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Vapor Pressure Measurements of Lanthanum–Bismuth Alloys by Mass-Spectrometric Method[1]

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Vapor pressures of Bi_2 (g) over $La_{0.03}Bi_{0.97}$ and two-phase mixtures of $Bi + LaBi_2$, $LaBi_2 + LaBi$, $LaBi + La_4Bi_3$, $La_4Bi_3 + La_5Bi_3$, and $La_5Bi_3 + La_2Bi$ were measured in the temperature range from 795 to 1066 K with a time-of-flight mass spectrometer equipped with a tungsten Knudsen cell. The vapor pressure of Bi_2 (g) over the two-phase mixtures of $La_2Bi + La$ could not be detected experimentally in this temperature range. The thermodynamic activity of bismuth was determined from the vapor pressure of Bi_2 (g). Thermodynamic activities of lanthanum over alloys were derived from those of bismuth in the alloys in this study and that of lanthanum in the bismuth in a previous study by graphic integration of the Gibbs–Duhem equation. Thermodynamic quantities such as Gibbs free energy of formation, excess enthalpy, etc., were also calculated from the thermodynamic activities.

KEY WORDS: La–Bi alloy; thermodynamic activity; thermodynamic quantity; vapor pressure.

1. INTRODUCTION

A dry process has been adapted to separate transuranium (TRU) elements from other fission products, mainly composed of rare earth elements, in nuclear fuel reprocessing. In this process using liquid metal molten chlorides (cadmium or bismuth), some rare earth elements are thought to be recovered together with TRU in the liquid metal, since rare earth

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elements are chemically similar to TRU. In order to estimate the separation efficiency between TRU and rare earth elements, thermodynamic data on the lanthanum–bismuth system are important since the light rare earth element lanthanum is one of the main components of the fission products.

There are few thermodynamic data available for the lanthanum–bismuth system. Two experimental values of the thermodynamic activity coefficient of lanthanum which were determined by the electromotive force are $10^{-13.39}$ [1] and $10^{-13.44}$ [2] at 773 K. The enthalpy of the lanthanum–bismuth system was measured with a direct isoperibol calorimeter [3].

In this study, lanthanum was selected as the rare earth elements and bismuth as the selected liquid metal. The vapor pressures over the lanthanum–bismuth alloys were measured by mass spectrometry in an attempt to derive the thermodynamic activities and the thermodynamic properties for the estimation of the thermodynamic stability of the intra-rare earth alloys.

2. EXPERIMENTAL

The metals used as starting materials for the preparation of the alloys were 99.9% pure lanthanum (Rare Metallic Co. Ltd., Japan) and 99.9999% pure bismuth (Niraco Co., Japan). Oxygen contents in the lanthanum metals were determined to be in the range of 300 to 1500 ppm by weight by mass-spectrometric evolved-gas analysis. The samples of $La_{0.03}Bi_{0.97}$ and the two-phase mixtures of $Bi + LaBi_2$, $LaBi_2 + LaBi$, $LaBi + La_4Bi_3$, $La_4Bi_3 + La_5Bi_3$, and $La_5Bi_3 + La_2Bi$ were prepared by mixing pure lanthanum and bismuth metals in desired proportions and melting them by an arc melting method under a pure argon atmosphere. Arc melting was performed several times with the specimen turned upside down to assure homogeneity. The samples, except for $La_{0.03}Bi_{0.97}$, were wrapped in tantalum foil and sealed in a silica tube under 1 Pa. When making samples with a bismuth content of more than 40 at%, the samples were annealed at about 800 K for 7 to 10 days. For samples with a bismuth content of less than 40 at%, the samples were annealed at about 1000 K. Phase identification was performed by *x*-ray diffraction, and no phase change was observed before and after the vapor pressure measurements.

The vapor pressures were determined with a time-of-flight mass spectrometer (CVC Model MA-2) equipped with a tungsten Knudsen cell, contained in a tantalum holder. The sample was heated in the tantalum holder by radiation. The temperature was determined with a Pt/Pt–13% Rh thermocouple. The Knudsen cell had a 7 mm internal diameter and a height of 7 mm, and the diameter of the effusion orifice was 0.5 mm. The electron energy used to ionize the gaseous species was 12 eV. The absolute pressure of dimer bismuth gas species was determined by comparing the intensity of its ionic current with that of monomer bismuth vapor over a pure bismuth metal [4]. The values of the atomic ionization cross section of lanthanum and bismuth were taken from the table by Mann [5]. The value for dimer bismuth was 1.5 times larger than that of monomer bismuth [6–8]. The relative multiplier gain was calculated by assuming inverse proportionality to the square root of the mass of the vaporizing species [9].

3. RESULTS AND DISCUSSION

3.1. Vapor Pressure

In this study the major species over pure bismuth is Bi_2 (g). The temperature dependence of the partial vapor pressure of Bi_2 (g) over pure bismuth obtained in this study was in good agreement with that reported previously [4, 10, 11].

