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Letter to the Editors

Activity coefficients of Dy dissolved in liquid Bi

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Abstract

Using an electromotive force technique, activity coefficients of Dy dissolved in liquid Bi in the 820–1101 K range and at Dy concentrations of 10^{-5}–10^{-2} mole fractions have been determined. The dependence of activity coefficient on concentration for each investigated temperature was linear, and the activity coefficient increased with the temperature increase. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Implementation of partitioning and transmutation (P&T) is intended to reduce the inventories of actinides and long-lived fission products in nuclear wastes. The reductive liquid–liquid extraction of f-elements between molten chloride and liquid metal deserves an examination as a possible technique for the group separation of lanthanides and actinides in the irradiated fuel reprocessing industry [1,2]. In support of the establishment of this group separation process, thermodynamic behavior of lanthanides and actinides in molten chloride and liquid metal are needed to be determined. The activity coefficients of the elements in the metal phase and the molten chloride phase greatly influence the separation efficiency. However, there are insufficient data related to the chemical activities of lanthanides and actinides in the liquid Bi. In this study, the activity coefficient of metallic Dy in liquid Bi was determined by an electromotive force (EMF, hereafter) measurement. The concentration and temperature dependency have been investigated.

2. Experimental

EMF measurement method was applied to the following electrochemical cell:

$$(-)\mathrm{Dy(solid)} \mid \mathrm{DyCl_3\ in\ KCl–LiCl} \mid \times \mathrm{Dy(in\ Bi\ solution)}(+).$$

The Dy electrode was prepared by welding a tantalum lead to a small rod of 99.9% pure Dy metal (3 × 3 × 25 mm). The alloy electrode was prepared by directly dissolving a small piece of Dy metal in 99.999% pure Bi. The electrolyte was KCl–LiCl eutectic (mole ratio of emlithium and potassium = 51/49) that was purchased from Anderson Physics Laboratory Engineered Materials Inc. with a purity of 99.9%. Other reagents used were of analytical grade purchased from Wako Pure Chemicals Co. Ltd. The experiments were performed in a glove-box filled with purified argon where the humidity and oxygen were kept <1 ppm. Before starting the experiment, the crucible was heated up to 773 K for several hours under vacuum in order to remove the humidity. In the experiment, 133 g of Bi with about 1 g of Dy was loaded into a sintered alumina crucible, and then about 36 g KCl–LiCl eutectic was loaded. The $DyCl_3$ in KCl–LiCl salt was directly extracted from liquid Bi. The achieved concentration of $DyCl_3$ was not measured because the EMF of the cell is not affected by

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the $DyCl_3$ concentration in the molten salt. The crucible was heated to a temperature range from 820 to 1101 K in an electric furnace. After achieving the distribution equilibrium of solutes (>6 h), the cell EMF was measured with a potentiometer (HG5100, Hokutodenko Co. Ltd.). The fluctuation of EMF was $<\pm 1$ mV within 10 min, and the temperature was controlled to be within the range of ±1 K. At each temperature, the concentration of Dy in liquid Bi was changed several times. At every concentration after the EMF measurement, a small portion of the metallic phase was taken as a sample. The samples were dissolved with diluted nitric acid, and concentration of Dy in Bi was analyzed by ICP-AES (ICPS-1000III, Shimadzu).

3. Results and discussion

In general, the lanthanides in chloride melts in contact with a metal were trivalent in most case except for Eu [3–6]. It is reported that Nd metal reacts with Nd^{3+} in LiCl–KCl to form Nd^{2+} [7]. However, Nd^{2+} is considered to disproportionate into Nd and Nd^{3+} again in the bulk of the salt phase. The Nd formed in the bulk by this mechanism is considered to be a 'metal fog', which is dispersed in the bulk, and we consider that this does not make a significant disturbance to the electrochemical activity at the surface of Nd metal and liquid Bi. Such reactions may also be found in the Dy–Bi system. What we observed during the measurement is the presence of a fractuation of EMF, which we consider is due to the disturbance of the diffusion layer at the electrode surface by the presence of the 'metal fog'. However, the EMF got stabilized during the settling time, and thus it shows that an equilibrium between Dy electrode and Dy–Bi electrode was achieved. The valence of Dy at the salt/Dy metal interface is not very clear in our experimental conditions. The Dy ion in molten salt was considered to be trivalent, not only because of the low concentration of $DyCl_3$ in the molten salt but also due to the lower activity of Dy in Bi. According to the above discussions, the Dy ion was considered as trivalent, and then the following equilibrium between the molten salt phase and Dy–Bi solution was attained.

