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Diffusivity, activity and solubility of oxygen in liquid lead and lead–bismuth eutectic alloy by electrochemical methods

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Abstract

The diffusivity of oxygen in liquid lead and lead–bismuth eutectic (LBE) alloy was measured by a potentiostatic method and is given by $\log(D_O^{Pb}/\text{cm}^2\,\text{s}^{-1}) = -2.554 - 2384/T\ (\pm 0.070)$, 818–1061 K, and $\log(D_O^{LBE}/\text{cm}^2\,\text{s}^{-1}) = -0.813 - 3612/T\ (\pm 0.091)$, 811–980 K. The activity of oxygen in lead and LBE was determined by coulometric titration experiments. Using the measured data, the standard free energy of dissolution of oxygen in liquid lead and LBE was derived and is given by

$$G_{O(Pb)}^{xs} = -121\,349 + 16.906T\ (\pm 560)\text{J(g atom O)}^{-1},\quad 815\text{–}1090\ \text{K},$$

$$G_{O(LBE)}^{xs} = -127\,398 + 27.938T\ (\pm 717)\text{J(g atom O)}^{-1},\quad 812\text{–}1012\ \text{K}.$$

Using the above data, the Gibbs energy of formation of PbO(s) and equilibrium oxygen pressures measured over the oxygen-saturated LBE alloy, the solubility of oxygen in liquid lead and LBE were derived. The solubility of oxygen in liquid lead and LBE are given by $\log(S/\text{at.\%O}) = -5100/T + 4.32\ (\pm 0.04)$, 815–1090 K and $\log(S/\text{at.\%O}) = -4287/T + 3.53\ (\pm 0.06)$, 812–1012 K respectively.

1. Introduction

Liquid lead and lead–bismuth eutectic (LBE) alloy (44.1 at.% Pb and eutectic temperature of 398 K) are the candidate coolant materials for accelerator driven systems (ADS) as they can also serve as spallation targets to produce high-energy neutrons [1]. LBE has been extensively used as a coolant in compact nuclear reactors of submarines in Russia [2]. Because of their low chemical reactivity, Pb and LBE are proposed for use as coolant in advanced fast breeder reactors [3]. These coolants are highly corrosive towards structural steels, but this corrosion can be minimised by suitable control of the oxygen potential in the coolant and thereby forming a protective oxide layer on the steels [2]. Oxygen control systems (OCS), which essentially

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employ a mixture of hydrogen and water vapour with argon carrier gas, are used for this purpose [4]. The time scale of the oxygen control process via OCS is determined by the kinetics of reaction of the gases with liquid metals and by the diffusivity of oxygen in liquid metal. Nature and extent of formation of the oxide layer on structural steels would depend on the thermochemistry of oxygen in the coolant in addition to the nature of processes on the steel–coolant interface. As part of our studies [5–7] on the chemical behaviour of oxygen in lead, bismuth and LBE, the diffusivity, activity and solubility of oxygen in liquid lead and LBE have been measured by electrochemical methods and are described in this work.

2. Literature review

2.1. Pb–O system

The diffusivity of oxygen in liquid lead has been measured by several investigators [8–14]. Details of the electrochemical techniques employed, the results obtained and the temperature range of measurements in these works are listed in Table 1. Recently Zhang and Li [3] have estimated the diffusivity of oxygen in lead based on the Stokes–Einstein relation. As it is seen from the table, a considerable discrepancy exists among the reported data, and data at temperatures below 973 K are not available.

The activity of oxygen in liquid lead and hence $G^{xs}_{O(Pb)} (= RT \ln \gamma_O)$ has been measured by several authors [11,14–22] using electrochemical methods, the details of these literature data are given in Table 2. In these works, the oxygen concentration in liquid lead has been varied either by adding a known amount of PbO or by coulometric titration of oxygen into liquid lead. Henry's law was assumed to be valid up to the saturation limit of oxygen in lead by the majority of the research workers except by Charle and Osterwald [14] and Isecke [18].

The solubility of oxygen has been measured in the past mainly by two methods, viz., sampling and electrochemical methods. The sampling method is an age-old method. Although literature data based on the sampling method exist from the last century, the method suffers from large uncertainty due to possible inclusion of Pb or impurity oxides in the lead oxide taken for analysis [23]. Literature data on the solubility of oxygen in liquid lead

Table 1
Literature data on the diffusivity of oxygen in liquid lead

S. no.	Electrochemical cell	Method	Diffusivity (cm² s⁻¹) $D = D_0 \exp(-E_a^*/RT)$		Temp. range (K)	Diffusivity (cm² s⁻¹)		Author and Year
			D_0 (cm² s⁻¹)	E_a (J mol⁻¹)		1075 K	1175 K	
1	Solid electrolyte emf method using CSZ	Potentiostatic	$^{a}6.32 \times 10^{-5}$	$^{a}14979$	973–1173	1.18×10^{-5}	$^{b}1.36 \times 10^{-5}$	Arcella and Fitterer, 1968 [8]
2	SS, $[O]_{Pb}$ |CSZ| Ni, NiO, SS	Potentiometric	$^{a}1.29 \times 10^{-5}$	–	1023 (single point)	–	–	Bandyopadhyay and Ray, 1971 [9]
3	Ir, $[O]_{Pb}$ |CSZ| Ni, NiO, Pt	Potentiometric	$(9.65 \pm 0.71) \times 10^{-5}$	20083 ± 6067	1073–1373	1.02×10^{-5}	1.23×10^{-5}	Honma et al., 1971 [10]
4	Chromel, $[O]_{Pb}$ |CSZ| air, Pt	Potentiostatic	$(1.44^{+0.46}_{-0.34}) \times 10^{-3}$	25941 ± 2803	1012–1353	7.90×10^{-5}	1.01×10^{-4}	Szwarc et al., 1972 [11]
5	$[O]_{Pb}$ |CSZ| Ni, NiO or Mo, MoO_2	Galvanostatic	$^{a}1.30 \times 10^{-5}$	–	1063 (single point)	–	–	Kawakami and Goto, 1973 [12]
6	Nichrome, Pt, Ni, NiO |CSZ| $[O]_{Pb}$ |CSZ| FeO, Fe_3O_4, SS	Combined potentiostatic and potentiometric techniques	$(1.48^{+0.62}_{-0.44}) \times 10^{-3}$	19497 ± 10711	1153–1408	$^{b}1.67 \times 10^{-4}$	2.01×10^{-4}	Otsuka and Kozuka, 1975 [13]
7	Ir, $[O]_{Pb}$ |stab.ZrO_2| air, Pt	Potentiometric or galvanostatic	$^{a}1.90 \times 10^{-3}$	$^{a}20920$	1173–1323	$^{b}1.83 \times 10^{-4}$	2.23×10^{-4}	Charle and Osterwald, 1976 [14]

[a] Error not given.
[b] Extrapolated data.