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Critical assessment and thermodynamic modeling of the Al-C system

G. Deffrennes, B. Gardiola, M. Allam, D. Chaussende, A. Pisch, J. Andrieux, R Schmid-Fetzer, O. Dezellus

Abstract

The Al-C system is the backbone of wide variety of applications in multicomponent systems, and was therefore studied intensively. Yet, considerable disagreements remain in the reported data, and the Al-C phase equilibria as well as the standard enthalpy of formation of Al_4C_3 are still debated. In order to establish a reliable thermodynamic description of the Al-C system a critical assessment of the literature was conducted. The data on the solubility of carbon in liquid Al and on the thermodynamic properties of Al_4C_3 were assessed, and the peritectic decomposition temperature of Al_4C_3 was confirmed at 2425 ± 15 K by thermal analysis. Thermodynamic modeling of the Al-C system is provided and compared to previous works. The proposed description was found to be more robust and to carry more physical meaning than any previous modeling of the system, which imply an easier extrapolation of the binary into higher-order systems.

1. Introduction

The Al-C system is of great interest as it is a cornerstone in a wide variety of applications in multicomponent systems. Carbon in aluminum is relevant for carbon materials reinforced aluminum composites [1]. The Al-C-O ternary is of industrial interest for the carbothermic reduction of alumina [2–6]. Aluminum and carbon reacts with early transition metals to form the so-called MAX phases [7] as for instance Ti_2AlC and Ti_3AlC_2 [8]. The Mg-Al-C system is of interest as carbon inoculation is the major industrial technique to refine the microstructure of Mg-Al alloys [9,10]. Recently, aluminum was used in the design of advanced lightweight steels alloys [11–13].

Thermodynamic modeling of the Al-C system was conducted on the basis of the same experimental information by Qiu et al. [14], Gröbner et al. [15,16] and Ohtani et al. [17]. This system is rather simple as Al_4C_3 is the only stable compound [18]. Therefore, solid aluminum and graphite together with a liquid phase and the Al_4C_3 carbide are considered in this work.

For the solubility of carbon in liquid aluminum, two conflicting trends can be observed in the literature data for temperatures above 2330 K. Different choices were made in the most recent modeling of the system [14,15,17]. For the Al_4C_3 phase, there are significant discrepancies on the reported standard enthalpy of formation of the phase as well as its thermal stability. Regarding its standard enthalpy of formation, a compelling discrepancy ranging from $-17.9 \text{ kJ}\cdot\text{mol}^{-1}$ of atoms to $-37.8 \text{ kJ}\cdot\text{mol}^{-1}$ of atoms is highlighted in the experimental literature. Regarding its peritectic decomposition temperature, the debate was left open by Schuster [18] who called into question the value of 2408 K measured by Gitelsen et al. [19], suggesting a decomposition temperature roughly 150 K lower. These temperatures are close to the 1 bar boiling point of liquid Al which makes any experimental investigation difficult.

In conclusion, considerable disagreements remains in the literature regarding the Al-C phase equilibria as well as the standard heat of formation of Al_4C_3 making the data selection in the scope of a thermodynamic modeling delicate. In the present work, the literature regarding the solubility of carbon in liquid Al, the thermal stability of the Al_4C_3 phase and its standard enthalpy of formation is critically reviewed and selected. The decomposition temperature of Al_4C_3 is confirmed by the mean of simple thermal analysis. Finally, the thermodynamic properties of the liquid and Al_4C_3 phases are modeled, and the proposed description is compared to the previous modeling of the system of the Al-C system [14,15,17].

2. Critical assessment of the experimental literature data

2.1 Solubility of carbon in liquid Al

The solubility of carbon in liquid Al was reported by various authors. In the high-temperature range, the available literature data [2,19–23] are plotted in Fig. 1. The literature data are consistent with each other in the 1700 – 2330 K range, however two conflicting trends can be observed in the 2330 – 3000 K range. The liquidus reported by Baur et al. [20] and Gjerstad [22] is significantly aluminum richer than the one reported by Stroup [2], Ginsberg et al. [21], Gitlesen et al. [19] and Oden et al. [23]. It is to note that there is a typing mistake in Gjerstad manuscript [22]. The solubility at 2633 K is reported to be 28.57 at% instead of being 22.57 at% as corrected in a figure in the manuscript [22] as well as in the figure reported by Gjerstad co-workers [6].

In the low-temperature range, the solubility of C in liquid Al was measured by Simensen [24]. In addition, Dorward [25] deduced the low-temperature liquidus from the literature data. However, Dorward [25] noted that his estimation is somewhat doubtful, and as the proposed values are two orders of magnitude higher than the measurements from Simensen [24], they were discarded.

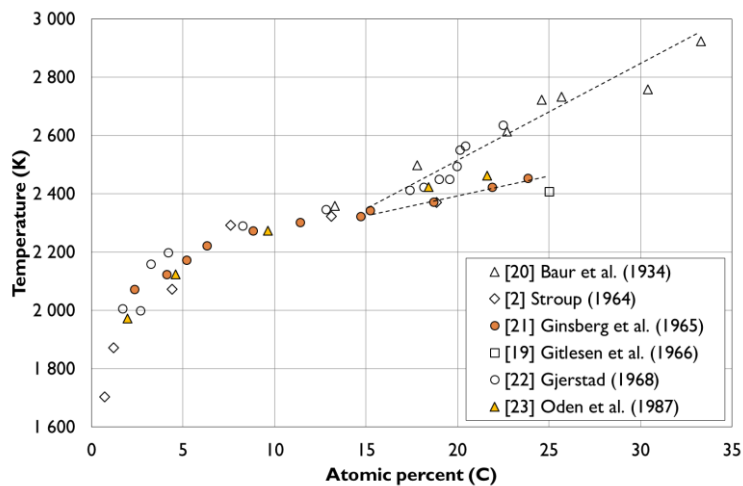


Fig. 1 Literature data on the solubility of carbon in liquid Al in the high-temperature range. The two conflicting trends above 2330 K are highlighted by dashed lines. The solid symbols represent the data selected in the present assessment.

The available details regarding the literature experimental solubility measurements are reviewed in Tables 1, 2 and 3. Stroup [2] plotted the unpublished solubility data measured by Long without giving any experimental information. Therefore, those data are not selected in the present assessment. The experimental details regarding the measurements made by Gitlesen et al. [19] were described by the authors in a previous study [26]. Gjerstad [22] reported in his manuscript two different experimental methods depending if the temperature was below or above the Al_4C_3 decomposition temperature of 2408 K reported by Gitlesen [19].

Three sources of error, and therefore of disagreements, are investigated: first, the fact that the equilibrium may not have been reached, then the uncertainties on the temperature measurements, and finally the uncertainties on the composition measurements.

Table 1 Materials, crucible and oven atmosphere as reported in the literature on the experimental determination of carbon solubility in liquid Al.

Ref	Materials	Crucible	Atmosphere
[20] 34Bau	2g samples (Al powder and 91wt% pure Al ₄ C ₃ with 9wt% of Al ₂ O ₃ and AlN<0.5wt% as impurities)	Graphite	Hydrogen
[2] 64Str	-	-	-
[21] 65Gin	99,99wt% pure Al ingots	Thick graphite crucibles (150g after being filled)	Argon
[19] 66Git	97wt% pure Al ₄ C ₃ with C and Al as impurities	Graphite	Argon
[22] 68Gje	20g 99.998wt% pure Al lumps, 99.92wt% pure graphite, 96.0wt% pure Al ₄ C ₃ with 1.7wt% Al and 2.3wt% C as impurities	T<2408K : Porous homemade Al ₄ C ₃ inner crucible placed inside of a graphite crucible T>2408K : “High-density” graphite crucible with a screwed lid	Argon
[23] 87Ode	99.99 wt% pure Al	Sealed Graphite crucible	99.995 wt% pure argon
[24] 89Sim	0.5g samples taken from electrolysis cells	-	-

Table 2 Temperature range, holding time and methods of temperature measurements as reported in the literature on the experimental determination of carbon solubility in liquid Al.

