Solubility and Activity of Oxygen in Pb–Bi Melts

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In order to obtain the solubility and activity of oxygen in Pb–Bi melts, the research for oxygen analysis and oxygen partial pressure measurement in a lead–bismuth eutectic alloy (LBE) was performed. The analytical condition of oxygen in low melting metals by an inert gas fusion-infrared absorption method was established using Pb or Bi equilibrated with its corresponding oxide at 973 K as a standard sample for the oxygen analysis. After establishing the analytical condition, oxygen analysis in liquid LBE in equilibrium with solid PbO at various temperatures was done. The temperature dependence of oxygen solubility in liquid LBE was expressed by the following equation,

$$\log(C_O/\text{mass ppm}) = -4.74 \times 10^3/T + 7.06(\pm 0.03) \quad (878 \leq T/\text{K} \leq 1073)$$

Oxygen partial pressure in LBE–(PbO and/or PbO + Bi₂O₃) equilibrium was measured using an oxygen sensor of a zirconia solid electrolyte (ZrO₂ – Y₂O₃), and obtained as a function of temperature as

$$\log(p_{O_2}/P^\circ) = 10.96 - 2.259 \times 10^4/T \quad (720 \leq T/\text{K} \leq 1098)$$

$$\log(p_{O_2}/P^\circ) = 2.49 - 1.330 \times 10^4/T \quad (1098 \leq T/\text{K} \leq 1252)$$

From the results, the oxygen potential in LBE at the oxygen unsaturated region was estimated as,

$$RT \ln(p_{O_2}/P^\circ)/(\text{J/mol}) = -58.59T - 2.510 \times 10^5 + 38.29T \log(C_O/\text{mass ppm})$$

The activity coefficient of oxygen in liquid LBE obtained using Blander's oxygen dissolution model was compared with these experimental data and those of other investigators.

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1. Introduction

In recent years, the development of a candidate coolant to take the place of sodium has been focused on in order to improve the safety of nuclear reactors.

The boiling point of LBE is higher and its reactivity with water and air is lower than those of sodium. However, if LBE is used as a coolant, the problem of the pipe corrosion, which originates in the dissolution of the metal into LBE, occurs. According to the IPPE report,¹⁾ it may be possible to prevent this corrosion by controlling the oxygen concentration in LBE and forming an oxide protection film on the inner wall of the cooling pipe. To do this, it is necessary to construct a potential diagram of the LBE–oxygen system.

In this study, the solubility of oxygen in LBE in equilibrium with PbO was obtained by a quenching and analyzing method, and then the equilibrium oxygen partial pressure in LBE–PbO equilibrium was measured using an oxygen sensor of zirconia solid electrolyte (ZrO₂ + Y₂O₃). From the results, an oxygen potential and temperature diagram in liquid LBE at the oxygen unsaturated region was estimated.

2. Experimental

2.1 Materials

A lead sheet of 99.99 mass% and bismuth grains of

99.99 mass% pure, both from Mitsubishi Metal. Co., were used. PbO, Bi₂O₃, copper powder and copper(II) oxide powder were all guaranteed reagent grade supplied by Wako Pure Chemical Ind. Ltd.

2.2 Quenching method

To prepare a sample of uniform oxygen concentration in the metal, three melting methods were tried using 25 g of LBE.

Fig. 1 Schematic apparatus to check the cooling rate of the Pb–Bi eutectic alloy (LBE).

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Fig. 2 Schematic apparatus to prepare samples for oxygen analysis.

- ① LBE was melted directly in one closed end silica glass tube (22 mm OD, 100 mm L).
- ② LBE was melted in an alumina crucible (15 mm OD, 12 mm ID and 100 mm L) placed in a silica glass tube.
- ③ LBE was melted in an alumina crucible placed in a silica glass tube with tin between the alumina and the silica glass to accelerate the cooling rate as shown in Fig. 1.

After melting, the silica glass tube was quenched in water. The sample temperature of the cooling process was measured continuously by a thermocouple dipped in the metal and recorded by a mobile type recorder (Keyence NR1000).

2.3 Oxygen analysis

The analytical condition of oxygen in low melting metals, using the inert gas fusion method, was established using Pb or Bi equilibrated with its corresponding oxide at 973 K as a standard sample for oxygen analysis. A schematic diagram of preparing sample for oxygen analysis is shown in Fig. 2. About 25 g of lead in contact with 1.5 g of PbO pellet was held in an alumina crucible placed in a silica glass tube at 973 K and 25 g of bismuth in contact with a Bi₂O₃ pellet of 1.5 g was held directly in the one closed end of a silica glass tube. Pb was held at 973 K for 54 ks and Bi for 36 ks at the same temperature. The holding times, 54 and 36 ks, were decided from the result between holding time and oxygen content in liquid LBE in equilibrium with solid PbO, as shown in Fig. 3. The silica glass tube was quenched in water. Each metal ingot was cut into pieces of about 0.2–0.8 g. Just before the oxygen analysis, the sample was washed with nitric acid (1 + 4) for Pb and hydrochloric acid (1 + 3) for Bi, dipped in ethanol, then acetone, and dried.

