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# Solubility of carbon in liquid Al and stability of $\text{Al}_4\text{C}_3$

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## Abstract

Using thermodynamic models the properties of the Al–C liquid phase have been evaluated from experimental information on the carbon solubility in liquid Al. After slight modification of the description of  $\text{Al}_4\text{C}_3$  presented by Gluschko and Gurvitch [1], the solubility has been described very well from 950 to 2500 °C with a regular solution model for the liquid phase. Stability of  $\text{Al}_4\text{C}_3$  was examined through thermodynamic calculations under various conditions. It has been shown that the description of  $\text{Al}_4\text{C}_3$  can account very well for most thermochemical measurements in a wide temperature range.

**Keywords:** Thermodynamics; Aluminium; Carbon solubility; Aluminium carbide

## 1. Introduction

The Al–C system is an important binary system. The carbide  $\text{Al}_4\text{C}_3$  is now known as the only intermediate compound in the system. Thermodynamic properties of the Al–C system and stability of  $\text{Al}_4\text{C}_3$  are essential for the carbothermic reduction of alumina and for ceramic processing where  $\text{Al}_4\text{C}_3$  often exists as a common substance.

In 1981 Gluschko and Gurvitch [1] assessed the thermodynamic properties of  $\text{Al}_4\text{C}_3$  based on thermochemical measurements from literature. Unfortunately, their work is not well known outside Russia. In a recent study on the thermodynamic analysis of the Al–C–Fe system, Kumar and Raghavan [2] presented a description of the Al–C system including the liquid and  $\text{Al}_4\text{C}_3$ . Although this description gives quite reasonable agreement with experiment in some cases, it is still not acceptable in several aspects such as the carbon solubility in liquid Al around 1000 °C and the heat capacity of  $\text{Al}_4\text{C}_3$  because the relevant experimental data were not considered in their evaluation.

The main motivation for this work is to obtain a reasonable thermodynamic description of liquid  $\text{Al}_4\text{C}_3$ , which is necessary for later studies when applying an ionic-liquid model [3] to the liquid phase in the  $\text{Al}_4\text{C}_3$ –AlN,  $\text{Al}_4\text{C}_3$ – $\text{Al}_2\text{O}_3$ , and  $\text{Al}_4\text{C}_3$ –AlN– $\text{Al}_2\text{O}_3$  systems. This requires reasonable descriptions of the liquid phase and solid  $\text{Al}_4\text{C}_3$ . The former can be evaluated from experimental information on the carbon solubility in liquid Al, whereas the latter is basically accepted

from the previous work [1] but slight modifications will be made in the present study. The evaluation approach makes use of the thermodynamic models for the molar Gibbs energy of the liquid and  $\text{Al}_4\text{C}_3$  phases. Some parameters in the models are to be determined by using the THERMO-CALC program [4].

## 2. Thermodynamic models

Two phases (i.e. liquid and  $\text{Al}_4\text{C}_3$ ) are considered in the present work. The liquid was treated by a substitutional solution model [5] in which Al and C atoms were assumed to substitute for each other. The model yields the following expression for the molar Gibbs energy:

$$G_m^{\text{liq}} = x_{\text{Al}} \circ G_{\text{Al}}^{\text{liq}} + x_{\text{C}} \circ G_{\text{C}}^{\text{liq}} + RT \times (x_{\text{Al}} \ln x_{\text{Al}} + x_{\text{C}} \ln x_{\text{C}}) + {}^E G_m^{\text{liq}} \quad (1)$$

Here  $R$  is the gas constant and  $T$  is temperature in kelvin. The variable  $x_i$  ( $i = \text{Al}, \text{C}$ ) is the mole fraction of component “ $i$ ” in the liquid phase, and  $\circ G_i^{\text{liq}}$  is the Gibbs energy of the pure component in the liquid state. The quantity  $\circ G_i^{\text{liq}}$  presented in Table 1 is taken from previous work [6]. The last term  ${}^E G_m^{\text{liq}}$  represents the excess Gibbs energy and is given as follows according to the Redlich–Kister power series [7]:

$${}^E G_m^{\text{liq}} = x_{\text{Al}} x_{\text{C}} \sum_{k=0}^n {}^{(k)} L_{\text{Al},\text{C}} (x_{\text{Al}} - x_{\text{C}})^k \quad (2)$$