Ref	Temperature range	Holding time	Temperature measurements
[20] 34Bau	2358-2923 K	As fast as possible to prevent Al evaporation	Optical pyrometer through water-cooled windows after a visual determination of the liquidus. The reported value are the mean of three measurements.
[2] 64Str	1700-2370 K	-	-
[21] 65Gin	2073-2453 K	Based on a visual observation, see discussion below	Optical micro-pyrometer
[19] 66Git	2408 K	Temperature ramp	Disappearing-filament optical pyrometer calibrated using a tungsten-strip lamp. The radiations from the sample passed through a silica glass window and were reflected by a mirror before reaching the pyrometer. Absorption was corrected using a temperature source at 2273 K
[22] 68Gje	2000-2636 K	T<2408K : 7-20 min T>2408K : 3-11 min	Similar to [19] 66Git
[23] 87Ode	1973-2463 K	From 90 min at 1973 K to 10 minutes at 2463 K	Thermocouple (W – 5% Re / W – 26% Re)
[24] 89Sim	1233-1275 K	-	-

Table 3 Aluminum evaporation, cooling condition and methods of composition measurements as reported in the literature on the experimental determination of carbon solubility in liquid Al

Ref	Al evaporation	Cooling condition	Composition measurements
[20] 34Bau	A significant part of the sample is lost	-	Gas analysis (H ₂ and CH ₄) after dissolution of the samples in a strong base
[2] 64Str	-	-	-
[21] 65Gin	<6w% when T>2423 K	Natural cooling	The graphite crucible was removed and the samples were ball milled under Ar atmosphere. Repeated and averaged gas combustion analysis (H ₂ and CH ₄) after dissolution of the samples in hot diluted hydrochloric acid.
[19] 66Git	-	-	Chemical analysis after extracting the liquid from the crucible and the Al ₄ C ₃ layers. Unknown method.
[22] 68Gje	<3w%	Quench by making the samples fall in a cooled chamber	Repeated and averaged analysis after careful extraction of the metal layer from the crucible layer. Unknown method.
[23] 87Ode	-	23°K/s	Combustion method after removing the crucible and 65µm of the samples outer surface
[24] 89Sim	None (low temperature)	Natural cooling	Gas-chromatographic method developed to calculate ppm of Al ₄ C ₃ from the amount of CH ₄ released by the reaction in hot sodium hydroxide

Due to the ever increasing vaporization of Al in the high-temperature range, long holding times are not possible and therefore thermodynamic equilibrium may not be obtained. This may be the case in the work of Baur et al. [20] where the carbon content is therefore likely to be underestimated. To support the fact that the equilibrium was reached, Gjerstad [22] performed two measurements at different holding times (3 – 7 min when $T < 2408$ K, 3 – 11 min for $T > 2408$ K) and highlighted the fact that similar results were found in both cases. This is the most rigorous check that was performed in the literature and Gjerstad's [22] holding times are therefore taken as a reference. Ginsberg et al. [Gin65] ensured the equilibrium was reached by observing the precipitation and dissolution of solids when the temperature regulator was oscillating around the set point. As soon as it became apparent that the precipitates would not dissolve completely during heating-up periods, the induction furnace was switched off. Although visual determination can be misleading in the studied temperature range, the method implies that the samples were held at least for a few minutes which is equivalent to Gjerstad [22] holding times. Oden et al. [23] used a molten Al plug to seal the graphite crucible, however the temperature was held for only 10 minutes at the highest temperature of 2463 K, probably due to the Al loss through the crucible porosities and to the fact that the plug itself would evaporate. Nonetheless, this holding time is comparable to the maximum holding time used by Gjerstad [22] at similar temperatures, and the equilibrium was therefore likely to be reached. In conclusion, only Gjerstad [22] and Ginsberg et al. [21] tried to ensure that equilibrium was reached. Although the visual determination from the later [21] can be misleading, Gjerstad results [22] suggest that holding times of only 3 minutes are enough above 2000 K. Therefore no results are discarded on this basis, although carbon contents measured by Baur et al. [20] may be underestimated.

Another source of error comes from the temperature measurements. Indeed, measuring temperatures in the 1700 – 3000 K temperature range using an optical pyrometer can lead to tremendous uncertainties. First of all, the temperature difference between the crucible and the sample and between the inner and the outer parts of the crucible can be of several tens of degrees. In addition, the calibration of the sample emissivity is also delicate in this temperature range, and ideally it should be adjusted using the melting point of a reference. Plus, additional corrections to take into account the absorption of the radiation along the optical path between the sample and the pyrometer should be considered. Finally, aluminum vapors may change the absorption directly or indirectly through condensation on the sight window. Ginsberg et al. [21] estimated the uncertainties on the temperature measurements to be ± 15 K around 2273 K and ± 20 K around 2373 K without giving any details of the calibrations performed. Experimental uncertainties are not given by Gjerstad [22], but the pyrometer was calibrated using a tungsten-strip lamp and the initial pyrometer's galvanometer was replaced by a more sensitive one. It was mentioned in Gjerstad manuscript [22] that the pyrometer corrections for absorption by the silica window and mirror was determined in separate trials, and was of the order of 30-70 K depending on the temperature. A very similar set-up was used by Gitlesen et al. [19,26] who worked in the same laboratory as Gjerstad. Oden et al. [23] took specific care in having isothermal conditions, and they are the only authors in the available high-temperature range liquidus literature who measured the temperature by the mean of a thermocouple. This solves the problems of calibrating the emissivity and the absorption in the case of using a pyrometer. However, aging of the thermocouple is a new source of uncertainties. The temperature gradient along the 2.54 cm long crucible used by Oden et al. [23] was estimated to be less than ± 15 K. Simensen [24] did not detail how the temperature measurements were performed in his study, however uncertainties are quite smaller in the lower temperature range investigated of 1233 – 1275 K. A standard deviation in temperature of 2 K is reported by the author [24]. Besides the uncertainties related to the measurement itself, Baur et al. [20] followed the liquidus recording the temperature when they visually estimated that the pellets were totally melted. A visual determination of the liquidus above 2300 K can be very misleading. Plus, a significant amount of Al_2O_3 , ranging from 3 to 6.4 w%, was found in the samples after the experiments. Therefore those results [20] are considered questionable and are discarded. In conclusion, significant uncertainties can come from the temperature measurements, especially as none of the literature studies refer to the use of a reference material for calibration, even though this is implied by Gitlesen et al. [19]. All the investigators except Oden et al. [23] used optical pyrometers and condensation of Al vapors on the sight window is a source of errors. Nonetheless, only the results from Baur et al. [20] are discarded, mainly because of the measurement procedure.

Last but not least, the composition measurements are another source of errors. In all the high-temperature literature studies where experimental details are available [19–23], chemical analysis was performed after the removal of the crucible to determine the final composition of the samples. Those results may be overestimations of the solubility if the reaction layer between the crucible and the sample was not completely removed, or if particles would detach from the liquid/crucible interface into the sample. Notably, Gitlesen et al. [19] reported that they had to separate a liquid layer from a mixed layer of liquid and Al_4C_3 and a graphite layer and noted that this composition point is therefore likely to be an upper limit of the liquidus. This might also be true in the case of Gjerstad work below 2408 K [22]. Various authors specified that the samples were inhomogeneous and that they performed repeated and averaged sampling to deal with this [21–23]. It is noteworthy that Oden et al. [23] could not find a correlation between the composition and the position of the analyzed samples along the length of the ingots. Ginsberg et al. [21] made the hypothesis that the high standard deviation was due to a significant hydrolysis of Al_4C_3 by moisture, which occurred even after careful processing of the samples. Indeed, aluminum carbide reacts strongly with water, and this is a possible source of underestimation of the carbon solubility for all the literature results. Oden et al. [23] evaluated the carbon content uncertainty to be about 5 % using repeated sampling and a combustion method. Simensen gave similar uncertainties of 3 – 5 % when using the gas-chromatographic method developed specifically to measure at the ppm level carbide content in magnesium and aluminum [27]. In conclusion, the measured carbon content can to be overestimated as all investigators worked with graphite crucibles, and the datapoint from Gitlesen et al. [19] is discarded for this reason. It is to note that only Ginsberg et al. [21] mentioned about trying to protect Al_4C_3 from hydrolysis, and it could not be prevented by the authors nonetheless.

