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Activity Measurements of Solid Ni–In Alloys by EMF Method with Zirconia Solid Electrolyte

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Summary. The EMF of galvanic cells with stabilized zirconia solid electrolyte was measured to determine the activity of indium in solid Ni–In alloys in the temperature range of 970–1170 K and composition range of 5–55 mol% In. Activity of indium increases sharply in the ζ phase and $Ni_{13}In_9$ phase. The activity values are compared with literature data.

Keywords. Nickel–indium alloy; Activity; EMF method; Thermodynamics; Solid electrolyte.

Introduction

Thermodynamic properties of solid alloys and compounds in wide composition ranges have been studied by many scientists. Lattice defect structures in the phases and existing regions of the phases in the phase diagram are the interest to be clarified in basic study.

Ni–In alloys have been studied by several authors. *Vinokurova* and *Geiderikh* [1, 2] used fused salt (chloride) EMF method to obtain the thermodynamic properties in the temperature range 360–670°C and composition range 25–40 at.% In. *Bhattacharya* and *Masson* [3, 4] measured vapor pressures in the range 902–1058 K and 24.97–60.00 at.% In by atomic absorption technique. *Sommer et al.* [5, 6] used zirconia based solid electrolyte EMF method with Fe,Fe_xO as reference electrode to determine the activity of In in the solid and liquid states up to 70 at.% In.

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Some discrepancy can be found in the thermodynamic values obtained by several researchers by several experimental techniques. *Waldner* and *Ipser* [7, 8] used thermodynamic modeling to describe the thermodynamic properties and phase diagram of the complete Ni–In system.

The aim of this study is to measure the activity of In in solid Ni–In alloys by stabilized zirconia EMF method in the temperature range 970–1170 K. The reference electrode is the mixture of In and In_2O_3.

Results and Discussion

EMF measurement of the following cell (I) was performed:

$$(-)\text{Kanthal,Re/In,}In_2O_3\ |ZrO_2(+Y_2O_3)|\ \text{Ni}-\text{In,}In_2O_3\text{/Re,Kanthal}(+) \quad \text{(I)}$$

The experimental results are shown in Table 1. The data shown by italic letters are obtained from another experimental run, which show the reproducibility of the data. All the data points distributed around a linear line for each composition within the same field, and the relation between EMF (E/mV) and temperature (T/K) are obtained by least-squares regression analysis. As the alloys in the same two phase fields show the same EMF values, the data were treated in the same group. Experimental data are shown in Fig. 1a and b. The number in the figure corresponds to the data points obtained in one experimental run. The temperature dependence of the EMF is shown in Table 2. The break points in the E:T plot correspond to the phase boundaries in the phase diagram of the Ni–In system.

The activity of indium a_{In} (reference state is liquid indium saturated with In_2O_3) is obtained by Eq. (1), where F is the Faraday constant, R is the gas constant, and $\Delta\overline{G}_{In}/\text{J mol}^{-1}$ is the partial molar *Gibbs* energy of mixing of In.

$$-3EF = RT\ln a_{In} = \Delta\overline{G}_{In} \quad (1)$$

Uncertainty limits in the activity values can be easily derived from those in the EMF values. The activities of indium in the alloys at 1000, 1050 and 1100 K are shown in Table 3 and Fig. 2. In the figure phase boundaries at 1000 K are shown. It is found that activity increases sharply in the ζ phase and $Ni_{13}In_9$ phase. Figure 3 shows the activity values at 1000 K by several researchers. *Bienzle* and *Sommer* [5] measured activity at 1080–1280 K ($x_{In} = 0.02$, 0.03, 0.04, 0.05 and 0.07). In the figure extrapolated values by them are shown in the α-Ni solid solution range. Our data (at $x = 0.05$ and 0.15) in the two phase region (α-Ni + Ni_3In) are in good agreement with extrapolated values by *Vinokurova* and *Geiderikh* ($x_{In} = 0.151$–0.20). In the ζ phase the results in this work agree well with the values by *Bhattacharya* and *Masson* [3]. In higher concentration range of In large discrepancy can be found in the experimental data. Much more experimental data seem necessary to clarify the thermodynamic properties of this system. Some of the points to be considered may be picked up: in EMF method, production of In_2O gas at

