Thermodynamics of Alon I: Stability at Lower Temperatures

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Abstract

The formation and stability of Alon under various circumstances are described using Ellingham and activity diagrams. With the help of these diagrams the connection between seemingly uncorrelated experimental observations on the stability of Alon from the literature can be understood. Thermodynamic data sets for Alon are critically reviewed. It is shown that Alon is stable only within a small region of oxygen and nitrogen pressures, and that it is not stable below 1640 ± 10°C.


La formation et la stabilité de l’Alon sous diverses conditions sont décrites en utilisant les diagrammes d’Ellingham et les diagrammes d’activité. À l’aide de ces diagrammes, un rapport entre des observations expérimentales apparentement sans corrélation sur la stabilité de l’Alon dans la littérature peut être trouvé. Des données thermodynamiques sur l’Alon sont passées en revue de façon critique. Il est montré que l’Alon est stable uniquement dans un petit domaine de pression en oxygène et en azote, et qu’il n’est pas stable en dessous de 1640 ± 10°C.

1 Literature Review

Although a considerable number of articles on γ-aluminium oxynitride (Alon) have been published, the thermodynamics of Alon are still not very well known. In the first place there is some disagreement about the temperature at which Alon can be formed and whether below this temperature a kinetic or a thermodynamic limitation occurs. Secondly, the proper formula for Alon (which is not a stoichiometric compound) gives some difficulty as to how the reactions should be balanced.

Table 1 contains the data given in the literature concerning the temperature at which an Alon-producing (or consuming) reaction is observed to proceed, along with its reactants and atmosphere. Some additional data on an Alon-like substance (TiAlON system) and AlN production are also included. From this table it is clear that in most cases temperatures higher than 1500–1700°C are needed for the formation of Alon. Ish-Shalom1 observes that at 1480°C only AlN is formed, but that at a temperature of 1580°C Alon and AlN are formed. A similar conclusion can be drawn from the data on the TiAlON system.

Lejus2 and Gilles3 mentioned that at temperatures below 1600°C Alon decomposes into Al2O3 and AlN; most probably the two articles are referring to the same experiment: according to Lejus a graphite boat and temperatures of 1450 and 1550°C were used. This experiment would prove that Alon is not stable below 1600°C and decomposes. Unfortunately, no reproduction of this experiment could be found in literature.

Table 1. Literature overview of reaction temperatures and related conditions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product</th>
<th>Atmosphere</th>
<th>Graphite</th>
<th>Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ + C</td>
<td>γ-Alon</td>
<td>Air</td>
<td>Yes</td>
<td>&gt;1650</td>
<td>17</td>
</tr>
<tr>
<td>Al₂O₃ + Al</td>
<td>γ-Alon</td>
<td>Air</td>
<td>Yes</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ + C</td>
<td>γ-Alon</td>
<td>Air</td>
<td>Yes</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>Argon</td>
<td>Yes</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>Argon</td>
<td>Yes</td>
<td>2000</td>
<td>19</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>NH₃</td>
<td>Yes</td>
<td>1400</td>
<td>20</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>NH₃</td>
<td>Yes</td>
<td>2000</td>
<td>17</td>
</tr>
<tr>
<td>Al₂O₃ + C</td>
<td>AI₂N</td>
<td>N₂</td>
<td>Yes</td>
<td>&gt;1600</td>
<td>17</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>N₂ or argon</td>
<td>Yes</td>
<td>&gt;1600</td>
<td>18</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>N₂ or argon</td>
<td>Yes</td>
<td>&gt;1600</td>
<td>22</td>
</tr>
<tr>
<td>γ-Alon</td>
<td>Al₂O₃ + AlN</td>
<td>N₂</td>
<td>Yes</td>
<td>1450/1550</td>
<td>2</td>
</tr>
<tr>
<td>γ-Alon</td>
<td>Al₂O₃ + AlN</td>
<td>N₂ or air</td>
<td>Yes</td>
<td>&lt;1600</td>
<td>3</td>
</tr>
<tr>
<td>Al₂O₃ + Al</td>
<td>γ-Alon</td>
<td>N₂ or air</td>
<td>Yes</td>
<td>&gt;1500</td>
<td>23</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>N₂</td>
<td>Yes</td>
<td>&gt;1700</td>
<td>24, 25</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>N₂</td>
<td>Yes</td>
<td>&gt;1650</td>
<td>26, 27</td>
</tr>
<tr>
<td>Al₂O₃ + C</td>
<td>γ-Alon</td>
<td>N₂</td>
<td>Yes</td>
<td>&gt;1580</td>
<td>1</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>AlN</td>
<td>N₂</td>
<td>Yes</td>
<td>1480</td>
<td>1</td>
</tr>
<tr>
<td>Al₂O₃ + BN</td>
<td>γ-Alon</td>
<td>N₂</td>
<td>Yes</td>
<td>&gt;1700</td>
<td>28</td>
</tr>
<tr>
<td>Al₂O₃ + AlN</td>
<td>γ-Alon</td>
<td>N₂</td>
<td>No</td>
<td>&gt;1650</td>
<td>4</td>
</tr>
<tr>
<td>Al₂O₃ + TiN</td>
<td>(Ti)Alon</td>
<td>N₂</td>
<td>Yes</td>
<td>1800</td>
<td>29</td>
</tr>
<tr>
<td>Al₂O₃ + TiN</td>
<td>No spinel</td>
<td>N₂</td>
<td>Yes</td>
<td>1470</td>
<td>29</td>
</tr>
</tbody>
</table>

