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Vaporization study on lanthanum–neodymium alloys by mass-spectrometry

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Abstract

Partial vapor pressure of Nd(g) over La_xNd_{1-x} alloys ($x = 0.10$, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90) was measured with a time-of-flight mass-spectrometer equipped with a tungsten Knudsen cell over the temperature range of 1474–1767 K. Thermodynamic activity of neodymium in the liquid alloys was determined by comparing the partial vapor pressure of Nd(g) over the alloys with that over the pure metal. The thermodynamic activity of lanthanum in the alloys was calculated from that of neodymium obtained experimentally in this study by graphic integration using the Gibbs–Duhem equation. Both activities for each element, thus obtained, showed positive deviations from Raoult's law over the entire compositional range. Thermodynamic quantities such as Gibbs free energy of formation, excess enthalpy etc. were also calculated from the thermodynamic activities. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pyrometallurgical partitioning of long-lived radioactive nuclides contained in high level radioactive waste from the reprocessing of spent fuels generated from light water reactors is being developed. The major parts of the long-lived nuclides are transuranium elements (TRU). According to the proposed concept of this partitioning, a reductive extraction process using a molten salt/liquid metal system can be employed for the extraction of TRU from the molten salt and for the separation of TRU from other fission products, mainly composed of rare earth elements. In this process, some rare earth elements are thought to be recovered together with TRU, since rare earth elements are chemically similar to TRU. The thermodynamic properties of TRU and rare earth elements are important to estimate separation efficiency between TRU and rare earth elements.

Some studies on the thermodynamic properties of the intra-rare earth alloy systems have been reported. The vapor pressures over the lanthanum–cerium and lanthanum–gadolinium alloys have been carried out recently by present authors and the thermodynamic activities of lanthanum and cerium for lanthanum–cerium alloys and those of lanthanum and gadolinium for lanthanum–gadolinium alloys were determined at 1673 K, respectively [1,2]. The vaporization studies of the praseodymium–neodymium and samarium–gadolinium alloys have been also performed by Lundin et al. [3,4] and thermodynamic activities of the praseodymium–neodymium alloys were determined at 1748, 1773 and 1798 K. The thermodynamic activity of samarium for the samarium–gadolinium alloys was determined from the vapor pressure of samarium and that of gadolinium was calculated using the Gibbs–Duhem equation at 1173 K. The lanthanum–cerium and praseodymium–neodymium systems (the light–light rare earth systems) were found to behave essentially as almost ideal solution since the elements in the alloy have the similar electronic structure. On the other hand, the lanthanum–gadolinium and samarium–gadolinium systems (the light–heavy

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rare earth systems) were observed to show the deviation from ideal solution model since the elements have the different electronic structure.

The aims of this study were not only to measure the vapor pressures of rare earth binary alloys but also to obtain the systematic knowledge of the rare earth binary alloys using the Miedema's model. In this study, neodymium was selected among the rare earth elements between cerium and gadolinium in a periodic table.

2. Experimental

The metals used as starting materials for the preparation of the alloys were 99.9% pure lanthanum and neodymium (Rare Metallic, Japan). Oxygen contents in the lanthanum and neodymium metals were determined to be in the range of 300–1500 ppm in weight by mass-spectrometric evolved-gas analysis. The samples of La_xNd_{1-x} alloys ($x = 0.10$, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90) were prepared by mixing pure metals in a desired proportion and melting them in a tungsten Knudsen cell installed in a mass spectrometer.

The experimental procedure of the vapor pressure over alloys has been fully described elsewhere [1,2].

3. Results and discussion

3.1. Vapor pressure

The temperature dependences of vapor pressure of Nd(g) over La_xNd_{1-x} alloys obtained in this study are shown in Fig. 1 and given in Table 1. It is seen in Fig. 1 that the vapor pressure of neodymium over the alloys becomes lower with decreasing mole fractions of the constituent element in the alloys as was expected.

Temperature dependence of partial vapor pressure of Nd(g) over the pure neodymium metal obtained in this study was in good agreement with that of Ref. [5].

