Letters

Thermogravimetric study of the non-stoichiometry of cuprite Cu_2O

Cuprous oxide, Cu_2O, is known to be a metal deficient p-type semi-conductor [1, 2]. Its non-stoichiometry has been investigated by gas volumetric analysis [3], thermogravimetry [4], chemical analysis of quenched samples [5], and more recently by a coulometric titration method [6]. These studies indicate that the predominant ionic defects at high temperature and high oxygen activities are neutral copper vacancies. Conversely, in low oxygen activity regions of the cuprous oxide homogeneity field, some authors [6, 7] have proposed the existence of oxygen deficient cuprite. Tretyakov *et al.*, in particular, have found deviations from stoichiometry as large as $\gamma = 2 \times 10^{-2}$ in $Cu_2O_{1-\gamma}$ at 1000° C (Fig. 1). These results are inconsistent with the p-type semiconductivity of Cu_2O in all its domain of existence, as found by conductivity measurements [1, 2, 8, 9]. In order to clarify this point a thermogravimetric reinvestigation has been undertaken particularly in the supposedly oxygen deficient cuprite field (Fig. 1) at as low as possible oxygen pressures to be compatible with weight change measurability.

Cuprous oxide was prepared by a floating zone technique [10, 11] from 10 mm diameter rods obtained by oxidation of high purity copper (Johnson Matthey Specpure) containing 2 ppm Ag, 1 ppm Fe and 1 ppm Si. A cylinder shaped specimen with alternate notches, 0.7 mm apart was suspended from one arm of the microbalance at the end of a thin silica wire. Experiments were carried out at five different temperatures (905, 940, 995, 1015 and 1030° C) and at partial pressures of oxygen ranging from 5×10^{-2} to

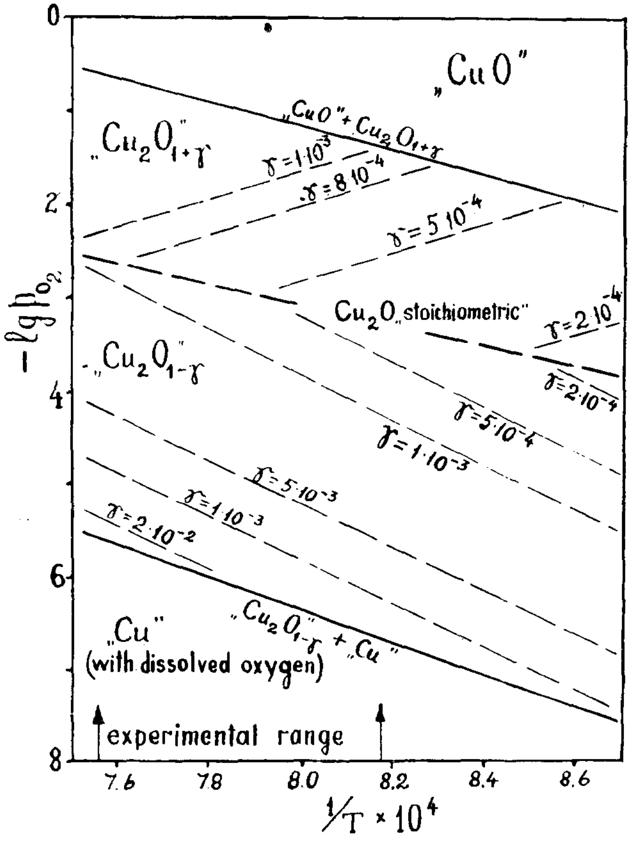

Figure 1 P_{O_2} (atm), T diagram for cuprite Cu_2O [6].

