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Vaporization study on lanthanum–cerium alloys by mass-spectrometric method

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Abstract

The partial vapor pressures of La(g) and Ce(g) over La_xCe_{1-x} alloys ($x = 0.00$, 0.05, 0.29, 0.50, 0.80, 1.00) were measured with a time-of-flight mass-spectrometer equipped with a tungsten Knudsen cell over the temperature range of 1592–1781 K. The thermodynamic activities of lanthanum and cerium in the liquid alloys were determined by comparing the partial vapor pressures of La(g) and Ce(g) over the alloys with those over the pure metals, respectively. The thermodynamic activities were also calculated from the ion intensity ratios of two components (lanthanum and cerium) in the alloys using the equation derived by Belton and Fruehan. Both activities for each element, thus obtained, were in good agreement with each other and almost obeyed Raoult's law. The partial molar Gibbs free energy, and the Gibbs free energy of formation were calculated from the thermodynamic activity values. © 1998 Elsevier Science B.V.

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1. Introduction

A molten salt electrorefining process has been adapted to separate the transuranium elements (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. There exist, however, few researches on the thermodynamic properties of the intra-rare earth alloy systems. In the binary alloys composed of the light and light rare earth elements (the rare earth element, the number of 4f electrons of which is less than 8, is called as the light element), the vapor pressures over the praseodymium–neodymium alloy have been measured by mass-spectrometric effusion method with a Knudsen cell [1]. From the thermodynamic activities determined from the vapor pressures, this system was found to behave essentially as an ideal solution. On the other hand, in the binary alloys composed of the light and heavy rare earth elements, the vaporization study on the lanthanum–gadolinium alloys has been recently carried out by the present authors [2], and this system was observed to show the positive deviation from an ideal solution model.

In this study, lanthanum (the light rare earth element and one of the main components of the fission products) and cerium (the light rare earth element and a possible stand-in for neptunium) were selected among rare earth elements. The vapor pressures over the lanthanum–cerium 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 and cerium (Rare Metallic Co., Japan). Oxygen contents in the lanthanum and cerium metals were determined to be in the range of 300–1500 ppm in weight by mass-spectrometric evolved-gas analysis. The samples of La_xCe_{1-x} alloys ($x = 0.00$, 0.05, 0.29, 0.50, 0.80 and 1.00) were prepared

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by mixing pure lanthanum and cerium metals in a desired proportion and melting them by arc melting method under purified argon atmosphere. Arc melting was performed several times with the specimen being turned upside down to assure homogeneity. Even after melting several times, the change in the sample weight was found to be negligibly small. The homogeneity (distribution) and the absolute value of the composition in the alloys were determined to be 0.01 in atomic ratios by electron probe microanalysis (EPMA).

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 tungsten holder. The sample was heated in the tungsten holder by electron bombardment. The temperature was determined with a Leeds and Northrup disappearing-filament optical pyrometer, of which error was estimated to be within 10 K by comparison with the melting point of platinum metal and emf values of a Pt/Pt–13%Rh thermocouple. The observation for the temperature measurement was made through an orifice of the Knudsen cell. The Knudsen cell had a 7 mm internal diameter, 7 mm in height 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 each gas species was determined by comparing the intensity of its ionic current with that of silver vapor over a pure silver metal [3]. The value of atomic ionization cross section of silver, lanthanum and cerium were taken from the table by Mann [4]. The relative multiplier gain was calculated by assuming inverse proportionality to the square root of the mass of the vaporizing species [5].

3. Results and discussion

3.1. Vapor pressure

Both temperature dependences of partial vapor pressures of La(g) and Ce(g) over the pure metals La and Ce, respectively, obtained in this study were in good agreement with those over pure metals reported previously [6,7].

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 La(g) or Ce(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

$$-(R \ln P_{\mathrm{M}} + \Delta\mathrm{fef})T = \Delta_{\mathrm{f}} H^{\circ}_{298} \ (\mathrm{M} = \mathrm{La\ or\ Ce}), \qquad (1)$$