Finally, after discarding the results from Stroup [2], Baur et al. [20] and Gitlesen et al. [19], the data regarding the solubility of carbon in liquid Al are consistent with each other up to 2450 K. Above this temperature, a sudden change of trend can be observed for the data reported by Gjerstad [22] which is in conflict with the other selected datasets [21,23]. This change of trend was not commented by Gjerstad in his manuscript [22]. Considering the experimental conditions reported by the authors, it could be explained by a burst of gas that would lead to the fogging of the sight glass, making a sudden change in the window absorption coefficient. Indeed, based on a critical literature review along with experimental observations, Schuster [18] made the assumption that the C-saturated Al liquid evaporates at temperatures around 2473 K. Last but not least, it has to be noted that Simensen’s measurements at low temperature [24] are in very good agreements with the extrapolation of the results of Oden et al. [23], which further support their validity. For these reasons, it was decided to discard the results from Gjerstad [22].

2.2 Thermal stability of Al_4C_3

The two high-temperature conflicting trends observed in the liquidus data (cf. Fig. 1) feed another debate regarding the thermal stability of the Al_4C_3 phase. Indeed, the decomposition temperature of Al_4C_3 was often estimated from slope breaks in solubility measurements. There are two distinct slope breaks reported in the literature: the one occurring around 2273 K that Schuster [18] attribute to the decomposition of the Al_4C_3 phase, and the one occurring around 2423 K accounted by the same author for the vaporization of liquid aluminum [18]. The literature results regarding the decomposition temperature of Al_4C_3 are listed in Table 4. No details are available regarding Searcy’s work [2] as the original patent could not be found.

Table 4 Literature results on the decomposition temperature of Al_4C_3

Ref.	Al_4C_3 Decomposition temperature in K	Means of determination
Searcy as reported by [2] 64Str	2298	Unknown method
Long as reported by [2] 64Str	2253	Slope break in C solubility in liquid Al
[21] 65Gin	2323±20	Slope break in C solubility in liquid Al
[19] 66Git	2408	Thermal analysis
[23] 87Ode	2428±12	Thermal analysis
[18] 91Sch	2263±20	Interpretation of a burst of vapor

The main uncertainty lies in the temperature measurements. The arguments discussed in the previous section still hold. Meticulous work was performed and detailed by Oden et al. [23]. The measurements were performed using a pyrometer calibrated using a tungsten-strip lamp in a similar set-up as previously described for Gitlsen et al. [19] in Table 2. However, Oden et al. [23] calibrated their set-up using Pt, Rh and Al₂O₃ references. In addition, the authors [23] used an Ar flow countercurrent to the Al vapors to avoid fogging of the sight window. Schuster [18] used a micro-pyrometer and calibrated his set-up using various references.

Another source of uncertainty is the purity of the samples. It was roughly evaluated by X-ray diffraction by Oden et al. [23] and Schuster et al. [18]. No impurities could be detected except for free graphite. The details regarding the chemical analysis performed by Gitlsen et al. [19] were given on Table 1.

In conclusion, two contradictory dataset can be found regarding the thermal stability of Al₄C₃. According to the estimations from liquidus slope break and experimental observations the decomposition of the aluminum carbide occurs around 2273 K. However, all the data supporting this temperature are based on either interpretation of burst of vapor [18] or of liquidus data [2,26], as well as some unknown method for Searcy's results [2], which can be misleading. Therefore this dataset is less reliable than the thermal analyses pointing towards a decomposition temperature around 2423 K. It has to be noted that thermal arrests were observed both at cooling and heating by both Gitlesen et al. [26] and Oden et al. [23], whereas no signal could be observed around 2273 K. Nonetheless, significant uncertainties may be expected on this temperature range as discussed earlier.

2.3 Thermodynamic properties of Al₄C₃

To begin with, the heat capacity of the Al₄C₃ carbide was measured by Furukawa et al. [28] in the 18-380 K range using an adiabatic calorimeter. In addition, the authors measured the heat content of the phase from 273 to 1173 K in a Bunsen ice calorimeter by the drop method [28]. The samples used had a purity close to 95 wt% with Al, C, AlN and Al₂O₃ as main impurities and the results were corrected accordingly. Binford et al. [29] also measured the heat content of Al₄C₃ over the 363-1774 K range using an homemade drop calorimeter. The amount and nature of impurities were found to be almost identical to the samples used by Furukawa et al. [28], and the authors [29] specified that the maximum correction applied was less than 0.5% of the measured values. The reported results are in very satisfying agreements with the dataset from Furukawa et al. [28] except for two data points at 1277 and 1672 K that were discarded by Binford et al. [29] due to unusually high deviations. Those datasets were recently further confirmed by determination of the heat capacity of Al₄C₃ both experimentally by the step-scan method in the 300 – 873 K range and from phonon calculations [30]; the two methods leading to a fairly good agreement with the already existing literature [28,29]. In fact, the entropy of formation of Al₄C₃ at 298 K that was found to be 88.97 J.K⁻¹.mol⁻¹ from integrating the ab-initio heat capacity [30] is in excellent agreement with the experimental value of 89.12 J.K⁻¹.mol⁻¹ proposed by Saba and Furukawa [31] and with their fitted value of 88.97 J.K⁻¹.mol⁻¹ [28].

Then, the standard heat of formation of Al₄C₃ was intensively investigated, however the reported values are highly scattered. The literature results [30,32–47] are displayed in Table 5.

Table 5 Literature results on the standard enthalpy of formation of Al₄C₃

Ref.	Method	$\Delta_f H^0_{298.15\text{ K}} \text{ Al}_4\text{C}_3$ in kJ.mol of atoms ⁻¹	Note
[32, 33] 34Mei, 42Rot	Combustion calorimetry	-23.9±1.8	
[34] 64Kin	Combustion calorimetry	-29.7±0.7	
[35] 64Mah	Combustion calorimetry	-31.9±1.2	
[45] 01Ber	Combustion calorimetry	-132.0	Discarded
[46] 33Wöh	Combustion calorimetry	-145.8	Discarded
[36] 70Bla	Solution calorimetry	-29.6±0.3	
[37] 95Mes	Direct reaction calorimetry	-18.3±1	
[38] 66Pla	Vapor-pressure measurements (2 nd law)	-30.6±2.8	
[39] 66Pot	Vapor-pressure measurements (2 nd law)	-35.2±2.5	
[40] 59Mes	Vapor-pressure measurements (2 nd law)	-35.3±3.3	
[41] 27Pre	Vapor-pressure measurements (2 nd law)	-36.0	Discarded
[42, 43] 28Pre, 37Sat	Vapor-pressure measurements (2 nd law)	-37.8	
[44] 80Rin	Vapor-pressure measurements (3 rd law)	-24.9±2.4	
[45] 64Tho	DTA (3 rd law)	-17.9±2.4	
[30] 19Pis	DFT (SCAN functional)	-26.2	