Table 1

Thermodynamic parameters for the Al–C liquid and Al<sub>4</sub>C<sub>3</sub>. Values are given in SI units (J, mole, K) and correspond to one mole of formula units

## Liquid

$$298.15 < T < 933.60$$

$${}^{\circ}G_{\text{Al}}^{\text{liq}} - {}^{\circ}G_{\text{Al}}^{\text{fcc}} = 11\,005.553 - 11.840\,873\,T + 7.9401 \times 10^{-20}\,T^7$$

$$933.60 < T < 2900$$

$${}^{\circ}G_{\text{Al}}^{\text{liq}} - {}^{\circ}G_{\text{Al}}^{\text{fcc}} = 10\,481.974 - 11.252\,0014\,T + 1.234\,264 \times 10^{28}/T^9$$

$$298.15 < T < 6000$$

$${}^{\circ}G_{\text{Al}}^{\text{liq}} - {}^{\circ}G_{\text{C}}^{\text{gr}} = 117\,369 - 24.63\,T$$

$$L_{\text{Al,C}}^{\text{liq}} = -4426 - 11.1007\,T$$

Al<sub>4</sub>C<sub>3</sub>

$${}^{\circ}G_{\text{m}}^{\text{Al}_4\text{C}_3} - 4H_{\text{Al}}^{\text{SER}} - 3H_{\text{C}}^{\text{SER}} = -265\,234 + 939.7257\,T - 148.7345\,T \ln T - 0.016\,733\,605\,T^2 + 3.633\,333\,33 \times 10^{-10}\,T^3 + 1863\,682/T$$

## Symbols:

$$298.15 < T < 700.00$$

$${}^{\circ}G_{\text{Al}}^{\text{fcc}} - H_{\text{Al}}^{\text{SER}} = -7976.15 + 137.071\,542\,T - 24.367\,1976\,T \ln T - 0.001\,884\,662\,T^2 - 8.776\,64 \times 10^{-7}\,T^3 + 74\,092/T$$

$$700.00 < T < 933.60$$

$${}^{\circ}G_{\text{Al}}^{\text{fcc}} - H_{\text{Al}}^{\text{SER}} = -11\,276.24 + 223.026\,95\,T - 38.584\,4296\,T \ln T + 0.018\,531\,982\,T^2 - 5.764\,227 \times 10^{-6}\,T^3 + 74\,092/T$$

$$933.60 < T < 2900.00$$

$${}^{\circ}G_{\text{Al}}^{\text{fcc}} - H_{\text{Al}}^{\text{SER}} = -11\,277.683 + 188.661\,987\,T - 31.748\,192\,T \ln T - 1.234\,264 \times 10^{28}/T^9$$

$$298.15 < T < 6000.00$$

$${}^{\circ}G_{\text{C}}^{\text{gr}} - {}^{\circ}H_{\text{C}}^{\text{SER}} = -17\,368.441 + 170.73\,T - 24.3\,T \ln T - 4.723 \times 10^{-4}\,T^2 + 2562\,600/T - 2.643 \times 10^8/T^2 + 1.2 \times 10^{10}/T^3$$

where the parameter  ${}^{(k)}L_{\text{Al,C}}$  accounts for the interaction between Al and C which can vary with temperature according to  $L = a + bT$ . The constants  $a$  and  $b$  will be evaluated in the present work.

The carbide Al<sub>4</sub>C<sub>3</sub> is treated as a stoichiometric phase with respect to its composition, and the description of its molar Gibbs energy has evaluated by Gluschko and Gurvitch [1] as follows:

$$\begin{aligned} {}^{\circ}G_{\text{m}}^{\text{Al}_4\text{C}_3} - H^{\text{SER}} &= -265\,234 + 937.1572\,T \\ &- 148.7345\,T \ln T - 0.016\,733\,605\,T^2 \\ &+ 3.633\,333\,33 \times 10^{-10}\,T^3 + 1863\,682/T \end{aligned} \quad (3)$$

where  $H^{\text{SER}}$  is the enthalpy of a selected state at 298.15 K and 1 bar (10<sup>5</sup> Pa) denoted as SER (Stable Element Reference). This expression is basically accepted but a slight modification is introduced in the present work.