Takebe et al.⁴ showed that the homogeneity region of Alon becomes smaller with lower temperatures. This can be an explanation for the difference in the temperatures that were found for the onset of the formation of Alon. It also can be interpreted as an indication of a eutectoid, below which Alon is unstable. The present authors’ own results with respect to the homogeneity region of Alon will be published shortly.⁵

Not entered in Table 1 are publications by Irene et al.⁶ and Silvestri et al.⁷ on the chemical vapour deposition of Al₉O₅N₂ films on silicon. In these publications films containing aluminium, oxygen and nitrogen made at temperatures of 770 and 900°C are described. In a certain composition range the films produced at 900°C exhibit γ-Al₂O₃-like electron diffraction patterns which would indicate that Alon can be formed at low temperatures. According to the authors, the deposition products are kinetically rather than thermodynamically controlled and therefore no conclusions about the thermodynamic stability of Alon at these low temperatures can be drawn from these experiments.

Corbin⁸ states that Alon is formed in graphite-heated as well as in tungsten-heated furnaces and that the atmosphere can be either nitrogen or argon, the only difference being that weight losses in argon are somewhat higher because of the instability of AlN in argon.

In many publications Alon is mentioned as being an intermediate phase, which disappears as the reaction proceeds. In reactions where carbon is used to reduce aluminium oxide in a reducing or inert atmosphere containing nitrogen, AlN is the final product (see, for instance, Ref. 1); at the same time, if the reaction is carried out in air, aluminium oxide is the resulting phase (if the reaction time is long enough; see, for instance, Ref. 20). From these results it seems clear that the (partial) oxygen pressure plays an important role in the formation (and the stability) of the Alon phase.

2 Data Sets for Alon

In the following calculations are in J mol⁻¹ unless otherwise stated. Thermochemical data are taken from the JANAF tables except for the values of Alon, Al₂O₃ and AlN. For Alon two sets of data are available: one from Dörner et al.,⁹ the other from Kaufman.¹⁰ Both assume the formula of Alon to be (stoichiometric) Al₂O₅N.

Dörner et al. used the eutectoid decomposition of Alon into α-Al₂O₃ and AlN at 1600°C according to the results of Lejus and assumed a positive value of 1 J K⁻¹ g atom⁻¹ for the entropy of formation from α-Al₂O₃ and AlN. According to his calculations, the Gibbs energy of formation of Alon is

\[ \Delta G_f(\text{Al}_5\text{O}_5\text{N}) = -5315.2132 + 1054.520 T \] (1)

When using this value for the Gibbs energy of formation of Alon, it is necessary to use the Gibbs energies of formation of aluminium oxide and aluminium nitride used by Dörner et al. in further
calculations, because these values are strongly related. The data used by Dörner et al. were:

\[ \Delta G_f(Al_2O_3) = -1673913.8 + 318.940T \]
\[ \Delta G_f(AlN) = -325854.1 + 114.990T \]

Kaufman described the system by using lattice stability, solution and compound phase parameters. He calculated the Gibbs energy of reaction (\(\Delta G'_r\)) for the reaction

\[
(3/17)Al_2O_3(C) + (1/17)AlN(N) = (1/17)Al_7O_9N(SP)
\]

(2)

in which C indicates corundum-, N indicates hexagonal- and SP indicates spinel-type structure. He estimates the Gibbs energy of reaction to be

\[ \Delta G'_r = -515.0'259T \] (3)

From this result Corbin computed the Gibbs energy of formation of Alon using

\[
\Delta G'_f(Al_7O_9N) = \Delta G'_r + 3\Delta G_f(Al_2O_3) + \Delta G_f(AlN)
\]

(4)

where the latter two values are taken from the JANAF tables. This method clearly is not correct. Not only does the value from Kaufman apply to 1 g atom instead of 1 mol, it is also not correct to mix the data from Kaufman with those obtained from the JANAF tables because of the intimate relationships between the data for \(Al_2O_3\), \(AlN\) and Alon. The correct value of the Gibbs energy of formation can be found by applying the formalism of Kaufman 'backwards' (see Appendix for further details) The results are:

\[
\Delta G'_f(Al_7O_9N) = -5356902.8 + 1070.58T \] (5)
\[
\Delta G'_f(Al_7O_9N) = -5357102 + 1052.21T \] (6)

Expression (5) results when using the basic data, expression (6) when using the intermediate results explicitly stated by Kaufman. The differences between these expressions amount to \(\pm 50\) kJ mol\(^{-1}\) in the temperature region of interest (about 1900 K) (see Table 2).