In the first place, several calorimetric techniques have been used to determine the heat of formation of Al₄C₃. The earlier measurements obtained by Berthelot [46] and Wöhler et al. [47] using combustion calorimetry of respectively -132.0 and -145.8 kJ.mol of atoms⁻¹ are significantly more exothermic than the accepted order of magnitude and are discarded. In both cases the observed reaction product was not a single phase and contained a mixture of oxides and carbides both of unknown structure making the reported values highly unreliable. In the later combustion calorimetry studies [32–35] the authors took particular care in the characterization of the reactants and products to take into account the amount and nature of all observed phases in the calculation of the heat of formation. Yet, the results display a discrepancy ranging from -23.9 to -31.9 kJ.mol of atoms⁻¹. Blachnik et al. [36] used acid solution calorimetry in 20.21 wt.% HCl at 110°C to determine the heat of formation of Al₄C₃. The sample used had a purity of 95.8 / 97.2 wt.% with free carbon and alumina as main impurities and the results were corrected accordingly. Finally, the most recent calorimetric value was reported by Meschel et al. [37] using direct reaction calorimetry. Al/C mixtures and reacted Al₄C₃ samples are dropped from room temperature into the calorimeter held at 1473±2 K. The reaction was not complete because residual carbon was detected in the analysis of the reaction products. The reported heat of formation was therefore corrected with respect to the measured carbon content. The debate was left open after this measurement as the reported result of -18.3 kJ.mol of atoms⁻¹ is among the less exothermic experimental values, and it is rather delicate to discriminate among them. An insufficient knowledge of the products and reactants involved and the use of additional data in the processing of the results can be a source of systematic errors. This is especially true as Al₄C₃ is unstable in contact of humidity to form Al(OH)_{3(s)} and CH_{4(g)} [48,49] and have to be handled carefully. Another source of errors lies in the fact that the heat of formation obtained are the small difference between roughly 10 times greater heats of solution and combustion, hence 1% of experimental uncertainty would for instance represent 10% of the final value.

In the second place, the heat of formation of Al₄C₃ was intensively studied by the means of vapor-pressure measurements. Prescott and Hincke [41] measured the equilibrium pressure from 1968 K to 2293 K and considered the following equation:

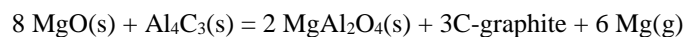


The authors performed a 2nd law analysis to obtain a heat of formation of -36.0 kJ.mol of atoms⁻¹. However, it is now known that there are two ternary compounds in the Al₄C₃-Al₂O₃ quasi binary section, namely Al₂CO and Al₄CO₄ [50]. The observed reaction product may therefore not be pure Al₄C₃(s) but a mixture of the carbide and one or both of the oxycarbides, and this result is therefore discarded. Prescott and Hincke [42] also measured the equilibrium pressure of Al₄C₃ under nitrogen atmosphere in the scope of determining the enthalpy of formation of AlN using their previous result for Al₄C₃. However, v. Stackelberg and Spiess [51] highlighted the existence of a new ternary phase in the system shortly after, namely Al₃C₃N. Therefore, the equilibrium equations proposed by Prescott and Hincke [42] were once again incomplete and were corrected by v. Stackelberg et al.

[52]. On the basis of the pressure measured by Prescott and Hincke [42], and using the corrected equations proposed by v. Stackelberg et al [52], Satoh [43] recalculated the enthalpy of formation of Al_4C_3 at -37.8 kJ.mol of atoms⁻¹ using his own experimental data for the enthalpy of formation of AlN.

Finally, the vapor pressure over pure Al_4C_3 in graphite crucibles were measured by torsion effusion [39,40], in a rotating Knudsen cell [38] and by Knudsen effusion mass spectrometry [44]. Al_4C_3 shows incongruent vaporization with Al(g) and C-graphite as reactions products and a minor contribution of the $\text{Al}_2(\text{g})$ dimer. It is noteworthy that the results from Meschi et al. [40], Plante et al. [38] and Rinehart et al. [44] reported in this study are different from the originally published values as they were re-calculated using more recent thermodynamic data for Al(g) [53]. There are two difficulties in these measurements: the presence of small amounts of oxygen leading to higher observed total pressures at the beginning of the reaction due to formation of CO(g), and the formation of a C-graphite layer on the surface of the sample which may act as a diffusion barrier for Al(g). Therefore, reliable data are only obtained if sufficient holding times are maintained and constant values for the measured pressures are observed while assuring by post-measurement analysis that free Al_4C_3 surfaces were available to avoid a pressure drop. These two experimental difficulties may explain the dispersion in the reported heats of formation for Al_4C_3 from the Al(g) pressure data ranging from -24.9 to -35.3 kJ.mol of atoms⁻¹.

Lastly, a few authors [54–57] have reported on the Gibbs energy of formation of Al_4C_3 from liquid Al and C-graphite. Campbell [54] obtained this data at 1193 K from measurements of the activity of Al in Al_4C_3 obtained by comparison of AlF pressure over reacted mixtures of AlF₃/Al and AlF₃/ Al_4C_3 . Grjotheim et al. [55] measured the Mg equilibrium pressure from 1324 K to 1452 K over the following reaction:



The Gibbs energy of formation of Al_4C_3 was calculated at 1400 K from those measurements. Choudary and Belton [56] calculated the Gibbs energy of formation of Al_4C_3 at 1873 K from the activity of Al measured in carbon-saturated Fe-Al melts by Knudsen cell-mass spectrometry. Finally, the Gibbs energy of formation of Al_4C_3 was obtained from 653 to 803 K by Obata et al. [57] based on electromotive force measurements over a (Mo)Al/ β -Alumina/ Al_4C_3 ,C(Mo) galvanic cell. All in all, those measurements cover a wide temperature range, however they are in rather poor agreement as it is highlighted latter in section 5.1.

In conclusion, the heat capacity of Al_4C_3 is very well known from 18 to 873 K and consistent heat content experimental data are available up to 1774 K. However, regarding the heat of formation of the aluminum carbide a systematic and significant scattering in the reported results is highlighted both within and between the experimental methods used. In fact, after discarding the earlier combustion calorimetry results [46,47] and the data from [41], statistics lead to a mean value of $-28.6 \pm 14.2 \text{ kJ.mol}$ of atoms⁻¹ with an expanded uncertainty with 0.95 level of confidence. Therefore, to select the most reliable value is not an easy task. In this purpose, the enthalpy of formation of Al_4C_3 was recently investigated using DFT calculations and a value of $-26.2 \text{ kJ.mol}^{-1}$ of atoms was determined [30]. The SCAN many-body interaction functional was used and a correction was applied to account for some limitations in the prediction of the ground state properties of C-graphite. This value is in good agreement with the vapor-pressure measurements from Rinehart et al. [44] and in acceptable agreement with the data obtained by combustion calorimetry by Meichsner and Roth [32,33]. It was selected in the present study in order to assess the debated experimental data.

3. Determination of the thermal stability of Al_4C_3

3.1 Materials and methods

The experimental set-up is based on a high-temperature crystal growth furnace and was developed for the seeded sublimation growth of semiconductor grade SiC single crystalline ingots. The assembly is similar to the one described in Ariyawong et al. [58]. The device is characterized by high thermal inertia, low inner thermal gradients and a fine and accurate control of the furnace temperature. Fig. 2 schematically presents the design of the furnace. It consists of a water-cooled quartz chamber. All the different crucible parts are made of high density and high purity isostatic graphite, and the set is insulated with graphite felt. The crucible is heated by induction, using a 50 kW generator operating at a frequency of 22 kHz. At such a frequency, most of the Joule losses are generated in the susceptor. The graphite sleeve and the measurement crucible are thus mainly heated by radiation from the susceptor. Temperatures are measured at two different locations. The first measurement from the top of the measurement crucible (T_F) is used to monitor the temperature of the furnace. The second one from the bottom of the measurement crucible (T_P) is the probe that collects the sample temperature. Both temperatures are measured using 2-colors infrared pyrometers from Fluke-Raytek (Endurance series) adapted for the 1273-3273 K temperature range. They have both been calibrated on 5 reference black bodies covering all the temperature range. The sample temperature (probe) is collected after a 1 mm thick graphite wall, which is the bottom of the measurement crucible. The associated thermal resistance is extremely low in comparison with the investigated temperature range. Therefore, in this configuration the temperature is measured very close to the sample, but the measurements are performed assuming blackbody radiations as the two cavities are made of graphite. This is advantageous compared to a direct measurement on the sample as its emissivity is most of the time unknown. As a result, no correction on emissivity or on the slope between the two wavelengths (two colours) is applied. The raw signal of the pyrometers is used, with a sampling time of 100 ms. The induction coil is adjusted in order to have isothermal conditions between the two measurement points once the thermal equilibrium is reached at high temperatures.