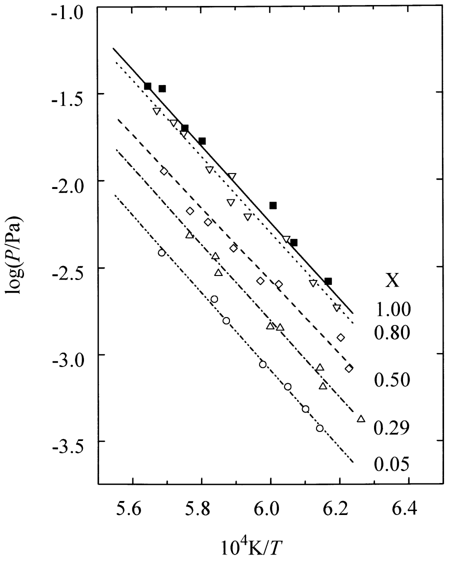

Fig. 1. Temperature dependence of the vapor pressure of La(g) over $\mathrm{La}_x\mathrm{Ce}_{1-x}$ ($x = 0.00$–1.00) alloys. ————: over pure metal, - - -: $\mathrm{La}_{0.80}\mathrm{Ce}_{0.20}$, – – –: $\mathrm{La}_{0.50}\mathrm{Ce}_{0.50}$, – · –: $\mathrm{La}_{0.29}\mathrm{Ce}_{0.71}$, – • –: $\mathrm{La}_{0.05}\mathrm{Ce}_{0.95}$.

where Δfef is the change in the free energy function. The heat content and the free energy function have been assessed by Barin [7] and Hultgren et al. [8]. The third law enthalpies of vaporization ($\Delta_{\mathrm{f}} H^{\circ}_{298}$) were obtained to be 431.3 ± 1.1 kJ mol^{-1} for lanthanum and 426.9 ± 1.1 kJ mol^{-1} for cerium in this study. The value for lanthanum was in good agreement with the literature values (431.8 ± 0.3 kJ mol^{-1} [6] and 433.6 ± 2.9 kJ mol^{-1} [9]). But the third law value for cerium has not been reported previously. Since the absolute value of the vapor pressure of cerium in this study was in good agreement with the literature value [6], the third law enthalpy for cerium obtained in this study was thought to be reliable.

Table 1
Equations for the vapor pressures of lanthanum and cerium over $\mathrm{La}_x\mathrm{Ce}_{1-x}$ alloys $\log(P(\mathrm{Pa})) = (-A \times 10^3)/T + B$, $1592 \leqslant T(\mathrm{K}) \leqslant 1781$

Sample	Gas species	A	B
La	La	22.05 ± 0.46	10.99 ± 0.26
$\mathrm{La}_{0.05}\mathrm{Ce}_{0.95}$	La	22.37 ± 0.07	10.15 ± 0.40
	Ce	22.75 ± 0.07	11.37 ± 0.41
$\mathrm{La}_{0.29}\mathrm{Ce}_{0.71}$	La	22.07 ± 0.08	10.43 ± 0.49
	Ce	22.43 ± 0.10	11.07 ± 0.53
$\mathrm{La}_{0.50}\mathrm{Ce}_{0.50}$	La	21.79 ± 0.10	10.51 ± 0.60
	Ce	22.28 ± 0.14	10.83 ± 0.84
$\mathrm{La}_{0.80}\mathrm{Ce}_{0.20}$	La	21.95 ± 0.10	10.85 ± 0.59
	Ce	22.48 ± 0.07	10.63 ± 0.43
Ce	Ce	22.84 ± 0.68	11.45 ± 0.47

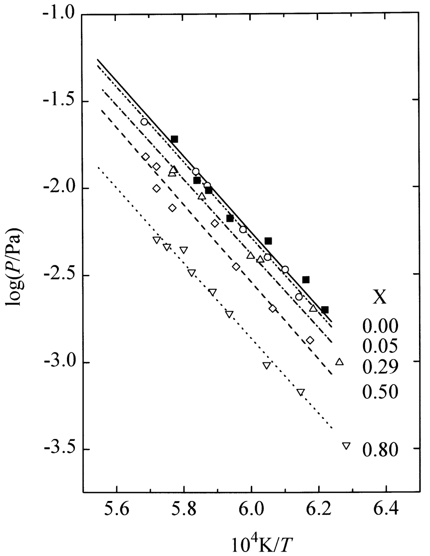

Fig. 2. Temperature dependence of the vapor pressure of Ce(g) over La_xCe_{1-x} ($x = 0.00$–1.00) alloys. ————: over pure metal, - - -: $La_{0.80}Ce_{0.20}$, — — —: $La_{0.50}Ce_{0.50}$, — · —: $La_{0.29}Ce_{0.71}$, — • —: $La_{0.05}Ce_{0.95}$.

The temperature dependencies of vapor pressures of La(g) and Ce(g) over La_xCe_{1-x} alloys obtained in this study are shown in Figs. 1 and 2, respectively. The equations for the vapor pressures obtained by the least-squares treatment are given in Table 1. It is seen in these figures that the vapor pressures of both lanthanum and cerium over the alloys become lower with decreasing mole fractions of the respective constituent elements in the alloys as was expected.