$$Dy^{3+}(\text{in salt}) + 3e^- = Dy\ (\text{in Bi solution}). \tag{1}$$

According to Nernst's equation, the observed EMF, ΔE, between metallic Dy and Dy in Bi can be expressed as the following equation [4–6]:

$$\begin{aligned}\Delta E &= \frac{1}{3F}\Delta G^{\text{fusion}}(\text{Dy}) - \frac{2.3RT}{3F}\log a_{\text{Dy–Bi}}\\ &= \frac{1}{3F}\Delta G^{\text{fusion}}(\text{Dy}) - \frac{2.3RT}{3F}\log x_{\text{Dy}}\frac{2.3RT}{3F}\log \gamma_{\text{Dy}},\end{aligned} \tag{2}$$

where $\Delta G^{\text{fusion}}(\text{Dy})$ is the fusion energy of metallic Dy, which can be deduced from literature [4]; R is the gas constant; T is the absolute temperature of cell (K); F is the Faraday constant; $a_{\text{Dy–Bi}}$ is the activities of metallic Dy in Bi solution, where $a_{\text{Dy–Bi}} = x_{\text{Dy}} \times \gamma_{\text{Dy}}$; x_{Dy} mole fraction of Dy in Bi solution; and γ_{Dy} is the activity coefficient of Dy in Bi solution. Then the γ_{Dy} can be obtained according to the Eq. (2), using the values of ΔE, x_{Dy} and T obtained in this study along with other constants.

Fig. 1 shows the dependence of ΔE on $\log x_{\text{Dy}}$. For all temperatures tested, observed EMF showed a roughly linear dependence on $\log x_{\text{Dy}}$, suggesting that the variation of ΔE approximately obeys Eq. (2). The lines drawn in Fig. 1 were obtained by applying the least-square fitting method to the experimental data of every temperature. Since the slopes of drawn lines in Fig. 1 showed a close value as the theoretical slopes from Nernst's equation, we believed that this is the evidence that the observed EMF gives the potential difference of Dy in Bi and Dy^{3+} in molten chloride.

By the way, the observed points were found to be slight deviated from the theoretical slopes $(2.3RT/3F)$. This suggests that the third term of Eq. (2) be not thoroughly constant over the tested concentration range at a given temperature, and that γ_{Dy} may depend on the concentration. Fig. 2 presented the activity coefficients of Dy dissolved in liquid Bi at varied temperatures and concentrations. A linear relationship between the $\log \gamma_{\text{Dy}}$ and $\log x_{\text{Dy}}$ was clearly observed at all temperatures. Therefore, when a small amount of Dy dissolved in Bi, the liquid phase was not a regular solution. It is interest that the experimental data at varied temperatures can

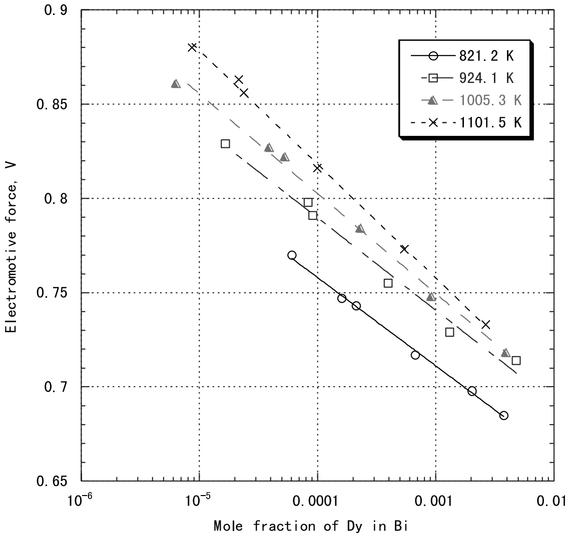

Fig. 1. Concentration dependence of EMF.