### 3. Experimental information and parameter evaluation

The solubility of carbon in liquid Al has been measured many times and most results [8–12] are essentially consistent with each other in the temperature range 1600–2600 °C. However, experimental measurements at lower temperatures show a large discrepancy. It has been pointed out that the solubility data reported by Obinata and Komatsu [13] and by Dorward [14] seem too high by one or two orders of magnitude. Recently,

Simensen [15] remeasured the solubility from 960 to 1000 °C and found that it changes from 6 ppm to 12.5 ppm accordingly, which agrees very well with the extrapolation from the data of Oden and McCune [12] at higher temperature. As a consequence, these data [15] together with all others [8–12] at higher temperatures were used in the present work in order to evaluate the properties of the liquid phase.

There is also disagreement on the decomposition temperature of Al<sub>4</sub>C<sub>3</sub> as stated by Schuster [16], but recent experimental work [12] shows that Al<sub>4</sub>C<sub>3</sub> decomposes to carbon-saturated melt and graphite at about 2150 °C. This is adopted in the evaluation. Experimental information on thermochemical data of Al<sub>4</sub>C<sub>3</sub> was already taken into account when evaluating its properties in the previous work [1] and thus will no longer be included in this evaluation.

After selecting the experimental information from various sources as input data with a certain weight, evaluation was made through the THERMO-CALC program [4] during which the parameters in the model (see Eq. (2)) were optimized by minimizing the sum of squares of the differences between experimental and calculated values. Initially, it was attempted to keep the description of Al<sub>4</sub>C<sub>3</sub> presented by Gluschko and Gurvitch [1] and to evaluate the interaction parameters for the liquid phase. Optimization showed that it was necessary to apply a subregular solution model to the liquid phase, in which the parameter  ${}^{\circ}L_{\text{Al,C}}$  was evaluated as a linear function of temperature whereas  ${}^1L_{\text{Al,C}}$

was treated as a constant. With this treatment, the carbon solubility in liquid Al could be well described from 950 to 2500 °C except for the temperature range between 1700 and 2000 °C where the calculated solubility indicates a somewhat higher carbon content relative to experimental results. This is demonstrated by the dashed lines in Fig. 1. Much effort has been spent on fitting these data better, but no significant improvement could be reached without modifying the description of  $\text{Al}_4\text{C}_3$ , so it was decided to alter the description slightly. Trials were carried out to examine which term in Eq. (3) gives the best results with the least effect on the thermodynamic properties of  $\text{Al}_4\text{C}_3$ . It was found that the best choice is the second term and the modification is from 937.1572 to 939.7257 J mol<sup>-1</sup> K<sup>-1</sup>. Further, a regular solution model is now sufficient for the liquid phase. The final results together with other thermodynamic parameters are given in Table 1, which will be used to calculate the Al–C phase diagram, carbon solubility, and other thermodynamic properties.

## 4. Results and discussion

### 4.1. The Al–C phase diagram and carbon solubility

The calculated phase diagram of the Al–C system above 1600 °C is presented in Fig. 1 in comparison with experimental solubility data from various sources. In Fig. 1 the solid lines were calculated according to the final description presented in Table 1, whereas the

