A Thermodynamic Study of the Liquid Cu-Sn and Cu-Cr Alloys by the Knudsen Cell-Mass Filter Combination

By Katsutoshi Ono*, Seiji Nishi** and Toshio Oishi*

A study of the thermodynamics of the liquid alloy systems Cu-Sn and Cu-Cr has been made with the combination of Knudsen cell and quadrupole mass spectrometer. From the data obtained, the activities in the liquid Cu-Sn and Cu-Cr systems, and the heats of mixing in the liquid Cu-Sn system were calculated.

The activities and the heats of mixing for Cu-Sn alloys showed a good agreement with those of other investigators.

The activity of Cr in Cu-Cr alloys showed a large positive deviation from Raoult's law. The liquidus line of the Cu-Cr system in the Cu-rich concentration range was determined from the break points of the ion current ratios in the mass spectrometric measurements as well as the differential thermal analysis.

(Received June 4, 1984)

Keywords: thermodynamics, activity measurement, mass spectrometry, copper-tin system, copper-chromium system, liquidus line, differential thermal analysis

I. Introduction

The mass spectrometric analysis of Knudsen cell effluents has made possible measurements of the thermodynamic properties of liquid alloy systems. Belton and Fruehan⁽¹⁾ have introduced a useful method for determining the activities and the partial molar heats of mixing with the Knudsen cell-mass spectrometer combination. This method consists of measuring the ratio of ion currents due to the two monatomic vapors above a binary alloy and substituting the ratio for the activity term in the Gibbs-Duhem relation.

Recent development of a small, inexpensive quadrupole mass filter makes interesting to use it as a mass spectrometer for alloy studies. In the present investigation, the activities in the liquid Cu-Sn system which had so far been studied by many authors using different experimental methods were firstly determined by this technique to check its reliability. Subsequent measurements were made on the Cu-Cr system

in the temperature range from 1523 to 1673 K where no comparable activity measurements have been conducted.

II. Experimental Method

For a binary liquid metallic solution which vaporizes as free atoms, the following relationships are derived by Belton and Fruehan.

$$\ln \gamma_1 = - \int_{N_1=1}^{N_1=N_1} N_2 d[\ln(I_2^+/I_1^+) - \ln(N_2/N_1)], \quad (1)$$

$$\ln a_1 = - \int_{N_1=1}^{N_1=N_1} N_2 d \ln(I_2^+/I_1^+), \quad (2)$$

and

$$\Delta \bar{H}_1 = -R \int_{N_1=1}^{N_1=N_1} N_2 d \left[\frac{d \ln(I_2^+/I_1^+)}{d(1/T)} \right], \quad (3)$$

where γ_1 is the activity coefficient of the component 1, defined as $\gamma_1 = a_1/N_1$. a_1 , N_1 and $\Delta \bar{H}_1$ are the activity, the atom fraction and the partial molar heat of mixing of the component 1, respectively, and I^+ is the ion current of a mass filter proportional to the partial pressure of the components in the Knudsen cell containing the liquid alloy.

A NEVA quadrupole mass filter, type NAG-531, was combined with a high-temperature vacuum furnace with a cylindrical tantalum

* Department of metallurgy, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

** Graduate Student, Kyoto University, Kyoto. Present address: Central Research Lab., Kobe Steel Co., Ltd., Wakino-hama, Fukiai-ku, Kobe 651, Japan.

Fig. 1 Assembly for Knudsen cell-mass filter measurement.

heater 20 mm in diameter and 100 mm long. An assembly for Knudsen cell-mass filter measurements is shown in Fig. 1. The temperature of the cell was measured by means of a W/Re 5-26 thermocouple.

The alumina crucible was 11 mm in o.d., 9 mm in i.d. and 7 mm in height, and the lid had a thickness of 0.5 mm and an orifice diameter of 0.5 mm. The cells were suspended with tungsten wires in the tantalum heater.

As principal mass peaks 63, 120 and 52 were used for Cu, Sn and Cr, respectively. The ionization potential of 22 eV was employed for both the Cu-Sn and Cu-Cr systems. The ion currents at a desired mass peak were recorded on a chart recorder, the background ion currents being determined by the shutter technique. The temperature was alternately decreased and increased between a maximum and a minimum.

The Cu-Sn alloys were prepared *in-situ* by melting together a total of 1 g of the 99.9% purity component metals. The Cu-Cr alloys were made beforehand by melting together weighed samples of 99.9% purity by a levitation method. The Cu-Cr alloy compositions were determined by subsequent chemical analysis.

III. Results and Discussion

1. Cu-Sn system

As an example, the ionic intensities and ion current ratio for the Cu-50 atom pct Sn alloy

Fig. 2 Ionic intensities and ion current ratio as a function of temperature for the Cu-50 atom pct Sn alloy.

Fig. 3 Ion current ratios for the Cu-Sn system.

are plotted in Fig. 2 as a function of temperature. The ion current ratios for the Cu-Sn alloys of different compositions are presented in

Fig. 4 Integration plot for the calculation of activity coefficients in the Cu-Sn system at 1573 K.

Fig. 5 Activities for the Cu-Sn system at 1573 K.