Table 1. Experimental EMF data of cell: (−)In,In_2O_3 |$ZrO_2(+Y_2O_3)$| Ni–In,In_2O_3(+)

T/K	*E*/mV
Ni-5.0 at.% In	
1004	108.74
1053	103.03
1029	105.72
1076	103.51
1124	103.92
1100	103.66
1148	104.07
1172	104.20
952	*114.20*
969	*112.40*
980	*110.90*
996	*109.30*
1016	*107.40*
1027	*106.00*
1038	*104.80*
1051	*103.30*
Ni-15.0 at.% In	
1010	108.10
1047	103.70
1035	105.20
1076	100.90
1066	102.10
1103	97.70
1089	99.50
Ni-20.0 at.% In	
1111	95.91
1121	95.06
1144	92.64
1130	94.01
1139	93.16
1121	94.86
1171	90.09
Ni-27.0 at.% In	
1117	95.28
1150	92.31
1126	94.33
1178	89.86
1023	*95.70*
1065	*96.30*
1104	*96.90*
1034	*96.40*
1066	*96.50*
1083	*96.50*
1092	*97.00*
1044	*96.30*
1106	*96.90*
1044	*96.80*
1080	*97.50*
1108	*96.40*
1085	*96.00*
1105	*95.80*
1168	90.01
Ni-32.5 at.% In	
1015	93.10
1102	87.60
1025	90.70
1064	89.00
1112	86.50
955	96.20
984	94.10
Ni-33.5 at.% In	
1106	82.60
1063	85.20
1084	83.80
993	89.60
1046	86.00
1023	88.60
1074	84.90
1037	86.30
1094	83.20
1046	86.10
Ni-34.6 at.% In	
1083	79.60
1026	82.90
983	85.00
1026	82.00
1095	77.80
Ni-35.5 at.% In	
1010	81.00
1103	74.20
1053	77.60
1082	75.80
1015	80.80
1065	77.60
1025	80.40
1092	76.00
981	82.80
1042	78.90
1101	74.90
Ni-36.5 at.% In	
994	78.10
1096	71.20
1046	74.10
1076	71.90
969	80.20
1025	75.50
1104	70.00
Ni-37.0 at.% In	
1043	69.50
1085	66.80
1042	69.80
1076	67.70
1021	71.50
1069	68.20
1074	67.50
1033	70.60
1054	69.30
1041	70.60
Ni-37.5 at.% In	
1095	63.70
1023	69.40
1106	62.70
1056	66.50
1005	71.20
1055	67.50
1017	69.50
951	*78.40*
991	*72.80*
Ni-38.0 at.% In	
1100	56.47
1124	54.80
1171	51.75
1146	53.32
1075	58.62
1004	*62.10*
1051	*59.72*
981	*63.56*
1026	*60.44*
Ni-42.0 at.% In	
1134	42.86
1169	40.81
1123	42.93
1154	41.04
1023	57.53
1054	52.87
1102	46.42
Ni-45.0 at.% In	
1085	49.27
1124	42.84
1106	45.07
1145	41.01
1165	40.23
1027	57.80
Ni-48.0 at.% In	
1144	41.79
1051	54.80
1074	51.19
1104	46.09
1004	62.21
1032	57.67
1092	48.34
1091	*48.29*
1152	*41.38*
1105	*45.02*
1131	*41.92*
1162	*40.85*
Ni-50.0 at.% In	
1161	36.66
Ni-52.0 at.% In	
1092	35.30
1051	32.53
1083	34.03
993	35.31
1145	39.02
1111	36.90
1133	39.94
1004	34.27
1055	31.96
1134	39.11
1093	34.54
1162	36.00
1179	34.09
1124	38.54
Ni-55.0 at.% In	
1075	34.10
1122	31.74
995	35.73
1013	34.10
1085	34.65
1152	28.49
1113	31.81
1165	26.90
1083	34.58
1142	29.29
1065	32.92
1156	*28.10*
965	*38.12*
1122	*31.73*
966	*38.27*
1055	*32.38*
1173	*26.39*