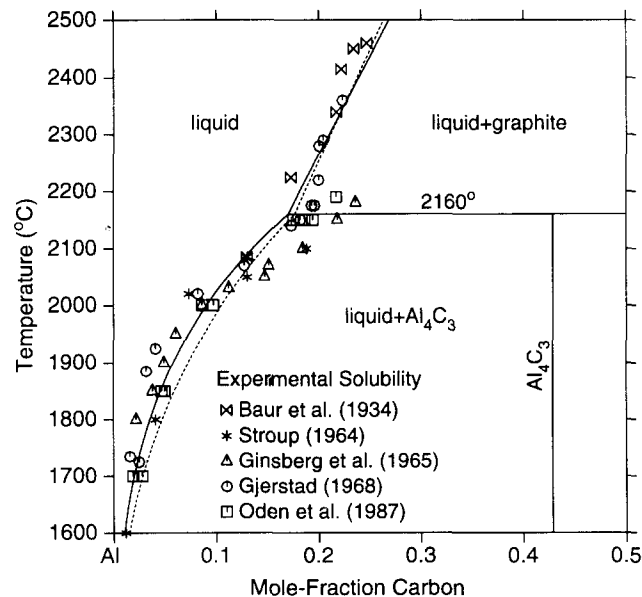


Fig. 1. Calculated phase diagram of the Al–C system in comparison with experimental solubility data from various sources. Solid lines were calculated from the description presented in Table 1, whereas dashed lines were calculated by using a subregular solution model to the liquid phase ( ${}^0L_{\text{Al,C}} = 32\,000 - 24.1517 T$  and  ${}^1L_{\text{Al,C}} = -21\,000$  J mol<sup>-1</sup>) together with the description of  $\text{Al}_4\text{C}_3$  in Eq. (3).

dashed lines were calculated by using the subregular solution model for the liquid ( ${}^0L_{\text{Al,C}} = 32\,000 - 24.1517 T$  and  ${}^1L_{\text{Al,C}} = -21\,000$  J mol<sup>-1</sup>) together with the description of  $\text{Al}_4\text{C}_3$  in Eq. (3). In general, there is satisfactory agreement between the calculation (solid lines) and experiments. The calculated peritectic melting temperature 2160 °C for  $\text{Al}_4\text{C}_3$  is close to the experimental one reported by Oden and McCune [12]. However, the dashed lines cannot account well for experimental results in the temperature range 1700–2000 °C for the reason already mentioned in Section 3. The description of the Al–C system presented by Kumar and Raghavan [2] gives similar results to the dashed lines except for a slightly higher peritectic temperature (2173 °C).

A comparison between the experimental [15] and calculated solubility at lower temperatures is presented in Fig. 2, which shows that the carbide solubility in liquid Al in the temperature range 950–1000 °C is also described very well. According to the calculation the carbon solubility increases from 6.4 ppm to 11.7 ppm as temperature increases from 960 to 1000 °C. In contrast, the description given by Kumar and Raghavan [2] is not able to describe such behavior. It gives solubility lower by two orders of magnitude than the experiments.

### 4.2. Stability of $\text{Al}_4\text{C}_3$

As already mentioned in Section 3, thermochemical measurements for  $\text{Al}_4\text{C}_3$  were considered in the previous work [1] when assessing its thermodynamic description. It is now interesting to examine its properties and compare them with experiments through thermodynamic calculation after a small modification of that description.

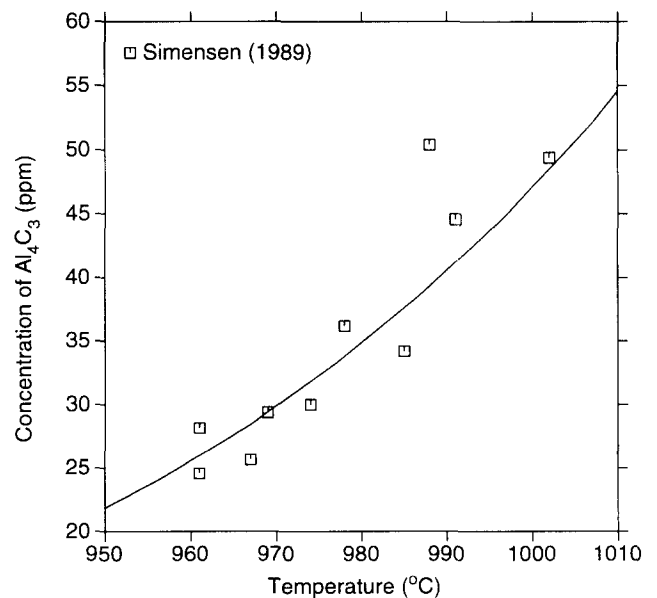


Fig. 2. Comparison between calculated and experimental carbide solubility in liquid Al.

