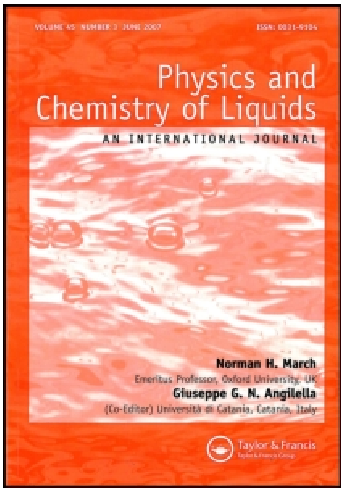

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DIFFUSION OF OXYGEN IN LIQUID TELLURIUM AND Sb–Te ALLOYS

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The diffusivity of oxygen in liquid tellurium and tellurium-antimony alloys was determined from potentiostatic experiments. In the temperature range 773–923 K the diffusivity of oxygen in liquid tellurium is:

$$D_O^{Te} = (6.8 \cdot 10^{-2}) \exp\left(\frac{-19417}{RT}\right) [\mathrm{cm^2 \cdot s^{-1}}]$$

while the isothermal D_O^{Te} vs. alloy composition plot shows an s-shape dependence with a sudden rise in oxygen diffusivity around the alloy composition $X_{Te} = 0.3$.

KEY WORDS: Fick's law, electrochemical cells.

INTRODUCTION

Electrochemical cells with solid oxide electrolytes have been successfully used to measure diffusivity, D_O, of oxygen in a number of liquid metals. Consequently, oxygen diffusivity in liquid Ag[1-3], Cu[2,4], Ni and Fe[5], Sn[6], Pb[7], In and Ga[8,9], Sb[8,10], and Bi[8,11] has been determined. However, there have been relatively few studies made so far on binary alloy systems[12-14].

In order to find out how the structure evolution in the liquid binary alloy may influence oxygen diffusivity, the antimony-tellurium alloys were chosen for the present study. Liquid tellurium exhibits the variation of structure depending on the temperature[15], while added antimony exhibits a compound-forming tendency towards tellurium. There is experimental evidence[16] that Sb_2Te_3 structure is retained in the liquid state after melting. Since in this system experiments can be carried out over the whole alloys composition range, one can investigate the diffusivity of oxygen as a function of both temperature and an alloy composition.

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EXPERIMENTAL DETAILS

Antimony (purity, 99.999%) was supplied by the Unitra-Cemi (Poland) while tellurium (purity, 99.9999%) was obtained from ASARCO (USA). Respective alloys were prepared by melting proper amounts of pure metals inside the electrolyte tube. Solid electrolyte tubes, closed at one end, and made of either calcia- or yttria-stabilized zirconia (outside diameter 8 mm and inside diameter 5 mm) were obtained from Friatec AG (Div. Frialit-Degussit)-Germany.

A potentiostatic method was employed for the determination of oxygen diffusivity in the liquid state. The experimental method and procedure have been described previously[10,11]. A schematic diagram of experimental arrangement of the cell:

$$\text{Pt, air } |O^{-2}| \text{ O in Te or Sb—Te, W or Re}$$

is presented in Figure 1. The tube of solid electrolyte contained about 4 g of metallic alloy of the chosen composition. The outer part of the solid electrolyte tube coated with

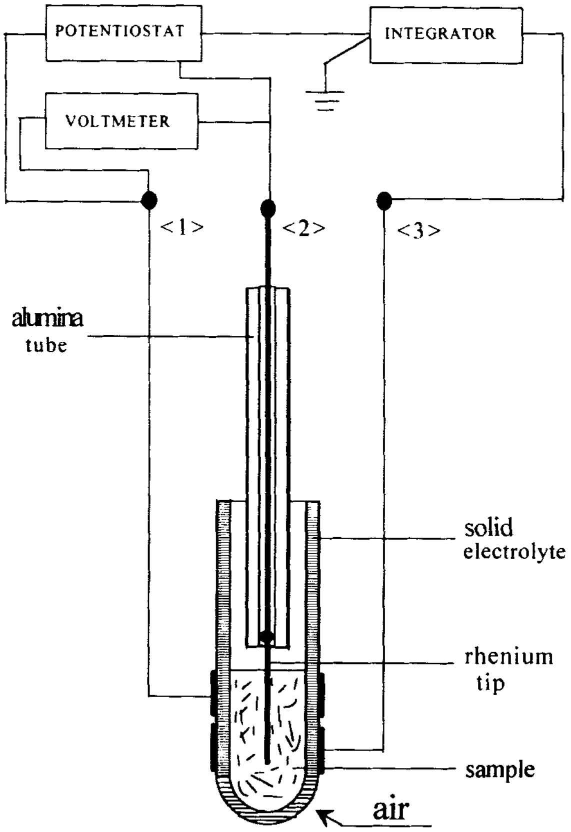

Figure 1 Schematic diagram of the experimental arrangement. ⟨1⟩-reference electrode, ⟨2⟩-working electrode, ⟨3⟩-current electrode.

