A Thermodynamic Study of Cu_2O -CaO Melts in Equilibrium with Liquid Copper

By Toshio Oishi*, Yasuhiro Kondo** and Katsutoshi Ono*

Oxygen partial pressure of the Cu_2O -CaO melts in equilibrium with liquid copper under a magnesia saturated condition was measured at 1573 K by means of a solid electrolyte galvanic cell technique. The chemical composition of quenched oxide samples taken at 1573 K was determined by chemical analysis for copper, oxygen combined with copper, magnesium and calcium.

The CaO content in CaO saturated cuprous oxide was 11.55 mass%. Solubilities of MgO in the Cu_2O -CaO melts were less than 0.62 mass%. The activities of Cu_2O and CaO in the oxide melts were calculated using the obtained oxygen partial pressures.

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I. Introduction

The liquid Cu_2O -CaO system has so far been treated from standpoint of phase relationship. Wartenberg *et al.*⁽¹⁾ investigated the melting points of Cu_2O -CaO mixtures and found that this system shows a simple eutectic type diagram with the eutectic temperature of 1413 K and the CaO concentration of about 27 mass%. Kuxmann and Kurre⁽²⁾ determined the solubilities of CaO in the CaO saturated Cu_2O -CaO melts in equilibrium with liquid copper using a CaO crucible in the temperature range from 1421 to 1746 K. They obtained the eutectic point with the temperature of 1419 K and the CaO concentration of about 10 mass%.

In the present investigation, Cu_2O -CaO mixture and copper were melted in a magnesia crucible, and the oxygen potential measurements were carried out under a magnesia-saturated condition at 1573 K using a zirconia solid electrolyte dipped in the liquid copper. Together with the chemical analysis of oxide melts, the results were used to determine the activities of Cu_2O and CaO in the oxide melts.

II. Experimental

Emf measurements employing solid electrolyte were made on the following galvanic cell at 1573 K:

The cell arrangement used is shown in Fig. 1. Zirconia solid electrolyte used was

Fig. 1 Cell arrangement.

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

** Graduate Student, Kyoto University, Kyoto.

ZrO₂ + 11 mole pct CaO, 10 mm in OD, 7 mm in ID and 100 mm long. The electrical lead dipped in the melt was made of Cr₂O₃. After mixed with a small amount of water, the Cr₂O₃ powder and a platinum wire were contained in an alumina protection tube. This alumina tube and the zirconia solid electrolyte were, respectively, covered by a magnesia tube to avoid direct contact with the oxide melts. The crucible for the melts was made from magnesia (40 mm in OD and 100 mm height).

Approximately 100 g of oxygen free copper and 80 g of oxide mixtures of a given composition were contained in the magnesia crucible which was placed in a mullite reaction tube, 60 mm in ID and 550 mm long. The oxide mixtures were prepared from commercially pure copper oxide wires and CaO powder. The whole arrangement was heated to 1573 K in an argon atmosphere. At this temperature, the cell was kept for 25 to 30 ks to attain the equilibrium among the liquid copper, the oxide melts and the magnesia crucible. During this period, the zirconia solid electrolyte and the Cr₂O₃ conducting lead were held just above the melts. After the electrolyte and the conducting lead were immersed slowly in the liquid copper through the oxide melt, emf measurements were made with an accuracy of ± 0.1 mV by a digital multimeter with an input impedance of 1000 M Ω . The emfs were regarded as stable, when the variation was within ± 0.1

mV over a period of about 1 ks.

At the end of each experimental run, the oxide sample was withdrawn into an alumina tube which had a small opening (approximately 1 mm in diameter) on the closed end. The samples were quenched in water and kept immediately in a glass tube in vacuum.

The samples were analyzed for copper, oxygen combined with copper, calcium and magnesium. Hydrogen reduction-weight loss method was used for the analysis of oxygen combined with copper. Copper was analyzed by the electro-gravimetric method. Ca and Mg were determined by the volumetric and atom-absorption procedure, respectively.

III. Results and Discussion

The analytical results for the samples taken at 1573 K and the emf values of the cell(I) are listed in Table 1. The percentages of Cu + O + CaO + MgO were between 98.5 and 99.6, so were corrected to total percentages up to 100.

