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Phase Relations in the Aluminum Carbide-Aluminum Nitride-Aluminum Oxide System

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The phase diagram of the pseudobinary Al4C3–AlN system was predicted using thermodynamic models. It was combined with previous thermodynamic descriptions of the pseudobinary Al4C3–Al2O3 and AlN–Al2O3 systems, and then thermodynamic properties of the pseudoternary Al4C3–AlN–Al2O3 system were assessed by modeling the Gibbs energy of the various phases. An ionic-liquid model was applied to the liquid phase and a compound-energy model was applied to the solid-solution phase (2H) that formed between Al2OC and AlN. A series of isothermal sections of the system were calculated in the temperature range of 1000°C–2100°C, and reasonable phase relations were established. The calculated isothermal section at 1600°C showed satisfactory agreement with experimental results. The calculated liquidus projection in the Al2O3-rich corner can explain the experimental observation of the microstructure after solidification very well. However, the present description cannot account for the phase segregation inside the solution phase but could be modified in the future, when more experimental information would be available.

I. Introduction

Aluminum carbide (Al4C3), aluminum nitride (AlN), and aluminum oxide (α-Al2O3, simply denoted as Al2O3) are important substances in ceramic materials. They can react with the environment to decompose or form complex compounds during ceramic processing under certain circumstances. The decomposition of the compounds and/or formation of new compounds will strongly affect various properties of the ceramic materials. Phase diagrams of the pseudoternary Al4C3–AlN–Al2O3 system are essential for understanding the reactions and for further development of the ceramic materials, because the diagrams can illustrate the phase relations and phase stability under different conditions.

An initial attempt to investigate the Al4C3–AlN–Al2O3 system was made by Henry et al.1 to search for the composition that may exhibit desirable high-temperature properties, and different phases in the system were classified. Recently, Green and coworkers2–4 explored new ceramics with high thermal conductivity and/or silicon.21 Therefore, only Al5C3N will be considered in this system when hot pressing samples at 1800°C. Groen and coworkers15,16 found the intermediate phase Al5C3N with a layer structure of Al4C3 and AlN. Later, Jeffrey and Wu17,18 reported three new compounds (Al5C3N2, Al7C3N3, and Al8C3N4) in this system. The occurrence of Al5C3N has been confirmed by several investigators,1,17–21 whereas the existence of the other three compounds remains controversial because they are likely to be stabilized by oxygen and/or silicon.21 Therefore, only Al5C3N will be considered in this work.

In the Al4C3–AlN–Al2O3 system, a solid-solution phase (denoted as 2H) that formed between Al2OC and AlN was observed under certain circumstances. In addition, Henry et al.1 found a phase with a diffraction pattern that was very similar to that of α-Al2O3 and at least three unidentified phases inside this system when hot pressing samples at 1800°C. Groen and coworkers2–4 also found three new quaternary compounds.

II. Thermodynamic Models

Thermodynamic models for various phases in the Al4C3–Al2O3 and AlN–Al2O3 systems have already been discussed in previous works.10,11,14 In the Al4C3–AlN system, Stackelberg and coworkers17,18 found the intermediate phase Al5C3N with a layer structure of Al4C3 and AlN. Later, Jeffrey and Wu17,18 reported three new compounds (Al5C3N2, Al7C3N3, and Al8C3N4) in this system. The occurrence of Al5C3N has been confirmed by several investigators,1,17–21 whereas the existence of the other three compounds remains controversial because they are likely to be stabilized by oxygen and/or silicon.21 Therefore, only Al5C3N will be considered in this work. In the Al4C3–AlN–Al2O3 system, a solid-solution phase (denoted as 2H) that formed between Al2OC and AlN was observed under certain circumstances. In addition, Henry et al.1 found a phase with a diffraction pattern that was very similar to that of α-Al2O3 and at least three unidentified phases inside this system when hot pressing samples at 1800°C. Groen and coworkers2–4 also found three new quaternary compounds.
One, with the composition Al$_2$O$_3$N$_2$C$_6$, crystallizes in a diamond-related structure and the other two (Al$_2$O$_3$N$_2$C$_5$ and Al$_2$O$_3$N$_2$C$_4$) are under investigation. Because of a lack of additional experimental information on the thermodynamic properties of all the quaternary compounds, it would be very uncertain to model them and evaluate their properties. As a consequence, it was decided not to include them in the present study. All the phases that are considered in this work were modeled as follows, and the models are summarized in Table I.

