

## **ACTIVITY MEASUREMENT OF Ga IN LIQUID Ga-Pb ALLOYS BY EMF METHOD WITH ZIRCONIA SOLID ELECTROLYTE**

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*(Received 30 September 2002; accepted 2 November 2002)*

### **Abstract**

*EMF measurement of the electrochemical cell with zirconia as solid electrolyte was performed to determine the gallium activity from 950 to 1150K in the entire composition range of liquid Ga-Pb alloys. In the whole concentration range, activity of Ga shows moderately positive deviations from ideality, and activity of Pb which is derived by Gibbs-Duhem equation shows also positive deviation from ideality. These are compared with published data obtained by different experimental methods.*

*Keywords:* thermodynamics, activity, Ga-Pb alloy, emf method, zirconia solid electrolyte, liquid binary alloy.

### **1. Introduction**

Thermodynamic properties and the phase diagrams of alloys are very important from the scientific and technological point of view, and the data have been

accumulated. Recently some studies [1] were made to establish a respectable understanding between the experimental results, theoretical approaches and empirical models for the liquid alloys with miscibility gap.

Activity data in liquid Ga-Pb alloys have been reported by Kwong and Munir [2] in the temperature range 950 to 1050K over the whole composition range using the torsion effusion method, by Desideri and Piacente [3] from 1130 to 1160K by the same technique, by Kononenko *et al.* [4] at 1100K and by Sommer *et al.* [5] from 900 to 1050K by a Knudsen effusion method. Ansara and Ajersch [6] evaluated phase diagram and thermodynamic properties of this system. Activity of lead in this system showed positive deviations from ideality in each paper, but large discrepancy can be found between reported values. Mathon *et al.* [7] determined the molar enthalpy of formation and the molar heat capacity of the liquid alloys by a high temperature calorimeter and a differential scanning calorimeter, and the phase diagram was assessed.

In this study, emf measurement of the electrochemical cell with zirconia as solid electrolyte was performed from 950 to 1150K in the entire composition range of liquid Ga-Pb alloys. This method is effective for obtaining the gallium activity directly, because the difference in Gibbs energy of formation of each oxide ( $\text{Ga}_2\text{O}_3$  and  $\text{PbO}$ ) per mole of  $\text{O}_2$  is large enough. It is assumed that the oxygen solubility in the liquid alloys is negligibly small under the experimental conditions.

## 2. Experimental

### 2.1. Materials

The alloys used in this study were prepared from high-purity elements (Ga:99.99mass% purity, Pb:99.999 % from Mitsubishi Materials Co.Ltd.).  $\text{Ga}_2\text{O}_3$  powder (99.99 % purity from Mitsubishi Materials Co.Ltd.) was added to the mixture in a mass ratio 7:93. The reference electrode was the mixture of Ga and  $\text{Ga}_2\text{O}_3$  in the similar ratio as the alloy electrode. Zirconia solid electrolyte crucibles ( $0.92\text{ZrO}_2+0.08\text{Y}_2\text{O}_3$ , o.d.8 mm, i.d.5 mm and length 50 mm) were obtained from Nikkato Co.Ltd.

### 2.2. Experimental apparatus and procedures

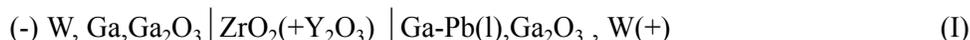
The experimental equipment and procedure used in this study are quite similar to the previous one for Ga-Sb-Sn alloys [8] and Ga-In-Bi alloys [9]. The alloy elements, weighed to give mixtures with desired compositions, and  $\text{Ga}_2\text{O}_3$  powder were put in

a zirconia crucible with a tungsten lead wire ( $\phi 0.5\text{mm}$ ), and the crucible was settled in the reference electrode ( $\text{Ga}, \text{Ga}_2\text{O}_3$ ) put in an alumina crucible in which another tungsten wire was settled as a lead wire for reference electrode.

After the cell was assembled in the homogeneous temperature region in the reaction tube settled in the vertical type electric-resistance furnace, the reaction tube was evacuated and then filled with purified argon gas. This operation was two or three times repeated. After that the temperature was raised to a desired value. Immediately after the cell temperature became constant, the alloy electrode was stirred by the tungsten lead wire to shorten the equilibrium time required and emf measurement started and this operation was very important to get reproducible emf. The cell temperature was raised and lowered, alternatively, and controlled to  $\pm 1$  K at each temperature with a thermo-controller (Thermo-let, Eiko Electric Co.Ltd., TPC-A202C2) and a Pt-13RhPt thermocouple. The emfs of the cell and the cell temperature were measured with a digital voltmeter (Multi-Logging Meter AD-5311, A and D Co.Ltd.) with a printer.

### 3. Results and Discussion

The emfs of cell I for the alloys were measured.



After the cell temperature reached desired one, the cell emfs were measured and printed out. Normally the stable equilibrium emf was obtained within 1 to 5 h depending on the alloy composition and temperature for the first time, and after that it took a very short period of time to get stable emf of the cell at the new temperatures.

