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Vapor pressure measurements of La–Gd alloys

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Abstract

The vapor pressures of La(g) and Gd(g) over La_xGd_{1-x} alloys ($x = 0.00$, 0.12, 0.22, 0.45, 0.70, 0.74, 0.85, 1.00) were measured with a time-of-flight mass spectrometer equipped with a tungsten Knudsen cell over the temperature range 1588 to 1797 K. The chemical activities of lanthanum and gadolinium in the alloys were determined by comparing the vapor pressures of La(g) and Gd(g) over the alloys with those over the pure metals. The chemical activities, thus obtained, showed positive deviations from Raoult's law over the entire compositional range. The interatomic force between gadolinium and lanthanum was thought to be repulsive. The partial molar Gibbs free energy and the Gibbs free energy, enthalpy and entropy of formation were calculated from the activity values. © 1997 Elsevier Science B.V.

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 a separation efficiency between the TRU and rare earth elements. However, only limited researches have been reported on the thermodynamic properties of intra-rare earth alloy systems. In binary alloys composed of the light and heavy rare earth elements, the vapor pressures over the samarium–gadolinium and the samarium–yttrium alloys have been measured by mass-effusion method with a Knudsen cell [1]. The chemical activities of these systems deviated from Raoult's law over all compositions.

In this study, lanthanum (one of the main components of the fission products) and gadolinium (a possible stand-in for curium) were selected among the rare earth elements. The vapor pressures over the lanthanum–gadolinium alloy were measured by mass spectrometry to derive the chemical activities and the thermodynamic properties for estimating the thermodynamic stability of intra-rare earth alloys.

2. Experimental

The 99.9% pure metals of lanthanum and gadolinium supplied by Rare Metallic Co., Japan were used for the preparation of the samples. The oxygen content of the lanthanum and gadolinium pure metals was determined to be in the range of 300–1500 ppm in weight by mass-spectrometric evolved-gas analysis. The La_xGd_{1-x} alloys ($x =$ 0.00, 0.12, 0.22, 0.45, 0.70, 0.74, 0.85, 1.00) were made by mixing pure lanthanum and gadolinium metals in the desired proportion and then arc melting the mixtures several times in a purified argon atmosphere. Even after melting several times, the change in the sample weight was negligible. The homogeneity of the composition and the atomic ratios in the alloys were confirmed by electron probe microanalysis (EPMA).

The vapor pressures were measured with a time-of-flight mass-spectrometer (CVC model MA-2) equipped with a tungsten Knudsen cell in a tungsten holder heated by electron bombardment. The Knudsen cell had a 7 mm internal diameter, was 7 mm in height and the diameter of the effusion orifice was 0.5 mm. The electron energy used

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to ionize the gaseous species was 12 eV. The absolute vapor pressure of each species was determined by comparing the intensity of its ionic current with that of silver vapor over pure silver metal [2]. The atomic ionization cross-section of silver, lanthanum and gadolinium were taken from the table by Mann [3]. The relative multiplier gain was calculated by assuming the inverse proportionality to the square root of the mass of the vaporizing species [4]. Temperature measurements were made with a Leeds and Northrup disappearing-filament optical pyrometer and the error was determined to be ± 5 K by comparison with the melting point of Pt 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.

3. Results and discussion

3.1. Ionization efficiency curves

As the predominant vapor species, La and Gd were identified over all compositions of the La_xGd_{1-x} samples. The ionization efficiency curves of La^+ and Gd^+ ions were very similar to each other. By the linear extrapolation of the ionization efficiency curves to zero intensity, the appearance potentials of La^+ and Gd^+ were determined to be 4.2 ± 0.5 and 4.8 ± 0.5 eV, respectively. The appearance potentials of La^+ and Gd^+ were a little smaller than the literature values (5.5 ± 0.5 [5] and 5.98 ± 0.1 eV [6], respectively). In order to provide a sufficiently high ion current, an ionization electron energy of 12 eV was chosen for the measurements. The ion intensities of La^+ and Gd^+ used for the calculation of the absolute vapor pressures of La(g) and Gd(g) were determined by converting the ion intensities measured at 12 eV to those at 9.4 and 8.8 eV, respectively, both of which are higher than the respective appearance energies by the same 4.6 eV according to the ionization efficiency curves.