(1) Liquid

The liquid that is formed in the Al$_4$C$_3$–AlN–Al$_2$O$_3$ system is described by an ionic two-sublattice model, 22 (Al$^{3+}$)$_n$(C$^{4−}$, N$^{3−}$, O$^{2−}$)$_m$ where the anions are assumed to substitute for each other on the second sublattice. To maintain electroneutrality, $P$ and $Q$ vary with composition according to the following equations:

$$ P = \sum y_j(-v_j) = 4y_{c^+} + 3y_{N^−} + 2y_{O^−} $$  \hspace{1cm} (1a)

$$ Q = \sum y_j v_j = 3y_{Al^3+} = 3 $$  \hspace{1cm} (1b)

where the variables $y_i$ and $v_j$ are the so-called site fractions of anion $i$ and cation $j$ in the compositional sublattice, respectively. The valency of anion $i$ and cation $j$ are represented by $v_i$ and $v_j$, respectively. The molar Gibbs energy of the liquid (denoted as “liq”) is expressed as follows:

$$ G_{m^{liq}} = y_{c^+} e^{G_{m^{liq}}^{c^+}} - c^+ + y_{N^−} e^{G_{m^{liq}}^{N^−}} - N^− + y_{O^−} e^{G_{m^{liq}}^{O^−}} - O^− + QRT(y_{c^+} \ln y_{c^+} + y_{N^−} \ln y_{N^−} + y_{O^−} \ln y_{O^−}) + e^{Fm{liq}} $$

where $Q$ is given by Eq. (1b); $R$ is the gas constant, and $T$ is temperature (in Kelvin). The variables $e^{G_{m^{liq}}^{c^+}}$, $e^{G_{m^{liq}}^{N^−}}$, and $e^{G_{m^{liq}}^{O^−}}$ are the Gibbs energies of 1 mol of Al$_2$C$_2$, 3 mol of AlN, and 1 mol of Al$_2$O$_3$ in the liquid state, respectively. They are referred to the enthalpy ($\Delta H^{SER}$) of the selected state at 298.15 K and 1 bar (10$^5$ Pa), denoted as SER (Stable Element Reference), as shown in the Appendix. All of them are accepted from previous studies. 23-25 The last term in Eq. (2), $e^{Fm{liq}}$, represents the excess Gibbs energy and is dependent on the interaction among the C$^{4−}$, N$^{3−}$, and O$^{2−}$ anions on the anion sublattice as follows:

$$ e^{Fm{liq}} = y_{c^+} e^{y_{N^−} L_{Al^{3+}}^{liq} c^+ - c^+} + y_{N^−} e^{y_{O^−} L_{Al^{3+}}^{liq} c^+ - O^−} + y_{O^−} \ln y_{O^−} $$

Here, $L_{Al^{3+}}^{liq} c^+ - c^+$ is the interaction parameter, in which the comma separates anions interacting on the same sublattice and the colon separates the cations from the anions on different sublattices. The parameter $L_{Al^{3+}}^{liq} c^+ - O^−$, which represents the interaction between C$^{4−}$ and O$^{2−}$ anions in the Al$_4$C$_3$–Al$_2$O$_3$ liquid, was evaluated by Qiu and Metselaar 10 using a subregular model. In the first evaluation of the AlN–Al$_2$O$_3$ system, Hillert and Jonsson 11 adopted the ionic two-sublattice model to describe the liquid; however, the parameter $L_{Al^{3+}}^{liq} c^+ - N^−$ was omitted, because of a lack of experimental information. Later, Dumitrescu and Sundman 14 treated the phase as a substituitional solution between AlN and AlO$_{1.5}$ in the new evaluation of the AlN–Al$_2$O$_3$ system, which is not consistent with the present treatment. When applying the ionic sublattice model to the AlN–Al$_2$O$_3$ system, it is now necessary to introduce the parameter $L_{Al^{3+}}^{liq} c^+ - N^−$. There is no experimental information available for estimation of the parameter $L_{Al^{3+}}^{liq} c^+ - N^−$ in the Al$_4$C$_3$–AlN system; however, it is still necessary, because of additional requirements. The parameter estimation is discussed later.

