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Standard molar enthalpies of formation of PdAl, PtAl, $ScAl_{1.78}$, YAl_2 and $LaAl_2$

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Abstract

The standard molar enthalpies of formation of PdAl, PtAl, $ScAl_{1.78}$, YAl_2 and $LaAl_2$ have been determined using a high temperature calorimeter at 1473 ± 2 K: $\Delta H_f^\circ(\text{PdAl}) = -182.5 \pm 9.3$ kJ mol^{-1}, $\Delta H_f^\circ(\text{PtAl}) = -195.1 \pm 10.1$ kJ mol^{-1}, $\Delta H_f^\circ(\text{ScAl}_{1.78}) = -132.6 \pm 2.6$ kJ mol^{-1}, $\Delta H_f^\circ(\text{YAl}_2) = -151.2 \pm 3.8$ kJ mol^{-1} and $\Delta H_f^\circ(\text{LaAl}_2) = -149.6 \pm 6.2$ kJ mol^{-1}. Comparisons are made with some available data and with predicted values.

1. Introduction

During recent years there has been a greatly increased interest in the phase stability and chemical bonding of intermetallic compounds. Evidence for this interest can be found in the number of theoretical and semiempirical models [1–8] which have been developed in order to predict the enthalpies of formation of binary alloy phases formed by transition metals. However, owing to the scarcity of experimental information, it has been very difficult to test many of these predictions.

We have for a long time pursued a research program which attempts to provide reliable experimental information on the thermochemistry of binary alloy systems. In the course of these investigations we have determined the enthalpies of formation of a number of borides, silicides, germanides and intermetallic compounds of transition metals. In the present work we extend this study to transition metal aluminides and have determined the standard enthalpies of formation of five compounds: PdAl, PtAl, $ScAl_{1.78}$, YAl_2 and $LaAl_2$. Comparisons will be made with earlier reported experimental data and with predicted values.

2. Experimental details

The experiments were carried out at 1473 ± 2 K in a modified Setaram-type high temperature calorimeter. Details of this apparatus and of the

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calorimeter liner assembly have already been given in earlier publications [9, 10]. Because of the possibility of reduction of the boron nitride (BN) crucible by aluminum, a beryllium oxide (BeO) crucible was used in the direct combination experiments. A survey of the phase diagrams of the considered binary systems [11–13] showed that the compounds of interest are all congruent melting and have quite high melting temperatures (above 1673 K). However, since very strong chemical interaction was expected in these alloy systems, the direct combination method was applied as well as solute–solvent drop calorimetry.

Table 1 reports the metallic purity and describes the materials used in the direct combination experiments. Palladium and aluminum powders were purchased from Johnson–Matthey AESAR: Lot#19901 and Lot#18918 respectively. Platinum powder was purchased from Baker & Co. Inc. (Lot#145). Scandium, yttrium and lanthanum in lump form were purchased from Johnson–Matthey AESAR: Lot#19065, BM1817 and BM2282 respectively. Scandium and yttrium powders were obtained by shaving on a milling machine, and the lanthanum powder by hand filing the lump just before making the pellets. In this way contamination of the sample by oxidation was avoided as far as possible

Table 2 describes the materials used in the solute–solvent experiments. Palladium metal and platinum metal were purchased from Engelhard as 2 mm wire. We also made use of palladium foil 0.025 mm thick, purchased

TABLE 1

Metallic purity and description of materials used in direct combination measurements

Metal	Metallic purity (%)	Description
Pd	99.95	200-mesh powder
Pt	99.9	325-mesh powder
Sc	99.9	80-mesh shavings
Y	99.9	80-mesh shavings
La	99.9	80-mesh shavings
Al	99.5	325-mesh powder

TABLE 2

Metallic purity and description of materials used in solute–solvent drop calorimetry

Metal	Metallic purity (%)	Description
Pd	99.99	2 mm wire
Pt	99.99	0.025 mm foil
Al	99.5	2 mm wire
Ge	99.999	2–3 mm pieces
		2–3 mm pieces

from Engelhard, and semiconductor grade germanium. Prior to the calorimetric experiments the palladium foil was annealed overnight at 1100 K in an inert atmosphere.

The PdAl and PtAl compounds used in the solute–solvent experiments were synthesized by arc melting on a water-cooled copper hearth in an inert atmosphere. The arc-melted buttons were turned over and remelted several times in order to obtain a homogeneous phase. The compounds were checked by scanning electron microscopy (SEM) and by energy-dispersive X-ray (EDX) analysis. The analysis indicated that both samples were homogeneous and of stoichiometric composition. For the calorimetric experiments samples were crushed into small pieces, ground in a mortar and sifted through 100-mesh sieves.

