



Thermochemistry of Pd–In, Pd–Sn and Pd–Zn alloy systems

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ABSTRACT

The standard enthalpy of formation of several Pd–M alloys (M = In, Sn and Zn) has been measured using a high temperature direct drop calorimeter. The reliability of the calorimetric results has been determined and supported by using different analytical techniques: light optical microscopy, scanning electron microscopy equipped with electron probe microanalysis (EPMA with EDS detector) and X-ray powder diffraction analysis. The values of $\Delta_f H$ (kJ/mol atoms) for the following phases were obtained for the formation in the solid state at 300 K: PdIn (49 at.%In): -69.0 ± 1.0 ; Pd₂In₃ -57.0 ± 1.0 ; Pd₃In₇: -43.0 ± 1.0 ; PdSn₂: -50.0 ± 1.0 ; Pd₂Zn₉ (77 at.%Zn): -33.7 ± 1.0 ; Pd₂Zn₉ (78 at.%Zn): -34.0 ± 1.0 ; Pd₂Zn₉ (80 at.%Zn): -35.0 ± 1.0 . The results show exothermic values which increase from the Pd–Zn to the Pd–Sn and Pd–In systems; the data obtained have been discussed in comparison with those available in literature.

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1. Introduction

Palladium thin films on copper contacts represent an improved method of protecting copper contacts from oxidizing. Interconnected solder joints containing a palladium or palladium–nickel layer are being introduced into selected areas of application by the electronics industry, and investigations on the interaction of this substrate material with solder could be important for processing and operation of lead-free solder contacts [1–3]. The main components of new lead-free solders are in most cases tin-based alloys (Sn–Ag, Sn–Ag–Cu, Sn–Bi). However, the addition of about 1 at.% Zn improves the mechanical properties of Sn–Ag [4] and often In is considered as a component which improves ductility of the solder [5].

In the framework of the European COST Action 531 “Lead-free solder materials”, our contribution was devoted to the investigation of the thermodynamic properties of several alloys of the Pd–In, Pd–Sn and Pd–Zn binary systems. In particular, Sn-rich, In-rich and Zn-rich palladium alloys have been considered and the enthalpies of formation of the solid alloys determined.

2. Literature data

In the following the thermodynamic data available in literature for the different Pd–M systems are reported. The relevant

enthalpies of formation data of the solid alloys are summarized in Table 1.

2.1. The Pd–In system

The phase diagram has been reported by Massalski et al. [17]. However, as far as the In-rich region, according to a crystal structure analysis, Häusermann et al. stated that the composition of the phase “PdIn₃” should be shifted towards Pd₃In₇ [18]. More recent information concerning the phase relationships in this region of the Pd–In phase diagram has been reported by Flandorfer [19] who gave a detailed literature overview, ruled out the existence of the PdIn₃ phase and determined the existence of the new Pd₃In₇ phase having a cI40–Ir₃Sn₇ type structure for which a peritectic temperature formation of 945 K was proposed. Besides, the temperature of 427 K was confirmed for the In-rich eutectic reaction and a value of 986 K was reported for the peritectic formation of the Pd₂In₃ phase.

The literature data available for the enthalpies of formation of solid Pd–In alloys are summarized in Table 1. Tin solution calorimetry has been used by Bryant and Pratt [7] to investigate the heats of formation of solid Pd–In alloys. Values have been obtained for the Pd-rich α (fcc) solid solution and for the intermediate phases Pd₃In, Pd₂In, Pd₅In₃, PdIn, Pd₂In₃ and a value was interpolated for “PdIn₃” (see above). These are the only results reported in the In-rich region.

Vogelbein et al. [9] employing lead solution calorimetry determined the enthalpies of formation at 1000 K for Pd-rich alloys.

