Thermodynamic Activity of Ga in Ni$_2$Ga$^{*1}$

Ayako Kushida$^{*2}$, Teruyuki Ikeda$^{*3}$, Hiroshi Numakura and Masahiro Koiwa$^{*4}$

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

Thermodynamic activity of Ga in the L1$_2$-ordered intermetallic phase Ni$_2$Ga has been determined by measuring the electromotive force of a galvanic cell with zirconia solid-electrolyte,

Ni-Ga, Ga$_2$O$_3$(ZrO$_2$ + Y$_2$O$_3$)/Ga, Ga$_2$O$_3$

in the temperature range between 1050 and 1300K for six compositions. The activity of Ga varies with composition most steeply at the stoichiometric composition (25 mol% Ga), the dependence being more pronounced at low temperatures. By applying a thermodynamic model based on the Bragg-Williams approximation (Ikeda et al.: Acta Mater. 46 (1998) 6605–6613), the effective pair interaction energy between Ni and Ga atoms has been determined to be $9.75 \pm 0.19$ kJ/mol. The thermodynamic factor in chemical diffusion in the L1$_2$ phase has been derived from the composition dependence of the thermodynamic activity.

(Received November 13, 2000; Accepted January 22, 2001)

Keywords: electromotive-force measurements, solid electrolyte, galvanic cell, thermodynamic activity, intermetallic compound, inter-atomic interaction energy, thermodynamic factor in diffusion

1. Introduction

Intermetallic compounds such as transition-metal aluminides and silicides attract much attention in recent years as high-temperature structural materials. To establish the fundamentals, e.g. phase diagrams and reaction rates, knowledge of their thermodynamic properties is essential. Measurements of the thermodynamic activities of components of alloys are important as they constitute the basis of the thermodynamics of the material. Data of thermodynamic activities also provide useful information for evaluating the concentrations of point defects, which play important roles in atomic diffusion. Furthermore, the composition dependence of the thermodynamic activity gives the thermodynamic factor in chemical diffusion.$^2$

The thermodynamic activity of Ga in the L1$_2$-ordered intermetallic compound Ni$_2$Ga was reported by Katayama et al.$^{3,4}$ and by Pratt and Bird.$^5$ Katayama et al. determined the activity of Ga in Ni-Ga alloys by measuring the electromotive-force (EMF) of the following solid-electrolyte cells

$$\text{Ni-Ga, Ga}_2\text{O}_3(\text{ZrO}_2(\text{+CaO}))/\text{Fe, Fe}_{1-x}\text{O}$$

$$\text{Fe, Fe}_{1-x}\text{O}(\text{ZrO}_2(\text{+CaO}))/\text{Ga, Ga}_2\text{O}_3$$

They made measurements on compositions ranging from 5 to 58 mol% Ga, encompassing the primary solid solution (Ga), the Ni$_2$Ga phase (Ga') and the B2-ordered NiGa phase (B), at temperatures between 1100 and 1300 K and evaluated thermodynamic functions. Pratt and Bird carried out similar EMF measurements on seventeen Ni-Ga alloys, whose compositions were in the range from 6 to 95 mol% Ga, at temperatures between 873 and 1100 K. For Ga concentrations up to 55 mol% they determined the activity of Ga from the EMF of the cells

$$\text{Ni-Ga, Ga}_2\text{O}_3(\text{ZrO}_2(\text{+CaO}))/\text{O}_2\text{ (air)}$$

$$\text{O}_2\text{ (air)}(\text{ZrO}_2(\text{+CaO}))/\text{Ga, Ga}_2\text{O}_3$$

These two studies gave the activity of Ga at three or four compositions in the L1$_2$-ordered Ni$_2$Ga phase, and the two sets of data at 1100 K are in reasonable agreement with each other.

The aim of the present work is to investigate the thermodynamic activity of Ga in Ni$_2$Ga in more detail, with particular emphasis on the composition-dependence. We have determined the activity of Ga in Ni-Ga alloys at six compositions, four in the L1$_2$ phase and two in the two-phase regions at both sides, in the temperature range from 1050 to 1300 K.

