THE FORMATION AND REACTIVITY OF ALUMINIUM NITRIDE AND RELATED MATERIALS

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by

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Abstract

The preparation and properties of aluminium nitride are reviewed with special reference to the newer production methods and fabrication techniques.

Information so far available on the sintering of materials is summarised. For nitrides the sintering is influenced by additives or impurities such as oxides formed by partial hydrolysis and oxidation. Resistance to oxidation is increased by sintering and hot-pressing the refractories.

The kinetics and products of oxidation of nitrides so far studied depend mainly on the intrinsic reactivity of the material and available surface at which oxidation can occur.

In the present research conditions are investigated for preparing aluminium nitride from ammonium hexafluoroaluminate. The x-ray characteristics and the thermal stability of a new compound, $\gamma$-AlF$_3$ are established. Attempts to study the kinetics of the commercial methods of aluminium nitride formation are summarised. The reactivity of aluminium nitride is examined by correlating changes in phase composition, surface area, crystallite and aggregates sizes with hydrolysis and oxidation time and temperature. The kinetics and rates of reaction are influenced by the crystallite and aggregate sizes of the aluminium nitride, by differences in type of crystal structure, by the molecular volume of the oxide products, and by fluoride additives. Ageing and sintering of the aluminas are additional factors. The activation energy of the oxidation of aluminium nitride in air is determined as 53 k.cals/mole.
Acknowledgements

I wish to thank Dr. A. B. Meggy for the help, comment and general supervision of this work. I also wish to acknowledge the helpful discussions I have had with Dr. D. R. Glasson. Thanks are also due to Miss I. Gratton, the Polytechnic Librarian, and her staff, for their patient and willing cooperation. The help of Mr. E. Tapper with the computation has been gratefully appreciated. I would also like to thank Mrs. E. Adams, J.A.C., A. Down, Dr. S. A. A. Jayaweera and Margaret Sheppard for their assistance and cooperation. I am indebted to the Governors of the Polytechnic for the research award and the facilities.

Finally, I would like to express my thanks to Anne for her understanding and encouragement throughout this work.
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CHAPTER I Literature survey of aluminium nitride and related minerals

The survey is divided into four sections as listed below:

1. The formation and chemical properties of aluminium nitride.
2. The crystallography and the heat of formation and thermal stability of aluminium nitride.
3. The physical properties of aluminium nitride.
4. The fabrication and uses of aluminium nitride.

I.1 The formation and chemical properties of aluminium nitride

The formation and chemical properties of aluminium nitride

I.1.1 The formation of aluminium nitride

The preparation of aluminium nitride is confined to four main processes;

(a) The formation of the nitride from its elements.
(b) The formation of the nitride from the decomposition of alumina with carbon in the presence of nitrogen, i.e. the Serpek process.
(c) The thermal decomposition of ammonium hexafluoroaluminate in the presence of ammonia.
(d) The thermal decomposition of the aluminium halides, hydride and sulphide with ammonia.

I.1.1(a) The formation of aluminium nitride from its elements

The solubility of aluminium for nitrogen has been discussed by many authors, and it is the key factor to this method of formation. Pitcher (1) and others (2-4, 13, 14, 157) have reported that at temperatures between 530 and 820°C aluminium absorbs nitrogen to give the nitride, although the reaction appeared to be more vigorous at 1300-1400°C. These statements were contradicted by Claus (6) and Laffite et al (8) who concluded that nitrogen was almost insoluble in aluminium both in its liquid and solid
state. Rontgen and Braun (7), however, stated that although nitrogen is almost insoluble in aluminium in the crystalline state, the absorption increases with temperature. The preparation of the nitride using ammonia instead of nitrogen has also been studied (15). The use of ammonia to nitride steels is well known, and the resultant formation of aluminium nitride in fully-killed steels has been established.

The earliest reference to formation of the nitride from the elements is the work of Briegleb and Geuther (10) in 1862, who stated that aluminium nitride is formed when "aluminium turnings are heated in an atmosphere of nitrogen". Arous (11) stated that if aluminium is heated by electrical current in the presence of nitrogen, aluminium nitride is formed. Aluminium nitride was formed (12) when aluminium was burnt in oxygen, and nitrogen substituted for oxygen while the aluminium is still burning. The purity of any nitride formed by this method is questioned, as the presence of alumina is anticipated. The formation of crystals of the nitride from its elements at elevated temperatures is reported (120).

The use of a catalyst was introduced in 1953 (16). Finely-divided aluminium was heated with 1-5 wt. percent of a fluoride catalyst in the presence of nitrogen to give aluminium nitride. Long and Foster (17) have stated that high purity nitride can be made by striking an arc between two pure aluminium electrodes in a nitrogen atmosphere, with a final treatment in argon to increase its stability towards water.

I.1.i(b) The formation of the nitride from the decomposition of alumina with carbon in the presence of ammonia or nitrogen

This method was extensively investigated by Serpek (45) in 1914, and was later to be known as the Serpek process. Prior to Serpek's work,
Caro (30) using aluminium carbide prepared the nitride. Although this process proceeds efficiently at high temperatures, it was found that very little nitride was formed at 1600°C and sulphur dioxide was detrimental to the process (31). The Serpek process has been discussed by a number of authors (32-43); Frankel (44) stated that when using producer gas instead of nitrogen, a higher temperature is required. The nitride, according to the Serpek reaction, is best formed by a mixture of nitrogen and hydrogen (45). Carbo-nitrides have been formed during this process (46). The earliest reference which is related to this method of preparation is reported in 1876 by Mallet (47). Aluminium was heated in a carbon crucible and impure aluminium nitride was formed. Various additions to alumina in the process such as zinc chloride, ferric oxide (48), and iron (49) used as catalysts, have been reported as benefiting the formation of the nitride. A vitrified refractory consisting of alumina and aluminium nitride has been reported where the method used was to heat the materials in a graphite crucible at about one hundred degrees above the softening point of the refractory (50). Crystals of aluminium nitride have been prepared according to the Serpek process (51). The revival of the process by Pechiney (52, 164) in 1956-7, led other people (56) to re-investigate the process. The nitride has been prepared by this method using calcium aluminate as a binder (53-55). When aluminium nitride is prepared by the Serpek process, the product is impure and has been known to contain up to 12% carbon (102). Methods have been described for removal of such impurities (101-5).

More recently the Serpek process has been adapted using a nitrogen plasma source (59, 98, 99).
The thermal decomposition of ammonium hexafluoroaluminate in ammonia

Ammonium hexafluoroaluminate \((\text{NH}_4)_3\text{AlF}_6\) can be prepared from molar solutions of aluminium chloride and ammonium fluoride (78).

\[
\text{6NH}_4\text{F} + \text{AlCl}_3 \rightarrow (\text{NH}_4)_3\text{AlF}_6 + 3\text{NH}_4\text{Cl}
\]

This ammonium complex can also be prepared from ammonium fluoride and freshly precipitated aluminium hydroxide (79, 96, 97). The salt has been mentioned as a by-product of various other reactions, such as the ammonation of phosphoric acid (81), anion exchange in clays (82), the formation from alumina and ammonium fluoride (80, 83), the formation from aluminium nitrate and ammonium fluoride (79), and the formation from ammonium alum and hydrofluoric acid (5). The complex is the ammonium salt of fluorosalvinic acid or hydro-fluoroaluminic acid, as it was previously known (83). Despite its obvious association with cryolite \((\text{Na}_3\text{AlF}_6)\), ammonium hexafluoroaluminate is related to perovskite and the potassium hexafluoroplutinate \((\text{K}_2\text{PtCl}_6)\) in its structure (84).

The existence of ammonium hexafluoroaluminate has been verified by a number of authors (85-89). When heated in ammonia it decomposes in stages to aluminium nitride. The stages are summarised as follows:

\[(\text{NH}_4)_3\text{AlF}_6 \xrightarrow{\text{NH}_3} \text{NH}_4\text{AlF}_4 \] (1)

\[\text{NH}_4\text{AlF}_4 \xrightarrow{\text{NH}_3} \text{AlF}_3 \] (2)

\[\text{AlF}_3 \xrightarrow{\text{NH}_3} \text{AlN} \] (3)

In the present work, the temperatures at which these reactions occur are found to differ from the results of Shinn et al (90) and Maak (91). Reaction temperatures according to Shinn et al:

(1) \(170^\circ\text{C}\)  
(2) \(300^\circ\text{C}\)  
(3) \(720^\circ\text{C}\)
Reaction temperatures according to Maak:

(1) 300°C     (2) 600-700°C     (3) 800°C

Shinn et al also reports the existence of $\gamma$-AlF$_3$.

The decomposition of the fluoroaluminate to form aluminium nitride has also been studied by Funk and Boehland (93).

I.i.i(d) Miscellaneous methods of preparation

There have been reported various methods of preparing aluminium nitride which do not appear to have a wide commercial application, but are reported here as possible alternatives to the more common methods. Perhaps the most noted of these methods is the reaction of anhydrous aluminium chloride with ammonia, known as the Grove process. This method is principally used to prepare single crystals of aluminium nitride which are to be used for electronic devices.

Tiede et al (57) reported that when ammonia is passed over pure aluminium chloride the monoammoniate is formed, and when the salt is decomposed on a tungsten spiral at 1000°C aluminium nitride is produced. This process has been studied more recently by Renner (58), whose results confirm the work of Tiede and others. This method can also be used to prepare the nitrides of silicon (63, 66), boron, gallium and indium (68), and it has been adapted by Popper (60), in his study of the formation of non-oxide coatings by pyrolysis. The method has also been used to coat various ceramic materials with aluminium nitride. If the temperature is raised to 2500°C, it is reported that aluminium nitride of high purity and desired particle size can be prepared from the chloride and ammonia (62).
It has been observed (64) that if aluminium is reacted with the aluminium chloride mono-ammoniate, an aluminium chloride-aluminium nitride complex is formed:

$$\text{AlCl}_3 \cdot \text{NH}_3 + \text{Al} \rightarrow \text{AlCl}_3 \cdot \text{AlN} + 3\text{H}_2$$

which is apparently so stable that it does not decompose when strongly heated. It therefore may well be that this compound is more resistant to oxidation than the pure nitride.

Viberg and May (65) have reported that aluminium nitride can be produced from the addition compound of aluminium hydride and ammonia. The reduction of hydrides using ammonia has recently been studied by Berg et al (66) using silicon hydride. Components which are corrosion-resistant and which possess mechanical strength have been prepared from aluminium hydride and ammonia or nitrogen, using such processes as slip casting, extruding, or hot pressing (67).

Aluminium nitride has been prepared in a non crystalline form by passing dry ammonia over aluminium phosphide at 1000-1100°C (68).

$$\text{AlP} + \text{NH}_3 \rightarrow \text{AlN} + \frac{1}{2}\text{P}_4 + \text{H}_2$$

The phosphorus produced by this reaction condenses in the system. It is removed by passing an excess of nitrogen through the system at 1375-1600°C. The phosphorous is carried away, separated from the nitrogen, and reacted with aluminium powder at 1250°C to give aluminium phosphide. The phosphide can be returned to the system, thus making the process continuous (69).

If ammonia is passed over alumina, heated at a 1000°C, aluminium nitride is formed (70). However, the product is impure due to formation of oxy-nitrides (71). This preparation is questioned as it is thermodynamically unfavourable at a 1000°C.
There have been early reports that if aluminium sulphide is heated in nitrogen, aluminium nitride is formed (72, 73). Borchers and Beck (74) have reported a process involving electrolysis. Impure nitride is formed when mixtures using powdered aluminium are nitrided (18); when liquid aluminium is nitrided (19), and also by the thermal evaporation of aluminium in vacuo (2), presumably due to the presence of residual nitrogen. Aluminium nitride can be prepared industrially by nitriding a mixture of aluminium powder with 30% aluminium nitride (20). High purity nitride has been prepared by nitriding aluminium, aluminium nitride and aluminium fluoride mixtures (22-24). The fluoride is used as a carrier or catalyst and volatilises at 1140°C. Aluminium nitride is formed by nitriding aluminium alloys, principally iron-aluminium (24), silicon-aluminium (26), aluminium-zinc (27), and lithium-aluminium (91) alloys. The combustion of aluminium with nitrous oxide (28) and a nitrogenous organic chemical, such as the thiocarbamide (29) to form the nitride have been reported. Aluminium nitride has been formed from alumina using a nitrogen plasma jet (100) or by heating aluminium phosphate and carbon (75), or orthoclase (76) in an atmosphere of nitrogen. Jander and Weiss (77) have reported that stannous nitride and aluminium bromide react together to form aluminium nitride.

I.1.ii The chemical properties of aluminium nitride

It has been reported that when aluminium nitride is heated in air it turns grey. It was also reported that aluminium nitride hydrolyses to give the hydroxide (56, 114), and the action of dilute sulphuric acid results in the formation of aluminium hydroxide. Hardtung (105) reported that hydrogen does not react with aluminium nitride. The
original observation of Mallet that when aluminium nitride is heated to redness it decomposes to give alumina, was confirmed by Pitcher (106).

Pitcher and Spengel (107) in 1925 reported that dry halogens reacted slowly with aluminium nitride, and in fact at 760°C aluminium nitride forms the chloride in the presence of chlorine. Bromine is observed to react slowly with the nitride only at high temperatures (56). Contrary to these reports, Flament (109) has observed that the halogens do not react with aluminium nitride, but no physical conditions were given.

Bradshaw and Matthew (110) reported in 1958 that the nitride oxidizes in oxygen at temperatures greater than a thousand degrees. Taylor and Lenie (111) have studied the properties of aluminium nitride extensively (see Table 1), and have reported that it is not highly resistant to corrosion by mineral acids, and it starts to oxidise in air at 600°C. A review of the oxidation of aluminium nitride in different atmospheres and temperatures, and for varying intervals of time, has been described (112), and will be compared with the present work later. Aluminium nitride has been produced which is in fact stable to moist air (113). The oxidation of the nitride was investigated in 1962 by Cooper et al (115), but the activation energies for oxidation vary considerably even for the same specific surface. The oxidation is said to follow a parabolic law.
### Table 1

The effect of various media on aluminium nitride

<table>
<thead>
<tr>
<th>Water</th>
<th>Acid</th>
<th>Alkali</th>
<th>Miscellaneous</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposes</td>
<td>Attacked by</td>
<td>Decomposes</td>
<td>Gaseous chlorine</td>
<td>(177)</td>
</tr>
<tr>
<td></td>
<td>concentrated</td>
<td>completely</td>
<td>at normal pressure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sulphuric. acid.</td>
<td></td>
<td>decomposes it</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>completely.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrolyses</td>
<td></td>
<td></td>
<td>(78, 114)</td>
</tr>
<tr>
<td></td>
<td>easily with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaOH.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Resistant to</td>
<td></td>
<td></td>
<td>(182)</td>
</tr>
<tr>
<td></td>
<td>common acids.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Partially</td>
<td>Decomposed</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>resists</td>
<td>by NaOH.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mineral acids.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decomposes</td>
<td></td>
<td>Resistant to B_2O_3</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>in hot</td>
<td></td>
<td>molten aluminium and cryolite Na_3AlF_6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HNO_3, H_2PO_4</td>
<td></td>
<td>No effect with</td>
<td>(180, 181)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>chlorine, bromine or iodine.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Unaffected by</td>
<td>(117)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>molten aluminium, iron or silicon.</td>
<td></td>
</tr>
</tbody>
</table>

9.
I.2. The crystallography and the heat of formation and thermal stability of aluminium nitride

1.2.1. The crystallography of aluminium nitride

The crystal structure of aluminium nitride was first studied by Ott (125) in 1934. He reports that it crystallizes in the hexagonal system with a c/a ratio of 1.601 and an aluminium-nitrogen inter-atomic distance of 1.894 Å. The ionic charges in single crystals of aluminium nitride have been studied (130), and the electronic structure has been discussed (131). The unit cell dimensions were later reported by a number of workers (73, 111, 122, 128, 132-6) (see Table 2). The term, ideal wurtzite structure, (i.e. hexagonal structure of zinc sulphide), has been used to describe aluminium nitride by several authors (117, 123), but Parry et al (117) from their structural investigations of aluminium nitride, confirmed the early proposals (129) and revealed a distortion along the c-axis and the structure of the nitride has latterly been compared with the ZnO structure. The influence of the bonding forces on this deviation from an ideal structure has been studied by Zdanov and Brysneva (136).

Data has been published on the existence of cubic aluminium nitride (a = 4.104 Å) formed by nitriding a steel containing aluminium (94), but the formation of a cubic nitride is questioned by Kohn et al (118). However, when the nitride is subjected to high static and dynamic pressures a modification of the structure is observed, but no conclusive evidence of a possible wurtzite-sphalerite transformation is reported (9).
Table 2

The lattice parameters of aluminium nitride

<table>
<thead>
<tr>
<th>(a (\text{\AA}))</th>
<th>(c (\text{\AA}))</th>
<th>(c/a) ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.113</td>
<td>4.984</td>
<td>1.601</td>
<td>(132)</td>
</tr>
<tr>
<td>3.104</td>
<td>4.965</td>
<td>1.599</td>
<td>(132)</td>
</tr>
<tr>
<td>3.10 ± 0.1</td>
<td>4.965 ± 0.01</td>
<td>1.601</td>
<td>(134)</td>
</tr>
<tr>
<td>3.10 ± 0.01</td>
<td>4.968 ± 0.01</td>
<td>1.602</td>
<td>(122)</td>
</tr>
<tr>
<td>3.111</td>
<td>4.980</td>
<td>1.601</td>
<td>(111)</td>
</tr>
<tr>
<td>3.110 ± 0.002</td>
<td>4.980 ± 0.002</td>
<td>1.601</td>
<td>(135)</td>
</tr>
<tr>
<td>3.08 ± 0.04</td>
<td>4.93 ± 0.06</td>
<td>1.601</td>
<td>(128)</td>
</tr>
<tr>
<td>3.214</td>
<td>4.968</td>
<td>1.595</td>
<td>(78)</td>
</tr>
</tbody>
</table>
The heat of formation and thermal stability of aluminium nitride

The heat of formation of aluminium nitride has been studied by a number of workers extending over a period of some fifty years. Matignon (139) in 1914 was the first to look at this feature. Six years later, Moldenhawe (140) again looked at the heat of formation, but no results are given in the literature. Prescott and Hencke (141) quote a figure of -80.43 k.cal/mole (see Table 3). Mellor (97) gives a value for the specific heat of aluminium nitride as

\[ C = 0.1803 + 2.750 \times 10^{-3} T + 1.937 \times 10^{-7} T^2 \]

This term involves a power of $10^{-7}$ and later expressions do not involve any terms smaller than $10^{-5}$. From Table 3 there is a wide range of values for the heat of formation. This is probably due to the experimental methods used by each author. For example Neugebauer et al (147), using a bomb calorimeter, gives a value which is in agreement with Sato (143), whereas Neumann et al (142) used sodium fluoride as a "catalyst". Apin et al (148) used aluminium and lead nitride in an explosive method to determine the heat of formation. Schissel and Williams (149) deduced their value using the mass-spectrometry third law. From Table 3 a statistical analysis suggests that the heat of formation is in the region of -76 k.cals/mole.

