THERMODYNAMIC BEHAVIORS OF Pd-In ALLOYS①

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ABSTRACT Some thermodynamic parameters of Pd-In alloys with 2% to 70% (mole ratio) indium were determined in the temperature range 800 ℃ to 1000 ℃ from *e. m. f.* measurements on galvanic cells with an oxygen-conducting solid electrolyte. Heats of mixing calculated from the activities are in excellent agreement with calorimetric data. The relative partial excess free energy of indium assumes unusually large negative values up to − 174 kJ/mol for Pd-rich alloys. Two effects were discussed to account for the non-ideal properties: the rise of Fermi energy as the valence electrons of indium enter the 4*d* and 5*sp* bands of the alloy and the lattice distortion brought about by the different molar volumes of the components; the rise of the Fermi energy, as determined from the activity data, indicates a strict adherence of the alloys to the rigid band model.

Key words galvanic cell activity data Fermi energy lattice distortion rigid band model

1 INTRODUCTION

Pd alloy is a useful subject for relating thermodynamic properties with electronic and elastic quantities of the components. The thermodynamic functions of a number of interstitial and substitutional Pd alloys exhibit analogous characteristics and may be interpreted in the same manner.

Two effects were discussed to account for the non-ideal properties. The first is "elastic" effect which is associated with the lattice distortion brought about by the dissolved particles. The energy of elastic strain fields of two separate solute atoms is changed if the particles enter adjacent sites. The another is "electronic" effect which is based on the observation that a number of alloy components behave as electron donors with respect to Pd. The increase of the electron concentration leads to a rise of the Fermi energy.

The rigid band model permits a detailed description of the activity coefficients not only of interstitially dissolved hydrogen and boron but also of cadmium and tin in substitutional α-Pd alloys. The object of this study is to demonstrate the applicability of this approach to other substitutional Pd alloys as well[1].

Heats of formation of three Pd-rich Pd-In alloys were determined by Darby *et al*[2]. The partial molar properties of In in β′-Pd-In alloys were measured by atomic absorption spectroscopy[3]. The activity of In in Pd-In alloys was obtained from *e. m. f.* studies employing the solid oxide electrolyte technique[4]. Free energies and heats of formation were calculated from the activity data.

2 EXPERIMENTAL

The thermodynamic properties of the Pd-In systems were determined on cells of the following type:

Pd-In, In_2O_3| ZrO_2− CaO| Ni, NiO (A)

Ni-NiO rather than In-In_2O_3 reference electrodes were used in order to avoid the experimental problems associated with liquid In.

The oxygen partial pressures of the electrodes employed in this investigation fulfill the conditions of pure ionic conductivity in the electrolyte[5].

With this provision, the unknown oxygen partial pressure p_{O_2}(Pd-In, In_2O_3) can be calculated from the known pressure p_{O_2}(Ni, NiO)[6]

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by means of Nernst's equation. Finally, since the standard free energy of formation of In_2O_3 is also known[6], the activity of In, α_{In}, can be calculated from p_{O_2}(Pd-In, In_2O_3) by the law of mass action.

The starting materials for the electrodes were obtained from commercial sources in the following stated purities: Pd 99.8% (in mass), Degussa; In and In_2O_3 99.999% (in mass), Halewood Chem.; Ni and NiO 99.998% (in mass), Koch-Light, Germany, respectively. The alloys were prepared by induction melting in an argon atmosphere. The samples were annealed for about 10 days in evacuated quartz capsules at 1 000 ℃.

The temperature of the cell was measured with a Pt/Pt10Rh thermocouple calibrated against the melting points of Ag and Au by means of a thermal-voltage-free Diesselhorst potentiometer, and controlled to within ±0.5 K. The heating coils were partly shunted to provide an extended region of constant temperature (±1 K within 20 cm). The electromotive force was also measured with a potentiometer, using a sensitive zero-voltmeter with an input impedance of 10^{12} Ω. A protective atmosphere was maintained in the apparatus by passing Ar over $Mg(ClO_4)_2$ at 25 ℃ and over Zr turnings at 1 000 ℃.

3 RESULTS

The potentials of the Pd-In alloys relative to the Ni-NiO reference electrode and the corresponding temperatures are given in Table 1. The *e. m. f.* values are reproducible within ±3 V, as checked by running independent cells.

