JOUNRAL OF MATERIALS SCIENCE 26 (1991) 5221–5228

Thermodynamic investigations of liquid Bi–Na and Sn–Na alloys by coulometric titration using β″-alumina

MITSURU ITOH*, ZENSAKU KOZUKA
Department of Materials Science and Processing, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

The following double galvanic cell was assembled and the thermodynamic properties of liquid Bi–Na and Sn–Na alloys, and the ion selectivity of β″-alumina during coulometric titration, were investigated.

$$\mathrm{Mo,\ Na(l)\,|\,\beta''\text{-alumina}\,|\,M\text{–}Na(l),\ Mo} \qquad [\mathrm{I}]$$

$$\mathrm{M\text{–}Na(l)\,|\,\beta''\text{-alumina}\,|\,Au + Au_2Na,\ Mo} \qquad [\mathrm{II}]$$

$$(\mathrm{M} = \mathrm{Bi\ or\ Sn})$$

where M–Na(1) and Au + $\mathrm{Au_2Na}$ were used as the common electrode and reference electrode, respectively. Sodium was coulometrically titrated through the β″-alumina electrolyte of cell I both ways, and the EMFs were measured. It was found that no ion-exchange reaction occurs between the liquid alloys and the β″-alumina, and only Na was transferred in the β″-alumina during coulometric titrations. The thermodynamic properties of liquid Sn–Na and Bi–Na alloys were found to be in agreement with the literature.

1. Introduction

Beta-alumina has been applied as a solid electrolyte for various kinds of investigations in materials science. A typical application in metallurgy is the measurement of the thermodynamic properties of liquid alloys. Using the beta-alumina solid electrolyte, the *in situ* preparation of a liquid alloy with a desired composition is possible by means of coulometric titration. In such an application, perfect ion selectivity is required during titration. In order to confirm the perfect ion selectivity of beta-alumina, a study was previously carried out for liquid Pb–Na alloys [1]. In addition to ion selectivity, the spontaneous reaction between beta-alumina and liquid alloy must be taken into account [2]. Iwase *et al.* [3] have reported the following equilibrium reaction between the β-alumina and liquid Bi:

$$\mathrm{Na_2O\ (in\ \beta\text{-alumina})} = \mathrm{2Na\ (in\ Bi)} + \tfrac{1}{2}\mathrm{O_2\ (g)} \qquad (1)$$

Therefore when beta-alumina is applied as a solid electrolyte to investigate the thermodynamic properties of liquid alloys containing sodium, the reaction between the beta-alumina and the liquid alloys should be checked before the experiments, especially in the case where the thermodynamic properties of Na are investigated in the dilute solution range. In our previous paper [1], perfect ion selectivity of the $\mathrm{Na^+}$ ion through β- and β″-alumina for liquid Pb–Na was confirmed by the coulometric titration experiments using a double galvanic cell:

$$\mathrm{Mo,\ Na(1)\,|\,\beta''\text{-alumina}\,|\,Pb\text{–}Na(1)}$$

$$\mathrm{Pb\text{–}Na(1)\,|\,\beta''\text{-alumina}\,|\,Au + Au_2Na,\ Mo}$$

In this paper, we report the results of thermodynamic investigations of liquid Bi–Na and Sn–Na alloys, and the measurement of the ion selectivity of β″-alumina, during coulometric titration.

2. Experimental procedure

The following galvanic cells were assembled and their EMFs were measured:

$$\mathrm{Mo,\ Na(1)\,|\,\beta''\text{-alumina}\,|\,M\text{–}Na(1)} \qquad [\mathrm{I}]$$

$$\mathrm{M\text{–}Na(1)\,|\,\beta''\text{-alumina}\,|\,Au + Au_2Na,\ Mo} \qquad [\mathrm{II}]$$

$$(\mathrm{M} = \mathrm{Bi,\ or\ Sn})$$

The EMF of cell I, E_I is represented by

$$\Delta\bar{G}_\mathrm{Na} = -FE_\mathrm{I} = \mathrm{RT}\ln\,[a_\mathrm{Na}(\mathrm{Na\text{–}M})] \qquad (1)$$

where F is Faraday's constant, R is the gas constant, T is the absolute temperature, and a_Na is the activity of Na. When E_I against temperature is represented by the

---

* *Present address*: Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan.

0022-2461/91 $03.00 + .12 © *1991 Chapman & Hall*

following straight line in a narrow temperature range,

$$E_{\mathrm{I}} = A + BT \tag{2}$$

the partial molar enthalpy and entropy of mixing, $\Delta\bar{H}_{\mathrm{Na}}$ and $\Delta\bar{S}_{\mathrm{Na}}$ are given by

$$\Delta\bar{H}_{\mathrm{Na}} = -FA \tag{4}$$

and

$$\Delta\bar{S}_{\mathrm{Na}} = FB \tag{5}$$

Since the temperature dependence of Na activity in the Au + Au_2Na mixture has already been determined [4], Na activity in the Bi–Na alloys can also be determined from the open circuit EMF of cell II, E_{II}. The simultaneous measurement of E_{I} and E_{II} makes it easier to detect the reaction between β″-alumina and liquid alloys.

2.1. Bi–Na alloys

Thermodynamic properties of liquid Bi–Na alloys and the ion selectivity of β″-alumina during coulometric titration were investigated by two experimental runs of the EMF measurement of galvanic cells using β″-alumina. In the run 1, the following galvanic cell was assembled and the EMFs were measured:

Mo, Na(1) | β″-alumina | Bi–Na(1), Mo [I]

Sodium was coulometrically titrated through the β″-alumina both ways. In the run 2, the following double galvanic cell was assembled and the EMFs were measured:

Mo, Na(1) | β″-alumina | Bi–Na(1) [I]

Bi–Na(1) | β″-alumina | Au + Au_2Na, Mo [II]

The Bi–Na(1) were used as the common electrode. Sodium was transferred between the Na and the Bi–Na electrodes by coulometric titration through the β″-alumina of cell I. Details of the experimental apparatus are explained in our previous paper [1].

