

ACTIVITY MEASUREMENT OF SOLID Cu-In ALLOYS BY EMF METHOD WITH SOLID ELECTROLYTE

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Abstract

The thermodynamic activity of indium in the solid Cu-In alloys was obtained from the emf measurement of cell: $In, In_2O_3 | ZrO_2(+11mol\%CaO) | Cu-In, In_2O_3$ for 16 alloys in the temperature range 773 to 900K. Activity changes with composition at 823K are very large in the δ and η phase regions. Activity and free energies of formation are derived and compared with the published data.

Keywords: copper-indium alloys, activity, emf method, thermodynamic property, intermetallic compound

1. Introduction

Thermodynamic properties of intermetallic compounds have been accumulated, and those of the alloy systems with B2 type structures were systematically measured and analyzed by model calculations [1]. Some of the L1₂ and B8 type compounds have wide composition ranges and the thermodynamic properties in the regions become important from the theoretical view points

related to the lattice defects, but the experimental data are not adequate or some discrepancy can be found for some systems.

In this study Cu-In alloys are picked up. In the phase diagram of Cu-In system by Hansen and Anderco [2] there are 5 intermetallic compounds, and the aim of this study is to obtain the thermodynamic properties in the α , δ and η -phases.

Predel and Schallner [3] measured the indium activity in the α region by the emf method with $0.85\text{ThO}_2+0.15\text{Y}_2\text{O}_3$ electrolyte and Ni,NiO reference electrode from 2.0 to 9.5 at% In at 1000K. Jacob and Alcock [4] determined the chemical potential of indium in the α region at 900K by use thin foils of Cu embedded in In_2O_3 equilibrated with controlled streams of $\text{CO}+\text{CO}_2$ mixtures followed neutron activation analysis.

Bhattacharya and Masson [5] used atomic adsorption spectroscopy to measure the vapor pressure of indium in the α region between 921-1076K. The shape of the activity curves by these three groups are different and the agreement of the activity value is not good even if the temperature is considered. Vinokuroba and Geiderikh [6] measured the activity of indium in the temperature range 655 to 853K and 8.6 to 39.0 at%In by the fused salt emf method. Recently Legendre and coworkers [7,8] determined heat content,heat capacity and enthalpy of formation of $\text{Cu}_{0.7}\text{In}_{0.3}$ and $\text{Cu}_{0.64}\text{In}_{0.36}$ by drop calorimetry and solution calorimetry precisely. They compared the enthalpy of formation with the literature data.

This study was intended to determine the activity of indium in the solid state in the whole composition range by emf method using galvanic cell with the solid electrolyte $\text{ZrO}_2(+\text{CaO})$ and In, In_2O_3 reference electrode.

2. Experimental

The materials used in the preparation of the alloys were 99.98 mass % Cu and 99.99 mass% In (both from Mitsubishi Materials Co Ltd). The surface of the copper was cleaned in dilute HNO_3 solution, washed with water and CH_3OH , and dried. After both of the materials was weighed (about 15g) they were held in an evacuated and enclosed silica ampoul (1×10^{-5} torr) to be melted and mixed enough at 1073K for higher than 25 at%In alloys and at 1373K for