Calibration was achieved by dropping small pieces of high purity copper wire 2 mm in diameter from room temperature into the calorimeter at 1473 K. The enthalpy of pure copper was taken from ref. 14: 46 465 J mol^{-1} at 1473 K. Within a single series of measurements the calibrations were reproducible to $\pm 1.5\%$.

3. Results and discussion

The standard enthalpies of formation were determined by the direct combination method for all compounds investigated in the present study. For comparison, solute–solvent drop calorimetry was also applied to PdAl and PtAl. In the direct combination experiments the well-mixed powders of transition metal and aluminum, which were weighed carefully in the desired ratio, were compressed into pellets 4 mm in diameter. These pellets were dropped from room temperature into the calorimeter at 1473 ± 2 K and the enthalpy effects determined. After the experiments the alloy products were removed from the crucible and broken into smaller pieces, which were used for the heat content measurements and also for analysis by SEM and EDX and by powder X-ray diffraction. The experimental procedures can be expressed through the following equations, here shown for MeAl, where Me represents the transition metal:

$$\mathrm{Me(s,\ 298\ K) + Al(s,\ 298\ K) = MeAl(s,\ 1473\ K)} \tag{1}$$

$$\mathrm{MeAl(s,\ 298\ K) = MeAl(s,\ 1473\ K)} \tag{2}$$

From reactions (1) and (2) we get

$$\mathrm{Me(s,\ 298\ K) + Al(s,\ 298\ K) = MeAl(s,\ 298\ K)} \tag{3}$$

and the standard enthalpy of formation is obtained from

$$\Delta H_f^\circ(\mathrm{MeAl}) = \Delta H_m(1) - \Delta H_m(2) \tag{4}$$

where $\Delta H_m(1)$ and $\Delta H_m(2)$ represent the molar enthalpy changes for reactions (1) and (2) with respect to MeAl.

Since the PdAl and PtAl alloy products could not be removed completely from the crucible, compounds synthesized by arc melting were used in the heat content measurements (reaction (2)). These arc-melted samples were also checked by SEM and EDX along with reaction products. The analyses indicated that for PdAl only one phase was present in both reaction product and arc-melted sample. while for PtAl a very small amount of a second phase (Pt_3Al_2) was detected in both samples. We believe that this small amount of an undesired phase does not significantly influence the measured enthalpy of formation. This is confirmed by the agreement with the results obtained by solute–solvent drop calorimetry for the same compounds.

Liquid (Pd + Ge) alloy was used as solvent in the solute–solvent drop experiments. The standard enthalpy of formation was obtained from the enthalpy effects associated with forming a liquid alloy of the same composition from the elements and from the compound. For PdAl the reactions in the calorimeter were

$$0.35\mathrm{Pd(s,\ 298\ K)} + 0.60\mathrm{Ge(s,\ 298\ K)} + 0.05\mathrm{Al(s,\ 298\ K)}$$
$$= \mathrm{Pd_{0.35}Ge_{0.60}Al_{0.05}(l,\ 1473\ K)} \tag{5}$$

$$0.30\mathrm{Pd(s,\ 298\ K)} + 0.60\mathrm{Ge(s,\ 298\ K)} + 0.05\mathrm{PdAl(s,\ 298\ K)}$$
$$= \mathrm{Pd_{0.35}Ge_{0.60}Al_{0.05}(l,\ 1473\ K)} \tag{6}$$

where (s) and (l) denote solid and liquid respectively. From reactions (5) and (6) we get

$$0.05\mathrm{Pd(s,\ 298\ K)} + 0.05\mathrm{Al(s,\ 298\ K)} = 0.05\mathrm{PdAl(s,\ 298\ K)} \tag{7}$$

Hence the standard enthalpy of formation can be obtained from

$$\Delta H_f(\mathrm{PdAl}) = \Delta H_m(5) - \Delta H_m(6) \tag{8}$$

where $\Delta H_m(5)$ and $\Delta H_m(6)$ represent the molar enthalpy changes for reactions (5) and (6) with respect to PdAl. Similar equations can be written for PtAl forming the liquid alloy $Pd_{0.30}Ge_{0.60}Pt_{0.05}Al_{0.05}$. After the experiments the solidified ingots were examined by SEM and EDX analyses; these examinations confirmed the complete dissolution of the elements and the compounds in the melts.