All samples from the present experiment were analyzed by inert gas fusion and infrared absorbing methods (Horiba Co. Ltd., type EMGA620W).

A tin bath (mol fraction: 0.6) was used to lower the vapor pressure of Pb and Bi, and the oxygen extraction temperature of the oxygen analyzer was set to 1873 K.

Fig. 3 Change in oxygen contents in liquid LBE with holding time at 878 and 973 K.

2.4 Oxygen partial pressure measurements

Galvanic cells used in this study can be represented as follows:

A schematic diagram of the cell arrangement is shown in Fig. 4. About 60 g Pb or Bi with 3 g of PbO or Bi₂O₃, or about 100 g of LBE with 6 g of PbO was held in an alumina crucible (40 mm OD, 35 mm ID and 100 mm H) at a constant temperature zone in a mullite reaction tube (70 mm OD) closed at one end. In the temperature region where PbO melted, ZrO₂ + MgO crucible instead of alumina was used. The cell, consisting of a ZrO₂ – Y₂O₃ (8 mm OD, 6 mm ID and 80 mm L) solid electrolyte tube, contained a mixture of

Fig. 4 Schematic arrangement of the cell for EMF measurements.

Cu and CuO as a reference electrode. At the experimental temperature, Cu reacts with CuO, changing to $\text{Cu} + \text{Cu}_2\text{O}$ equilibrium. The spiral end of a platinum lead wire was pushed into the reference electrode using an alumina protection tube for the platinum lead, thus good contact being obtained between the reference electrode and the electrolyte.

Two kinds of electrical lead dipped in the melt were used for the melt. LaCrO_3 rod (2 mm dia. and 10 mm long) was used as an electrical contact for cells [I] and [III], and Ir wire (0.5 mm dia. and 10 mm long) was for cell [II]. The LaCrO_3 rod was placed at the end of the alumina protection tube, electrical contact being made via a platinum lead wound round one end and iridium was spot welded at the tip of the Pt wire. Both contact parts were covered by alumina cement to prevent the contact of Pt lead with the melt, as shown in Fig. 4.

The upper end of the mullite reaction tube was sealed with a water-cooled stainless cap provided with openings for evacuation and protection tubes for the lead wire of the cell and a thermocouple.

A silicon carbide resistance furnace was used, and its temperature was controlled within ± 1 K using a PID controller.

After the cell was assembled, the reaction tube was evacuated and heated slowly to about 500 K to ensure gas tightness and dehydration. Ar gas was introduced into the reaction tube and then heated to the temperature for emf measurement under a stream of Ar.

3. Results and Discussion

3.1 Cooling rate

Figure 5 shows a comparison of the cooling rate among the

Fig. 5 Comparison of cooling rate among methods ①, ② and ③.

three different melting methods, ①, ② and ③. As is clear from the figure, it took 15 s from 1000 to 400 K for method ①, and 40 s for method ③.

According to these results, method ① was adopted for Bi, and method ③ for Pb and LBE to avoid reaction between PbO and SiO_2 .

3.2 Solubility of oxygen in Pb, Bi and LBE

Table 1 shows oxygen concentrations in liquid Pb and Bi equilibrated with the respective oxide at 973 K with the results of other investigators.²⁻⁹⁾ Oxygen concentrations in Pb and Bi at 973 K in this study agree well with those of other investigators, although the agreement among the references for Bi is not good.

From this result, the analytical condition of oxygen using the inert gas fusion-infrared absorption method was found to be suitable for low melting metals.

Figure 6 demonstrates the XRD pattern of PbO equilibrated with LBE at 873, 923, 973, 1023 and 1073 K for 36 ks. Only PbO (yellow + red) was identified; it seemed that the yellow PbO was generated during cooling. Furthermore, ICP analysis proved that the Bi content in PbO was 0.01–0.2 mol%. From this fact, the oxide equilibrated with LBE was determined to be a solid solution of PbO below 1098 K, with a very small amount of Bi_2O_3 .

