

Standard enthalpies of formation of AlB_{12} and Al_4C_3 by high temperature direct synthesis calorimetry

S.V. Meschel, O.J. Kleppa

The James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA

Received 2 March 1995

Abstract

The standard enthalpies of formation of $\alpha\text{-AlB}_{12}$ and of Al_4C_3 have been determined by high temperature direct synthesis calorimetry at 1473 ± 2 K. The experiments were carried out in two different calorimeters of similar but not identical constructions. The following average values of ΔH_f^0 are reported: for $\alpha\text{-AlB}_{12}$, -11.4 ± 0.6 kJ (mol of atoms) $^{-1}$; for Al_4C_3 , -18.3 ± 1.0 kJ (mol of atoms) $^{-1}$. The results are compared with earlier experimental values reported in the literature and with values predicted from Miedema's semi-empirical model.

Keywords: Enthalpies of formation; Direct synthesis calorimetry

1. Introduction

The borides and carbides of aluminum have been the subject of significant scientific interest for a number of years. The electrical and optical properties of AlB_{12} were reviewed by Berezin et al. [1]. Among its crystalline modifications, $\alpha\text{-AlB}_{12}$ has been considered a promising compound for high temperature thermoelectric applications. Its potential utilization to provide light-weight armor for aircraft protection was considered by Wilkins [2].

Al_4C_3 is an important compound in the production technology of aluminum metal. Its thermochemical properties are of special interest in connection with the possible development of new technologies in the production of this metal; they have been studied by a wide range of different experimental methods since the turn of the century. However, in spite of this, we found to our surprise that there is still considerable uncertainty about the value for the enthalpy of formation Al_4C_3 . Since the 1930s, the reported and/or calculated enthalpy values for this compound given in the literature range from about -12 to -54.5 kJ (mol of atoms) $^{-1}$; most of the values fall between -18 and -32 kJ (mol of atoms) $^{-1}$ [3].

The enthalpy of formation of AlB_{12} has been derived by Kant and Moon (4) from vapor pressure–mass spectroscopy data and has been measured by fluorine bomb calorimetry by Domalski and Armstrong [5,6]. The reported values for the enthalpy of formation of Al_4C_3 from the elements have been

derived from equilibrium measurements, oxygen bomb calorimetry, vapor pressure–mass spectroscopy, e.m.f. measurements and acid solution calorimetry at 110°C . The available data for this compound were reviewed by King and Armstrong [3] and more recently by Rinehart and Behrens [7].

However, since there is considerable uncertainty about which value(s) should be accepted, particularly for Al_4C_3 , we decided to attempt to measure the standard enthalpies of formation for both of these compounds by high temperature direct synthesis calorimetry.

During recent years, communications from this laboratory have reported new information on the standard enthalpies of formation, based on this technique, for several borides, germanides and carbides of transition metals, as well as for some aluminum intermetallic compounds [8–13]. We have found this technique to be quite useful, even when the enthalpies of formation are numerically quite small, as is the case, for example, for Cu_3Ge , OsGe_2 and W_2B_5 [9,11,13]. The present investigation also provided us with an opportunity to carry out our measurements on the two binary compounds in two different high temperature calorimeters of similar but not of identical designs.

The phase diagrams and the structural information for the binary systems $\text{Al} + \text{B}$ and $\text{Al} + \text{C}$ are readily available in the published literature [14–19]. We shall compare our new calorimetric values with data reported in the published literature and with values predicted from the semiempirical model of Miedema and coworkers [20].