2.2. Sn–Na alloys

The following double galvanic cell was assembled and the EMFs were measured:

Mo, Na(1) | β″-alumina | Sn–Na(1) [I]

Sn–Na(1) | β″-alumina | Au + Au_2Na, Mo [II]

The dimensions of the β″-alumina crucible used for cell I were 15 mm OD, 13 mm ID, and 120 mm in height. The dimensions of the β″-alumina crucible used for cell II were 7 mm OD, 5 mm ID, and 70 mm in height. The β″-alumina crucible used for cell I was connected to an alumina tube by alumina cement to prevent contamination of the liquid Bi–Na and Sn–Na alloys by Na vapour over the liquid Na of cell I. Three normal-purity Na and 5N-purity Bi and Sn were used for the experiments. The mixture of Au + Au_2Na was made by heating a mixture of 4N-purity Au granules and a Na ingot (molar ratio 7:3) in argon atmosphere [4]. After evacuating the galvanic cell system, titanium-gettered argon was introduced and the system was heated to 673 K. Residual oxygen was removed by metallic calcium which was placed just under the Ni crucible containing liquid Na. The temperature of the furnace was controlled to ± 0.1 K by a proportional controller with a chromel–alumel thermocouple. The temperature of the cell was measured by a Pt/Pt–13% Rh thermocouple. The open-circuit EMFs between the electrodes were measured by a Yokogawa 2502A digital multimeter. Coulometric titration was carried out using a Hokuto HA301 potentiostat/galvanostat and a Hokuto HF201 Coulomb/amperehour meter. In the experimental run 1 of Bi–Na alloys, sodium was coulometrically titrated into bismuth (normal direction) through β″-alumina of cell I to the composition $X_{\mathrm{Na}} = 0.0001$ (100 p.p.m. Na), then the titration was carried out in the reverse direction to the composition $X_{\mathrm{Na}} = 0.000001$ (1 p.p.m.). After that the coulometric titration in the normal direction was carried out again to the composition $X_{\mathrm{Na}} = 0.0001$. Coulometric titration in the normal direction was carried out using a constant current (current density 9×10^{-2} A m^{-2}), and in the reverse direction a constant voltage of 1.6–2.0 V.

In the run 2, the coulometric titrations were always carried out with a constant current (current density 30–100 A m^{-2}). A voltage between 0.4 and 1.0 V was then applied between the electrodes. After each coulometric titration, a constant EMF was obtained between the time 0.2 and 1.8 ks. After the constant EMF was obtained in experimental run 2, the cell temperature was increased to be higher than the liquidus temperature of that alloy composition. At that temperature, EMF was also measured and the next coulometric titration was carried out. When the composition of Na reached $X = 0.35$, the β″-alumina crucible containing the Au + Au_2Na electrode was immersed in the liquid Bi–Na alloy, and simultaneous measurements of E_{I} and E_{II} were begun.

The coulometric titrations of Sn–Na alloys were always carried out with a constant current (current density 30–100 A m^{-2}). A voltage between 0 and 0.8 V was then applied between the electrodes. After each coulometric titration, a constant EMF was obtained between 3.6 and 7.2 ks. Coulometric titration was carried out in the composition range $0 \leqq X \leqq 0.31$ in both ways. When the composition of the alloy reached $X_{\mathrm{Na}} = 0.31$, the β″-alumina crucible containing an Au + Au_2Na electrode was immersed into the Sn–Na alloy and a simultaneous EMF measurement of cells I and II was begun.

After the experiments, the compositions of β″-alumina crucibles were examined using a Hitachi X-650 electron probe X-ray microanalyser (EPMA).

3. Results and discussion

3.1. Experimental run 1 for Bi–Na alloys

When the cell was heated to 673 K and kept at that temperature, a constant EMF of cell I was not obtained within 18 days. Therefore the following reaction apparently does not occur between the liquid bismuth and the β″-alumina curcible:

$$\mathrm{Na_2O}\ (\text{in } \beta''\text{-alumina}) = 2\,\mathrm{Na}\ (\text{in Bi}) + \tfrac{1}{2}\mathrm{O_2} \qquad (6)$$

$$\mathrm{Na^+}\ (\text{in } \beta''\text{-alumina}) + \tfrac{1}{3}\mathrm{Bi} = \tfrac{1}{3}\mathrm{Bi^{3+}}\ (\text{in } \beta''\text{-alumina}) + \mathrm{Na}\ (\text{in Bi}) \qquad (7)$$

Part of the experimental results are shown in Table I. Figs 1–3 show the results obtained by coulometric titration in both directions. The arrows represent the directions of coulometric titration, in the normal (→) and reverse (←) directions. The accompanying number represents the number of times for a series of coulometric titrations in that direction. The EMF values obtained after the coulometric titrations in both directions agreed with each other. Henry's law holds between a_{Na} and X_{Na} in the composition range $X_{\mathrm{Na}} < 0.0001$ (100 p.p.m. Na), and the activity coefficient was calculated as $\gamma^\circ = 1.91 \times 10^{-5}$ at 673 K. Fig. 3, an enlarged a_{Na} against X_{Na} relation, shows that an irreversible reaction occurs between the β″-alumina and liquid bismuth during the coulometric titration. However, the maximum error in the Na composition originated from the irreversible reaction corresponding to a compositional change within 1 p.p.m. Discrepancies between the EMF values measured after the coulometric titrations in the different directions were observed in the other experimental runs, in which different amounts of Bi were used: the value inversely depended on the amount of Bi used. Too small an amount of Na or Bi associated with the

