Thermodynamic Study of the Liquid Cu–O System*

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The phase relationships in the liquid Cu–O system were determined by the following three experimental techniques, (1) Water quenching of the samples in crucible, (2) Water quenching of the samples after suction into an alumina tube, (3) Emf measurements combined with the suction-water quenching.

The cells used were as follows: Pt/Ni, NiO/ZrO₂(+CaO)/O in Cu(l) or copper oxide (1)/LaCrO₃/Pt, Pt/Ni, NiO/ZrO₂(+CaO)/O in Cu(l)+copper oxide (s or l)/LaCrO₃/Pt.

It was confirmed that the miscibility gap exists between liquid copper and liquid copper oxide and it seems to disappear at higher temperature than 1620 K.

From emf measurements, the activities of oxygen and copper were calculated at 1573 K, and the standard free energies of formation of solid and liquid Cu₂O were determined in the temperature range from 1370 to 1600 K. Relative partial molar entropy of oxygen in the liquid Cu–O system showed a minimum value at or close to the stoichiometric Cu₂O composition.

The oxygen potential-temperature-composition (P-T-X) diagram for the Cu–O binary system was determined from the results of this study.

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I. Introduction

The Cu–O system is one of the fundamental systems for copper smelting processes and many thermodynamic studies of this system have been reported. In early studies for the equilibrium phase diagram^{(1)~(4)}, the miscibility gap between liquid copper and copper oxide has been reported to exist even at higher temperature than 1673 K.

In recent years, Kuxmann and Kurre⁽⁵⁾, Gerlach, Osterwald and Stichel⁽⁶⁾, and Sadat-Darbandi⁽⁷⁾ have reported that the oxygen solubility in liquid copper at the lower temperature than 1473 K is in good agreement with the early studies, but the miscibility gap disappears at the temperature near 1620 K and the homogeneous liquid phase is stable at the high temperatures. It has been supposed that in the early studies quenching of samples was not rapid enough to freeze the dissolved oxygen,

and solution of refractory materials into the liquid oxide also occurred.

In the present investigation, the equilibrium phase diagram for the Cu–O binary system mainly in the liquid field was determined using three different experimental techniques and compared with the previous works.

The H₂/H₂O^{(8)~(11)} and CO/CO₂⁽¹²⁾⁽¹³⁾ gas equilibrium methods and the emf method with solid electrolytes^{(6)(7)(14)~(35)} have been employed to study the thermodynamic properties of the Cu–O binary system. In the present investigation, the relationship among oxygen potential, temperature and oxygen concentration was determined using the zirconia solid electrolyte galvanic cells in the oxygen concentration range from 3 to 34 at% and at the temperatures from 1430 to 1600 K. From the results of emf measurements, the activities of oxygen and copper, the standard free energies of formation of solid and liquid Cu₂O and the relative partial molar entropy of oxygen in the liquid Cu–O system were also obtained.

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II. Determination of the Cu–O Phase Diagram

1. Experimental method

The samples taken with three different

techniques were analysed for oxygen to determine the Cu-O phase diagram of the liquid copper and oxide equilibrium field.

(1) An alumina crucible, 13 mm OD, 10 mm ID and 100 mm long, which contains oxygen free copper of about 10 g and copper oxide weighed so as to make an oxygen concentration of about 6 wt% was included in a silica tube. The system was evacuated and purified argon was introduced. The sample was then heated and maintained at a given temperature for 15 ks. This holding period was determined from the emf measurements which will be described in the following section. The silica tube containing the alumina crucible and the sample was quenched in water and the sample was analysed for oxygen.

(2) About 220 g in total weight of copper and copper oxide were equilibrated in an alumina crucible, 40 mm OD and 34 mm ID,

and the liquid copper and oxide were sampled separately using a 4 mm ID alumina tube and then quenched in water. The alumina tube for sampling of liquid oxide has a small opening of about 1 mm in diameter at the position of about 20–30 mm from the closed bottom end. These copper and copper oxide samples were analysed for oxygen.