platinum paste worked as an air reference electrode and was connected to the electric system with a platinum wire. The electric circuit contained a potentiostat model 550 and a chargemeter (integrator) model 721, both produced by AMEL (Italy), and the digital voltmeter 197 A made by Keithley (USA). Purified argon was allowed through the cell just above the surface of the liquid metal. Either tungsten wire or Kanthal Al wire with welded rhenium tip acted as electric contacts with the liquid metal electrode.

After the chosen temperature had been reached and the equilibrium electromotive force (emf) of the cell E_1 was recorded, the preselected additional potential ΔE was applied by the potentiostat. Then, the equilibrium voltage suddenly jumped to level E_2, so that concentration of oxygen $C_{O(2)}$ was established instantaneously at the metal-solid electrolyte interface. The diffusion of oxygen could then be followed by recording the current through the external circuit as a function of time. The experimental run was repeated several times at the same temperature, then the temperature was changed.

RESULTS

The diffusion of oxygen in the liquid metal electrode contained in solid electrolyte tube is described by Fick's second law for cylindrical coordinates:

$$\frac{\partial C_O}{\partial t} = \frac{1}{r}\left[r D_O \frac{\partial C_O}{\partial r} \right] \qquad (1)$$

where C_O represents the oxygen concentration in the metal in g atom/cm^3, D_O is the diffusion coefficient of oxygen in the metal in cm^2/s, t is the time in seconds, and r is the radius of the tube in cm.

The solution of Eq. 1 was given by Crank[17], and, after necessary differentiation and rearrangements Rapp *et al.*[6] arrived at the expression:

$$I_{\text{Ion}} = 8hF\, D_O \cdot (C_{O(1)} - C_{O(2)}) \exp\left(\frac{-2.405 \cdot D_O t}{r} \right) \qquad (2)$$

where I_{Ion} represents ionic current determined experimentally, h is the height of the liquid metal column, F is the Faraday constant, $C_{O(1)}$ and $C_{O(2)}$ represent initial and final (i.e. a steady—state) oxygen concentrations during titration experiment, and the constant 2.405 is the first root of the Bessel function of zero order. The logarithm of Eq. 2 takes the form:

$$\ln I_{\text{Ion}} = A + B \cdot t \qquad (3)$$

and from the value of B the diffusion coefficient D_O can be obtained. The relation (3) can be derived from experimental decay curves I_{Ion} vs. time, which recorded examples for pure tellurium and the alloy of $X_{\text{Te}} = 0.6$ composition are shown in Figure 2. Calculated values of $\ln D_O^{\text{Te}}$ in tellurium are shown in Figure 3 as a function of reciprocal