Using the data from Dörner et al., the Gibbs energy of reaction for reaction (2) is

\[ \Delta G'_r = 1905 - 1.017T \] (7)

This \(\Delta G'_r\) value is greater than zero below 1600°C and lower than zero above this temperature. Equations (5) and (6) result in \(\Delta G'_r\) values which are negative for all temperatures.

The present authors tried to estimate the value of the entropy of Alon by taking into account the defect structure of the material. From Goursat et al.\(^{12}\) it is known that Alon has a spinel-type crystal structure (\(Fd\overline{3}m\)) with vacancies in the octahedral positions. Thus the \(Al_2O_2N_5\) composition that was proposed by McCauley,\(^{13}\) and has been generally accepted, has eight aluminium ions on the tetrahedral sites and 15 on the octahedral sites of the cationic lattice. The charge of the aluminium ions is always 3+.

Therefore:

\[ A^{2+}_{[\text{tet}]} + [B^{3+}_{16\text{[oct]}},O^{2-}_{3}]_{2} \]

(normal spinel)
\[ B^{3+} + [A^{3+}_{8},B^{3+}_{8},O^{2-}_{3}]_{2} \]

(inverse spinel)
\[ Al^{3+}_{[Al^{3+}_{8},Al^{3+}_{8}]}O^{2-}_{27}N^{3-}_{15} \]

(one vacancy in the octahedra)

or, in Kröger-Vink notation,

\[ [\text{Al}^{3+}_{18,8}][\text{Al}^{3+}_{18,7},\text{Al}^{3+}_{18}]O^{2-}_{27}N^{3-}_{0.5} \]

If there is no correlation between the defects and \(W\) is the number of possible configurations, then

\[ W = \left(\frac{8}{8}\right) \times \left(\frac{16}{8}\right) \times \left(\frac{32}{1}\right) \times \left(\frac{32}{5}\right) = 2.07 \times 10^{10} \]

and

\[ S'_f = R \ln (W) = 197.5 \text{ J K}^{-1} \text{ mol}^{-1} (Al_{23}O_{27}N_5)^{-1} \]

\[ S'_f = 3.591 \text{ J K}^{-1} \text{ gat}^{-1} \]

In order to calculate the Gibbs energy of \(Al_{23}O_{27}N_5\), entropy values from JANAF and Gibbs energy values from Dörner et al. for aluminium oxide and aluminium nitride are used. The values from JANAF are extrapolated to 1873 K, the lowest temperature at which Alon is formed, according to the literature (Table 3).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Expression (1)</th>
<th>Expression (5)</th>
<th>Expression (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>-3522.529</td>
<td>-3536.917</td>
<td>-3568.337</td>
</tr>
<tr>
<td>1900</td>
<td>-3311.625</td>
<td>-3322.801</td>
<td>-3357.894</td>
</tr>
<tr>
<td>2100</td>
<td>-3100.721</td>
<td>-3108.685</td>
<td>-3147.451</td>
</tr>
<tr>
<td>2300</td>
<td>-2889.817</td>
<td>-2894.569</td>
<td>-2937.008</td>
</tr>
<tr>
<td>2500</td>
<td>-2678.913</td>
<td>-2680.453</td>
<td>-2726.565</td>
</tr>
</tbody>
</table>

Table 2. Comparison of the Gibbs energy of formation of Alon from the different equations in kJ mol\(^{-1}\)

Table 3. Values of \(S'_f\) (J K\(^{-1}\) mol\(^{-1}\)) and \(\Delta G'_f\) (kJ mol\(^{-1}\)) at 1873 K extrapolated from JANAF tables

\[ S'(Al) = 93.573 \]
\[ S'(O_2) = 266.179 \]
\[ S'(N_2) = 249.606 \]
\[ S'(AlN) = 301.239 (\pm 50.620 \text{ J K}^{-1} \text{ gat}^{-1}) \]
\[ S'(Al_2O_3) = 262.139 (\pm 52.428 \text{ J K}^{-1} \text{ gat}^{-1}) \]
\[ \Delta G'_f(Al_2O_3) = -1076.539 \]
\[ \Delta G'_f(AlN) = -110.478 \]
With these values

\[
S^\circ(1/55\text{Al}_2\text{O}_3\text{N}_5) = S^\circ(1/2\text{AlN})
+ 9/14[S^\circ(1/5\text{Al}_2\text{O}_3) \\
- S^\circ(1/2\text{AlN})] + S^\circ_f
\]

\[
S^\circ(1/55\text{Al}_2\text{O}_3\text{N}_5) = 55.373 \text{ J K}^{-1} \text{ g at}^{-1}
+ 3045.5 \text{ J K}^{-1} \text{ mol}^{-1}
\]