lower alloys than that. The alloys were again held in evacuated and enclosed silica ampouls to be homogenized at 873K for long period of time followed quenching in water. As the change in weight of each alloys was negligible small before and after these treatment, nominal composition was used as the alloy concentration. After the alloy powder was made by a diamond dental drill, In_2O_3 powder (99.9 mass% purity, Mitsubishi Materials Co.Ltd.) was added to the alloy powder in a mass ratio 1:7 and mixed. Each mixture was pressed into a pellet in a die of 9mm diameter under 4 tons/cm^2 , and enclosed in an evacuated silica ampoul to be held at 873K for over one week. The sintered pellet was used as the alloy electrode after being polished with emery papers. A stabilized zirconia crucible with the flat bottom ($0.89\text{ZrO}_2 + 0.11\text{CaO}$, size $8^{\text{od}} \times 5^{\text{id}} \times 50^{\text{length}}$ mm, produced at Nikkato Co.Ltd) was used as a solid electrolyte. The outer bottom surface of the crucible was polished by emery paper in order to keep good contact between the alloy electrode and the crucible. Re wire (about 10mm long) spot-welded to the end of Pt wire was used as a contact lead with electrodes, and it was effective to avoid the reaction between the lead wire and both electrodes. In an alumina crucible with flat bottom ($15^{\text{od}} \times 12^{\text{id}} \times 16^{\text{length}}$ mm) Re/Pt wire, alloy electrode and zirconia crucible in which In, In_2O_3 and Re/Pt were settled in the order in a cell holder, lower part of which a big hole was made for easy handling of the cell construction as shown in Fig.1. A spring was inserted between lower and upper alumina tubes on the electrolyte to keep good contact between the alloy electrode and the electrolyte. The reaction tube was evacuated and filled with purified argon gas at room temperature and 150°C .

Cell apparatus and experimental procedure were similar to those used for Ni-Ga [9], Co-Ga [10], Pd-Ga [11] solid alloys and Ga-Sb-Sn [12] liquid alloys. The inner part of the reaction tube was kept higher pressure than 1atm of purified Ar gas, and emf measurement was performed in the temperature range 773 to 900K for 16 alloy compositions.

3. Results and Discussion

After the cell temperature reached the desired value, it took 6 to 10 hours to reach stable emf of the cell. On changing the temperature, equilibration at a new temperature took shorter period of time (2 to 5 h).

