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Standard enthalpies of formation of 4d aluminides by direct synthesis calorimetry

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Abstract

The standard enthalpies of formation of aluminides in the binary systems Y + Al, Zr + Al, Nb + Al, Mo + Al and Pd + Al have been determined by direct synthesis calorimetry at 1473 ± 2 K. The results are compared with earlier experimental data and with predicted values from Miedema's semi-empirical model. In systematic graphs the enthalpies of formation of the **4d**-aluminides are compared with enthalpy data for the corresponding borides, germanides and silicides.

1. Introduction

The alloys of aluminum have been the subject of increasing interest for some time. One reason for this is that their resistance to high temperature oxidation make them very suitable for a wide range of technological applications. While there is now phase diagram information on most of the important binary alloys of aluminum, there is still a lack of reliable thermochemical information. In most earlier experimental work on the thermochemistry of aluminide compounds emphasis was placed on alloys of aluminum with the **3d** metals [1, 2].

In recent communications from this laboratory we have reported new thermochemical data for some aluminides formed by **4d** metals, notably for RuAl and RhAl [3] as well as for PdAl and YAl_2 [4]. The enthalpies of formation of these compounds were all measured by direct synthesis from the elements at 1473 ± 2 K. In addition to these measurements the heat of formation to PdAl was also determined by solute–solvent drop calorimetry [4]. In the present communication these earlier studies are extended to binary alloys in the systems Zr + Al, Nb + Al and Mo + Al. Apart from this we also report new heat of formation data for Pd_2Al and Y_2Al_3 which were not studied by Jung, Kleppa and Topor [4]. Our new data allow us to obtain a systematic picture of the influence of the number of d-electrons on the heat of formation of aluminides formed by the **4d** transition metals.

We will compare our results with data existing in the literature, with corresponding values for the **4d** transition metal borides, silicides and germanides (mostly determined in this laboratory) and with predicted values from Miedema's semi-empirical model [5].

2. Experimental details and materials

The experiments were carried out at 1473 ± 2 K in a single unit differential microcalorimeter which has been described in some detail in an earlier communication [6]. All the experiments were performed in a protective atmosphere of argon gas, which was purified by passing it over titanium powder at 900 °C. Within the liner of the calorimeter the gas was passed over zirconium tubing getters. A BN (Boron Nitride) crucible was used to contain the samples.

Table 1 summarizes the metallic purities and the particle sizes of the materials used in this study. The Zr, Al, Nb, Pd and Mo samples were all purchased from Johnson-Matthey/Æsar Group while the Y metal was obtained from Alfa/Ventron.

TABLE 1. Purities and particle sizes of the pure metals used in the calorimetric experiments

Element	Purity (%)	Particle size	Comment
Y	99.9	80 mesh	Filed from ingot
Zr	99.5	80 mesh	Filed from ingot
Nb	99.8	325 mesh	Powder
Mo	99.95	100 mesh	Powder
Pd	99.95	200 mesh	Powder
Al	99.5	325 mesh	Powder

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The calorimetric measurements on the Nb + Al alloys were carried out using both commercial metallic Nb powder and Nb powder freshly filed from ingot. The Zr and Y powders were both filed from ingot. All the pure components of the alloys were checked by X-ray diffraction in order to detect possible contamination from oxides and other impurities.

The powdered elements were carefully mixed in the appropriate molar ratios, pressed into 4 mm diameter pellets, and then dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were dropped into the calorimeter in order to measure their heat contents.

Calibration of the calorimeter was performed by dropping weighed pieces of 2 mm diameter high purity copper wire from room temperature into the calorimeter at 1473±2 K. The enthalpy of pure copper at this temperature was obtained from Hultgren *et al.* [7] 46 435 J mol^{-1}. The calibrations were reproducible within ±1.2%.

3. Measurements and results

The standard enthalpies of formation of the aluminides were obtained from the difference between the results of two sets of measurements. In the first set the following reaction took place in the calorimeter

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

where m represents the molar ratio Al/Me; Me is the considered metal and s denotes solid. The reacted aluminide pellets were recovered from the calorimeter and reused in a second set of measurements in order to determine their heat contents.