The electromotive force method, employing a (ZrO₂ + CaO) solid electrolyte, have been used by Bird et al. [20] to determine the ther-

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Table 1
Enthalpies of formation of solid Pd–M (M = In, Sn, Zn) alloys. Literature data, reference states: Pd (solid), M (Solid).

at.% In	Phase	Method and working temperature (K)	Reference temperature (K)	$\Delta_f H$ kJ/mol at.	Ref.
2.0	α	emf, 1073–1273	1173	–4.7	[6]
3.0	α	emf, 1073–1273	1173	–6.8	[6]
4.0	α	emf, 1073–1273	1173	–9.3	[6]
5.0	α	emf, 1073–1273	1173	–11.5	[6]
		Sn sol. cal., 656	320	–11.1	[7]
		vap. pressure	298	–10.8	[8]
7.5	α	emf, 1073–1273	1173	–17.1	[6]
9.0	α	emf, 1073–1273	1173	–20.5	[6]
10.0	α	emf, 1073–1273	1173	–22.1	[6]
		vap. pressure	298	–20.6	[8]
		Sn sol. cal., 656	320	–22.6	[7]
11.2		emf, 1073–1273	1173	–25.4	[6]
12.0		Pb sol. cal., 1000	1000	–30.2	[9]
12.5		emf, 1073–1273	1173	–28.4	[6]
15.0		emf, 1073–1273	1173	–33.7	[6]
		vapour press.	298	–29.7	[8]
		Sn sol. cal., 656	320	–32.6	[7]
17.0		emf, 1073–1273	1173	–37.5	[6]
		vap. pressure 1382–1495	298	–34.3	[10]
18.0		emf, 1073–1273	1173	–39.3	[6]
25.0	Pd ₃ In	Sn sol. cal., 656	320	–53.2	[7]
		vap. pressure 1382–1495	298	–53.5	[10]
		emf, 1073–1273	1173	–49.0	[6]
		Pb sol. cal., 1000	1000	–56.5	[9]
33.3	Pd ₂ In	emf, 1073–1273	1173	–54.6	[6]
	Pd ₂ In	Sn sol. cal., 656	320	–60.4	[7]
37.0	Pd ₅ In ₃	Sn sol. cal., 656	320	–60.7	[7]
40.0		Sn sol. cal., 656	320	–60.5	[7]
43.0		emf, 1073–1273	1173	–57.3	[6]
43.0	PdIn	Sn sol. cal., 656	320	–60.9	[7]
45.0		Sn sol. cal., 656	320	–61.1	[7]
46.0		Sn sol. cal., 656	320	–61.3	[7]
49.0		Sn sol. cal., 656	320	–61.4	[7]
50.0		Sn sol. cal., 656	320	–61.4	[7]
50.0		emf, 1073–1273	1173	–56.9	[6]
50.0		Dir. cal., 1273	298	–62.8	[11]
52.0		Sn sol. cal., 656	320	–60.1	[7]
54.0		Sn sol. cal., 656	320	–58.9	[7]
60.0	Pd ₂ In ₃	Sn sol. cal., 656	320	–55.2	[7]
87.5		Sn sol. cal., 656	320	–17.7	[7]
at% Sn	Phase	Method and working temperature (K)	Reference temperature (K)	$\Delta_f H$ kJ/mol at.	Ref.
10.0		Sn sol. cal., 900–1200	320	–25.9	[12]
15.0		Sn sol. cal., 900–1200	320	–38.3	[12]
		vap. pressure 1382–1495	298	–39.7	[10]
16.0		emf, 1073–1273	1173	–40.4	[13]
22.2	Pd ₇ Sn ₂	vap. pressure 1382–1495	298	–47.1	[10]
25.0	Pd ₃ Sn	Sn sol. cal., 900–1200	320	–58.6	[12]
		Dir. cal., 1473	298	–57.8	[14]
		emf, 1073–1273	1173	–55.7	[13]
33.0	Pd ₂ Sn	Sn sol. cal., 900–1200	320	–64.0	[12]
37.0		Sn sol. cal., 900–1200	320	–63.0	[12]
40.0	Pd ₃ Sn ₂	Sn sol. cal., 900–1200	320	–62.3	[12]
50.0	PdSn	Sn sol. cal., 900–1200	320	–61.1	[12]
		Sn sol. cal., 638–791	273	–60.3	[15]
66.0	PdSn ₂	Sn sol. cal., 900–1200	320	–44.1	[12]
		Sn sol. cal., 638–791	273	–43.7	[15]
75.0	PdSn ₃	Sn sol. cal., 900–1200	320	–33.9	[12]
80.0	PdSn ₄	Sn sol. cal., 900–1200	320	–27.8	[12]
		Sn sol. cal., 638–791	273	–28.3	[15]
at.% Zn	Phase	Method and working temperature (K)	Reference temperature (K)	$\Delta_f H$ kJ/mol at.	Ref.
40.0	β_1	Vap. pressure 750–1300	1273	–65.5	[16]
45.0				–70.1	
48.0				–72.5	
49.0				–73.3	
50.0				–73.9 ± 10.0	
51.0				–73.1	
52.0				–72.2	

