THERMODYNAMIC STUDIES ON ARSENIC–OXYGEN AND SELENIUM–OXYGEN INTERACTIONS IN MOLTEN COPPER

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ABSTRACT

The effect of arsenic and selenium on the activity coefficient of oxygen in liquid copper at 1150°C was determined by electrochemical methods using oxygen concentration cells. Arsenic increases the activity coefficient of oxygen and selenium decreases it, the first-order interaction parameters being $\epsilon_O^{As} = +4.0$ (± 0.5), and $\epsilon_O^{Se} = -14.0$ (± 0.5). Temperature dependencies of the parameters were estimated by using earlier assessments in dilute copper–oxygen alloys.

INTRODUCTION

Arsenic and selenium are harmful impurities in copper ores due to their difficult elimination by conventional pyrometallurgical methods. Their activity coefficients in molten copper at infinite dilution are small. Recently, Hino and Azakami [1] measured, by an isopiestic method, a limiting value $f_{As}^0 = 4 \times 10^{-4}$ referred to pure liquid arsenic. In a previous study, Hino et al. [2] determined the activity coefficient of selenium at infinite dilution in liquid copper at 1200°C to be $f_{Se}^0 = 2 \times 10^{-3}$.

The only information in the literature on solute–oxygen interactions for these elements in molten copper is from Staffansson et al. [3], who measured the first-order interaction parameter at 1200°C. According to their observations, selenium has an extraordinarily large negative effect on the activity coeffient of oxygen, the first-order interaction parameter being $\epsilon_O^{Se} = -745$.

EXPERIMENTAL

The experimental apparatus and the procedure used in this study have been described in detail previously [4,5]. The method is based on the utilization of an oxygen concentration cell with zirconia as the solid electrolyte. The cell can be described schematically as

$$Pt/Cr_2O_3/[O]_{Cu+Me}/ZrO_2(CaO)/air/Pt \qquad (I)$$
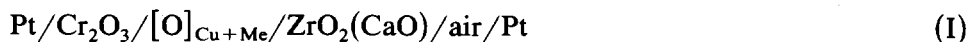
The electrolyte crucibles holding the molten alloy were of $ZrO_2 + 15$ mol% CaO and they were supplied by Yamari Trading Co. The gas train was similar to that in previous studies [5].

Arsenic and selenium were added to the copper–oxygen alloy in the form of Cu_3As and Cu_2Se, prepared in the laboratory. The starting materials were HCOF grade copper with a purity of 99.995% Cu, supplied by Outokumpu Oy, and 99.999% pure arsenic and selenium from Koch-Light Ltd. Weighted amounts of the elements to form the intermetallic compounds were sealed in a vacuum ampoule and heat treated in a laboatory tube furnace. The arsenide was first annealed for 2 days at 600°C and then 2 additional days at 600–840°C. The selenide was synthesized at 650°C by an anneal of 2 days.

Pure arsenic and selenium are easily volatilized at copper-making temperatures. Therefore, the volatilization of selenium during the runs was studied by sampling the molten alloy immediately after the runs by a quartz capillary tube and quenching the metal in water. Three parallel analyses were done assaying 2.12 ± 0.02 wt.% Se and 3.34 ± 0.1 wt.% Se for runs I and II, respectively. The corresponding values calculated from the added amounts were 2.16 wt.% Se and 3.28 wt.% Se, which indicate that the selenide added into the melt dissolved quantitatively and no vaporization losses occurred during the runs with a duration of 10–15 min only.