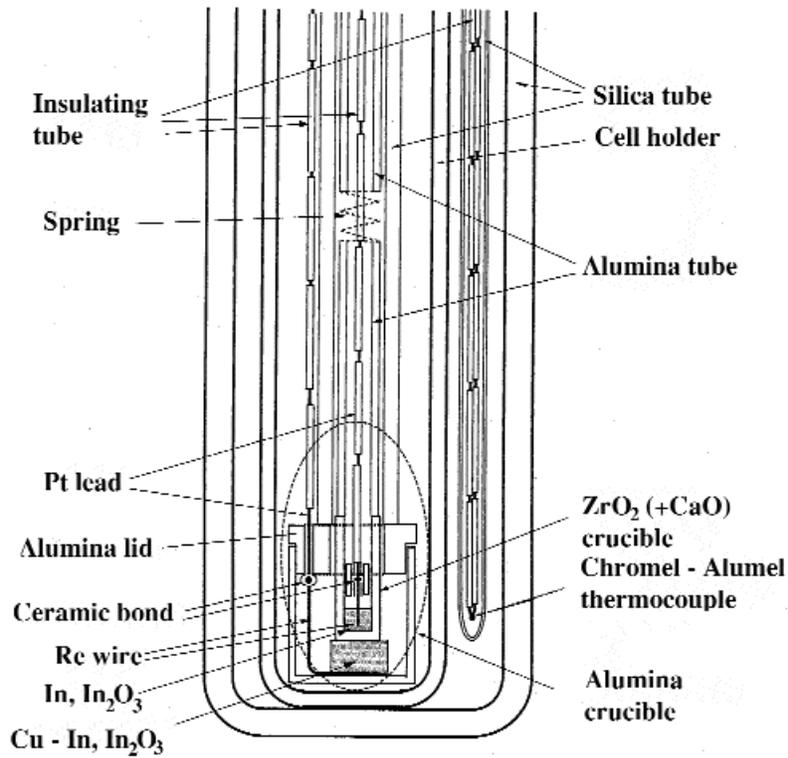


Fig.1 Partial schematic diagram of cell arrangement for emf measurement

The experimental results are shown in Fig.2. As all the data points distributed around a linear line for each composition (uncertainty limits of emf are within 1.5mV), the relations between emf (E/mV) and temperature (T/K) are obtained by least-squares regression analysis, and listed in Table 1. For the alloys within the same two phase region ($x_{In} = 0.15$ and 0.25), ($x_{In} = 0.39, 0.40$ and 0.60) data points are on the same lines as shown in Fig.2. In order to calculate the copper activity and free energy of formation of alloys the following values are used as the phase boundary concentration from the phase diagram of ref[2]; ($\alpha/\alpha+\delta$: $x_{In} = 0.10$; $\alpha+\delta/\delta$: $x_{In} = 0.285$; $\delta/\delta+\eta$: $x_{In} = 0.315^*$ (the value in ref[2] is 0.306); $\delta+\eta/\eta$: $x_{In} = 0.34$; $\eta/\eta+L$: $x_{In} = 0.39$). From the results in this study the value for $x_{In} = 0.31$ differs from those for $x_{In} = 0.32$ and 0.325 , and it is considered in the δ phase region.

Table 1. Temperature dependence of emf of cell (I) and activity of indium (reference state is liquid indium saturated with In_2O_3); (-) $In, In_2O_3 | ZrO_2(+CaO) | Cu_{1-x}In_xIn_2O_3(+)(I)$.

x_{In}	E/mV	$a_{In}, 800K$	$a_{In}, 823K$	$a_{In}, 873K$
0.05	$69.0 + 0.0162T/K$	0.0282	0.0308	0.0364
0.07	$67.6 + 0.0121T/K$	0.0346	0.0375	0.0442
0.15	$207.8 - 0.1655T/K, T/K < 847$	0.0376	0.0483	
0.15	$150.8 - 0.0975T/K, T/K > 847$			0.0728
0.25	$207.8 - 0.1655T/K, T/K < 847$	0.0376	0.0483	
0.25	$234.8 - 0.1973T/K, T/K > 847$			0.0824
0.29	$173.4 - 0.1294T/K$	0.0477	0.0590	0.0899
0.30	$149.8 - 0.1129T/K$	0.0751	0.0901	0.130
0.31	$48.9 - 0.0224T/K$	0.259	0.275	0.311
0.32:0.325	$6.0 + 0.0172T/K$	0.422	0.426	0.433
0.35	$80.0 - 0.0768T/K$	0.445	0.492	0.595
0.36	$28.2 - 0.0187T/K$	0.563	0.581	0.622
0.37	$32.8 - 0.0288T/K$	0.654	0.681	0.737
0.38	$13.7 + 0.0224T/K$	0.832	0.819	0.792
0.39:0.40:0.60	$32.7 + 0.0430T/K$	0.992	0.892	0.824

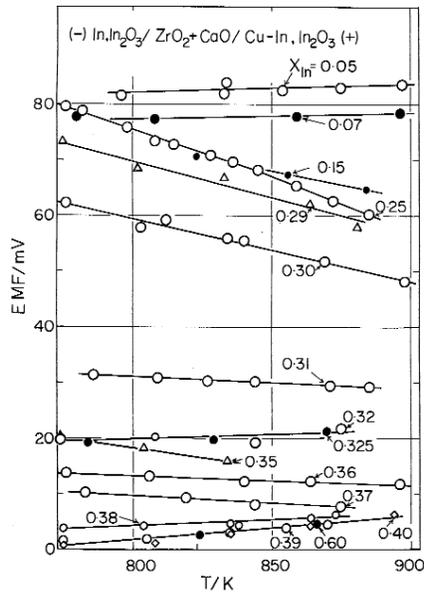
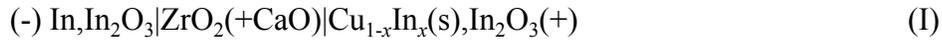


Fig.2. Temperature dependence of emf of cell (I) and activity of indium; (-) $In, In_2O_3 | ZrO_2(+CaO) | Cu_{1-x}In_xIn_2O_3(+)(I)$.