3.2. Thermodynamic quantities

3.2.1. Thermodynamic activity, partial molar Gibbs free energy of mixing

From the vapor pressures of La(g) and Ce(g) over the pure metals and alloys, the values of thermodynamic activities and partial molar Gibbs free energy of mixing were derived and are given in Table 2. In the calculation the following relations were used:

$$\Delta\overline{G}_i = RT\ \ln(a_i) = RT\ \ln\left(\frac{P_i}{P_i^{\mathrm{o}}}\right), \tag{2}$$

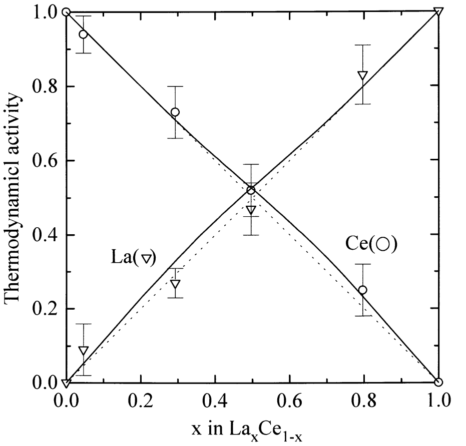

Fig. 3. Thermodynamic activities of La and Ce in La_xCe_{1-x} alloys at 1673 K. ▽: La, ○: Ce obtained from the vapor pressure ratios in this study, ————: calculated from the ion intensity ratios in this study, - - -: Raoult's law.

where $\Delta\overline{G}_i$ is the partial molar Gibbs free energy of mixing of the component i, a_i is the thermodynamic activity of the component i, R is the gas constant, P_i and P_i^{o} are the vapor pressures of component i over the alloys and pure metals, respectively. The thermodynamic activities for lanthanum and cerium at an average experimental temperature of 1673 K, for all compositions, are shown in Fig. 3.

The thermodynamic activities of the components were also calculated by the other method i.e. from the ion intensities using the following equation derived by Belton and Fruehan [10];

$$\ln(\gamma_i) = -\int_{x_i=1}^{x_i=x_i} x_j\, \mathrm{d}\left[\ln\left(\frac{I_j}{I_i}\right) - \ln\left(\frac{x_j}{x_i}\right)\right], \tag{3}$$

where γ_i, I_i, and x_i are the thermodynamic activity coefficient, ion intensity and mole fraction of component i, respectively.

The experimental values of the ion intensity ratios for La_xCe_{1-x} alloy are shown in Fig. 4. The relationship between $\ln(I_{La}/I_{Ce})$ and $1/T$ is seen to be linear for all compositions, showing the applicability of the Eq. (3). The compositions of alloys are plotted against the values obtained for $[\ln(I_{La}/I_{Ce}) - \ln(x_{La}/x_{Ce})]$ at average tempera-

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

Sample	a_{La}	a_{Ce}	$\Delta\overline{G}_{La}$ (kJ mol^{-1})	$\Delta\overline{G}_{Ce}$ (kJ mol^{-1})
$La_{0.05}Ce_{0.95}$	0.09 ± 0.06	0.94 ± 0.05	-33.0	-0.8
$La_{0.29}Ce_{0.71}$	0.27 ± 0.04	0.73 ± 0.06	-18.3	-4.3
$La_{0.50}Ce_{0.50}$	0.47 ± 0.05	0.52 ± 0.04	-10.4	-9.1
$La_{0.80}Ce_{0.20}$	0.83 ± 0.05	0.25 ± 0.07	-2.6	-19.4

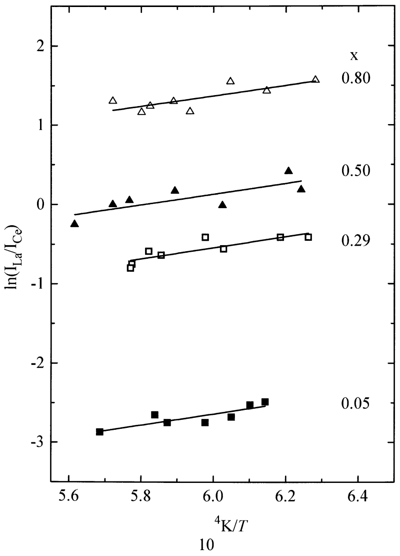

Fig. 4. Ion intensity ratios for the La_xCe_{1-x} alloys.