The activity of In as derived from the *e. m. f.* data was used to calculate the relative partial excess free energy of indium, $\Delta\overline{G}^{E}_{In}$,

$$\Delta\overline{G}^{E}_{In} = RT\ln\alpha_{In} - RT\ln x_{In} \quad (1)$$

and the relative partial excess entropy of indium, $\Delta\overline{S}^{E}_{In}$,

$$\Delta\overline{S}^{E}_{In} = -\left(\frac{\partial\Delta\overline{G}^{E}_{In}}{\partial T}\right)_{x_{In}} \quad as \quad (2)$$

Values of $\Delta\overline{G}^{E}_{In}$ determined on α-Pd alloys at 800, 900, and 1 000 ℃ are plotted in Fig. 1.

Table 1 Electromotive force for cell (A) at different temperatures (mV)

x_{In}	Temperature/ ℃				
	800	850	900	950	1000
0.02	469.2	472.0	474.4	477.2	479.6
0.03	450.0	–	457.1	–	461.0
0.04	440.0	445.0	449.0	449.9	451.0
0.05	440.5	444.1	447.3	450.3	453.6
0.075	428.6	430.0	431.4	432.9	434.0
0.09	420.0	–	420.3	–	420.0
0.10	411.8	413.3	415.2	415.3	414.0
0.112	391.5	392.2	392.9	393.1	393.5
0.125	370.4	368.5	372.5	367.8	372.3
0.15	326.5	330.4	332.6	333.3	334.2
0.17	303.0	304.2	304.8	305.2	305.4
0.18	286.5	285.5	287.0	288.5	288.6
0.25	121.4	125.2	131.0	135.8	139.0
0.325	– 5	– 25	– 40	4.9	10.0
0.426	– 108.7	– 106.4	– 104.6	– 101.4	– 96.8
0.5	– 171.5	–	– 176.2	–	– 177.0
0.6	– 328.0	–	– 227.6	–	– 210.0
0.7	– 240.0	–	– 237.0	–	– 234.0

The partial quantities for Pd were obtained by integrating the Gibbs-Duhen equation[7].

The partial and integral thermodynamic properties of the Pd-In system are listed in Table 2.

The integral molar heat of mixing ΔH^{M} and the integral quantities ΔS^{E} and ΔG^{E} at 900 ℃ are plotted in Fig. 2. For comparison, the three ΔH^{M} values of Darby *et al*, determined calorimetrically at 425 ℃ and recalculated for 25 ℃, are also shown. The two sets of ΔH^{M} data are in good agreement. The observed difference may quite possibly be due to the different temperatures of measurement. The agreement between calorimetric and *e. m. f.* determinations of ΔH^{M} is even better in the system Pd-Sn. In that case, the *e. m. f.* derived data lie between two sets of calorimetric data[8], Darby's values are likewise slightly more positive. Consequently, *e. m. f.* measurements on such alloys appear to be a reliable method to obtain ΔH^{M} values.