Sol. cal. = solution calorimetry, Dir. cal.: direct synthesis calorimetry; vap. pressure = vapour pressure measurements; emf = electromotive force measurements.

mododynamic activities and Gibbs free energies of formation at 873 K of the α (fcc)-solid-solution and of intermediate phases.

The thermodynamic properties of the Pd–In alloys with 2–70 at.% In were also determined by galvanic cell measurements with an oxygen-conducting solid electrolyte in the 1073–1273 K temperature range by Schaller and Brodowsky [6].

The vaporization behaviour and some thermodynamic properties of the Pd–In and Pd–Sn systems have been studied by Ciccioli et al. [10] and the enthalpies of formation data have been reported. Enthalpies of formation of liquid Pd–In alloys were obtained by El Allam et al. [21] and a discussion concerning the correlation between the enthalpy of mixing and the Fermi energy was given by Hayer and Bros [22].

Perring et al. [23] carried out heat capacity measurements for several intermediate phases in the Pd–In and Pd–Sn systems using differential scanning calorimetry.

Standard enthalpy of formation of PdIn phase was more recently determined by high temperature direct synthesis calorimetry at 1273 K by Meschel and Kleppa [11] and a value of -62.8 ± 1.7 kJ/mol of atoms was reported for the solid alloy at 298 K.

A thermodynamic description of the Pd–In system was subsequently obtained by using the CALPHAD approach by Jiang and Liu [24].

2.2. The Pd–Sn system

The phase equilibria of the Pd–Sn system is very complex due to the presence of numerous intermediate phases. This has been compiled by Massalski et al. [17] while thermodynamic data of Pd–Sn alloys have been assessed by Hultgren et al. [25]. In comparison with the previous assessments, however, the existence of the Pd₇Sn₂ phase was suggested by Durussel [26] which was not confirmed, nor ruled out by Ciccioli et al. [10] while studying thermodynamic properties of Pd–Sn alloys by vapour pressure using a Knudsen-effusion-cell coupled with mass-spectrometry. From these measurements the authors derived and reported the standard enthalpies of formation at 298 K of the solid phases Pd₃Sn,

Pd₇Sn₂ and Pd_{1-x}Sn_x. On the basis of the thermodynamic experimental data available, Ghosh [27] calculated the enthalpy of mixing of liquid Pd–Sn alloys at 1850 K. The experimental enthalpies of formation of the liquid Pd–Sn alloys between 952 and 1372 K and heat capacities of intermediate phases have been reported by Mathon et al. [28] and partial and integral enthalpies of mixing of liquid alloys at 1173 K were also determined by Luef et al. [29]. Heat capacity measurements in the Pd–Sn and Pd–In systems have been performed by Perring et al. [23]. Enthalpy of formation of solid Pd₃Sn alloy has also been determined by high temperature calorimetry [14]. All these data are summarized in Table 1.

2.3. The Pd–Zn system

Thermodynamic investigations of the Pd–Zn system are quite limited in the literature.