(2) Solid-Solution Phase (2H)

In the previous work on the Al$_4$C$_3$–AlN–Al$_2$O$_3$ system, Qiu and Metselaar 10 applied a compound-energy model 26 to Al$_2$OC. This model, with two sublattices, can be extended to describe the solid-solution phase that forms among Al$_2$OC, AlN, and SiC. All these compounds have the same crystal structure, which is based on the wurtzite-type lattice, which consists of two hexagonal-close-packed (hcp) sublattices that are displaced from each other. 70 When applying this model to the solution phase between Al$_2$OC and AlN, it becomes (Al$^{3+}$)$_{y_1}$(C$^{4−}$, N$^{3−}$, O$^{2−}$)$_{y_2}$, where the anions can be substituted for each other on the anion sublattice (following a certain rule to maintain electroneutrality). The molar Gibbs energy of the 2H phase is obtained from

$$ G_{m^{2H}} = y_{c^+} e^{G_{m^{2H}}^{c^+}} + y_{N^−} e^{G_{m^{2H}}^{N^−}} + y_{O^−} e^{G_{m^{2H}}^{O^−}} + 2RT(y_{c^+} \ln y_{c^+} + y_{N^−} \ln y_{N^−} + y_{O^−} \ln y_{O^−}) + y_{c^+} y_{N^−} L_{Al^{3+}}^{2H} c^+-c^+ \ln y_{2H} + y_{c^+} y_{O^−} L_{Al^{3+}}^{2H} c^+-O^− \ln y_{2H} + y_{N^−} y_{O^−} L_{Al^{3+}}^{2H} c^+-N^− \ln y_{2H} $$

Here, $y_{c^+} = y_{N^−}$, which ensures that the composition of the 2H phase varies to maintain electroneutrality. Al$_4$C$_3$ and Al$_2$OC are hypothetical substances with the same structure as the 2H phase, and their Gibbs energies ($e^{G_{m^{2H}}^{Al_4C_3}}$ and $e^{G_{m^{2H}}^{Al_2OC}}$) were discussed by Qiu and Metselaar, 10 i.e., the value of $e^{G_{m^{2H}}}$ was set at zero as a reference, and the value of $e^{G_{m^{2H}}^0}$ was obtained from the $G_{m^{Al_2OC}}$, which was evaluated from experimental information. The Gibbs energy of AlN$_2$ ($e^{G_{m^{Al_2OC}}}$) can be expressed as twice the value for AlN that was assessed by Hillert and Jonsson. 11 The interaction parameters $L_{Al^{3+}}^{2H} c^+-j$ have similar meanings as those in Eq. (3). Among the three parameters, the value of $L_{Al^{3+}}^{2H} c^+ c^+$ was set at zero in the previous work on the Al$_4$C$_3$–Al$_2$O$_3$ system, 10 and the other two can be set equal to each other, because of the condition $y_{c^+} = y_{N^−}$. They are to be evaluated from experimental information.

Table I. Summary of Thermodynamic Models, Showing the Sublattice Occupation Scheme for Various Phases in the Pseudoternary Al$_4$C$_3$–AlN–Al$_2$O$_3$ System