Table 2 Partial and integral thermodynamic properties of solid Pd-In alloys

x_{In}	$\Delta\bar{G}^{E}_{In}$ / kJ·mol^{-1}	$\Delta\bar{S}^{E}_{In}$ / J·mol^{-1}·K^{-1}	$\Delta\bar{G}^{E}_{Pd}$ / kJ·mol^{-1}	ΔG^{E} / kJ·mol^{-1}	ΔS^{E} / J·mol^{-1}·K^{-1}	ΔH^{M} / kJ·mol^{-1}	Phase
0.02	- 172.9	- 52	0.0	- 3.5	- 1.0	- 4.7	α
0.03	- 171.8	- 49	0.2	- 5.0	- 1.6	- 6.8	α
0.04	- 172.3	- 49	0.0	- 6.9	- 2.1	- 9.3	α
0.05	- 174.0	- 40	0.2	- 8.6	- 2.5	- 11.5	α
0.075	- 173.3	- 44	0.1	- 12.9	- 3.5	- 17.1	α
0.09	- 171.9	- 55	0.0	- 15.5	- 4.3	- 20.5	α
0.1	- 171.5	- 50	- 0.2	- 17.2	- 4.8	- 22.1	α
0.112	- 166.1	- 51	- 0.4	- 19.1	- 5.4	- 25.4	α
0.125	- 161.2	- 50	- 1.5	- 21.3	- 6.1	- 28.4	α
0.15	- 151.5	- 37	- 2.9	- 25.3	- 7.2	- 33.7	α
0.17	- 144.6	- 46	- 4.3	- 28.2	- 8.0	- 37.5	α
0.18	- 140.0	- 43	- 5.2	- 29.5	- 8.4	- 39.3	α
0.25	- 98.1	- 21	- 16.5	- 36.9	- 10.4	- 40.0	Pd_3In
0.325	- 62.6	- 22	- 30.9	- 41.2	- 11.4	- 54.6	Pd_2In
0.426	- 35.1	- 22	- 47.2	- 42.1	- 13.0	- 57.3	PdIn
0.5	- 15.9	- 48	- 63.9	- 39.9	- 15.0	- 56.9	PdIn
0.6	- 2.8	-	- 80.0	- 33.7	-	-	Pd-In(liquid)
0.7	- 0.6	-	- 84.3	- 25.7	-	-	Pd-In(liquid)

Reference states: Pd (solid) and In (solid)

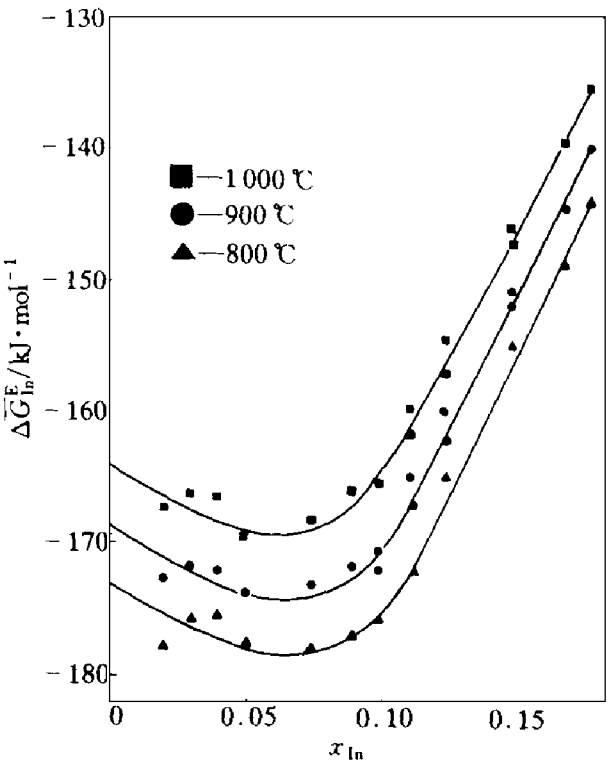

Fig. 1 Values of $\Delta\bar{G}^{E}_{In}$ of α-Pd alloys vs x_{In} at different temperatures

Reference state: In (solid)

4 DISCUSSION

The most noteworthy characteristics of the thermodynamic properties of Pd-In system are the extremely large negative deviations from ideal mixing behavior as illustrated by the representation of the relative partial excess free energies in Fig. 1 and of the heats of mixing in Fig. 2.

Very large negative deviations are also exhibited by the alloys of Pd with polyvalent solutes Cd and Sn. The pronounced increase of the effect from Cd to In to Sn suggests that the mixing behavior is correlated with the electronic configuration of the solute. Although the electronic effects are quite noticeable in the experimental values as obtained, it is useful to apply a relatively small correction in order to separate out the contribution of lattice distortion to the excess functions.

In principle, a separation into electronic (underscript "e" in superscript E_e) and elastic or dilatational (underscript "d" in superscript E_d) parts is possible with all excess functions.

The function

$$\frac{\partial \Delta G^{E}}{\partial x_{In}} = \Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd} = (\Delta \overline{G}^{E_e}_{In} - \Delta \overline{G}^{E_e}_{Pd}) + (\Delta \overline{G}^{E_d}_{In} - \Delta \overline{G}^{E_d}_{Pd}) \quad (3)$$

suggested by Redlich and Kister[9] is selected as most practicable for this purpose. An advantage of this choice is that the term $\Delta \overline{G}^{E_e}_{In} - \Delta \overline{G}^{E_e}_{Pd}$ directly describes the rise of the Fermi energy upon substituting In for Pd.