2. Experimental and materials

The initial experiments were carried out at 1473 ± 2 K in a single-unit differential microcalorimeter which has been described in an earlier communication from this laboratory [21] (calorimeter I). All the experiments were performed under a protective atmosphere of argon gas, purified by passing it over titanium chips at about 900 °C. A crucible made from boron nitride was used to contain the samples. The aluminum and carbon were purchased from Johnson Matthey–Aesar, while boron was obtained from Alfa Products–Ventron. The purities were 99.0% for C, 99.5% for Al and 99.7% for B. The particle sizes of the powders as purchased were – 300 mesh for C, – 325 mesh for Al and – 60 mesh for B. The boron sample consisted of crystalline material in the rhombohedral form. Prior to use, it was ground in an agate mortar to reduce the particle size and to provide fresh surfaces for the reactions. The powder was sifted through a 150 mesh sieve to obtain particles suitable for the calorimetric experiments.

The second set of experiments was carried out at the same temperature (1473 ± 2 K) in a second high temperature calorimeter which has a furnace which is a revised version of the earlier unit (calorimeter II).

The two components were carefully mixed in the appropriate molar ratio, pressed into 4 mm pellets and dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were also dropped into the calorimeter from room temperature in order to measure their heat contents. Between the two sets of experiments the samples were kept in a vacuum desiccator to prevent any possible reaction with oxygen or moisture. The weight stability of Al_4C_3 was tested over a period of 3 weeks and no change was observed.

Calibration of the calorimeter was achieved by dropping weighed segments of high purity copper wire of 2 mm outside diameter from room temperature into the calorimeter at 1473 ± 2 K. The enthalpy of pure copper at this temperature, 46465 J mol^{-1} , was obtained from Hultgren et al. [22]. The calibrations were reproducible to within $\pm 1.2\%$.

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

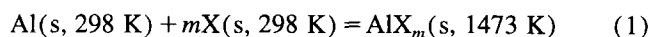
The phase diagram of the Al + B system shows one congruently melting compound, AlB_{12} , which melts at 2150 °C [14]. Carlson [16] discusses the differences of opinions voiced in the literature regarding the stability of the different crystalline modifications of this compound. AlB_{12} exists in three structural forms: the tetragonal α - AlB_{12} , the body-centered orthorhombic β - AlB_{12} , and γ - AlB_{12} which has a primitive orthorhombic cell [17]. Samsonov et al. [18] state that β - AlB_{12} is stabilized by impurities and as such may not be a true binary compound. We prepared AlB_{12} in the calorimeter. The X-ray diffraction pattern of our sample matched well the

pattern of the α tetragonal form in the ASTM *Powder Diffraction File*. We found no evidence of any unreacted elements or of other phases such as AlB_2 or β - AlB_{12} .

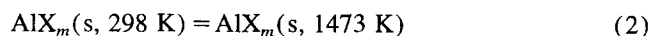
The phase diagram of the Al + C system shows the formation of a single compound, namely Al_4C_3 , which melts peritectically at about 2500 °C [14]. However, melting temperatures of 1990 °C and 1850 °C have been reported by Schuster [15] and by Carlson [16] respectively. The X-ray diffraction pattern of a stoichiometric mixture of Al + C, reacted in the calorimeter to form Al_4C_3 , matched well the pattern in the ASTM *Powder Diffraction File*. However, we found also about 7–10% of unreacted Al. We therefore decided to prepare another sample with some excess carbon. The addition of an excess of one of the two components may aid the completion of the reaction, as we found in the preparation of some transition metal borides and carbides [11,12]. The X-ray diffraction pattern of this modified sample showed no unreacted Al. It yielded an excellent match with the pattern in the ASTM *Powder Diffraction File*. While a small amount of carbon could be observed, SEM and X-ray microprobe analyses confirmed that this sample was a single phase, apart from the surplus carbon.

3. Results and discussion

The standard enthalpies of formation determined in this study were obtained as a difference between the results of two sets of measurements. In the first set the following reaction took place in the calorimeter:



Here m is the molar ratio of X to Al, X represents B or C and s denotes solid. The reacted pellets were re-used in a subsequent set of measurements to determine their heat contents:



The standard enthalpy of formation is given by

$$\Delta H_f^0 = \Delta H(1) - \Delta H(2) \quad (3)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per mole of atoms associated with reactions (1) and (2).