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

The standard enthalpy of formation is given by

$$\Delta H_f^0 = \Delta H_m(1) - \Delta H_m(2) \tag{3}$$

where $\Delta H_m(1)$ and $\Delta H_m(2)$ are the molar enthalpy changes associated with reactions (1) and (2).

The aluminide samples were examined by X-ray powder diffraction to assess their structures and to ascertain the absence of unreacted metals. In addition the samples were also subjected to scanning electron microscopy (SEM) and X-ray microprobe analyses.

The phase diagram of the Zr + Al system indicates the existence of $ZrAl_2$ and $ZrAl_3$ phases with congruent melting points [8]. X-ray diffraction examination of both phases showed excellent agreement with the crystal structures given in the ASTM powder diffraction file and in the published literature [9–11]. The results of the SEM and X-ray microprobe analyses confirmed that these samples were single phase. The SEM of $ZrAl_2$ also indicated the presence of less than 0.3% of Ta and Sn as impurities.

The phase diagram of the Nb + Al system indicates the existence of a stable compound with the composition $NbAl_3$, which has a congruent melting point and narrow range of homogeneity [8]. Nb_3Al and Nb_2Al have also been reported to form peritectically. The crystal structures have been studied by Brauer [11], Lundin and Yamamoto [12] and by Jorda *et al.* [13]. We prepared $NbAl_3$ both from commercial 325 mesh Nb powder and from niobium metal freshly filed from ingot. The formation reaction (eqn. (1)) with filed powder was considerably slower than the reaction using the commercial powder. Moreover, the X-ray diffraction analyses also indicated significant differences. The $NbAl_3$ compound made from the fine powder showed excellent agreement with the pattern in the ASTM powder diffraction file, while the pattern from $NbAl_3$ prepared from filed Nb metal exhibited more than one phase. SEM and X-ray microanalyses confirmed that the sample made from fine Nb powder was single phase, while the samples made from filed Nb powder had at least 20% Nb_2Al. Our experience with these preparations illustrates the importance of particle size in influencing the reaction at the temperature of the calorimeter. In the present study we are reporting the results for $NbAl_3$ prepared from commercial niobium powder.

An attempt to prepare Nb_2Al at 1200 °C showed an incomplete reaction. We also prepared Nb_3Al. X-ray diffraction of this product matched quite well the pattern in the ASTM powder diffraction file. However, we detected also about 5% of Nb_2Al. In order to improve the purity of the sample we also carried out the preparation with a slight excess of Nb, corresponding to the composition $Nb_{3.2}Al$. X-ray analysis of this sample showed about 3% Nb_2Al. The SEM analysis of this sample was inconclusive. The analysis also indicated the presence of Nb_4Al; this compound has not previously been found in phase diagram and/or crystallographic work on this system.

The phase diagram of the Mo + Al system shows one congruently melting compound, namely Mo_3Al_8 [8]. In addition Mo_3Al which forms peritectically is also listed as stable. We prepared both Mo_3Al_8 and Mo_3Al. The X-ray diffraction patterns of both compounds showed excellent agreement with the patterns in the ASTM powder diffraction file and the published literature [14, 15]. The SEM and microprobe analyses confirmed that Mo_3Al_8 was single phase. However, the analysis of Mo_3Al was not conclusive due to the high porosity of the sample.

The enthalpy of formation of PdAl was determined both by direct synthesis calorimetry and by the solute–solvent drop method [4]. However, the phase diagram shows another stable phase in this system, Pd_2Al, which melts congruently at 1700 °C. The X-ray diffraction pattern of this compound agreed with the ASTM powder diffraction file and with the published literature [16, 17]. SEM and X-ray microprobe analysis indicated that the sample was essentially single phase.

The enthalpy of formation of YAl_2 was measured by Jung, Kleppa and Topor [4]. However, the phase diagram of Y + Al shows another, congruently melting stable phase, Y_3Al_2 [8, 18]. The crystal structure of this compound was determined by Dagerhamn [19, 20]. Y_3Al_2 melts congruently at 1100 °C, *i.e.* below the temperature of the calorimeter. We prepared the compound from our filed yttrium powder; the resulting sample was single phase. Since Y_3Al_2 can not readily be removed from the BN crucible, the heat content measurements were carried out on Y_3Al_2 samples prepared by arc-melting in an argon atmosphere. The arc-melted samples were tested by X-ray diffraction and SEM. The X-ray diffraction pattern agreed well with the pattern in the ASTM powder diffraction file. SEM and X-ray microprobe analyses confirmed that this sample was essentially single phase.