Fig. 1 shows that  $\text{Al}_4\text{C}_3$  melts following the peritectic reaction  $\text{Al}_4\text{C}_3 \rightarrow \text{liquid} + \text{graphite}$  at 2160 °C with the decomposition enthalpy  $341.531 \text{ kJ mol}^{-1}$  and entropy  $140.371 \text{ J mol}^{-1} \text{ K}^{-1}$ . The former is about 2.5 times the value reported by Oden and Beyer [17]. In contrast, the heat content calculated for  $\text{Al}_4\text{C}_3$  agrees very well with experimental results [18] at temperatures up to 1500 °C, as will be seen later. Therefore, the difference in the decomposition enthalpy should not be taken as evidence for suspecting the present description of  $\text{Al}_4\text{C}_3$  unless more independent experiments become available. From this description one can also calculate the congruent melting temperature of  $\text{Al}_4\text{C}_3$  by applying the condition  $7G_m^{\text{liq}} - {}^\circ G_m^{\text{Al}_4\text{C}_3} = 0$  in which the liquid has the same composition as  $\text{Al}_4\text{C}_3$ . This calculation gives the temperature 2339 °C with melting enthalpy  $587.717 \text{ kJ mol}^{-1}$  and entropy  $224.984 \text{ J mol}^{-1} \text{ K}^{-1}$ . Such quantities could be used to describe the stability of liquid  $\text{Al}_4\text{C}_3$  if neglecting the difference of heat capacity between liquid  $\text{Al}_4\text{C}_3$  and solid  $\text{Al}_4\text{C}_3$ . This strategy has been applied to liquid  $\text{AlN}$  [19] and liquid  $\text{Si}_3\text{N}_4$  [20].

The heat capacity of  $\text{Al}_4\text{C}_3$  is calculated as function of temperature in Fig. 3, which shows excellent agreement with the experimental results by Furukawa et al. [21]. However, it should be noticed that the present description cannot yield correct heat capacity values at temperatures below 250 K, which are beyond the range of the description. Instead, the Debye model can be applied in this range.

After reviewing the experimental results on the enthalpy of formation of  $\text{Al}_4\text{C}_3$ , Rinehart and Behrens [22] pointed out that the enthalpy data derived from vapor pressure measurements are in no better agreement with the calorimetric values and the reason remains

unknown. The present calculation gives  $-206.900 \text{ kJ mol}^{-1}$  for the enthalpy of formation of  $\text{Al}_4\text{C}_3$  at 298.15 K, which is very close to the calorimetric measurements reported by King and Armstrong [23] and confirmed by Blachnik et al. [24]. The heat content calculated for  $\text{Al}_4\text{C}_3$  at various temperatures is shown in Fig. 4, which is in accord with experimental data by Furukawa et al. [21] and by Binford et al. [18] over a wide temperature range.

The calculated standard Gibbs energy of formation of  $\text{Al}_4\text{C}_3$  at 298.15 K is  $-194.403 \text{ kJ mol}^{-1}$ . Its temperature dependence is shown in Fig. 5 according to the calculation following the reaction  $4\text{Al}(\text{liq}) + 3\text{C}(\text{gra}) = \text{Al}_4\text{C}_3$ . The calculated value at 1873 K is  $-72.919 \text{ kJ mol}^{-1}$ , which is less negative than the value  $-88.8 \text{ kJ mol}^{-1}$  derived from Al activity measured in the Fe–Al melt at the same temperature by Choudary and Belton [25]. This can be considered as reasonable if taking into account the experimental uncertainty.