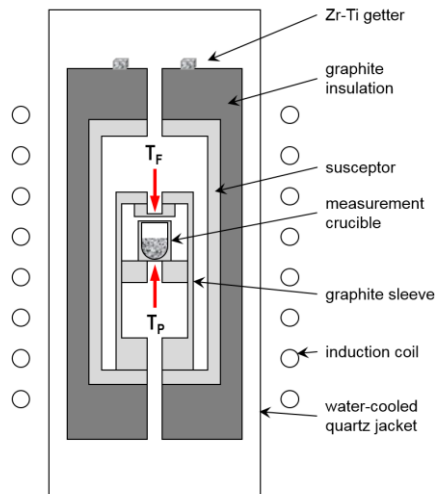


Fig. 2 Schematic drawing of the high temperature thermal analysis set-up. Light and dark grey parts consist of high density graphite and graphite insulation, respectively. The two red arrows indicate the two temperature measurements, T_F and T_P for furnace and probe, respectively.

The temperature calibration is performed using various carbide-based invariant points. The measurement crucible is loaded with high purity Si, Ti, Cr or Nb, and the carbon is supplied by the crucible itself. The volume of samples is typically 2 cm^3 . After loading, the chamber is placed under vacuum for a few hours. The heating stage is then composed of three main steps. In a first step, the crucible is slowly heated up and kept at 1473 K for 30 minutes under vacuum. This ensures a good outgassing of the different graphite parts. The chamber is then filled with high purity argon, and the pressure is kept constant all along the run, and typically set at 800 mbar. In a second step, the temperature is raised to a temperature approximately 200 K higher than the targeted invariant point at a rate of

20 K/min. This is done to promote the reaction between the load (pure Si or metal) and the graphite crucible. Finally, in a third step, measurements cycles are performed at controlled heating and cooling rates. Besides the graphite environment, which helps reducing the residual oxygen content in the load by carbo-thermal reduction of the residual oxides, Ti-Zr getters are placed on top of the graphite insulation part. The measurement of Al_4C_3 decomposition temperature has been performed on a 99+% pure Al_4C_3 powder supplied from Alfa Aesar and conditioned under inert gas. It is worth noting that for all this study, only the values collected during heating up have been considered, as the signal upon cooling showed unclear features.

3.2 Calibration and Results

The thermal analysis set-up has been calibrated on a series of carbon-based invariant points (Figure B). The first four points (a-d) have been accurately determined in the literature (less than 1K as uncertainty). The last one (d) is given with an uncertainty of ± 10 K, though it is not clear in Smith et al. paper [59] where this value came from. The measurements performed in this study, collected at the back side of the crucible, are found very close to the reference points, leading to a calibration curve with a slope almost equal to one and an intercept of a few degrees. To assess the repeatability of the measurements, each invariant point has been measured 5 consecutive times. All the values have been reproduced quite closely, in a ± 1 K window, even for the high temperature invariant point of the Nb-Nb₂C eutectic at 2613 K. This shows that the present procedure (experiments, measurements and treatment of the data) has a high reproducibility.

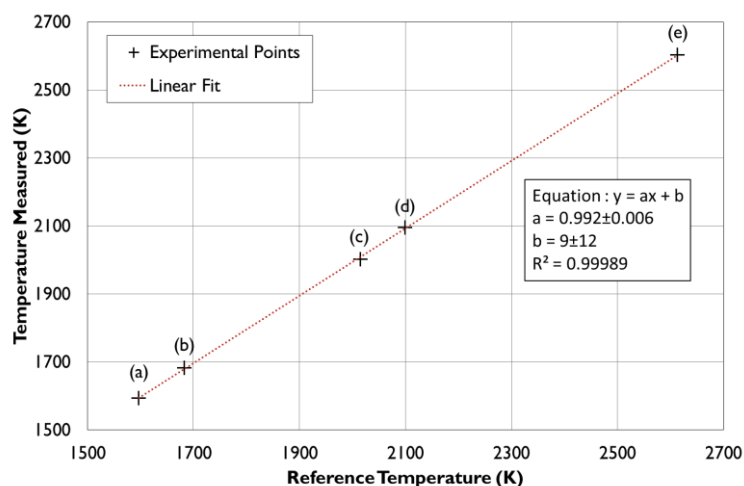


Fig. 3 Calibration curve of the thermal analysis device used in this study on a series of fixed points : (a) Co-C eutectic given at 1597K [60], (b) Si-SiC eutectic 1683 K [61], (c) Cr_7C_3 - Cr_3C_2 eutectic 2015 K [62], (d) Cr_3C_2 -C peritectic 2099 K [62], (e) Nb-Nb₂C eutectic 2613 K [59]. Reference Temperature stands for the published values of the fixed points, Temperature Measured corresponds to our measurements.

Based on five different measurements from 3 different material loads, the decomposition of Al_4C_3 has been found at 2425 ± 15 K. This uncertainty is the one associated to the pyrometer accuracy (0.5% of the measured value + 2, in °C), which might be the largest source of error. The reproducibility of the measure is lower, at about ± 5 K (standard deviation on the 5 measurements). This result further support the validity of the measurements performed by thermal analysis by Gitlesen et al. [19] and Oden et al. [23], at respectively 2408 K and 2428 ± 12 K. Therefore, the dataset pointing toward a decomposition around 2273 K supported by estimations from liquidus slope break [2,21] and experimental observations [18] is discarded.

4. Thermodynamic modeling and optimization procedure

The Liquid and the Al_4C_3 phases were the only ones modeled in this work. The Gibbs energies of the pure elements were taken from the SGTE database [63], and the one of the Gas phase was taken from the NIST Chemistry WebBook [64]. All calculations were performed using both software packages Pandat [65] and Thermocalc [66], and the results were checked for agreement.

The aluminum carbide Al_4C_3 was treated as a stoichiometric phase and its Gibbs energy was modeled according to Eq. 1. The expression for the heat capacity of the phase is given in Eq. 2 from Eq. 1.

$$G_m^{Al_4C_3}(T) - 4H_{Al}^{SER} - 3H_C^{SER} = A + BT + CT \ln(T) + DT^2 + ET^{-1} + FT^3 \quad (1)$$

$$C_p^{Al_4C_3}(T) = -C - 2DT - 2ET^{-2} - 6FT^2 \quad (2)$$

The Liquid phase was treated as a substitutional solution (Al, C), and the excess Gibbs energy parameter was described using the Redlich-Kister polynomial [67] according to Eq. 3, 4 and 5. A binary excess parameter of order 1 (sub-regular solution) was used in order to obtain a satisfactory fit for the very small solubility of C in liquid Al in the order of 20 ppm-atomic around 1250 K and its sudden increase above 1900 K.

$$ex G_m^{Liq} = x_{Al}x_C \left({}^0L_{Al,C}^{Liq} + {}^1L_{Al,C}^{Liq}(x_{Al} - x_C) \right) \quad (3)$$

$${}^0L_{Al,C}^{Liq} = {}^0a_{Al,C}^{Liq} + {}^0b_{Al,C}^{Liq}T \quad (4)$$

$${}^1L_{Al,C}^{Liq} = {}^1a_{Al,C}^{Liq} \quad (5)$$

First of all the C, D, E and F coefficients of Eq. 2 were determined from the heat capacity and heat content measurements made by Furukawa et al. [28], the heat capacity measured by DSC by the authors [30], and the heat content measured by Binford et al. [29] except for the data points at 1277 and 1672 K. Four temperature ranges were used to describe the heat capacity energy of Al_4C_3 , and the continuity of the function was ensured at each junctions. The reason behind this choice is that it reduced the number of parameters to be used, and it avoided aberrations at extreme temperatures caused by the use of the powers of T terms. It is to note that for the highest temperature range function, no T^2 nor T^{-2} terms were needed to obtain a good fit for the high temperature heat contents.

