

INTERACTION BETWEEN OXYGEN AND TIN DISSOLVED IN LIQUID COPPER

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ABSTRACT

Using the cell

Ni, NiO | ZrO₂ + CaO | Cu + Sn + O, Cr-cermet

the effect of tin on the activity of oxygen in solution in liquid copper has been measured at 1373 and 1473 K. It was found that the activity of oxygen in liquid copper decreased with the addition of tin and the interaction parameter $\epsilon_{\text{O}}^{\text{Sn}}$ was determined as

$$\epsilon_{\text{O}}^{\text{Sn}} = -\frac{58044}{T} + 35.375$$

The results obtained are in satisfactory agreement with those predicted by a quasi-chemical model.

INTRODUCTION

The discovery of copper ores and the development of the production of copper in Poland has resulted in research on the thermodynamic properties of copper alloys. In previous papers [1,2], results of investigations of Cu + O and Cu + Ag + O systems by use of the oxygen concentration cell with solid electrolyte were reported. In order to check existing data on the effect of tin on the activity of oxygen dissolved in liquid copper, the interaction parameter $\epsilon_{\text{O}}^{\text{Sn}}$ was measured in the temperature range 1373–1473 K.

EXPERIMENTAL

Materials

Copper MOOB (Polish symbol for oxygen-free copper) was 99.99% pure. Cuprous oxide of chemical purity was obtained from Baker's Chemical Co., U.K., while tin was supplied by Polskie Odczynniki Chemiczne, Poland, and was 99.999% pure. Solid electrolyte tubes of ZrO₂ + CaO (fully stabilized) were obtained from Yamari Trading Co., Japan, and chromium cermet was supplied by Morgan Refractories Ltd., U.K. High-purity nickel and nickel oxide were obtained from BDH Chemicals Ltd., U.K.

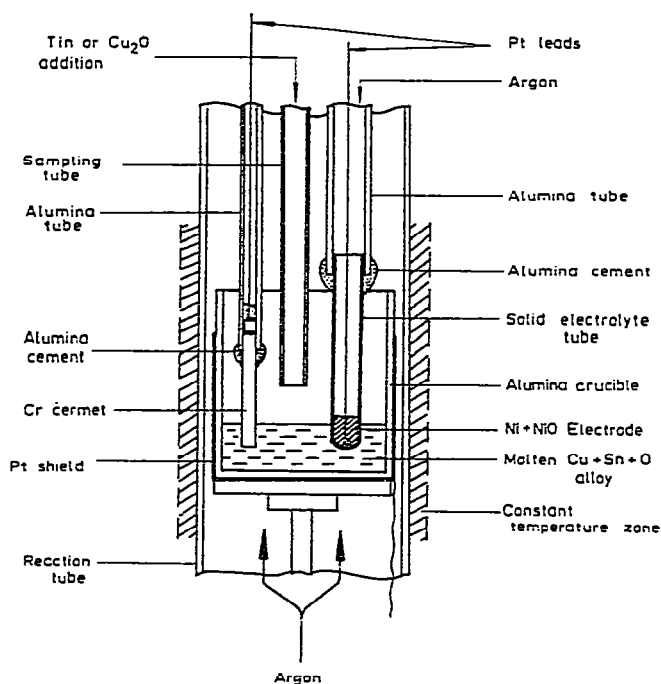


Fig. 1. Cell used to measure EMF in liquid Cu + Sn + O solution.

Apparatus and procedure

Experiments were performed in a resistance furnace produced by Metals Research Ltd., U.K. The cell was kept in the mullite tube of the furnace. The internal cell arrangement is shown in Fig. 1. Approximately 100 g of high-purity copper were held in an alumina crucible placed in the constant temperature zone of the furnace (about 10 cm long). Both ends of the tube were closed with water-cooled brass heads. The brass head on the top held the different tubes going into the cell and permitted electrical connections.

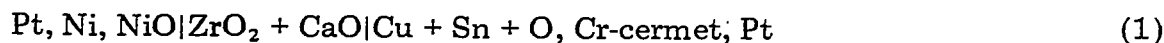
The metal-metal oxide mixture for the reference electrode was prepared by mixing equimolar fractions of Ni and NiO and then packing them into the bottom of the electrolyte tube (150 mm long \times 8 mm outer diameter) which was closed at one end. A platinum lead wire was inserted into the powder. The electrolyte tube was attached to a tight-fitting alumina tube by use of alumina cement. This tube was suspended from the brass head. The conductivity lead of chromium cermet was arranged in a similar manner; it was about 35 mm long and was pre-oxidized in air at 1200°C before the experiments. An inert atmosphere was maintained by flushing the furnace tube with purified argon. The argon was pre-purified by passing the gas over copper and titanium chips at 450 and 800°C, respectively. Metal samples were withdrawn by means of a syringe into 3 mm inner diameter quartz tubes and analyzed for oxygen content.

