Thermodynamic Activity and Gibbs Energy of Mixing of Rare Earth Alloys

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Thermodynamic activities of rare earth alloys such as La–Ce, La–Nd, and La–Gd alloys obtained with a mass-spectrometer by the present authors were summarized together with other reported values of Pr–Nd and Sm–Gd. Gibbs energy of mixing, which was calculated from the thermodynamic activity values, was compared to each other. The minimum regions of Gibbs energy of mixing in all La–Ln (Ln=Ce, Nd, Gd) alloys seem to be attained in almost equal molar compositions. The Gibbs energies of mixing and interaction parameters of the alloys were compared to each other and discussed with the Miedema’s model. The difference in the electron density for elements was recognized as the important term for rare earth alloys.

1. Introduction

A dry process has been adapted to separate the transuranium elements (TRU) from other fission products, mainly composed of rare earth elements in nuclear fuel reprocessing. In this process using molten chlorides–liquid metal (cadmium or bismuth), some rare earth elements are thought to be recovered together with TRU in liquid metal, since rare earth elements are chemically similar to TRU. In order to estimate separation efficiency between TRU and rare earth elements, the thermodynamic data on the rare earth binary systems are important since rare earth metals are the main components of the fission products.

The lanthanide and actinide elements which are characterized by 4f or 5f electrons are a matter of interesting. The rare earth elements are classified into light rare earth (lanthanum–europium) and heavy rare earth (gadolinium–lutetium) elements, as the heavy rare earth element has more than half-filled 4f level differently from the light rare earth element. There exist a few researches on the thermodynamic properties of the intra-rare earth alloy systems. The vapor pressures over the praseodymium–neodymium and samarium–gadolinium alloys have been measured by mass-spectrometric effusion method with a Knudsen cell. From the thermodynamic activity determined from vapor pressures, the praseodymium–neodymium system was found to behave essentially as an ideal solution. On the other hand, the samarium–gadolinium system was observed to show the deviation from ideal solution model. The vapor pressures over the lanthanum–gadolinium system have been measured by the present authors. The thermodynamic activities of lanthanum and gadolinium in the lanthanum–gadolinium alloys were calculated directly from the comparison of the vapor pressures of the constituent elements in the alloy to those over the pure metal in our previous paper.

In this study, the thermodynamic activity of the lanthanum–gadolinium system was re-calculated using the equation derived by Belton and Fruehan based on our previous vapor pressure data. This calculation method for the thermodynamic activity is thought to be more reliable than that based on the comparison of the vapor pressure for the component in the alloys to that over the pure metal. The thermodynamic activities of the La–Ln (Ln=Ce, Nd, Gd) alloys determined by the present authors, the Pr–Nd alloys and the Sm–Gd alloy were also summarized. The Gibbs energies of mixing and interaction parameters of the La–Ln (Ln=Ce, Nd, Gd) alloys were compared to each other and discussed with the Miedema’s model.

2. Thermodynamic Activity

The thermodynamic activities and the partial molar enthalpy of mixing of the constituent components in the alloys were calculated from the ion intensities measured by mass-spectrometry using the following equations derived by Belton and Fruehan:

\[ \ln(\gamma) = -\int_{x_i}^{x_{max}} x_i d\left[ \ln\left(\frac{I_{x_i}}{I_{x_{max}}}ight) \right] \]  

and

\[ \Delta H_i = -R \int_{x_i}^{x_{max}} x_i d\left[ \ln\left(\frac{I_{x_i}}{I_{x_{max}}}ight) \right] \]

where \(\gamma\), \(I\), \(x\), and \(\Delta H_i\) are the thermodynamic activity coefficient, ion intensity, molar fraction of component \(i\) and partial enthalpy of mixing of component \(i\), respectively. The thermodynamic activities in the lanthanum–gadolinium system, thus calculated, are shown in Fig. 1. The previous results on the lanthanum–cerium, lanthanum–neodymium, praseodymium–neodymium, and samarium–gadolinium systems are shown in Figs. 2–5 for comparison. As seen in these figures, the thermodynamic activities of the lanthanum–cerium and praseodymium–neodymium systems behave as almost ideal solution (Raoult’s law). However those of lanthanum–gadolinium, lanthanum–neodymium and samarium–gadolinium systems have the deviation of the activities from Raoult’s law; i.e., the positive deviation for the lanthanum–neodymium.
and lanthanum-gadolinium systems, while the negative deviation for the samarium–gadolinium system.

From these results it is thought that the thermodynamic activities of the alloys composed of light and heavy rare earth elements such as lanthanum–gadolinium and samarium–gadolinium systems deviate from Raoult’s law. On the other hand, those for the light rare earth–light rare earth systems such as lanthanum–cerium and praseodymium–neodymium systems obey Raoult’s law since the elements in the alloy have the similar electronic structure. The result of the lanthanum–neodymium system (the light rare earth–light rare earth system)\(^{6}\) is different from the ideal behavior (Raoult’s law) although this system is composed of the light–light rare earth elements. The lanthanum–cerium and the praseodymium–neodymium systems seem to be more close to the ideal solution, since the components of lanthanum–cerium and praseodymium–neodymium alloys are the next elements in the periodic table and their properties are similar to each other.