2. Experimental Procedure

The same experimental method as the former two studies has been adopted, i.e. EMF measurements using zirconia solid-electrolyte. The activity of Ga in Ni-Ga alloys has been obtained directly from a single galvanic cell, by using a mixture of pure gallium and gallium oxide as the reference electrode. Yttria-stabilized zirconia was used as the solid electrolyte. The constitution of the cell used is

$$\text{(+)}\text{Ni-Ga, Ga}_2\text{O}_3(\text{ZrO}_2(\text{+Y}_2\text{O}_3))/\text{Ga, Ga}_2\text{O}_3(\text{–})$$

From the EMF of the cell, $E$, the thermodynamic activity of Ga in the Ni-Ga alloy is derived using the relation

$$\mu_{\text{Ga}}(\text{in alloy}) - \mu_{\text{Ga}}^\circ = RT \ln a_{\text{Ga}} = -3FE,$$

where $\mu$ denotes chemical potential, $R$ the gas constant, $T$ temperature, $a$ activity, $F$ the Faraday constant. The standard state for the activity of Ga is oxygen-saturated gallium (liquid).

Six Ni-Ga alloys, whose nominal compositions are in the range of 21 to 32 mol% Ga, were prepared from pure nickel (nominal purity 99.9 mass%) and pure gallium (99.999 mass%) by argon arc melting. The alloys, each being a button weighing about 10 g, were sealed in an evacuated...
quartz capsule and were annealed at 1273 K for 11 d for homogenization. After the annealing the compositions of the alloys were determined by inductively-coupled plasma (ICP) analysis. The results are shown in Table 1.

Specimens used for the EMF measurements were powders ground to 3 to 6 μm using a diamond mill. About 1 g of the powder was mixed with about 0.1 g of Ga₂O₃ powder, and the mixture was annealed at 1170 K for 24 h in a zirconia crucible under dynamic evacuation by an oil-diffusion pump. This heat-treatment was aimed at saving equilibration time at the beginning of an EMF measurement run. The mixture sintered by the pre-annealing was pulverized again and was used as the test electrode.

The instrument for EMF measurements was newly constructed for the present investigation. Figure 1 shows the structure of the galvanic cell. The innermost crucible (outer diameter 7.5 mm, inner diameter 4.5 mm, height 50 mm) is made of zirconia stabilized by 8 mol% yttria, which was purchased from Nittako Corp., Osaka (8-YSZ). The crucible is half-filled with the test-electrode material, and is immersed in the other electrode material, a mixture of pure gallium (about 3 g) and Ga₂O₃ powder (about 0.3 g), within the outer crucible (inner diameter 12 mm, outer diameter 15 mm, height 27 mm) made of alumina. A disc of alumina is placed at the top of the test-electrode material to maintain the compactness and to prevent transfer of oxygen through the atmosphere. The disc is pressed downwards by a Mullite tube, which is equipped with a coil spring at the top-end. The potential leads are Kanthal wires with rhenium wires (0.25 mm in diameter and 20 mm in length) welded at the ends; the extended parts are inserted in the electrode materials.

The cell is fixed in an air-tight quartz tube and the assembly is mounted on a vertical tube-furnace, whose zone of homogeneous temperature is about 40 mm long. Prior to measurements the assembly was evacuated by an oil-diffusion pump and kept at 420 K for 10 min for degassing. The tube was then filled with a high-purity argon gas and, after several times of substitution, was sealed under a pressure of 100 kPa. The assembly was heated to the temperature of the first measurement at a rate of 5 K per min, and the EMF of the cell was measured at various temperatures between 1050 and 1300 K. After reaching a desired temperature, the EMF of the cell was measured as a function of time until the equilibrium has been established. For a given temperature such a procedure was made at least twice, once by heating up and once by cooling down to the temperature. The equilibrium values obtained by heating and cooling were usually in good agreement with each other.

3. Results

3.1 Preliminary experiments

To verify the performance of the newly built instrument, two preliminary experiments were carried out. The first is a standard measurement on the cell

\[
(+\text{)}\text{Ni, NiO}\vert \text{ZrO}_2(\text{+Y}_2\text{O}_3)\vert \text{Ga, Ga}_2\text{O}_3(\text{−})
\]  

The second is a set of two standard measurements

\[
(+\text{)}\text{Ni, NiO}\vert \text{ZrO}_2(\text{+Y}_2\text{O}_3)\vert \text{Fe, Fe}_{1-x}\text{O}(\text{−})
\]

\[
(+\text{)}\text{Fe, Fe}_{1-x}\text{O}\vert \text{ZrO}_2(\text{+Y}_2\text{O}_3)\vert \text{Ga, Ga}_2\text{O}_3(\text{−})
\]

Note that the sum of the EMFs of these two must be equal to the EMF of cell (7). In the temperature range of interest, the EMF of cell (7) is as large as 0.5 V, which corresponds to a ratio of the partial pressures of oxygen at the two electrodes of the order of 10². It was pointed out earlier that when the partial pressures were very different the EMF could be affected by transfer of oxygen through the atmosphere. To avoid such undesirable effects, Katayama et al. measured the EMFs of cells (1) and (2), both of which are smaller in magnitude, and derived the EMF of the hypothetical cell consisting of the alloy and pure Ga. In the present work we made direct measurements on cell (5) to exclude possible errors arising from such a procedure. The second set of experiments was undertaken to ascertain whether the direct measurements give correct values of EMF, irrespective of the magnitude.