Oxygen partial pressures (p_{O_2}/p°) in the Table were calculated using the standard free energy of formation of NiO according to eq. (1):

$$\log (p_{O_2}/p^\circ) = \frac{1}{19.145} (-4EF + 2\Delta G^\circ_{NiO}), \quad (1)$$

where $p^\circ = 101325$ Pa, T is the absolute temper-

Table 1 Experimental Data at 1573 K.

Run No.	emf/mV	$\log (p_{O_2}/p^\circ)$	chemical analysis of oxide* mass%			
			Cu	O	CaO	MgO
1	-247.3	-3.48	90.32	9.61	0	0.07
2	-244.2	-3.52	88.20	10.01	1.64	0.15
3	-240.9	-3.56	86.06	10.67	2.78	0.49
4	-236.3	-3.62	85.53	10.32	3.89	0.26
5	-230.2	-3.70	83.59	10.08	6.01	0.32
6	-232.8	-3.66	82.93	10.26	6.29	0.52
7	-224.5	-3.77	81.93	9.88	7.81	0.38
8	-227.0	-3.74	80.94	9.95	8.84	0.27
9	-225.5	-3.76	79.73	10.10	9.55	0.62
10	-219.1	-3.84	79.50	9.70	10.37	0.43
11	-223.3	-3.78	79.04	9.81	10.85	0.30
12**	-221.1	-3.81	78.34	9.63	11.55	0.48

* Average values from duplicate analyses corrected 100%

** CaO saturated

Fig. 2 Relationship between oxygen partial pressure and mass% CaO in oxide melt at 1573 K.

ature, F the Faraday constant and ΔG_{NiO}^0 the standard free energy of formation of NiO: $\Delta G_{\text{NiO}}^0/\text{kJ} \cdot \text{mol}^{-1} = -235.10 + 0.08586T^{(3)}$.

Solubility of MgO in the Cu_2O -CaO melt was 0.62 mass% at the highest.

The oxygen partial pressure for $\text{Cu(l)}-\text{Cu}_2\text{O(l)}$ two phase equilibrium at 1573 K (No. 1 in the Table 1), $\log(p_{\text{O}_2}/p^0) = -3.48$, agrees very well with values of other investigators⁽⁴⁾⁻⁽⁶⁾.

Kuxmann and Kurre⁽²⁾ have determined the CaO solubilities in the Cu_2O melts under the existence of liquid copper using a CaO crucible in the temperature range from 1421 to 1746 K. The interpolated value was 11.6 mass% at 1573 K, which was in excellent agreement with that of the present result.

The oxygen partial pressures are plotted against mass pct CaO in the oxide melts at 1573 K in Fig. 2. With an increase in the CaO content, the oxygen partial pressure decreases slowly to the CaO saturated point.

Two of the authors and their co-workers have obtained the activity of oxygen in liquid copper⁽⁴⁾. Using their data, one can calculate the oxygen concentrations in the liquid copper from the oxygen partial pressures in Table 1 considering that the contents of Mg and Ca in the liquid copper are negligibly small: The activities of Ca and Mg at CaO saturation may be calculated from the Gibbs free energies of formation of CaO and MgO⁽⁷⁾ to be 1.5×10^{-14}

Fig. 3 Variation of oxygen contents in liquid copper with CaO contents in oxide melt. The oxygen contents were calculated using the data from ref. (4).

Fig. 4 Conjugation lines of the two-phase region between liquid copper and Cu_2O -CaO melt in the system Cu-O-CaO at 1573 K.

and 2.7×10^{-13} , respectively. The mass pct oxygen concentration in the liquid copper thus calculated is plotted against the mass% CaO concentration in the oxide in Fig. 3.

Figure 4 shows the phase relationships and the conjugation lines in the Cu-O-CaO ternary isothermal section. In this figure, the mass percentages of Cu + O + CaO in the oxides were corrected to 100%, because the solubilities of MgO were relatively small. The composition of the oxide melts in equilibrium with liquid copper changes from point A to B along line AB, and CaO is saturated at point B. With increasing CaO content, the O/Cu

weight ratio increases to the stoichiometric Cu₂O value, 0.126. Accordingly the oxygen content in the liquid copper changes from point C to D. In this field, the oxygen partial pressure, p_{O_2}/p° , changes from 3.35×10^{-4} of the line AC to 1.55×10^{-4} of the line BD. Two or three conjugation lines intersect each other. This may result from the analytical error of CaO in the oxide.