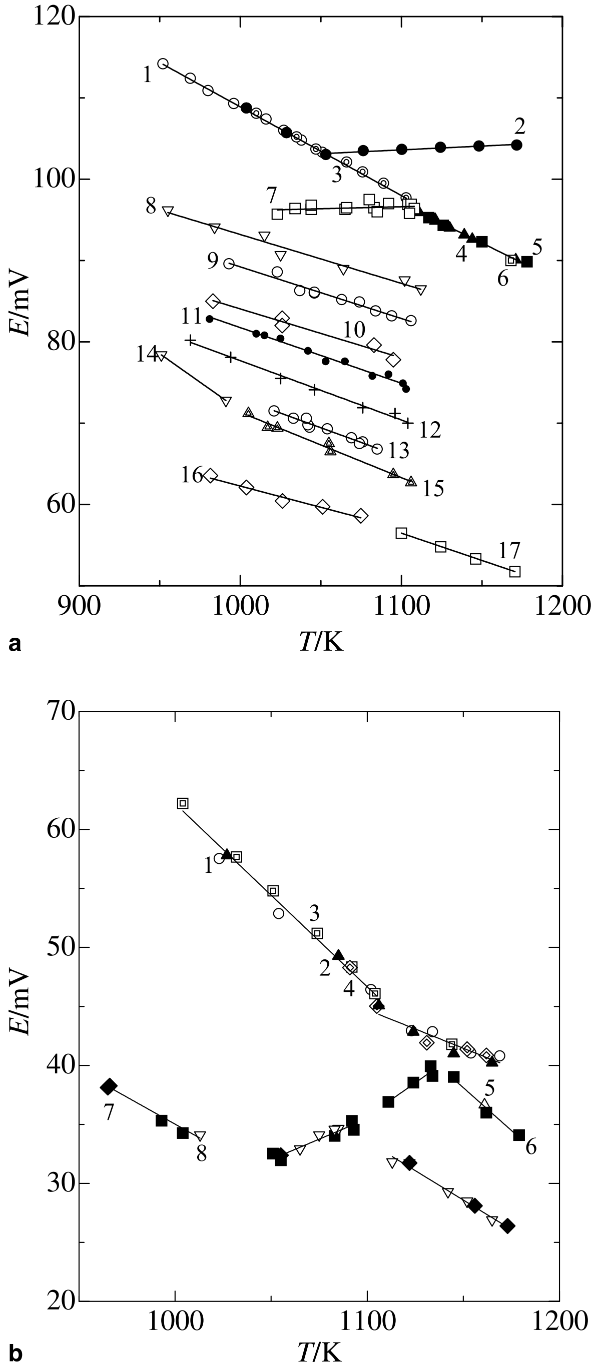

Fig. 1. (a) Temperature dependence of EMF of cell In,In_2O_3 $|ZrO_2(+Y_2O_3)|$ Ni–In,In_2O_3 in Ni–In alloys with $x_{In} = 0.05$ to 0.38: (1, 2) Ni-5.0 at.% In; (3) Ni-15.0 at.% In; (4) Ni-20.0 at.% In; (5, 6, 7) Ni-27.0 at.% In; (8) Ni-32.5 at.% In; (9) Ni-33.5 at.% In; (10) Ni-34.6 at.% In; (11) Ni-35.5 at.% In; (12) Ni-36.5 at.% In; (13) Ni-37.0 at.% In; (14, 15) Ni-37.5 at.% In; (16, 17) Ni-38 at.% In; (b) temperature dependence of EMF of cell In,In_2O_3 $|ZrO_2(+Y_2O_3)|$ Ni–In,In_2O_3 in Ni–In alloys with $x_{In} = 0.42$ to 0.55: (1) Ni-42.0 at.% In; (2) Ni-45 at.% In; (3, 4) Ni-48 at.% In; (5) Ni-50.0 at.% In; (6) Ni-52 at.% In; (7, 8) Ni-52 at.% In