In a second step the B coefficient of Eq. 1 was determined for the temperature range starting at 298.15 K using the experimental standard entropy of formation ($\Delta_f S^\circ_{298}$) measured by Furukawa et al. [28,31]. For all other temperature ranges the value of the parameter B was determined using the condition of continuity of the entropy function of Al_4C_3 . Then, the A coefficient of Eq. 1 was adjusted for the temperature range starting at 298.15 K using the standard enthalpy of formation ($\Delta_f H^\circ_{298}$) evaluated by DFT calculation [30]. Finally, the A parameter was determined for all other temperature ranges using the condition of continuity of the Gibbs energy function of Al_4C_3 .

In a last step, the Liquid parameters of Eq. 4 and 5 were optimized together with the parameters of the highest temperature range function of Al_4C_3 using the liquidus data from Ginsberg et al. [21] and Oden et al. [23], the decomposition temperature of Al_4C_3 determined in this work, the heat content [28,29] and DSC C_p [30] data available above 800 K, as well as the calculated enthalpy and entropy of formation of Al_4C_3 at 800 K. It is to note that a high weight was selected for the calculated entropy of formation during this process. Finally, the continuity over the different temperature ranges of the thermodynamic functions of Al_4C_3 was ensured afterwards. Extensive details regarding the uncertainties and the weights used in the optimization can be found elsewhere [68].

The thermodynamic parameters obtained for the Al_4C_3 and liquid phases are presented in Table 6 along with the results from previous modeling of the system.

Table 6 Thermodynamic parameters determined in the modeling of the Al-C system and compared with previous modeling of the system. Parameters are given in $\text{J}\cdot\text{mol}^{-1}$ in the form $A + BT + C\ln(T) + DT^2 + ET^{-1} + FT^3$

Term	Ref.	A	B	C	D.10 ³	E.10 ⁻⁶	F.10 ⁶
Al₄C₃, Stoichiometric, Al₄C₃							
$G_m^{Al_4C_3}(T) - 4H_{Al}^{SER} - 3H_C^{SER}$	[14] Qiu et al. (1994)	-265234	+939.726	-148.735	-16.73361	+1.86	+3.6E-4
	[15] Gröbner et al. (1995)	-286001	+1030.273	-161.709	-11.5228	+2.45	+0.7
	[17] Ohtani et al. (2004)	-265237.816	+938.2003131	-148.7408	-16.72941	+1.8639755	-6.53485E-5
	This Work (18-60 K)	-209609.2	+11.74423	-3.98514	+137.076	+0.0001394	-987.67
	This Work (60-298.15 K)	-207459.8	-199.2384	+47.03837	-413.864	-0.0171756	+156.251
	This Work (298.15-800 K)	-237336.07	+643.8029	-100.6823	-83.9832	+1.133215	+15.8781
	This Work (800-3000 K)	-240446.3	+866.8532	-139.40526	-19.4607	-	-
Liquid, Redlich-Kister, (Al, C)							
${}^0L_{Al,C}^{Liq}$	[14] Qiu et al. (1994)	-4426	-11.1007				
	[15] Gröbner et al. (1995)	+40861.02	-33.21138				
	[17] Ohtani et al. (2004)	+29910	-25.586				
	This Work	-48892	+1.15				
${}^1L_{Al,C}^{Liq}$	This Work	+32543	-				

5. Results and discussion

5.1 The Al₄C₃ phase

The calculated heat content of Al₄C₃ are presented in Fig. 4 along with the experimental data [28,29] and the results from Gröbner et al. [15]. The fit obtained in this work is in very good agreement with the ones proposed by Qiu et al. [14] and Ohtani et al. [17], therefore those were not plotted in Fig. 4 for the sake of clarity. A very satisfying fit of the literature data was obtained over the whole 363 – 1774 K range. The results from Gröbner et al. [15] lead to an underestimation of the experimental heat content data above 1000 K.

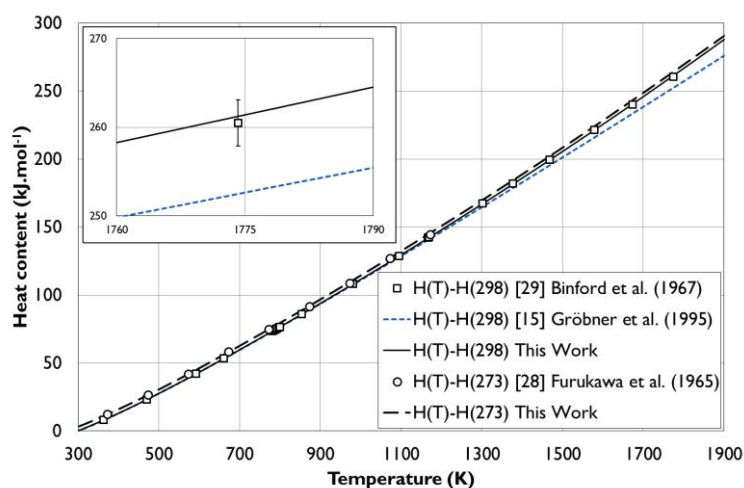


Fig. 4 Calculated heat content of Al₄C₃ compared with experimental data and previous modeling of the system. Inlet: focus on the data at 1774 K with its associated uncertainty (open square, [29]), previous thermodynamic calculation (dotted blue line, [15]) and calculated heat content H(T)-H298 (solid black line).

The calculated heat capacity of Al₄C₃ is presented in Fig. 5 along with the experimental data [28,30] and the results from the previous modeling of the system [14,15,17]. For the sake of clarity, only one third of the experimental data are reproduced. Plus, as the Cp function proposed by Ohtani et al. [17] is almost identical to

the one assessed by Qiu et al. [14], both functions are represented by the same line in Fig. 5. The function proposed in this work is in very good agreement with the experimental data over the whole 18 to 870 K range, whereas results from previous modeling of the system are not valid below 298.15 K. Starting from 900 K and above, the function proposed by Gröbner et al. [15] is lower than for other modeling, which come from a less satisfying fit of the heat content data as seen in Fig. 4.

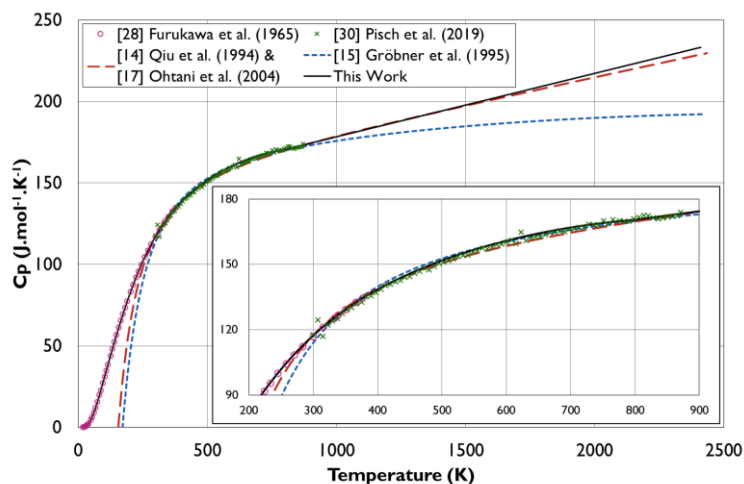


Fig. 5 Calculated heat capacity of Al_4C_3 compared with experimental data and previous modeling of the system. Inlet: focus on the agreement between calculated and experimental data between 200 and 900 K.