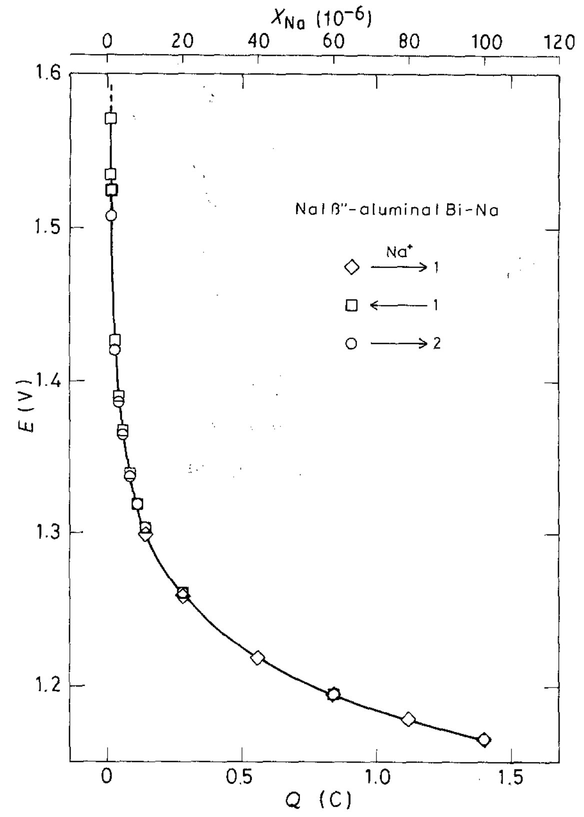

Figure 1 E_{I} against net quantity of electricity Q passed in the normal direction (experimental run 1) at 673 K. (→) and (←) represent the directions of coulometric titrations in the normal direction, from Na to Bi–Na alloy in cell I; and in the reverse direction, from Bi–Na alloy to Na, respectively. Numbers represent the times of a series of coulometric titrations in that direction.

TABLE I Results of experimental run 1 for Bi–Na alloys. $T = 673.2$ K; Bi = 30.26272 g.

$X_{\mathrm{Na}}/10^{-6}$	Q(C)[a]	E_{I}(V)
10	0.1379	1.2998
20	0.2794	1.2595
40	0.5589	1.2185
60	0.8384	1.1948
80	1.1179	1.1780
100	1.3973	1.1650
60	0.8384	1.1950
20	0.2794	1.2609
10	0.1397	1.3040
8	0.1118	1.3186
6	0.0838	1.3379
4	0.0559	1.3670
3	0.0419	1.3895
2	0.0279	1.4262
1	0.0140	1.5246
0.94	0.0131	1.5248
0.90	0.0126	1.5351
0.80	0.0112	1.5708
0.70	0.0098	–[b]
1	0.0140	1.5074
2	0.0279	1.4200
3	0.0419	1.3861
4	0.0559	1.3649
6	0.0839	1.3370
8	0.1118	1.3282
10	0.1397	1.3039
20	0.2794	1.2609
60	0.8384	1.1952
100	1.3973	1.1653

[a] Net quantity of electricity passed in the normal direction.

[b] Equilibrium EMF was not obtained.

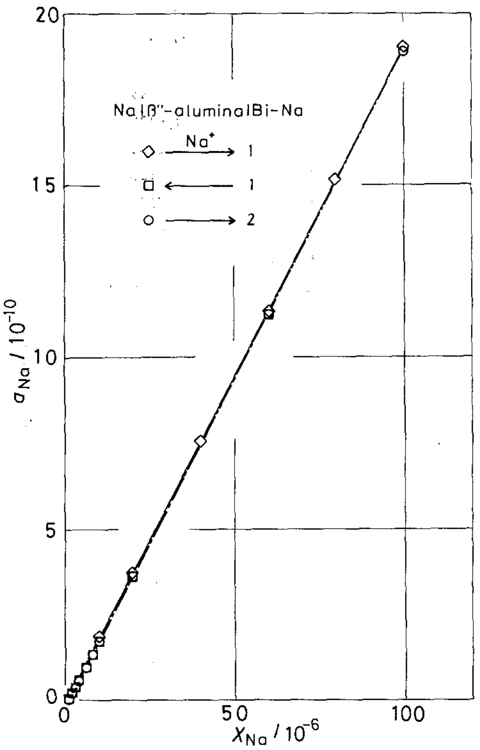

Figure 2 a_{Na} against X_{Na} in the composition $X_{\mathrm{Na}} < 0.0001$ at 673 K.

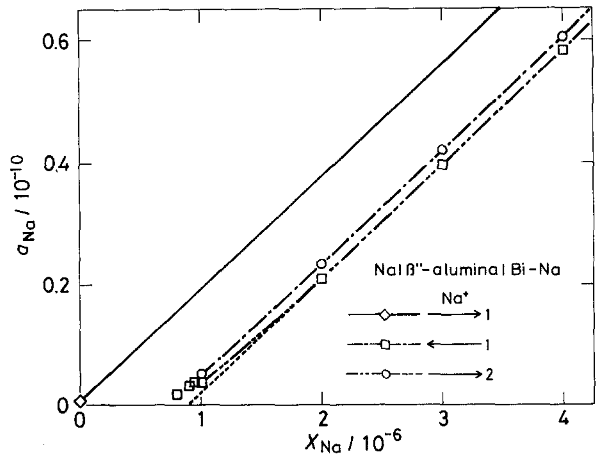

Figure 3 a_{Na} against X_{Na} in the composition $X_{Na} < 0.00001$ at 673 K.

irreversible reaction makes it difficult to elucidate the reaction.