The enthalpy of vaporization at 298 K was calculated by the second and the third law treatments. The second law enthalpy of vaporization at the median temperature of the measurements was obtained directly from the slope of the logarithmic plot of the vapor pressure of Nd(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 was calculated as the averaged value of the standard enthalpies derived from each individual experimental data point with the relation:

$$-(R\ln P_{\mathrm{Nd}} + \Delta\mathrm{fef})T = \Delta_{\mathrm{f}}H^0_{298}, \qquad (1)$$

where Δfef is the change in the free energy function. The values of heat content and the free energy function have been assessed by Barin [6] and Hultgren [7]. The second and third law enthalpies of vaporization ($\Delta_{\mathrm{f}}H^0_{298}$) were obtained to be 330.0 ± 7.7 kJ mol^{-1}, 327.8 ± 1.6 kJ mol^{-1} for neodymium in this study, respectively. The values for neodymium were in good agreement with the literature value of 328.2 ± 0.8 kJ mol^{-1} for third law

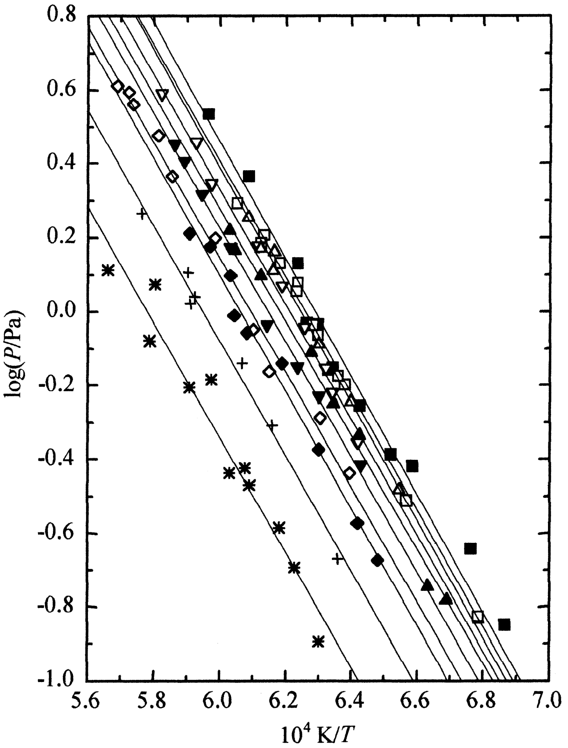

Fig. 1. Temperature dependences of the vapor pressure of Nd(g) over La_xNd_{1-x} ($x = 0.00 - 0.90$) alloys. ■: Nd, □: $La_{0.10}Nd_{0.90}$, △: $La_{0.20}Nd_{0.80}$, ▽: $La_{0.30}Nd_{0.70}$, ▲: $La_{0.40}Nd_{0.60}$, ▼: $La_{0.50}Nd_{0.50}$, ◇: $La_{0.60}Nd_{0.40}$, ◆: $La_{0.70}Nd_{0.30}$, +: $La_{0.80}Nd_{0.20}$, and ✱: $La_{0.90}Nd_{0.10}$.

Table 1
Equation for the vapor pressures of neodymium over lanthanum–neodymium alloys

$\log(P/\mathrm{Pa}) = (-A \times 10^3)/T + B, 1474 \leqslant T/K \leqslant 1767$

Sample	A	B
Nd	10.05 ± 0.30	22.05 ± 0.98
$La_{0.10}Nd_{0.90}$	9.85 ± 0.20	15.74 ± 0.32
$La_{0.20}Nd_{0.80}$	9.96 ± 0.31	15.95 ± 0.50
$La_{0.30}Nd_{0.70}$	9.69 ± 0.29	15.60 ± 0.47
$La_{0.40}Nd_{0.60}$	9.50 ±0.33	15.37 ± 0.53
$La_{0.50}Nd_{0.50}$	9.55 ± 0.24	15.54 ± 0.40
$La_{0.60}Nd_{0.40}$	9.47 ± 0.32	15.54 ± 0.53
$La_{0.70}Nd_{0.30}$	9.59 ± 0.41	15.82 ± 0.67
$La_{0.80}Nd_{0.20}$	9.28 ± 0.45	15.60 ± 0.76
$La_{0.90}Nd_{0.10}$	8.99 ± 0.70	15.55 ± 1.17

treatment but a little different from that of 341.5 ± 1.7 kJ mol^{-1} for second law treatment [5]. The present values are thought to be more reliable due to the consistency of the second and the third law values.