As the Gibbs energy change for the reaction of aluminium oxide and aluminium nitride to form Alon is zero at 1873 K:

\[
\Delta G^\circ_f(\text{Al}_2\text{O}_3\text{N}_5) = 9\Delta G^\circ_f(\text{Al}_2\text{O}_3) + 5\Delta G^\circ_f(\text{AlN})
\]

\[
\Delta G^\circ_f(\text{Al}_2\text{O}_3\text{N}_5) = -10241.242 \text{ kJ mol}^{-1}
\text{ (at 1873 K)}
\]

The formation reaction of Alon from the elements

\[
23\text{Al} + 13.5\text{O}_2 + 2.5\text{N}_2 = \text{Al}_2\text{O}_3\text{N}_5
\]
gives, with the values from Table 3,

\[
\Delta G^\circ_f = -16467302 + 3324111 T \text{ J mol}^{-1}
\text{ (Al}_2\text{O}_3\text{N}_5)^{-1}
\text{ (8)}
\]

This expression is used in the next section and the results compared with results from the Dörner et al. and Kaufman expressions.

3 Ellingham and Activity Diagrams

With the data from Section 2 three Ellingham diagrams were constructed: Fig. 1 with the data from Dörner et al., Fig. 2 with the data from Kaufman (eqn (6)) and Fig. 3 with the present authors' own data.

In all of these diagrams the stability region of Alon is fairly small. With the data set of Kaufman, Alon is stable at all temperatures, while for the other datasets Alon is stable above 1873 K only. In Fig. 2 the Alon phase is energetically stabilized while in Figs 1 and 3 Alon is stabilized by entropy. The latter is, in the authors' opinion, nearer the truth for a highly defective material like Alon. Figures 1 and 3 are very much alike and therefore will be referred to as the 'Dörner diagrams' in the remaining part of the article, whereas Fig. 2 will be referred to as the 'Kaufman diagram'.

Activity diagrams were drawn according to the method used by Wada to estimate the oxygen and nitrogen pressures at which Alon is stable. In Fig. 4 these diagrams are drawn for a carbon activity of 1 (Fig. 4(a)) of and 10\(^{-4}\) (Fig. 4(b)) at a temperature of 2000 K. Under these circumstances Alon is stable within the small area indicated with 'Alon'. The data-

![Fig. 1. Ellingham diagram drawn with the data set from Dörner et al.](image-url)
set used was that of Dörner et al., but the other data sets give almost the same results at this temperature. Again it can be seen that the stability region of Alon is very small.

4 Experiments

4.1 Starting materials and equipment

Some experiments with aluminium oxide (Rubis synthétique des Alpes, Jarrie, France, A15Z)/aluminium nitride (H. C. Starck, Berlin, Germany, grade C) and with aluminium oxide/carbon (Cabot, Rozenburg, The Netherlands, Elftex 125) mixtures were performed to check the data from literature. Experiments were done in different furnaces (for abbreviations used see Table 4).

The temperature of the GPSF and HFF were controlled using two-colour pyrometers. In the GPSF temperature was measured in a ‘black hole’ some distance (about 5 cm) from the sample. In the HFF the pyrometer was focused on the outside of the crucible, no more than 5 mm from the sample. The ASF was controlled with a tungsten/tungsten–rhenium thermocouple between the elements; the actual temperature of the sample was measured with.

<table>
<thead>
<tr>
<th>Furnace</th>
<th>Code</th>
<th>Heating elements</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-pressure</td>
<td>GPSF&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Graphite</td>
<td>Nitrogen (3 and 80 bar)</td>
</tr>
<tr>
<td>Astro</td>
<td>ASF&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Tungsten</td>
<td>Nitrogen/hydrogen (88%/12%, 1 bar)</td>
</tr>
<tr>
<td>High-frequency</td>
<td>HFF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Graphite</td>
<td>Nitrogen (1 bar)</td>
</tr>
<tr>
<td>Vertical tube</td>
<td>VTF&lt;sup&gt;d&lt;/sup&gt;</td>
<td>/</td>
<td>Nitrogen (1 bar)</td>
</tr>
<tr>
<td>Horizontal tube</td>
<td>HTF&lt;sup&gt;e&lt;/sup&gt;</td>
<td>/</td>
<td>Nitrogen (1 bar)</td>
</tr>
</tbody>
</table>