Finally, the decomposition pressure of  $\text{Al}_4\text{C}_3$  calculated according to the equilibrium  $\text{Al}_4\text{C}_3 = 4\text{Al}(\text{g}) + 3\text{C}(\text{gra})$  is plotted as a function of temperature in Fig. 6 in comparison with experimental data [22,26]. In the calculation the gaseous phase was treated as the ideal gas including the species  $\text{Al}_1$ ,  $\text{Al}_2$ ,  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{AlC}$ ,  $\text{AlC}_2$ , and  $\text{Al}_2\text{C}_2$ , and their descriptions were taken from the SGTE (Scientific Group Thermodata Europe) substance database [27] which is based on JANAF tables [28]. Fig. 6 shows that the calculated Al vapor pressures at higher temperatures are in good agreement with the experimental data by Plante and Schreyer [26], but at lower temperatures the calculation falls consistently below the measurements by Rinehart and Behrens [22]. Thermodynamic calculations indicates

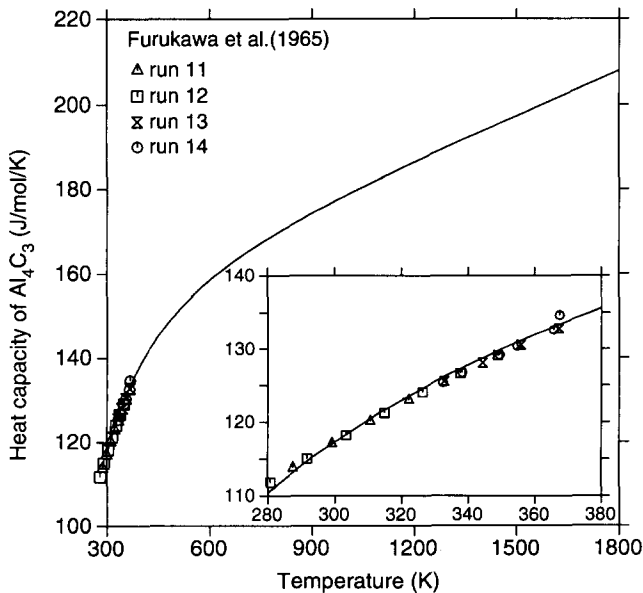


Fig. 3. Calculated heat capacity ( $C_p$ ) of  $\text{Al}_4\text{C}_3$  compared with experimental measurements.

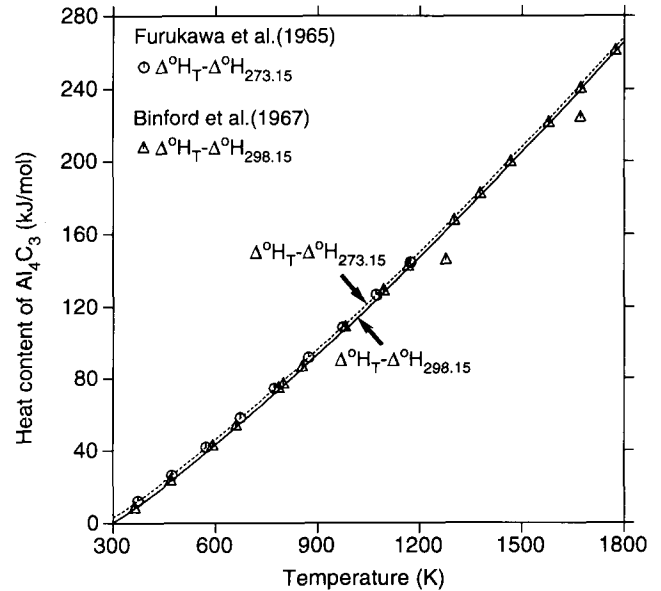


Fig. 4. Heat content ( $\Delta^{\circ}H$ ) of  $\text{Al}_4\text{C}_3$  calculated as a function of temperature in comparison with experimental data.