The calculated standard entropy and enthalpy of formation of Al_4C_3 are displayed in Table 7 along with the selected literature data [30,31] and the results from previous modeling of the system [14,15,17]. The calculated standard entropy of formation is in perfect agreement with the experimental value of $89.12 \text{ J.K}^{-1}.\text{mol}^{-1}$ proposed by Saba and Furukawa [31]. The calculated standard enthalpy of formation is significantly less exothermic than in the previous modeling of the system [14,15,17]. The calculated standard enthalpy of formation could not perfectly agree with the selected DFT value [30] as a compromise was necessary to fit the decomposition temperature of Al_4C_3 presented later in the discussion. The calculated equilibrium vapor pressure of Al over a $\text{Al}_4\text{C}_3/\text{C}$ mixture is presented in Fig. 6 along with the literature data [38,40,44] and the results from the previous modeling of the system [14,15,17]. This equilibrium pressure is directly linked to the standard enthalpy of formation. The calculated value lead to a mean between Plante et al. [38] and Rinehart et al. [44] measurements whereas the DFT enthalpy of formation lead to a good agreement with the dataset from Rinehart et al. [44].

Table 7 Calculated standard entropy and enthalpy of formation of Al_4C_3 compared with the selected literature data and results from previous modeling of the system

Ref.	Method	$\Delta_f S^\circ_{298.15 \text{ K}} \text{ Al}_4\text{C}_3$ in $\text{J.K}^{-1}.\text{mol}^{-1}$	$\Delta_f H^\circ_{298.15 \text{ K}} \text{ Al}_4\text{C}_3$ in kJ.mol of atoms $^{-1}$
[31] 62Sab	Experimental	89.1	-
[30] 19Pis	DFT	88.9	-26.2
[14] 94Qiu	Thermodynamic assessment	87.4	-29.6
[15] 95Grö		89.0	-31.5
[17] 04Oht		87.0	-29.6
This Work		89.1	-27.6

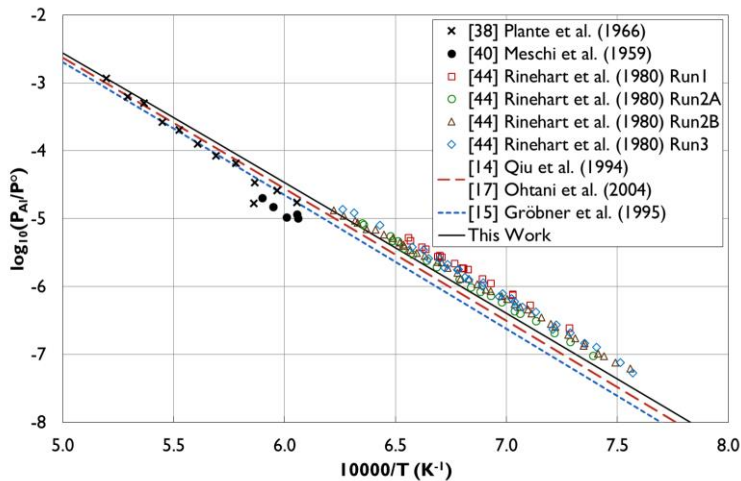


Fig. 6 Calculated equilibrium vapor pressure of Al over a $\text{Al}_4\text{C}_3/\text{C}$ mixture compared with experimental data and previous modeling of the system

The calculated Gibbs energy of formation of Al_4C_3 from liquid Al and C-graphite is presented in Fig. 7 along with the experimental data [54–57] and the results from the previous modeling of the system [14,15,17]. A good agreement is obtained between the description proposed in this work and the results from Obata et al. [57]. The measurements from Grjotheim and Herstad [55] are in a better agreement with the proposed description than with previous modeling of the system of the system [14,15,17], whereas the results from Campbell [54] and Choudary et al. [56] support the later.

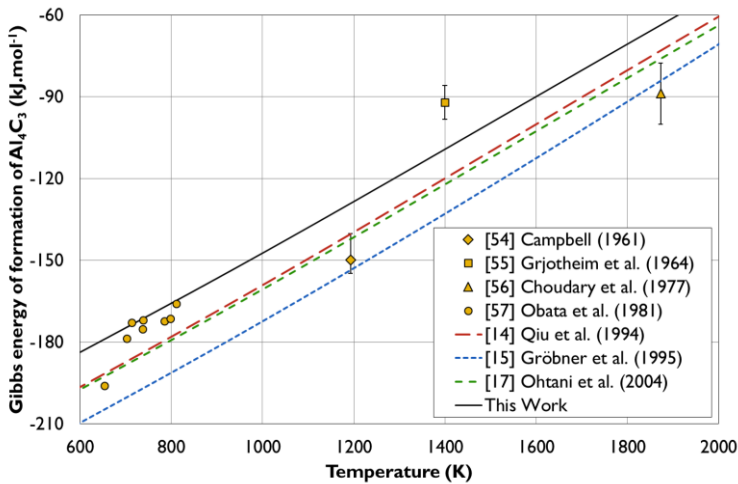


Fig. 7 Calculated Gibbs energy of formation of Al_4C_3 from liquid Al and C-graphite compared with experimental data and previous modeling of the system

5.2 The Al-C phase diagram

The calculated Al-C liquidus is presented in Fig. 8 and 9 along with the experimental data [2,19–24] and the results from previous modeling of the system [14,15,17]. In the high-temperature range, the proposed description leads to a carbon richer liquidus than in the modeling from Qiu et al. [14] and Ohtani et al. [17] and is in rather good agreement with the results from Gröbner et al. [15]. In the low-temperature range, the calculated liquidus is in good agreement with the results from Qiu et al. [14] but not with the ones of Gröbner et al. [15] and Ohtani et al. [17] who omitted the data measured by Simensen [24] in their assessment. The introduction of a sub-regular parameter as presented in Eq. 5 enabled a better fit of the limited solubility of C in liquid Al at low temperatures and its sudden increase above 2000 K in comparison with previous modeling of the system of the system [14,15,17].

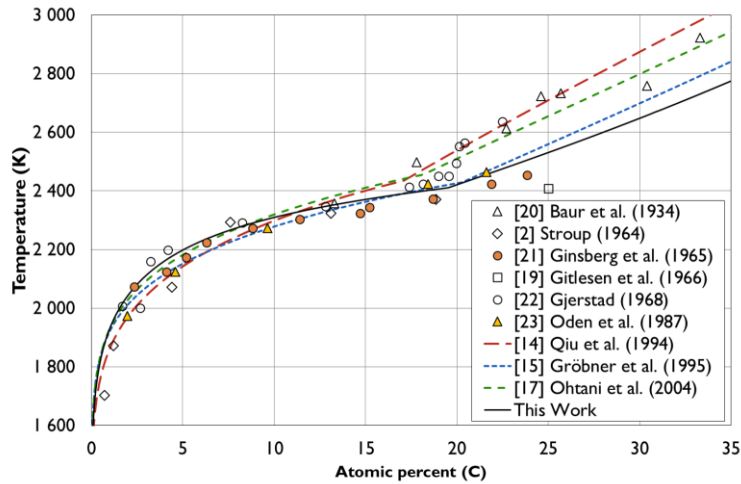


Fig. 8 Calculated high-temperature liquidus compared with experimental data and previous modeling of the system. The solid symbols represent the data selected in the assessment.

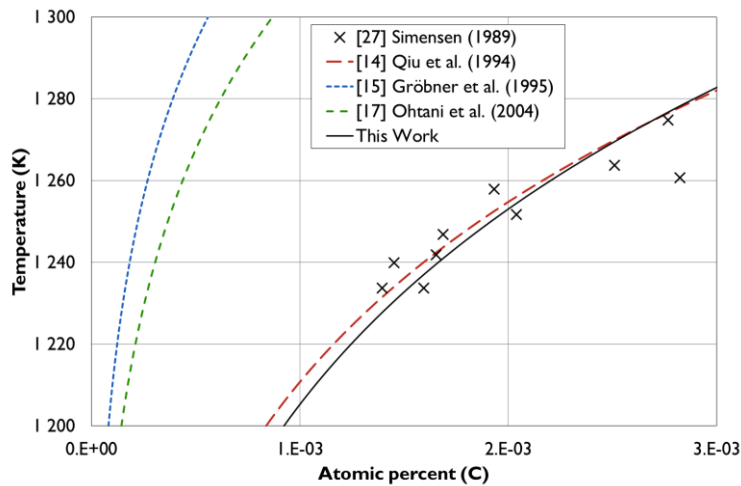


Fig. 9 Calculated low-temperature liquidus compared with experimental data and previous modeling of the system

The measured and calculated temperature of decomposition of Al_4C_3 is presented in Table 8 along with the selected experimental results from literature [19,23] and the ones from previous modeling of the system. The temperature calculated in this work is in satisfying agreement with the experimental data.