The enthalpy of formation of Bi_2 (g) at 298 K was calculated by second- and the third-law treatments. The second-law enthalpy of vaporization at the median temperature of the measurement was obtained directly from the slope of the logarithmic plot of the vapor pressure of Bi_2 (g) versus inverse temperature and the difference between the heat content at the median temperature and that at the standard state (298 K). The third-law enthalpy of formation was calculated as the averaged value of the standard enthalpies derived from each individual experimental data point with the relation

$$-(R \ln P_{\mathrm{Bi}_2} + \Delta fef)\,T = \Delta_f H^0_{298} \tag{1}$$

where Δfef is the change in the free energy function, P_{Bi_2} is the vapor pressure of Bi_2, R is the gas constant, and T is the absolute temperature. The heat content and the free energy function have been assessed by Barin [12]. The third-law enthalpy of formation was calculated to be $110.0 \pm 3.5\ \mathrm{kJ \cdot mol^{-1}}$ for Bi_2 (g) in this study, which was in good agreement with the literature values of 110.4 [4], 110 ± 4 [10], 110 ± 4 [11] and $111.3\ \mathrm{kJ \cdot mol^{-1}}$ [13]. The temperature dependence of the vapor pressure of Bi_2 (g) over La–Bi alloys obtained in this study is shown in Fig. 1. The coefficients in the equation for the vapor pressure obtained by least-squares treatment are given in Table I. The vapor pressure of Bi_2 (g) over two-phase mixtures of $La_2Bi + La$ could not be detected experimentally in this temperature range. It is seen in Fig. 1 that the vapor pressure of dimer bismuth over the alloys becomes lower with decreasing mole fraction of the constituent element Bi in the alloys, as expected.

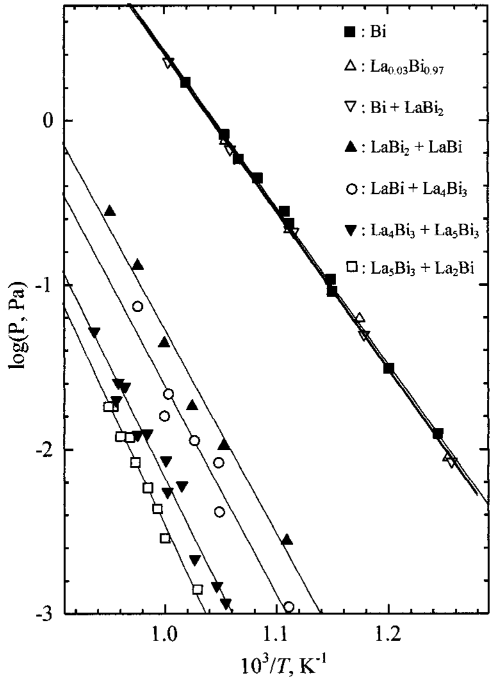

Fig. 1. Vapor pressure of Bi_2 (g) over La–Bi alloys.

3.2. Thermodynamic Quantities

3.2.1. Thermodynamic Activity and Partial Molar Gibbs Energy of Mixing

From the vapor pressure of Bi_2 (g) over the pure metal and alloys, the values of thermodynamic activities and the partial molar Gibbs energy of

Table I. Coefficients in the Equation for the Vapor Pressure of Dimer Bismuth over La–Bi Alloys: $\log(P/[\mathrm{Pa}]) = (-A \times 10^3)/T + \mathrm{B}$, $795 \leqq T \leqslant 1066$ K

Sample	A	B
Bi	9.54 ± 0.13	9.97 ± 0.14
$La_{0.03}Bi_{0.97}$	9.60 ± 0.33	10.01 ± 0.38
$Bi + LaBi_2$	9.58 ± 0.11	9.97 ± 0.12
$LaBi_2 + LaBi$	12.42 ± 0.58	11.15 ± 0.60
$LaBi + La_4Bi_3$	12.75 ± 0.57	11.15 ± 0.61
$La_4Bi_3 + La_5Bi_3$	13.74 ± 0.77	11.57 ± 0.76
$La_5Bi_3 + La_2Bi$	14.72 ± 0.70	12.27 ± 0.68

mixing for bismuth were derived and are given in Table II. The following relation was used for the calculation of $\Delta\bar{G}_{\mathrm{Bi}}$:

$$\Delta\bar{G}_{\mathrm{Bi}} = RT\ln(\alpha_{\mathrm{Bi}}) = \frac{RT}{2}\ln\left(\frac{P_{\mathrm{Bi}_2}}{P^0_{\mathrm{Bi}_2}}\right) \tag{2}$$

where a_{Bi} is the thermodynamic activity of Bi, P_{Bi_2} is the vapor pressure of Bi_2 over the sample, and $P^o_{\mathrm{Bi}_2}$ is the vapor pressure of Bi_2 over pure Bi metal. For the calculation of the thermodynamic activities of bismuth over $\mathrm{La}_2\mathrm{Bi} + \mathrm{La}$ and lanthanum over La–Bi alloys, there were several assumptions:

(a) The thermodynamic activity coefficient of lanthanum in the lanthanum plus liquid bismuth system is constant in this liquid region.