Warner (146) for the reaction of the elements to give aluminium nitride at 1800°C reports a value of the equilibrium gas constant (Kp) as \[ \log K_p = 1.46. \] Kubaschewski and Evans (150) equated the free energy of formation of AlN as

\[ G = -154,000 + 44.5T \]

for the equation 2Al + N₂ = 2AlN.
<table>
<thead>
<tr>
<th>$\Delta H_{298}$ kcal/mol $^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80.43</td>
<td>(141)</td>
</tr>
<tr>
<td>-57.4</td>
<td>(142)</td>
</tr>
<tr>
<td>-73.7</td>
<td>(143)</td>
</tr>
<tr>
<td>-62.0</td>
<td>(144)</td>
</tr>
<tr>
<td>64.0</td>
<td>(145)</td>
</tr>
<tr>
<td>-76.17 ± 0.20</td>
<td>(147)</td>
</tr>
<tr>
<td>-57.6</td>
<td>(148)</td>
</tr>
<tr>
<td>-63.0</td>
<td>(149)</td>
</tr>
<tr>
<td>-75.5 ± 1.0</td>
<td>(150)</td>
</tr>
<tr>
<td>73.0</td>
<td>(180)</td>
</tr>
</tbody>
</table>
Olette and Mme. Ancey-Moret (151) in a recent article have studied the variation of free energy of formation of the some oxides and nitrides, among them aluminium nitride.

It has been reported that aluminium nitride has no melting point and dissociates in the range of 2200-2400°C in agreement with the equation:

\[ \text{AlN} \rightarrow \text{Al}_2(g) + \frac{3}{2}\text{N}_2(g) \]

In fact, no melting has been observed as high as 2700°C (158). The vapourisation behaviour of aluminium and boron nitride has been studied using an effusion method (152). This method appears to be complex and not totally relevant to the present studies. Mah et al (153) have shown from their thermodynamic calculations, that aluminium nitride is stable at 1727°C (2000K) which agrees with established facts. The vapourisation pressure (154) and the decomposition of aluminium nitride (154, 160, 161) have been studied. The activation energy of sublimation for gallium nitride has been studied using mass spectrometry methods (155). The vapourisation behaviour (155, 159) and the kinetics of vapourisation of aluminium nitride have also recently been discussed (156).

1.3 The physical and mechanical properties of aluminium nitride and related materials

Several nitrides including aluminium nitride have been placed in a diamond shape pattern and theories put forward to relate their properties with reference to their positions in this table (124).

Matignon (37) stated that aluminium nitride does not melt, but in fact dissociates at 2200°C. Herzer (115) in 1927 reported that it decomposes at greater than 1400°C, and since then various research workers (108, 111, 117, 146) have reported the decomposition temperature
<table>
<thead>
<tr>
<th>Decomposition Temp.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2150^\circ C \oplus 4$ atmospheres</td>
<td>(108)</td>
</tr>
<tr>
<td>$2230-2240^\circ C$</td>
<td>(138)</td>
</tr>
<tr>
<td>$2400^\circ C$</td>
<td>(111)</td>
</tr>
<tr>
<td>$2200^\circ C \oplus 4$ atmospheres</td>
<td>(116)</td>
</tr>
<tr>
<td>$2230^\circ C$</td>
<td>(117)</td>
</tr>
</tbody>
</table>
of aluminium nitride. The density of aluminium nitride has been reported as 3.049, 3.004 (115), 3.25 (117), 3.30 (123), and 3.26 (111).

Crystals of aluminium nitride have been reported as white (108, 122), pale yellow (97), and blue (97, 108, 122, 134), and in fact the growth and properties of single crystals of aluminium nitride has been studied by Witzke (119) and Matsumara and Tanake (120). The occurrence of blue crystals has been attributed to cobalt impurities (121).

The electrical properties of aluminium nitride have been studied (124, 126-128). It has been reported that aluminium nitride is a "typical dielectric" (125), and the epitaxial growth on several single crystals substrates of aluminium nitride has been studied (128).

### I.3.1i The mechanical properties of aluminium nitride and related materials

Ceramic materials have such desirable properties as resistance to wear, mechanically hard, good electrical insulation, and resistance to corrosive environment, but the machinability of the ceramic is such that to produce articles with close dimensional tolerances requires an expensive operation.

However, a material has been established which not only possesses the reputed ceramic properties, but also has resistance to thermal shock and is capable of being produced with an improved degree of dimensional accuracy. This new material is silicon nitride. A comparison of the formability with respect to mechanical characteristics of aluminium nitride, with silicon nitride and other ceramic materials (see Table 5) suggests the possible use of aluminium nitride in a similar field.
**Table 5**

A comparison of the mechanical properties of aluminium nitride with certain ceramics

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminium nitride</td>
<td>27</td>
<td>25</td>
<td>1230</td>
<td>35050</td>
<td>5.64</td>
<td>2400</td>
</tr>
<tr>
<td></td>
<td>18.95</td>
<td>1000</td>
<td></td>
<td>32300</td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>1400</td>
<td></td>
<td>28100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silicon nitride</td>
<td>1.5</td>
<td>20</td>
<td>16</td>
<td>3337</td>
<td>4.60</td>
<td>1900</td>
</tr>
<tr>
<td></td>
<td>2.75</td>
<td>14.7</td>
<td>1200</td>
<td>(120g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tantalum carbide</td>
<td>2.3</td>
<td></td>
<td></td>
<td>29100</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>titanium boride</td>
<td>24.5</td>
<td>20</td>
<td></td>
<td>54000</td>
<td>6</td>
<td>2980</td>
</tr>
<tr>
<td>molybdenum di tlicide</td>
<td>28</td>
<td>980</td>
<td>21</td>
<td>735</td>
<td>8</td>
<td>2030</td>
</tr>
<tr>
<td></td>
<td>29.4</td>
<td>1200</td>
<td>6</td>
<td>3100</td>
<td>9.2</td>
<td></td>
</tr>
</tbody>
</table>
It is reported that aluminium nitride has high thermal conductivity, low thermal expansion, and good thermal shock resistance. It is observed that the mechanical properties of aluminium nitride and silicon nitride decrease with temperature, but when compared with molybdenum disilicide, the drop in shear strength is not so drastic. However, the tensile strength of molybdenum disilicide increases slightly with temperature. The difference in crystal structure is noted as a possibility for the explanation of these observations (see Table 7).

The knoop hardness figures suggest that aluminium nitride is not so resistant to mechanical deformation as silicon nitride. Aluminium nitride has a lower modulus of elasticity than most of the ceramics considered, but is nevertheless compatible with the materials in terms of its elastic deformation. The bending strength, however, reduces rapidly with respect to temperature for aluminium nitride as values of 38,500 p.s.i. at 25°C falling to 18,000 p.s.i. at 1400°C are reported. The thermal stability range of aluminium nitride, however, is reported to be higher than that of silicon nitride, but not so high as titanium boride.

A comparison of the coefficient of thermal expansion of aluminium and silicon nitrides shows that with respect to temperature, aluminium nitride will expand more than silicon nitride. However, this is still less than that of the other ceramics considered (see Table 6).

The thermal shock characteristics of aluminium nitride are better than all the ceramics considered, except silicon nitride, and it is concluded that the use of aluminium nitride as an engineering material has distinct possibilities, especially as the properties could be enhanced by hot pressing the material as observed with boron nitride. In fact,
Table 6
The thermal expansion of certain materials (92)

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage expansion from 250°C to</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1) 500</td>
</tr>
<tr>
<td>aluminium nitride</td>
<td>0.23</td>
</tr>
<tr>
<td>α-silicon nitride</td>
<td>0.10</td>
</tr>
<tr>
<td>β-silicon nitride</td>
<td>0.07</td>
</tr>
<tr>
<td>molybdenum silicide</td>
<td>0.37</td>
</tr>
<tr>
<td>α-quartz</td>
<td>0.92</td>
</tr>
<tr>
<td>alumina</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Table 7
A comparison of the crystal structures of certain materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Type</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a(\text{Å}))</td>
</tr>
<tr>
<td>aluminium nitride</td>
<td>hexagonal</td>
<td>(\text{ZnS} )</td>
<td>3.104</td>
</tr>
<tr>
<td>(\alpha)-silicon nitride</td>
<td>hexagonal</td>
<td>(\text{ZnO} )</td>
<td>7.76</td>
</tr>
<tr>
<td>(\beta)-silicon nitride</td>
<td>hexagonal</td>
<td></td>
<td>7.59</td>
</tr>
<tr>
<td>tantalum carbide</td>
<td>cubic</td>
<td>NaCl</td>
<td>4.456</td>
</tr>
<tr>
<td>titanium boride</td>
<td>hexagonal</td>
<td>AlB(_2)</td>
<td>3.026</td>
</tr>
<tr>
<td>molybdenum disilicide</td>
<td>tetragonal</td>
<td>MoSi(_2)</td>
<td>3.203</td>
</tr>
</tbody>
</table>
it has been shown that the thermal shock parameters of aluminium nitride are improved by this technique.

I.4 The fabrication and uses of aluminium nitride and related materials

I.4.1 The fabrication of aluminium nitride

Rey (117) suggested the possibilities of aluminium nitride as a refractory material, and it was established that aluminium nitride could in fact be used as a container for aluminium up to 2000°C (17). Sintered aluminium nitride objects (162) were produced by placing powder around a graphite core and heating the assembly to 2000-2500°C. The shape of the article was determined by the design of the core. Porous refractory bricks and nitrided articles were also obtained by heating a mixture of corundum, coke, calcium aluminate cement, and water or bauxite at 1600°-1800°C in nitrogen. The products were found to have density of greater than 1 and contained more than 30% nitrogen. Compacted aluminium nitride crystals bonded by aluminium nitride and containing small impurities were heated to 1500°C in a pure nitriding atmosphere, resulting in sintered objects, details of composition and conditions being given (163). Aluminium nitride powders were heated as a compacted mass to 2000-2500°C in a nitrogen atmosphere. The vapour phase of aluminium nitride is formed and on cooling AlN recrystallizes around the grains of the compacted mass. Another method of producing a moulded article, was to add a suitable organic binder to the powdered mixture of aluminium nitride and a small amount of mineraliser. The mixture was heated in an oxidising atmosphere below 500°C to eliminate the binder and maintained in ammonia to remove the oxygen, and the temperature raised.

21.
Contrary to the report of Rey (117), that the conductivity of aluminium nitride up to 1500°C is so low that it could be used as an insulating material, electrodes of aluminium nitride have been prepared (165), and could be substituted for graphite in the Hall process (17, 166). A refractory material similar in composition to these electrodes was produced by hot pressing a titanium carbo-nitride - aluminium nitride mixture to give a bulk density of 2.6 gram cc⁻¹ and an electrical resistance of 250-5000 x 10⁻⁶ ohm-ins. (167).

Objects of aluminium nitride were produced by calcining aluminium and aluminium nitride powders together with a catalyst in nitrogen atmosphere (168). Aluminium nitride articles were prepared by mixing aluminium with 7-50% cyanamide, dicyanamide or melamine and heating for 30-90 minutes in nitrogen at 1200-1400°C (169). To stabilise the nitride against water, the product was heated in oxygen before or after pressing and sintering at 2050-2150°C.

Sintered refractory mixtures of aluminium nitride and titanium boride have been prepared (170). Refractories were obtained from a mixture of aluminium and silicon powders with 2-10% paraffin binder and a fluoride catalyst in a nitrogen atmosphere and heating in stages to 1420°C (184). Aluminium nitride and a solid solution of aluminium nitride and silicon carbide, together with approximately 2% water were hydrostatically pressed to give a hard dense and strongly bonded refractory (171). Silicon carbide is also reported to benefit the properties of aluminium nitride (174, 190, 191). Crucibles were formed by extruding the product after it had been slowly heated to remove the water. The sintering of the aluminium nitride-aluminium system has recently been studied (147). The results were
applied in the manufacture of aluminium nitride crucibles. The mechanism of sintering in general and factors influencing sintering has recently been reviewed (173). A vitrified refractory composed of alumina and aluminium nitride was made by fusing the two compounds in a graphite crucible at 2000-2300°C (153). Care was taken not to exceed 2300°C, because the nitride may start to decompose in this temperature region.

I.4.ii The uses of aluminium nitride and related materials

Since the discovery that silicon nitride has properties similar to both a conventional ceramic material and a semi-conducting material, the interest in the possible applications of aluminium nitride has grown. Silicon nitride, from the virtue of its physical, chemical and mechanical properties, has been used as high temperature electrical insulators, refractory for aluminium, engineering components, furnace linings and barings, where the coefficient of friction compares with such materials as P.T.F.E. and glazes (174).

Aluminium nitride is resistant to most common acids and alkalis and in fact articles specifically to be used in corrosive environment have been made (176).

The applications of aluminium nitride have generally been directed in producing refractory articles of aluminium nitride (17, 118, 183, 194, 186) such as crucibles, or combining aluminium nitride with titanium carbon-nitride (182), silicon nitride (185, 187) and silicon carbide (204) to form such articles. Aluminium nitride has been used to coat graphite (15), quartz (61), and alumina (188), and other refractory materials (133), to improve the surface properties of the ceramic matrix.

Silicon nitride has been used as a binder for refractory oxides (189) and there is possible use of aluminium nitride in this field.

Aluminium nitride has been used as a carrier for molten aluminium (17) and in this respect is more resistant to cryolite-alumina melts than silicon nitride or some metal borides and carbides (190).
As aluminium nitride in compact form is non-reactive up to $1600^\circ$C, it has been developed for use in connection with nuclear reactors (192, 193) and has a high temperature insulation material (196). Aluminium nitride has been used in the production of radioactive isotopes (194, 195).

Titanium salts have been added to improve the conductance of aluminium nitride. The resulting cermet has been used as electrodes to produce aluminium by the Hall process (197, 198). Semi-conductors have been produced using co-axial films of aluminium nitride with the elements of compounds of germanium and silicon when the difference in lattice parameters is less than 40% (199). The precipitation of aluminium nitride in low carbon steel benefits the deformation characteristics of that particular steel (200). Aluminium nitride has been used as a slow-working fertiliser (203), as a secondary accelerator in the vulcanization of a co-polymer (200), and in the production of aromatic hydro-carbons (201). Thin refractory layers of alumina, aluminium nitride and silicon nitride have been used as covering layers for electronic devices (175). Aluminium nitride has been used in connection with reinforced filaments (5, 95).

In this thesis the author has studied and compared existing and newer processes for the production of aluminium nitride, viz.

(a) Serpek process;
(b) the preparation of the nitride from its elements;
(c) the reaction of ammonium hexafluoroaluminate in ammonia.

The formation of aluminium nitride has been investigated thermodynamically using the available thermal data. The reactivity of aluminium nitride has been examined with regard to atmospheric oxidation and possible hydrolysis by steam or liquid water, particularly for samples of size ranges possibly suitable for sintering or hot-pressing. Changes in phase composition and crystal structure on milling and oxidation or hydrolysis of aluminium nitride have been investigated by X-ray, optical and electron-micrographic methods. Surface area determinations have been made by gas sorption and correlated with changes in crystal structure and crystallite size on oxidation or hydrolysis. Some comparisons have been made with the reactivity of silicon nitride.
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1953, 29, 439.
1968, (1-2), 56.
CHAPTER II. Experimental Techniques

This chapter is devoted to the experimental techniques used in the present work. Reference will be made to this chapter when the results of a particular section are considered.

The methods observed were:

1. The formation of ammonium hexafluoroaluminate.
2. Chemical analysis.
3. Thermal analysis.
4. Infra-red analysis.
5. X-ray analysis.
7. Particle size analysis.
8. Surface area determination.

II.1 The preparation of ammonium hexafluoroaluminate

Ammonium hexafluoroaluminate was prepared by the following methods.
(1) Reaction of aqueous ammonium fluoride with an aqueous suspension of Bayer hydrate, Al₂O₃·3H₂O. (2) By reacting aqueous ammonium fluoride with aqueous solutions of aluminium fluoride, and aluminium chloride.
(3) By reacting alcoholic ammonium fluoride with alcoholic aluminium bromide or aluminium nitrate.

The method selected was to dissolve aluminium foil in aqueous HF to give a solution of aluminium fluoride, and after filtration to react the solution with aqueous ammonium fluoride. Details are given in Appendix I.
II.2 Chemical analysis

The chemical analysis of the ammonia content in ammonium hexafluoroaluminate was carried out using the Kjeldahl technique (3). The nitrogen content in aluminium nitride was determined using the method of Passer et al (4). The fluoride content of ammonium hexafluoroaluminate was determined using the Willard-Winter technique on a micro-scale. This method was found not to be satisfactory for the fluoride analysis of aluminium fluoride and a method based on the report of Bognar and Nagy (6) was adopted. The aluminium content of all the compounds was determined by precipitating the aluminium as aluminium oxinate (2, 7).

Details of the analytical methods are given in Appendix II.

II.3 Thermal analysis

The thermoanalytical techniques used in the present study were (a) Thermogravimetric Analysis, (b) Differential Thermal Analysis.

II.3.1 Thermogravimetric analysis

Thermogravimetry is the continuous or frequent measurement of weight at a particular temperature, or as a function of temperature change. The measurement of weight and temperature as the specimen is being heated is not simple, several errors tending to distort the system (21).

The balance used in this analysis was based on a suggestion of Gregg and Winsor (22), using a null point thermo-balance design. The balance (Stanton's A49) could record weights to an accuracy of 0.2 mg and was supported on a dexion frame above the furnace. The furnace was constructed in the following manner. Nichrome windings was placed in double turns round a grooved silica tube of 1 inch I.D. The tube was supported in a mixture of vermiculite and asbestos contained in a cylindrical stainless steel case. One end of the silica tube was sealed. The nichrome windings
were attached to a temperature controller (Sunvic (A.E.I.)). The specimen to be heated was suspended in the furnace by nichrome wire connecting the base of a weighting pan to the nichrome crucible holder. Nichrome was used, as it does not begin to oxidise appreciably in wire form until 1100°C (24). The specimen was placed in a 10 c.c. porcelain crucible, placed in the crucible holder and suspended in the furnace. A chromel-alumel couple, capable of recording temperatures up to a 1100°C was placed a few centimetres from the specimen.

The furnace was brought to temperature and the weight changes were observed at a particular temperature.