The experimental results are summarized in Table 1. The heat effects associated with reactions (1) and (2) are given in kilojoules per mole of atoms as the averages of five to seven consecutive measurements with the appropriate standard deviations. The last column shows the standard enthalpies of formation of the considered phases. The standard deviations in this column also reflect the contribution from the uncertainty in the calibrations. As Table 1 shows, the measurements for both compounds were carried out in two different calorimeters (I and II) of similar design but of somewhat different constructions. The table shows that the agreement between the two sets of values is quite good. Binford et al. [23] measured the heat content of Al_4C_3 up to about 1800 K. From their measurements its heat content at

Table 1
Summary of standard enthalpies of formation for α -AlB₁₂ and Al₄C₃

Compound	<i>m</i>	Calorimeter used ^a	$\Delta H(1)$	$\Delta H(2)$	ΔH_f°
α -AlB ₁₂	12.0	I	15.7 ± 0.4(6)	27.5 ± 0.4(6)	-11.8 ± 0.6
		II	15.7 ± 0.3(6)	26.7 ± 0.2(6)	-11.0 ± 0.4
Al ₄ C ₃ ^b	0.75 + 0.08 0.75 + 0.11	I	8.5 ± 0.4(6)	27.0 ± 0.5(6)	-18.5 ± 0.5
		II	8.7 ± 0.6(6)	26.7 ± 0.8(6)	-18.0 ± 1.0

^a I and II refer to the two different calorimeters of similar designs.

^b In calculating $\Delta H(1)$ and $\Delta H(2)$ for Al₄C₃, corrections were made for the surplus carbon based on its heat content as given by Hultgren et al. [22].

1473 K is 28.7 kJ (mol of atoms)⁻¹. Table 1 shows that our two values are slightly less endothermic.

In Table 2 we compare the standard enthalpies of formation reported in the present work with a wide range of experimental values from the published literature and with predicted values from the semiempirical model of Miedema and coworkers [20]. Our value for the heat of formation of α -AlB₁₂ agrees well with the value derived from the mass spectrometry determination by Kant and Moon [4] but is somewhat less exothermic than the values of Domalski and Armstrong [5,6] obtained by fluorine bomb calorimetry. In their earlier study these workers discussed the uncertainties arising from the impurities present as well as due to the uncertainties in the heats of formation of the combustion products. According to the cited references, the sample con-

sisted of 96–97% α -AlB₁₂. Among the major impurities were Al, B₂O₃, BN and B₄C. Since our starting materials were 99.5–99.7% pure and the compounds were prepared by direct synthesis, we are confident that we were able to avoid these problems. It is worth noting that our experimental precision is considerably better than given in the fluorine bomb calorimetry study. Table 2 also shows that our experimental value for the enthalpy of formation of α -AlB₁₂ differs very much from the predicted value; in fact, even the algebraic sign is different. This may be because the model of Miedema and coworkers does not take the boron–boron bonding in the compound into consideration. This is expected to contribute significantly to the stability of compounds with high boron content. In our earlier communication on rare earth borides and carbides we noted that the predicted values often differ

Table 2
Comparison of the standard enthalpies of formation reported in this study with experimental values in the published literature and with predicted values from the semiempirical model of Miedema and coworkers