<sup>a</sup> KCE Sondermachinen GmbH, type FPW 100/150-2200-100 DIL (Rödental, Germany).
<sup>b</sup> Astro (Thermal Technology Inc.), type 1100V-4080-W2 (Santa Rosa, California, USA).
<sup>c</sup> Philips, type PH 1012 (Eindhoven, The Netherlands).
<sup>d</sup> Purpose built by Isoheat (Worksop, UK).
<sup>e</sup> Heraeus GmbH, type R0S4/50 (Hanau, Germany).
<sup>f</sup> Elements on the outside of an aluminium oxide tube.
Fig. 3. Ellingham diagram drawn with the present authors' data set.

an additional thermocouple of the same kind. In the tube furnaces temperature was measured using platinum/platinum-rhodium thermocouples that were placed as close to the samples as possible. In the VTF Pt/6% Rh versus Pt/30% Rh was used, in the HTF pure platinum versus Pt/10% Rh.

4.2 Synthesis experiments
For the first set of experiments aluminium oxide/nitride mixtures were used with a O/N ratio in the Alon domain corresponding to 73 mol% Al₂O₃. The mixed powders were pressed into tablets 12 mm in diameter and 10 mm in height. The furnaces with graphite elements (GPSF and HFF) gave the same results: Alon could be formed at high temperatures only. The HFF experiments were performed in a carbon crucible under flowing nitrogen at 1630 and 1650°C: Alon was only found in the sample sintered at 1650°C. In the GPSF a boron nitride crucible was used and the experiments were performed at temperatures of 1600, 1700, 1750, 1800 and 1850°C under a stationary nitrogen pressure of about 3 bar. Alon was found in the samples sintered at temperatures higher than or equal to 1700°C. The outer surface of the samples consisted mainly of AlN with some Alon as minor phase; inside, pure Alon was found.

When a powder bed (consisting of AlN mixed with Al₂O₃ and BN) was used, the amount of AlN on the surface decreased. When a higher nitrogen pressure was used in the GPSF (80 instead of 3 bar) a lower end-point density resulted; this was attributed to a higher amount of AlN in the sintered sample, for AlN has a lower density compared to Alon (3.26 and 3.70 g cm⁻³ respectively). This expectation was confirmed by X-ray diffraction.

In the ASF a boron nitride crucible was used and the experiments were performed at 1600, 1700, 1750, 1800 and 1850°C in flowing nitrogen. Alon was again found in the samples sintered at temperatures higher than or equal to 1700°C. The samples sintered in the ASF showed only very small differences in composition between the inside and the outer surface of the sample.

The samples that were sintered in the VTF under flowing nitrogen in an aluminium oxide crucible (3 h at 1750°C) had an outer surface that consisted of Alon with Al₂O₃ as a minor phase. If a graphite crucible was used (the other conditions were the same) the outer surface consisted of Alon with some AlN. In both cases the inside of the sample consisted of pure Alon.

In the second set of experiments tablets made of
aluminium oxide/carbon mixtures (74 wt% Al₂O₃, 26 wt% C) were sintered without a powder bed in the HFF in a carbon crucible under flowing nitrogen. Temperatures from 1570 up to 1800°C were used. At temperatures higher than 1640°C (+10°C) Alon was formed, always accompanied by AlN. At lower temperatures only AlN was formed.

4.3 Annealing experiments
Alon and AlN samples were heated in the HTF to determine the stability of Alon at lower temperatures (1400 and 1450°C). The Alon samples used were synthesized previously at 1880 or 1850°C, had a composition of 73 mol% Al₂O₃/27 mol% AlN and were translucent. The AlN samples were also translucent. In these experiments flowing nitrogen gas which contained ±400 ppm of oxygen was passed over the samples. AlN was placed 'downstream' from Alon to prevent contamination of Alon by AlN as much as possible.

In one set of experiments an aluminium oxide crucible was used as a container. After 100h at 1400°C both Alon and AlN were completely converted (at least on the surface) into Al₂O₃. Consequently both the Alon and the AlN lost their translucency.

In another set of experiments a crucible of glassy carbon with a layer of carbon powder in it was used as a container. After 16 h at 1450°C Al₂O₃, AlN and Alon were found on the surface of the Alon sample using X-ray diffraction. After 84 h at that temperature no Alon phase could be detected on the surface of the no longer translucent Alon sample; the surface consisted of Al₂O₃ and AlN only. The weight of the sample decreased slightly (0.02 wt%). After 100 h the surface of the sample consisted of about 55 mol% of Al₂O₃ and 45 mol% of AlN. An Al₂O₃ sample treated for the same period of time under the same circumstances showed about 4 mol% AlN on the surface. On the AlN no Al₂O₃ could ever be detected during the experiments with the graphite container and the samples remained translucent.