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum-rich liquid</td>
<td>(Al, C)$_1$</td>
<td>Substitutional solution</td>
<td>Qiu and Metselaar</td>
</tr>
<tr>
<td>Liquid</td>
<td>(Al$^{3+}$)$_n$(C$^{4−}$, N$^{3−}$, O$^{2−}$)$_m$</td>
<td>Ionic two-sublattice</td>
<td>This work</td>
</tr>
<tr>
<td>Solid solution (2H)</td>
<td>(Al$^{3+}$)$_n$(C$^{4−}$, N$^{3−}$, O$^{2−}$)$_m$</td>
<td>Compound-energy model</td>
<td>Dumitrescu and Sundman</td>
</tr>
<tr>
<td>Al$_4$C$_3$</td>
<td>(Al$^{3+}$)$_n$(C$^{4−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Qiu and Metselaar</td>
</tr>
<tr>
<td>AlN</td>
<td>(Al$^{3+}$)$_n$(N$^{3−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Hillert and Jonsson</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>(Al$^{3+}$)$_n$(O$^{2−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Taylor et al.</td>
</tr>
<tr>
<td>Al$_4$C$_3$N</td>
<td>(Al$^{3+}$)$_n$(C$^{4−}$,N$^{3−}$)$_m$</td>
<td>Solution phase</td>
<td>This work</td>
</tr>
<tr>
<td>Al$_4$C$_3$O$_3$</td>
<td>(Al$^{3+}$)$_n$(C$^{4−}$,O$^{2−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Dumitrescu and Sundman</td>
</tr>
<tr>
<td>12H</td>
<td>(Al$^{3+}$)$_n$(N$^{3−}$)$_m$(O$^{2−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Dumitrescu and Sundman</td>
</tr>
<tr>
<td>21R</td>
<td>(Al$^{3+}$)$_n$(N$^{3−}$)$_m$(O$^{2−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Dumitrescu and Sundman</td>
</tr>
<tr>
<td>27R</td>
<td>(Al$^{3+}$)$_n$(N$^{3−}$)$_m$(O$^{2−}$)$_m$</td>
<td>Stoichiometric compound</td>
<td>Dumitrescu and Sundman</td>
</tr>
</tbody>
</table>
The description of the spinel phase in the MgO–Al₂O₃ system has been illuminated in detail by Hallstedt using the compound-energy model. Later, the same model was adopted by Hillert and Jonsson to treat the spinel phase based on Al₂O₃ in the AlN–Al₂O₃ system, and it has the following form: (Al³⁺)(Al³⁺,Va)(N³⁻,O²⁻). This model and its thermodynamic description that was given by Dumitrescu and Summan were accepted in the present study, and no carbon solubility was considered in the spinel phase.

Other Phases
All other compounds are treated as stoichiometric phases, with respect to their compositions. The thermodynamic descriptions of Al₄C₃, Al₂O₃, Al₄O₄C, 12H (Al₆O₄N₃), 21R (Al₇O₅N₃), and 27R (Al₉O₇N₃) have been obtained in previous evaluations, whereas the molar Gibbs energy for Al₅C₃N is given by

\[ G_m^{Al₅C₃N} = G_m^{Al₄C₃} + G_m^{AlN} + a + bT \]

Here, the quantities \( G_m^{Al₄C₃} \) and \( G_m^{AlN} \) are the molar Gibbs energies for Al₄C₃ and AlN, respectively. The constants \( a \) and \( b \) are to be estimated by examining the thermodynamic stability of Al₅C₃N in this work.

The liquid metal has been modeled as a substitutional solution between aluminum and carbon. Although a very small amount of nitrogen and oxygen can be dissolved in liquid aluminum, their solubilities are much lower than the solubility of carbon. Therefore, the dissolution of nitrogen and oxygen in liquid aluminum has been neglected for simplicity in the present case, and then the previous description of the aluminum–carbon liquid phase can be directly used in this work.

III. Experimental Information and Parameter Evaluation
From the processing section, it has been shown that there are several parameters in the thermodynamic models to be evaluated on the basis of experimental information. The evaluation was made using a computerized optimization program that is available in the Thermo-Calc databank. This program can simultaneously treat various types of input data, and the parameters are obtained by searching for the best fit to the selected experimental data, within an expected uncertainty. The parameters that are obtained in this way also are required to be self-consistent and to yield reasonable phase relations and stabilities of various phases in the entire system.

The first step in the evaluation is to assess the Al₅C₃N–AlN system. To evaluate the model parameters, it is necessary to have relevant experimental information. Oden and McCune observed the melting of a sample of a mixture of Al₅C₃N and AlN at 2195°C, using thermal analysis during heating, and then suggested that the observed arrest was probably eutectic melting of Al₅C₃N and AlN. Later, Schuster found that Al₅C₃N melted incongruently to graphite, AlN, and an aluminum-rich liquid at 2185°C (with an uncertainty of 15°C) under 10⁵ Pa of pure argon. If a eutectic reaction AlN + Al₅C₃N \( \rightarrow \) liquid does exist at 2195°C, then the incongruent melting of Al₅C₃N must occur at a temperature of >2195°C. In fact, the melting that was observed was found to be 2175°C.
determined by Schuster at 2185°C may be caused by the presence of Al$_4$C$_3$, which will melt incongruently to graphite and an aluminum-rich liquid at ~2160°C. The presence of Al$_4$C$_3$ can be the result of decomposition of Al$_5$C$_3$N during heating. As a consequence, the melting that was determined by Schuster may not be considered as the incongruent melting of Al$_5$C$_3$N; thus, his observation was not considered. Instead, the results by Oden and McCune were used in the present evaluation.