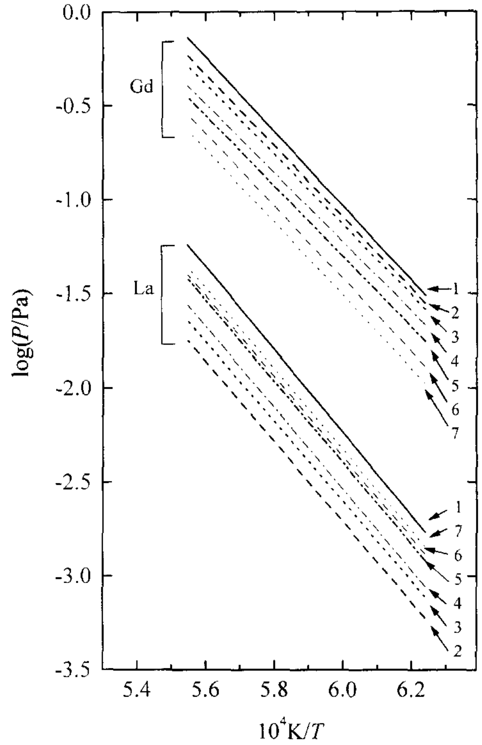

Fig. 1. Vapor pressures of La(g) and Gd(g) over La_xGd_{1-x} ($x = 0.12$–0.85) alloys and pure lanthanum and gadolinium metals. (————) Over pure metals; (— — —) $La_{0.12}Gd_{0.88}$; (– – –) $La_{0.22}Gd_{0.78}$; (– · –) $La_{0.45}Gd_{0.45}$; (– · · –) $La_{0.70}Gd_{0.30}$; (---) $La_{0.74}Gd_{0.26}$; (· · ·) $La_{0.85}Gd_{0.15}$.

3.2. Vapor pressure

The vapor pressures of La(g) over La(l) and Gd(g) over Gd(l) determined in this study are shown in Fig. 1 and were in good agreement with those over reported previously [7–9]. The equations for the vapor pressures obtained by the least-squares treatment are given in Table 1. 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 Gd(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

$$-(R \ln P_{\mathrm{M}} + \Delta \mathrm{fef})T = \Delta_{\mathrm{f}} H_{298}^{\circ} \quad (\mathrm{M} = \mathrm{Gd\ or\ La}), \quad (1)$$

where Δfef is the change in the free energy function. The

Table 1
Equations for the vapor pressures of La(g) and Gd(g) over La_xGd_{1-x} alloys. $\log(P/\mathrm{Pa}) = (-A \times 10^{-3})/T + B$

Sample	Gas species	A	B
Gd	Gd	19.79 ± 0.41	10.84 ± 0.24
$La_{0.12}Gd_{0.88}$	La	21.28 ± 0.58	10.05 ± 0.34
	Gd	19.00 ± 0.58	10.30 ± 0.34
$La_{0.22}Gd_{0.78}$	La	21.16 ± 0.52	10.09 ± 0.31
	Gd	18.71 ± 0.51	10.09 ± 0.30
$La_{0.45}Gd_{0.55}$	La	21.61 ± 0.80	10.43 ± 0.58
	Gd	18.36 ± 0.75	9.79 ± 0.44
$La_{0.70}Gd_{0.30}$	La	21.56 ± 0.73	10.54 ± 0.43
	Gd	18.75 ± 0.65	9.94 ± 0.59
$La_{0.74}Gd_{0.26}$	La	21.42 ± 0.32	10.48 ± 0.19
	Gd	19.35 ± 0.21	10.18 ± 0.41
$La_{0.85}Gd_{0.15}$	La	21.45 ± 0.72	10.54 ± 0.44
	Gd	19.44 ± 0.88	10.15 ± 0.42
La	La	22.05 ± 0.46	10.99 ± 0.26