One experiment was done in a vacuum furnace under a pressure of 10⁻⁹ bar. After heating at 1400°C for 100 h, Alon was the main phase detectable by X-ray diffraction. Some aluminium oxide and some molybdenum (from the heating elements) were also present on the surface of the sample. The sample had a blue colour, although this was partly obscured by the molybdenum on the surface. No other phases were detected. The intensities of the reflections in the X-ray diffractogram of the resulting Alon phase were somewhat different from the normal intensities, the highest being the 440 reflection and not the 311 reflection as usual.

5 Discussion
In this section the relationship between the experiments described in Sections 1 and 4, and the Eillingham diagrams from Section 3, is discussed. For clarity the line of thought followed here is illustrated in Fig. 5, which is nearly the same as Fig. 1, apart from the fact that some extra lines are entered (ΔG° value of WO₃ and H₂O (-- -- --); lines of constant oxygen pressure (-- -- --); and a line at $T = T_c$ (---)).

The process considered here is as follows: in a...
furnace with graphite heating elements a sample of $\text{Al}_2\text{O}_3/\text{AlN}$ (with a proper O/N ratio) is placed. The furnace is closed, evacuated and then filled with nitrogen gas to a pressure of 1 bar (for the rest of the process the total pressure is kept at 1 bar). The gas contains 100 ppm of oxygen (the partial oxygen pressure is $10^{-4}$ bar).

Now the heating up of the furnace is started. At first, the carbon/carbon dioxide equilibrium is the most important equilibrium. At point A in Fig. 5 $\text{CO}$, $\text{CO}_2$ and $\text{O}_2$ are in equilibrium with each other. The partial oxygen pressure at point A is about $10^{-25}$ bar (remember that all the lines in Ellingham diagrams are drawn for 1 bar partial pressure of the gaseous species involved except for $\text{O}_2$). At higher temperatures the equilibrium carbon/carbon monoxide will become the most important equilibrium.

By the time the temperature above which Alon is stable ($T_c$ in the diagram) is reached Alon is formed, due to the solid-state reaction between $\text{Al}_2\text{O}_3$ and AlN. At point B the oxygen pressure is about $10^{-23}$ bar. Because this oxygen pressure is very low the reaction

$$\text{AlN} + \text{O}_2 = \text{Alon} + \text{N}_2$$

(the lower line of the Alon stability region) is forced to the left and AlN is formed. The oxygen released is consumed by the carbon. This process will only stop when the equilibrium oxygen pressure over carbon and over Alon are the same and, as can be seen from Fig. 5, this region is very small. If the $\Delta G^\circ$ of this reaction at, say, 2000 K is considered, its value is almost equal to the $\Delta G^\circ_c$ of the carbon/carbon monoxide reaction and therefore $K_p$ for the overall reaction ($= P(\text{N}_2)^{2/3}/P(\text{CO})^3$) is almost unity. From this result it is clear that in flowing nitrogen no equilibrium can be reached and Alon is not stable but will react to form AlN. In a closed system it should be possible to reach equilibrium when there are enough reactants. In any case there always has to be some production of AlN in this kind of system when pure nitrogen gas is used (meaning no CO is mixed with it beforehand).

Now, if Alon would have been stable down to room temperature, what would have happened? Let us consider an aluminium oxide/carbon mixture with a surplus of carbon. The oxygen pressure is low, so the stable phase will be AlN. From the Kaufman diagram it would be expected that Alon is formed as...
an intermediate phase at all temperatures. However, according to the experiments, Alon is not formed below a certain temperature and for that reason the Kaufman diagram cannot be correct. There is no reason why Alon is formed at higher temperatures only unless it is not (thermodynamically) stable in the lower region. If it is not formed due to kinetic reasons, then AlN should also not form; also the (relatively) sharp transition point (Alon formation/no Alon formation versus temperature) contradicts this kind of inhibition. From these considerations it seems clear that Alon is not stable at low temperatures.

If the nitrogen pressure is increased, AlN is formed more rapidly (kinetically) and thus the amount of AlN in the product will be increased. As the intersection of the three lines that make up the Alon region is not dependent on pressure (specific volume change of solids is assumed to be zero), Alon is formed at the same temperature.