II.3.ii Differential thermal analysis

Introduction

Differential thermal analysis is a technique by which thermal effects are measured, usually as the sample is heated or cooled. In basic technique it is related to calorimetry. As heat is added to a calorimeter or isolated system, the temperature of the system will rise approximately linearly. With a specimen present, the specimen has to be heated as well so there will be a decrease in the rate of temperature increase. If the specimen undergoes some transformation, additional heat must be added to the system to change the specimen to its new form. If a reference junction is present within the system, the temperature difference after the transition will be zero. If the temperature difference was plotted against temperature instead of heat input, and if the thermocouple was inserted in the specimen and reference thermocouple in an inert material, this would result in the essentials of differential thermal analysis. The thermal transformation taking place can be detected by such a system from the plot of temperature difference against temperature.
The sample shape and size will affect the shape of the plot, or peak, as it is known.

An account of the experimental factors which affect the shape of a differential curve has been given elsewhere (21).

**Apparatus**

The apparatus used was based on the design of Grimshaw et al (18).

28 gauge wire thermocouples (nichrome and alumel) was placed in the double holder with each section containing a common lead which was placed in identical position to its neighbour.

The sample under test was packed into one of the two cubical compartments (1 cm wide) of the thin walled refractory holder, the other being filled with inert material. This holder was fitted into the lower half of a refractory block, the upper half forming the cover. When assembled, the cylindrical block was placed in a tube furnace (Griffin & George) of similar diameter. The thermocouples were connected to a recording instrument (Cambridge Instruments Ltd.). The temperature of the specimen was measured by inserting a similar refractory block in the other side of the furnace. The block contained the same inert material as used in the sample block and the temperature was read by placing a nichrome thermocouple in the block and connecting it to a directly calibrated temperature recorder, using self compensating thermocouple leads.

The rise in temperature was recorded for three temperature settings and for a heating rate of 10-15°C per min a furnace setting of 180 V was used.

**II.4 Infra-red analysis**

The instrument used for this work was a Unicam SP 200 double beam spectrophotometer. The instrument had an air cooled Nernst glower as its
source of radiation, and a monochromator of the Littrow arrangement. The
detector was a Golay pneumatic type. The chart recorder was of the flat
bed type. The instrument operated over a range of 650 \text{ cm}^{-1} \text{ to } 5000 \text{ cm}^{-1}
with a change in scale at 2000 \text{ cm}^{-1}. Sodium chloride prisms were used
throughout this work.

Sample preparation

Several techniques have been developed for obtaining infra red
absorption spectra of solids. These include milling or suspending the
solid in a liquid medium and the pressing the sample in alkali halides.
The liquid technique was employed throughout this work. The common
technique is to suspend a few milligrams in a commercial Nujol mull.
However, the reported values of the absorption spectra of the ammonium
fluoride and its complexes are in the range 1420 - 1490 \text{ cm}^{-1}, and 3000 -
3300 \text{ cm}^{-1}. Nujol gave strong absorption peaks at 1460 \text{ cm}^{-1} and 2850 \text{ cm}^{-1}.
Tetrachloroethylene gives strong absorption peaks at 780 \text{ cm}^{-1}, so it was
decided to use the Nujol mull in the range 650 - 1200 \text{ cm}^{-1} and
tetrachloroethylene in the range 1200 - 5000 \text{ cm}^{-1}.

A few milligrams of each specimen were ground in an agate and mortar.
A few crops of the solvent was added and the mixture was reground and
placed between the sodium chloride plates. The plates were mounted in
the holder and the assembly placed in the instrument using a reference
beam of air.

II.5. X-ray analysis

Two methods of identification were used; powder diffractometry and
a 9 cm x-ray powder camera.

II.5.1 Powder diffractometry

In the present work most of the compounds could be indexed on
orthogonal axes.
From \( n\lambda = 2d\sin \theta \) \hspace{1cm} (1)

and \( 1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \) \hspace{1cm} (2)

where \( h, k, l \) and the crystal indices and \( a, b, c \) and the crystal parameters and by substituting equation (2) in equation (1), it is possible to show a relationship between the Bragg angle and the intrinsic crystallographic properties of a particular system, the length of the equation depending on the symmetry of the crystal system

\[
\text{i.e. } \sin^2 \theta = \frac{1}{4} \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

The agreement between the calculated \( \sin^2 \theta \) values or \( d \)-spacings and those observed will indicate the accuracy of estimating the cell parameters \( a, b, c \).

Intensity of radiation emitted by an element is proportional to the atomic scattering factor \( f \) and \( f = Z \), the atomic number of the element, when \( \theta \) is zero, but falls off as \( \theta \) increases. In the present study compounds such as aluminium nitride, aluminium fluoride and alumina were x-rayed and as \( Z \) for aluminium is 13, the observed intensity will decrease with increasing \( \theta \). Consequently, it was anticipated that the \( d \)-spacings at high \( \theta \) angles would be too weak to make accurate measurements. For low \( \theta \) angles greater accuracy is obtained with the recordings of a diffractometer.

**Sample preparation and instrumental technique**

Techniques for sample preparation have been given (23), but as the identification of the sample only is required, a far less complicated technique than those described was used.
To a sample of powder placed on a watch glass was added a small amount of "durofix" and acetone. The presence of these two substances did not alter the x-ray characteristics of the sample and serve to coalesce and maintain the powder on a flat glass slide. This glass slide was supported in the x-ray beam and rotated from 4° to 40°. The refracted beam was collected by a geiger or proportional counter and translated to the chart recorder by means of a panax ratemeter or Berthold ratemeter/discriminator, depending which diffractometer was used. The chart was calibrated in intervals according to the speed of rotation of the sample, from which a direct reading of θ could be made.

II.5.ii Powder camera

A 9 cm-radius Unicam powder camera was used with the Van Arkel arrangement (see Fig. 2a).

A powder film (Kodirex 3.5 cm x 2.8 cm) was cut to the required dimension using a guillotine (Unicam S.61) placed around the sample in the camera support and the lid set in position. The camera was mounted adjacent to the x-ray tube and evacuated for two to three minutes before the x-ray generator was switched on. A working voltage of 40 kV and 6 mA was used in all cases for exposures of 2 to 4 hours.

After exposure, the powder films were developed for 4 minutes, (Kodax D19b), rinsed in water and fixed for 4 minutes (Kodax FX40), washed for half an hour, and left hanging to dry.

II.5.iii Errors in powder photographs

The possible errors in powder photographs are (a) the non-coincidence of the axis of the camera and the rotation axis of the specimen; this error can be easily accounted for and will be discussed later, (b) the finite height of the specimen; in a 9 cm camera only approximately 2 mm of specimen is irradiated and hence this error was neglected.
Fig 2 Van Arkel arrangement.
(c) absorption and divergence of the x-ray beam; the errors produced by these effects are similar, for with absorption only a specimen in which this error is negligible can the centres of the powder lines be taken as the correct positions, and usually the measured value of $\Theta$ is too large (91). Hence the observed d-spacing will be too small when compared with the standards. The opposite of this effect is true with divergence of the x-ray beam.

From the equation

$$ n \lambda = 2 d \sin \Theta $$

when considering first order wavelengths

$$ d = \left( \frac{\lambda}{2} \right) \cosec \Theta $$

$$ \Delta d = - \frac{\lambda}{2} \cosec \Theta \cot \Theta. \ \Delta \Theta $$

Now in the Van Arkel arrangement $\Theta = 90 - \frac{S}{4R}$ where $S$ is the distance between corresponding diffraction arcs and $R$ is the radius of the camera. So when $S$ is large $\Delta \Theta$ will be large. An extensive mathematical survey for this error has been cited (9). To compensate for the error, a plot of the unit cell parameter against the Nelson-Riley function could be made (8), (d) film shrinkage; when the film is developed depending on, among other factors, the temperature of the developer, the film may shrink. To compensate for this it was assumed that the shrinkage was uniform throughout the film and the error could be calculated if the knife edge angle ($\phi_k$) was known for the camera.

Measurements were made using micrometer callipers of the knife edge at the point opposite to the emergent x-ray beam termed as $C$ in Fig. 2b, and of the camera radius.
From Fig. 2b

\[ \frac{C}{2R} = \sin 2\phi \]

\[ 4 \phi_i = 2 \sin^{-1} \frac{C}{2R} \]

\[ 4 \phi_k = 360 - 2 \sin^{-1} \frac{C}{2R} \]

\[ \phi_k = 90 - \frac{1}{2} \sin^{-1} \frac{C}{2R} \]

\[ \phi_k = 86.40 \pm 0.01 \circ \]

from which the film constant will be

\[ \frac{\phi_k}{S_k} \]

Measurement of the film

The powder films were measured using an instrument constructed from two metre rules separated and ribbed together by varnished three ply wood. Adequate allowance was made for placing the film between the two metre rules and a plastic cursor was placed over the rules. Any tolerance in the cursor was compensated by a small piece of watch spring between the rule and the cursor. A vernier scale of 1 mm intervals was made in the cursor enabling measurement to be made to the second decimal place.

Accuracy of measurement was \( \pm 0.01 \) cm.

As a result of careful measurement the estimation of the crystallographic parameters were made using a computer program based on Ito's method (see Appendix III).

II.6. Electron microscopy techniques

The microscope

The Philips EM 100 B electron microscope with a resolution of 25 Å was used in this study. The microscope is usually operated at 80 KV. The pumping system consists of a prevacuum rotary pump, a mercury diffusion pump and an oil diffusion pump. The magnification is altered by adjusting
the currents to the electromagnetic lenses. Focussing of the image is controlled when varying the strengths of the magnetic fields, by changing the currents generating them. The image of the sample is projected onto a fluorescent screen directly in front of the observer. There are facilities provided for photographing this image with a 35 mm camera which can be lowered into position immediately in front of the screen. Generally, a four second exposure is used and the magnification of the photomicrographed image obtained from comparing the instrumental and the illumination settings with calibrated standard tables. The camera constant $\lambda L$ is calculated using a compound of known unit cell dimensions, but if the same accelerating voltage is maintained then $\lambda L$ remains constant. $\lambda L$ is the effective camera length.

**Sample preparation**

Specimens were prepared by placing a film of carbon on a copper grid in the normal manner. The grid was supported under an infra red lamp. A few milligrams of the sample were placed in distilled water or acetone in a test tube and placed in an ultra-sonic medium to ensure that the sample was thoroughly mixed. A single drop of the suspension was placed on the grid, the heat from the lamp evaporated the water leaving a dispersion of the sample on the carbon film.

Finally the grid was placed in a specimen holder to be introduced into the microscope.

**II.7 Estimation of particle size**

The particle size was estimated using electron and optical microscopy.

**II.7.1 Electron microscopical technique**

Electron micrographs of the relevant samples were taken using a 35 mm camera.
From the print obtained and knowing the total magnification (i.e., the magnification of the microscope and the magnification characteristics of the enlarger), an equivalent distance to 1 μm could be measured on the photograph. The dimensions of the irregular particles were measured with respect to the 1 μm equivalent distance and the mean given to represent the particle dimension. As the particles were ill-formed, a range of size is quoted.

II.7.ii Optical microscopical techniques

The method has been described in great detail (10). The instrument used was a Vickers polarising microscope with magnifications 400x and 1600x. The samples were spread on a glass slide and placed on the microscope. The sizes were estimated by comparing the particles with standard dimensions on an eyepiece graticule (11). The graticule dimensions were calibrated to represent different μm sizes for each magnification. Again, as the particles are irregular, a range of size is quoted.

With both techniques of measurement, care must be taken when measuring, that the sample is representative of the total mass. This involves precise and careful observation of the sample characteristics.

II.8 Surface area measurements

Gas sorption measurements give information as to the specific surface and the average crystallite size of a powder. A general treatise of the subject has been given by Gregg and Sing (12).

The method used to determine surface areas was due to Brunauer, Emmett & Teller and is known as the B.E.T. procedure (13). The B.E.T. equation gives:

\[
\frac{p}{x(p_0 - p)} = \frac{c - 1}{xM c} \cdot \frac{p}{p_0} + \frac{1}{xM c}
\]
where $p$ is the pressure of the adsorbate vapour in equilibrium with absorbent; $p_0$ the standard vapour pressure of adsorbate vapour; $x$ is the amount of vapour adsorbed; $x_m$ is the capacity of filled monolayer; $c$ is a constant.

Adsorption isotherms are classified into five types of which type II isotherms give the best agreement with the B.E.T. equation over limited ranges of vapour pressure (14). Thus a plot of $\frac{p}{x(p_0 - p)}$ against $\frac{p}{p_0}$ would give a straight line of slope $\frac{c}{x_m^2}$ and intercept $\frac{1}{x_m}$. From the quantities a value of $x_m$ can be found. The specific surface $S$ is related to $x_m$ by the equation;

$$S = \frac{x_m}{M} \cdot N \cdot A_m$$

where $M$ is the molecular weight of the adsorbate

$N$ is Avogadro's number

$A_m$ is the cross sectional area of an adsorbate molecule in a completed monolayer.

The specific surface is related to the average particle size $l$ by;

$$S = \frac{6}{\rho l}$$

where $\rho$ is the density of adsorbent.

Apparatus

The sorption balance is based on the design of Gregg (15, 16). The balance arms are made of glass and supported on needles. One arm of the balance supports buckets for the sample and counterweights, the other arm either a solenoid or magnet enclosed in glass and surrounded by an external solenoid. The whole assembly is enclosed in glass and connected to a system of evacuation pumps and gas reservoirs. The pressure readings were made
with a graduated mercury manometer. The current in the external solenoid is varied to obtain the balance point, which is noted by comparing the position of a horizontal metal pointer with a reference pointer. The instrument is calibrated by measuring the current required to observe the null point for known weights. Buoyancy corrections were made to the readings again by comparison with a standard material.

**Technique**

The sample was placed in the specimen bucket and out-gassed to remove physically adsorbed vapour. This was carried out at 200° by surrounding the balance limb with a furnace (17).

A Dewar flask containing liquid oxygen was placed around the balance limb. The absorbate was nitrogen gas. The isotherms were measured at -183°C. The weight of the sample was determined in vacuo. Nitrogen was introduced into the system and equilibrium was achieved before simultaneous readings of sample weights and gas pressure were taken.

From the results the surface area measurements were found with the aid of a computer program devised by P. O’Neill and Denise Harris (5) in Fortran IV using an I.B.M. 1130 computer as detailed in Appendix IV.

**II.9 Ball milling**

The aluminium nitride was milled in cylindrical porcelain pots containing a number of balls of the same material. The pot had radiused ends to present a smooth interior surface free from corners and crevices. Having placed the material in the pot, the open end was secured with a lid and quick-release bar. The pot was placed in a jig and lay in a horizontal position, and mechanically rotated so as to ensure effective contact with the porcelain ball.
Following the milling period, the process of recovery was as follows:
The pot was held vertically above a sieve positioned on a large dish. The porcelain balls were collected on the sieve and the powdered nitride collected in the dish. The balls and the inside of the pot were brushed vigorously to remove the nitride. Any remaining nitride was brought out by rotating the closed pot with a portion of acetone, whereupon the nitride and acetone were removed from the pot and the nitride was freed from acetone by drying in an oven at 70°C overnight. 80% recovery or better was achieved with this operation.

II.10 Experimental techniques used in preparing aluminium nitride

II.10.1 Preparation from ammonium hexafluoroaluminate

The preparation of aluminium nitride was attempted by the thermal decomposition of ammonium hexafluoroaluminate in gaseous ammonia.

The removal of gaseous impurities

When decomposing the hexafluoroaluminate compound in air it was noted that after periods of an hour at higher temperatures (> 500°C) the formation of compounds similar in x-ray characteristics to basic fluorides (24) were formed. The removal of the moisture in the system was therefore vital.

The air was passed through two dreschel bottles and a horizontal glass tube containing potassium hydroxide pellets. The glass tube was used to improve contact between the hydroxide and the air. As a consequence, the removal of moisture from the system appeared to be effective, for in 18 hours at 62°C no basic fluoride was formed when decomposing the hexafluoroaluminate.

The presence of a small percentage of oxygen was anticipated in the nitrogen gas used and to remove it the gas was bubbled through pyrogallol solution. To prepare pyrogallol solution, 15 grams of A.R. pyrogallol were
added to a quickfit test tube. A tube was inserted via a side arm piece and 100 mls of 40% aqueous potassium hydroxide was added under nitrogen. The solution was prepared in this manner because of its active affinity for oxygen. The nitrogen was bubbled through the pyrogallol solution and passed through a U-tube containing magnesium perchlorate, prior to passing it through the drying system.

**Furnace**

The furnace was a horizontal tube type using chromel-alumel thermocouples with a maximum temperature of 1000°C.

When ammonium hexafluoroaluminate is thermally decomposed, ammonium fluoride is present. At temperatures above 520°C it will exist in its dissociated state as ammonia gas and hydrofluoric acid gas. However, the recombination of these two gases takes place at temperatures less than 520°C giving ammonium fluoride which condenses on the colder parts of the purox tube. It appeared to condense in one particular region and the build up of the compound was sufficient to vigorously attack the purox until the tube fell apart. Hence the tube life is drastically shortened. To overcome this problem, the tube end was maintained above the decomposition temperature of ammonium fluoride in the following manner. The tube end was wound with several turnings of nichrome wire on a layer of paper asbestos. A thick layer of alumina cement was placed on the windings and left to set hard. The ends of the windings were connected through an ammeter to a variac with a maximum current of six amps. The excess load on the tube was compensated by supporting the tube below the alumina cement layer.

The variac was set just below its maximum rating and a temperature of 600°C was observed in the furnace end. This initially upset the thermal equilibrium and the discrepancies were accounted for by allowing the gas to
be used, to pass through the system for a period of some 30 minutes.

The ammonium fluoride condensate was therefore collected in a six inch length of copper tubing which was rigidly set in the purox tube with alumina cement. Less than half of the copper tube was cooled by placing a few turnings of thinner copper tubing around it and passing water through them.

After each run, the copper tubing where the ammonium fluoride was now observed to condense was cleaned with a small brush.

The exit gases were passed through (a) a plastic bottle containing glass wool, (b) a dreschel bottle containing potassium hydroxide pellets, and (c) a plastic bottle containing distilled water.

The first plastic bottle was required to prevent any fluoride attacking the dreschel bottle which in turn was required to prevent moisture diffusing back into the system. The ammonia exit gas was partially dissolved in the distilled water; any excess was passed to a fume cupboard.

The ammonium hexafluoroaluminate and its derivatives were placed in a purox boat which was inserted into the horizontal tube furnace and placed in the hot zone under the gas in question. The rate of gas flow was measured using calibrated flowmeter tubes.

II.10.11 Preparation by the Serpek reaction

There are innumerable problems, such as temperature control and fluctuations, thermocouple materials and system design, when studying chemical reactions at elevated temperatures. The possibility of designing a high temperature furnace was considered, but for the reasons stated above, an alternative method was desirable.
The use of optical microscopy appeared to offer a suitable method for examining the reaction.

The microscope used in the investigation was a Griffin-Telin hot stage microscope which has the following advantages;
(a) Elaborate water-cooling arrangements for the protection of the microscope are unnecessary and the instrument can be adapted to examine the behaviour of materials at high temperature by x-ray diffraction as well as by optical microscopy.
(b) The method of mounting the sample makes provision for examination of the internal structure by transmitted light. Crystals present in a melt can be viewed in normal and in polarised light.
(c) The instrument provides specifically for very high temperature observations and reproducibility of results reported to be within ± 1°C.