The results of the second experiment are shown first in Fig. 2(a). The values of the EMF of cells (8) and (9) are in good agreement with those reported by Kiukkola and

![Fig. 1 Schematic illustration of the solid-electrolyte cell.](image-url)
Wagner\(^3\) and by Katayama \textit{et al.}\(^3,4\) respectively. The EMF of cell (7) measured directly is compared in Fig. 2(b) with the sum of these two. The data denoted as ‘indirect’ have been calculated from linear expressions for the EMFs on cells (8) and (9), i.e. the solid lines in Fig. 2(a). The dotted line shows the EMF derived from the values of the standard free-energy of formation of the oxides compiled in a reference book.\(^7\) All the data in the figure are in good agreement. Thus, the basic performance of the instrument and its applicability to measurements of large EMFs are substantiated. The expressions for the EMFs of cells (7), (8) and (9) obtained in this work are summarized in Table 2.

### 3.2 Experiments on Ni–Ga alloys

The EMF of cell (5) was measured on the six Ni–Ga alloys. Stable EMF was attained at 2 to 5 h after the temperature was equilibrated. The equilibrium EMF for the six alloys is summarized in Fig. 3, where the EMF is shown as a function of temperature. At every composition the EMF varies linearly with temperature. For the alloy of 31.6 mol% Ga the slope changes at a temperature between 1220 and 1230 K, which must be associated with the transformation of the phase coexisting with Ni\(_2\)Ga from \(\gamma\)-Ni\(_2\)Ga\(_2\) (at low temperatures) to \(\beta\)-Ni\(_2\)Ga (at high temperatures). The solid lines in the figure are linear equations fitted to the respective data sets; the expressions are given in Table 3. (There were some errors in the expressions given in the earlier publication of the present work [Kushida \textit{et al.}: J. Japan Inst. Metals 64 (2000) 202–206]). In Fig. 3, the data by Katayama \textit{et al.}\(^3,4\) at three compositions are also shown for comparison. (The percent compositions given in the figure refer to mol% Ga.) The present data at 20.5% and 31.6%, which actually represent the activity of Ga at the phase boundary compositions, are close to those at 20% and 30%, respectively, reported by Katayama \textit{et al.}. The data at 25.2% are slightly but systematically larger.

---

**Table 2** Temperature dependence of the EMF of cells (7), (8) and (9). Temperature \(T\) is in K.

<table>
<thead>
<tr>
<th>Cell</th>
<th>EMF, (E/\text{mV})</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)</td>
<td>(E = (683.6 \pm 6.7) - (0.1377 \pm 0.0058)T)</td>
<td>1058–1285</td>
</tr>
<tr>
<td>(8)</td>
<td>(E = (169.9 \pm 2.2) + (0.0911 \pm 0.0018)T)</td>
<td>1060–1294</td>
</tr>
<tr>
<td>(9)</td>
<td>(E = (508.0 \pm 3.6) - (0.2215 \pm 0.0030)T)</td>
<td>1067–1297</td>
</tr>
</tbody>
</table>

**Table 3** Temperature dependence of the EMF of cell (5). Temperature \(T\) is in K.

<table>
<thead>
<tr>
<th>Alloy composition (mol% Ga)</th>
<th>EMF, (E/\text{mV})</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>(E = (513.5 \pm 6.1) - (0.1955 \pm 0.0052)T)</td>
<td>1063–1292</td>
</tr>
<tr>
<td>23.7</td>
<td>(E = (468.3 \pm 8.0) - (0.1623 \pm 0.0069)T)</td>
<td>1068–1252</td>
</tr>
<tr>
<td>25.2</td>
<td>(E = (432.2 \pm 2.9) - (0.1449 \pm 0.0025)T)</td>
<td>1114–1252</td>
</tr>
<tr>
<td>25.9</td>
<td>(E = (269.7 \pm 3.1) - (0.0273 \pm 0.0026)T)</td>
<td>1114–1295</td>
</tr>
<tr>
<td>26.6</td>
<td>(E = (214.0 \pm 3.2) + (0.0067 \pm 0.0028)T)</td>
<td>1114–1252</td>
</tr>
<tr>
<td>31.6</td>
<td>(E = (238.5 \pm 4.9) - (0.0339 \pm 0.0042)T)</td>
<td>1059–1218</td>
</tr>
<tr>
<td></td>
<td>(E = (143.6 \pm 1.8) + (0.0444 \pm 0.0144)T)</td>
<td>1218–1288</td>
</tr>
</tbody>
</table>

---

Fig. 2  (a) EMF of cells (8) and (9). (b) EMF of cell (7) measured directly and those obtained indirectly from the EMF of cells (8) and (9). Solid line indicates linear regression for the present results.