3.2. Experimental run 2 for Bi–Na alloys

Part of the experimental results are shown in Table II. EMF against X_{Na}, EMF against temperature, and $\Delta\bar{S}_{Na}$ against X_{Na} are shown in Figs 4–6, respectively.

TABLE II Results of experimental run 2 for Bi–Na alloys. Bi 5.54507 g

X_{Na}	$Q(C)$[a]	$T(K)$	$E_I(V)$	$E_{II}(V)$
0.005	12.86	673.2	0.93682	–
		573.2	0.90246	–
0.02	52.25	673.2	0.85444	–
		573.2	0.83255	–
0.05	137.74	673.2	0.79644	–
		573.2	0.78350	–
0.10	284.46	673.2	0.74577	–
		573.2	0.74030	–
0.15	451.78	673.2	0.70946	–
		573.2	0.70879	–
0.20	640.03	673.2	0.67832	–
		573.2	0.68149	–
0.250	853.37	673.2	0.64951	–
		573.2	0.65619	–
0.300	1097.19	673.2	0.62156	–
		623.2	0.62628	–
0.350	1378.52	673.2	0.59304	–
		628.2	0.42387	–
0.300	1097.19	673.2	0.62161	0.040337
		623.2	0.62634	0.051605
0.250	853.37	673.2	0.64962	0.012680
		573.2	0.65631	0.036412
0.200	640.03	673.2	0.67844	– 0.015819
		573.2	0.68162	0.010658
0.150	451.78	673.2	0.70961	– 0.047366
		573.2	0.70891	– 0.016181
0.100	284.46	673.2	0.74591	– 0.083813
		573.2	0.74040	– 0.047590
0.050	134.74	673.2	0.79664	– 0.134570
		573.2	0.78366	– 0.090861
0.020	52.25	673.2	0.85495	– 0.192780
		573.2	0.83301	– 0.10423
0.005	12.86	673.2	0.93915	– 0.27705
		573.2	0.90435	– 0.21157
0.001	0.2560	673.2	1.18517	– 0.52332
		573.2	1.11476	– 0.42287

[a] Net quantity of electricity passed in the normal direction.

The experimental data obtained in this study are in close agreement with data in the literature [3, 5, 6], except for the data of Hultgren [7], in the whole composition range.

Fig. 7 shows the relation between the EMF values and the net quantity of electricity passed in the normal direction. In the composition range $X_{Na} < 0.020$, a difference becomes conspicuous between the EMF values measured after coulometric titration in the normal direction (from Na to Bi–Na in cell I), and the EMF values measured after coulometric titration in the reverse direction. The difference in electrical quantity corresponded to a value $|\Delta Q| \sim 1$ C. Since

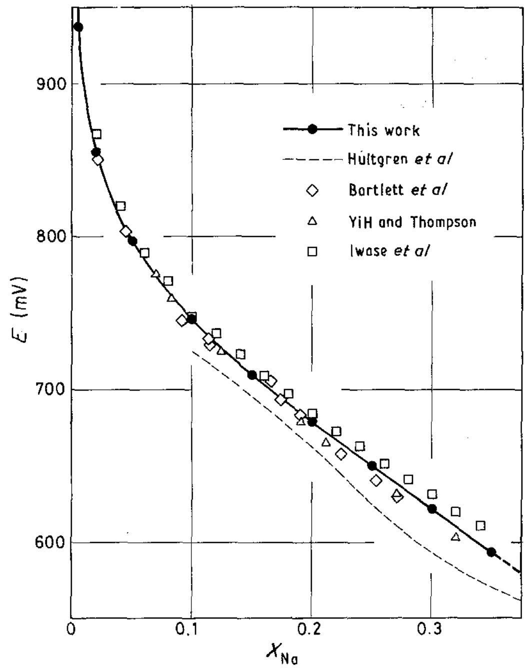

Figure 4 Comparison of the EMF of cell I with the literature (Bi–Na, experimental run 2, 673 K). EMF values measured after coulometric titrations in the normal direction are shown.

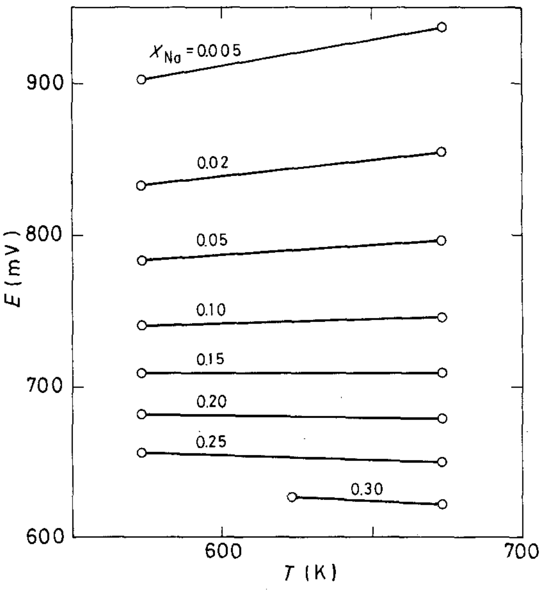

Figure 5 EMF against T. EMF values measured after coulometric titrations in the normal direction are shown.