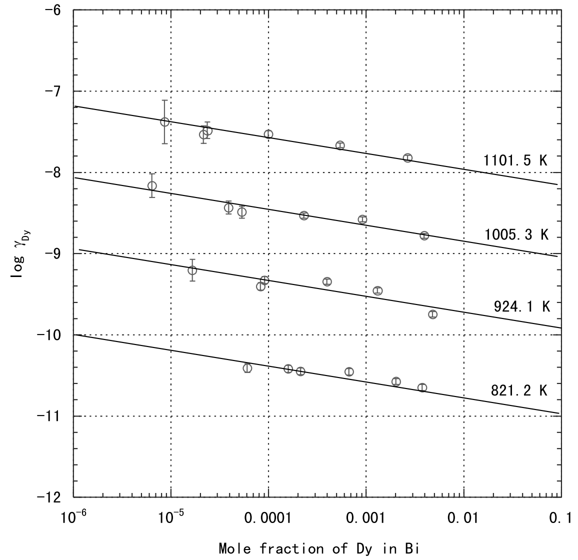

Fig. 2. Variation of the activity coefficient as a function of concentrations.

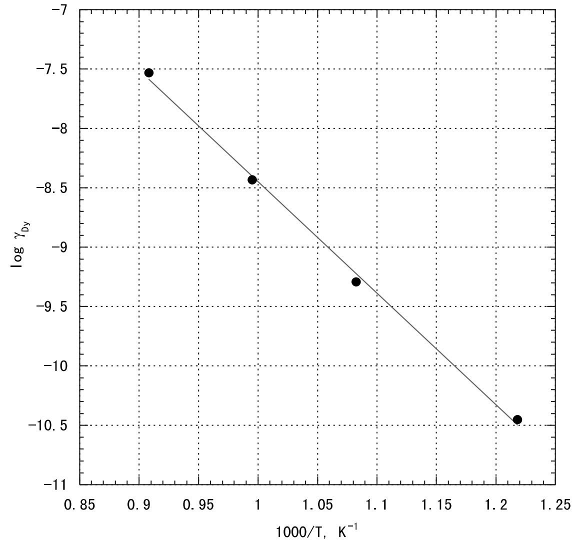

Fig. 3. Temperature effects on the activity coefficients.

be well fitted using the lines having same slope (slope $= -0.161$).

A considerable increase in the γ_{Dy} with the temperature was observed. In order to evaluate the temperature-dependent tendency, mole fraction $x_{Dy} = 0.005$ was chosen as the representative concentration. The calculated values of the activity coefficient were plotted in Fig. 3 as a function of temperature, where a good linearity was observed. The activity coefficient through the range 820–1101 K may be represented by Eq. (3).

$$\log \gamma_{Dy} = 1.003 - \frac{9470.6}{T}, \tag{3}$$

When the temperature variation is known, then it is possible to calculate the change in excess partial molar thermodynamic quantities of Dy in the formation of Dy–Bi solutions from liquid components [6]. The calculation was not included in this letter.

4. Conclusion

The EMF measurement method was successfully used to determine the activity coefficients of Dy in liquid Bi at Dy concentrations of $10^{-5} < x_{Dy} < 10^{-2}$ mole fraction and in a temperature range from 820 to 1101 K. The activity coefficient was concentration dependent at the varied temperatures. The activity coefficient decreased with the concentration increase at a given temperature. The activity coefficients were increased with the temperature increase as $\log \gamma_{Dy} = 1.003 - (9470.6/T)$ at a constant Dy concentration.

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