4. Discussion

The experimental results are summarized in Table 2. The enthalpies of formation are given as the differences between $\Delta H_m(1)$ and $\Delta H_m(2)$ (eqns. (1) and (2)) with the appropriate standard deviations. The numbers in parentheses represent the numbers of experiments averaged. The enthalpy of formation of Nb_3Al was measured both at the stoichiometric composition and with a slight excess of Nb. We reported the technique of adding a small excess of one of the components to facilitate completion of the reaction in an earlier communication [21]. It will be seen that the two reported values are in excellent agreement.

Table 3 presents a comparison of the enthalpies of formation reported in this study with corresponding values in the literature; this table also gives the values predicted from Miedema's semiempirical model [5]. We see that generally the experimental values deviate from the predicted ones. For $ZrAl_2$, $ZrAl_3$ and Y_3Al_2 the predicted values are considerably more exothermic than the experimental data, while for $NbAl_3$, Mo_3Al_8, Mo_3Al and Pd_2Al the opposite situation holds.

The heat of formation of Y_2Al_3 does not agree with the value advanced by Kober *et al.* measured by chronopotentiometry [22]. It is worth noting that Jung, Kleppa and Topor found the enthalpy of formation of the YAl_2 to be -50.4 kJ (g atom)$^{-1}$ [4]. In view of the fact that the melting point of Y_2Al_3 (1100 °C) is considerably lower than that of YAl_2 (1483 °C), the difference between the two values seems reasonable. Also, earlier measurements by Yamshchikov *et al.* [23] on YAl_3 give $\Delta H_f^0 = -47.5 \pm 1.0$ kJ (g atom)$^{-1}$.

Our values for $ZrAl_2$, $ZrAl_3$, Nb_3Al, Mo_3Al_8 and Mo_3Al are in reasonable agreement with thermodynamic data recorded in the literature [15, 24–30]. It will be noted, however, that most of the earlier data are not based on calorimetric measurement but derived indirectly from vapor pressure data or other measurements. For the three compounds for which the earlier data were obtained by calorimetry the agreement is good ($ZrAl_3$) to excellent ($NbAl_3$, Pd_2Al).

In previous communications from this laboratory Jung and Kleppa [3] and Jung, Kleppa and Topor [4] reported on the enthalpies of formation of several **4d** transition metal aluminides. In Fig. 1 we present a systematic plot of the enthalpies of formation of all **4d** aluminides studied in this laboratory compared with corresponding data for **3d** transition metal aluminides. The values for the **3d** aluminides are cited from De Boer *et al.* [5]

TABLE 2. Summary of standard enthalpies of formation of **4d** aluminides. All data in kJ (g atom)$^{-1}$

Compound	m = Al/Me	$\Delta H_m(1)$	$\Delta H_m(2)$	ΔH_f^0
Y_3Al_2	0.67	10.2 ± 1.1 (6)	50.2 ± 1.2 (5)	−40.0 ± 1.6
$ZrAl_2$	2.0	−20.6 ± 1.4 (6)	31.5 ± 0.8 (6)	−52.1 ± 1.6
$ZrAl_3$	3.0	−18.0 ± 0.4 (5)	30.4 ± 1.2 (6)	−48.4 ± 1.3
$NbAl_3$	3.0	−10.5 ± 0.5 (6)	30.0 ± 0.4 (6)	−40.5 ± 0.6
Nb_3Al	0.33	16.0 ± 0.7 (6)	29.7 ± 0.7 (6)	−13.7 ± 1.0
	0.31*	14.9 ± 0.7 (6)	28.2 ± 0.6 (4)	−13.3 ± 0.9
Mo_3Al_8	2.67	−2.3 ± 0.3 (6)	30.7 ± 0.6 (6)	−33.0 ± 0.7
Mo_3Al	0.33	8.1 ± 1.0 (6)	30.4 ± 1.2 (6)	−22.3 ± 1.6
Pd_2Al	0.50	−52.0 ± 1.6 (5)	35.3 ± 0.9 (5)	−87.3 ± 1.8

Numbers in parentheses indicate numbers of experiments averaged.