(3) The emf measurement-oxygen analysis combination method was employed to determine the oxygen solubility in liquid copper. The emf values changed linearly with temperature both in the one- and two-phase regions in emf vs temperature diagram. After the intersection temperature of these two straight lines was obtained, the melt was heated to the homogeneous liquid region and sampled for oxygen analysis.

A hydrogen reduction method was used for oxygen analysis in copper and copper oxide.

Fig. 1 Equilibrium phase diagram for the Cu-O system.

The oxygen in copper oxide was determined both by weight gain of phosphorus pentoxide and by weight loss of samples. Both results were in good agreement. The oxygen in copper was determined only from the weight gain of phosphorus pentoxide.

2. Results

The experimental results obtained by the three different techniques are shown in Fig. 1. In this figure, the quadrangles, the closed circles and the open circles represent the data obtained by the first, second and third techniques, respectively. The temperature dependence of the miscibility gap from the results of first method is very small. It seems that the quenching rate was not rapid enough, because the relatively large volume of sample was in the double wall of alumina crucible and silica tube, so that during quenching the oxygen diffused too fast to keep the state at high temperatures. Whereas the closed and the open circles locate on the same oxygen solubility line. From these results, it was considered that the state at high temperature could be kept by using the second and third sampling methods.

The monotectic temperature was found to be 1495 K from the results of emf measurements. It is supposed from Fig. 1 that the immiscibility disappears at higher temperature than 1620 K. The data are in good agreement with those of Kuxmann *et al.*,⁽⁵⁾ Gerlach *et al.*⁽⁶⁾ and Sadat-Darbandi⁽⁷⁾.

III. Thermodynamic Properties of Oxygen in the Liquid Cu-O System

1. Experimental apparatus and procedure

In the present investigation, emf measurements employing solid electrolyte were made on the following galvanic cells in the temperature range from 1370 to 1600 K:

Fig. 2 Cell arrangement.

oxide (s or l)/LaCrO₃/Pt. (II)

The cell arrangement used is shown in Fig. 2. The cell consisted of a ZrO₂+11 mole per cent CaO solid electrolyte tube, made by Nippon Kagaku Togyo Co., Ltd., which contained the mixtures of nickel and nickel oxide as a reference electrode. The reference electrode was prepared by mixing equal weights of nickel and nickel oxide powders with a small amount of water and packing the mixtures into the bottom of the zirconia solid electrolyte tube. The spiral end of platinum wire was pushed to the Ni, NiO electrode. Good contact was thus obtained between the reference electrode and the electrolyte.

The lead dipped in the melts was made from commercial LaCrO₃ rod of about 40–50 mm long. JACO spectrograph analysis showed that the solubility of LaCrO₃ in liquid copper or copper oxide was confirmed to be ignorable.

An alumina was used as a crucible material. In the preliminary experiments, the solubility of alumina in liquid copper oxide showed below 0.5% at 1573 K.

The furnace used was of the silicon carbide resistance type and its temperature was controlled within an error of ± 1 K.

Oxygen free copper of about 100 g and

Fig. 3 Variation of emf with temperature for the cell, Ni, NiO/ZrO₂(+CaO)/Cu-O liquid alloys.

copper oxide weighed so as to make a certain oxygen concentration were contained in an alumina crucible and placed in a mullite reaction tube, 60 mm ID. The upper end of the mullite tube was sealed with a water-cooled brass head. After the cell was evacuated at about 670 K to ensure complete dehydration, purified argon was introduced into the cell. The furnace was then heated to the temperature of experiment. Initial equilibrium of each experimental run was generally attained in several hours after reaching the desired temperature. The emf readings were made with both ascending and descending temperatures in the range from 1370 to 1600 K.

The emf measurements were made with an accuracy of ± 0.1 mV using a digital voltmeter (Kuwanon Electrical Instruments Co., Ltd.) of input impedance 100 M Ω . The emf values were considered to be steady if the variations were within ± 0.5 mV over a period of about 1.2 ks.