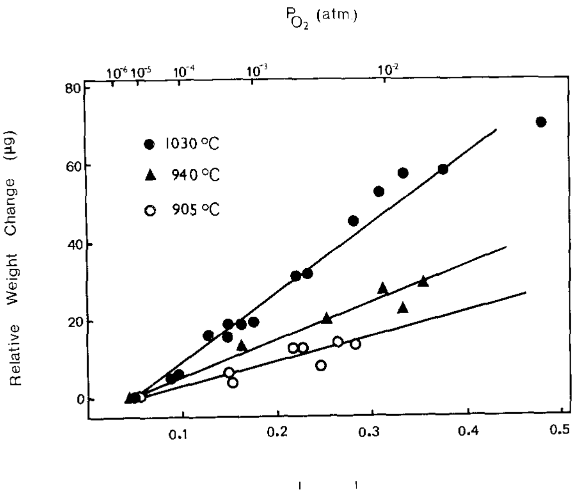

Figure 2 Weight change data as a function of $P_{O_2}^{1/4}$.

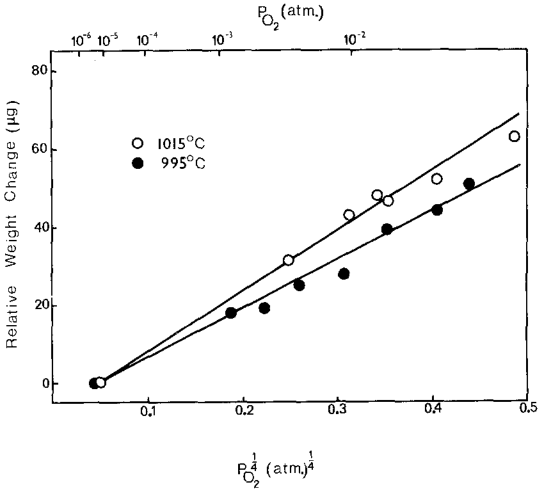

Figure 3 Weight change data as a function of $P_{O_2}^{1/4}$.

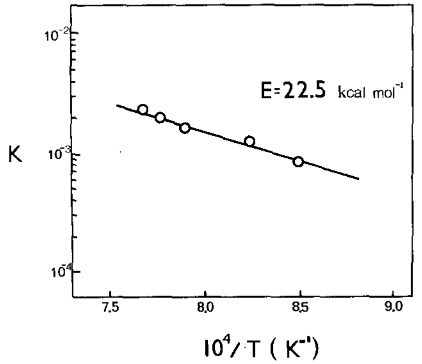

Figure 4 Arrhenius plot of mass action constant K from weight change data.

about 5 x 10^{-6} atm.

Constant P_{O_2} was achieved by a flow of an argon/oxygen mixture at a total pressure of 1 atm. This method allowed the elimination of the problems encountered at low pressures, i.e. thermomolecular flow and vaporization of Cu_2O [4]. The partial pressure of oxygen was measured at the inlet of the microbalance by a zirconium oxide oxygen gauge.

The presence of gas, flowing at about 8 litre h^{-1} around the specimen necessitated a weight correction due to minute changes of the flow rate at the different values of P_{O_2}. This correction was of 50 $\mu g\, l^{-1}$. Weight losses due to vaporization of cuprite were measured at high temperatures above 900° C: 0.6 $\mu g\, h^{-1}$ at 940° C and 2 $\mu g\, h^{-1}$ at 1030° C. After these cumulative corrections the accuracy of the weight change measurements was estimated at ± 5 μg.

Using the Kröger and Vink notation [12], the equation for copper vacancies formation is:

$$\frac{1}{4} O_2 \rightleftharpoons \frac{1}{2} O_O^x + V_{Cu}^x \tag{1}$$

Thus, the deviation γ from stoichiometry in $Cu_2O_{1+\gamma}$ may be written:

$$\gamma = \frac{1}{2}\left[V_{Cu}^x\right] = K \cdot P_{O_2}^{1/4} \tag{2}$$

the mass action constant K being related to the temperature by the relation

$$K = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is a constant, T the absolute temperature and E the enthalpy of formation of copper vacancies.

The weight change ΔW corresponding to a variation $\Delta\gamma$ of the stoichiometry may then be written:

$$\Delta W = \frac{16 \cdot g}{M} \cdot \Delta\gamma = \frac{16 \cdot g}{M} K \cdot \Delta\,(P_{O_2}^{1/4}) \tag{4}$$

where g is the sample weight and M the molecular weight of Cu_2O.