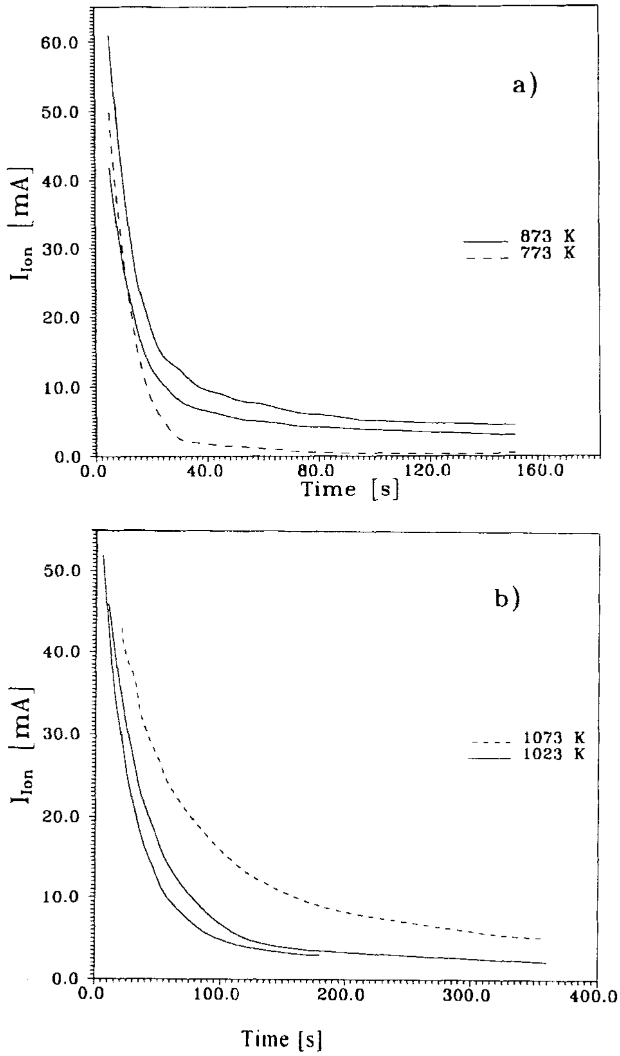

Figure 2 Cell current I_{Ion} as a function of time in the potentiostatic experiment. a) pure tellurium, b) $X_{\mathrm{Te}} = 0.6$.

temperature. They can be represented by the equation:

$$D_0^{\mathrm{Te}} = (6.8 \cdot 10^{-2}) \exp\left(\frac{-19417}{RT}\right) [\mathrm{cm}^2 \cdot \mathrm{s}^{-1}] \tag{4}$$

in the temperature range 773–823 K. In Eq. 4 R is the gas constant equal to 8.314 J/K mole.

Composition dependence of D_0^{Te} derived from experiments conducted for seven alloy compositions (Table 1) at constant temperature 923 K is shown in Figure 4. The value of D_0^{Sb} in pure, liquid antimony is taken from the previous study[10].

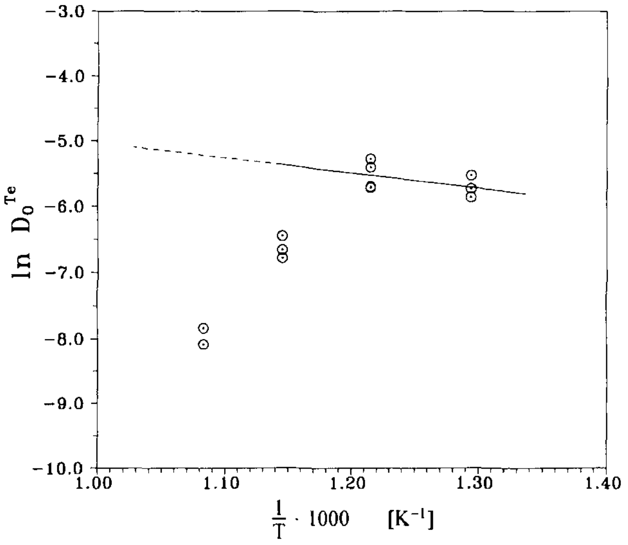

Figure 3 Diffusion coefficient of oxygen in liquid tellurium as a function of reciprocal temperature.

Table 1 Results of diffusion experiments performed on liquid Sb—Te—O solutions.

X_{Te}	$\ln D_O = A + B \cdot (R \cdot T)^{-1}$		*Experimental temperature range* *[K]*	*MSE* *(mean square error)*
	A	*B*		
1.0	−2.6884	−19416.6	773-823	0.134
0.9	−7.2310	−7147.5	773-973	0.104
0.8	1.0512	−73961.7	973-1073	0.134
0.6	−12.8663	4815.6	1023-1123	0.188
0.5	−3.0296	−41726.0	1023-1123	0.309
0.4	−2.4471	−38140.7	1023-1123	0.205
0.3	0.3641	−56603.7	1023-1123	0.265
0.2	−5.4678	−17222.2	1023-1123	0.124
0.1	−2.4393	−32903.2	1023-1123	0.195
0.0	−8.089	−16410.4	from Ref. [10]	—

DISCUSSION

The potentiostatic electrochemical method was found to be suitable for the investigation of the diffusion of oxygen, D_O, in the liquid metal Sb–Te system. In general, the experiments on oxygen diffusivity were difficult, since due to high tellurium pressure they had to be run in different temperature ranges depending on the alloy composition (e.g. 773–923 K for pure tellurium and 973–1073 K for $X_{Te} = 0.8$). Then, isothermal D_O^{alloy} vs. compostion plot was obtained partly by extrapolation, which may introduce additional error into the calculated values.