The instrument is composed of a power supply, which incorporates a 5 inch scale meter calibrated directly for use with 20% Rh-Pt/5% Rh-Pt thermocouples and a Beck petrological binocular-type microscope.

The instrument is provided with a gas tight cell which houses the thermocouple elements and at the same time permits the use of any desired atmosphere. At high temperatures oxidation of the thermocouple may occur and the volatilisation of the thermocouple will impair vision of the sample. Passing of nitrogen obviates this effect and the use of this gas is also desirable for the Serpek reaction.

The inlet and outlet posts of the cell were guarded from moisture by U-tubes containing calcium chloride.

The thermocouple units are provided with neoprene gaskets which make an efficient seal when the retaining nuts on the guide rods are tightened.
The cell was attached to the microscope stage by means of slotted arms, which in the locked position exert a slight pressure on the cell to ensure good thermal contact with the revolving microscope stage, and so any heat radiated which is small, will be conducted away and dissipated in the body of the instrument.

The alignment of the instrument was checked before each operation to ensure optimum visibility.

When using the instrument the behaviour of any material and the accuracy of temperature measurement is dependent on two factors, (a) the correct fabrication of the microfurnace assembly, (b) temperature gradient within the sample.

(a) Fabrication of the thermocouple elements

The optimum performance of the microfurnace assembly is dependent upon the thermojunctions being formed in an exact and reproducible manner.

A length of 5% Rh-Pt alloy (approximately 3 cm) is placed in the negative terminal designated by a small red dot and secured by the clamping screw. The other extremity of the wire was such that when placing the thermocouple unit into the cell, it extended just to the edge of the window aperture. A similar length of 0.5 mm diameter 20% Rh-Pt alloy wire was clamped to the positive terminal. These two wires form the supports for the heater element proper, which is composed of 0.2 mm diameter wires of the same alloy composition. To join the two respective wires together, the operation requires a small oxy-coal gas flame. The thinner diameter wire is first placed in flame and a small bead compatible in dimension to the diameter of the thicker wire is formed.
The bead is placed adjacent to the head of the thicker wire and the wires placed in the flame until fusion is complete. The operation, which requires a certain amount of skill, is repeated with the other two wires of differing diameters. The fine wires are then trimmed to approximately 1.5 cm and the supporting wires turned inward until the fine wires are crossed. The fine wires are trimmed in this position using a guillotine and jig and the welding of the juxtaposed fine wires is completed in the flame. Any final trimming may be done using the guillotine. Finally, the fine wires were squeezed together in the neighborhood of the junction over a length of 5 mm. A rigid observation of the procedure enables reproducible results to be obtained.

(b) Temperature gradient in the sample

Due to a finite width between the thermocouple wires adjacent to the point of junction of the 0.2 mm diameter wires, and the presence of the sample in this region, there will be a temperature gradient within the sample. This is reported to be of the order of 4°C (i.e. ± 2°C from the junction point at which the actual temperature is measured. It is therefore necessary not to overload the thermocouple with the material to be investigated. The materials were ground to less than 200 mesh.

To calibrate the thermocouple A.R potassium sulphate was used as it has a sharp and reproducible melting point at 1072°C. It also undergoes a polymorphic transition at 580°C.

To mount the standard and materials to be examined, the thermocouple was dipped in solution of an inert solvent and placed in powdered sample. It was found that a column of approximately 0.5 mm gave the optimum results with the standard, and this dimension was adopted with the materials to be examined.
The thermocouple and sample were placed in the gas tight cell and the assembly mounted on the microscope stage. Nitrogen at a moderate flow rate was passed through the system for a few minutes to remove any air present. The rate of gas flow was found as in the previous technique using a flowmeter. The connection between the power unit and the thermocouple was made and the heat input increased gradually until the temperature required was obtained.

After the run, careful removal of the sample was made. A small amount of collodion was added to the sample and it was mounted on a very thin glass fibre and left to dry for 30 minutes. The fibre with the sample was then placed in the 9 cm powder camera and a powder photograph was taken as previously described.

The thermocouples were cleaned by inserting them first in concentrated hydrochloric acid and drying them and placing them in water, then acetone, and a final drying in an oven at 60°C.

II.10.iii Preparation of the nitride from its elements

Reports that aluminium can be nitrided below its melting point, i.e. above 400° were investigated. The microcrystallinity of aluminium films and their changes on attempted nitridation were studied by electron microscopy and diffraction.

The aluminium film was prepared by first depositing a carbon film on mica. The mica plate was then fixed inside the high vacuum unit at about 10 cm from a helical tungsten filament. Aluminium powder was placed in the filament and the system evacuated. The filament current was increased sufficiently slowly to avoid rapid temperature changes, thus avoiding any unnecessary stresses in the film. After the aluminium had evaporated, the resultant film and carbon base were stripped from the mica plate and placed
on a copper grid in the normal manner. The film was observed under the microscope and a diffraction pattern was taken.

The copper grid with the deposited aluminium film was placed in a glass vessel which was flushed with nitrogen gas at room temperature. The nitrogen pressure was reduced to 0.2 atmospheres by pumping out the excess gas from the vessel. The whole assembly was lowered into a furnace preset at 500°C. The films were heated for 3 hours and re-examined under the microscope.


16. ibid., 1955, 1438.


CHAPTER III  

The formation of aluminium nitride

In the present research, three methods for the formation of aluminium nitride were tried. They were (1) thermal decomposition of ammonium hexafluoroaluminate in ammonia, (2) the formation of the nitride from an intimate mixture of $\alpha$-alumina and carbon in the presence of nitrogen, and (3) the nitriding of pure aluminium.

III.1  The thermal decomposition of ammonium hexafluoroaluminate in various atmospheres

The thermal decomposition of the ammonium-aluminium-fluorine complex was studied in air, dried air, and dried ammonia.

III.1.1  The thermal decomposition of ammonium hexafluoroaluminate in air

Approximately 0.25 grams of ammonium hexafluoroaluminate was weighed out in a purox (recrystallised alumina) boat and placed in the tube furnace as described in Chapter II. Air was pumped through the furnace at a moderate rate to allow sufficient removal of any volatile matter. When the air was to be dried it was passed through a potassium hydroxide drying system. The complex was heated in air at various temperatures for set intervals of time and subsequent weight losses were determined. A plot of percentage weight loss against time for different temperatures was made (see Fig. 3). At various intervals in the heating cycle, samples were removed for x-ray analysis to determine the phases present (see Fig. 4). The thermal and x-ray analysis gave the following results.

Ammonium hexafluoroaluminate is stable in air up to $130^\circ C$, when a weight loss of $\frac{3}{4}$ was observed. This decomposition is probably due to loss of water present in the system. From the results of the differential thermal analysis a small peak is recorded at $100^\circ C$ (see Fig. 5a). At $220^\circ C$ the formation of ammonium tetrafluoroaluminate begins to take
Fig. 3. The percentage wt. loss of ammonium hexafluorocryolminate heated in dried air for various temperatures and times.
place. The weight loss at this temperature is therefore due to the
volatilisation of ammonium fluoride. The characteristic d-spacings for
\((\text{NH}_4)_3\text{AlF}_6\) are 5.2 and 4.47. From Table 8 the d-spacings are 5.07 and
4.4 respectively after 3 hours at 220°C, which suggests that the number
of moles of ammonium fluoride present in the sample is slightly less
than three. After 4 hours at this temperature, the tetrafluoroaluminate
phase is prevalent (see Table 8). As the temperature is increased the
loss of ammonium fluoride continues and at 340°C d-spacings intermediate
between those recorded for ammonium tetrafluoroaluminate and those of a
phase identified as \(\gamma\)-aluminium fluoride were observed (see Table 9,
Fig. 8). This intermediate compound exists even after 5 hours at 340°C.

The thermal analysis curve at 420°C confirms the existence of this
intermediate as the percentage weight changes for ammonium tetrafluoro-
aluminate and \(\gamma\)-aluminium fluoride are 38% and 57% respectively, and a
weight change of 51.2% is observed after 4 hours at 420°C. To verify
the nature of the intermediate, infra-red analysis gave peaks at 1430
and 3240 cm\(^{-1}\) which are due to \(\text{NH}_4^+\) ions and hence this intermediate is
of the type \(\text{AlF}_3(\text{NH}_4\text{F})_x\). To determine the stoichiometry of the compound,
a chemical analysis of the ammonia content was made. The percentage
ammonia present was determined as 4.32% and the theoretical ammonia
content of ammonium tetrafluoroaluminate is 14.04%. The formula of the
intermediate observed was therefore \(\text{AlF}_3(\text{NH}_4\text{F})_{0.3}\) which is in
agreement with the 51.2% weight loss. Furthermore, from the differential
thermal analysis of ammonium hexafluoroaluminate a peak over the
temperature range 200 to 420°C with a maximum at 335°C is observed.
Ammonium tetrafluoroaluminate therefore does not appear to exist as a
### Table 8

**Ammonium hexafluoroaluminate heated at 220°C in dry air**

<table>
<thead>
<tr>
<th>3 hours</th>
<th>4 hours</th>
<th>( d_{(NH_4)_3AlF_6} )</th>
<th>( d_{NH_4AlF_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
</tr>
<tr>
<td>6.284</td>
<td>11</td>
<td>6.231</td>
<td>4</td>
</tr>
<tr>
<td>5.07</td>
<td>4</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>4.398</td>
<td>2</td>
<td>4.47</td>
<td></td>
</tr>
<tr>
<td>3.577</td>
<td>13</td>
<td>3.549</td>
<td>2</td>
</tr>
<tr>
<td>3.122</td>
<td>11</td>
<td>3.080</td>
<td>2</td>
</tr>
<tr>
<td>2.523</td>
<td>4</td>
<td>2.496</td>
<td>2</td>
</tr>
<tr>
<td>2.345</td>
<td>4</td>
<td>2.328</td>
<td>2</td>
</tr>
<tr>
<td>2.218</td>
<td>4</td>
<td>2.197</td>
<td>2</td>
</tr>
<tr>
<td>2.104</td>
<td>3</td>
<td>2.090</td>
<td>2</td>
</tr>
<tr>
<td>1.97</td>
<td>2</td>
<td>1.958</td>
<td>1</td>
</tr>
<tr>
<td>1.815</td>
<td>4</td>
<td>1.805</td>
<td>3</td>
</tr>
<tr>
<td>1.788</td>
<td>8</td>
<td>1.778</td>
<td>5</td>
</tr>
<tr>
<td>1.725</td>
<td>2</td>
<td>1.708</td>
<td>2</td>
</tr>
<tr>
<td>1.596</td>
<td>3</td>
<td>1.591</td>
<td>2</td>
</tr>
<tr>
<td>1.578</td>
<td>2</td>
<td>1.571</td>
<td>1</td>
</tr>
<tr>
<td>1.549</td>
<td>3</td>
<td>1.542</td>
<td>3</td>
</tr>
</tbody>
</table>

- 63 -
Table 9

Ammonium hexafluoroaluminate heated at 340°C in dry air

<table>
<thead>
<tr>
<th>½ hour</th>
<th>5 hours</th>
<th>$d_{\text{NH}_4\text{AlF}_4}$</th>
<th>$d_{\text{AlF}_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>d</td>
<td>$d_{\text{NH}_4\text{AlF}_4}$</td>
<td>$d_{\text{AlF}_3}$</td>
</tr>
<tr>
<td>6.224</td>
<td>s</td>
<td>6.111</td>
<td>6.4</td>
</tr>
<tr>
<td>3.535</td>
<td>ms</td>
<td>3.620</td>
<td>3.60</td>
</tr>
<tr>
<td>3.083</td>
<td>m</td>
<td>3.039</td>
<td>3.12</td>
</tr>
</tbody>
</table>

$s = $ strong

$ms = $ moderately strong

$m = $ moderate.
stable phase in the decomposition, but may be considered the end member of the series $\text{AlF}_3\cdot\text{NH}_4\text{F} \rightarrow \gamma\text{AlF}_3$. Shinn et al. (12) concluded from x-ray results that the tetrafluoroaluminate is a distinct phase in the decomposition even though dynamic thermogravimetric analysis revealed a point of inflection corresponding to a weight loss of 2.1 - 2.25 moles of ammonium fluoride. Other workers (13, 14) also report the existence of stable tetrafluoroaluminate phase in the thermal decomposition and it seems that their conclusions are wrong.

Differential thermal analysis of the starting complex revealed a peak with a maximum at 470°C. X-ray analysis gave d-spacings comparable to those of Shinn et al. (12). However, Shinn et al. (12) were not able to make full chemical analysis of $\gamma\text{-AlF}_3$ due to the resistance of the compound to decomposition. They managed to prepare an impure form of $\gamma$-aluminium fluoride by passing gaseous hydrogen fluoride over aluminium bromide or chloride at temperatures from 150 to 500°C, as indicated by the x-ray pattern. The x-ray pattern however, was generally amorphous, but the transition to $\alpha$-aluminium fluoride was observed when the impure fluoride was heated in nitrogen at 730°C. In the present work infra red analysis showed the absence of any ammonium ions in the compound $\gamma\text{-AlF}_3$. A chemical analysis for aluminium and fluoride was made (see Appendix II), and the compound was therefore unequivocally established as $\gamma$-aluminium fluoride. The x-ray characteristics of the compound will be discussed later.

When the temperature was raised to 530°C the formation of $\gamma$-aluminium fluoride was evident after a quarter of an hour. However, at 620°C after 1 hour the formation of a phase which gave a number of spacings which did not fit with the previous data was observed (see Table 11). To
Table 10
Comparison of the observed and calculated d-spacings for $\gamma$-AlF$_3$
($a = 3.53 \pm 0.01 \text{\AA}; \quad \gamma = 6.02 \pm 0.01 \text{\AA}$).

<table>
<thead>
<tr>
<th>(d_{\text{obs}})</th>
<th>(d_{\text{calc}})</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.03</td>
<td>6.02</td>
<td>001</td>
</tr>
<tr>
<td>3.54</td>
<td>3.53</td>
<td>100</td>
</tr>
<tr>
<td>3.05</td>
<td>3.04</td>
<td>101</td>
</tr>
<tr>
<td>2.00</td>
<td>2.01</td>
<td>003</td>
</tr>
<tr>
<td>1.92</td>
<td>1.92</td>
<td>112</td>
</tr>
<tr>
<td>1.76</td>
<td>1.76</td>
<td>200</td>
</tr>
<tr>
<td>1.70</td>
<td>1.69</td>
<td>201</td>
</tr>
<tr>
<td>1.54</td>
<td>1.53</td>
<td>211</td>
</tr>
<tr>
<td>1.50</td>
<td>1.50</td>
<td>004</td>
</tr>
<tr>
<td>1.38</td>
<td>1.38</td>
<td>104</td>
</tr>
<tr>
<td>1.33</td>
<td>1.32</td>
<td>203</td>
</tr>
<tr>
<td>1.24</td>
<td>1.24</td>
<td>213</td>
</tr>
</tbody>
</table>
establish the nature of this compound the sample was x-rayed after 4 hours, 18 hours and 65 hours at this temperature. The results are given in Table 11. A comparison of the d-spacings observed with those reported for basic fluorides (15, 16) revealed the possibility of a basic fluoride being formed due to the moisture content in the air. A fluoride analysis of the specimen heated for 18 hours at 620°C gave a percentage fluoride content of 41.7% which corresponds to a formula AlF$_2$. Hence to the balance the stoichiometry OH$^-$ ions will substitute in the lattice to give the empirical formula $\text{Al OH}_{x} F_{3-x}$ where $x = 0.81$, and as the time of heating in increased the loss of fluorine increases and $x$ in the empirical formula will increase. A formula in which $x = 2$ (i.e. $\text{Al(OH)}_{2} F$) for a basic fluoride has been reported (15). From Table 11 as the time of heating is increased the ionic fraction of (OH)$^-$ increases and peaks are observed after 65 hours which are not present in the previous cases of 1, 4 and to a lesser extent 18 hours. The Al-F bond lengths in aluminium fluoride are of the order of 1.7 Å and this is increased to 1.84 Å for the basic fluoride $\text{Al(OH)}_{1.35} F_{1.65} 1.09$.H$_2$O, so the introduction of hydroxyl ions will weaken the crystal lattice, and will finally result in the total removal of fluorine. This forms the basis for the analytical method to determine the fluoride content of aluminium fluoride by pyrohydrolysis (17, 18). There are conflicting reports as to the temperature at which the thermal hydrolysis of aluminium fluoride initially takes place, but temperatures as low as 300°C have been reported (19). It is noted that as the time of heating in moist air is increased the d-spacings respectively decrease and there is significant change after 65 hours (see Table 11). Furthermore, the density of the fluoride heated in moist air for 18 hours was measured as
Table 11

Comparison of the d-spacings of ammonium hexafluoroaluminate heated in moist air at 620°C for 1, 4, 18 and 65 hours with \( \gamma - \text{AlF}_3 \), a basic fluoride, aluminium hydroxide and alumina

<table>
<thead>
<tr>
<th>( \gamma - \text{AlF}_3 )</th>
<th>1 hour</th>
<th>4 hours</th>
<th>18 hours</th>
<th>65 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{\text{obs}} )</td>
<td>6.029</td>
<td>3.547</td>
<td>2.999</td>
<td>2.500</td>
</tr>
<tr>
<td>( d_{\text{obs}} )</td>
<td>5.93 w</td>
<td>3.51 vs</td>
<td>3.51 vs</td>
<td>2.68 vvw</td>
</tr>
<tr>
<td>5.32 w</td>
<td>3.51 vs</td>
<td>3.46 ms</td>
<td>3.53 vvw</td>
<td>2.68 vvw</td>
</tr>
<tr>
<td>5.31 vs</td>
<td>3.46 ms</td>
<td>3.46 ms</td>
<td>3.52 m</td>
<td>2.67 w</td>
</tr>
<tr>
<td>5.29 s</td>
<td>3.46 ms</td>
<td>3.37 s</td>
<td>3.31 m</td>
<td>2.51 m</td>
</tr>
<tr>
<td>4.90 s</td>
<td>3.31 m</td>
<td>3.53 m</td>
<td>3.47 m</td>
<td>2.67 m</td>
</tr>
<tr>
<td>5.53 s</td>
<td>3.48 m</td>
<td>3.53 m</td>
<td>3.53 m</td>
<td>2.69 m</td>
</tr>
<tr>
<td>4.72 s</td>
<td>3.19 m</td>
<td>3.53 m</td>
<td>3.53 m</td>
<td>2.69 m</td>
</tr>
<tr>
<td>2.270</td>
<td>2.22 m</td>
<td>2.18 w</td>
<td>2.18 w</td>
<td>2.18 w</td>
</tr>
<tr>
<td>2.129</td>
<td>2.11 m</td>
<td>2.09 w</td>
<td>2.09 w</td>
<td>2.09 w</td>
</tr>
<tr>
<td>2.003</td>
<td>1.915</td>
<td></td>
<td>1.97 w</td>
<td>1.96 w</td>
</tr>
<tr>
<td>1.773</td>
<td></td>
<td>1.83 w</td>
<td>1.89 w</td>
<td>1.83 w</td>
</tr>
<tr>
<td>1.736</td>
<td>1.75 mw</td>
<td></td>
<td>1.74 mw</td>
<td>1.74 mw</td>
</tr>
<tr>
<td>1.707</td>
<td></td>
<td>1.75 mw</td>
<td>1.73 mw</td>
<td>1.76 mw</td>
</tr>
<tr>
<td>1.582</td>
<td>1.58 w</td>
<td></td>
<td>1.55 w</td>
<td>1.55 w</td>
</tr>
<tr>
<td>1.532</td>
<td></td>
<td>1.50 w</td>
<td>1.51 w</td>
<td>1.50 w</td>
</tr>
<tr>
<td>1.379</td>
<td></td>
<td>1.38 w</td>
<td>1.37 w</td>
<td>1.37 w</td>
</tr>
<tr>
<td>1.332</td>
<td>1.25 vvw</td>
<td></td>
<td>1.28 vvw</td>
<td>1.28 vvw</td>
</tr>
</tbody>
</table>

Note: w = weak, s = strong, vs = very strong, mw = medium weak, ms = medium strong.
vs = very strong
s = strong
m = moderate
w = weak
vw = very weak etc.

\[ d_x = \text{Al}_2\text{O}_3 \]
\[ d_y = \text{Al(OH)}_2 \text{F} \cdot \text{H}_2\text{O} \]
\[ d_z = \text{Al(OH)}_3 \text{ (Bayerite)} \]
2.44 ± 0.06 g·cc⁻¹ which compares well with the reported values for basic aluminium fluorides (15), i.e. 2.25 and 2.45 ± 0.2 (20).