The experimental results for PdAl and PtAl by the direct combination method are summarized in Tables 3 and 4 and by the solute–solvent drop method in Tables 5 and 6. The enthalpies of formation of PdAl and PtAl obtained by the two different methods are in good agreement with each other: -181.2 ± 4.4 and -183.8 ± 8.2 kJ mol^{-1} for PdAl and -189.8 ± 4.9 and -200.4 ± 8.8 kJ mol^{-1} for PtAl. Furthermore, these values agree well with the calorimetric values of Ferro and coworkers [15, 16]: -187.2 kJ mol^{-1} for PdAl and -200.8 kJ mol^{-1} for PtAl.

In Tables 3–6 the average values of ΔH_m for each reaction are given with their standard deviations δ_1 and δ_2. The uncertainties in ΔH_f were calculated from $\delta = (\delta_1{}^2 + \delta_2{}^2)^{1/2}$. From the standard enthalpies of formation

TABLE 3

Standard enthalpy of formation of PdAl by direct combination method at 1473 ± 2 K

Exp. no.	n(Pd) (mmol)	n(Al) (mmol)	n(PdAl) (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1–1	1.2878	1.2878		−141.9	−110.2	
1–2	1.7069	1.7069		−202.3	−118.5	
1–3	1.0607	1.0607		−121.5	−114.5	
1–4	1.2466	1.2466		−151.2	−121.3	
1–5	1.7384	1.7384		−206.3	−118.7	
2–1			1.1274	72.8		64.6
2–2			2.0967	134.5		64.2
2–3			1.6297	104.1		63.9
2–4			2.3635	151.6		64.1
2–5			2.5704	169.3		65.9
					−116.6 ± 4.3	64.5 ± 0.8

$\Delta H_f^\circ = (-116.6 \pm 4.3) - (64.5 \pm 0.8) = -181.2 \pm 4.4$ kJ mol^{-1}

TABLE 4

Standard enthalpy of formation of PtAl by direct combination method at 1473 ± 2 K

Exp. no.	n(Pt) (mmol)	n(Al) (mmol)	n(PtAl) (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1–1	0.9011	0.9011		−121.3	−134.7	
1–2	0.9583	0.9583		−118.1	−123.2	
1–3	0.8826	0.8826		−112.2	−127.1	
1–4	1.0439	1.0439		−135.3	−129.6	
1–5	0.7399	0.7399		− 92.4	−124.8	
2–1			1.0929	65.7		60.1
2–2			0.8682	56.1		64.6
2–3			0.9493	59.4		62.6
2–4			1.0439	63.1		60.5
					−127.9 ± 4.5	61.9 ± 2.1

$\Delta H_f^\circ = (-127.9 \pm 4.5) - (61.9 \pm 2.1) = -189.8 \pm 4.9$ kJ mol^{-1}

for PdAl or PtAl obtained by the two different methods we calculated the average of the two results. In this way the mean values of the standard molar enthalpy of formation of PdAl and PtAl were found to be

$\Delta H_f^\circ(\text{PdAl}) = -182.5 \pm 9.3$ kJ mol^{-1}

$\Delta H_f^\circ(\text{PtAl}) = -195.1 \pm 10.1$ kJ mol^{-1}

For the direct combination experiments on group III metal aluminides we adopted the $MeAl_2$ composition (Me ≡ Sc, Y, La). Examination by SEM

TABLE 5

Standard enthalpy of formation of PdAl obtained by generating the liquid alloy $Pd_{0.35}Ge_{0.60}Al_{0.05}$ at 1473±2 K

Exp. no.	n(Pd) (mmol)	n(Ge) (mmol)	n(Al) (mmol)	n(PdAl) (mmol)	ΔH_{obs} (J)	$\Delta H_m(5)$ (kJ mol^{-1})	$\Delta H_m(6)$ (kJ mol^{-1})
1–1	1.5545	3.1718		0.2643	162.7		615.6
1–2	1.5633	3.1266		0.2605	156.6		601.2
1–3	1.5859	3.1090		0.2590	157.9		609.7
2–1	2.8552	4.8946	0.4078		173.6	425.7	
2–2	2.9187	5.0034	0.4169		175.4	420.7	
2–3	2.8505	4.8865	0.4072		174.5	428.5	
						425.0±4.0	608.8±7.2

$\Delta H_f^\circ = (425.0 \pm 4.0) - (608.8 \pm 7.2) = -183.8 \pm 8.2$ kJ mol^{-1}