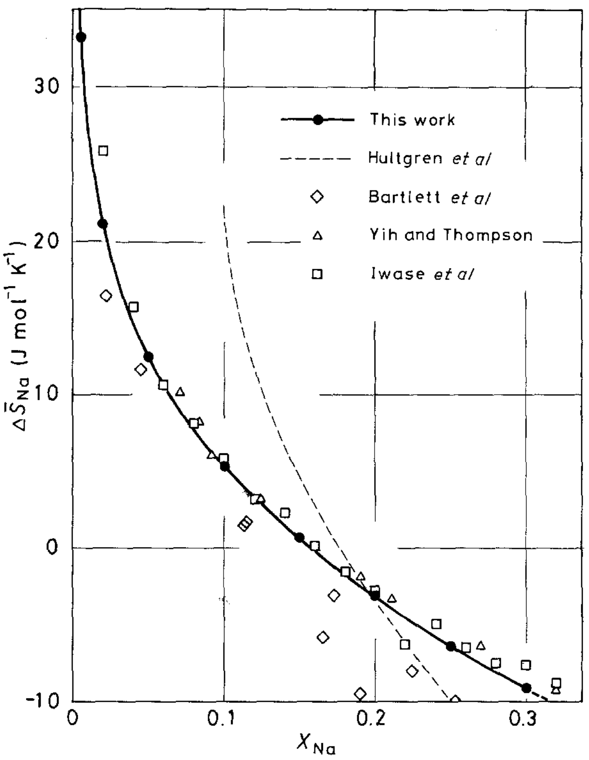

Figure 6 Comparison of the $\Delta\bar{S}_{Na}$ values for Bi–Na with the literature. $\Delta\bar{S}_{Na}$ values were calculated from the EMF values in Fig. 5.

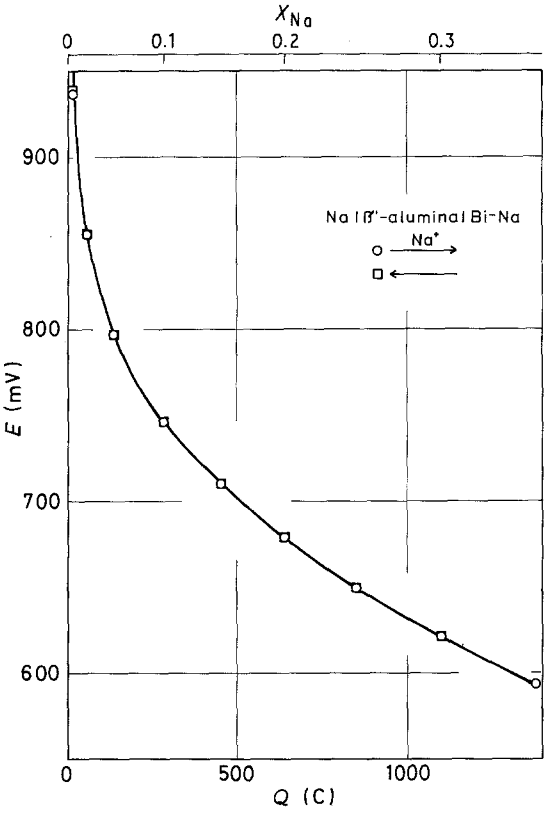

Figure 7 E_I against net quantity of electricity Q passed in the normal direction; 673 K.

the EMF values measured after coulometric titrations in the reverse direction were larger than those measured after titrations in the normal direction, the difference in EMF would be due to a Na loss during the experiment, especially at the higher Na concentrations. The vapour pressure of Na at $X_{Na} = 0.35$ at 673 K was calculated as 1.72×10^{-3} Pa (1.79×10^{-8} atm) using the EMFs given in Table I and the vapour pressure data [8] of liquid Na. The experimental results given in Fig. 7 show that no reaction occurs between the β″-alumina and Bi–Na alloy during coulometric titration.

Fig. 8 shows Na activity in the Bi–Na alloys calculated from E_I and E_{II}. The Na activities calculated from E_I and E_{II} agree with each other, and show that the transport number of Na^+ ion in the β″-alumina is unity.

3.3. Sn–Na alloys

When the cell was heated to 623 K and kept at that temperature, a constant EMF of cell I was not obtained within 7 days. Therefore the following reaction apparently does not occur between the liquid tin and the β″-alumina crucible:

$$Na_2O \text{ (in } \beta''\text{-alumina)} \rightarrow 2Na \text{ (in Sn)} + \tfrac{1}{2}O_2 \qquad (8)$$

$$Na^+ \text{ (in } \beta''\text{-alumina)} + \tfrac{1}{2}Sn = \tfrac{1}{2}Sn^{2+} \text{ (in } \beta''\text{-alumina)} + Na \text{ (in Sn)} \qquad (9)$$

Part of the experimental results are shown in Table III. EMF against X_{Na}, EMF against temperature, and $\Delta\bar{S}_{Na}$ against X_{Na} are shown in Figs 9–11, respectively. The experimental data obtained in this study were in close agreement with the results obtained by Iwase *et al.* [9] and Rivier and Pelton [10] in the composition range $X_{Na} < 0.27$. According to the equilibrium phase diagram by Hansen [11], the liquidus temperature of the Sn–Na system at $X_{Na} = 0.31$ is 673 K. However, this study has proved that the liquidus temperature at $X_{Na} = 0.31$ is 696 K, which can be detected by the bending appearance of the linear temperature dependence of the EMF, as shown in Fig. 12. The measured EMF below 696 K was larger than that obtained by extrapolating the data above 696 K.