After each run of emf measurements, the furnace temperature was raised to 1593 K and the sample was taken by use of a 4 mm ID silica tube for the liquid copper and 3 mm ID alumina tube for the liquid oxide, respectively and quenched in water. These samples were analysed for oxygen.

2. Results

Figure 3 shows the temperature dependences of emf values for 9 different oxygen concentrations in liquid copper. Open and black

Fig. 4 Variation of emf with temperature for the cell, Ni, NiO/ZrO₂(+CaO)/Cu-O liquid oxides.

circles indicate the emf values measured at ascending and descending temperatures, respectively. The emf values in the single phase region were found to change linearly with temperature. The coefficients of temperature dependence are positive and decrease with increasing oxygen concentration. The lines (I) and (II) correspond to the emf values for the $\text{Cu(l)}-\text{Cu}_2\text{O(s)}$ and $\text{Cu(l)}-\text{copper oxide(l)}$ equilibria, respectively. The intersection temperature of the lines (I) and (II) shows the monotectic temperature and was obtained to be 1495 K.

It is apparent from Fig. 1 that the liquid copper oxide in equilibrium with liquid copper is not stoichiometric. Therefore, in order to determine accurate standard free energy of formation of stoichiometric $\text{Cu}_2\text{O(l)}$, emf

measurements in both the liquid copper and the oxide fields are needed.

Figure 4 shows emf-temperature relationships for the liquid copper oxide field. The coefficients of temperature dependence are positive and show a minimum at or close to the stoichiometric Cu_2O composition.

Figure 5 shows the relationship between emf and mole fraction of oxygen N_{O} at 1573 K obtained from Figs. 3 and 4. With increasing oxygen content, the emf values decrease at first sharply and then slowly in the liquid copper field, and stay constant in the two phase region. In the liquid oxide field, the emf values decrease slowly up to the oxygen mole fraction of about 0.31 and fall sharply in a higher oxygen content field. Also shown in Fig. 5 are the data of Osterwald *et al.*⁽²³⁾ and

Fig. 5 Relationship between emf and N_{O} at 1573 K.

Sadat-Darbandi⁽⁷⁾. Their original data are transformed to the equivalent of the cells (I) and (II) by using the standard free energy of formation of NiO.

The activities of oxygen and copper in the Cu-O system are shown in Fig. 6. The activity of copper was obtained by applying the Gibbs-Duhem relation. The activity of oxygen shows a negative deviation from Henry's law. Whereas the activity of copper in the liquid copper field shows a positive deviation from Raoult's law.

3. Discussions

As was previously stated, liquid copper is in equilibrium with stoichiometric solid Cu₂O at temperatures below 1495 K and in equilibrium with nonstoichiometric liquid Cu₂O at higher temperatures. The oxygen potentials in these two phase equilibria may be expressed as

$$\begin{aligned} \text{Cu(l)}-\text{Cu}_2\text{O(s)}: \log(p_{\text{O}_2}/p_{\text{O}_2}^\circ) \\ = -\frac{2.129 \times 10^4}{T} + 10.323 \end{aligned}$$

$$\begin{aligned} \text{Cu(l)}-\text{copper oxide(l)}: \log(p_{\text{O}_2}/p_{\text{O}_2}^\circ) \\ = -\frac{1.424 \times 10^4}{T} + 5.606, \end{aligned}$$

where $p_{\text{O}_2}^\circ$ denotes 101325 Pa.

Fig. 6 Activities of oxygen and copper in the liquid Cu-O system at 1573 K. Standard states of oxygen and copper are pure gas at 101325 Pa and pure liquid copper, respectively.