The phase diagram was determined by using thermal, micrographic and X-ray methods [30,31]. As for the Zn-rich corner, two different versions are presented in the Hansen and Anderko [32] and Massalski et al. [17] compilations. Nowotny and Bauer [31] reported evidence for the presence, in this region, of a phase having a hexagonal compact structure with an axial ratio $c/a = 1.55$, which is reported in the Hansen compilation as η phase decomposing at ~ 703 K. In the Massalski compilation this phase was not reported and the Zn-richest phase corresponds to the γ phase (extending from 76 to 85.5 at.% Zn) which forms congruently at 1153 K. On the basis of a single crystal investigation, Edström and Westman [33] reported a cubic c152-Cu₅Zn₈-type structure having a lattice constant 9.1022 Å for this phase (indicated also as Pd₂Zn₉ phase). More recently Gourdon and Miller [34], using single-crystal diffraction and tight-binding electronic-structure calculations, described a series of γ -brass related structure in the Zn-rich portion of the Pd–Zn phase diagram. The sample having a composition below 20 at.% Pd was solved as a cubic γ -brass phase having a lattice constant ~ 9.1 Å, while those that exceeded 20 at.% Pd gave data sets that were consistent with an orthorhombic structure. Additional

Table 2

Heat of formation of solid Pd–M (M = In, Sn, Zn) alloys at 300 K obtained by high temperature drop calorimetry for the reaction: $(1-x)\text{Pd}(\text{cr}, 300\text{K}) + x\text{M}(\text{cr}, 300\text{K}) \rightarrow \text{Pd}_{1-x}\text{M}_x(\text{cr}, 300\text{K})$.

Sample	SEM analysis composition x_M	Calorimeter working $T(\text{K})$	Q_1' (kJ mol at.)	Q_2' (kJ mol at.)	$\Delta_r H^\circ / \text{kJ mol at} \pm 0.5$	Remarks and observed phases
Pd–In	0.49 ₀	1173	-50.1	19.2	-69.3	Single phase PdIn
	0.60 ₀	913	-4.6	22.2	(-26.8) ^a	Reaction not complete
	0.60 ₅	978	-36.3	21.0	-57.3	70%Pd ₂ In ₃ + 20%Pd ₃ In ₇ + 5%Pd + 5%In
	0.64 ₀	948	-7.1	33.7	(-40.8) ^a	90%Pd ₂ In ₃ + 10%Pd ₃ In ₇
						Not uniform sample (Pd ₂ In ₃ + Pd ₃ In ₇ + In), incomplete equilibrium state
	0.68 ₀	960	-11.5	26.8	-38.3	30%Pd ₂ In ₃ + 70%Pd ₃ In ₇ incomplete equilibrium state, the value may be considered as a limiting value
	0.78 ₀	913	-2.1	22.1	(-24.2) ^a	Reaction not complete
	0.81 ₀	908	-0.3	24.1	-24.4	2%Pd ₂ In ₃ + 70%Pd ₃ In ₇ + 28%In
	0.85 ₀	900	4.2	26.1	-21.9	60%Pd ₃ In ₇ + $\sim 40\%$ In and traces of Pd ₂ In ₃ and Pd
	Pd–Sn	0.65 ₀	823	-22.9	26.7	-49.6
0.65 ₀		823	-19.3	15.6	(-34.9) ^a	Reaction not complete
0.66 ₀		843	-23.8	26.2	-50.0	Nearly single phase PdSn ₂
Pd–Zn	0.77 ₀	1073	-9.5	24.2	-33.7	Single phase sample
	0.78 ₀	1073	-12.2	21.8	-34.0	Single phase sample
	0.79 ₀	1073	-8.4	21.8	-30.2	Nearly single phase sample + small quantity of unreacted Pd
	0.80 ₀	1073	-11.6	23.5	-35.1	Single phase sample
	0.80 ₀	1073	-14.1	-2.1	(-12.0) ^a	Reaction not complete

^a Samples for which the reaction inside the calorimeter was not complete; these heat effects were not considered for the final evaluation.

experiments probably have to be done in order to clarify the real stable phase diagram in the Zn-rich region.