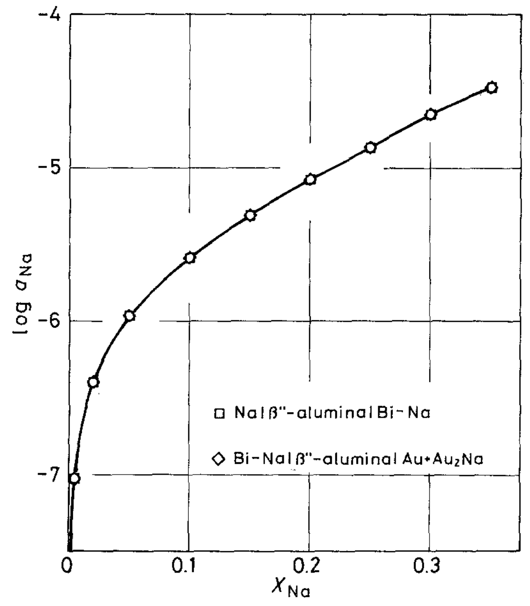

Figure 8 Logarithmic activity of Na in liquid Bi–Na alloys against X_{Na} at 673 K. Activities were calculated based on data obtained by coulometric titrations in the reverse direction.

TABLE III Results for Sn–Na alloys. Sn 9.40626 g

X_{Na}	Q(C)[a]	T(K)	E_I(V)	E_{II}(V)
0.005	38.42	728.0	0.64650	–
		627.6	0.61728	–
0.020	156.02	728.2	0.55542	–
		628.2	0.54017	–
0.050	402.38	728.3	0.49546	–
		628.3	0.48843	–
0.100	849.06	728.2	0.44743	–
		628.2	0.44765	–
0.150	1349.15	728.2	0.41707	–
		628.3	0.42224	–
0.200	1911.29	728.2	0.39302	–
		628.2	0.40269	–
0.250	2548.39	729.2	0.37131	–
		653.2	0.38137	–
0.260	2686.14	728.2	0.36712	–
		653.2	0.37779	–
0.280	2973.12	728.2	0.35872	–
		678.2	0.36605	–
0.290	3122.68	728.2	0.35435	–
		678.1	0.36205	–
0.300	3276.50	728.2	0.35000	–
		678.2	0.36129	–
0.310	3434.79	728.2	0.34544	–
		703.2	0.34947	–
0.300	3276.50	728.2	0.35028	0.29758
0.290	3122.68	728.2	0.35486	0.29311
		678.2	0.36246	0.29910
0.280	2973.12	728.2	0.35921	0.28864
		678.2	0.36655	0.29507
0.260	2686.14	728.2	0.36796	0.27990
		653.2	0.37838	0.29010
0.250	2548.39	728.2	0.37236	0.27590
		653.2	0.38207	0.28643
0.200	1911.29	728.2	0.39437	0.25373
		628.2	0.40380	0.27161
0.150	1349.15	728.2	0.41901	0.22902
		628.2	0.42387	0.25152
0.100	849.46	728.2	0.45082	0.19739
		628.2	0.45045	0.22503
0.050	402.38	728.2	0.50322	0.14504
		628.2	0.49511	0.18042
0.020	156.02	728.2	0.58035	0.06784
		628.2	0.56144	0.11411

[a] Net quantity of electricity passed in the normal direction of cell I.

Using such values below 696 K, the $\Delta\bar{S}_{Na}$ value becomes a larger negative value. This is the main reason for the difference between the data in this study and in the literature [9].

Fig. 13 shows the relation between the EMF values and the net quantity of electricity passed in the normal direction. In the composition range $X_{Na} < 0.20$, a difference becomes conspicuous between the EMF values measured after coulometric titration in the normal direction (from Na to Sn–Na in cell I) and the EMF values measured after titrations in the reverse direction. The difference in electrical quantity corresponded to a value $|\Delta Q| \sim 40$ C. The difference in EMFs would be due to a Na loss during the experiment, especially at the higher Na concentrations. The vapour pressure of Na at the composition $X_{Na} = 0.31$ was calculated as 0.827 Pa (8.157×10^{-6} atm) at 728 K using the EMF value given in Table III and the vapour-pressure data of liquid Na [8]. The experimental results given in Fig. 13 show that no reaction occurs between the β″-alumina and Sn–Na alloy during the coulometric titrations.

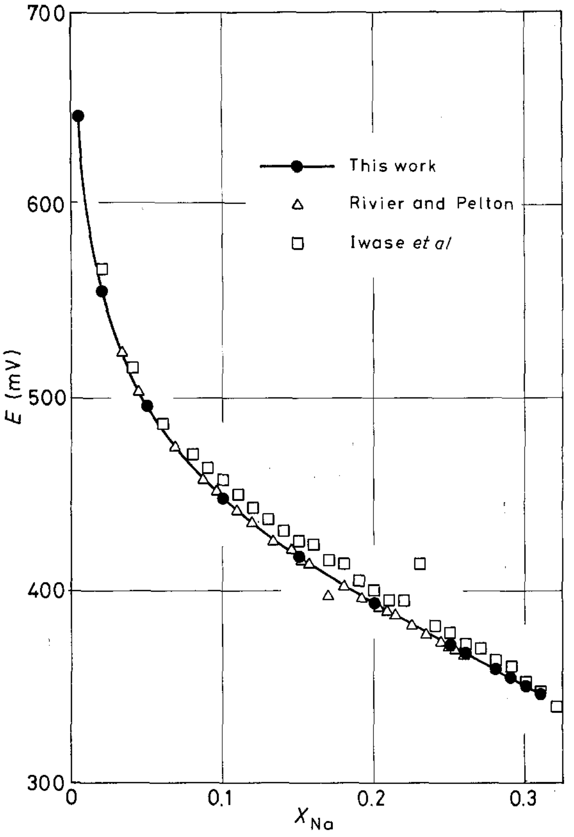

Figure 9 Comparison of the EMF of cell I with the literature. EMFs obtained by coulometric titrations in the normal direction are shown; 728 K.