TABLE 6

Standard enthalpy of formation of PtAl obtained by generating the liquid alloy $Pd_{0.30}Ge_{0.60}Pt_{0.05}Al_{0.05}$ at 1473±2 K

Exp. no.	n(Pd) (mmol)	n(Ge) (mmol)	n(Pt+Al) (mmol)	n(PtAl) (mmol)	ΔH_{obs} (J)	$\Delta H_m(5)$ (kJ mol^{-1})	$\Delta H_m(6)$ (kJ mol^{-1})
1–1	1.1499	2.2998		0.1916	116.4		607.5
1–2	1.1217	2.2434		0.1869	114.6		613.2
1–3	1.1654	2.3308		0.1942	119.8		616.9
1–4	1.1273	2.2546		0.1878	114.1		607.6
1–5	1.2114	2.4228		0.2019	121.9		603.8
2–1	1.7443	3.4886	2(0.2907)		121.0	416.2	
2–2	1.7344	3.4688	2(0.2890)		115.7	400.3	
2–3	1.7377	3.4754	2(0.2896)		118.8	410.2	
2–4	1.7321	3.4642	2(0.2896)		116.6	404.0	
2–5	1.7481	3.4962	2(0.2913)		121.2	416.1	
						409.4±7.1	609.8±5.2

$\Delta H_f^\circ = (409.4 \pm 7.1) - (609.8 \pm 5.2) = -200.4 \pm 8.8$ kJ mol^{-1}

and EDX analysis indicated that 99% YAl_2 or 96% $LaAl_2$ was present in these two reaction products. However, the $ScAl_2$ sample showed a large deviation from this stoichiometry. On the basis of this analysis we carried out our measurements on $Sc_{0.36}Al_{0.64}$ ($ScAl_{1.78}$).

The calorimetric results for $Sc_{0.36}Al_{0.64}$, YAl_2 and $LaAl_2$ obtained by the direct combination method are given in Tables 7–9. The standard molar enthalpies of formation are

$$\Delta H_f^\circ(ScAl_{1.78}) = -132.6 \pm 2.6 \text{ kJ mol}^{-1}$$

TABLE 7

Standard enthalpy of formation of $Sc_{0.36}Al_{0.64}$ by direct combination method at 1473 ± 2 K

Exp. no.	n(Sc) (mmol)	n(Al) (mmol)	$n(Sc_{0.36}Al_{0.64})$ (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ (g atom)$^{-1}$)	$\Delta H_m(2)$ (kJ (g atom)$^{-1}$)
1–1	1.6928	3.0094		−53.7	−11.7	
1–2	1.6683	2.9659		−55.7	−12.3	
1–3	1.6372	2.9105		−52.3	−11.8	
1–4	1.9419	3.4523		−69.0	−13.1	
1–5	1.9041	3.3850		−63.4	−12.2	
2–1			3.7725	132.3		35.1
2–2			4.3882	157.1		35.8
2–3			4.3075	152.6		35.4
2–4			5.4644	199.1		36.4
2–5			5.5451	191.4		34.5
					−12.2 ± 0.6	35.5 ± 0.7

$\Delta H^\circ_f = (-12.2 \pm 0.6) - (35.5 \pm 0.7) = -47.7 \pm 0.9$ kJ (g atom)$^{-1}$

TABLE 8

Standard enthalpy of formation of YAl_2 by direct combination method at 1473 ± 2 K

Exp. no.	n(Y) (mmol)	n(Al) (mmol)	$n(YAl_2)$ (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1–1	1.2214	2.4428		−71.9	−58.9	
1–2	1.7911	3.5822		−104.4	−58.3	
1–3	1.5847	3.1694		−94.9	−59.9	
1–4	1.7953	3.5906		−102.9	−57.3	
1–5	1.5140	3.0280		−98.9	−65.3	
1–6	1.4657	2.9314		−91.5	−62.4	
2–1			1.1073	97.7		88.2
2–2			1.1948	108.4		90.7
2–3			1.7659	164.5		93.1
2–4			2.3602	219.9		93.2
2–5			1.4734	131.0		88.9
					−60.4 ± 3.0	90.8 ± 2.3

$\Delta H^\circ_f = (-60.4 \pm 3.0) - (90.8 \pm 2.3) + -151.2 \pm 3.8$ kJ mol^{-1}

$$\Delta H\text{of}(YAl_2) = -151.2 \pm 3.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f(LaAl_2) = -149.6 \pm 6.2 \text{ kJ mol}^{-1}$$

where the value for $ScAl_{1.78}$ was calculated by multiplying (-47.7 ± 0.9) by $(1 + 1.78)$. The experimental results obtained in the present work are shown in Fig. 1, where they are compared with available values. Because two different compositions are compared in this figure, ΔH°_f is presented in kilojoules per