Table 8 Calculated Invariant decomposition temperature of Al_4C_3 compared with the selected experimental data, and results from previous modeling of the system

Ref.	Method	Decomposition temperature of Al_4C_3 in K
[19] 66Git	Thermal analysis	2408
[23] 87Ode		2428 ± 12
This Work		2425 ± 15
[14] 94Qiu	Thermodynamic assessment	2433
[15] 95Grö		2429
[17] 04Oht		2456
This Work		2411

Finally, the calculated Al-C phase diagram is presented in Fig. 10. The robustness and consistency of the proposed thermodynamic description was a strong basis to extrapolate thermodynamic phase equilibria at higher temperature.

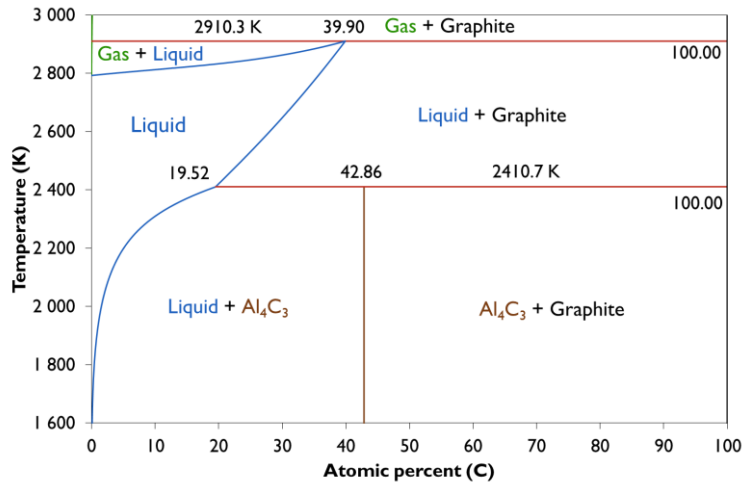


Fig. 10 Calculated Al-C phase diagram at 1 bar pressure

5.3 The Liquid phase

The choices made in this assessment lead to significant differences regarding the description of the Al-C Liquid phase when compared to the previous ones.

The enthalpy of mixing in the Liquid phase is presented in Fig. 11 along with the results from previous modeling of the system [14,15,17]. The negative value found in this work roughly suggest attractive interaction between Al and C in the liquid as opposed to the positive values from Gröbner et al. [15] and Ohtani et al. [17] and the values very close to ideality from Qiu et al. [14]. Considering that Al and C react together to form the Al_4C_3 carbide stable up to 2425 K one can expect attractive interaction between the elements in the Liquid phase.

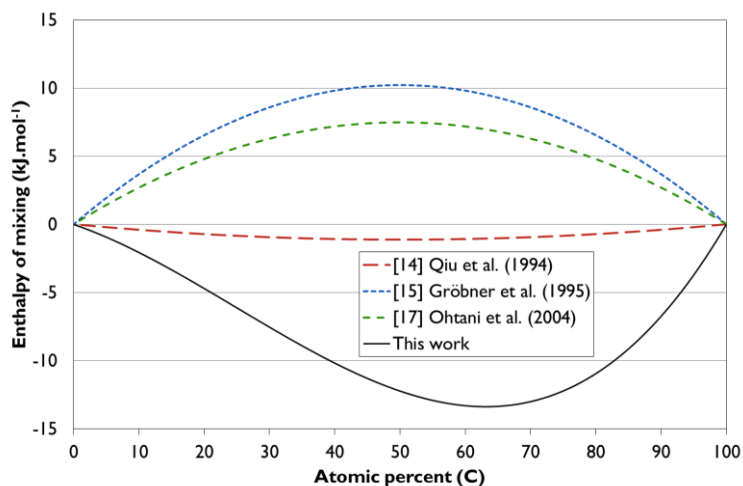


Fig. 11 Calculated enthalpy of mixing in the Liquid phase compared with previous modeling of the system

The entropy of mixing in the Liquid phase is presented in Fig. 12 along with the results from previous modeling of the system [14,15,17]. The value found in this work is very close to the configurational entropy and roughly suggest a statistical ordering of the elements in the Liquid phase. The results from Gröbner et al. [15] leads to an approximately 3 times greater entropy of mixing than in the ideal case. This can suggest short-range ordering

which is more common in ionic liquid than in metallic ones, and which is usually not described by a simple substitutional model.

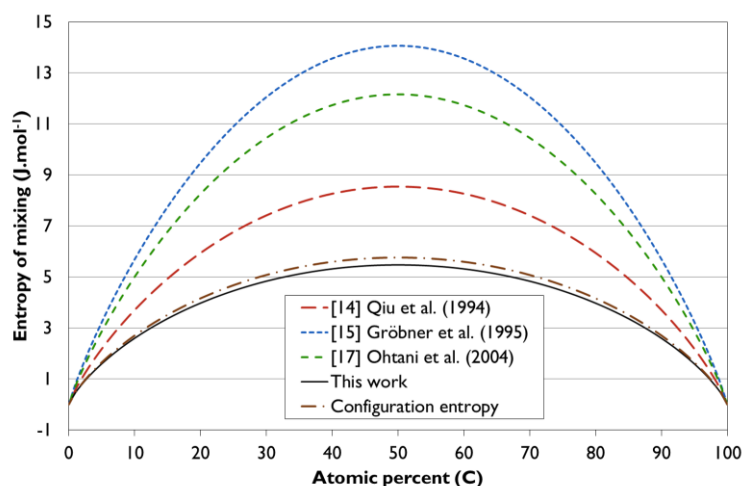


Fig. 12 Calculated entropy of mixing in the Liquid phase compared with previous modeling of the system

It is very interesting to note that the assessments from Qiu et al. [14] and Ohtani et al. [17] are very similar, except that the former took into account the low-temperature liquidus data from Simensen [24]. As a result, the entropy and enthalpy of mixing are significantly reduced as this dataset provides a valuable anchor point. All in all, in the proposed thermodynamic modeling of the Al-C binary, the description of the Liquid phase is suggested to be more reasonable than in the previous modeling of the system of the system.

Conclusions

The Al-C system is the cornerstone to numerous applications, however open debate can be found on key data in the literature making it delicate to assess this binary. In this work, the literature data regarding the Al-C liquidus and the standard enthalpy of formation of Al_4C_3 were critically reviewed and selected. Regarding the liquidus, the data leading to a carbon richer liquid above the decomposition temperature of Al_4C_3 were preferred. Regarding the standard enthalpy of formation of Al_4C_3 , a value of $-26.2 \text{ kJ.mol of atoms}^{-1}$ was assessed from DFT calculations rather than from the very conflicting experimental results. In addition, the thermal stability of Al_4C_3 , which was also debated in the literature, was confirmed by the means of simple thermal analysis at $2425 \pm 15 \text{ K}$. Based on this selection a thermodynamic description of the Al_4C_3 and Al-C liquid phases was proposed. Concerning the calculated phase diagram, a relatively good agreement can be found between this work and the previous modeling of the Al-C system. However, regarding the thermodynamic data relative to the phases, significant differences were highlighted. Compared to previous works the enthalpy of formation of Al_4C_3 is less exothermic, and the thermodynamic description of the liquid phase with a much smaller excess entropy, is found to be more reasonable.

Data availability

The datasets analyzed during the current study will be made available from the corresponding author on request.

Acknowledgments

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