Fig. 3. Values of $\log(I_{Cu}^+/I_{Sn}^+) - \log(N_{Cu}/N_{Sn})$ derived from the data in Fig. 3 are plotted against Cu compositions in Fig. 4. Graphical integration of the area under the curve gives, according to eq. (1), the activity coefficient of Sn. The activities of Cu and Sn, thus determined, are compared with data from other investigations in Fig. 5.

It is evident from Fig. 5 that the activity of Sn exhibits a slight positive departure from ideality for $N_{Sn} > 0.5$ and a negative departure for $N_{Sn} < 0.5$. The activity of Cu, on the other hand, shows a negative deviation over the entire composition range.

From the derived slopes in Fig. 3 the values

Fig. 6 Integration plot for the calculation of partial molar heats of mixing in the Cu-Sn system.

Fig. 7 Integral and partial molar heats of mixing of the liquid Cu-Sn alloys.

Fig. 8 Integral molar heat of mixing of the liquid Cu-Sn alloys.

of $R[d \ln (I_{\text{Cu}}^+/I_{\text{Sn}}^+)/d(1/T)]$ have been calculated. The results are shown in Fig. 6 as a function of N_{Cu} . The partial molar heats of mixing have been calculated from eq. (3) using the integrated areas in Fig. 6. The results of the integral and partial molar heats of mixing are shown in Fig. 7. Figure 8 shows a comparison between the integral molar heats of mixing obtained by various investigators. It is to be noted that the partial molar heat of mixing of Sn varies from a large negative to positive with increasing Sn content, and the integral quantity shows a small positive at high Sn concentrations.

2. Cu-Cr system

The relationships between the ion current ratios and $1/T$ are presented in Fig. 9. For the alloys of 3.7, 4.5 and 6.4 at%Cr, breaks were observed. These break points would correspond to the liquidus line. The experimental points for the higher Cr alloys of 9.8 and 21.7 at% correspond, therefore, to values of liquid alloys and solid Cr in the two phase equilibrium region. The liquidus temperature thus obtained

Fig. 9 Ion current ratios for the Cu-Cr system.

Fig. 10 Liquidus line at the Cu-rich side in the system Cu-Cr.

Fig. 11 Integration plot for the calculation of the activity of Cr in the Cu-Cr system at 1573 K.

differed considerably from that of Siedschlag⁽⁷⁾ in Hansen's Handbook⁽⁸⁾. The differential thermal analysis was then used to check this large difference. It was made on four different Cu-Cr alloy compositions. The results are shown in Fig. 10. The liquidus lines by the two different techniques lie very close to each other.

In this system eq. (2) was used to obtain the activity of Cr. The interpolated ion current ratios at 1573 K were plotted against the mole fraction of Cu in Fig. 11. According to Fig. 11, the phase boundary at this temperature should be situated at 4.7 at%Cr.

The activities of Cu and Cr at 1573 K are

Fig. 12 Activities in the Cu-Cr system at 1573 K.

shown in Fig. 12. The activity of Cr in the two-phase field was taken to be unity, the solubility of Cu in solid Cr being regarded as negligible.

IV. Summary

Thermodynamic studies of the liquid Cu-Sn and Cu-Cr systems have been made with the combination of Knudsen cell and quadrupole mass spectrometer. The study of the liquid Cu-Sn system was made to check the reliability of this technique.

The ion current ratios for the alloy components were measured through the whole range of composition for the Cu-Sn and in the range of composition, $N_{Cr} < 0.22$, for the Cu-Cr system. The thermodynamic values were calculated by the modified Gibbs-Duhem equation.

The activities and the heats of mixing for the Cu-Sn alloys showed a good agreement with

those of other investigators.

The activity of Cr in the Cu-Cr alloys at 1573 K showed a large positive deviation from Raoult's law. The liquidus line of the Cu-Cr system at the Cu-rich concentration range was determined from break points of the ion current ratios in the mass spectrometric measurements as well as the differential thermal analysis. The liquidus lines obtained by the two different techniques lie very close to each other, but differed considerably from that in the literature.

After the submission of this manuscript, the authors noticed the presence of a paper by L. Timberg and J. M. Toguri; "A thermodynamic study of (copper+chromium) by mass spectrometry.", J. Chem. Thermodynamics, 14 (1982), pp. 193-199. A correction of the liquidus temperature of the Cu-Cr system has been suggested by them. They indicated that the liquidus temperature of this system located higher than that of Hansen's Handbook. The present results have been raised considerably over those of them.

REFERENCES

- (1) G. R. Belton and R. J. Fruehan: J. Phys. Chem., **71** (1967), 1403.
- (2) C. B. Alcock, R. Sridhar and R. C. Svedberg: Acta Met., **17** (1969), 839.
- (3) J. P. Hager, S. M. Howard and J. H. Jones: Met. Trans., **1** (1970), 415.
- (4) T. Azakami and A. Yazawa: J. Min. Met. Inst. Japan, **86** (1970), 377.
- (5) T. Oishi, T. Hiruma and J. Moriyama: J. Japan Inst. Metals, **36** (1972), 481 (in Japanese).
- (6) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley: *Selected Values of the Thermodynamic Properties of Binary Alloys*, American Society for Metals, (1973), p. 795.
- (7) E. Siedschlag: Z. anorg. Chem., **131** (1923), 173.
- (8) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, McGraw-Hill, New York, 2nd ed., (1958), p. 524.