TABLE 9

Standard enthalpy of formation of $LaAl_2$ by direct combination method at 1473±2 K

Exp. no.	n(La) (mmol)	n(Al) (mmol)	n($LaAl_2$) (mmol)	ΔH_{obs} (J)	$\Delta H_m(1)$ (kJ mol^{-1})	$\Delta H_m(2)$ (kJ mol^{-1})
1–1	1.2983	2.5966		−74.6	−57.5	
1–2	1.5321	3.0642		−79.5	−51.9	
1–3	1.5005	3.0010		−88.4	−58.9	
1–4	1.6197	3.2394		−90.6	−56.0	
2–1			1.0312	95.8		92.9
2–2			1.0027	85.9		85.7
2–3			1.6005	153.3		95.8
2–4			1.2210	113.1		92.7
2–5			1.7291	173.6		100.4
					−56.1±3.0	93.5±5.4

$\Delta H_f^\circ = (-56.1 \pm 3.0) - (93.5 \pm 5.4) = -149.6 \pm 6.2$ kJ mol^{-1}

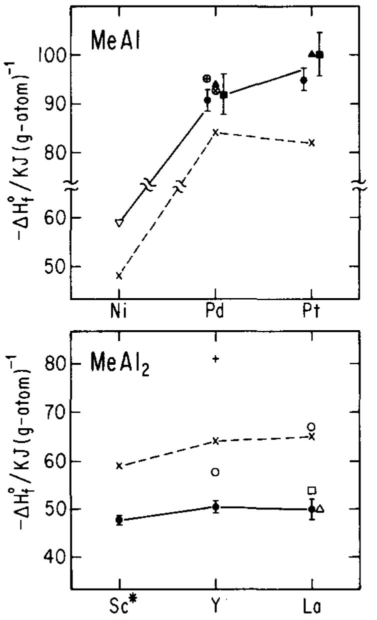

Fig. 1. Standard enthalpies of formation for MeAl and $MeAl_2$ from present investigation compared with available values: ●, present work (direct combination method); ■, present work (solute–solvent drop method); ×, de Boer *et al.* [8] (estimated); ∇, Hultgren *et al.* [17] (assessment); ▲, Ferro and coworkers [15, 16]; ⊕, Ettenberg *et al.* [18] (vapour pressure); ⊗, Pratt and Bryant [19]; +, Snyder [21]; ○, Kober *et al.* [20, 24] (e.m.f.); □, Colinet *et al.* [22]; △, Canneri and Rossi [23]. *, $ScAl_{1.78}$.

gram atom. The value for NiAl given in the figure is that selected by Hultgren *et al.* [17], though the reported experimental values were -59 to -71 kJ (g atom)$^{-1}$. The predicted values of de Boer *et al.* [8] show considerable discrepancy from our experimental values; however, the general trends are in fair agreement with experiment. Our results for PdAl agree well with those of Ettenberg *et al.* [18] (-95 kJ (g atom)$^{-1}$) and Pratt and Bryant [19] (-92.5 kJ (g atom)$^{-1}$). To the best of our knowledge an experimental value for $ScAl_{1.78}$ is not found in the literature. Our new value for YAl_2 is smaller in magnitude than those of Kober *et al.* [20] (-57.7 kJ (g atom)$^{-1}$) and Snyder [21] (-81 kJ (g atom)$^{-1}$), which were obtained by the e.m.f. method and combustion calorimetry respectively. Our value for $LaAl_2$ agrees well with those of Colinet *et al.* [22] (-54.2 kJ (g atom)$^{-1}$) and Canneri and Rossi [23] (-50 kJ (g atom)$^{-1}$), both obtained by calorimetry, but not with that of Kober *et al.* [24] (-67 kJ (g atom)$^{-1}$) obtained by the e.m.f. method.

Finally, it may be mentioned that our values for $ScAl_{1.78}$ (-47.7 kJ (g atom)$^{-1}$) and YAl_2 (-50.4 kJ (g atom)$^{-1}$) may be compared in magnitude with the calorimetric results of Kubaschewski and Heymer [25] for $TiAl_3$ (-36 kJ (g atom)$^{-1}$) and with the third-law vapor pressure data of Kematick and Franzen [26] for $ZrAl_2$ (-46 kJ (g atom)$^{-1}$).

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