When the sample was heated in carefully-dried air (see Chapter II) at 620°C, the specimen was identified as γ-AlF₃. The d-spacings of a sample heated at 700°C no longer agreed with those for γ-aluminium fluoride. A comparison with the values reported for α-aluminium fluoride (21) showed that in fact a crystallographic transformation had taken place. Differential thermal analysis also showed this change and a small peak was established at 690°C (see Fig. 5a). To check this fact a sample analysed as γ-AlF₃ was heated under similar conditions (see Chapter II) and a peak was observed at 700°C (Fig. 5b). Chemical analysis of the product concluded that α-aluminium fluoride was formed at 695°C ± 5°C.

There are several reports in the literature that aluminium fluoride undergoes a phase transition at 445°C (22, 23) and 460 ± 4°C (24). Repeated experiments between room temperature and 700°C with ammonium hexafluoroaluminate and γ-aluminium fluoride gave no evidence of a phase transformation for aluminium fluoride other than that at 695°C ± 5°C as previously described. It should be noted that the existence of γ-AlF₃ over a wide region of temperature (420-695°C). The aluminium fluoride transformation is irreversible as a specimen of α-aluminium fluoride was heated at 600°C and the d-spacings of α-aluminium fluoride were maintained. The presence of α-aluminium fluoride is observed at temperatures up to 880°C. However, when α-aluminium fluoride is heated for 18 hours at 710°C in dry air, d-spacings other than those for α-aluminium fluoride are observed (see Table 12). This is probably due to removal of fluorine from the fluoride and substitution by oxygen.
Table 12
Ammonium hexafluoroaluminate heated at 710°C for 18 hours in dried air

<table>
<thead>
<tr>
<th>(d_{\text{obs}})</th>
<th>(d_{\alpha-\text{AlF}_3})</th>
<th>(d_{\alpha-\text{Al}_2\text{O}_3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.50</td>
<td>3.52</td>
<td>3.48</td>
</tr>
<tr>
<td>2.65</td>
<td></td>
<td>2.55</td>
</tr>
<tr>
<td>2.17</td>
<td>2.12</td>
<td>2.16</td>
</tr>
<tr>
<td>1.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>1.51</td>
</tr>
<tr>
<td>1.45</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>1.36</td>
<td>1.40</td>
</tr>
</tbody>
</table>
The thermal decomposition of ammonium hexafluorogallate is said to take two courses (see Fig. 6). Firstly gallium fluoride can be formed as is observed with the aluminium compound or the second course resulting in gallium nitride, which was proposed by Hanneböhm & Klemm (46) to explain the weight changes observed when heating the sample in vacuo. In the present work when ammonium hexafluoroalumininate was heated in vacuo at 430°C, a white x-ray amorphous compound was formed for which no chemical analysis was made. This investigation was not continued as means of qualitative identification of the product was not possible.

Two different forms of gallium trifluoride are reported to exist, one obtained as above and one by the fluorination of gallium oxide as 600°C (25). Recently a crystal structure of gallium fluoride has been reported (5).

It was concluded that the decomposition of ammonium hexafluoroalumininate in air took the following course:

\[ (NH_4)_3\text{AlF}_6 \xrightarrow{\text{430°C}} 3\text{NH}_3 + \text{AlF}_3 \xrightarrow{\text{420-530°C}} 3\text{AlF}_3 \xrightarrow{\text{695°C}} \alpha\text{-AlF}_3 \]

III.i.i The thermal decomposition of ammonium hexafluoroalumininate in ammonia

It has been reported (13, 26) that aluminium nitride is formed when ammonium hexafluoroalumininate is heated in ammonia. Due to the ease of formation of the fluoride complex and that fact that aluminium fluoride is a waste product in the phosphate industry, and could therefore be subsequently converted to a useful source, this method of forming the nitride was extensively investigated.
Fig. 6

Thermal decomposition of ammonium hexafluorogallate (NH₄)₃ GaF₆

\[
(\text{NH}_4)_3 \text{GaF}_6 \xrightarrow{\text{NH}_4\text{F}} (\text{NH}_4)_2\text{GaF}_5 \xrightarrow{\text{NH}_4\text{F}} \text{NH}_4\text{GaF}_4 \xrightarrow{\text{NH}_4\text{F}} \text{GaF}_3
\]

\[
-2\text{HF}
\]

\[
\text{Ga(NH}_2\text{)F}_2 \xrightarrow{\text{HF}} \text{Ga(NH)}\text{F} \xrightarrow{\text{HF}} \text{GaN}
\]
As in the decomposition of the complex in air the complete removal of ammonium fluoride was not observed until 530°C when an x-ray trace of a sample heated for 2 hours at this temperature was positively identified as \( \gamma \)-AlF\(_3\). When the temperature was increased, the thermal decomposition in carefully dried ammonia was analogous to decomposition in air. At 620°C \( \gamma \)-aluminium fluoride was observed which converted to \( \alpha \)-aluminium fluoride at 700°C in ammonia. The \( \alpha \)-phase was still observed at 840 and 880°C. The temperature was raised to 960°C and the specimen was heated for an hour and cooled to 400°C under a flow of ammonia to prevent oxidation of the sample when removing it from the furnace. An x-ray trace of the product revealed aluminium nitride in the presence of aluminium fluoride (see Table 13). To study the effect of the rate of flow of ammonia on the reaction at this temperature, half gram samples were weighed out and placed in the tube furnace under a current of ammonia at 960°C.

A plot of percentage weight loss against rate of flow of ammonia was made (see Fig. 7). A weight loss of 61.58% was recorded when the flow rate of ammonia was zero. The theoretical weight loss for the transformation of ammonium hexafluoroaluminata to aluminium fluoride is 57%. According to the reaction

\[
(NH_4)_2 AlF_6 + LNH_2 \rightarrow AlN + 6NH_4F
\]

the theoretical weight loss for the formation of aluminium nitride is 78.98%. An x-ray trace of the product revealed two peaks which gave d-spacings comparable with those established for aluminium nitride. The presence of aluminium nitride in a zero flow rate of ammonia can be explained as follows:
Table 13

Ammonium hexafluoroaluminate heated in dried ammonia at 960° for 1 hour and cooled to 400°C in ammonia.

<table>
<thead>
<tr>
<th>d_{obs.}</th>
<th>Intensity*</th>
<th>d_{AlN}</th>
<th>d_{α-AlF_3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48</td>
<td>2</td>
<td></td>
<td>5.52</td>
</tr>
<tr>
<td>2.68</td>
<td>3</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>2.53</td>
<td>3</td>
<td></td>
<td>2.51</td>
</tr>
<tr>
<td>2.46</td>
<td>1</td>
<td>2.49</td>
<td></td>
</tr>
<tr>
<td>2.35</td>
<td>2</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>3</td>
<td></td>
<td>2.07</td>
</tr>
<tr>
<td>1.83</td>
<td>1</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>1.73</td>
<td>1</td>
<td></td>
<td>1.76</td>
</tr>
<tr>
<td>1.59</td>
<td>4</td>
<td></td>
<td>1.59</td>
</tr>
<tr>
<td>1.54</td>
<td>1</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td>1.48</td>
<td>1</td>
<td></td>
<td>1.46</td>
</tr>
</tbody>
</table>

* Intensity measured as the peak height.
Fig. 7. The thermal decomposition of ammonium hexafluoroalumina in various flow rates of ammonia.
Aramon fluoride sublimes at 520°C to give ammonia and gaseous hydrofluoric acid according to the reaction

\[ \text{NH}_4\text{F} \rightleftharpoons \text{NH}_3 + \text{HF} \]

Hence the formation of aluminium nitride in this case will be a result of the reaction of aluminium fluoride and ammonia according to the reactions

\[ (\text{NH}_4)_3 \text{AlF}_6 \rightarrow \text{AlF}_3 + \text{NH}_3 \]

\[ \text{NH}_3 + \text{HF} \]

\[ \text{AlF}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{HF} \]

To verify this statement an independently prepared specimen of α-aluminium fluoride was heated in ammonia at 960°C and aluminium nitride was positively identified.

From the reaction

\[ \text{AlF}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{HF} \]

the equilibrium constant with respect to partial pressure of the gases present \( K_p \) will be given by

\[ K_p = \frac{P_{\text{HF}}}{P_{\text{NH}_3}} \]

Reducing the partial pressure of gaseous hydrofluoric acid in the system will therefore promote the formation of the nitride. The ammonia gas flowing through the system will therefore remove the gaseous HF as the condensate ammonium fluoride and hence the increase in rate of flow of ammonia will result in increase of the nitride formation which is observed as an increase in weight loss. A comparison of the peak intensities of diffractometer traces of samples also showed the relative increase of
nitride with respect to fluoride as the flow rate of ammonia is increased (see Table 14). At a rate of 50 cc/min a weight loss of 78% is observed. This corresponds to 98.8% conversion to aluminium nitride. A nitrogen analysis (see Chapter II) of a sample heated in ammonia at a rate of 48 cc/min gave a nitrogen content of 33.61%, which corresponds to 98.5% aluminium nitride. As the rate is increased there is a marginal increase in nitride content as is shown in Fig. 7. At a rate of 160 cc/min a nitride content of 98.7% was analysed. Further increase in rate did not increase the percentage conversion of the complex to aluminium nitride. A specimen heated for 4 hours at 120 cc/min was analysed and gave a nitride content of 99.1%.

It appears that the thermal decomposition of ammonium hexafluoroaluminate in dry ammonia gives a nitride yield of the order of 99%. Aluminium fluoride, present here as an impurity, is reported to be used as a binder when sintering the nitride so the presence of the fluoride would not be detrimental when the nitride is to be used in this manner. However, the presence of the fluoride is shown to increase rapidly the rate of oxidation of aluminium nitride (see Chapter IV). The only disadvantage of the preparation is the rapid attack on the purox tube by ammonium fluoride seriously reducing the furnace tube life. If this problem could be overcome the successful industrial application of this method may be possible.

Reports that aluminium nitride is formed from ammonium hexafluoroaluminate in ammonia at 500°C (26) are not verified. These workers report the presence of brown and green aluminium nitride which would suggest undesirable impurities present in the nitride. In the present study the nitride formed was a white crystalline powder of excellent purity.
Table 1.

Comparison of the observed x-ray intensities of ammonium hexafluoroaluminate heated at 960°C in various flow rates of ammonia.

<table>
<thead>
<tr>
<th>d_{dAlF₃}</th>
<th>d_{AlN}</th>
<th>d_{obs} (±0.01)</th>
<th>5</th>
<th>8.1</th>
<th>23.3</th>
<th>40</th>
<th>71</th>
<th>96.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.52</td>
<td>3.48</td>
<td></td>
<td>12</td>
<td>8</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>2.70</td>
<td>2.69</td>
<td></td>
<td></td>
<td>12</td>
<td>12</td>
<td>28</td>
<td>36</td>
<td></td>
</tr>
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<td>2.51</td>
<td>2.49</td>
<td>2.51</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>4</td>
<td>16</td>
<td>16</td>
</tr>
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<td>2.37</td>
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<td>4</td>
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<td>8</td>
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<td>18</td>
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<td>2.119</td>
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</tr>
<tr>
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<td>2.07</td>
<td></td>
<td>4</td>
<td>12</td>
<td>I</td>
<td>I</td>
<td>I</td>
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</tr>
<tr>
<td>1.759</td>
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</tr>
<tr>
<td>1.587</td>
<td>1.59</td>
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<td>8</td>
<td>4</td>
<td>2</td>
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<td>1.557</td>
<td>1.56</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>12</td>
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<td></td>
</tr>
<tr>
<td>1.460</td>
<td>1.48</td>
<td></td>
<td>4</td>
<td>8</td>
<td>12</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1.431</td>
<td>1.44</td>
<td>1.40</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.355</td>
<td>1.348</td>
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</tbody>
</table>
It has been reported that gallium and indium nitride (27) are formed when the corresponding hexafluorometallate compound is heated in ammonia at high temperatures. Gallium nitride is also reported to be formed from ammonium hexafluorogallate at lower temperatures (28). The complex is heated in argon at 175°C initially to ammonium tetrafluorogallate. The tetrafluorogallate is heated in ammonia at 130°C to form the adduct ammonium tetrafluorogallate mono-ammoniate. As the temperature is raised, mono-amino gallium fluoride (GaF$_3$.NH$_3$) is formed which loses gaseous hydrofluoric acid in the presence of ammonia at 300°C to form gallium nitride. As this offers a low temperature alternative to formation of nitrides from their corresponding hexafluorometallates, a similar program was adopted for ammonium hexafluoroaluminate.

Ammonium tetrafluoroaluminate was made according to the reaction

$$\text{HBF}_4 + \text{Al(OH)}_3 + \text{NH}_4\text{OH} \rightarrow \text{NH}_4\text{AlF}_4 + \text{H}_2\text{BO}_3 + \text{H}_2\text{O}$$

details are given in Appendix I.

Ammonium tetrafluoroaluminate was heated in ammonia at 110°C for periods up to 30 hours, but no difference in structure was detected by infra-red and x-ray analysis. To continue the method of Mermant et al. (28), attempts were made to prepare aluminium fluoride mono-ammoniate.

The ammoniates of the chlorides (29), bromides (30), and iodides (39) are known, and it is reported that the mono-ammoniate can be prepared by adding aluminium fluoride very slowly to liquid ammonia (31).

To prepare the aluminium fluoride mono-ammoniate, liquid ammonia was prepared by passing dried ammonia gas into a quickfit test tube placed in an ice trap (a dewar containing solid CO$_2$). To the other side of the trap was connected a drying tube containing potassium hydroxide.
pellets to prevent moisture from entering the system. \( \alpha \)-Aluminium fluoride (prepared by heating ammonium hexafluoroaluminate in purified nitrogen at 740°C) was very slowly added to the liquid ammonia and the mixture was left in a fume cupboard to reach equilibrium. The quick fit test tube was gradually removed from the ice trap such that induced temperature difference was sufficient to remove any excess liquid ammonia. The white powder was examined using x-ray and infra-red analysis and no structural differences from \( \alpha \)-aluminium fluoride were observed. Hence the work of Clark (31) was not confirmed.

Attempts were made to prepare the mono-ammoniate by passing ammonia gas over \( \gamma \)-aluminium fluoride at 110° and 160°C for periods up to 100 hours but no structural changes were observed. It was anticipated that \( \gamma \)-aluminium fluoride had a more open structure, but no mono-ammonium fluoride adduct was observed using the above methods.

Using the Schomaker-Stevenson relationship (32) the bonding for the known \( \alpha \)-aluminium fluoride structure (33) was calculated as 66% ionic in character, whereas aluminium chloride, iodide and bromides are prevalently covalent in character. Boron trifluoride mono-ammoniate is readily formed from boron trifluoride and ammonia and the resulting chemical bonding in the adduct is characteristically covalent. Furthermore, aluminium fluoride is reported to have the highest lattice energy of the group IIIb metal trihalides (34). The absence of formation of aluminium fluoride mono-ammoniate is therefore attributed to inherent chemical nature of aluminium fluoride bonding.

Other routes for the formation of aluminium nitride from ammonium hexafluoroaluminate than those established are not possible, and the
method of formation analogous to the work of Mermant et al. (28) on the
gallium compound is not confirmed.

Due to the similarity between ammonolysis and hydrolysis a study of
the solubility of aluminium fluoride in distilled water was made. Also
the structure of γ-aluminium fluoride is not yet evaluated and the
formation of any hydrates with the compound may give information about
the lattice space within the fluoride. The solubility of aluminium
fluoride in water is reported as 0.55\% (2) presumably as the α-trihydrate.
The hydrates of aluminium fluoride are numerous (see Table 15) and
Bogachov and Myasmkov (36) showed that 0.19\% water of crystallization was
present in aluminium fluoride when left in air of varying relative
humidity. There is a report that when aluminium fluoride trihydrate is
dehydrated, a new catalytic form of aluminium fluoride (β-AlF₃) is
formed (37). A comparison of the d-spacings of γ-aluminium fluoride with
those reported for this catalytic fluoride (see Table 16) shows certain
similarities, but contains a number of lines not present in γ-aluminium
fluoride. The possible hydrolysis of the aluminium fluoride to form a
basic fluoride may also occur.

It has been proposed (12) that this β-aluminium fluoride is in fact
an open γ structure with a residual amount of water present.