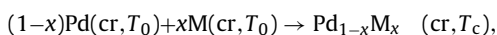
Vapour pressure of Zn in Pd–Zn alloys with a composition between 0 and 83 at.% Zn were determined by two different isopiestic methods in the 750–1300 K temperature range [16]. From these data, the relevant partial molar and integral quantities were derived as well as the values of the enthalpy of formation for the β_1 Pd–Zn phase, which are summarized in Table 1. DTA experimental measurements in the Zn-rich region and a critical evaluation of Pd–Zn phase and thermodynamic data were performed by Vizdal et al. [35].

3. Experimental procedure

All the alloys were prepared from powders obtained by filing rods of the elements with a purity of 99.95 mass% Pd, 99.999 mass% In, 99.99 mass% Zn and 99.999+ mass% Sn. Mixed powders weighing about 0.7 g, were pressed to obtain the pellets and then enclosed in a tight-sealed tantalum crucible. The preparation of the calorimetric samples starting from a mixture of fine powders guarantees a fast reaction between different elements, avoiding any Zn evaporation. Besides, the use of sealed crucibles prevents any Zn loss as confirmed in the subsequent micrographic and microprobe analysis.

For what concerns the Pd–In system, the investigated range of composition was 49–85 at.% In; for Pd–Sn, 65–66 at.% Sn and for Pd–Zn system a composition close to 80 at.% Zn. The composition of the investigated samples and the measured calorimetric data are reported in Table 2.

The calorimetric measurements were carried out in a high temperature direct reaction calorimeter working up to 1273 K [36]. The calorimetric alloys were dropped under an argon atmosphere from a room temperature thermostat T_0 (300 K) into the high temperature calorimeter T_c . Following the composition of the alloys, the working calorimeter temperature was set at values between 823 and 1173 K. Each sample was dropped twice into the calorimeter from the room temperature thermostat. In the first run (reaction run) a mixture of the two selected pure metals is dropped and the heat effect is due to the heat of the reaction:



at temperature T_c

and also due to the increment of enthalpy of Pd and M (M = In, Sn and Zn) and of the tantalum crucible.

$$Q_1 = \frac{(1-x)(H_{T_c} - H_{T_0})(\text{Pd}, \text{cr}) + x(H_{T_c} - H_{T_0})(\text{M}, \text{cr}) + m_{\text{cruc}}}{180.95(H_{T_c} - H_{T_0})(\text{Ta}, \text{cruc}) + \Delta_f H(\text{Pd}_{1-x}\text{M}_x, \text{cr}, T_c)} \quad (1)$$

Subsequently, with the same procedure, a reference run is performed. This is made by dropping into the calorimeter (working with the same values of T_c and T_0) the reacted sample. The heat effect Q_2 , evaluated as usual by means of a number of calibration drops (consisting in dropping four weighed silver or nickel spheres, two before and two after the alloy), is due to the enthalpy increments of the compound and of the tantalum crucible

$$Q_2 = \frac{(H_{T_c} - H_{T_0})(\text{Pd}_{1-x}\text{M}_x, \text{cr}) + m_{\text{cruc}}}{180.95(H_{T_c} - H_{T_0})(\text{Ta}, \text{cruc})} \quad (2)$$

by taking the difference ($Q_1 - Q_2$), the crucible effects cancel out. The result is the $\Delta_f H(\text{Pd}_{1-x}\text{M}_x, \text{cr}, T_c)$, corrected for the difference in the heat contents of metals and compound, that is the $\Delta_f H(\text{Pd}_{1-x}\text{M}_x, \text{cr}, T_0)$.

$$Q_1 - Q_2 = \Delta_f H(\text{Pd}_{1-x}\text{M}_x, \text{cr}, T_0)$$

Table 3

Interpolated $\Delta_f H^\circ$ (kJ/mol at) referred to a temperature of 300 K, reference states: Pd (solid), M (solid), obtained from the listed data in Table 2 and their trend vs. composition.

	x_M	Phase	$\Delta_f H^\circ$ (kJ/mol at.) (± 1.0) this work
Pd–M	0.49	PdIn	–69.0
	0.60	Pd ₂ In ₃	–57.0
	0.70	Pd ₃ In ₇	–43.0
	0.66 ₇	PdSn ₂	–50.0
	0.77	Pd ₂ Zn ₉	–33.7
	0.78	Pd ₂ Zn ₉	–34.0
	0.80	Pd ₂ Zn ₉	–35.0

The measurement errors related to the performance and characteristics of the instrument, are estimated to correspond to ± 0.3 – 0.5 kJ/mol in any run.

