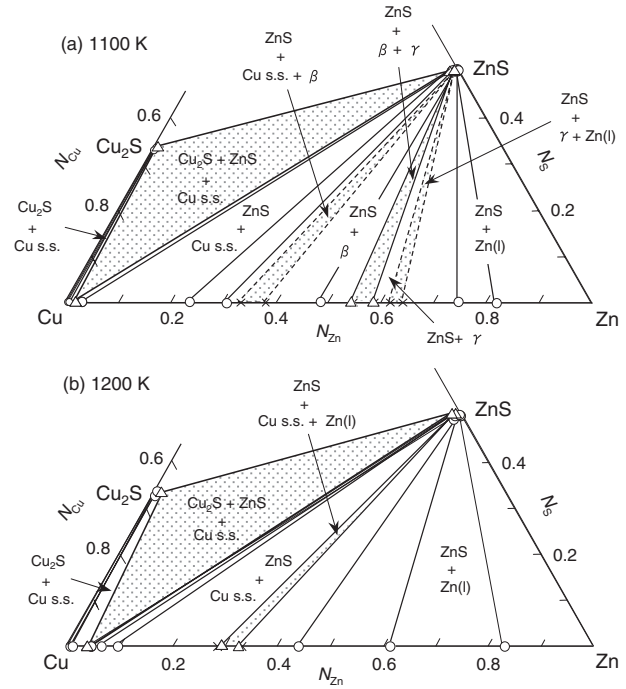


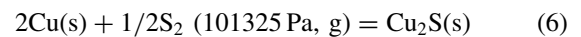
Fig. 3 Phase diagram of the copper-zinc-sulfur ternary system at 1100 and 1200 K. where  $N_i$ : mole fraction (—), ×: Massalski *et al.*,<sup>9)</sup> △: Present work (three-phase combinations), ○: Present work (two-phase combinations).

$$\log(P_{\text{S}_2}/10^5 \text{ Pa}) = \log(P_{\text{S}_2}/10^5 \text{ Pa})_{N_{\text{Cu}}=1} + 2 \int_{N_{\text{Cu}}=1}^{N_{\text{Cu}}} y d \log a_{\text{Cu}} \quad (4)$$

where  $(P_{\text{S}_2}/10^5 \text{ Pa})_{N_{\text{Cu}}=1}$  is the equilibrium partial pressure of sulfur in the system Cu-Cu<sub>2</sub>S at the temperature  $T$  and the following relation defines  $y$ :

$$y = \frac{N_{\text{Cu}} N'_{\text{Zn}} - N_{\text{Zn}} N'_{\text{Cu}}}{N_{\text{Zn}} N'_{\text{S}} - N_{\text{S}} N'_{\text{Zn}}} \quad (5)$$

The equilibrium partial pressure of sulfur in the system Cu-Cu<sub>2</sub>S was substituted using the standard Gibbs energy of Cu<sub>2</sub>S formation reaction described as eq. (6) in the present work. The standard Gibbs energy of Cu<sub>2</sub>S formation is given as eq. (7).<sup>10)</sup>



$$\Delta G^0/\text{kJ}\cdot\text{mol}^{-1} = -132650 + 31.28T/\text{K} \quad (1074\text{--}1283 \text{ K}) \quad (7)$$

For the activity of copper in eq. (4), the value of copper-zinc binary alloys<sup>11,12)</sup> was employed, since the sulfur solubilities in metal were negligibly small as mentioned above.

The relations between the partial pressure of sulfur and the composition of condensed phase at 1100 and 1200 K are illustrated in Fig. 4(a) and (b), where  $X_{\text{Zn}} = N_{\text{Zn}}/(N_{\text{Cu}} + N_{\text{Zn}})$  and  $X'_{\text{Zn}} = N'_{\text{Zn}}/(N'_{\text{Cu}} + N'_{\text{Zn}})$  denote the molar ratio in metal and sulfide phase, respectively. The triangles (△) and circles (○) correspond to the three-condensed-phase and two-condensed-phase combinations, respectively. The small solid circles are literature data.<sup>10,13)</sup> Since the system has two three-condensed-phase fields at 1200 K, there are two



Table 5 Calculated zinc partial pressures in the reaction:  $\text{ZnS(s)} + 2\text{Cu(s)} = \text{Zn(g)} + \text{Cu}_2\text{S(s)}$  at various temperatures.

$T/\text{K}$	$P_{\text{Zn}}/\text{kPa}$
1100	0.049
1200	0.52
1180	0.33
1210	0.64
1240	1.2

condensed-phase field ( $a_{\text{Cu}_2\text{S}} = 0.97$ ,  $a_{\text{ZnS}} = 1.0$ ,  $a_{\text{Cu}} = 0.96$ ) then reaching the  $\text{Cu}_2\text{S}$  composition ( $a_{\text{Cu}_2\text{S}} = 1$ ).

By assuming the activities of  $\text{Cu}_2\text{S}$ ,  $\text{ZnS}$  and copper to be almost unity in the temperature range of 1100 to 1240 K, the zinc partial pressure in the reaction of eq. (10) was calculated as shown in Table 5. The equilibrium partial pressure of zinc is 1.2 kPa at the temperature of 1240 K, indicating that the process is practicable under inert gas stream as well as vacuum.

The activity of  $\text{Cu}_2\text{S}$  in the copper sulfide that will be formed in the process can be regarded as unity. Zinc content in the copper sulfide is expected to be small, and the copper sulfide can be sent to conventional copper smelter, especially, copper converter. Roasting and sintering of zinc sulfide to zinc oxide calcine or sinter are not required. Therefore, utilization of a copper scrap as reducing agent leads to the reduction of the energy consumption and sulfur fixation with sulfide dioxide free in the zinc extraction process. This process enables cyclical use of resources and reduction of environmental burdens.

The kinetic experiments were conducted to confirm the possibility of zinc sulfide reaction with metallic copper under vacuum (about 1 Pa) in the temperature range of 1180 to 1240 K.<sup>14)</sup> The reaction rate increased with increasing temperature. As a result, the zinc distillation process utilizing zinc sulfide reaction with metallic copper is considered to be practicable.

## 5. Conclusions

The phase relations and the activities of components in the copper-zinc-sulfur ternary system, which are fundamental data on the new zinc distillation process where zinc sulfide is directly reduced to zinc vapor with metallic copper, and sulfur in zinc sulfide is fixed as copper sulfide, have been determined at temperatures of 1100 and 1200 K. The results are summarized as follows:

(1) Sulfur solubility in metal coexisting with sulfide is

negligibly small, and sulfide phases lie on the  $\text{Cu}_2\text{S}$ - $\text{ZnS}$  pseudo-binary system. The mutual solid solubility between  $\text{Cu}_2\text{S}$  and  $\text{ZnS}$  is small.

- (2) Relation between the partial pressure of sulfur and the composition of the condensed phase was determined. The activities of  $\text{Cu}_2\text{S}$  and  $\text{ZnS}$  were obtained using the equilibrium partial pressure of sulfur and the activities of copper and zinc in copper-zinc binary alloys.
- (3) The activity of  $\text{Cu}_2\text{S}$  in the copper sulfide that will be formed in the process can be regarded as unity. Zinc content in the copper sulfide formed in the process is expected to be small, and the copper sulfide can be sent to conventional copper smelter, especially, copper converter.

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