*Measurements refer to the $Nb_{3.2}Al$ composition. Both $\Delta H_m(1)$ and $\Delta H_m(2)$ were corrected for the heat content of the excess Nb.

TABLE 3. Comparisons of ΔH_f^0 from present work with earlier experimental data and with predicted values from Miedema's semi-empirical model

Compound	ΔH_f^0 (exptl.) kJ (g atom)$^{-1}$ This work	ΔH_f^0 (exptl.) kJ (g atom)$^{-1}$ Literature	Method	ΔH_f^0 (predicted) kJ (g atom)$^{-1}$
Y_3Al_2	−40.0	−87.9 (22)	Chronopotentiometry	−60
$ZrAl_2$	−52.1	−45.8 (24) −56.9 (25)	Vapor pressure Free energy, ΔG	−72
$ZrAl_3$	−48.4	−40.8 (24) −44.4 (26)	Vapor pressure Calorimetry	−57
$NbAl_3$	−40.5	−33 (27) −41.0 (2) −36.4 (28, 29)	Vapor pressure Calorimetry Calculated from volume change	−29
Nb_3Al	−13.7	−19 (27) −21 (28, 29)	Vapor pressure Calculated from volume change	−28
Mo_3Al_8	−33.0	−39.3 (15)	Vapor pressure	−17
Mo_3Al	−22.3	−21.4 (15)	Vapor pressure	−15
Pd_2Al	−87.3	84.9 (30)	Calorimetry	−68

Numbers in parentheses are reference numbers.

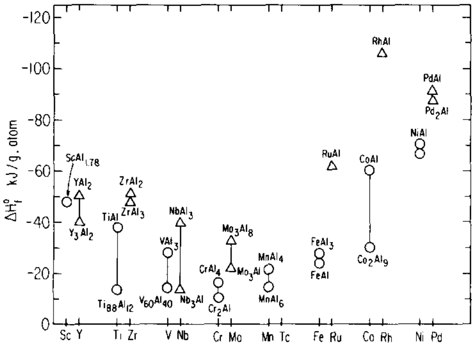

Fig. 1. Comparison of the enthalpies of formation of **3d** and **4d** aluminides.

and from Hultgren *et al.* [7]. The data show that the **4d** aluminides generally are somewhat more exothermic than the corresponding **3d** compounds. However, the trends are very similar in both sets of alloys.

Pasturel *et al.* [31] developed a theory which aims at the prediction of the energies of formation of alloys of transition metals with elements which have only s and p electrons in their outer shells. In this paper they specifically considered **3d** aluminides. Comparing the data in Fig. 1 with their predictions we observe some similarities. In our systematic plots of ΔH_f^0 we find the roughly parabolic shape of the curve predicted by the theory. Thus both in theory and in experiment we find the most weakly bound compounds in the middle of the transition series while the most strongly bound alloys are located near the end of the series. However, an important difference is found in the fact that while the enthalpy of formation of NiAl is roughly comparable to that of CoAl, RhAl is definitely more exothermic than PdAl.

In Fig. 2 we compare the **4d** aluminides with the corresponding **4d** borides. If more than one compound in a binary system was studied, we selected to plot the value for the compound with the larger amount of Al. The enthalpies of formation of MoB, NbB_2, $RuB_{1.1}$ and $RhB_{1.1}$ were reported by Meschel and Kleppa [21, 32, 33]; the heats of formation of YB_4 and Pd_5B_2 are those of Topor and Kleppa [34, 35], while the plotted value for ZrB_2 is cited from Johnson *et al.* [36]. It is evident from Fig. 2 that the trends of the thermochemical data for aluminides and borides differ considerably in spite of the fact that boron and aluminum are immediate neighbors in Column III of the periodic table.

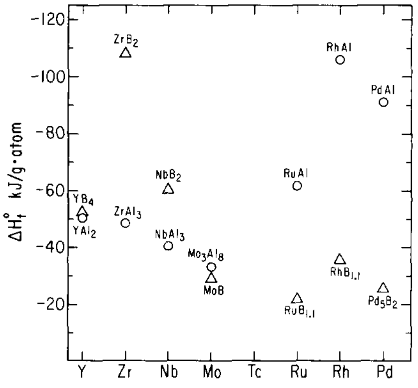

Fig. 2. Comparison of the enthalpies of formation of **4d**-aluminides with corresponding borides.