At the beginning of each experiment the oxygen content in liquid copper was adjusted by addition of cuprous oxide to the melt. Weighed samples of oxygen-free tin were dropped into the Cu + O solution in the cell. The

oxygen-free tin samples were prepared by reducing metallic tin with dry hydrogen at 1000°C for 4 h. After each addition an approximately constant EMF (± 1 mV) was recorded after 15–20 min by means of a digital voltmeter V 534 (Elwro, Poland). A sample of the melt corresponding to this EMF was withdrawn for oxygen analysis. The ends of the sample were cut off and rejected. Samples were etched in hydrofluoric acid for several hours to remove any silica traces and analyzed using a Leco RO-16 Oxygen Analyzer. The tin content of the alloy was calculated from the mass balance.

RESULTS

The effect of the addition of tin on the activity coefficient of oxygen dissolved in liquid copper can be calculated from the EMF measurements and oxygen analysis of Cu + O and Cu + Sn + O samples taken during the measurements. The oxygen potential of an unsaturated liquid solution was measured with the solid oxide galvanic cell



The experimental results are summarized in Table 1. The effect of the addition of tin on oxygen activity is related to the change in EMF and oxygen concentration

$$\log \gamma_{\text{O}(\text{alloy})} = \frac{2F(E - E')}{4.575T} + \log \left(\frac{X_{\text{O}(\text{Cu})}}{X_{\text{O}(\text{alloy})}} \right) \quad (2)$$

where $\gamma_{\text{O}(\text{alloy})}$ denotes the effect of tin on the activity coefficient of oxygen, E and E' are the EMFs of the cell (1) in volts without and with the addition of tin, respectively, and $X_{\text{O}(\text{Cu})}$ and $X_{\text{O}(\text{alloy})}$ are the mole fractions of oxygen in liquid copper and alloy, respectively.

As the oxygen concentration of the melt was about 0.1 at.% O, the variation of the activity coefficient of oxygen with its concentration may be neglected. Taking into account a tin concentration up to $X_{\text{Sn}} = 0.1$, the Wagner's interaction parameters at 1373 and 1473 K were calculated as

$$\epsilon_{\text{O}}^{\text{Sn}} = \sum_{i=1}^n X_{\text{Sn}} \ln \gamma_{\text{O}(\text{alloy})} / \sum_{i=1}^n X_{\text{Sn}}^2 \quad (3)$$

Results of the experiments are shown in Figs. 2 and 3, and from eqn. (3) values of the interaction parameters $\epsilon_{\text{O}}^{\text{Sn}} = -6.9$ at 1373 K and $\epsilon_{\text{O}}^{\text{Sn}} = -4.03$ at 1473 K were established. From the relation between $\epsilon_{\text{O}}^{\text{Sn}}$ and $1/T$ the following equation was calculated

$$\epsilon_{\text{O}}^{\text{Sn}} = -\frac{58044}{T} + 35.375 \quad (4)$$

which represents the variation of the interaction parameter $\epsilon_{\text{O}}^{\text{Sn}}$ with temperature.