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

Sample	a_{La}	a_{Gd}	$\Delta\bar{G}_{La}$ (kJ mol^{-1})	$\Delta\bar{G}_{Gd}$ (kJ mol^{-1})
$La_{0.12}Gd_{0.88}$	0.33 ± 0.04	0.86 ± 0.10	−15.4 ± 1.6	−2.1 ± 1.7
$La_{0.22}Gd_{0.78}$	0.43 ± 0.05	0.79 ± 0.08	−11.7 ± 1.5	−3.3 ± 1.3
$La_{0.45}Gd_{0.55}$	0.51 ± 0.07	0.64 ± 0.07	−9.4 ± 1.8	−6.2 ± 1.5
$La_{0.70}Gd_{0.30}$	0.70 ± 0.06	0.53 ± 0.07	−5.0 ± 1.2	−8.8 ± 1.7
$La_{0.74}Gd_{0.26}$	0.74 ± 0.05	0.41 ± 0.06	−4.2 ± 0.9	−12.4 ± 0.9
$La_{0.85}Gd_{0.15}$	0.81 ± 0.10	0.33 ± 0.08	−2.9 ± 1.6	−15.4 ± 3.1

heat content and the free energy function have been assessed by Hultgren table [10] and Barin [11]. The third law enthalpies of vaporization ($\Delta_f H_{298}°$), thus obtained (431.3 ± 1.1 kJ mol^{-1} for lanthanum and 395.5 ± 1.1 kJ mol^{-1} for gadolinium) were in good agreement with the literature values [7–9].

The temperature dependencies of the vapor pressures of La(g) and Gd(g) over the La_xGd_{1-x} alloys obtained in this study are also shown in Fig. 1. It is seen from Fig. 1 that the vapor pressure of both lanthanum and gadolinium over the alloys becomes lower with decreasing mole fractions of parent metal, as was expected.

3.3. Thermodynamic quantities

3.3.1. Chemical activity, partial molar Gibbs free energy of mixing

From a comparison of the vapor pressures of La(g) and Gd(g) over La_xGd_{1-x} alloys with those over pure lanthanum and gadolinium metals, chemical activities and partial molar Gibbs free energies of mixing were derived and are given in Table 2. In these calculations, the following relations were used:

$$\Delta\bar{G}_i = RT\ln(a_i) = RT\ln(P_i/P_i^0), \qquad (2)$$

where $\Delta\bar{G}_i$ is the partial molar Gibbs free energy of mixing for the component i, a_i is the chemical activity of the component i, R is the gas constant and P_i and P_i^0 are the vapor pressures of component i over alloys and pure metal, respectively. The chemical activities for lanthanum and gadolinium at an average temperature of 1673 K, for all compositions, are shown in Fig. 2. In Fig. 2 the positive deviation of the activities from Raoult's law is seen, suggesting the presence of a repulsive interaction between lanthanum and gadolinium atoms in the alloys. The chemical activities of the samarium–gadolinium system (the light rare earth–heavy rare earth system) were also reported to show a deviation from Raoult's law [1], although the deviation was different (negative) from that of the lanthanum–gadolinium system. The difference in the deviation between the two light–heavy rare earth systems is possibly related to the configuration of 4f electrons (La: $4f^0$, Sm: $4f^6$), but is not clearly explained at moment.

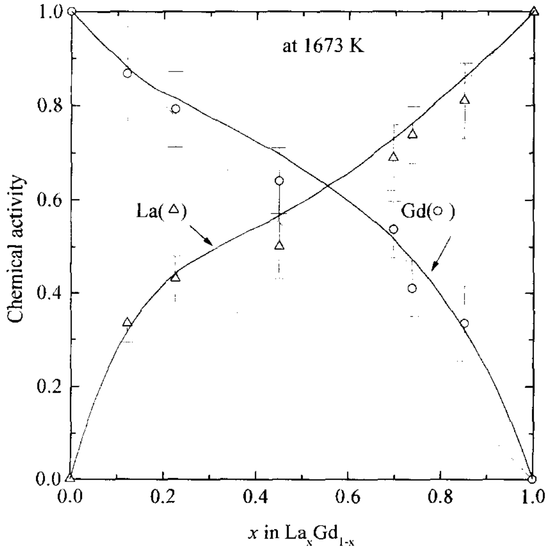

Fig. 2. Chemical activities of La and Gd in La_xGd_{1-x} alloys at 1673 K. (○) Gd, (△) La, (————) Raoult's law.