For kinetic reasons, in the experiments where the samples were heated at a rate of 10°–13°C/min, the observed melting temperature should be slightly higher than the equilibrium melting temperature. A temperature lower than 2195°C was then chosen as the temperature for the eutectic reaction AlN + Al$_5$C$_3$N → liquid. In addition, Al$_5$C$_3$N is also assumed to remain stable below its incongruent melting temperature. With these treatments, the stability of Al$_5$C$_3$N could be assessed preliminarily by estimating the parameters $a$ and $b$ in Eq. (5). During the course of this work, an additional requirement has been derived for these two parameters; i.e., their values should make the stability of Al$_5$C$_3$N consistent with other phases in the Al$_4$C$_3$–AlN–Al$_2$O$_3$ system, to establish reasonable phase relations at various temperatures. This requires the term $a + bT$ to have a value of approximately −15000 J/mol at 1600°C; this was introduced as a condition in the optimization. At the same time, the interaction parameter $L_{\text{liq} \text{Al}^{3+}:N^{3-},O^{2-}}$ was adjusted to obtain a better fit to the eutectic temperature. The final values that are estimated here are presented in the Appendix.

The next step is to estimate the interaction parameter $L_{\text{N}^{3-},O^{2-}}$ in the AlN–Al$_2$O$_3$ system. Because the stability of the spinel phase is well described and all other compounds except Al$_{22}$N$_3$O$_2$ with $d$-spinel structure are included in the new evaluation of the AlN–Al$_2$O$_3$ system, it is straightforward to accept the descriptions of all these phases. Nevertheless, the liquid has been described with a substitutional-solution model in the new evaluation, which is not compatible with the present ionic model. Then, $L_{\text{N}^{3-},O^{2-}}$ is required.

Fig. 4. Calculated isothermal sections of the pseudoternary Al$_2$O$_3$–Al$_4$C$_3$–AlN system at various temperatures ((a) 1000°, (b) 1200°, (c) 1400°, and (d) 1600°C; data for Fig. 4(d) is from Lührmann et al.8).
when applying the ionic model, and its value should be such that the invariant reactions that are calculated using the ionic model are as close as possible to the previous calculations using the substitutional model, specially for those reactions that are in good agreement with experimental results. Based on this consideration, the temperatures for the reactions \( 27\text{R} + \text{liquid} \rightarrow 12\text{H} \) and \( \text{liquid} \rightarrow 12\text{H} + \text{spinel} \) were fitted to the previous calculations, and the parameter \( L_{\text{liq}}^{\text{Al}_{3}^{3+} \text{N}_{3}^{2-} \text{O}_{2}^{-}} \) was evaluated as a linear function of temperature (see the Appendix).

The final step is to combine the descriptions of the three subsystems and then evaluate the \( \text{Al}_{4}\text{C}_{3} - \text{AlN} - \text{Al}_{2}\text{O}_{3} \) system. Experimental information on this system, as mentioned earlier, is very limited. Henry et al. examined the phase constituents of the samples with various compositions that were hot pressed at \( \sim 1800^\circ\text{C} \). Unfortunately, equilibrium was not attained in most cases; thus, such information could not be used for thermodynamic evaluation. The experimental results by Lihmann et al., showing the effect of AlN addition on the stability of \( \text{Al}_{2}\text{OC} \), were used to evaluate the interaction parameters in Eq. (4), which can adjust the stability range of the solution phase that is formed between \( \text{Al}_{2}\text{OC} \) and AlN. The parameter values that have been evaluated in this work are given in the Appendix. Segregation of the solution phase has been observed in a certain composition range. A description of such behavior requires complicated thermodynamic and kinetic treatments; experimental information is insufficient to allow such treatments. Consequently, the segregation has not been considered, and the solution phase is treated as a complete solid solution between \( \text{Al}_{2}\text{OC} \) and AlN.