To study the solubility of the fluorides weighed amounts were placed
in two separate 100 ml quickfit conical flasks. 50 mls of distilled water
were added to each flask and the flasks sealed with firmly fixed stoppers.
The flasks were gently shaken in a water bath set at 25°C for 17 days.
Intermittently samples were extracted, carefully dried by washing in
acetone and placing in an oven at 50°C and weighed. X-ray and infra-red
Table 15
X-ray data of basic aluminium fluorides and aluminium fluoride hydrates

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF$_3$·9H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td>44.</td>
</tr>
<tr>
<td>AlF$_3$·H$_2$O</td>
<td>3.610</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>AlF$_3$·1.33H$_2$O</td>
<td>11.42</td>
<td>21.18</td>
<td>8.54</td>
<td>41</td>
</tr>
<tr>
<td>AlF$_3$·3H$_2$O</td>
<td>9.20</td>
<td>9.30</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>AlF$_3$·3H$_2$O</td>
<td>7.734</td>
<td>7.330</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>7.734</td>
<td>3.665</td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>Al(F$<em>{1.75}$OH$</em>{1.25}$)$_6$/16H$_2$O</td>
<td>9.83</td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Al(F$<em>{1.65}$OH$</em>{1.35}$)$_6$/16H$_2$O</td>
<td>9.849</td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Al F$<em>{0.7}$OH$</em>{2.3}$ 6/16H$_2$O</td>
<td>9.87</td>
<td></td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>
Table 16

Comparison of the d spacings of the reported $\beta$-AlF$_3$ (37) and $\gamma$-AlF$_3$.

<table>
<thead>
<tr>
<th>$d_{\beta}$AlF$_3$ (calc)</th>
<th>$d_{\gamma}$AlF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.02</td>
<td>6.002</td>
</tr>
<tr>
<td>3.53</td>
<td>3.563</td>
</tr>
<tr>
<td>3.04</td>
<td>3.063</td>
</tr>
<tr>
<td>2.01</td>
<td>2.001</td>
</tr>
<tr>
<td>1.92</td>
<td>1.914</td>
</tr>
<tr>
<td>1.76</td>
<td>1.782</td>
</tr>
<tr>
<td>1.69</td>
<td>1.708</td>
</tr>
<tr>
<td>1.53</td>
<td>1.532</td>
</tr>
<tr>
<td>1.50</td>
<td>1.500</td>
</tr>
<tr>
<td>1.38</td>
<td>1.377</td>
</tr>
<tr>
<td>1.32</td>
<td>1.310</td>
</tr>
<tr>
<td>1.24</td>
<td>1.242</td>
</tr>
<tr>
<td>1.21</td>
<td>1.216</td>
</tr>
<tr>
<td>1.20</td>
<td>1.200</td>
</tr>
<tr>
<td>1.18</td>
<td>1.188</td>
</tr>
<tr>
<td>1.14</td>
<td>1.148</td>
</tr>
<tr>
<td>1.13</td>
<td>1.134</td>
</tr>
</tbody>
</table>
analysis of the dried sample were made. After the period of 17 days, there was no overall change in weight and no structural differences were observed. It appears that α and γ-aluminium fluorides are resistant to hydrolysis under these conditions. However, basic fluorides are formed as shown at higher temperatures.

III.i.iii X-ray analysis of ammonium hexafluoroaluminate

To determine the lattice parameters of the complex a powder specimen was prepared and placed in the 9 cm camera (see Chapter II). After a 2 hour exposure, the developed film was measured as previously described. The intensity of the powder lines are dependant on the arithmetic mean of the scattering factor \( f \), (i.e. \( f \) is the ratio of the amplitude of scattering of an atom to the amplitude of scattering of a single electron) and as the Bragg angle \( \theta \) increases, \( f \) decreases. Consequently, for an accurate value of the lattice parameter, Cohen's least squares method was employed (8), as this method reduces the statistical error involved when using a small number of powder lines.

The lattice parameter of ammonium hexafluoroaluminate was determined as 8.93 ± 0.01 Å, which agrees well with established values (see Table 17).

III.i.iv The structural rearrangements during the formation of aluminium nitride from the thermal decomposition of ammonium hexafluoroaluminate.

Ammonium hexafluoroaluminate has a tetramolecular unit cell of dimension 8.93 ± 0.01 Å. The space group has been assigned as \( \text{Fm} \overline{3} \text{m-} \text{O}^5_h \) with atoms in the positions:

\[
\text{NH}_4 (1) : (4b) \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.
\]

\[
\text{NH}_4 (2) : (8c) \frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}.
\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit Cell Dimensions (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>(NH$_4$)$_3$FeF$_6$</td>
<td>9.17</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$Fe$_5$F$<em>6$O$</em>{4}$H$_2$O</td>
<td>9.10</td>
<td></td>
</tr>
<tr>
<td>Na$_2$FeF$_6$</td>
<td>9.26</td>
<td></td>
</tr>
<tr>
<td>K$_3$FeF$_6$</td>
<td>9.93</td>
<td></td>
</tr>
<tr>
<td>Rb$_3$FeF$_6$</td>
<td>10.23</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_3$SiF$_6$</td>
<td>8.39</td>
<td></td>
</tr>
<tr>
<td>Rb$_3$SiF$_6$</td>
<td>8.44</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_3$AlF$_6$</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_3$GaF$_6$</td>
<td>8.93</td>
<td></td>
</tr>
<tr>
<td>Na$_3$AlF$_6$</td>
<td>7.80</td>
<td>5.61</td>
</tr>
<tr>
<td>Na$_3$AlF$_6$·(500°θ)</td>
<td>7.95</td>
<td></td>
</tr>
<tr>
<td>K$_3$AlF$_6$</td>
<td>8.468</td>
<td>5.944</td>
</tr>
<tr>
<td>K$_2$AlF$_5$·0.1H$_2$O</td>
<td>8.435</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_3$InF$_6$</td>
<td>6.53</td>
<td>9.49</td>
</tr>
<tr>
<td>(NH$_4$)$_3$GaF$_6$</td>
<td>9.04</td>
<td></td>
</tr>
</tbody>
</table>

Table 17
Lattice parameters of some complex hexafluorides
\[ \text{Al} : (4a) \ O_x \ O_y \ O_z \\
\text{F} : (24e) \ x_0 \ x_0 \ x_0 ; 0 \ x_0 \ x_0 ; 0 \ x_0 \ x_0 ; \bar{x}_0 \ x_0 ; \bar{x}_0 \ x_0 ; 0 \ x_0 \bar{x}_0 \]

where \( x = 0.23 \).

There is an octahedral arrangement of fluorine atoms around each aluminium atom with face centred cubic distribution.

The first thermal transition of the above system is the removal of ammonium fluoride from the system. If it is considered that at any instant below \( 420^\circ \text{C} \) in the decomposition, the phase ammonium tetrafluoroaluminate exists then the following observation can be made.

Ammonium tetrafluoroaluminate has been assigned to space group \( \text{Pm} \overline{1} \text{mmm} - \frac{1}{4} \text{h} \) with atoms in special positions

\[ \text{NH}_4 : (1a) \ 0_0 \ 0_0 \]

\[ \text{Al} : (1d) \ \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2} \]

\[ \text{F} : (1) : (2e) \ 0_0 \ \frac{1}{2} \ \frac{1}{2} ; \ \frac{1}{2} \ 0_0 \]

\[ \text{F} : (2) : (2h) \ \frac{1}{2} \ \frac{1}{2} \ z ; \ \frac{1}{2} \ \frac{1}{2} \ z. \text{ where } z = 0.21 \]

From structural considerations the removal of two moles of ammonium fluoride would be followed by contraction of the cubic lattice in two directions to form layers of AlF\(_6\) octahedra joined by shared corners (47). The major adsorption in the infra-red analysis has been assigned to \( \gamma_1 \). The sharing of the fluoride ions does not distort the AlF\(_6\) octahedra as the \( \gamma_3 \) band is not appreciably affected (see Table 18a). The NH\(_4\) groups would lie between these layers. The removal of the two moles of ammonium fluoride distorts the M-F and F-F octahedral interatomic distances by less than 2.5% which suggests the AlF\(_6\) octahedron is not unaffected in the initial decomposition. Thus it would seem possible the ammonium atoms associated with special position (8c) in ammonium hexafluoroaluminate.
### Table 18a

**Infra-red analysis of the thermal decomposition of ammonium hexafluoro-aluminate**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_3$</th>
<th>$\nu_2 + \nu_4$</th>
<th>$2\nu_4$</th>
<th>$\nu_4 + \nu_6$</th>
<th>$\nu_4$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(NH_4)_3AlF_6$</td>
<td>3240</td>
<td>3050</td>
<td></td>
<td></td>
<td></td>
<td>14.30</td>
</tr>
<tr>
<td>Heated 2 hr.</td>
<td>3240</td>
<td>3050</td>
<td></td>
<td></td>
<td></td>
<td>14.35</td>
</tr>
<tr>
<td>at 220°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated 4 hr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 420°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$NH_4F$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.84 (4)</td>
</tr>
<tr>
<td>$(NH_4)_2AlF_6$</td>
<td>3250</td>
<td>3060</td>
<td></td>
<td></td>
<td></td>
<td>14.28 (4)</td>
</tr>
<tr>
<td>$NH_4AlF_4$</td>
<td>3230</td>
<td>3120</td>
<td>2905</td>
<td>1800</td>
<td>14.35</td>
<td>(4)</td>
</tr>
</tbody>
</table>
Table 18b

Densities of some aluminium compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (g·cc⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{(NH}_4\text{)}_3\text{AlF}_6)</td>
<td>1.84</td>
</tr>
<tr>
<td>(\gamma\text{-AlF}_3)</td>
<td>1.98</td>
</tr>
<tr>
<td>(\alpha\text{-AlF}_3)</td>
<td>3.25</td>
</tr>
<tr>
<td>(\text{AlF}_3\cdot\text{H}_2\text{O})</td>
<td>2.17</td>
</tr>
<tr>
<td>(\text{AlF}_3\cdot\frac{\text{3}\frac{1}{2}}{2}\text{H}_2\text{O})</td>
<td>1.914</td>
</tr>
<tr>
<td>AlN</td>
<td>3.47</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>3.97</td>
</tr>
</tbody>
</table>
are initially removed in the decomposition. However, these suppositions are not conclusive.

The total removal of ammonium fluoride results in the $\gamma$-AlF$_3$ structure which indexes satisfactorily with a tetragonal cell of unit cell dimensions $a = 3.53 \pm 0.01 \, \text{Å}$, $c = 6.02 \pm 0.01 \, \text{Å}$ (see Table 10). The basic structure of tetrafluoroaluminate is unchanged in the decomposition to $\gamma$-AlF$_3$. The contraction of the lattice is essentially concerned with the $c$-axis as shown by Figs. 8a and 8b. A greater distortion of the $d_{001}$ spacing with increasing temperature is observed. The removal of ammonium fluoride from the tetrafluoroaluminate phase by the ammonium atoms and one of the non-bridging fluorine atoms would result in a structure composed of planar AlF$_4$ groups with fourfold coordination, sharing corners with each aluminium atom being connected by an unshared fluorine atom (see Figs. 8c and 8d). White and Roy (48) have proposed a formula connecting the infrared spectrum with the metal-fluoride interatomic distance $r$:

$$F = \frac{\lambda^2}{2} \text{ where } F = \frac{\lambda^2}{2} \frac{\mu}{Z_1 Z_2}$$

where $\lambda$ = main metal-fluoride frequency

$\mu$ = reduced mass of the metal-fluoride ion pair

$Z_1 Z_2$ = product of the effective charge

$r$ = metal-fluoride interatomic distance.

By comparison with interatomic distances in $\alpha$-aluminium fluoride (see Table 19) and using the reported metal-fluoride vibrations (12) for $\gamma$ and $\alpha$-aluminium fluorides an Al-F interatomic distance in $\gamma$-AlF$_3$ is calculated as 1.77 Å.
Fig. 8. (a-d) The ammonium tetrafluroaluminate $\alpha$-alumina
fluoride crystallographic transition,
- 91 -
**Table 19**

Interatomic distances in α-aluminium fluoride and related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Al-Al interatomic distance</th>
<th>Al-F interatomic distance</th>
<th>F-F interatomic distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₃AlF₆</td>
<td>38</td>
<td>6.31</td>
<td>1.76</td>
<td>2.49</td>
</tr>
<tr>
<td>Al₄H₄F₄</td>
<td></td>
<td>1.35, 1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-AlF₃</td>
<td>33</td>
<td>3.508</td>
<td>1.79</td>
<td>2.503</td>
</tr>
<tr>
<td>(γ-AlF₃)</td>
<td>present work</td>
<td>1.77, 3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al OH₁.₃₅ F₁.₆₅</td>
<td>15</td>
<td>1.84</td>
<td></td>
<td>2.61</td>
</tr>
</tbody>
</table>

* a should be Al-F, OH and F-Al-OH interatomic distances.
The calculated x-ray density of \( \gamma \)-aluminium fluoride is 1.98 g.cc\(^{-1} \) which agrees well with the observed value of 1.92 \( \pm \) 0.04 g.cc\(^{-1} \). This agreement suggests that the proposed aluminium-fluorine configuration (see Fig. 8d) is four planar fluorine atoms at a distance 1.77 \( \AA \) from the aluminium atom and two fluorine atoms at a distance of 3.01 \( \AA \) from the aluminium atom. The Al-F configuration in \( \alpha \)-AlF\(_3\) is a regular octahedron of Al-F interatomic distance 1.79 \( \AA \). The collapse of the \( \gamma \) face-centred tetragonal structure to form the rhombohedral \( \alpha \)-AlF\(_3\) structure is again probably associated with the c-axis and a contraction of the Al-F spacing of 3.01 \( \AA \) to 1.77 \( \AA \) would result in a cube of side 3.54 \( \AA \) and a calculated density is 3.48 g.cc\(^{-1} \). The reported density of \( \alpha \)-AlF\(_3\) is 3.25 and the lattice parameters is 5.029 \( \AA \) (\( \alpha = 58^\circ 31' \)), so the transition to \( \alpha \)-AlF\(_3\) involves a slight distortion of the pseudo-cubic cell. This rearrangement of Al-F configuration is also shown from the results of differential thermal analysis. The resultant \( \alpha \)-AlF\(_3\) structure is represented in Fig. 9a. The splitting of the \( \gamma \) band (see Table 18) is attributed to the presence of the two octahedra. Moreover the difference in densities of the \( \gamma \) and the \( \alpha \) modification of aluminium fluoride suggests that ammonia or water might be substituted in the more open \( \gamma \)-AlF\(_3\) structure. This was not experimentally verified at 25 and 60\(^\circ\). However the \( \gamma \)-AlF\(_3\) is seen to take up moisture more readily than \( \alpha \)-aluminium fluoride at elevated temperatures, Moreover attempts to form aluminium nitride from ammonium hexafluoroaluminate and gaseous ammonia at 520\(^\circ\)C were unsuccessful. These observations would suggest that the kinetics for the reaction

\[
\text{AlF}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{HF}
\]

as well as the thermodynamics (see Fig. 33) are unfavourable.
Fig. 9. Atomic arrangements in
a) AlF₃ - 95 b) AlN
III.2 The formation of aluminium nitride by the Serpek process

Serpek (49) patented a process of making aluminium nitride formed from the reaction of gaseous nitrogen with an intimate mixture of alumina and carbon:

\[ \text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow \text{AlN} + 3\text{CO} \]

This method of nitride formation is now known as the Serpek process. Other workers have studied the reaction and there is great conflict in the literature as to the exact process variables required to bring about the optimum aluminium nitride yield.

Tucker and Read (50) reported the absence of aluminium nitride from the above reaction at 1600°C, but Frankel (51) showed that 10% nitride formation is observed as low as 1400°C, and this percentage nitrogen fixation initially increases with increasing temperature.

The presence of impurities is reported to catalyse the reaction according to Mellor (52) such that the nitride is formed at 1550°C using bauxite in place of alumina, but Repenko et al. (53) did not confirm this report.

Peacock and du Pont (54) concluded that the reaction at 1500°C and 500 mm Hg was

\[ \text{Al}_2\text{O}_3 + 6\text{C} + \text{N}_2 \rightarrow \text{Al}_2\text{C}_3\text{N}_6 + 3\text{CO} \]

The compound Al$_2$C$_3$N$_6$ would contain 49% nitrogen and Frankel using the same conditions as Peacock and du Pont observed 19.4% nitrogen fixation at pressures as low as 100 mg Hg.

It has been previously stated that increasing the reaction temperature increases the yield but too high a temperature appears to be detrimental.
This was observed by Pechiney (55) from an analysis of the reaction product. The residual alumina content decreased with increasing temperature to a minimum of 1.8% at 1725°C but increased to 4.2% at 1825°C in three quarters of the original time. Residual carbon was also present in the charge which was removed by roasting in air at 700 to 800°C. From the present work 4% conversion to α-alumina is observed in 5 hours at 800°C and this suggests that the residual alumina content would be increased by roasting. Furthermore at temperatures in the region 1600-1800°C the side reaction
\[ \text{AlN} + \text{C} \Leftrightarrow \text{AlCN} \]
is reported (56). 0.2% aluminium sub-cyanide content is analysed at 1600°C and this increases to 1% at 1800°C. Nevertheless Tucker and Read (51) stated that the reaction is best completed in the temperature range 1800-2000°C.

The presence of other impurities than aluminium sub-cyanide is expected. Accordingly Frankel observed that aluminium carbide (Al₄C₃) is formed as a sublimate when alumina and carbon are heated together in air from the reaction
\[ 2 \text{Al}_2\text{O}_3 + 9\text{C} \rightarrow \text{Al}_4\text{C}_3 + 6\text{CO} \]
This would suggest that the reaction is strongly exothermic as the sublimation temperature is reported as 2100°C. Also compounds of the general formula \((\text{AlN})_n\cdot\text{Al}_4\text{C}_3\) where \(n=1\) to 6 are formed when aluminium nitride is heated in a carbon crucible in the presence of nitrogen (57). Repenko et al. (53) reported that a spinel of the type \(\text{Al}_0.\text{Al}_2\text{O}_3\) is formed in the reaction. Yamaguchi & Yanagida (58) however reported that a spinel of the type \(\text{AlN}\cdot\text{Al}_2\text{O}_3\) is formed in a reducing atmosphere above 1650°C (see...
Table 20). Oxycarbides are also reported to be formed in the reaction.

Pechiney (59) have reported that better than a 99% yield of aluminium nitride is observed after a purification process which involves a final chlorinating stage at 450-650°C. Chlorine is reported to attack aluminium nitride at 900°C forming aluminium chloride and so unnecessary impurities may be introduced by this purification stage. Hence the inherent impurities likely to be present as a result of the reaction are detrimental to the process. However Repenko et al. (53) has shown that under the same experimental conditions a greater percentage of nitride is formed if the initial reaction mixture contains the spinellide $\text{Al}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ rather than alumina. They also showed that prolonged heating increased the nitride content which is a direct contradiction of the results of Frankel (51).

It would seem that temperatures in the region 1700-1750°C give the optimum results, especially as it is reported that the reaction velocity of alumina reduction by carbon increases at a faster rate than the diffusion velocity of nitrogen in the diffusion mass above 1750°C.