Figs. 2 and 3 represent the relative weight

TABLE I Non-stoichiometry in $Cu_2O_{1+\gamma}$

P_{O_2} (atm)	$\gamma \times 10^4$							
	[4]		[5]		[6]		This work	
	900° C	1000° C	900° C	1000° C	900° C	1000° C	900° C	1000° C
4.3×10^{-2}	–	9.1	–	11.4	7.3	13.1	–	7.4
8.5×10^{-3}	2.8	5.9	5.4	8.3	4.6	8.7	2.3	4.9
9.6×10^{-4}	1.6	3.2	3.0	5.2	2.8	5.1	1.3	2.9
1×10^{-5}	–	–	–	–	−8.77	−55	0.43	0.92

change of the sample plotted versus a $P_{O_2}^{1/4}$ dependence at different temperatures and at pressures ranging from 5×10^{-2} to 5×10^{-6} atm. From Fig. 2 it may be seen that the linear relationship extends below 10^{-3} atm pressure, at which for a temperature around 1000° C a change of the type of non-stoichiometry should occur [6]. This would indicate that the copper vacancy defect model is valid over the whole range of oxygen partial pressure considered.

The plot of log K versus $1/T$ represented in Fig. 4 gives values of A and E of Equation 3: $A = 11.9$ and $E = 22.5$ kcal mol^{-1}. Using these values the deviation from stoichiometry in $Cu_2O_{1+\gamma}$ has been calculated for different partial pressures of oxygen and compared to values derived from results and equations in [4–6] in Table I.

In conclusion it seems that the predominant ionic defect in Cu_2O at high temperature is V_{Cu}^x down to oxygen pressures of at least 5×10^{-6} atm, the enthalpy of formation of copper vacancies with respect to oxygen gas at 1 atm being 22.4 kcal mol^{-1}.

References

1. R. S. TOTH, R. KILKSON, D. TRIVICH, *Phys. Rev.* **122** (1961) 482.
2. P. KOFSTAD, "Non-Stoichiometry diffusion and electrical conductivity in binary metal oxides" (Interscience, New York, 1972) p. 328
3. H. DUNNWALD and C. WAGNER, *Z. Physik. Chem.* **B22** (1933) 212.
4. M. O'KEFFE and W. J. MOORE, *J. Chem. Phys.* **36** (1962) 3009.
5. C. WAGNER, H. HAMMEN, *Z. Physik, Chem.* **B40** (1938) 197.
6. YU. D. TRETYAKOV, V. F. KOMAROV, N. A. PROSVIRNINA, I. B. KUTSENOK, *J. Solid State Chem.* **5** (1972) 157.
7. J. BLOEM, *Philips Res. Rep.* **13** (1958) 167.
8. K. STECKER, *Ann. Physik* **7** (1959) 70.
9. J. DELLACHERIE, Thesis, University of Nancy (1973).
10. A. REVCOLEVSCHI, *Rev. Int. Hautes Temp. et Ref.* **7** (1970) 73.
11. R. D. SCHMIDT-WHITLEY, M. MARTINEZ-CLEMENTE and A. REVCOLEVSCHI, *J. Crystal Growth* **23** (1974) 113.
12. F. A. KROGER and H. J. VINK, "Solid State Physics", Vol. 3, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956).

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The effect of grain size on the occurrence of cleavage fatigue failure in 316 stainless steel

Highly reflective mirror like cleavage facets occur on the fatigue fracture surfaces of austenitic type 316 stainless steel [1]. The influence of grain size on this failure mode has been examined for the grain sizes of 3, 20 and 37 grains/mm. Tests at 140 Hz used an Amsler vibrophore and standard compact tension [2] specimens to produce crack propagation in the stress intensity range $\Delta K = 5 - 30$ MN m$^{-3/2}$ at a stress ratio of $R = 0.33$.

A cleavage facet is shown for the 3 grains/mm