In addition, Lihmann reported the microstructure of the \( \text{Al}_{4}\text{C}_{3} - \text{AlN} - \text{Al}_{2}\text{O}_{3} \) samples after solidification. Because the compositions of the samples fall in the \( \text{Al}_{2}\text{O}_{3} \)-rich corner, their solidification processes and microstructure are mainly governed by the eutectic and peritectic reactions in the \( \text{Al}_{4}\text{C}_{3} - \text{Al}_{2}\text{O}_{3} \) system. Although such experimental information was already considered when the \( \text{Al}_{4}\text{C}_{3} - \text{Al}_{2}\text{O}_{3} \) system was evaluated by Qiu and Metselaar, further examination also was made during the present evaluation.

The thermodynamic parameters for the liquid, \( 2\text{H} \) phase, and

Fig. 5. Calculated isothermal sections of the pseudoternary \( \text{Al}_{2}\text{O}_{3} - \text{Al}_{4}\text{C}_{3} - \text{AlN} \) system at various temperatures ((a) 1800°, (b) 2000°, and (c) 2100°).
IV. Results and Discussion

The phase diagram of the pseudobinary $\text{Al}_4\text{C}_3$–$\text{AlN}$ system was calculated by excluding the gas phase, as shown in Fig. 1. The calculated temperature for the liquid $\rightarrow$ $\text{AlN} + \text{Al}_5\text{C}_3\text{N}$ eutectic reaction, 2180°C, is slightly lower than 2195°C, which is the temperature at which the melting of the mixture of $\text{AlN}$ and $\text{Al}_5\text{C}_3\text{N}$ was determined by Oden and McCune. This is very reasonable if the kinetic effect and heating rate in the experiments are considered. Only one intermediate compound—$\text{Al}_5\text{C}_3\text{N}$—appears in Fig. 1, and it remains stable until it melts incongruently at 2253°C. The incongruent melting of $\text{Al}_4\text{C}_3$ occurs at 2160°C, which is just below the temperature at which Schuster observed melting of the $\text{Al}_5\text{C}_3\text{N}$ sample. This observation of melting most likely can be considered as the incongruent melting of $\text{Al}_4\text{C}_3$ rather than $\text{Al}_5\text{C}_3\text{N}$. As mentioned in Section II, other possible compounds (e.g., $\text{Al}_6\text{C}_3\text{N}_2$, $\text{Al}_7\text{C}_3\text{N}_3$, $\text{Al}_8\text{C}_3\text{N}_4$) have been ignored in the evaluation of the $\text{Al}_4\text{C}_3$–$\text{AlN}$ system. The present $\text{AlN}$–$\text{Al}_4\text{C}_3$ phase diagram should be regarded only as a provisional version that may be modified in a future evaluation of the $\text{Al}_4\text{C}_3$–$\text{AlN}$ system when new experimental data that concern the stabilities of $\text{Al}_5\text{C}_3\text{N}_2$, $\text{Al}_7\text{C}_3\text{N}_3$, and $\text{Al}_8\text{C}_3\text{N}_4$ become available.

For convenience of discussion, the phase diagrams of the pseudobinary $\text{Al}_2\text{O}_3$–$\text{Al}_4\text{C}_3$ and $\text{Al}_2\text{O}_3$–$\text{AlN}$ systems also have been calculated, as shown in Figs. 2 and 3. The present $\text{Al}_2\text{O}_3$–$\text{AlN}$ diagram is very similar to the previous diagram that was calculated using the substitutional model for the liquid. The calculated temperatures for the invariant reactions liquid $\rightarrow$ 21R $\rightarrow$ 12H, liquid $\rightarrow$ 12H + spinel, and liquid $\rightarrow$ $\text{Al}_2\text{O}_3 +$ spinel are the same as the corresponding temperatures in the previous calculations. However, the present liquidus of spinel falls slightly above the previous one, and the liquid of the 12H and 21R phases also are shifted slightly to the $\text{AlN}$ side. Other differences between the present diagram and previous calculations are the temperatures of the congruent melting of the 27R phase and the invariant reactions liquid $\rightarrow$ $\text{AlN} +$ 27R and liquid $+ 27R$ $\rightarrow$ 21R, which are unknown from experiments.