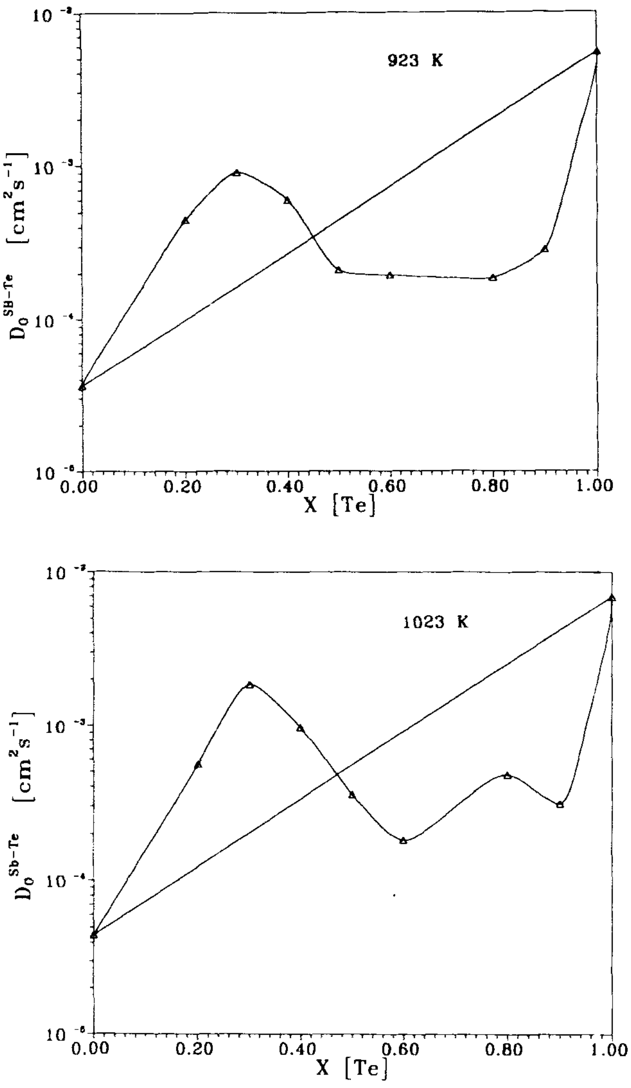

Figure 4 Diffusion coefficient of oxygen in the liquid Sb–Te alloys.

The diffusion coefficients for liquid tellurium, obtained in this study, indicate the change in temperature dependence of $\ln D_O^{Te}$ vs. reciprocal of temperature (Fig. 3). Though, in the same temperature range, there is a change of a structure of liquid Te which becomes simple hard sphere mixture between 823 and 873 K[15,18], it is unlikely that this process may slow down oxygen diffusion.

Contrary, at high temperature, liquid Te should behave as a simple metal with oxygen diffusion typical for this kind of solutions. Therefore, we assumed that this abrupt change is caused by a rising pressure of tellurium, which disturbed our experiments above 823 K. Consequently, Eq. 4 was calculated from a least-squares analysis of experimental data from 773 and 823 K only.

Then, the value of $\ln D_O^{Te}$ used at 923 K was obtained by extrapolation of Eq. 4. Next, using plots similar to that shown in Figure 3, temperature dependence of $\ln D_O^{Te}$ was established for seven alloy compositions ranging from $X_{Te} = 0.2$ to $X_{Te} = 0.9$, and consequently, composition dependence of D_O^{Te} at constant temperature $T = 923$ K and $T = 1023$ K was derived. For pure antimony, we accepted the value of D_O^{Sb} obtained previously in our laboratory[10]. At 923 K, this value is higher ($3.62 \cdot 10^{-5}$) than that ($8.4 \cdot 10^{-7}$) determined by Heshmatpour and Stevenson[8].

These results, shown in Figure 4, indicate that oxygen diffusivity in liquid tellurium rapidly decreases with the addition of antimony, and then it is held approximately constant up to $X_{Te} = 0.5$.

The investigations of the physical properties (viscosity[19] and electrical conductivity[16] of liquid Sb-Te alloys, indicate that in this composition range a residual structure in the liquid still exists. For antimony-rich alloys however, diffusivity increases, and at the same time electrical conductivity increases[20] as well having its maximum for the composition $X_{Te} = 0.25$. Since in the Darken equation:

$$D_O = RTB_O \left\{ 1 + \frac{d \ln \gamma_O}{d \ln X_O} \right\} \tag{5}$$

(where B_O is the mobility of oxygen) the thermodynamic factor is unity due to Henry's law behaviour of oxygen in the dilute solution, diffusivity is practically governed by the oxygen mobility. In turn, a change in mobility depends on characteristics of bonding between solute and metallic solvent, which seems to depend on the availability of free electrons in the liquid metal. Judging from the electrical conductivity measurements, this factor apparently varies with the composition of the alloy in the Sb–Te solution.

So far, we have found only two studies which reported D_O dependence on the alloy composition over the whole concentration range, namely in Cu—Pb—O[13], and In—Ga—O[12] systems. Their results show departures from linear dependence; however, this experimental evidence is not broad enough to suggest a theoretical model to predict D_O in liquid alloys. Its development requires more experimental research on a number of liquid alloys.

Acknowledgements

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