TABLE 1

Effect of tin on the activity coefficient of oxygen in liquid copper

System	EMF (mV)		Oxygen in at. % (analyzed)	X_{Sn} (calc.)	$\log \gamma_{O(\text{alloy})}$
	E	E'			
1373 K					
Cu + O	-21		0.0410		
Cu + Sn + O		+29	0.0552	0.143	-0.49637
Cu + Sn + O		+98	0.0222	0.186	-0.60752
Cu + O	-110		0.146		
Cu + Sn + O		-95	0.142	0.009	-0.09668
Cu + Sn + O		-72	0.109	0.018	-0.15298
Cu + Sn + O		-59	0.097	0.027	-0.19697
Cu + Sn + O		-37	0.068	0.046	-0.20428
Cu + Sn + O		-30	0.063	0.078	-0.22252
Cu + O	-100		0.125		
Cu + Sn + O		+56	0.043	0.177	-0.67543
Cu + Sn + O		+73	0.021	0.209	-0.48497
Cu + Sn + O		+86	0.026	0.241	-0.69050
Cu + O	-62		0.079		
Cu + Sn + O		-36	0.076	0.027	-0.17265
Cu + Sn + O		+22	0.033	0.109	-0.23279
Cu + Sn + O		+53	0.051	0.164	-0.65144
Cu + Sn + O		+68	0.023	0.192	-0.41246
Cu + Sn + O		+80	0.0544	0.222	-0.88062
1473 K					
Cu + O	-34		0.104		
Cu + Sn + O		-33	0.125	0.011	-0.09015
Cu + Sn + O		-29	0.095	0.024	+0.00508
Cu + Sn + O		-25	0.093	0.036	-0.01648
Cu + Sn + O		-21	0.110	0.048	-0.11677
Cu + Sn + O		-16	0.102	0.062	-0.11479
Cu + Sn + O		-10	0.115	0.077	-0.20795
Cu + Sn + O		-1	0.094	0.094	-0.18542
Cu + O	-38		0.115		
Cu + Sn + O		-33	0.098	0.015	+0.03524
Cu + Sn + O		-26	0.104	0.031	-0.03849
Cu + Sn + O		-20	0.105	0.048	-0.08164
Cu + Sn + O		-14	0.090	0.065	-0.05783
Cu + Sn + O		-6	0.090	0.083	-0.11260
Cu + Sn + O		+18	0.078	0.121	-0.21475

DISCUSSION AND CONCLUSIONS

The effect of the addition of tin on the activity of oxygen in liquid copper was measured by Jacob et al. [3], Oishi et al. [4], and Nanda and Geiger [5] using the EMF technique, and by Block and Stüwe [6] and Sano and Sakao [7] using the gas-liquid equilibrium measurement method. Their results are shown in comparison with the present study in Fig. 4. The present results are

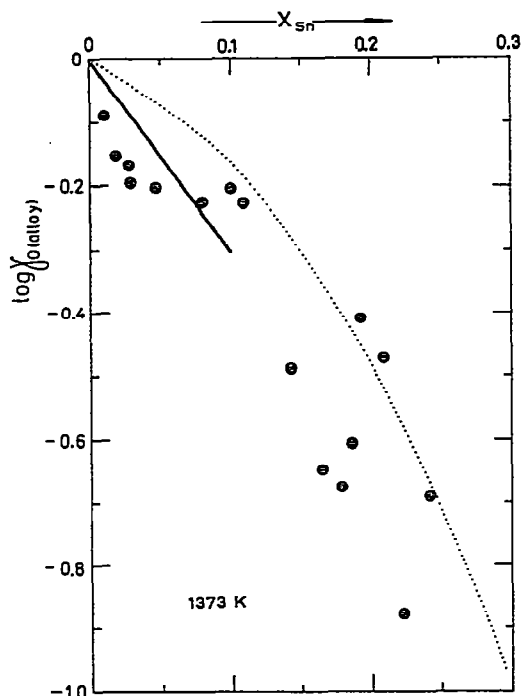


Fig. 2. Composition dependence of the activity coefficient of oxygen in liquid copper-tin alloys at 1373 K, relative to oxygen in pure copper (· · · · ·) and calculated from the quasi-chemical model eqn. (7) (—).

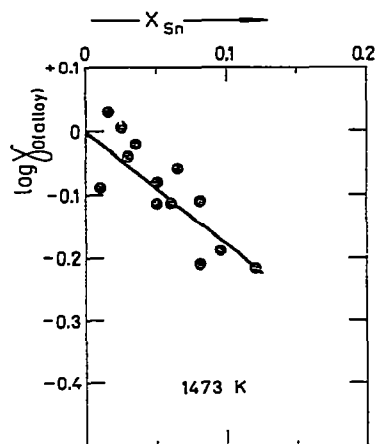


Fig. 3. Composition dependence of the activity coefficient of oxygen in liquid copper-tin alloys at 1473 K, relative to oxygen in pure copper.