Now, we shall discuss the pseudoternary $\text{Al}_4\text{C}_3$–$\text{AlN}$–$\text{Al}_2\text{O}_3$ system. A series of isothermal sections have been calculated at temperatures in the range of 1000°–2100°C and are presented in Figs. 4 and 5. These diagrams show that $\text{AlN}$ extends into the pseudoternary system to form the solid-solution phase 2H, and the solubility of $\text{Al}_2\text{O}_3$ in the 2H phase increases as the temperature increases until the complete solution forms between $\text{Al}_2\text{O}_3$ and $\text{AlN}$ in the temperature range of 1710°–1990°C, where $\text{Al}_2\text{O}_3$ becomes stable. After $\text{Al}_2\text{O}_3$ melts at 1990°C, the liquid becomes a dominant phase in the $\text{Al}_2\text{O}_3$-rich corner at higher temperatures. Among these isothermal sections, Fig. 4(d) shows a comparison with the experimental results at 2000°C. The experiments indicate that $\text{AlN}$ decomposes to $\text{Al}_4\text{O}_4\text{C}$ and $\text{Al}_4\text{C}_3$, however, it becomes stable after an addition of $\text{AlN}$. Meanwhile, the amount of $\text{Al}_4\text{O}_4\text{C}$ decreases as the $\text{AlN}$ addition to the sample increases. When the $\text{AlN}$ addition is 15 mol%, $\text{Al}_4\text{O}_4\text{C}$ does not exist in the samples anymore, which is clearly illustrated by the calculated
isothermal section in Fig. 4(d). However, the experiments also show phase segregation of the solid-solution phase when the AlN addition is >80 mol%, whereas the present calculation gives a complete solution. This difference is accepted because the segregation has not been considered in the present models.

The calculated section at 1800°C shows that Al$_5$C$_3$N exists only in the three-phase (Al$_5$C$_3$N + 2H + Al$_4$C$_3$) and two-phase (Al$_5$C$_3$N + 2H) regions (see Fig. 5(a)). These regions occupy only a small part of the entire composition triangle. The experimental observation of Al$_5$C$_3$N by Henry et al. indicates that Al$_5$C$_3$N forms only in a narrow composition region when the samples were hot pressed at $\sim$1800°C. Although equilibrium has not been attained in most cases of their experiments, such observation can still be used as a guideline in comparison with the calculation.

The projection of the liquidus surfaces in the Al$_2$O$_3$–Al$_4$C$_3$–AlN system has been calculated, together with isotherms, as shown in Fig. 6. In the diagram, each curve with an arrow that indicates decreasing temperature represents a univariant equilibrium, and a cross point of three such curves represents an invariant equilibrium. On each liquidus surface, the liquid is in equilibrium with only one solid phase; thus, only one solid phase is marked in each area, except the area with liquid + carbon (i.e., aluminum-rich liquid and graphite) that is caused by the decomposition of Al$_4$C$_3$. That solid phase will precipitate first during solidification when the sample composition falls in this area. The liquidus of the 2H phase notably covers a wide area; this is because the 2H phase has been modeled as a complete solid solution between Al$_2$OC and AlN, and its liquidus extends from the Al$_2$O$_3$–Al$_4$C$_3$ side to the AlN–Al$_4$C$_3$ side. Hence, the liquidus of the 2H phase has contact with all other liquids.

As stated before, the evaluation of the Al$_4$C$_3$–AlN liquid was based on very limited information. No interaction parameter was introduced for the quaternary liquid, because of a lack of experimental data. Therefore, the calculated liquidus projection in Fig. 6 should be regarded as an approximation. Nevertheless, it would be very useful when predicting the effect of a change in composition or temperature; thus, this may be used as a guideline for future experiments. Particularly, the calculated univariant equilibrium curves in the Al$_4$C$_3$–AlN rich corner are in good agreement with experimental microstructure observation, as demonstrated in Fig. 7. Two experimental samples were observed to have almost purely eutectic structures after solidification, and their compositions were near the calculated eutectic curve, liquid $\rightarrow$ Al$_4$O$_3$ + 2H, and eutectic point, liquid $\rightarrow$ Al$_4$O$_3$ + 2H + Al$_2$O$_3$C, at 1838°C; all of the liquid has solidified after the eutectic reaction at 1838°C. The other two samples after solidification exhibited primary crystal and eutectic structures, and their compositions were in the liquidus of the 2H phase. Therefore, the calculated univariant equilibrium curves in the Al$_4$O$_3$-rich corner seem reasonable, although the calculation showed some discrepancies with the experimental data on the liquidus temperatures.