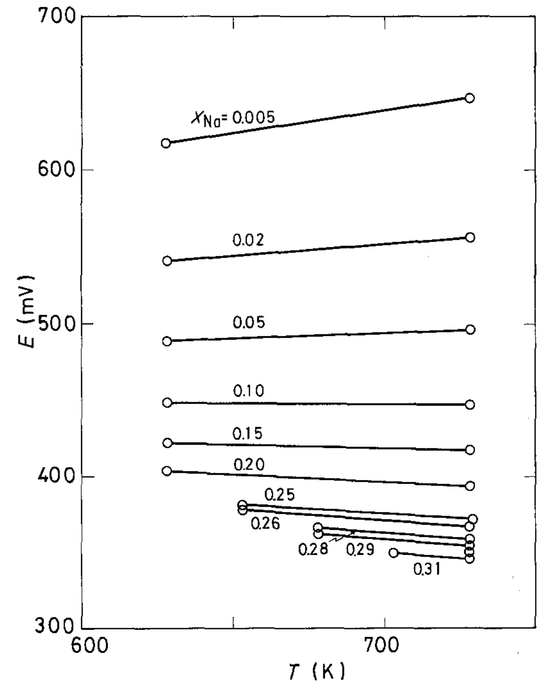

Figure 10 Temperature dependence of the EMFs of cell I obtained by coulometric titrations in the normal direction, for Sn–Na.

Figure 14 shows the Na activities in the Sn–Na alloys calculated from E_I and E_{II}. The Na activities calculated from E_I and E_{II} agreed with each other. These results also show that the transport number

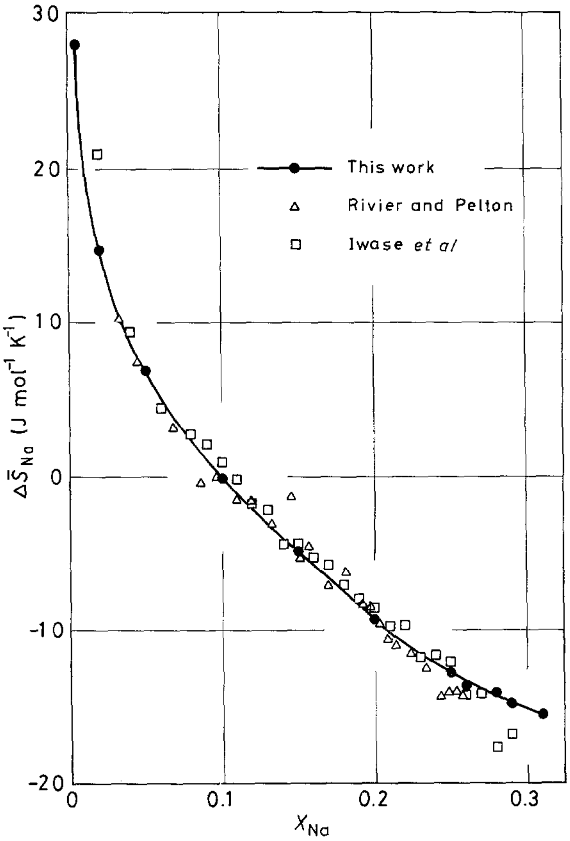

Figure 11 Comparison of the $\Delta\bar{S}_{Na}$ values with the literature. $\Delta\bar{S}_{Na}$ values were calculated from the EMFs.

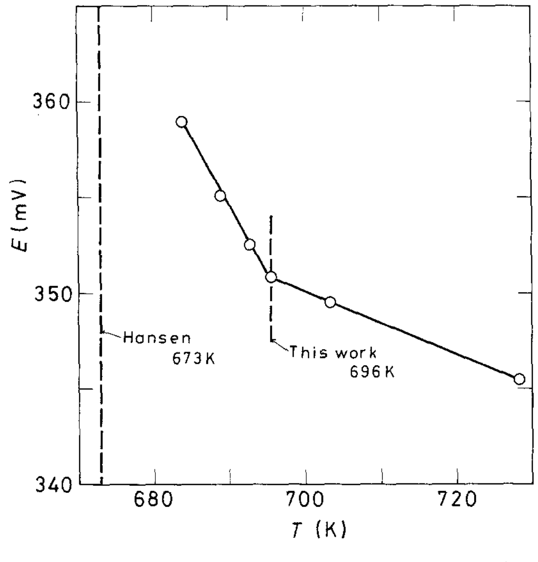

Figure 12 Temperature dependence of the EMFs of the alloy with the composition Sn–Na, $X_{Na} = 0.31$.

of Na^+ ions in the β″-alumina employed for cell I is unity.

Tin and bismuth were not detected anywhere in the cross-section of the β″-alumina crucible used for cell I by EPMA.