3.3.2. Gibbs free energy, enthalpy and entropy of formation

Thermodynamic properties (Gibbs free energy ($\Delta_f G°$), enthalpy ($\Delta_f H°$) and entropy ($\Delta_f S°$) of formation) of the La_xGd_{1-x} alloys were calculated from the partial thermo-

Table 3
Gibbs free energy, enthalpy and entropy of formation for La–Gd alloys

Sample	$\Delta_f G°$ (kJ mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f S°$ (J mol^{-1} K^{-1})
$La_{0.12}Gd_{0.88}$	−3.56	15.15	11.18
$La_{0.22}Gd_{0.78}$	−5.10	19.89	14.94
$La_{0.45}Gd_{0.55}$	−7.15	18.85	15.90
$La_{0.70}Gd_{0.30}$	−6.20	12.52	11.19
$La_{0.74}Gd_{0.26}$	−6.37	11.15	10.48
$La_{0.85}Gd_{0.15}$	−4.77	10.76	9.28

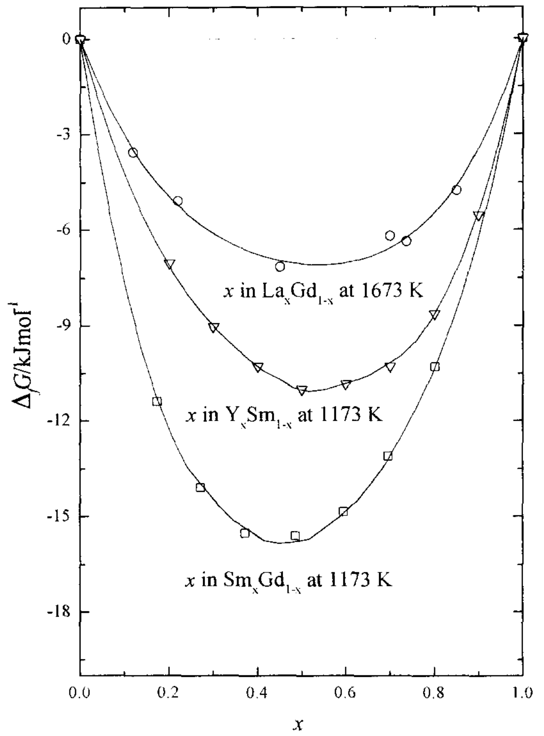

Fig. 3. Gibbs free energy of formation of La_xGd_{1-x} alloys and other related (light–heavy rare earth) compounds. (○) La–Gd alloys (this study), (□) Sm–Gd alloys [1], (▷) Y–Sm alloys [1].

dynamic properties at 1673 K from Eq. (3) and these are summarized in Table 3:

$$\Delta_f G^\circ = X\Delta\bar{G}_{La} + (1-X)\Delta\bar{G}_{Gd}. \qquad (3)$$

The compositional dependence of $\Delta_f G^\circ$ obtained in this study is shown in Fig. 3 in comparison with those of the samarium–gadolinium and the yttrium–samarium systems. As seen in Fig. 3, the values of the Gibbs free energy of formation obtained in this study showed the similar compositional dependence to two other systems, suggesting the homogeneous solution over all compositional range. The most thermodynamically stable composition in these light–heavy rare earth alloys seems to be attained at almost equal molar composition.

4. Conclusions

From the vapor pressure measurements over La_xGd_{1-x} alloys by mass-spectrometry, the following conclusions were obtained.

(1) The predominant vapor species over La_xGd_{1-x} alloys ($x = 0.00$, 0.12, 0.22, 0.45, 0.70, 0.74, 0.85, 1.00) were identified to be La(g) and Gd(g).

(2) The chemical activities showed positive deviations from Raoult's law over the entire compositional range. The interatomic force between gadolinium and lanthanum was thought to be repulsive.

(3) The Gibbs free energies ($\Delta_f G^\circ$) of the La_xGd_{1-x} alloys were calculated from the partial molar Gibbs free energy of mixing for each component obtained from the chemical activity. The most thermodynamically stable composition was obtained to be nearly equal molar composition ($x \simeq 0.5$).

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