V. Summary and Conclusions

An attempt has been made to predict the pseudobinary Al$_4$C$_3$–AlN phase diagram by applying thermodynamic models. In the prediction, only one intermediate phase—Al$_5$C$_3$N—was considered, whereas other possible intermediate phases were not considered, because their existence remains controversial. The thermodynamic properties of the Al$_4$C$_3$–AlN system were then combined with those of the pseudobinary Al$_4$C$_3$–Al$_2$O$_3$ and AlN–Al$_2$O$_3$ systems, and the pseudoternary Al$_4$C$_3$–AlN–Al$_2$O$_3$ system was evaluated after considering the experimental information. In the evaluation, an ionic-liquid model was applied to describe the liquid phase, and a compound-energy model was applied to describe the solid-solution 2H phase that formed between Al$_4$OC and AlN. A series of isothermal sections of the Al$_4$C$_3$–AlN–Al$_2$O$_3$ phase diagrams were calculated within the temperature range of 1000°–2100°C, and reasonable phase relations were well established. The isothermal section that was calculated at 1600°C showed satisfactory agreement with experimental results. The calculated liquidus projection also was presented, which could explain very well the microstructure observation of the experimental samples in the Al$_4$O$_3$-rich corner after solidification.

The 2H phase also has been treated as a complete solid solution from Al$_2$OC to AlN, based on the present thermodynamic model, and this cannot account for the phase segregation that is observed inside the solution in the experiments within a certain composition range. This treatment can be modified in the future, when more experimental information is available.
APPENDIX

Thermodynamic Parameters for the Liquid, Solid-Solution (2H), and Al₄C₃N Phase in the Pseudoternary Al₄C₃–AlN–Al₂O₃ System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression/value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid with formula (Al₄C₃)m(C⁺,N⁻,O²⁻)ₙ</td>
<td>[ G_{\text{liq}}^{\text{m}} ]</td>
</tr>
<tr>
<td>3°/2°</td>
<td>[ G_{\text{liq}}^{\text{3°/2°}} = -4H_{\text{SER}}^{\text{3°/2°}} - 3H_{\text{SER}}^{\text{3°/2°}} ]</td>
</tr>
<tr>
<td>3°/2°</td>
<td>[ G_{\text{liq}}^{\text{3°/2°}} = -3H_{\text{SER}}^{\text{3°/2°}} - 3H_{\text{SER}}^{\text{3°/2°}} ]</td>
</tr>
<tr>
<td>Solid-solution phase (2H) with formula (Al₄C₃)m(C⁺,N⁻,O²⁻)ₙ</td>
<td>[ G_{\text{m}}^{\text{LOC}} = 4RT \ln 0.5 ]</td>
</tr>
<tr>
<td>3°/2°</td>
<td>[ G_{\text{m}}^{\text{3°/2°}} = 2G_{\text{m}}^{\text{AIN}} ]</td>
</tr>
<tr>
<td>3°/2°</td>
<td>[ G_{\text{m}}^{\text{3°/2°}} = 2G_{\text{m}}^{\text{AIN}} + 2G_{\text{m}}^{\text{LOC}} - 2H_{\text{SER}}^{\text{3°/2°}} + 2H_{\text{SER}}^{\text{3°/2°}} ]</td>
</tr>
<tr>
<td>Solid-solution phase (2H) with formula (Al₄C₃)m(C⁺,N⁻,O²⁻)ₙ</td>
<td>[ G_{\text{AlC₃N}} = G_{\text{m}}^{\text{Al₄C₃}} + G_{\text{m}}^{\text{AIN}} + 20120 \pm 187.5T ]</td>
</tr>
</tbody>
</table>

Values are given in SI units (J, mol, K) and correspond to 1 mol of formula units. Parameters for the other phases can be found in relevant references.

References