The logarithms of oxygen concentration in liquid LBE equilibrated with PbO at 878, 973, 1023 and 1073 K against the reciprocal of absolute temperature are plotted in Fig. 7 together with the data of Gromov *et al.*¹⁾ Their oxygen solubilities show fairly low compared with our data. The straight line of $\log(\text{Co}/\text{mass ppm})$ against $1/T$ in this study can be expressed by eq. (1).

$$\log(\text{Co}/\text{mass ppm}) = -4.74 \times 10^3/T + 7.06 (\pm 0.03) \quad (878 \leq T/\text{K} \leq 1073) \quad (1)$$

3.3 Oxygen partial pressures in Pb/ PbO , Bi/ Bi_2O_3 and LBE/(PbO and/or $\text{PbO} + \text{Bi}_2\text{O}_3$) equilibria

Emf measurements were carried out using cells [I], [II] and [III], respectively. A steady emf was obtained several hours after reaching the desired temperature. When the

Table 1 Oxygen solubility limit in Pb and Bi.

	$\log(C_O/\text{mass ppm})$ $= A/T + B$		$C_O/\text{mass ppm}$ $T/K = 973$	Temp. (K)	References
	A	B			
Pb	–5201	7.34	98.8	601–1073	Otsuka and Kozuka ²⁾
	–5240	7.44	113	600–1153	Alcock and Belford ³⁾
	–5000	7.20	115	673–973	Gromov ¹⁾
	–5443	7.60	101	—	Charle and Osterwald ⁴⁾
	–5062	7.23	107	773–1773	Richardson and Webb ⁵⁾
	–4884	7.03	102	—	Risold, Nagata, and Suzuki ⁶⁾
	—	—	91	973	This study
Bi	–4820	7.26	202	545–979	Otsuka and Kozuka ²⁾
	–4660	7.02	170	—	Risold, Hallstedt and Gauckler ⁷⁾
	–3400	5.48	96.8	673–1023	Griffith and Mallett ⁸⁾
	–4388	6.70	155	—	Isecke and Osterwald ⁹⁾
	—	—	178	973	This study

Fig. 6 XRD patterns of the oxide equilibrated with LBE.

Fig. 7 Relationship between oxygen content in LBE and temperature.

temperature was changed, a new steady emf was obtained after 10.8 ks.

Figure 8 shows the temperature dependencies of emf values for cells [I], [II] and [III]. The break point in the emf of

Fig. 8 EMF of cells (I), (II), and (III).

cell [II] corresponds to the transformation of solid Bi_2O_3 , and that for cell [III] to the melting of PbO and making $\text{PbO} + \text{Bi}_2\text{O}_3$ melt.

Least square linear regression analyses gave eqs. (2) to (4) for cells [I], [II] and [III], respectively.

$$E/\text{mV} = 262.8 - 0.1416T/K (\pm 0.21) \quad (709 \leq T/K \leq 970) \quad (2)$$

$$E/\text{mV} = 131.4 - 0.1251T/K (\pm 0.12) \quad (771 \leq T/K \leq 1012) \\ = 74.31 - 0.0687T/K (\pm 0.06) \quad (1012 \leq T/K \leq 1067) \quad (3)$$

$$E/\text{mV} = 256.3 - 0.1792T/K (\pm 0.18) \quad (720 \leq T/K \leq 1098) \\ = -204.5 + 0.2406T/K (\pm 0.86) \quad (1098 \leq T/K \leq 1252) \quad (4)$$

The standard Gibbs energy of formations of PbO and Bi₂O₃ can be obtained by combining the Gibbs energy of formation of Cu₂O according to Charette and Flengas.¹⁰⁾

$$\Delta G_f^\circ(\text{PbO})/\text{kJ}\cdot\text{mol}^{-1} = -217.5 + 0.0986T \quad (709 \leq T/\text{K} \leq 970) \quad (5)$$

$$\Delta G_f^\circ(\text{Bi}_2\text{O}_3)/\text{kJ}\cdot\text{mol}^{-1} = -576.5 + 0.2863T \quad (771 \leq T/\text{K} \leq 1012) \quad (6)$$

$$= -543.4 + 0.2537T \quad (1012 \leq T/\text{K} \leq 1067) \quad (7)$$

The $\Delta G_f^\circ(\text{PbO})$ and $\Delta G_f^\circ(\text{Bi}_2\text{O}_3)$ of this study agreed very well with those of other investigators.^{3,9-16)}

Equations (8) and (9) show the relation between logarithms of partial pressure of oxygen and reciprocal temperature for cell [III].

$$\log(p_{\text{O}_2}/P^\circ) = 11.06 - 2.259 \times 10^4/T \quad (720 \leq T/\text{K} \leq 1098) \quad (8)$$

$$\log(p_{\text{O}_2}/P^\circ) = 2.60 - 1.330 \times 10^4/T \quad (1098 \leq T/\text{K} \leq 1252) \quad (9)$$

where P° is 101325 Pa.