The accuracy of the calorimetric measurements is related to the actual processes occurring in the calorimeter, e.g., completeness of the synthesis reaction, attainment of the equilibrium state, possible side reactions, etc. To this end, the composition of the samples and the working temperature of the calorimeter are selected taking into account the features of the phase diagram.

All samples were analysed using optical and electronic microscopy and electron probe microanalysis (EPMA) equipped with an EDS detector in order to check their equilibrium state.

The error of ± 1 kJ/mol of atoms reported for each interpolated enthalpy values listed in Table 3 is considered to include both the instrumental errors and any uncertainties due to small composition variation or inhomogeneities detected in the samples.

4. Results and discussion

The experimental results of the heats of formation obtained in the calorimetric measurements and at reference temperature of 300 K are listed in Table 2. The heat effects Q_1' and Q_2' associated with reactions (1) and (2) diminished by the enthalpy increments of the mass of the tantalum crucible calculated using the Dinsdale polynomials [37] are also reported in Table 1. These data, together with those of the literature (see Table 1) were used to trace a trend, reported in Figs. 1 and 2, of the $\Delta_f H^\circ$ (kJ/mol-atom).

As for the Pd–In system, measurements of the heat of formation of alloys in the range 49–85 at.% In were carried out. The analyses performed on the different synthesized calorimetric samples made it possible to evaluate their equilibrium state and, accordingly, to interpolate the enthalpy of formation values at 300 K for the PdIn, Pd₂In₃ and Pd₃In₇ phases, see Table 3. Due to the peritectic reactions and the high temperature involved, several samples showed an incomplete equilibrium state.

We may notice that our results suggest a more exothermic enthalpy of formation in the region around the equiatomic composition by comparison to the literature experimental values and the data calculated by Jiang and Liu using the CALPHAD approach [24].

The Pd–Sn samples prepared in the calorimeter was nearly homogeneous with the formation of PdSn₂ compound. The experimental results are reported as a function of the composition in Fig. 2 together with the literature data. A value of -50.0 ± 1.0 kJ/mol at. (see Table 3) was obtained for the enthalpy of formation at room temperature of the solid PdSn₂ phase, in good agreement with the general $\Delta_f H^\circ$ trend obtained from the literature data. This value resulted to be a little more exothermic than those obtained by Sn solution calorimetry [12,15].

For the Pd–Zn system, the microscopic analysis performed showed that the 77.0–80.0 at.% Zn calorimetric samples are single phase samples and from the XRD measurements the diffraction