Activity of indium a_{In} is related to the emf of cell (I) by the Eq. (1)



$$-3EF = RT \ln a_{\text{In}} \quad (1)$$

where F -Faraday constant, R - gas constant and T - absolute temperature in K.

The reference state of the a_{In} is liquid indium saturated with In_2O_3 .

Activity of indium can be calculated by Eq.(1) and that of copper is derived by the following Gibbs-Duhem equation with α -function.

Table 2. Thermodynamic values of Cu-In alloys at 823K.

x_{In}	a_{In}	a_{Cu}	$\Delta G_{\text{In}}/\text{J/mol}$	$\Delta G_{\text{Cu}}/\text{J/mol}$	$\Delta G/\text{J/mol}$	Phase
0	0	1		0	0	
0.05	0.0308	0.960	-23810	-281	-1458	α
0.07	0.0375	0.948	-22470	-366	-1913	α
0.10	0.0483	0.926	-20740	-525	-2546	$\alpha/ \alpha+\delta$
0.15	0.0483	0.926	-20740	-523	-3555	$\alpha+\delta$
0.20	0.0483	0.926	-20740	-523	-4567	$\alpha+\delta$
0.25	0.0483	0.926	-20740	-526	-5579	$\alpha+\delta$
0.285	0.0483	0.926	-20740	-527	-6288	$\alpha+\delta/ \delta$
0.29	0.059	0.854	-19370	-1079	-6384	δ
0.30	0.0901	0.715	-16470	-2291	-6545	δ
0.31	0.275	0.438	-8834	-5642	-6631	δ
0.315	0.426	0.359	-5839	-7003	-6636	$\delta/\delta+\eta$
0.32	0.426	0.359	-5839	-7003	-6630	$\delta+\eta$
0.33	0.426	0.359	-5839	-7003	-6619	$\delta+\eta$
0.34	0.426	0.359	-5839	-7003	-6607	$\delta+\eta/\eta$
0.35	0.492	0.333	-4853	-7522	-6588	η
0.36	0.581	0.304	-3716	-8148	-6552	η
0.37	0.681	0.277	-2629	-8773	-6499	η
0.38	0.819	0.248	-1366	-9530	-6428	η
0.39	0.892	0.235	-782	-9896	-6341	$\eta/\eta+\text{L}$
0.40	0.892	0.235	-782	-9896	-6250	$\eta+\text{L}$
0.50	0.892	0.235	-782	-9891	-5337	$\eta+\text{L}$
0.60	0.892	0.235	-782	-9887	-4424	$\eta+\text{L}$
0.70	0.892	0.235	-782	-9886	-3513	$\eta+\text{L}$

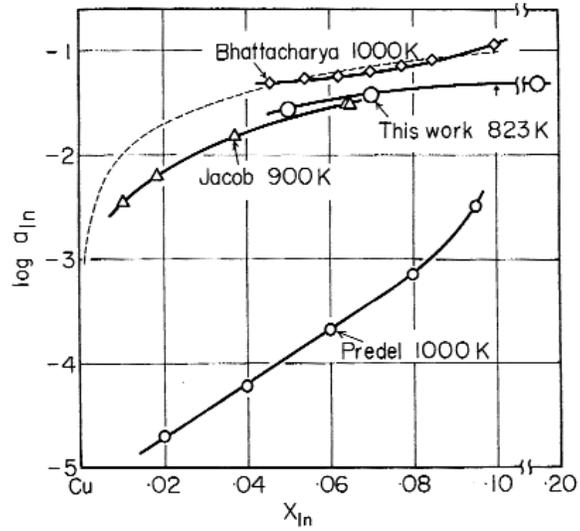


Fig.3 Activity of indium in the α -phase of Cu-In alloys.