3.2. Thermodynamic quantities

3.2.1. Thermodynamic activity and partial molar gibbs free energy of mixing

From the vapor pressures of Nd(g) over the pure metal and alloys, the values of thermodynamic activities were derived. In the calculation the following relation was used:

$$\Delta\bar{G}_{\mathrm{Nd}} = RT\ln(a_{\mathrm{Nd}}) = RT\ln\left(\frac{P_{\mathrm{Nd}}}{P^0_{\mathrm{Nd}}}\right), \quad (2)$$

where $\Delta\bar{G}_{\mathrm{Nd}}$ is the partial molar Gibbs free energy of mixing of neodymium, a_{Nd} the thermodynamic activity of neodymium, R is the gas constant, P_{Nd} and P^0_{Nd} the vapor pressures of neodymium over the alloys and pure metal, respectively. Thermodynamic activities of lanthanum in the alloys were calculated from the Gibbs–Duhem equation using the those of neodymium in the alloys. The thermodynamic activities of lanthanum and neodymium in the alloys at an average experimental temperature of 1673 K are shown in Fig. 2 and given in Table 2. In Fig. 2 the positive deviation of the thermodynamic activities from Raoult's law is seen, suggesting the presence of a repulsive interaction between lanthanum and neodymium atoms in the alloys.

The lanthanum and neodymium alloy can be regarded as substitutional solution, for which the excess Gibbs energy is given by

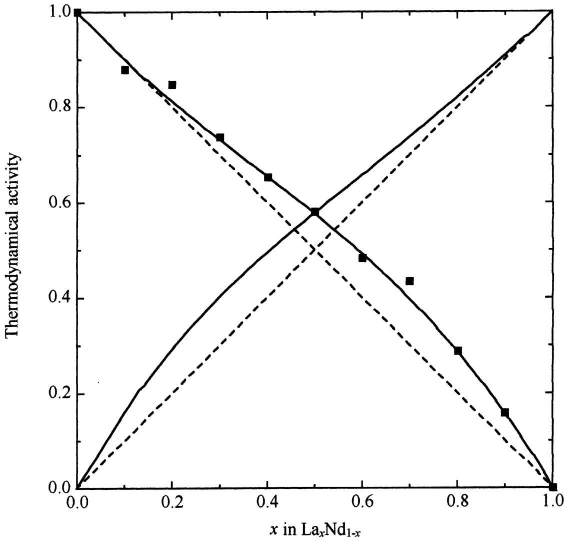

Fig. 2. Thermodynamic activities of La and Nd in La_xNd_{1-x} alloys at 1673 K. ■: This study, - - - -: Raoult's law.

$$\Delta G^{\mathrm{EX}} = \Omega x_{\mathrm{La}} x_{\mathrm{Nd}}, \quad (3)$$

where Ω is the interaction parameter. The numerical value of the interaction parameter (Ω) is usually determined by least-squares treatment using the equation of the thermodynamic activity coefficients (γ) for neodymium:

$$\ln(\gamma_{\mathrm{Nd}}) = \frac{\Omega}{RT}(1 - x_{\mathrm{Nd}})^2. \quad (4)$$