In Fig. 3 we compare the enthalpies of formation of the **4d** aluminides with corresponding data for germanides, also studied in this laboratory by Jung and Kleppa [37, 38]. This figure illustrates that the plotted data exhibit some interesting similarities. For both groups of compounds there is a decrease in the magnitude of the enthalpy of formation from Y to Mo and an increase from Mo to Pd. Even the sharp rise from Ru to Rh and the subsequent decrease to Pd is exhibited by both groups.

A comparison of the aluminide data with the corresponding silicides is presented in Fig. 4. In this figure the enthalpies of formation of Y_5Si_3, Zr_5Si_3, RuSi, RhSi and Pd_2Si are quoted from Topor and Kleppa [39–41], while the data for $MoSi_2$ and Nb_5Si_3 are taken from Robins and Jenkins [42] and Gorelkin *et al.* [43] respectively. The trend illustrated by Figs. 3 and 4 indicate that the enthalpies of formation of the transition metal compounds of Al, Ge and Si show considerable similarity.

We attempted to correlate the observed enthalpies of formation with the difference in the electronegativities of the elements and also with the melting point of the compounds. However, there is no clear correlation with these variables. For example, the electronegativity differences between the component elements in RuAl and RhAl are nearly the same, while the enthalpies of formation differ by a factor of two. Similarly, the melting points of PdAl, $NbAl_3$ and Mo_3Al_8 all fall within a range of ±50 °C. However, the enthalpies of formation differ by a factor of three. It is difficult to assess this effect completely since the melting point of RhAl is not known.

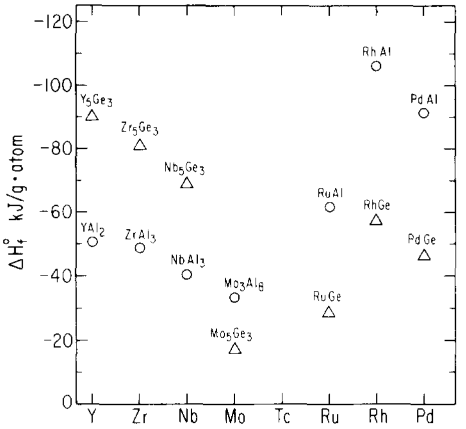

Fig. 3. Comparison of the enthalpies of formation of **4d**-aluminides with corresponding germanides.

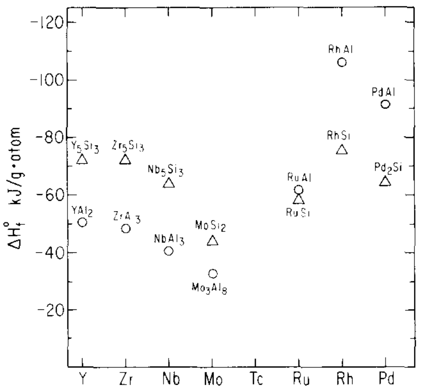

Fig. 4. Comparison of the enthalpies of formation of **4d**-aluminides with corresponding silicides.

Colinet, Bessoud and Pasturel [44] developed a statistical model based on interaction of clusters of atoms and their nearest neighbor shells. Since the predictions made in this theory apply for enthalpies of liquid–liquid mixing, we cannot make a direct comparison with our data. However, this study also considers the bonding character of Ni, Pd and Pt–Al alloys. Their calculations indicate that bonding in transition metal–aluminum compounds is more covalent than ionic which correlates with our observations. Moreover, Colinet *et al.* as well as Pasturel *et al.* [31] show that the formation of bonding hybrids between the d-electrons of the transition metal and the s and p electrons of Al contribute significantly to the heat of formation and hence to the stability of these compounds. This is consistent with the trends we observed where the predominant effect is the influence of the number of **4d** electrons of the transition metal component on the observed enthalpies of formation. We are planning to explore this further by extending this study to the enthalpies of formation of the aluminides of the **5d** transition metals.

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