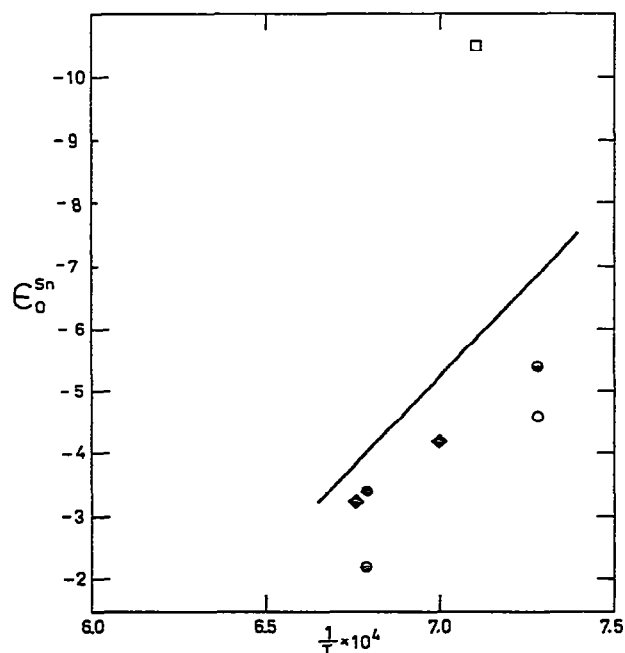


Fig. 4. Effect of temperature on the interaction parameter $\epsilon_{\text{O}}^{\text{Sn}}$. \circ , Ref. 3; \bullet , ref. 6; \blacklozenge , ref. 7; \square , ref. 5; —, this work.

somewhat lower than those discussed above, which is probably caused by the rather large scatter of experimental points due to the sampling method. Excluding the results of Nanda and Geiger, the results obtained are found to be in satisfactory agreement with previous data. Jacob et al. [3] obtained a value of $\epsilon_{\text{O}}^{\text{Sn}} = -4.6$ at 1373 K, while Oishi et al. [4] determined $\epsilon_{\text{O}}^{\text{Sn}}$ over the temperature range 1373–1473 K as

$$\epsilon_{\text{O}}^{\text{Sn}} = -\frac{64500}{T} + 41.57 \quad (5)$$

Block and Stüwe [6] obtained the value of $\epsilon_{\text{O}}^{\text{Sn}} = -3.4$ at 1473 K, which is nearly identical with that measured by Sano and Sakao [7] at 1479 K ($\epsilon_{\text{O}}^{\text{Sn}} = -3.2$). The results of Fruehan and Richardson [8] are not taken into account as they were previously shown [3] to be in error due to the formation of a separate oxide phase. It is worth mentioning that the assessment of the experimental results made by Chiang and Chang [9] led the authors to the expression

$$\epsilon_{\text{O}}^{\text{Sn}} = \frac{4600}{T} + 3.65 \quad (6)$$

which gives positive values for the interaction parameter over the temperature range under investigation.

The experimental values of $\log \gamma_{\text{O}(\text{alloy})}$ can be accounted for by a quasi-chemical model suggested by Jacob and Alcock [10]. According to this model the activity coefficient of oxygen in ternary solution can be predicted from the binary data by the equation

$$\frac{1}{\gamma_{\text{O}(\text{alloy})}^{1/n}} = X_{\text{Sn}} \frac{\gamma_{\text{Sn}(\text{alloy})}^{\alpha}}{\gamma_{\text{O}(\text{Sn})}^{1/n}} + X_{\text{Cu}} \frac{\gamma_{\text{Cu}(\text{alloy})}^{\alpha}}{\gamma_{\text{O}(\text{Cu})}^{1/n}} \quad (7)$$

where $\gamma_{\text{O}(\text{Sn})}$, $\gamma_{\text{O}(\text{Cu})}$ and $\gamma_{\text{O}(\text{alloy})}$ are the activity coefficients of oxygen at infinite dilution in liquid tin, copper and copper–tin alloy, respectively, $\gamma_{\text{Cu}(\text{alloy})}$ and $\gamma_{\text{Sn}(\text{alloy})}$ are the activity coefficients of tin and copper in the Cu + Sn binary system, and X_{Sn} and X_{Cu} are the mole fractions of tin and copper in the alloy.

It has been shown [10] that a large number of systems can be accounted for by this model, taking values $n = 4$ and $\alpha = 1/2$, which means that each oxygen atom is assumed to be interstitially coordinated to four metal atoms and the nearest neighbor metal atoms are assumed to lose approximately half of their metallic energies. Figure 2 compares the experimental results of this study at 1373 K with those calculated by Jacob and Alcock [10] from the model, and shows satisfactory agreement. Unfortunately, no model explains the nature of the bonds between oxygen and the metallic atoms in the solution.

Finally, the results obtained may be summarized as follows.

(1) The activity of oxygen in liquid copper was decreased by the addition of tin and its decrease became more pronounced at lower temperature.

(2) Wagner's interaction parameter $\epsilon_{\text{O}}^{\text{Sn}}$ was determined as

$$\epsilon_{\text{O}}^{\text{Sn}} = -\frac{58044}{T} + 35.375$$

(3) Agreement between the results obtained and previous data is satisfactory.

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