3. Thermodynamic Quantities of Mixing

Thermodynamic quantities (Gibbs energy \(\Delta G\)), enthalpy \(\Delta H\), and entropy \(\Delta S\) of mixing) of lanthanum–gadolinium were calculated from the partial thermodynamic quantities by the following Eqs. (3)–(6).

\[
\Delta G_i = RT \ln(a_i),
\]  

(3)
Gibbs energy of mixing show the similar compositional dependence. The minimum regions of free energy in these systems seem to be attained in absent equal molar compositions. The Gibbs energies of mixing for the La<sub>0.50</sub>Ln<sub>0.50</sub> (Ln = Ce, Nd, Gd) alloys are shown in Fig. 7 as a function of the difference in the metallic radius between La and Ln (Ln = Ce, Nd, Gd). As seen in this figure, the value of the Gibbs energy decreases with decreasing the difference in the metallic radii. The metallic radii of the rare earth elements decrease with the mass number (i.e., lanthanoid contraction). From this relationship the metallic radius or the mass number, i.e., the number of 4f electrons is thought to affect the Gibbs energy of mixing.

In the Miedema's model, a semi empirical model to calculate the enthalpy of mixing of the binary alloy AB has been proposed by the following expression:

\[ \Delta H^M = x_A f_B^\phi - \frac{V_B^2}{(n_V k_B)^2} \]  
\[ - P(D^\phi)^2 + Q(D^\eta)^2 \]  
(7)

and

\[ f_B^\phi = \frac{x_B V_B^3}{(x_B V_B^2 + x_A V_A^2)^{1/2}} \]

where \( f_B^\phi \) includes the factors such as concentration dependence, \( \phi \) and \( \eta_W \) are the material parameters representing the electronegativity of the metal and the electron density of the metal in the Wigner–Seitz cell, respectively, \( V_A \) and \( V_B \) are the molar volumes, and \( P \) and \( Q \) are empirically defined parameters. The enthalpies of mixing, thus calculated, for four systems (lanthanum–cerium, praseodymium–neodymium, samarium–gadolinium, and lanthanum–gadolinium systems) are given in Table 1 together with the experimental values.

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

\[ \Delta G^G = \Omega x_L x_A \]  
(8)

where \( \Omega \) is the interaction parameter. Numerical value of the interaction parameter (\( \Omega \)) is usually determined by a least-squares treatment using the equation of the thermodynamic activity coefficients (\( \eta \)) for component \( i \):

\[ \ln(\eta_i) = \frac{\Omega}{R T} (1 - x_i)^2 \]  
(9)

The interaction parameter (\( \Omega \)) was obtained to be 2.7 for lanthanum–cerium system, 7.8 for lanthanum–neo-

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**Table 1. The Experimental Results of the Enthalpy of Mixing and Calculated Values Using the Miedema's Model at \( x_A = x_B = 0.50 \)**

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H^M / \text{kJ mol}^{-1} ) (Experimental value)</th>
<th>( \Delta H^M / \text{kJ mol}^{-1} ) (Miedema's model)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La–Ce</td>
<td>0.7</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td>Pr–Nd</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>La–Gd</td>
<td>18.2</td>
<td>0.24</td>
<td>3</td>
</tr>
<tr>
<td>Sm–Gd</td>
<td>7.1</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

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Fig. 8. The values of $P(\Delta \phi)^2$, $Q(\Delta \xi)^2$, and interaction parameters in La-Ln systems (Ln=Ce, Nd, and Gd). $\nabla$, $P(\Delta \phi)^2$; $\triangle$, $Q(\Delta \xi)^2$; interaction parameter.

dium system, and $16.6 \text{ kJ mol}^{-1}$ for lanthanum–gadolinium system in this study, respectively. In rare earth elements, the difference of the electronegativity is small and the number of electrons increases with the mass number. The values of the first and the second terms in Eq. (7) and the values of the interaction parameter in La-Ln systems (Ln=Ce, Nd, and Gd) are shown in Fig. 8 as a function of the difference in the metallic radius between La and Ln (Ln=Ce, Nd, Gd). As seen in this figure, the difference in the electron density for the elements is recognized as the important term for the interaction parameter in these systems. From this relationship, the difference in the metallic radius, i.e., the number of 4f electron, is thought to affect the increase of the interaction parameter in these systems. It is, therefore, concluded that the values of the Gibbs energies of mixing, i.e., the interaction parameters in these rare earth alloys, are related to the difference in the metallic radius, i.e., the electron density for the elements. As seen in this Table 1, however, there are large differences between the values for Miedema’s model and experiment ones. These differences were thought to be caused from the parameters (i.e., $\phi$ and $n_{ws}$) in Miedema’s model (Eq. (7)) in the rare earth elements which were not derived from the binary rare earth–rare earth alloys but from the rare earth–non rare earth alloys. The thermodynamic studies on the binary rare earth alloys are, therefore, important to determine the behavior of $\phi$ and $n_{ws}$ values of the rare earth.

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References


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