Frankel (51) was able to show that in fact the Serpek process is reversible and thus the equation can be written

$$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightleftharpoons 2\text{AlN} + 3\text{CO}$$

He assumed that the solids alumina, carbon and aluminium nitride exist in their standard states and hence the equilibrium is a function of the partial pressures of the gases in the system, such that

$$f_p = \frac{P_{\text{CO}}^3}{P_{\text{N}_2}}$$  \hspace{1cm} (1)

However, due to impurities discussed above, this assumption is to a first approximation only valid for lower temperatures in the considered
Table 20

Comparison of the crystal properties of AlN with the possible impurities in the Serpekk process

<table>
<thead>
<tr>
<th>Compound</th>
<th>Refractive Index</th>
<th>Unit Cell Parameters, Å</th>
<th>Density</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>2.13 - 2.20</td>
<td>3.11 4.98</td>
<td>3.20</td>
<td>57</td>
</tr>
<tr>
<td>AlN·Al_2O_3</td>
<td>1.80</td>
<td>7.490</td>
<td>3.78</td>
<td>58</td>
</tr>
<tr>
<td>AlN·(Al_2O_3)_2</td>
<td></td>
<td></td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>Al_4C_3</td>
<td>2.70</td>
<td>3.330 24.89</td>
<td>3.00</td>
<td>57</td>
</tr>
<tr>
<td>Al_6C_3N_2</td>
<td></td>
<td>3.248 40.03</td>
<td>3.076</td>
<td>57</td>
</tr>
<tr>
<td>Al_3O_4</td>
<td>1.770 - 1.795</td>
<td></td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Al_2O</td>
<td></td>
<td></td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>AlCN</td>
<td></td>
<td></td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Al_2CO</td>
<td></td>
<td></td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>AlO·Al_2O_3</td>
<td>1.99 - 2.03</td>
<td></td>
<td></td>
<td>53</td>
</tr>
</tbody>
</table>
temperature range. Moreover Frankel (51) has stated the equilibrium constant incorrectly as \( K = \frac{C_{N_2}}{C_{CO}^3} \) where \( C \) is concentration. Hence by studying the effect of a gaseous mixture of carbon monoxide and nitrogen on an intimate mixture of alumina and carbon as evaluation of the chemical equilibrium could be made.

It has been reported (53) that the equilibrium constant can be calculated from the equation

\[
\log K_p = 14.71 - \frac{27743}{T} \tag{2}
\]

Consequently, at 1600°C and atmospheric pressure the gaseous mixture will contain up to 34% \( N_2 \). At 1700°C the nitrogen concentration would be expected to be 12% from the equations (1) and (2) assuming ideal conditions. These results agree with those of Frankel (51) who reports a gaseous mixture of 50-65% carbon monoxide at 1600°C. Frankel also established a weight ratio of 2:1 (\( Al_2O_3:C \)) was satisfactory to form the nitride. He also concluded that the rate of reaction is dependent on the form and reactivity of the carbon in the process.

From the above observations an attempt was made to carry out the reaction using the Griffin Tellin hot stage microscope described in Chapter II. A fine mixture of alumina and carbon in a weight ratio of 2:1 was made. To a small quantity was added a drop of sodium silicate, which moistened the mixture. The Pt/Rh thermocouple was inserted into the mixture and very carefully extracted to ensure that sufficient material was present in the thermocouple tip (see Chapter II). Any spurious material was carefully removed with a fine brush.

The thermocouple was inserted into the gas tight chamber and nitrogen was passed over at a rate of 50-60 cc per minute. The temperature was
gradually raised to 1700°C. Temperature fluctuations were noted. This is probably due to the strong endothermic reaction when aluminium nitride is formed in this manner. After 1 hour at 1700 ± 10°C the sample was removed and submitted to x-ray examination.

Aluminium nitride was observed but due to the very small quantity of material the powder lines were very weak. Some other weak powder lines were observed, but these could not be positively identified. It was hoped to study the gaseous equilibrium in the reaction by passing CO/N₂ mixtures over the alumina/carbon samples, but inherent problems arose concerning the chemical analysis of the reactants and products. Due to the small quantity of sample (less than 10 mg) quantitative analysis of solid components of the reaction proved impossible with the techniques available. It was intended to use an optical crystallographic to identify the amounts and the composition of the phases present, but this was not successful partly because of poor crystal formation and partly because the material was opaque. A total aluminium determination e.g. spectrographically, would not have yielded any useful information. The most profitable line would have been to develop a micro-method for the determination of combined nitrogen but there was insufficient time available at this stage of the work. Hence, due to the problems of chemical analysis, no further observations of the Serpek process could be made.

III.3 The formation of aluminium nitride from its elements

Introduction

III.3.1 Kinetics of metal nitridation

Metal nitridation is expected to conform to the principles applying to oxide growth. As discussed in Chapter IV, the oxidation of metals
Follow linear, parabolic, and logarithmic relationships and as is observed for the oxidation of aluminium (61), any combination of these laws may be used to describe a nitridation curve. The kinetics of the nitridation of aluminium is reported (62) to be initially linear but with increasing temperature becomes parabolic.

Factors affecting the rate of reaction

When a nitride is formed from a metal and its gaseous environment, the initial nitride layer may act as a barrier and for further reaction to take place the reactants must pass through this barrier. Therefore, factors which affect the overall rate of reaction are (a) the supply of gaseous reactant to the initial nitride layer and (b) transport of the reactants through the nitride layer. Each of these factors are governed by the effect of temperature, pressure and any defect structure in the nitride layer.

The mechanical stability of the nitride layer is also important in determining the extent of reaction. The strength of the nitride layer depends on the difference in molecular volume and type of crystal lattice of the product layer compared with the original metal (63).

Sintering of the nitride layer can also cause a change in lattice dimension e.g. $\text{Ca}_2\text{N}_2$, the lattice dimension falls from 11.42 to 11.38 Å on sintering (33).

For nitridation of aluminium there is a fractional volume change of $+0.19$ and hence a stable nitride film is anticipated.

III.3.11 The formation of the nitride from its elements

On heating aluminium films prepared as described in Chapter II in nitrogen under the described conditions, no nitridation appeared to take
place at temperatures up to 500°C. The microscopical examination revealed that crystallite growth had occurred to a limited extent as can be seen by comparison of Fig. 11a and b. However, the rings in Fig. 10b index for f.c.c. Al as in Fig. 10a.

The growth is nucleated at points such as a and b as shown in Fig. 11b. The film appears to have sintered as can be observed from the electron diffraction patterns of the "nitrided" film (Fig. 10b). The pattern is more spotty and this observation is consistent with previous work on metal films (64).

According to other workers the formation of aluminium nitride is reported to commence appreciably at 530°C (62) and 600-650°C (60) both at a partial pressure of 100 mm of mercury (0.12 atm.). The kinetics of nitridation are initially linear but change to parabolic in the temperature range 580-590°C. Attempts to nitride aluminium at 450°C were made by the same authors but with success, whereas aluminium is reported to oxidise at this temperature. Metal films when prepared, have a large surface area to weight ratio and are inherently unstable and highly defective in structure. As is observed in the case of iron films (11), the sintering of the aluminium film is probably due to the structural defects such as vacancies diffusing through the bulk material to the metal surface and reducing the overall crystallite area. This mode of diffusion is possible as the temperatures considered are well above the Tamman temperature.

This sintering minimises possible initiation of the reaction with nitrogen on the aluminium surface at 500°C. At 475°C and 515°C weight changes of 0.1 and 0.25 µg/cm² for the nitridation of aluminium have been reported (62). A comparison of the rates of nitridation and the rates of
Fig. 10a. Electron diffraction pattern of the aluminium film.

Fig. 10b. Electron diffraction pattern of the film heated in nitrogen.
Fig 11b. Electron micrograph of the film heated in nitrogen.

Fig 11c. Electron micrograph of the aluminium film.
oxidation (6) show that aluminium reacts more rapidly in the presence of oxygen, even at temperatures approaching the melting point of aluminium.

The formation of aluminium nitride from its elements has been studied in the temperature range 600-1800°C. At 600°C chemical analysis revealed that the powdered lump was saturated with nitrogen and yet the formation of aluminium nitride was not observed. Certain authors (3) consider that even at low nitrogen content (at 700°C 0.0064 - 0.0070% N, at 850°C 0.0058-0.014% N) the compound AlN is distributed on the surface of the molten metal as a very thin film. Repenko et al. (53) reports substantial nitride formation at temperatures greater than 1700°C where the high concentration of aluminium vapour and nitrogen gas is sufficient to produce single crystals of aluminium nitride.

The formation of aluminium nitride from molten aluminium and nitrogen gas has been described also by Cooper et al. (1). They emphasise the need for preventing the reaction being inhibited by layers of nitride formed on the surface of the molten metal.

An attempt to prepare aluminium nitride as previously described was made (see Chapter II). A portion of finely-divided aluminium powder was placed in a horizontal tube furnace at 1000°C under purified nitrogen. After two hours the sample was removed and cooled to room temperature. The surface of the sample was observed to be sintered. The sample was ground and replaced in the furnace under nitrogen at 1000°C for a further two hours. The cooled sample was x-ray amorphous and no appreciable weight change was recorded. Even with repeated cycling of the routine no nitride formation was observed.
It has been reported that aluminium nitride is formed from aluminium powder and nitrogen at temperatures as low as 650°C (60). The same authors report increasing the particle size of the aluminium powder decreases the rate of reaction to form the nitride. However, only at temperatures above 1000°C are yields of better than 90% observed. These observations are not confirmed from the present work, and it would therefore appear that the formation of the nitride from the elements is best facilitated at elevated temperature where the reaction takes place in the vapour state (b.p. Al = 2467°C). However, at temperatures in the region of the boiling point of aluminium, any nitride will be unstable and dissociate into its elements, thus making the reaction reversible and temperatures of 1500-1800°C are recommended as it observed in the work of Repenko et al. (53), at which temperature aluminium has an appreciable vapour pressure.
7. Tananayev, I.V., & Talipov, Sh., Zhokh., 1955, 1155.


38. Brosset, C., SB v1, 1938, 28, 95.


CHAPTER IV The reactivity of aluminium nitride

IV.1 Introduction

The development of sintering and hot-pressing techniques has enabled aluminium nitride, and the nitrides of silicon and boron, to be used more extensively as ceramics. The resistance of these nitrides to hydrolysis and oxidation is increased considerably when they are hot pressed up to temperatures approaching 2000°C. These conditions may bring about structural changes in the nitrides which may compact the crystal lattice thus altering the characteristics of the material.

However, the rates of hydrolysis and oxidation would seem to depend on the intrinsic reactivity and surface available for chemical reaction. Impedance of the reactions by layers of products surrounding the remaining nitride particles may become significant. In the present chapter, production and sintering of aluminium nitride are considered in relation to changes in, phase composition, surface area, and crystallite and aggregate sizes on hydrolysis and oxidation under various experimental conditions.

The chemical reactivity of nitrides is controlled considerably by the extent to which they have been sintered during their formation and any subsequent calcination. At present, there is more available literature on the sintering of oxides which is expected to resemble that of nitrides. The theories of sintering are well established (1-8), and the subject has recently been
reviewed (9). Sintering is enhanced by compacting the powdered nitride before calcining in vacuo to prevent possible hydrolysis and oxidation (10). This can be observed by comparison of the present work and the data reported for the oxidation of hot pressed aluminium nitride (16).

A prerequisite for sintering is the production of finely-divided material with a suitable particle size range. Development of sintering is limited by impurities such as the oxide impurities produced by partial nitride hydrolysis and oxidation, and particularly gas-producing containments such as hydroxides and carbonates. When boron nitride is purified at higher temperatures to reduce oxide content, the increased particle size make subsequent hot pressing more difficult (14), but the addition of silica glass will bond the material under these conditions (15).

Sintering is generally accelerated by low melting additives (13), but such additions may cause serious reductions in optical and mechanical properties.
IV.1.1. The hydrolysis and oxidation of nitrides.

The resistance of powdered refractory nitrides to the action of water and aqueous acids and alkalis has been summarised by Samsonov (16). In nitride production usually oxygen must be excluded, for it prevents nitrogen from reacting with clean metal surfaces. Occasionally, formation of an initial nitride surface layer protects against any subsequent oxygen attack, and permits nitridation to proceed. When the nitride layer is destabilised by hydrolysis, the nitride ions are replaced by hydroxyl ions and since one nitride is replaced by three hydroxyl ions, the film becomes very weak and ruptures whilst very thin (17). At higher temperatures, decomposition of the hydroxides to oxides causes further fragmentation (18). For example, in the nitridation of magnesium between \(400^\circ\) and \(650^\circ\), metal evaporation is promoted by traces of water vapour but inhibited by oxygen (19).

The formation, hydrolysis and oxidation of the ionic calcium nitride \((\text{Ca}_3\text{N}_2)\) and magnesium nitride \((\text{Mg}_3\text{N}_2)\) have been described (20). More recently it has been found that zinc and cadmium films do not nitride in nitrogen or ammonia at temperatures below their melting points, and are formed only at appreciable rates at temperatures above \(600^\circ\) (19). They are hydrolysed rapidly to ammonia soluble complexes, \(M(\text{NH}_3)_x(\text{OH})_2\) where \(x \approx 4\) for \(M = \text{Zn}\) or \(\text{Cd}\) (17). Comparison of the molecular susceptibilities of magnesium, zinc and cadmium nitrides shows that the polarising action of the metal ion decreases from magnesium to zinc to cadmium. Nitrides in Group III of the Periodic Table (boron, aluminium and gallium) and Group IV (silicon and tin) show covalent character and are more resistant to hydrolysis and oxidation than the nitrides of magnesium and beryllium (26).
Boron nitride appears to be more chemically-reactive than aluminium and silicon nitride. Finely divided boron nitride is hydrolysed slowly by hot water and dissolves completely in boiling 20% sodium hydroxide in thirty minutes. It is also observed to dissolve in acids and alkalis at 20°C (22). By comparison, the reactions of the nitrides of aluminium and silicon with hot water are inhibited by coatings of hydrous alumina or silica respectively.

Hydrolysis is generally slow in mineral acids and alkalis (23, 24), but there is complete dissolution of aluminium nitride in 30% sodium carbonate solution at 80°C, and of silicon nitride in boiling hydrofluoric acid (25). All the nitrides oxidize at higher temperatures above 600°C, the most resistant to oxidation being silicon nitride with respect to temperature.

IV.1.ii Materials

The higher temperatures generally required for the production of aluminium nitride (see Chapters III and V), cause sintering to the extent that samples generally have specific surfaces of below 1 m².g⁻¹ and average crystallite sizes of over 2 μm.

More finely-divided aluminium nitride was obtained by ball-milling. Thus, 5 gram batches of aluminium nitride were ball-milled for times up to 10 hours. Changes in specific surface and average crystallite size are shown in Fig. 12.

Electron micrographs showed that the original nitride consisted of single crystals and aggregates of about 1–2 μm size, see Fig. 24a. The single crystals were fractured in the earlier stages of the milling and the fragments were incorporated into the aggregates which remained approximately the same size throughout the periods of millings, see Fig. 24b.
The change in specific surface during the milling of AlN.

(b) The change in average crystallite size during the milling of AlN.

Fig. 12.
This the average crystallite size decreased rapidly at first and later slowly when
the crystallites became of sum micron size.

A closer x-ray examination of the milled materials showed that any
inherent line broadening was in fact mainly due to strain introduced by milling
rather than particle size (68, 69), since the average crystallite size was always above 0.4 \( \mu \) m.

IV. 2. The hydrolysis of aluminium nitride

The sample of aluminium nitride which had been milled for 5 hours
\( (S = 4.0 \text{ m}^2 \text{g}^{-1}, \text{average crystallite size} 0.47 \mu \text{m}) \) was hydrolysed in water at
95\(^{\circ}\)C and in steam at 580-520\(^{\circ}\)C and 680-640\(^{\circ}\)C.

IV 2.1. The hydrolysis in water ("Wet" hydrolysis).

The sample was hydrolysed in water at 95\(^{\circ}\)C for prespecified times,
after which the partially hydrolysed sample was filtered off. The residue was
washed twice with 50 ml portions of acetone to remove immediately most of
the water remaining in contact with the nitride. This would prevent further
hydrolysis and ageing (26). The last traces of acetone and water were removed
by outgassing the samples at 150\(^{\circ}\)C \( \text{in vacuo} \) on an electrical sorption balance (26), before measure-
ment of its surface area by determining the adsorption isotherm of nitrogen at
-183\(^{\circ}\)C.

Portions of each sample were thermally analysed at (a) 200\(^{\circ}\)C in air
when physically adsorbed water was completely removed, (b) 500\(^{\circ}\)C in air
when the bayerite (\( \alpha \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \)) and boehmite (\( \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} \) or \( \gamma \cdot \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} \))
were almost completely dehydrated (27), and (c) 10000\(^{\circ}\)C or 1200\(^{\circ}\)C in air
when the remaining aluminium nitride had been oxidised completely to
\( \alpha \cdot \text{Al}_2\text{O}_3 \); the final weight also gave the total amount of alumina formed.
The phases present were identified by x-ray diffractometry and infra-red spectroscopy. The presence of retained nitride and boehmite was revealed by the x-ray diffractometer traces. However, the bayerite was x-ray amorphous and was detected together with boehmite by using the X-ray amorphous and x-ray amorphous techniques with the SP 200 infra-red spectrophotometer. The results of the x-ray and infra-red analysis are given in Tables 21 and 22.

The products of hydrolysis by water contained approximately 1 molecule of bayerite to every 4 molecules of boehmite and their formation was consistent with the pH conditions in the surrounding solutions. It is reported that at pH values greater than 2 boehmite is formed from amorphous aluminium hydroxide, which will transform at pH 9 to bayerite. The bayerite-gibbsite transformation takes place at pH 12 at 40-60°C (28). The pH of the surrounding solution was estimated as being in the range 7-11 which is consistent with the findings of x-ray and infra-red analysis. It is reported also that a highly protective film of boehmite is formed when aluminium metal is dipped into boiling water (33).