Table 2. Temperature dependence of EMF of cell: $(-)In,In_2O_3\ |ZrO_2(+Y_2O_3)|\ Ni–In,In_2O_3(+)$

Alloys (at.%)	E/mV	Temperature range
Ni-(5% In–15% In)	$E = -0.1081T + 217.07 \pm 0.23$	952–1103 K
Ni-5% In	$E = 0.0076T + 95.35 \pm 0.06$	1076–1172 K
Ni-(20% In–27% In)	$E = -0.0950T + 201.35 \pm 0.42$	1111–1178 K
Ni-27% In	$E = 0.0049T + 91.23 \pm 0.98$	1023–1108 K
Ni-32.5% In	$E = -0.0601T + 153.30 \pm 1.00$	955–1112 K
Ni-33.5% In	$E = -0.0635T + 152.72 \pm 0.84$	993–1106 K
Ni-34.6% In	$E = -0.0602T + 144.25 \pm 0.55$	983–1095 K
Ni-35.5% In	$E = -0.0684T + 150.15 \pm 0.54$	981–1103 K
Ni-36.5% In	$E = -0.0728T + 150.48 \pm 0.51$	969–1104 K
Ni-37% In	$E = -0.0720T + 145.04 \pm 0.51$	1021–1085 K
Ni-37.5% In	$E = -0.1400T + 211.54$	951–991 K
Ni-37.5% In	$E = -0.0803T + 151.64 \pm 0.61$	1005–1106 K
Ni-38% In	$E = -0.0522T + 114.47 \pm 0.51$	981–1075 K
Ni-38% In	$E = -0.0671T + 130.29 \pm 0.04$	1100–1171 K
Ni-(42% In–48% In)	$E = -0.155T + 217.49 \pm 1.09$	1004–1105 K
Ni-(42% In–48% In)	$E = -0.0652T + 116.32 \pm 0.81$	1106–1169 K
Ni-(52% In–55% In)	$E = -0.0914T + 126.42 \pm 0.35$	965–1013 K
Ni-(52% In–55% In)	$E = 0.0689T - 40.32 \pm 0.49$	1051–1093 K
Ni-52% In	$E = 0.1147T - 90.51 \pm 0.50$	1111–1134 K
Ni-52% In	$E = -0.1450T + 204.86 \pm 0.37$	1145–1179 K
Ni-55% In	$E = -0.0997T + 143.24 \pm 0.50$	1113–1173 K

Table 3. Activity of indium in Ni–In Solid Alloys

1000 K		1050 K		1100 K		1150 K	
x_{In}	a_{In}	x_{In}	a_{In}	x_{In}	a_{In}	x_{In}	a_{In}
0.05	0.0225	0.05	0.0323	0.05	0.0375	0.05	0.0428
0.15	0.0225	0.15	0.0323	0.27	0.0470	0.2	0.0615
0.27	0.0352	0.27	0.0410	0.325	0.0633	0.27	0.0615
0.325	0.0390	0.325	0.0503	0.335	0.0726	0.38	0.2002
0.335	0.0448	0.335	0.0577	0.346	0.0846	0.42	0.5799
0.346	0.0536	0.346	0.0681	0.355	0.0934	0.45	0.5799
0.355	0.0581	0.355	0.0745	0.365	0.1077	0.48	0.5799
0.365	0.0669	0.365	0.0859	0.37	0.1245	0.52	0.6060
0.37	0.0786	0.37	0.1000	0.375	0.1348	0.55	0.6868
0.375	0.0834	0.375	0.1073	0.38	0.1674		
0.38	0.1144	0.38	0.1383	0.42	0.5266		
0.42	0.3906	0.42	0.4568	0.45	0.5266		
0.45	0.3906	0.45	0.4568	0.48	0.5266		
0.48	0.3906	0.48	0.4568	0.52	0.6126		
0.52	0.5890	0.52	0.6306	0.55	0.6304		
0.55	0.5890	0.55	0.6306				