If a furnace with tungsten heating elements is used with flowing nitrogen, as is the case in these experiments, it is very difficult to predict the partial oxygen pressure at $T_c$ because the WO$_3$ pressure is not known. In this case the partial oxygen pressure will be dependent on the gas flow rate and the furnace design. When argon is used in a furnace with tungsten heating elements, $P(N_2)$ is low. If the nitrogen pressure is lower than $10^{-5.1}$ bar (at 2000 K, see Fig. 4), AlN is no longer stable. Large weight losses will occur during the sintering process if the oxygen pressure is lower than $10^{-18.1}$ bar. If the oxygen pressure is higher than $10^{-18.1}$ bar then Al$_2$O$_3$ will be the stable phase and some of the AlN will be converted into Al$_2$O$_3$. In a furnace with graphite heating elements Al$_2$C$_3$ is formed if the nitrogen pressure is lower than $10^{-4.1}$ bar and the oxygen pressure is lower than $10^{-17.4}$ bar (at 2000 K). No Al$_2$C$_3$ formation has ever been reported in the literature on Alon, but then the necessary circumstances (an argon atmosphere with very low oxygen and nitrogen pressures in a furnace with graphite heating elements) are not often encountered.

The experiments in the HTF show that Alon is not stable if it is heated at 1450°C in flowing nitrogen when graphite is present. In this case the decomposition of Alon into aluminium oxide and aluminium nitride seems to be faster than the reduction of aluminium oxide by graphite, and thus Al$_2$O$_3$ and some AlN are found. This is the same result as reported by Lejus. If no carbon is present, only aluminium oxide is found on the surface of the sample. This difference can be attributed to the fact that AlN is not stable in the nitrogen used for these experiments (the partial oxygen pressure in the gas is too high) and is oxidized.

The experiments suggest that $\gamma'$-Alon is formed in the vacuum furnace (see Refs 24 and 29 for a discussion on $\gamma'$-Alon). The characteristic blue colour and the changed XRD intensities point in that direction. This $\gamma'$-Alon also seems to be an intermediate phase, brought about by the loss of nitrogen from $\gamma$-Alon. Because no thermodynamic data for $\gamma'$-Alon are available and it is not certain whether this is a stable phase in the system under consideration, no effort was made to enter this phase in Fig. 4. As the principal leakage of gas into the system stems from the surrounding air, the oxygen and nitrogen pressures are about $10^{-10}$ bar. The stable phase under these circumstances is Al$_2$O$_3$ (cf. Fig. 4), which is indeed found on the surface of the sample. The dissociation reaction seems to be much slower under these circumstances than in nitrogen at 1 bar.

6 Conclusion

The formation and stability of Alon under various circumstances can be adequately described using Ellingham and activity diagrams as presented in Section 3. It is shown that Alon is stable only within a small region of oxygen and nitrogen partial pressures, and that it is not stable below 1640 ± 10°C.

Acknowledgement

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References

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### Appendix

In this appendix the symbolic conventions of Kaufman are used; consequently for this appendix $G^\Psi$ is represented by $G$. The equation that is used by Kaufman to define the Gibbs energy of a compound phase $i_1 \rightarrow i_3 = i_2$ is

$$G^\Psi = (1 - x) G^\theta + x^2 G^\theta + x(1 - x) \times \{ (1 - x) L_1 J_2 + L_2 J_1 - C[T] \}$$

where $\Psi$ and $\theta$ refer to the base structure selected for the compounds, $C[T]$ (which is a temperature-dependent function) is the compound parameter, and $L_1 J_2$ and $L_2 J_1$ are interaction parameters that are functions of temperature but not of composition. Symbolic usage and values for the parameters are summarized in Table A1.

#### Table A1. Symbols and parameters used in this Appendix (in J g at\(^{-1}\)). Values marked with an asterix are from Ref. 27, others from Ref. 23

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO = 1/5AlO(_3)</td>
<td>N = Wurtzite</td>
</tr>
<tr>
<td>AN = 1/2AlN</td>
<td>B = $\beta$Si(_3)N(_4)</td>
</tr>
<tr>
<td>AL = Al</td>
<td>V = Vapour</td>
</tr>
<tr>
<td>NN = 1/2N(_2)</td>
<td>L = Liquid</td>
</tr>
<tr>
<td>OO = 1/2O(_2)</td>
<td>C = Corundum</td>
</tr>
<tr>
<td>AN(_0) = Al(_2)O(_3)N(_x)</td>
<td>S = Spinel</td>
</tr>
</tbody>
</table>

Lattice stability parameters

**Syntaxis:** $(\text{compound 1}) (\text{compound 2}) (\text{structure 1}) (\text{structure 2})$

- **ALALBB** = 628 – 6.69\(T\)
- **NNNBV** = 3.682 + 53.64\(T\)
- **ANANBNL** = 42.593 – 13.31\(T\)
- **ANANLS** = -8.377
- **AOAOLC** = -23.640 – 10.21\(T\)
- **AOAOLS** = 19.205 – 9.087\(T\)
- **OOOOVL** = 3.410 – 37.97
- **OOOOLB** = 230 – 4.27