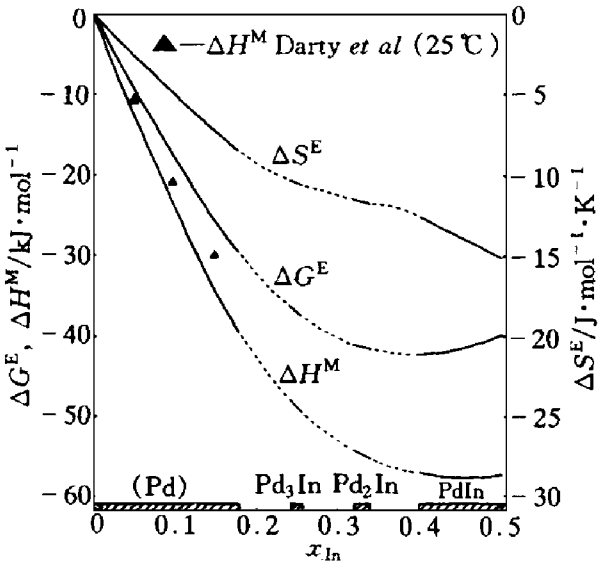

Fig. 2 Integral thermodynamic properties of Pd-In alloys vs x_{In} at 900 ℃

Reference states: Pd-In(solid) and In (solid)

The difference of the relative partial excess free energies $\Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd}$ at 900 ℃ is represented in Fig. 3 as a solid line. The values are referred to solid Pd and to hypothetically solid In as reference state, respectively. The $\Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd}$ vs x_{In} curve shows a minimum on the Pd-rich side at about $x_{In} = 0.07$, followed by a steep rise with increasing In content.

The occurrence of the minimum is attributed to opposing influences of electronic and elastic contributions. The electronic contribution shows a moderate rise in the $4d$ band regime (high density of states) and a steep rise in the $5s$ band regime (low density of state). The elastic contribution dominates as long as there are still holes in the $4d$ band available and brings about the negative gradient of $\Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd}$ on the Pd-rich side. The reversal of slopes is caused by the low density of $5s$ states, where the steep rise of the Fermi energy overcompensates the elastic part.

The elastic contribution in Eqn. (3) can be described according to the quasichemical method with a pair interaction parameter w_{H-H}:

$$\Delta \overline{G}^{E_d}_{In} - \Delta \overline{G}^{E_d}_{Pd} = -6w_{H-H} + 12RT \ln \frac{2 - 2x_{In}}{1 + \beta - 2x_{In}}$$

$$\beta = \{1 - 4x_{In}(1 - x_{In}) \times [1 - \exp(-\frac{w_{H-H}}{RT})]\}^{1/2} \quad (4)$$

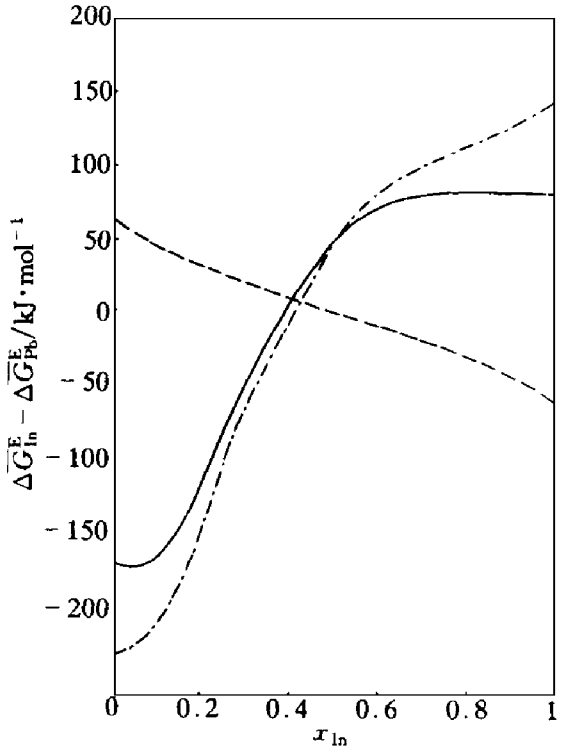

Fig. 3 Difference of excess potentials $\Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd}$ vs x_{In} at 900 ℃

——$\Delta \overline{G}^{E}_{In} - \Delta \overline{G}^{E}_{Pd}$;

—• —• —Electronic contribution;

- - - —Elastic contribution

In systems with clustering tenedency, the pair interaction parameter w_{H-H} is an energy of attraction.