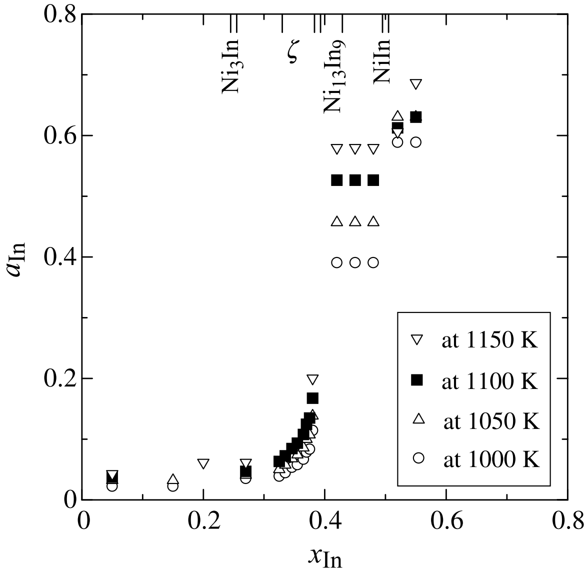

Fig. 2. Activity of In in the Ni–In alloys at 1000, 1050, 1100, and 1150 K (phase boundary at 1000 K)

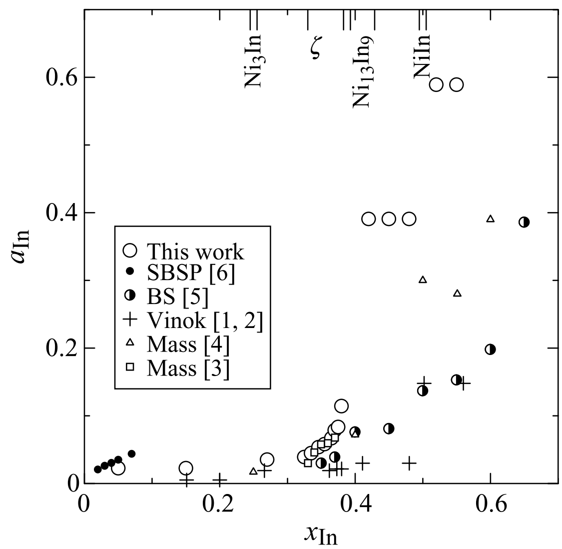

Fig. 3. Activity values obtained by several researchers at 1000 K (including values extrapolated from the original data)

higher temperatures from $In + In_2O_3$, the stability of indium chloride (+1 or +3) in the fused salt, *etc*., but at present the reason of the difference in the data is not clear.

Conclusions

Thermodynamic activity is measured in solid Ni–In alloys by stabilized zirconia EMF method with In,In_2O_3 as reference electrode in the temperature range

970–1170 K. Activity of In increases sharply in the ζ and $Ni_{13}In_9$ phase regions with increasing In concentration. The activity values are compared with the literature data at 1000 K.

Materials and Experimental Procedure

Alloys are made from pure Ni (99.98 mass% purity) and In (99.99 mass%) held and melt at 1323 to 1373 K, followed by aging at 1073 K for 7 days in an evacuated silica ampoule. The alloy powder and In_2O_3 powder (99.999 mass%) were mixed and pressed into a pellet to be heat-treated at 1023 to 1073 K for 3 to 5 days for equilibration before cell construction.

Cell apparatus and experimental procedure were quite similar to those used for the systems Cu–In [9], Pd–Ga [10], and Co–Ga–Sb [11] and described there in detail. A spring was inserted in the middle part of the alumina tube above the alloy electrode to keep good contact between the alloy electrode and the solid electrolyte. The reaction tube was kept at higher pressure than 1 atm of purified argon gas, and EMF measurement was performed in the temperature range 970–1170 K.

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