RESULTS

The effects of arsenic and selenium on the activity coefficient of oxygen in liquid copper were measured at 1150°C. The activity coefficient of oxygen, with oxygen in molten copper at infinite dilution as the reference state, was calculated from the equation

$$\ln f_O^{Me} = \frac{2F}{RT}(E' - E) + \ln(x_O'/x_O) + \epsilon_O^O(x_O' - x_O) \tag{1}$$

where the prime refers to the binary copper–oxygen alloy, E is the EMF of the cell [I], F is the Faraday constant, R is the gas constant, x_O is the mole fraction of oxygen, and ϵ_O^O is the first-order self-interaction parameter for oxygen in molten copper. The amount of oxygen in the alloy was calculated from mass balances and by using recent thermodynamic data for binary copper–oxygen alloys [5] with

$$\ln f_O^0 = 4.529 - \frac{8961.5}{T(K)} \tag{2}$$

$$\epsilon_O^0 = 16.18 - \frac{35\,550}{T(K)} \tag{3}$$

The primary results including the calculated $\ln f_O^{Me}$ values have been tabulated in Table 1. One can easily see that arsenic additions to the melt

TABLE 1

The measured EMF values of cell (I) and the corresponding activity coefficients of oxygen referred to oxygen in molten copper at infinite dilution

E (mV)	x_{Me}		x_O	$\ln f_O^{Me}$
As(I)		1150.2°C		
548.2	0		0.000368	0
548.1	0.00079		0.000367	+0.0053
548.0	0.00163		0.000366	+0.0109
548.2	0.00283		0.000364	+0.0133
548.3	0.00436		0.000362	+0.0189
548.8	0.00614		0.000359	+0.0192
548.9	0.00820		0.000357	+0.0275
549.0	0.01034		0.000353	+0.0361
549.4	0.01285		0.000350	+0.0353
As(II)		1150.4°C		
620.5	0		0.000113	0
620.5	0.00052		0.000113	+0.0022
620.5	0.00141		0.000113	+0.0064
620.2	0.00312		0.000112	+0.0187
620.4	0.00531		0.000111	+0.0235
620.9	0.00760		0.000110	+0.0256
621.4	0.01045		0.000109	+0.0305
Se(I)		1150.0°C		
526.5	0		0.000525	0
528.7	0.00211		0.000522	−0.0265
532.3	0.00575		0.000518	−0.0774
537.2	0.01063		0.000514	−0.1468
Se(II)		1148.9°C		
608.9	0		0.000136	0
611.1	0.00224		0.000135	−0.0286
614.6	0.00529		0.000134	−0.0756
618.2	0.00947		0.000132	−0.1203
622.4	0.01429		0.000130	−0.1725
627.5	0.01969		0.000128	−0.2372
633.3	0.02662		0.000125	−0.3076

increase the activity coefficient of oxygen, whereas selenium has the reverse effect. The present results are shown in Figs. 1 and 2 as a function of the arsenic and selenium concentrations, respectively.

DISCUSSION

The first-order interaction parameters, ϵ_O^{Me}, defined in general as

$$\epsilon_O^{Me} \equiv \lim_{x_{Cu} \to 1} \left(\frac{\partial \ln f_O^{Me}}{\partial x_{Me}} \right)_{P,T} \tag{4}$$
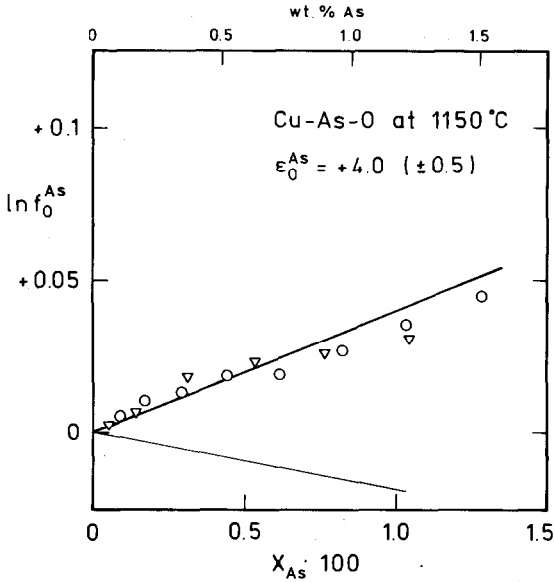
Fig. 1. Effect of dissolved arsenic on the activity coefficient of oxygen in molten copper at 1150°C; the thin line shows the additive behaviour of oxygen at infinite dilution in molten copper–arsenic alloys calculated according to refs. 5 and 9.
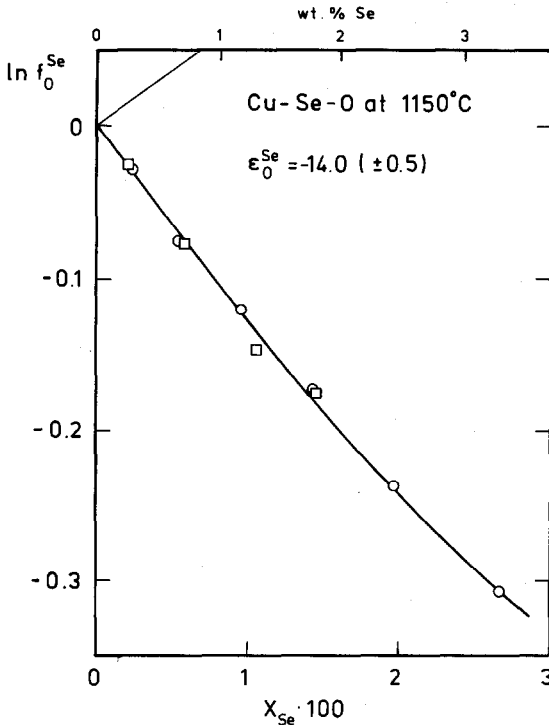