4. Conclusions

Thermodynamic properties of the liquid Bi–Na and Sn–Na alloys, and ion selectivity of β″-alumina during coulometric titration, were investigatd by the EMF measurement of the galvanic cells:

$$\text{Mo, Na(l)}\,|\,\beta''\text{-alumina}\,|\,\text{M–Na(l), Mo} \qquad [\text{I}]$$

$$\text{M–Na(l)}\,|\,\beta''\text{-alumina}\,|\,\text{Au} + \text{Au}_2\text{Na, Mo} \qquad [\text{II}]$$

$$(\text{M} = \text{Bi or Sn})$$

Sodium was coulometrically titrated through the β″-alumina electrolyte of cell I both ways, and EMFs

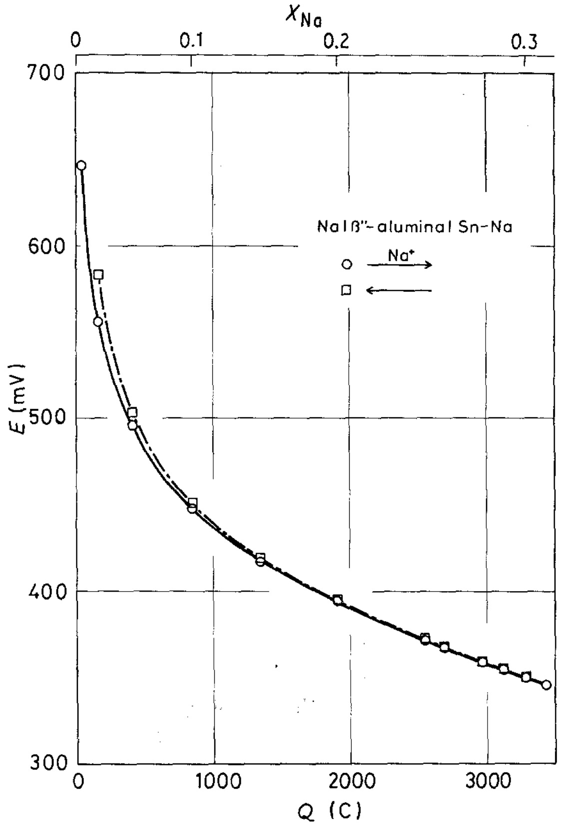

Figure 13 E_I against Q. (→) and (←) represent directions of coulometric titrations in the normal direction, from Na to Sn–Na alloy in cell I; and in the reverse direction, from Sn–Na alloy to Na, respectively; 728 K.

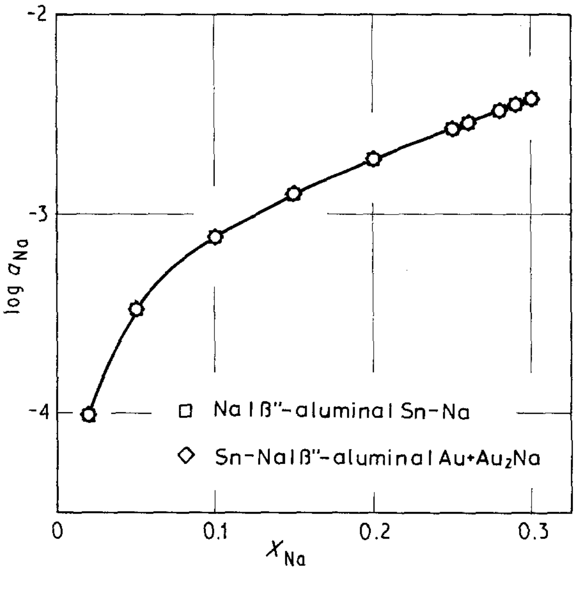

Figure 14 Logarithmic activity of Na in Sn–Na against X_{Na}. Activities were calculated based on data obtained by coulometric titrations in the reverse direction; 728 K.

were measured. It was found that no ion-exchange reaction occurs between the liquid alloys and the β″-alumina, and only Na was transferred in the β″-alumina during coulometric titrations. In Bi–Na alloys, equilibrium EMF was obtained to a minimum Na concentration of 1 p.p.m. In the dilute solution range of Na, an accuracy in the Na composition which is determined from the electricity passed through the β″-alumina is estimated to be of the order of ± 1 p.p.m. Henry's law was confirmed to hold in the composition range $X_{\mathrm{Na}} < 0.0001$, and the activity coefficient γ° was 1.91×10^{-5} at 673 K.

Thermodynamic properties obtained in this study were confirmed to agree with the data in the literature.

Acknowledgement

The authors wish to express their thanks to the NGK Spark Plug Company for supplying the β″-alumina crucibles and some financial support. Thanks are also due to Mr N. Takasawa for help in the experiments. Part of this work was supported by a Grant-in-Aid for Scientific Research from the Japanese Government's Ministry of Education.

References

1. M. ITOH and Z. KOZUKA, *J. Electrochem. Soc.* **135** (1988) 2238.
2. *Idem., J. Amer. Ceram. Soc.* **71** (1988) C36.
3. M. IWASE, S. SUGINO and E. ICHISE, *High Temp. Mater. Processes* **3&4** (1984) 143.
4. M. ITOH, E. SUGIMOTO and Z. KOZUKA, *Trans. Jpn Inst. Met.* **27** (1984) 504.
5. T.-S YIH and J. C. THOMPSON, *J. Phys. F* **12** (1982) 1613.
6. H. E. BARTLETT, A. J. NEETHLING and P. CROWTHER, *J. Chem. Thermodyn.* **2** (1970) 583.
7. R. HULTGREN, P. D. DESAI, D. T. HAWKINS, M. GLEISER and K. K. KELLEY, in "Selected Values of the Thermodynamic Properties of Binary Alloys" (American Society of Metals, Novelty, Ohio, 1973).
8. O. KUBASCEWSKII and C. B. ALCOCK, in "Metallurgical Thermochemistry", 5th edn (Pergamon, Oxford, 1979).
9. M. IWASE, S. SUGINO, E. ICHISE and Y. WASEDA, *J. Chem. Thermodyn.* **17** (1985) 603.
10. M. RIVIER and A. D. PELTON, *J. Electrochem. Soc.* **125** (1978) 1377.
11. M. HANSEN, in "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).

Received 19 April 1990
and accepted 15 January 1991