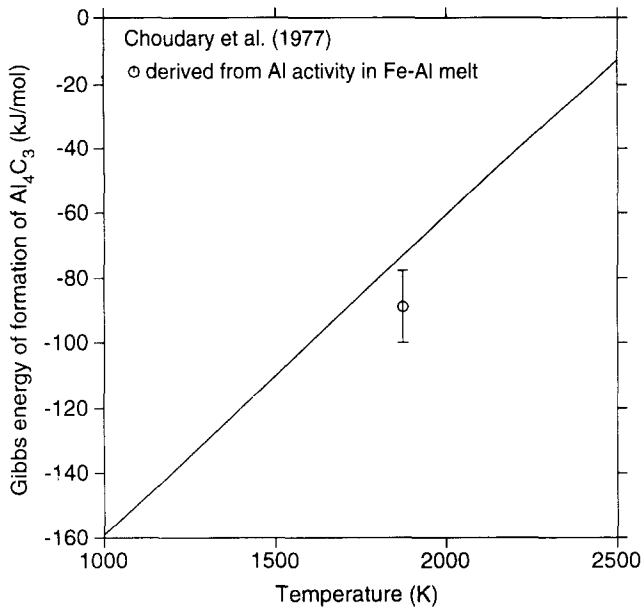


Fig. 5. Temperature dependence of the Gibbs energy ( $\Delta^{\circ}G$ ) of formation of  $\text{Al}_4\text{C}_3$  according to the present calculation following the reaction  $4\text{Al}(\text{liq}) + 3\text{C}(\text{gra}) = \text{Al}_4\text{C}_3$ .

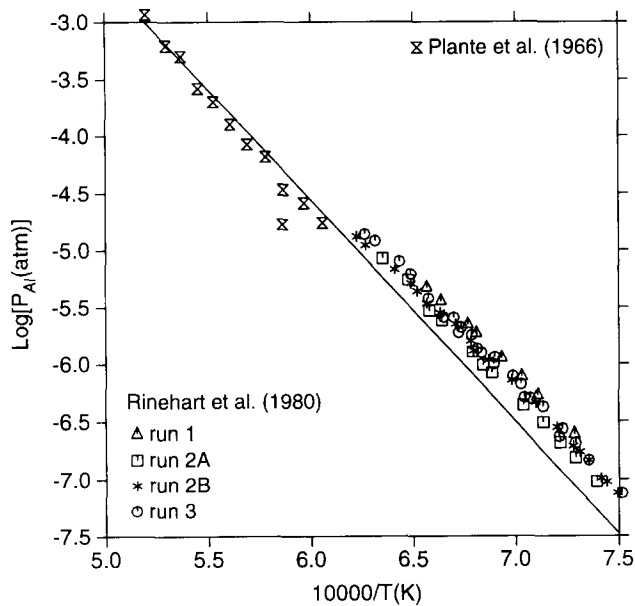


Fig. 6. Calculated decomposition pressure of  $\text{Al}_4\text{C}_3$  as a function of temperature according to the equilibrium  $\text{Al}_4\text{C}_3 = 4\text{Al}(\text{gas}) + 3\text{C}(\text{gra})$ , in comparison with experimental results.

that the vapor pressure data from Rinehart and Behrens correspond to an enthalpy value of around  $-180 \text{ kJ mol}^{-1}$  for the formation of  $\text{Al}_4\text{C}_3$  at 298.15 K, as derived by themselves. It appears that their results are neither consistent with the similar measurements [26] at higher temperatures nor with the calorimetric measurements [23,24].

## 5. Summary and conclusions

Using thermodynamic models the properties of the Al–C liquid phase have been evaluated based on experimental information on the carbon solubility in liquid Al. After slight modification of the description of  $\text{Al}_4\text{C}_3$  presented by Gluschko and Gurvitch [1], the solubility has been described very well from 950 to 2500 °C with a regular solution model for the liquid phase, which is not the case in the previous work [2].

Stability of  $\text{Al}_4\text{C}_3$  has been examined through thermodynamic calculations under various conditions. It has been shown that the description of  $\text{Al}_4\text{C}_3$  can account very well for most thermochemical measurements over a wide temperature range. Nevertheless, the vapor pressures for  $\text{Al}_4\text{C}_3$  decomposition measured by Rinehart and Behrens [22] at lower temperatures, which suggest a smaller value of enthalpy of formation of  $\text{Al}_4\text{C}_3$  at 298.15 K, could not be reproduced by the calculation since they are not consistent with other thermochemical measurements.

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