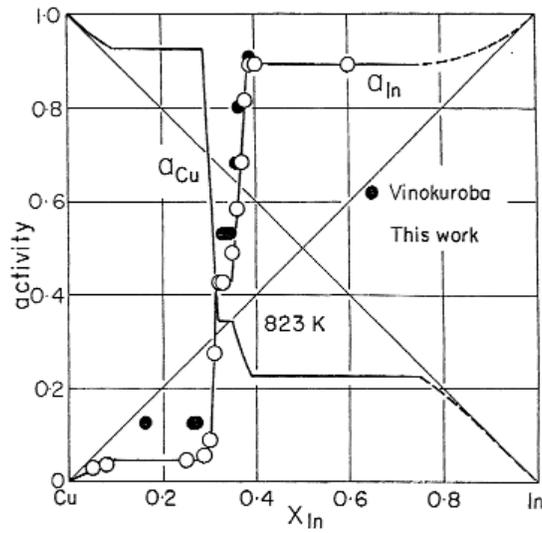


Fig.4 Activity curves in Cu-In alloys

$$\ln a_{\text{Cu}} = \ln x_{\text{Cu}} - x_{\text{Cu}} x_{\text{In}} \alpha_{\text{In}} + \int_0^{x_{\text{In}}} \alpha_{\text{In}} dx_{\text{In}} \quad (2)$$

$$\text{where } \alpha_i = \ln \gamma_i / (1 - x_i)^2 \quad (3)$$

$$\text{and } a_i = \gamma_i x_i \quad (4)$$

(γ_i is the activity coefficient of element i).

Integral free energy of formation of alloys from Cu and In are derived by eq.5.

$$\Delta G = RT \{x_{\text{In}} \ln a_{\text{In}} + (1 - x_{\text{In}}) \ln a_{\text{Cu}}\} \quad (5)$$

The thermodynamic functions are calculated and shown in Table 2.

Activity curves in logarithmic scale in the α phase by four groups are shown in Fig.3. The composition dependence of activity is reported differently. Activity values by Predel and Schallner [3] are too low. As they used Y_2O_3 -doped ThO_2 as a solid electrolyte and Ni_3NiO as the reference electrode, there might be no problem in the cell performance at about 1000K. Three groups report the similar values by different experimental methods, although the concentration dependence is a little different. The reasons of the discrepancy are not apparent.

Vinokuroba and Geiderikh [6] obtained the activity of indium in the regions ($\alpha + \delta$ to $\eta + L$) by fused salt electrolyte $\{(\text{KCl} + \text{LiCl}) + 0.2\% \text{InCl}\}$. Their results are shown in Fig.4 with our results. In the whole region their values are higher than those in this study, and the difference is larger in lower In concentration range. We calculate the possibility of coexistence of InCl and InCl_3 at 800K from the standard free energy of formation of InCl and InCl_3 [12]. Assuming $a_{\text{InCl}} = 1$, $a_{\text{InCl}_3} = 0.144$ at $a_{\text{In}} = 0.03$, $a_{\text{InCl}_3} = 0.052$ at $a_{\text{In}} = 0.05$ and $a_{\text{InCl}_3} = 1.4 \times 10^{-3}$ at $a_{\text{In}} = 0.3$. When a_{In} becomes bigger than 0.5, a_{InCl_3} becomes negligibly small. These result corresponds to the difference in activity values, i.e. the higher the content of InCl_3 in the electrolyte, the smaller emf values, and the bigger the activity.

4. Conclusion

Activity of indium in the Cu-In solid alloys is measured in the whole composition range at 773 to 900K by an emf method using galvanic cell with the solid electrolyte $ZrO_2(+CaO)$ and In, In_2O_3 reference electrode. At 823K activity of In in the α phase region shows small negative deviations from Raoult's law and changes sharply with the indium concentration in δ and η phase regions. Free energy change of formation of the alloy has a maximum near $x_{In} = 0.315$. They are compared with the published data.

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