Fig. 2. Effect of selenium on the activity coefficient of oxygen in molten copper at 1150°C; the thin line shows the additive behaviour of the activity coefficient calculated according to refs. 5 and 9.

were calculated as the limiting slopes of the $\ln f_O^{Me}$ vs. x_{Me} plots at $x_{Me} = 0$. The first-order interaction parameters $\epsilon_O^{As} = +4.0$ (± 0.5) and $\epsilon_O^{Se} = -14.0$ (± 0.5) were obtained in this work. Temperature dependencies of the first-order interaction parameters can be calculated by using the general relationship between the enthalpy and entropy interaction coefficients, suggested recently by Taskinen [6]. According to her assessment in copper–oxygen alloys

$$\eta_O^{Me}/\sigma_O^{Me} = \tau = 1830 \text{ K} \tag{5}$$

where η_O^{Me} and σ_O^{Me} are the enthalpy and entropy interaction coefficients, respectively. If τ is constant, the enthalpy interaction coefficient attains the form

$$\eta_O^{Me} = RT \frac{\epsilon_O^{Me}(T)}{1 - T/\tau} \tag{6}$$

where $\epsilon_O^{Me}(T)$ is the first-order interaction parameter at temperature T.

By using the present data, the first-order interaction parameter for arsenic and selenium in molten copper can be written as

$$\epsilon_O^{As} = 25.6 \times 10^3 \frac{1}{T \text{ (K)}} - 14.0 \tag{7}$$

$$\epsilon_O^{Se} = -89.6 \times 10^3 \frac{1}{T \text{ (K)}} + 49.0 \tag{8}$$

The corresponding terms with mass % as the composition coordinate, calculated according to Schenck et al. [7] from eqns. (7) and (8), have the forms

$$e_O^{As} = 94.2 \frac{1}{T \text{ (K)}} - 0.051 \tag{9}$$

$$e_O^{Se} = -314 \frac{1}{T \text{ (K)}} + 0.172 \tag{10}$$

The present observations on the selenium–oxygen interaction parameter in liquid copper differ significantly from the value suggested by Staffansson et al. [3]. The good reproducibility of this study as well as the fair agreement in the chemical analyses of selenium prove, however, that the present value is more reliable than that given by the previous authors. This is also supported by the recent observations on the tellurium–oxygen interaction parameter in liquid copper [8]. The chemical behaviour of selenium in molten copper is similar to that of tellurium, and thus interaction parameters of the same order of magnitude are expected for both the elements.

The additive behaviour of oxygen in copper–arsenic and copper–selenium alloys is shown in Figs. 1 and 2 as the thin line calculated on the basis of available literature data [5,9]. One can easily see that approximating the

alloys as additive systems with respect to $\ln f_O^0$ is inadequate for estimating the first-order interaction parameters without any further information on the system.

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