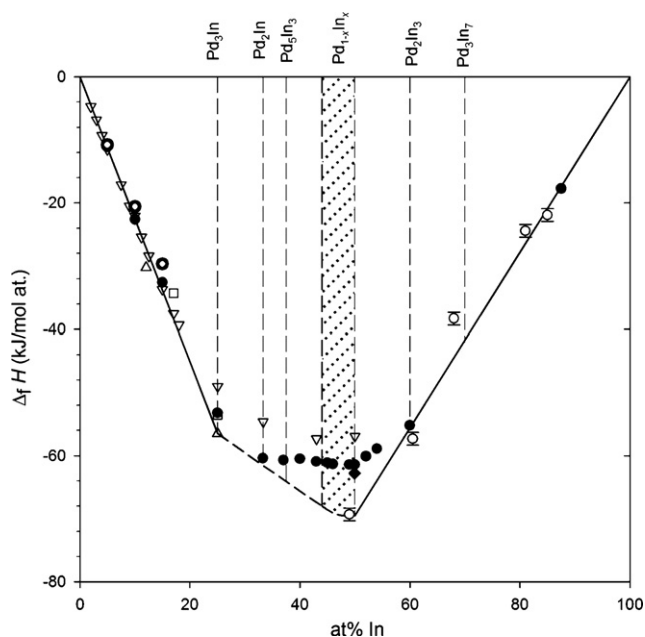


Fig. 1. Formation enthalpies for Pd–In alloys. Comparison between experimental (see Table 2) and literature data (see Table 1). The composition of the phases is indicated. ○ Dir. cal. this work, ▽ emf [6], △ Pb sol. cal. [9], □ vap. pressure [10]; ● Sn sol. cal. [7]; ◆ Dir. cal. [11], ● vap. pressure [8].

lines could be indexed on the basis of a cubic unit cell (cI52–Cu₅Zn₈-type) such as that proposed in literature. The lattice parameter value of $a = 9.098 \pm 0.007 \text{ \AA}$ was obtained for the Pd–78Zn sample, in good agreement with the literature value $a = 9.1022 \text{ \AA}$ reported by Edström and Westman [33].

An enthalpy of formation value included between -33.7 and -35.0 kJ/mol at. was obtained for these alloys, see Table 3.

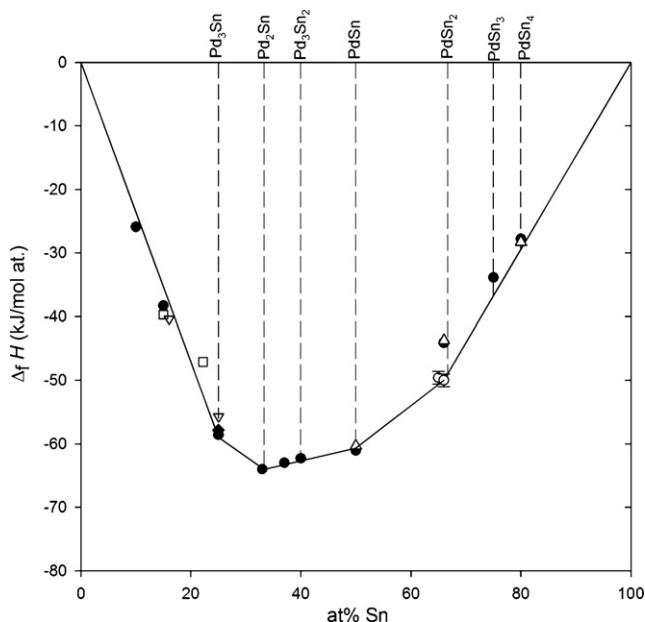


Fig. 2. Formation enthalpies for Pd–Sn alloys. Comparison between experimental (see Table 2) and literature data (see Table 1). The composition of the phases is indicated. ○ Dir. cal. this work, ▽ emf [13], △ Sn sol. cal. [15], □ vap. pressure [10]; ● Sn sol. cal. [12]; ◆ Dir. cal. [14].

5. Conclusions

A high temperature drop calorimeter was used to study the standard enthalpies of formation of solid Pd–M (M = In, Sn and Zn) alloys at 300 K in the M-rich region. Microscopy, electron probe microanalysis and X-ray diffraction analyses of the reacted alloys were performed for phase identification and for evaluating completeness of the synthesis reaction, attainment of the equilibrium state, presence/absence of side reactions, etc.

Measurements in the Sn-rich region for the phases PdSn₃ and PdSn₄ using another technique could be very useful. In fact owing to the low peritectic temperatures of reaction (618 and 568 K) of these phases, it is difficult to obtain completeness of the synthesis reaction and attainment of the equilibrium state using the direct calorimetry technique.

This work can be useful in the study of the metallurgical phases, which form on the pads on SMT (surface mount technology) circuit boards during the soldering operations.

As can be deduced from the exothermic enthalpy values obtained for the Pd–M alloys, the intermetallic phases that are in case formed between soldering material and substrate are very stable.

These data may be also very useful in a thermodynamic description and optimization of the binary and more complex systems.

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