By combining eqs. (1) and (8) and assuming that Sieverts' law is obeys up to the solubility limit of oxygen in LBE, the oxygen potential at the oxygen unsaturated region was estimated as a function of oxygen concentration and temperature as,

$$\begin{aligned} RT \ln(p_{\text{O}_2}/P^\circ) / (\text{J/mol}) \\ = -58.59T - 2.510 \times 10^5 \\ + 38.29T \log(C_{\text{O}}/\text{mass ppm}) \end{aligned} \quad (10)$$

To evaluate the formation of an oxide protection film on the inner wall of the cooling pipe in the lead–bismuth cooled fast reactor, which is basically made of the Fe–Cr alloy, the potential diagram of Pb–Bi–O and Fe–Cr–O systems was constructed in Fig. 9. The relation in eq. (10) can be seen in Fig. 9 together with the oxygen potentials of H₂–H₂O, Fe–FeO, FeO–Fe₃O₄, Fe–FeCr₂O₄–Cr₂O₃ and Cr–Cr₂O₃ equilibria, when considering the equilibrium between LBE and

Fig. 9 Potential diagram of Pb–Bi–O and Fe–Cr–O systems.

Table 2 Relationship between oxygen contents in LBE and oxides expected to precipitate on the surface of the Fe–10mass%Cr alloy at 873 K.

Oxygen content in LBE, Co/mass ppm	Oxides expected to precipitate	H ₂ /H ₂ O ratio
4×10^{-9}	None	$\sim 3 \times 10^5$
4×10^{-9} $\sim 3 \times 10^{-7}$	Cr ₂ O ₃	3×10^5 $\sim 3.6 \times 10^3$
3×10^{-7}	Cr ₂ O ₃ + FeCr ₂ O ₄ (spinel)	3.6×10^3
3×10^{-7} $\sim 3 \times 10^{-4}$	FeCr ₂ O ₄ (spinel)	3.6×10^3 ~ 3.6
3×10^{-4} $\sim 1 \times 10^{-3}$	FeO + FeCr ₂ O ₄ (spinel)	$3.6 \sim 1$
$1 \times 10^{-3} \sim 43$	FeCr ₂ O ₄ (spinel)	$1 \sim 2.9 \times 10^{-5}$
43	PbO precipitation	2.9×10^{-5}

Fe–Cr alloy containing about 10 mass% chromium. The oxygen potential of Fe–FeCr₂O₄–Cr₂O₃ equilibrium was obtained by extrapolating the data of Jacob *et al.*¹⁷⁾ down to the temperature region in Fig. 9.

The relation between the oxygen contents in LBE and oxide species, which may be expected to precipitate on the surface of the Fe–Cr alloys at a given temperature, can be seen in Fig. 9.

Table 2 shows the relationship between the oxygen contents in LBE and oxides expected to precipitate on the surface of the Fe–Cr alloy at 873 K, which is within the operating temperature.

3.4 Solution model

Several theories and models have been proposed to describe the compositional variation of the activity coefficient of oxygen, γ_{O} , in liquid binary alloys. In 1973, Wagner¹⁸⁾ derived an equation for activity coefficient using a chemical approach. The basic assumptions underlying this model are that the solvent atoms exhibit ideal solution behavior and the dissolved oxygen atoms occupy quasi-interstitial sites. In 1981, Blander¹⁹⁾ described the dissolution of a solute atom in a binary solvent in terms of four types of atomic interactions. By applying Blander's model to the system Pb–Bi–O, eq. (11) may be derived for γ_{O} .

$$\gamma_{\text{O}} = \left\{ \sum_{i=0}^Z \frac{Z!}{i!(Z-i)!} \left(\frac{x_{\text{Bi}} \gamma_{\text{Bi}}^t}{\gamma_{\text{O(Bi)}}^{1/Z}} \right)^{Z-i} \left(\frac{x_{\text{Pb}} \gamma_{\text{Pb}}^t}{\gamma_{\text{O(Pb)}}^{1/Z}} \right)^i \exp \left[-\frac{g_i^E}{RT} \right] \right\}^{-1} \quad (11)$$

$$g_i^E = i(Z-i)h_b/2 \quad (12)$$

Where

γ_{O} : Activity coefficient of oxygen

T : Temperature of the system

Z : Coordination number of dissolved solute atom

i : Number of B atom in coordination cluster

$Z-i$: Number of A atom in coordination cluster

t : Geometric parameter

x_{Bi} : Molar fraction of component Bi

x_{Pb} : Molar fraction of component Pb

γ_{Bi} : Activity coefficient of Bi in Pb–Bi binary alloy

Fig. 10 Compositional dependence of the activity coefficient of oxygen, γ_O , in liquid Pb–Bi alloys.