(b) The solubility limit is estimated to be $x = 0.96$ in the liquid solution of $\mathrm{La}_{1-x}\mathrm{Bi}_x$ at 900 K.

(c) Due to the almost zero solubility of lanthanum in bismuth, the thermodynamic activities of lanthanum in this region obey Raoult's law.

The thermodynamic activity of bismuth over $\mathrm{La}_2\mathrm{Bi} + \mathrm{La}$ was estimated from that of lanthanum over the liquid solution of lanthanum in bismuth in a previous study [1] and using the graphic integration of the Gibbs–Duhem equation. The thermodynamic activities of lanthanum over alloys were also calculated from the Gibbs–Duhem equation and are given in Table II. The thermodynamic activities of lanthanum and bismuth are shown in Fig. 2. This figure indicates that the thermodynamic activity of bismuth showed negative deviations from Raoult's law (ideal solution) for $x_{\mathrm{Bi}} \leqq 0.67$. The negative deviation from ideal behavior suggests the presence

Table II. Thermodynamic Activities and Partial Molar Gibbs Free Energies at 900 K

Sample	a_{Bi} (experimental value)	a_{La} (calculated value)	$\Delta\bar{G}_{\mathrm{Bi}}$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta\bar{G}_{\mathrm{La}}$ ($\mathrm{kJ \cdot mol^{-1}}$)
$\mathrm{La}_{0.03}\mathrm{Bi}_{0.97}$	0.98 ± 0.02	1.2×10^{-13} [1]	−0.2	−222.6
$\mathrm{Bi} + \mathrm{LaBi}_2$	0.96 ± 0.02	1.7×10^{-13}	−0.3	−219.8
$\mathrm{LaBi}_2 + \mathrm{LaBi}$	0.10 ± 0.08	1.7×10^{-11}	−17.5	−185.6
$\mathrm{LaBi} + \mathrm{La}_4\mathrm{Bi}_3$	0.06 ± 0.07	2.6×10^{-11}	−20.6	−182.4
$\mathrm{La}_4\mathrm{Bi}_3 + \mathrm{La}_5\mathrm{Bi}_3$	0.03 ± 0.07	4.6×10^{-11}	−26.4	−178.0
$\mathrm{La}_5\mathrm{Bi}_3 + \mathrm{La}_2\mathrm{Bi}$	0.02 ± 0.10	6.0×10^{-11}	−29.8	−176.1
$\mathrm{La}_2\mathrm{Bi} + \mathrm{La}^a$	6.9×10^{-23}	1.0	−381.6	0.0

[a] Estimated value.

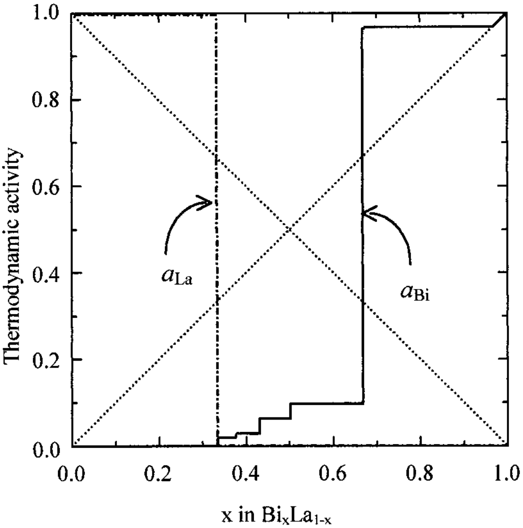

Fig. 2. Thermodynamic activities of Bi and La in Bi_xLa_{1-x} at 900 K.

of an attractive interaction between lanthanum and bismuth atoms in the alloys.

3.2.2. Gibbs Energy of Formation

The Gibbs energy of formation for lanthanum–bismuth alloys was calculated from the partial molar Gibbs energy at 900 K by the following equation, and the results are summarized in Table III:

$$\Delta_f G^\circ = x\bar{G}_{Bi} + (1-x)\,\Delta\bar{G}_{La} \tag{3}$$

Table III. Gibbs Energy of Formation for Lanthanum–Bismuth Alloys at 900 K

Sample	$\Delta_f G^\circ$ ($kJ \cdot mol^{-1}$)
$LaBi_2$	-73.4 ± 4
$LaBi$	-101.5 ± 11
La_4Bi_3	-113.5 ± 12
La_5Bi_3	-121.1 ± 13
La_2Bi	-127.2 ± 13

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