Compound	Reference	Method	ΔH_f° (kJ (mol of atoms) ⁻¹)	
			Experimental	Predicted
AlB ₁₂	Domalski and Armstrong [5]	Fluorine bomb calorimetry	-19.8 ± 3.5	+9
	Domalski and Armstrong [6]	Fluorine bomb calorimetry	-15.4 ± 3.2	
	Kant and Moon [4]	Vapor pressure–mass spectroscopy	-11.9 ± 1.3	
	This work	Direct synthesis calorimetry	-11.4 ± 0.6	
Al ₄ C ₃	Prescott and Hincke [24]	Equilibrium study	-32.1	-34
	Meichsner and Roth [25]	Oxygen bomb calorimetry	-12.0 ± 1.8	
	Roth [26]	Oxygen bomb calorimetry	-23.9 ± 1.8	
	Meschi and Searcy [27]	Vapor pressure–mass spectroscopy	-30.5 ± 6.0	
	Campbell [28]	Vapor pressure–mass spectroscopy (AlF ₃)	-21.5 ± 1.8	
	King and Armstrong [3]	Oxygen bomb calorimetry	-29.7 ± 0.7	
	Grjotheim et al. [29]	Vapor pressure–mass spectroscopy (ΔG ; 1400 K)	-13.1 ± 1.0	
	Thoburn [30]	Differential thermal analysis (third law)	-18.1 ± 0.4 ^a	
	Plante and Schreyer [31]	Vapor pressure–mass spectroscopy	-30.8 ^a	
	Blachnik et al. [32]	Solution calorimetry (HCl; 110 °C)	-29.6 ± 0.3	
	Choudary and Beldon [33]	Vapor pressure–mass spectroscopy (ΔG ; 1873 K)	-18.9 ± 1.6	
	Rinehart and Behrens [7]	Vapor pressure–mass spectroscopy (third law)	-25.1 ± 4.9 ^a	
	This work	Direct synthesis calorimetry	-18.3 ± 1.0	

^a Based on heat of vaporization of Al taken from Hultgren et al. [22] as 329.3 ± 2.1 kJ mol⁻¹.

considerably from the experimental measurements in these systems [12].

In Table 2 we are also comparing our value for the enthalpy of formation of Al_4C_3 with a number of values in the published literature. Table 2 shows that there is considerable discrepancy between the reported data. The reason for this is not immediately obvious. Some uncertainties may arise if the measured reaction is slightly incomplete or if the carbides are extensively exposed to air; many carbides react readily with moisture in the atmosphere [12]. In oxygen bomb calorimetry the enthalpy of formation is evaluated as the difference between two large numbers. ΔH_f^0 represents about 5% of these numbers. Hence, any small error in the measurements may give rise to a significant error in the ΔH_f^0 . The heats of formation calculated from the mass spectroscopy experiments are also influenced by the adopted value for the heat of vaporization of Al. In the combustion experiments the value is influenced by the value selected for the heats of formation of Al_2O_3 and AlF_3 . The uncertainties in these quantities contribute significantly to the total error. It is worth noting that the uncertainties cited in the literature usually reflect only experimental precision, rather than a total error estimate incorporating the uncertainties in the above mentioned quantities. The data in the literature were summarized by King and Armstrong [3] and more recently by Rinehart and Behrens [7]. Our measurements agree with one of the more recent values derived from mass spectrometry by Choudary and Belton [33] and with the differential thermal analysis study of Thoburn [30]. Table 2 shows that our value falls in the lower half of the reported data. It is worth noting that our work differs from previous studies in some significant aspects.

- (1) Elemental Al was completely absent.
- (2) The reactants had high purities.
- (3) There was no ambiguity regarding the crystalline form of reactant or product.
- (4) Samples were tested for weight stability in order to rule out reaction with moisture or with oxygen in air.
- (5) Completeness of reaction was proved by X-ray diffraction and by SEM.
- (6) The direct synthesis calorimetry methodology provided a considerable statistical advantage over evaluation from a difference between large numbers.
- (7) There was no need to use further terms or additional thermodynamic functions to evaluate the final result.

The predicted value for Al_4C_3 from the semiempirical model of Miedema and coworkers is considerably more exothermic than our experimental value. This is consistent with our earlier observations for rare earth carbides for which the predicted values are always more exothermic than our experimental values [12].

Acknowledgements

This study has been supported by the US Department of Energy under Grant DE-FG02-88ER45363 and has also ben-

efitted from the MRSEC facilities at the University of Chicago. We are indebted to Dr. A.M. Davis for help with the SEM work.