Fig. 3  Temperature dependence of the EMF of cell (5). The composition (mol% Ga) is indicated at the leftmost part of each curve.
than those at 25% by Katayama et al. A possible cause of this discrepancy is uncertainties in determining the actual composition; since the activity varies sensitively with composition, slight deviations in composition lead to large differences in the activity.

4. Discussion

4.1 Activity of Ga in Ni$_3$Ga

Figure 4 shows the activity of Ga in the Ni$_3$Ga phase as a function of composition at 1100, 1150, 1200 and 1250 K; the values of the activity have been calculated from formula (6) using the expressions in Table 3. The activity obtained from the two-phase alloys, viz. of 20.5 and 31.6 mol% Ga, represents the values at the phase boundary compositions, for which the recent reassessment of the Ni–Ga phase diagram by Ikeda et al.\textsuperscript{8}\) is referred to. The solid curves in the figure are theoretical curves based on the Bragg-Williams model; the expression for the thermodynamic activity in L1$_2$-ordered alloys given by Ikeda et al.\textsuperscript{2}\) has been fitted to the experimental data. The activity of Ga increases with increasing the concentration of Ga, most steeply around the stoichiometric composition. The composition dependence is more pronounced at lower temperatures.

In the statistical thermodynamic model by Ikeda et al.\textsuperscript{2}\) the fundamental parameter is the ordering energy, or the effective pair interaction (EPI) energy, $\varepsilon$, which is defined as

$$\varepsilon = \frac{g_{AA} + g_{BB}}{2} - g_{AB},$$

(10)

where $g_{ij}$ denotes the bond-energy between atoms $i$ and $j$ at the nearest-neighbour positions; the thermodynamic properties of the alloy are characterized essentially by the temperature scaled to this parameter, $RT/\varepsilon$. The activity versus composition curve is determined by $RT/\varepsilon$ and a reference value at a certain composition. The values of the ordering energy for the curves in Fig. 4 and those of $\ln a_{Ga,0}$, which refers to the stoichiometric composition, are summarized in Table 4(a). The ordering energy exhibits a decreasing trend with increasing temperature. The average value of $\varepsilon$ in this temperature range is $9.75 \pm 0.19$ kJ/mol.

The activity of Ga obtained in this work is compared with the data by Katayama et al.\textsuperscript{3,4}\) and those by Pratt and Bird\textsuperscript{5}\) in Fig. 5. The phase boundary compositions by Ikeda et al.\textsuperscript{8}\) are again adopted for the data at 1100 K and 1250 K by Katayama et al., while those in the phase diagram by Lee and Nash\textsuperscript{9}\) are assumed for the data at lower temperatures by Pratt and Bird (since the temperature range reexamined by Ikeda et al.\textsuperscript{3}\) was only from 1073 to 1373 K). At the temperature 1100 K, for which data are available from all the three studies, the agreement is reasonable, although deviations are recognized at high Ga concentrations. The statistical model\textsuperscript{2}\) has been applied to the two sets of literature data to draw the dotted curves and the dashed curves. The ordering energy and the reference value $\ln a_{Ga,0}$ for these curves are listed in Table 4(b). The data by Pratt and Bird, i.e. the variations of the activity with composition, are described very well by the model. However, the values of the ordering energy for the low-temperature data is significantly smaller than those at 1100 K. The origin of these variations is unclear; there seems to be no a priori reason for such strong dependence of the atomic interaction energies on temperature.

Ikeda et al.\textsuperscript{2}\) analysed the thermodynamic activity of Al in Ni$_3$Al in the same way as described here and evaluated the ordering energy of Ni$_3$Al to be 11.2, 10.5 and 9.7 kJ/mol at temperatures 1400, 1500 and 1600 K. The decreasing trend in the magnitude of the ordering energy is the same as in Ni$_3$Ga found in this study. As pointed out previously,\textsuperscript{2}\) the trend must be attributed primarily to the limitation of the Bragg-Williams model in describing the thermodynamic properties of alloys over a wide range of temperature.

![Graph](image)

Fig. 4 Thermodynamic activity of Ga in Ni$_3$Ga. The reference state is oxygen-saturated gallium (liquid).