The activities of Cu₂O and CaO in the oxide melt along line AB were calculated as follows.

The activity of Cu was determined using the Gibbs-Duhem equation neglecting the contents of Mg and Ca in the liquid copper as stated above,

$$N_O d \log p_{O_2}^{1/2} + N_{Cu} d \log a_{Cu} = 0, \quad (2)$$

where N is the mole fraction and a is the activity of the components in the liquid copper.

The activity of Cu₂O, the standard state being stoichiometric liquid Cu₂O, was calculated from the standard free energy of formation of Cu₂O(1)⁽⁴⁾ to be

$$\Delta G_{NiO}^\circ = -RT \ln a_{Cu_2O} / a_{Cu}^2 \cdot (p_{O_2}/p^\circ)^{1/2}. \quad (3)$$

Applying the Gibbs-Duhem equation to the oxide melts by taking the components as Cu, O, CaO and MgO, one obtains

$$N'_{Cu} d \log a_{Cu} + N'_O d \log p_{O_2}^{1/2} + N'_{CaO} d \log a_{CaO} + N'_{MgO} d \log a_{MgO} = 0, \quad (4)$$

where N' is mole fraction of the components in the oxide melts. The fourth term drops out for the oxide studied in this work, because a_{MgO} is always unity.

Upon combining eqs. (2) and (4), the activity of CaO can be calculated as follows:

$$\log a_{CaO} = \int_{N'_{CaO(sat.)}}^{N'_{CaO}} \left(\frac{N'_{Cu} \cdot N'_O - N'_{Cu} \cdot N'_O}{N'_{CaO} \cdot N'_{Cu}} \right) d \log p_{O_2}^{1/2}. \quad (5)$$

Figure 5 shows the activities of Cu, Cu₂O and CaO, along line AB in Fig. 4, obtained by eqs. (2), (3) and (5), respectively. The activity of CaO changed almost linearly with %CaO up to the CaO saturation.

At %CaO=0, the activities of both Cu and Cu₂O are not unity because of the mutual

Fig. 5 Changes in activities of Cu, Cu₂O and CaO in oxide melt with CaO concentration at 1573 K.

solubilities of Cu₂O and Cu.

IV. Summary

The oxygen partial pressure of the Cu₂O–CaO melts in equilibrium with liquid copper was measured at 1573 K by means of a solid electrolyte galvanic cell technique:

A MgO crucible was used for the melts, and both of the zirconia solid electrolyte and the alumina protection tube for the conducting lead were covered with a magnesia tube.

The chemical composition of quenched oxide samples taken at 1573 K was determined by chemical analysis for copper, oxygen combined with copper, magnesium and calcium.

The CaO content in CaO saturated cuprous oxide was 11.55 mass%. The solubility of MgO in the Cu₂O–CaO melt was 0.62 mass% at the highest. The oxygen partial pressure varied from 34 Pa for CaO free cuprous oxide to 16 Pa for CaO saturated oxide.

The activities of Cu₂O and CaO at 1573 K were also determined.

REFERENCES

- (1) H. V. Wartenberg, H. J. Reusch and E. Saran: *Z. anorg. allgem. Chem.*, **230** (1937), 257.
- (2) U. Kuxmann and K. Kurre: *Erzmetall*, **21** (1968), 199.
- (3) T. Oishi: Dr. thesis, Kyoto Univ. (1974).
- (4) Y. Kayahara, K. Ono, T. Oishi and J. Moriyama: *Trans. Japan Inst. Met.*, **22** (1981), 493.
- (5) S. H. Sadat-Darbandi: Dr. thesis, Berlin Tech. Univ. (1977).
- (6) J. Osterwald: *Z. phys. Chem. N. F.*, **49** (1966), 138.
- (7) O. Kubaschewski and C. B. Alcock: *Metallurgical Thermochemistry*, 5th. ed. Pergamon Press (1979), p. 378, 381.
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