Fig. 11 Compositional dependence of oxygen partial pressure in liquid Pb–Bi alloys.

γ_{Pb} : Activity coefficient of Pb in Pb–Bi binary alloy
 $\gamma_O(Bi)$: Activity coefficient of oxygen in pure Bi
 $\gamma_O(Pb)$: Activity coefficient of oxygen in pure Pb
 g_i^E : Excess free energy
 h_b : Enthalpy of solute for coordination cluster

Otsuka *et al.*²⁰ applied eq. (12) to oxygen in liquid Pb–Bi alloys at 1073 K with $h_b = -1.60$ kJ, $t = 0.33$ and $Z = 6$ and confirmed that the value $\gamma_O(Pb\text{–}Bi)$ obtained by the above model agreed very well with that from their experimental data. Saboungi²¹ pointed out that the temperature dependence of h_b may be ignored. According to his proposal, $\gamma_O(Pb\text{–}Bi)$ at 973 K in this study was calculated using h_b , t and Z to be -1.60 , 0.33 and 6 , respectively, and Moser's experimental data²² for the activity values of Pb–Bi alloys. Figure 10 shows the results together with those of other investigators.^{4,9,20,23} The curves in the figure, from this study at 973 K and from Otsuka *et al.* at 1073 and 1173 K, show γ_O obtained using Blander's model. It seems that the agreement between the experimental points and curves from the model calculation is good because the Pb–Bi system is regarded to obey the regular solution behavior.

Figure 11 shows the compositional dependence of p_{O_2} for the equilibrium between Pb–Bi alloys and PbO with the experimental data of Sugimoto *et al.*,²⁴ and of Kapoor and Mehrotra.²⁵ The results of this study agreed very well with those of other investigators. Logarithms of p_{O_2} were expressed as follows.

$$\log(p_{O_2}/P^\circ) = 1.70x_{Pb}^2 - 4.09x_{Pb} - 10.66 \quad (973 \text{ K}) \quad (13)$$

$$\log(p_{O_2}/P^\circ) = 1.19x_{Pb}^2 - 3.33x_{Pb} - 8.74 \quad (1073 \text{ K}) \quad (14)$$

Combining the p_{O_2} values and $\gamma_O(Pb\text{–}Bi)$ calculated by Blander's coordination cluster theory, a model calculation of composition dependence of solubility limit of oxygen in a Pb–Bi melt was performed and is shown in Fig. 12.

Fig. 12 Calculated and experimental oxygen solubility limits in liquid Pb–Bi alloys at 973 K.

4. Summary

In order to obtain the solubility and activity of oxygen in Pb–Bi melts, research for oxygen analysis and oxygen partial pressure measurement in lead–bismuth eutectic alloy (LBE) was performed. The analytical condition of oxygen in low melting metals was established using Pb or Bi equilibrated with its corresponding oxide at 973 K as standard samples.

The temperature dependence of oxygen solubility in liquid LBE was expressed by the following equation,

$$\log(C_O/\text{mass ppm}) = -4.74 \times 10^3/T + 7.06 (\pm 0.03) \quad (878 \leq T/\text{K} \leq 1073)$$

Oxygen partial pressure in LBE–(PbO–Bi₂O₃) equilibrium was measured using an oxygen sensor of a zirconia solid electrolyte (ZrO₂ – Y₂O₃), and obtained as a function of temperature as

$$\log(p_{O_2}/P^\circ) = 11.06 - 2.259 \times 10^4/T$$

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$$\log(p_{O_2}/P^\circ) = 2.60 - 1.330 \times 10^4/T$$

$$(1098 \leq T/K \leq 1252)$$

From the results, the oxygen potential in LBE at the oxygen unsaturated region was estimated as,

$$RT \ln(p_{O_2}/P^\circ)/(J/mol) = -58.59T - 2.510 \times 10^5$$

$$+ 38.29T \log(C_O/\text{mass ppm}).$$

Oxide species expected to precipitate on the Fe–Cr alloy were discussed when considering the equilibrium between LBE and Fe–Cr alloy from the relationship between oxygen partial pressure and oxygen content in LBE.

Compositional dependencies of the activity coefficient of oxygen, oxygen partial pressure and solubility of oxygen in LBE were calculated and compared with the literature data.

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