Experimental emf data for 8 kinds of alloys are shown in Fig.1 As all the data points distribute around a linear line for each composition, the relations between emf ( $E/\text{mV}$ ) and temperature ( $T/\text{K}$ ) are obtained by least squares regression analysis, and are listed in Table 1.

Using the data shown in Table 1, activities of Ga ( $a_{\text{Ga}}$ ) in the alloys are calculated from Eq.(1):

$$-3EF = RT \ln a_{\text{Ga}} (= \Delta \bar{G}_{\text{Ga}}) \quad (1)$$

where  $F$  is the Faraday constant,  $R$  is the gas constant and  $\Delta \bar{G}_{\text{Ga}} / \text{Jmol}^{-1}$  is partial

molar Gibbs energy of mixing of Ga. Uncertainty limits in the activity values can be easily derived from those in the emf values. The activity of Ga at 1000 and 1100K is shown in Table 2 and Fig.2. Activity of gallium shows large positive deviations from ideal behavior at both temperatures, values at higher temperature are lower than those at lower temperature, and temperature dependence of the activity is small.

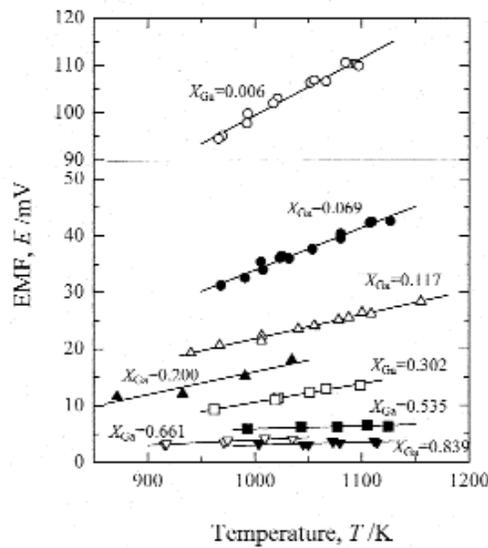


Fig. 1. Temperature dependence of emf of cell Ga,  $Ga_2O_3 / ZrO_2(+Y_2O_3) / Ga-Pb, Ga_2O_3$

Activities of Pb are derived from Eq.2 by use of  $\alpha$ -function(Eq.3)

$$\ln a_{Pb} = \ln x_{Pb} - x_{Ga} x_{Pb} \alpha_{Ga} + \int_0^{x_{Ga}} \alpha_{Ga} dx_{Ga} \quad (2)$$

$$\alpha_{Ga} = \frac{\ln \gamma_{Ga}}{(1-x_{Ga})^2} \quad (3)$$

where  $\gamma$  is the activity coefficient and  $x$  is the mole fraction. The activity values of Pb are also shown in Table 2 and Fig.2. In the whole concentration range, activity of Ga and Pb show positive deviations from ideality.

The activity,  $a_{Pb}$  obtained by the other researchers are shown in Fig.3 with the data in

this study. There can be seen large difference in the activity values, although the similar experimental techniques were used.

Table 1. Temperature dependence of emf of cell  $Ga, Ga_2O_3 | ZrO_2(+Y_2O_3) | Ga-Pb, Ga_2O_3$

$X_{Ga}$	$E/mV$	
0.006	$1.22+0.1207$	$T/K$
0.069	$1.22+0.0751$	$T/K$
0.117	$0.85+0.0426$	$T/K$
0.200	$0.22+0.0359$	$T/K$
0.302	$4.29+0.0248$	$T/K$
0.535	$0.86+0.0050$	$T/K$
0.661	$4.76+0.0086$	$T/K$
0.839	$2.27+0.0052$	$T/K$

Table 2 Activity and Gibbs free energy of mixing of liquid Ga-Pb alloys

$X_{Ga}$	$a_{Ga}$	$a_{Pb}$	$\Delta G^m / \text{Jmol}^{-1}$	$X_{Ga}$	$a_{Ga}$	$a_{Pb}$	$\Delta G^m / \text{Jmol}^{-1}$
0	0	1	0	0	0	1	0
0.006	0.0313	0.994	-223	0.006	0.0293	0.994	-248
0.069	0.307	0.937	-1181	0.069	0.27	0.939	-1362
0.117	0.469	0.898	-1526	0.117	0.439	0.895	-1777
0.200	0.574	0.866	-1880	0.200	0.532	0.861	-2249
0.302	0.693	0.815	-2108	0.302	0.645	0.807	-2580
0.535	0.815	0.733	-2111	0.535	0.818	0.703	-2482
0.661	0.875	0.662	-1897	0.661	0.862	0.651	-2229
0.839	0.903	0.592	-1414	0.839	0.897	0.566	-1672
1	1	0	0	1	1	0	0