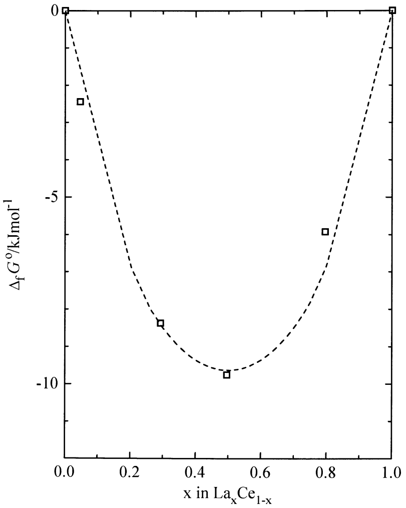

Fig. 6. Gibbs free energy of formation for La_xCe_{1-x} alloys at 1673 K. □: this study, ---: Ideal solution model.

ture 1673 K in Fig. 5. The graphical integration of curve in this figure gave the thermodynamic activity coefficients of lanthanum and cerium based on Eq. (3). The thermodynamic activities, thus calculated, are shown in Fig. 3 by the solid lines. This figure indicates that these activities almost obey Raoult's law. The almost ideal behavior of the lanthanum–cerium alloys found in this study is similar to that of the light rare earth-light rare earth system (praseodymium–neodymium) system previously reported by Lundin et al. [1]. However the light rare earth-heavy rare earth systems (lanthanum–gadolinium [2], samarium–gadolinium [11] and samarium–yttrium [11] systems) have been reported to have the deviation of the activities from Raoult's law. This difference in the thermodynamic activities is thought to be caused by the difference in the electronic structure of elements, as the heavy rare earth element has more than half-filled 4f level differently from the light rare earth element. For this reason, it is thought that the thermodynamic activities of the alloys composed of light and heavy rare earth elements deviate from Raoult's law. The thermodynamic activities for the light rare earth-light rare earth system, on the other hand, obey Raoult's law since the elements in the alloy have the similar electronic structure.

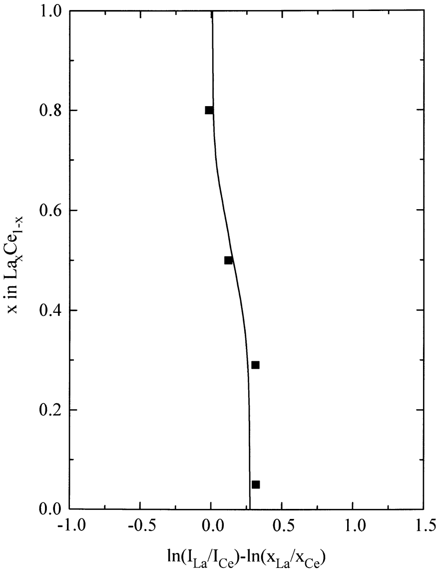

Fig. 5. Integration curve at 1673 K for the activity coefficients in the La_xCe_{1-x} alloys.

3.2.2. Gibbs free energy of formation

Gibbs free energy of formation ($\Delta_f G^o$) of the lanthanum–cerium alloys can be calculated from partial molar Gibbs free energies by the following Eq. (4):

$$\Delta_f G^o = x\Delta\overline{G}_{La} + (1-x)\Delta\overline{G}_{Ce}. \tag{4}$$

The compositional dependence of the Gibbs free energy of formation obtained in this study is shown Fig. 6, in comparison with those of the ideal model. As seen in this figure, the values of the Gibbs free energy of formation obtained in this study are almost equal to those of ideal model, and the most thermodynamically stable composition was found to be at nearly equal molar composition.

4. Conclusions

The vapor pressure of lanthanum and cerium over the lanthanum–cerium alloys were measured as a function of temperature by means of high temperature mass-spectrometry, and the following conclusions were obtained.

(1) The predominant vapor species over La_xCe_{1-x} alloys ($x = 0.00$, 0.05, 0.29, 0.50, 0.80 and 1.00) were identified to be La(g) and Ce(g).

(2) The thermodynamic activities of lanthanum and cerium in the alloys determined from the vapor pressures ratios and calculated from the ion intensity ratios were almost equal to each other and to mole fractions of components.

(3) The Gibbs free energies of formation of the lanthanum–cerium alloys were calculated from the partial molar Gibbs free energy of mixing for each component obtained from the thermodynamic activity. The most thermodynamically stable composition was found to be at nearly equal molar composition ($x \simeq 0.5$).

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