<table>
<thead>
<tr>
<th>Temperature, $T$/K</th>
<th>Ordering energy, $\varepsilon$/kJ mol$^{-1}$</th>
<th>$\ln a_{Ga,0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>9.500</td>
<td>-6.927</td>
</tr>
<tr>
<td>1200</td>
<td>9.734</td>
<td>-7.378</td>
</tr>
<tr>
<td>1150</td>
<td>9.850</td>
<td>-7.876</td>
</tr>
<tr>
<td>1100</td>
<td>9.956</td>
<td>-8.419</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature, $T$/K</th>
<th>Ordering energy, $\varepsilon$/kJ mol$^{-1}$</th>
<th>$\ln a_{Ga,0}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>9.640</td>
<td>-6.815</td>
<td>3, 4)</td>
</tr>
<tr>
<td>1100</td>
<td>9.528</td>
<td>-8.511</td>
<td>3, 4)</td>
</tr>
<tr>
<td>1100</td>
<td>9.657</td>
<td>-8.489</td>
<td>5)</td>
</tr>
<tr>
<td>873</td>
<td>8.961</td>
<td>-12.14</td>
<td>5)</td>
</tr>
<tr>
<td>773</td>
<td>7.395</td>
<td>-14.62</td>
<td>5)</td>
</tr>
</tbody>
</table>
4.2 Thermodynamic factor in diffusion

The thermodynamic factor in diffusion represents the effect of chemical potential gradient in interdiffusion; it was introduced by Darken in his analysis of chemical diffusion in binary alloys. Darken’s equation, or the Darken-Manning relation, which is an improvement of the former, relates the chemical diffusion coefficient $\bar{D}$ to the tracer diffusion coefficients of components $D_A^L$ and $D_B^L$ in an A–B alloy, i.e.

$$\bar{D} = (D_A^L x_B + D_B^L x_A) \Phi S,$$

where $x$ denotes the mole fraction. $S$ is the vacancy-wind factor describing the effect of a net-flow of vacancies, and is a function of the relative magnitudes of $D_A^L$ and $D_B^L$. $\Phi$ is the thermodynamic factor, which is defined as

$$\Phi \equiv \frac{\partial \ln a_i}{\partial x_i},$$

where $i$ is either A or B. While $S$ is of the order of unity, the thermodynamic factor may take a very large value in systems where interatomic interaction is strong. Therefore, proper evaluation of this factor is important in analysing chemical diffusion.

When data of the thermodynamic activity is available as a continuos function of composition, evaluation of the thermodynamic factor is straightforward according to eq. (12). (The statistical model by Ikeda et al. gives also analytical expressions for the thermodynamic factor, which are indeed compatible to the expressions for the thermodynamic activity through eq. (12).) Figure 6 shows the thermodynamic factor for Ni$_3$Ga calculated from the results of the present work (1100–1250 K); those at lower temperatures derived from the data by Pratt and Bird are also shown. At the stoichiometric composition, the magnitude of $\Phi$ in Ni$_3$Ga is found to be about 20 at 1100 K and about 10 at 1250 K. These results have been adopted in a recent study of diffusion in Ni$_3$Ga.

5. Summary and Conclusions

The thermodynamic activity of Ga in Ni$_3$Ga has been determined for six compositions in the temperature range from 1050 to 1300 K by measuring the EMF of the solid galvanic cell using zirconia solid-electrolyte. The value of the activity is, for example, $2 \times 10^{-4}$ at 1100 K and $1 \times 10^{-3}$ at 1250 K, referring to oxygen-saturated gallium, at the stoichiometric composition. The activity increases with increasing the concentration of Ga, particularly at compositions close to the stoichiometry. The dependence on the composition is more pronounced at lower temperatures.

The ordering energy in the Ni$_3$Ga phase is evaluated to be about 9.8 kJ/mol by fitting the analytic expression for the activity curve based on the Bragg-Williams model. The thermodynamic factor in diffusion has been calculated from the derivative of the activity versus composition curve. Its magnitude is about 20 at 1100 K and about 10 at 1250 K at the stoichiometric composition.

Acknowledgements

The authors are grateful to Dr. I. Katayama (Osaka University) for his invaluable help and advice, as well as persistent encouragement throughout the work. They thank Dr.
K. Tanaka (Kyoto University) for discussion and useful comments, and Mr. T. Aoyama (formerly undergraduate student, Kyoto University) for his contributions in the early stage of the research. This work was supported by the Grant-in-Aid for Scientific Research, Priority Area A 287 09242106, and Basic Research C 11650680, from the Ministry of Education, Science, Sports and Culture.

REFERENCES