The rise of Fermi energy ε_F (alloy) - ε_F (Pd)[10] as derived from these evaluations is plotted in Fig. 4 as a function of the valence electron concentration $v_i x_i$, where the valence v_i of the components is equal to the group number. The values for the Pd-Cd, Pd-In, and Pd-Sn alloys are consistent with common curve. The small deviations observed for the Pd-Cd and Pd-

In systems at high solute concentration are within the error limits to be expected of the Gibbs-Duhem integration. With this in mind, the agreement may be considered remarkably good. The virtual superposition of all three curves is a strong indication for the validity of the rigid band model for the three systems.

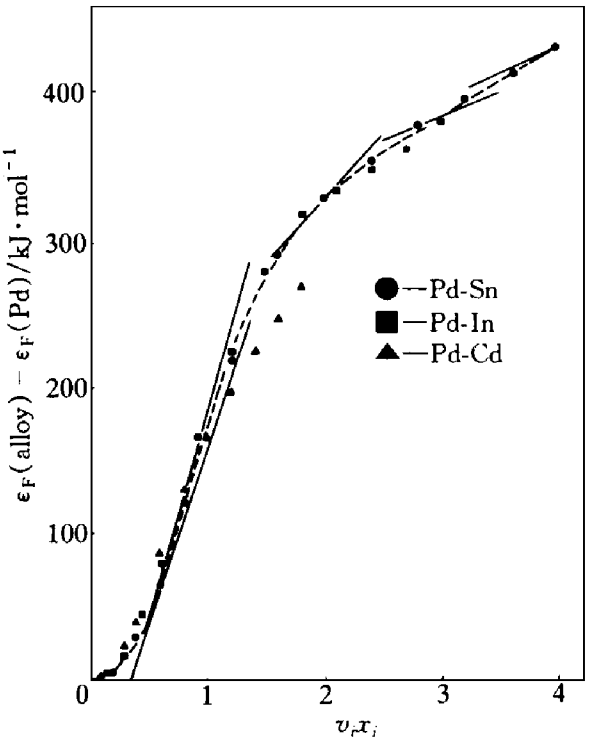

Fig. 4 Fermi energy rise vs electronic concentration $v_i x_i$ for several Pd alloys

……—From activity data;

—— —From electronic specific heat measurements

The steep rise of the Fermi energy in the concentration range $0.4 < v_i x_i < 1.2$ can be approximately represented by a straight line:

$$\varepsilon_F(\text{alloy}) - \varepsilon_F(\text{Pd}) = (250 \pm 40)(v_i x_i - 0.36)\ \text{kJ/mol} \qquad (5)$$

The slightly smaller slope at $v_i x_i > 1.3$ points to a higher density of states in the 5*p* band compared to the 5*s* band. The values of the Fermi energy rise as derived from the electronic specific heats of Cd, In, and Sn[11] are plotted as straight solid lines at the corresponding electron concentrations $v_i x_i = 2$, 3, and 4.

The straight line described by Eq. (5) intersects the abscissa at about $v_i x_i = 0.36$. The point of intersection indicates the filling of the 4*d* band. Since the measurements on pure Pd[12] also indicate 0.36 holes in the 4*d* band, the band structure of Pd is preserved in these alloys under the experimental conditions in question.

In most other instances, the experimental data or band calculations[13] do not indicate the strict adherence to the simple rigid band model. A "sliding band" model has been proposed[14] to account for the observations of a delayed 4*d* band filling and of an apparent increase of the density of 5*s* states. It is not fully understood, at present, why the rigid band concept is such a good approximation in the case of the Cd, In, and Sn alloys at high temperature.

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