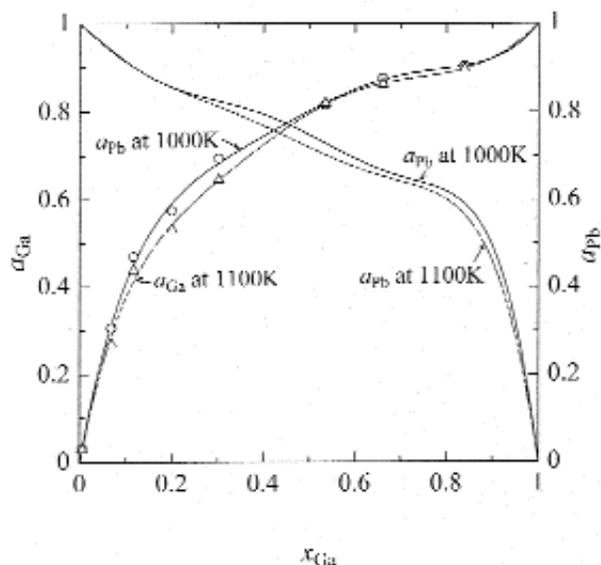


Fig. 2. Activity of Ga and Pb in Ga - Pb alloys at 1000K and 1100K

Experimental cell used in this study didn't work well sometimes without stirring the alloy electrode by the tungsten lead wire. Such tendency could be found often when the cell temperature was decreased.

The different condition exists between vapor pressure measurement and emf measurement: the former is for pure binary alloys and the latter for oxide saturated alloys, respectively. As for  $a_{\text{Ga}}$  values shown in the references, [3] shows largely positive deviation from ideality at 1143K, [2] shows small deviation from ideality at 1000K, and the values in this study are between those two. Directly obtained values of  $a_{\text{Pb}}$  [2-5] are scattered, and derived values of this work using the Gibb-Duhem equation with  $\alpha$  function show reasonably agreement with those by Sommer et al [5] in the whole composition range with one exception at  $x_{\text{Ga}}=0.839$ . This means that the scattered results obtained by another workers cannot be explained from the difference in the alloy condition described above nor experimental technique.

The assessed values of excess Gibbs energies of mixing of liquid alloys are taken from Refs.[6] and [7], respectively:

$$\Delta G^{\text{xs}}/\text{Jmol}^{-1} = x(1-x)[15390 + 1.5257T + (1887 - 1.38982T)(1-2x) + (6333.75 - 4.66476T)(1-2x)^2 + 0.475T(1-2x)^3], \text{ and}$$

$$\Delta G^{\text{xs}}/\text{Jmol}^{-1} = (1-x)[13667.22 + 3.02950T + (1366.42 - 1.29363T)(1-2x) + (5213.84 - 4.02277T)(1-2x)^2]$$

where  $x$  is mole fraction of Pb.

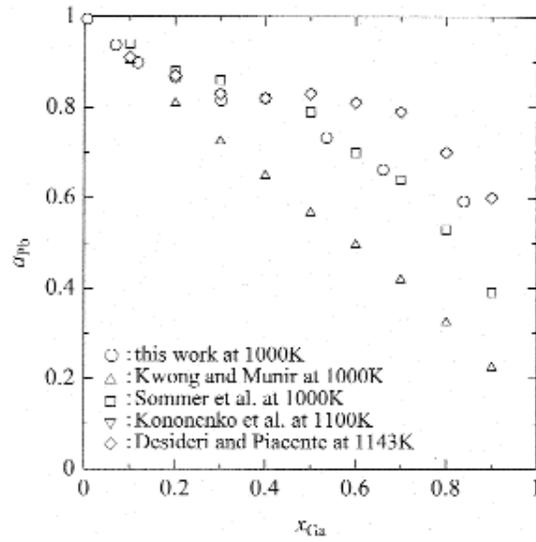


Fig. 3. Activity of Pb in Ga - Pb alloys

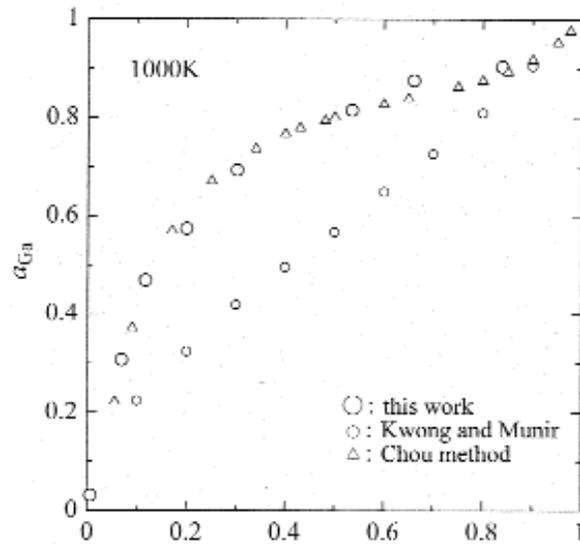


Fig. 4. Comparative review of Ga activity

Both of the assessed equations give very close values. Mathon *et al.* [7] show that the data [2] are not used in their assessment, the data [4] are in agreement with the calculation and that the data [5] are available only on the Pb-rich side of the alloys.

For the calculation of the activity of gallium, Chou's treatment [10] is applied, which is used for the phase diagram containing a miscibility gap, assuming  $\theta = H_i/S_i^E=3000$  in Richardson equation [11]. The process of the calculation will appear in detail later [12]. The calculated results are shown in Fig.4 with the experimental data in this study. The figure shows very good agreement between them.

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