References

- [1] A.A. Berezin, O.A. Golikova, V.R. Zaitsev, M.M. Kazanin, V.M. Orlov and E.N. Tkalenko in V.I. Matkovich (ed.), *Boron and Refractory Borides*, Springer, New York, 1977, pp. 52–64.
- [2] M.K. Wilkins, in V.I. Matkovich (ed.), *Boron and Refractory Borides*, Springer, New York, 1977, pp. 633–648.
- [3] R.C. King and G.T. Armstrong, *J. Res. Natl. Bur. Stand. A*, 68 (1964) 661–668.
- [4] A. Kant and K.A. Moon, *High Temp. Sci.*, 9 (1977) 131–145.
- [5] E.S. Domalski and G.T. Armstrong, *Rep. NBS-8962*, October 1965 (National Bureau of Standards, Washington, DC).
- [6] E.S. Domalski and G.T. Armstrong, *J. Res. Natl. Bur. Stand. A*, 71 (1967) 307–315.
- [7] G.H. Rinehart and R.G. Behrens, *J. Chem. Thermodyn.*, 12 (1980) 205–215.
- [8] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 177 (1991) 159–166.
- [9] S.V. Meschel and O.J. Kleppa, *Metall. Trans. A*, 22 (1991) 2162–2165.
- [10] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 197 (1993) 75–81.
- [11] S.V. Meschel and O.J. Kleppa, *J. Chim. Phys.*, 90 (1993) 349–354.
- [12] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 205 (1994) 165–168.
- [13] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 216 (1994) L13–L15.
- [14] T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak (eds.), *Binary Alloy Phase Diagrams*, 2nd edn., American Society for Metals, Metals Park, OH, 1990.
- [15] J.C. Schuster, *J. Phase Equilib.*, 12 (1991) 546–548.
- [16] O.N. Carlson, *Bull. Alloy Phase Diagrams*, 11 (1990) 560–566.
- [17] J.S. Kasper, M. Vlasse and R. Naslain, *J. Solid State Chem.*, 20 (1977) 281–285.
- [18] G.V. Samsonov, V.A. Neronov and L.K. Lamikhov, *J. Less-Common Met.*, 67 (1979) 291–296.
- [19] H. Duschaneck and P. Rogl, *J. Phase Equilib.*, 15 (1994) 543–552.
- [20] A.K. Niessen, F.R. de Boer, R. Boom, P.F. de Chatel, W.C.M. Mattens and A.R. Miedema, *Calphad*, 7 (1983) 51–70.
- [21] O.J. Kleppa and L. Topor, *Thermochim. Acta*, 139 (1989) 291–297.
- [22] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, OH, 1973, p. 154.
- [23] J.S. Binford, J.M. Strohmenger and T.H. Hebert, *J. Phys. Chem.*, 71 (1967) 2404–2408.
- [24] C.H. Prescott, Jr., and W.B. Hincke, *J. Am. Chem. Soc.*, 50 (1928) 3228–3237.
- [25] A. Meichsner and W.A. Roth, *Z. Elektrochem.*, 40 (1934) 19–26.
- [26] W.A. Roth, *Z. Elektrochem.*, 48 (1942) 267.
- [27] D.J. Meschi and A.W. Searcy, *J. Phys. Chem.*, 63 (1959) 1175–1178.
- [28] C.S. Campbell, *Proc. 7th Conf. of Metals Society, London, 1962*, pp. 412–416.
- [29] K. Grjotheim, O. Herstad and K. Stahl Johannessen, *Z. Anorg. Allg. Chem.*, 328 (1964) 267–271.
- [30] W.J. Thoburn, *Ph.D. Dissertation*, University of Toronto, 1964.
- [31] E.R. Plante and C.H. Schreyer, *J. Res. Natl. Bur. Stand. A*, 70 (1966) 253–257.
- [32] R.O.G. Blachnik, P. Gross and C. Hayman, *Trans. Faraday Soc.*, 66 (1970) 1058–1064.
- [33] U.V. Choudary and G.R. Belton, *Metall. Trans. B*, 8 (1977) 531–534.