Solution phase parameters

**Syntaxis:** $L(\text{compound 1}) (\text{compound 2})$

- **LALNN** = -50.208
- **LNNAL** = 912.112 + 256.48\(T\)
- **LOCAL** = -1287.830 + 147.77\(T\)
- **LANAO** = 29.28

Compounds structure parameters

- **AN**: $C[T]$ = 167.360 + 18.41\(T\), base = bcc
- **AO**: $C[T]$ = 96.650 – 2.51\(T\), base = bcc
- **AN\(_{0.18}\)AO\(_{0.82}\)**: $C[T]$ = 120.081 – 12.67\(T\), base = S

**NB:** **ALALBB** = **ALALBL**

- **ANANSN** = **ANANLN**
- **ANANLS**
- **OOOOVL** = **OOOOVL**
- **OOOOLB** = **AOAOLC**

* e.g. ANANLB is used to designate the Gibbs energy of pure liquid AlN minus the Gibbs energy of the $\beta$ form of AlN.

---

Using Table A1 the Gibbs energy of formation for AlN can be calculated:

\[
0.5\text{Al}(L) + 0.25\text{N}_2(V) \rightarrow \text{Al}_0.5\text{N}_0.5
\]

\[
G^\circ = (1 - 0.5)(G^0_{\text{Al}} - 0.5G^0_{\text{N}}) + (1 - 0.5)(0.5)G^0_{\text{ALNN}} + 0.5\text{LNNAL} - C[T]
\]

\[
\Delta^\circ G_f(\text{AN}) = G^\circ - (1 - 0.5)(G^0_{\text{Al}} - 0.5G^0_{\text{N}}) + (1 - 0.5)(0.5)G^0_{\text{ALNN}} + 0.5\text{LNNAL} - C[T]
\]

\[
= (1 - 0.5)\text{ALALBL} + 0.5\text{NNNNBV} + (1 - 0.5)(0.5)\text{LALNN} + 0.5\text{LNNAL} - C[T]
\]

\[
= -164285 + 576225 T \text{J g}^{-1}
\]

Kaufman himself gives the same value for \(\Delta^\circ H_f(\text{AN})\) and a value of 57625 for \(\Delta^\circ S_f(\text{AN})\), which is nearly the same.

For \(1/17\text{Al}_2\text{O}_3(\text{Al}_{0.4}\text{O}_{0.6})\) one finds, using the same kind of calculation,

\[
\Delta^\circ G_f(\text{AO}) = -3347104 + 639864 T \text{J g}^{-1}
\]

In a publication by Kaufman\(^\text{16}\) there is a table (Table 2) in which the calculated values correspond to a slightly different equation:

\[
\Delta^\circ G_f(\text{AO}) = -334720 + 62766 T \text{J g}^{-1}
\]

If the values from Table A1 are used to calculate the free energy for the reaction

\[
(1/17)\text{AlIN}(N) + (3/17)\text{Al}_2\text{O}_3(C) \rightarrow (1/17)\text{Al}_7\text{O}_9\text{N(SP)}
\]

which, written in the formalism used here, looks like

\[
0.118\text{AN} + 0.882\text{AO} \rightarrow \text{AN}_0.118\text{AO}_{0.882}
\]

using

\[
\Delta^\circ G_f = 0.118\text{ANANSN} + 0.882\text{AOAOSN}
\]

\[
+ (0.118)(0.882)[0.118\text{LANAO} + 0.882\text{LAOAN} - C[T]]
\]

then it amounts to

\[
\Delta^\circ G_f = -511728 - 0.26 T \text{J g}^{-1}
\]

while Kaufman states

\[
\Delta^\circ G_f = -515 - 0.259 T \text{J g}^{-1}
\]

From Fig. A1 it is clear that

\[
\Delta G_4 = \Delta G_1 + \Delta G_2 + \Delta G_3
\]

Note added in proof

It can be argued that the charged and uncharged aluminium ions are not discernable in the defect structure of Alon. In that case the number of possible configurations is

\[
W = \binom{16}{32} \binom{5}{15}
\]

and

\[
\Delta^\circ G_f(\text{Al}_{23}\text{O}_{27}\text{N}_4) = 16603843 + 3397011 T
\]

However, with these values, Fig. 3 changes only marginally and the conclusions drawn in the remaining part of the paper are still valid.

In Fig. 2 the labels ‘14/9 AlIN + 02 = 2/9 Al709N + 2/3 N2’ and ‘4/3 Al709N + 02 = 14/3 Al203 + 2/3 N2’ have inadvertently been interchanged.