The interaction parameter (Ω) was obtained to be 7.8 kJ mol^{-1} in this study. In the lanthanum–cerium and lanthanum–gadolinium systems, the values of the interaction parameter were calculated in this study using the Gibbs–Duhem equation from the values of thermodynamic activity of cerium and gadolinium, respectively, reported in our previous papers [1,2]. The value of the interaction parameter of lanthanum–neodymium system falls between those of the lanthanum–cerium (2.7 kJ mol^{-1}) and lanthanum–gadolinium systems (15.2 kJ mol^{-1}). In the Miedema's model [8], the following semi-empirical expression to calculate the enthalpy of formation of alloy AB ($\Delta_f H^0$) has been proposed:

$$\Delta_f H^0 \propto [-P(\Delta\phi)^2 + Q(\Delta n_{\mathrm{WS}}^{1/3})^2], \quad (5)$$

where ϕ is the material parameter representing the electronegativity of the metal (La: $\phi = 3.17$, Ce: $\phi = 3.18$, Nd: $\phi = 3.19$, Gd: $\phi = 3.20$ [8]). This was a similar concept to the electronegativity of the element proposed by Pauling [9] except for the absolute value. n_{WS} is the electron density of the metal in the Wigner–Seitz cell (La: $n_{\mathrm{WS}}^{1/3} = 1.18$, Ce: $n_{\mathrm{WS}}^{1/3} = 1.19$, Nd: $n_{\mathrm{WS}}^{1/3} = 1.20$, Gd: $n_{\mathrm{WS}}^{1/3} = 1.21$ [8]). This parameter, n_{WS}, was derived from the ratio of the experimental bulk modulus and the molar volume of pure metals by Miedema [8]. Δ is the difference in the values of ϕ or n_{WS} between the component elements of the alloy. P is a proportional constant related to the alloy type. The value of P for the lanthanum–neodymium alloy is 14.2. Q is a proportional constant, and the ratio Q/P has the value of 9.4 for all transition metal alloys. In rare earth elements, the difference of the electronegativity is small and the number of electrons increases with increasing mass number. The values of the terms for Eq. (5) are shown in Fig. 3 in comparison with the values of the interaction parameter in La–Ln systems (Ln = Ce, Nd and Gd). In Fig. 3 the values of the interaction parameter are determined from three methods. The first and second ones were obtained using the thermodynamic activities calculated by the Gibbs–Duhem and Belton–Fruehan equations, respectively. The last one was from the thermodynamic activity calculated from the ratio of the vapor pressure between pure metal and alloys. As seen in Fig. 3 the difference in the electron density for the elements is recognized as the important term for these systems. From this relationship, the mass number,

Table 2
Thermodynamic activities and partial molar Gibbs free energies at 1673 K

Sample	a_{La} (calculated)	a_{Nd}	$\Delta\bar{G}_{La}$ (kJ mol^{-1})	$\Delta\bar{G}_{Nd}$ (kJ mol^{-1})
$La_{0.10}Nd_{0.90}$	0.16	0.88 ± 0.08	−25.5	−1.8 ± 1.3
$La_{0.20}Nd_{0.80}$	0.29	0.85 ± 0.08	−17.2	−2.3 ± 1.4
$La_{0.30}Nd_{0.70}$	0.40	0.74 ± 0.06	−12.7	−4.2 ± 1.2
$La_{0.40}Nd_{0.60}$	0.49	0.65 ± 0.05	−9.9	−6.0 ± 1.1
$La_{0.50}Nd_{0.50}$	0.58	0.57 ± 0.05	−7.6	−7.8 ± 1.3
$La_{0.60}Nd_{0.40}$	0.66	0.48 ± 0.03	−5.8	−10.2 ± 0.9
$La_{0.70}Nd_{0.30}$	0.74	0.43 ± 0.03	−4.2	−11.7 ± 1.0
$La_{0.80}Nd_{0.20}$	0.82	0.29 ± 0.02	−2.8	−17.2 ± 1.0
$La_{0.90}Nd_{0.10}$	0.91	0.16 ± 0.02	−1.3	−25.5 ± 1.9