As can be seen in Fig. 1, the oxygen solubility in liquid copper and the copper solubility in liquid oxide at higher temperatures cannot be neglected. Considering pure copper and stoichiometric Cu₂O as standard states, the standard free energy of formation of Cu₂O can be calculated from the results of the present study in the following way. When the stoichiometric Cu₂O is in equilibrium with copper and oxygen, the standard free energy of formation of Cu₂O may be expressed by

$$\Delta G_{\text{Cu}_2\text{O}}^\circ = -RT \ln a_{\text{Cu}_2\text{O}}/a_{\text{Cu}}^2 \cdot (p_{\text{O}_2}/p_{\text{O}_2}^\circ)^{1/2}, \quad (1)$$

where $a_{\text{Cu}_2\text{O}}$ and a_{Cu} are activities of Cu₂O and Cu at the stoichiometric Cu₂O composition, respectively, and $a_{\text{Cu}_2\text{O}}$ is equal to unity. The values of a_{Cu} at the stoichiometric Cu₂O composition were calculated by the Gibbs-Duhem equation at given temperatures. Substituting these values in eq. (1), the standard free energies of formation of Cu₂O were obtained as a function of temperature and are shown in Fig. 7 together with the results of other investigators.

Fig. 7 Standard free energy of formation of Cu₂O.

The standard free energies of formation of Cu_2O obtained in the present investigation may be represented by the equations

$$\Delta G_{\text{Cu}_2\text{O}}^\circ(\text{s}) = -194.85 + 91.96 \times 10^{-3} T (\text{kJ/mol}),$$

$$\Delta G_{\text{Cu}_2\text{O}}^\circ(\text{l}) = -121.34 + 42.92 \times 10^{-3} T (\text{kJ/mol}).$$

The intersection temperature of the two straight lines for $\Delta G_{\text{Cu}_2\text{O}}^\circ(\text{s})$ and $\Delta G_{\text{Cu}_2\text{O}}^\circ(\text{l})$ in Fig. 7, 1499 K, is in good agreement with 1503 K by Osterwald⁽¹⁵⁾ and 1500 K by Sadat-Darbandi⁽⁷⁾.

Relative partial molar entropies of oxygen in Cu-O system calculated from the temperature dependences of the emf values at each oxygen content are plotted in Fig. 8. The relative partial molar entropy of oxygen decreases with increasing oxygen content and shows a minimum at or close to the stoichiometric Cu_2O composition. This may be interpreted by that the compound Cu_2O remains at least some extent even in the liquid state.

P-T-X diagram for the Cu-O binary system

Fig. 8 Relationships between $\Delta \bar{S}_O$ and N_O at 1573 K.

determined in the present study is shown in Fig. 9. Partial pressures of oxygen, $p_{\text{O}_2}/p_{\text{O}_2}^\circ$, were found to be $10^{-3.0} - 10^{-4.5}$ in the oxygen concentration range between 3 and 34 at% and at a temperature between 1423 and 1600 K.

Fig. 9 Oxygen potential-temperature-composition diagram for the Cu-O system.

IV. Summary

The phase relationship in the liquid Cu–O binary system was determined by the following three experimental techniques:

(1) Water quenching of the samples in crucible,

(2) Water quenching of the samples after suction into an alumina tube,

(3) Emf measurements combined with the suction-water quenching.

The cells used were as follows,

Pt/Ni, NiO/ZrO₂(+CaO)/O

in Cu(1) or copper

oxide(1)/LaCrO₃/Pt

Pt/Ni, NiO/ZrO₂(+CaO)/O

in Cu(1)+copper

oxide(s or 1)/LaCrO₃/Pt.

From oxygen analyses, it was found that the miscibility gap seems to disappear at higher temperature than 1620 K.

Using the galvanic cells above mentioned, the activities of oxygen and copper were calculated in the oxygen concentration range from 3 to 34 at % and the standard free energies of formation of solid and liquid Cu₂O were determined in the temperature range from 1370 to 1600 K.

Relative partial molar entropy of oxygen in the liquid Cu–O system showed a minimum at or close to the stoichiometric Cu₂O composition.

A P-T-X diagram for the Cu–O binary system was also obtained.

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