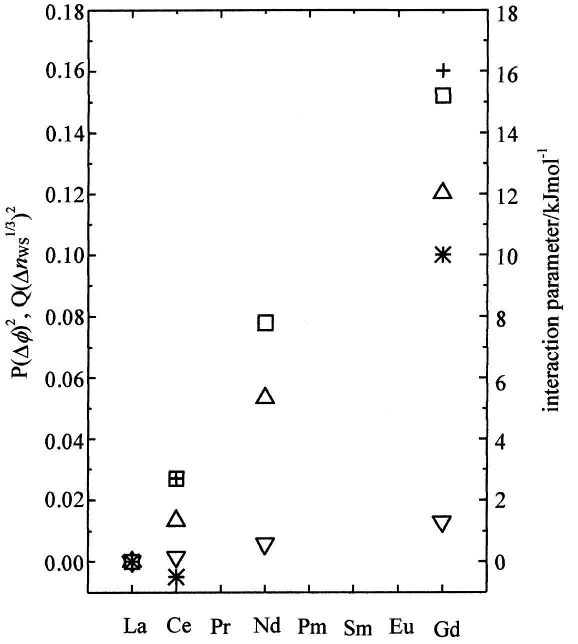

Fig. 3. The values of $P(\Delta\phi)^2$, $Q(\Delta n_{WS}^{1/3})^2$ and interaction parameters in the La–Ln systems (Ln = Ce, Nd and Gd). ∇: $P(\Delta\phi)^2$, Δ: $Q(\Delta n_{WS}^{1/3})^2$, □: interaction parameter calculated by the Gibbs–Duhem equation, +: interaction parameter calculated by the Belton–Fruehan equation, ✱: interaction parameter calculated from the ratio of the vapor pressure between pure metal and alloys.

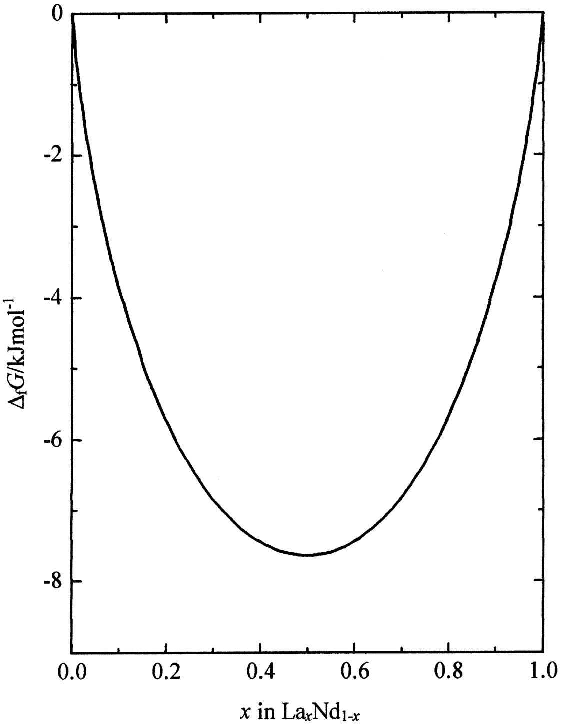

Fig. 4. Gibbs energy of formation of La_xNd_{1-x} alloys at 1673 K.

i.e. the number of 4f electron is thought to affect the increase of the interaction parameter in these systems.

3.2.2. Gibbs free energy of formation

Gibbs free energy of formation ($\Delta_f G^0$) of the lanthanum–neodymium alloys can be calculated from partial molar Gibbs free energies by the following Eq. (6):

$$\Delta_f G^0 = x\Delta\bar{G}_{La} + (1-x)\Delta\bar{G}_{Nd}. \qquad (6)$$

The compositional dependence of the Gibbs free energy of formation obtained in this study is shown Fig. 4. As seen in Fig. 4 the most thermodynamically stable composition was found to be at nearly equal molar composition.

4. Conclusions

The vapor pressure of neodymium over the lanthanum–neodymium system was measured by mass-spectrometry. The thermodynamic activities of lanthanum and neodymium showed positive deviation from Raoult's law. From the comparison of the terms for the Miedema's model with the interaction parameters, the term of the electron density was found to be important in these systems. The Gibbs energy of formation of the lanthanum–neodymium alloys was calculated from the thermodynamic activity. The most thermodynamically stable composition was found to be at nearly $x = 0.5$.

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