The 5 hour-milled sample of aluminium nitride was hydrolysed by about 80% at 95°C in water in 5 hours (Fig. 13(a)). Thereafter, hydrolysis was comparatively slow. The calculated increase in specific surface during the first 5 hours of hydrolysis (Fig. 13(a)) indicate that crystallites of alumina hydrate must split off from the nitride particles before their growth is promoted by ageing. The nucleation energy of these crystallites is a function of the initial nitride surface available for hydrolysis. The hydrous alumina crystallites grow as the hydrolysis is continued and there is a subsequent decrease in specific surface as the hydrous oxide crystallites coarsen on the nitride particles.
<table>
<thead>
<tr>
<th>aluminium-nitride</th>
<th>milled 5 hours</th>
<th>boehmite</th>
<th>gibbsite</th>
<th>bayerite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hydrolysed 5 hrs.</td>
<td>hydrolysed 10 hrs</td>
<td>hydrolysed 20 hrs</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>Intensity (I)</td>
<td>d</td>
<td>l</td>
<td>d</td>
</tr>
<tr>
<td>2.71</td>
<td>180</td>
<td>2.69</td>
<td>60</td>
<td>2.68</td>
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<td>120</td>
<td>2.47</td>
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<td>2.37</td>
<td>320</td>
<td>2.36</td>
<td>50</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Table 21
X-ray analysis of hydrolysed aluminium nitride
Table 22

Infra-red analysis of hydrolys*d aluminium nitride

<table>
<thead>
<tr>
<th></th>
<th>5 hrs. hydrolysis</th>
<th>10 hrs. hydrolysis</th>
<th>20 hrs. hydrolysis</th>
<th>boe units</th>
<th>ba erite</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3300 sh, m</td>
<td>3300 sh, m</td>
<td>3260 m</td>
<td>3260  346</td>
<td>3560</td>
<td>3540</td>
</tr>
<tr>
<td>3070 sh, w</td>
<td>3070 sh, w</td>
<td>3070 3039</td>
<td></td>
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<tr>
<td>1150 w</td>
<td>1150 w</td>
<td>1150</td>
<td>1150 1149</td>
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<tr>
<td>1070 b, s</td>
<td>1070 b, s</td>
<td>1070 w</td>
<td>1080 1063</td>
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<td>970 w</td>
<td>980 w</td>
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<td>975</td>
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<td>730 736</td>
<td>770-720</td>
<td>694</td>
</tr>
</tbody>
</table>

sh = shoulder
s = strong
b = broad
m = medium
w = weak
Figure 12: (b) Comparison of the specific surface area.

Note: Percentage hydrolysis.

Area and average perforation size.
The crystallites eventually form an impermeable layer of hydrous oxide which prevents any further appreciable hydrolysis Fig 13 (c). This behaviour is analogous to the wet hydrolysis of calcium and magnesium nitrides and the hydration of lime (20).

The actual variations in surface area, $S'$ when 1 gram of AlN is hydrolysed is shown in Fig. 13 (b). Changes in surface area of the unchanged nitride (represented by the dashed curve in Fig. 13 (b) are calculated on the basis of the reaction proceeding by inward advancement of the nitride-hydrous oxide interface (34). The surface area of the hydrous alumina (by difference) accounts for practically all of the total surface area (c.f. dashed curve). The corresponding average crystallite sizes of the hydrous alumina and the remaining nitride as shown in Fig. 13 (d) are 0.018 - 0.024 $\mu$m and about 0.25 $\mu$m respectively.

The hydrolysis involves change in crystal structure from the hexagonal structure of AlN to the orthorhombic structure of boshmite and the hexagonal structure of bayerite and a considerable volume increase (0.724 of the original volume). Since the nitride changes its volume 1.724 fold when it forms hydrous alumina, hydration of x gram in a 1 gram sample of aluminium nitride would cause the proportionate volume change

$$(1 - x) + 1.724x = (1 + 0.724 x)$$

The proportionate change in surface = $(1 + 0.724 x)^{2/3}$. In general, if $S$ and $S'$ are the surfaces of the aluminium nitride and its partly hydrolysed product, then,

$$S'/S = (1 + 0.724 x)^{2/3}$$

i.e. $$S'/S^{3/2} = (1 + 0.724 x)$$
Complete hydrolysis would give a surface change of \((1.724)^2 = 1.438\), if there was no splitting of crystallites to product. Increases in the number of crystallites can be estimated from the ratio \(S_1/S_2\) where \(S_1\) and \(S_2\) are the values of the surface area of the hydrous alumina and the specific surface of the original alumina nitride respectively, allowance being made for the change in lattice structure. Thus, after 5 hours hydrolysis each original AlN crystallite produces 14,500 crystallites of hydrous oxide which increases to 15,200 after 10 hours, although there is little further hydrolysis. Between 5 and 10 hours, increase in surface is caused by additional hydration and completion of the recrystallization of the newly formed hydrous alumina to their normal lattice structures; this is counterbalanced by ageing of the hydrous alumina which becomes more marked after 20 hours when the overall crystallite increase is reduced to 7,600.

Optical and electron micrographs show that the hydrolysed material consists of large aggregates of over 100 \(\mu\)m size compared with the smaller aggregates of about 1-2 \(\mu\)m size of the original milled nitride. The estimation of the partial size is described in Chapter II.

After hydrolysis for 5 hours the particle size is 100-130 \(\mu\)m and this is increased in range to 120-160 \(\mu\)m in a further 5 hours. The material sinters after this period to give large aggregate of 420-500 \(\mu\)m at 20 hours hydrolysis. These independent results agree with surface area characteristics of the milled material.

IV.2.11 The hydrolysis in steam ("Dry" hydrolysis)

The pyrohydrolysis of aluminium nitride was studied at temperatures in the range 580-520°C and 680-640°C respectively. The analysis of aluminium nitride for nitrogen can be carried out under similar conditions using sodium or potassium hydroxide pellets.
A weighed amount of nitride in a pyrex boat was placed in a horizontal tube furnace and steam supplied at an approximately constant rate. A blank run was made to determine the rate of steam passing through the system. This was established as 2.4 cc/min. As a result of the steam, a temperature drop of 40-60°C was observed.

Any ammonia given off by the pyro-hydrolysis was collected in a beaker in which was placed 25 ml of 2% boric acid and 5 drops of a mixed methyl red - toluocresol green indicator. The amount of ammonia evolved was determined by titrating the condensate against 0.1 M hydrochloric acid.

0.4% ammonia was formed in 10 hours at 560-520°C and 2.4% in 7 hours at 680-640°C. This corresponds 0.97% and 5.8% hydrolysis respectively. The amount of hydrolysis is low compared with liquid-solid reaction and it would suggest among other things that a different mechanism of hydrolysis is rate-controlling.

The results suggest that the steam promotes sintering of the nitride and prevents such a rapid hydrolysis as in the liquid-solid reaction. The sintering of the nitride is a barrier to further hydrolysis and the rate of hydrolysis is very much curtailed as a result.

IV.3  The oxidation of aluminium nitride

As AlN has application as a high temperature material, a study has been undertaken of (i) mechanism of reaction at these temperatures with particular reference to crystallite size, (ii) the change in surface properties as the reaction takes place. Aluminium nitride oxidises at temperatures above 600°C forming aluminium oxide in one of its crystallographic forms depending on the temperature at which the reaction is studied.
The kinetics of the oxidation of aluminium nitride and the effect of particle size on the rate of reaction was studied, using a thermogravimetric balance in the temperature range of 700°C to 1000°C. The experimental technique is described in Chapter II.

Although the initial mass of nitride does not appreciably affect the reaction rate (35), one-gram samples of aluminium nitride were used in the experiments for this weight is more convenient when interpreting the results.

One-gram samples were placed in a 10 cc porcelain crucible and suspended a few centimetres from the thermocouple. The same conditions were employed throughout the experiments.

IV.3i The oxidation reaction

Although moisture is known to increase the rate of oxidation (36,37) no attempts were made to dry the air in which the nitride was oxidised so that oxidation kinetics experimentally derived could be applied to the material when in general use.

Therefore as moisture is present in the system, ammonia will be produced according to the reaction:

$$2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{NH}_3.$$  

As the temperature increases, the amount of ammonia decreases and the amount of nitrogen increases according to the reaction:

$$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2.$$  

such that in the temperature range considered, the amount of ammonia present is very small compared with that of nitrogen. The activation energies for reaction of aluminium nitride with moist oxygen and moist nitrogen are 26.5 and 7.3 k. cal. mole⁻¹ respectively, and the rate determining step for the low activation energy for the reaction of moist nitrogen is attributed to absorption (38).
It was therefore assumed that the main reaction taking place was

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 + N_2$$

IV.3.ii The rate laws of oxidation

The rate laws of oxidation are classified into three main groups:

(a) Logarithmic Rate Equations:

(b) Linear Rate Equation:

(c) Parabolic Rate Equation.

These rate equations are dependent on a number of factors among which are temperature, oxygen pressure, elapsed time of reaction, surface preparation and pre-treatment of the system.

(a) Logarithmic Rate Equations

These equations can be mathematically expressed as

\[ x = k_1 \log(t + t_0) A \]

\[ 1 = B - k_2 \log t \]

where \( x \) is some measure of the oxide formed, \( A \) and \( B \) are constants and \( k_1 \) and \( k_2 \) are the respective rate constants and are known as a) direct logarithmic growth and b) inverse logarithmic growth respectively.

A number of theories have been put forward to explain these laws based on various rate determining mechanisms such as cavity formation in the oxide film or chemisorption.

(b) Linear Rate Equations

Linear oxidation can be described by

\[ \frac{dx}{dt} = k_3 \]

i.e. \( x = k_3 t + c \)

If a relationship is governed by linear oxidation, the surface reaction or phase boundary reaction is said to be rate determining.
(3) **Parabolic Rate Equations**

Parabolic oxidation is a diffusion-controlled process and the amount of oxide formed in an interval of time \( t \) is proportional to the square root of \( t \). It can be expressed as

\[
\frac{dx}{dt} = \frac{k_4}{x}
\]

i.e. \( x^2 = k_4 t \), \( x = k_4 t^{\frac{1}{2}} \)

IV.3.iii The kinetics of the oxidation of aluminium nitride

The factors which govern the kinetic laws for gas solid reactions are:

- the rates of nucleation and recrystallization,
- the chemical reaction at the phase boundary,
- and the rates of diffusion.

The gas-solid reaction initially takes place at the surface of the solid and the part played by a surface in a chemical reaction has been discussed by Gregg (43).

Gregg gives the classical example of the decomposition of calcium carbonate and considers the key to the continuation of the reaction

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

is the surface heterogeneity. On the surface of a solid there are regions of particularly high potential energy where the energy barrier opposing decomposition is lower than elsewhere, and these areas are the regions of nucleation or active sites. In other words, the points at which the chemical reaction can begin.

When discussing the reaction of powders, it is necessary to consider the influence of reactant particle size and shape on the reaction rate. By considering the assumption that a gas solid reaction may be controlled by rate of gas diffusion through a product layer Jander (44) derived the equation

\[
k = 1 - (1-F)^{\frac{1}{2}}
\]

where \( k \) is the 'parabolic' rate constant and \( t \) is the time in which a mass of reactant is converted to a mass of product \( F \) per unit mass.
However, Jander's equation did not consider that (i) the ratio of surface area of partially oxidised crystallite to area reaction interface progressively changes during the reaction (46), and (ii) the reactant and product molar volumes are not equal. Carter (45) modified Jander's equation to give
\[\left[1 + (\lambda-1)F^2 + (\lambda-1)(1-F)^3 \right] = Z + 2 (1-\lambda)^{\frac{kt}{r}}\]
where \(r\) is the initial radius of a particle and \(\lambda\) is the ratio of product and reactant molecular volumes.

Several kinetic equations have been derived and the equation which connects the kinetic parameter with the experimentally determined function is dependent on whether the original powder particles are considered to be disc-like (39), cubic (40), spherical (41), or needle shaped (42).

From electron microscopy, the particles to a first approximation could be supposed to be circular. The geometry of situation was limited to 2 dimensions by the instrument, and it was assumed that the particles were spherical rather than disc-like. The results of the thermogravimetric study of the oxidation of aluminium nitride fitted the equation derived for spherical particles.

**Kinetic equation**

The rate of reaction was considered to be experimentally expressed as the amount of aluminium nitride converted to alumina in time \(t\) as \(F\)

where
\[F = m_t - \frac{m_0}{m_0 + \frac{M_p}{M_r} - 1}\]

where \(m_t\) = mass of the sample at time \(t\)
\(m_0\) = initial mass
\(M_p\) = Molecular weight of the product
\(M_r\) = Molecular weight of the reactant
and the value of \(F\) will vary from \(0\) (\(t = 0\)) to 1.
It is assumed that the particles are spherical and so if \( V \) is the volume of a particle and \( r \) is the radius:

\[
V = \frac{4}{3} \pi r^3
\]

If \( V_t \) is volume of residual AlN at any time \( t \) and assuming that the shape of the particle does not change during oxidation, then

\[
V_t = V - VF
\]

where \( VF \) is the volume changed to alumina in time \( t \).

If \( r_t \) is the radius of the particle of residual AlN:

\[
r_t = r (1-F)^{\frac{1}{3}}
\]

The volume of alumina formed \( V_\alpha \) is equal to the difference in the initial volume and the volume of the residual AlN and there is a molecular volume change:

\[
V_\alpha = (V - V_t)\lambda
\]

where \( \lambda \) is the stoichiometric ratio of the molecular volumes of alumina and aluminium nitride according to the reaction:

\[
2 \text{AlN} + \frac{3}{2} O_2 \rightarrow \text{Al}_2\text{O}_3 + \text{N}_2.
\]

The total volume \( V \) at any time \( t \) is therefore equal to the sum of the volume of alumina formed and the volume of the residual nitride:

\[
V = V_\alpha + V_t
\]

\[
= (V - V_t)\lambda + V_t
\]

\[
= (V - (V - VF))\lambda + V - VF
\]

\[
= V(1 - F + \lambda F)
\]

Therefore \( r_x = r (1 - F + \lambda F)^{\frac{1}{3}} \) so the total thickness \( x \) of the layer of alumina will be

\[
x = x = \frac{x}{x}
\]

\[
= r \left( 1 + \frac{\lambda F}{3} \right) - (1 - F)^{\frac{1}{3}}
\]

\[
= 128
\]
If the rate of diffusion is very great in relation, the rate of reaction then is

\[
\frac{dN}{dt} = k_1 A
\]

where \( A \) is the surface area of the spherical particle

\[
A = 4\pi r^2
\]

\[
N = \frac{4}{3} \pi r^3 v_{\text{AlN}}
\]

where \( v_{\text{AlN}} \) is the molar volume of aluminium nitride.

\[
\frac{dN}{dt} = -4\pi \frac{r^2}{v_{\text{AlN}}} \frac{dr}{dt} = k_1 4\pi r^2
\]

\[
\Rightarrow \quad - \frac{dr}{dt} = k_1 v_{\text{AlN}}
\]

\[
\int_{t=0}^{t} dr = \int_{t=0}^{t} k_1 v_{\text{AlN}} dt
\]

\[
-r_0 + r = k_1 v_{\text{AlN}} t
\]

\[
1 - (1-F)^{\frac{1}{3}} = k_1 v_{\text{AlN}} \frac{t}{r}
\]

and if diffusion is not rate controlling \( 1 - (1-F)^{\frac{1}{3}} \) will vary linearly with time.

But if rate of diffusion controls the reaction, the derived parabolic law is expressed as:

\[
\frac{dx}{dt} = \frac{k_2}{x}
\]

which, when integrated, gives

\[
x^2 = 2k_2 t
\]

where \( x \) is the thickness of the product;
\[
\begin{align*}
  r (1-F + F)^{\frac{1}{3}} - (1-F)^{\frac{1}{3}} &= x \\
  r^2 (1-F + F)^{\frac{1}{3}} - (1-F)^{\frac{1}{3}} &= x^2 \\
  (1-F + F)^{\frac{1}{3}} - (1-F)^{\frac{1}{3}} &= \frac{2k_2t}{r^2} \\
  &= z^2
\end{align*}
\]
so a plot of \( z^2 \) with time will vary linearly if diffusion is the rate controlling process.

**Estimation of kinetic parameters**

Calculation of the mass converted in time \( t, F; \)

\[
F = \frac{m_t - m_o}{m_o} \frac{M_p}{M_r} - 1
\]

\( M_r = 2M_{\text{AlN}} \) where \( M_{\text{AlN}} \) is the molecular weight of aluminium nitride.

\( M_p = M_{\text{Al}_2\text{O}_3} \) the molecular weight of alumina

\[
\begin{align*}
M_r &= 82 \\
M_p &= 102 \\
\frac{M_p}{M_r} - 1 &= \frac{102}{82} - 1 = 0.244. \\
F &= \frac{m_t - m_o}{0.244m} = \frac{\Delta m}{0.244m}
\end{align*}
\]

**Calculation of \( \lambda \)**

\( \lambda \) is the stoichiometric ratio of the molar volumes of aluminium nitride and alumina. From the x-ray results of the product of oxidation, the alumina was identified as \( \alpha \)-alumina by comparison of observed d-spacings and the d-spacings given by the A.S.T.M. index see Table 25. Aluminium nitride is reported to convert to alumina at temperatures as low as 600°C (38) where the form of alumina is possibly \( \gamma \)-alumina.

The densities of aluminium nitride and \( \alpha \)-alumina were taken to be 3.27 and 3.97 g/cm\(^{-3} \) respectively.
These values gave the molar volumes of aluminium nitride and
\(\alpha\)-alumina as 27.55 and 12.57 \(\text{cm}^3\) respectively.

\[
\begin{align*}
\frac{v_{\text{Al}_2\text{O}_3}}{2} & = \frac{v_{\text{AlN}}}{2} \\
& = 1.19.
\end{align*}
\]

Hence, knowing \(\lambda\) and \(P\), the values of \(y\) and \(Z^2\) can be found.

The calculation of \(Z^2\) is particularly tedious and a computer
programme in Fortran IV for IBM 1130 Computer has been written to
calculate these functions (See Appendix V). Graphs of percentage
conversion (Fig. 14), \(y\) and \(Z^2\) (Figs. 17 and 19) for various times
at different temperatures were drawn and from the slope of \(Z^2\) against
time the reaction rate constants \((k_2)\) were found.

**The determination of the activation energy for the oxidation reaction**

The rate of reaction is proportional to the rate constant \(k\). The
relationship with the rate constant and the activation energy for the
process is given by the Arrhenius equation

\[
k = A \cdot e^{-E/RT}
\]

where \(A\) is the frequency factor or pre-exponential factor.

\(e^{-E/RT}\) is sometimes termed the Boltzman factor where \(E\) is the
activation energy, \(T\) is the temperature in degrees Kelvin, and \(R\) is the
gas constant.

From this equation

\[
\ln k = \ln A - \frac{E}{RT}
\]

\[
\log_{10} k = \log_{10} A - \frac{E}{2 \times 303RT}
\]

\[
= \log_{10} A - \frac{E}{4.56T}
\]

Hence a plot of \(\log_{10} k\) against \(1/T\) will give a straight line of slope
\(E/4.56\), from which the activation energy for the process can be calculated.
Fig. 14. The percentage conversion of aluminium nitride to α-alumina at various temperatures.
Many factors contribute the initial shape of an oxidation isotherm, and these have been enumerated by Gulbransen and Andrew (48). These factors are (i) the influence of the decrease of roughness or surface area as the reaction proceeds, (ii) the influence of the heat evolved in the reaction on the rate of reaction, (iii) the effect of impurities in the oxide as the reaction begins, (iv) the change in oxide composition, (v) the influence of potential fields at the gas oxide interface due to absorbed oxygen ions according to the mechanism of Mott (49).

It has been shown (46) that as the reaction proceeds, that the sample of initial surface area of \(1.1 \text{ m}^2 \text{ g}^{-1}\) increases to an estimated \(1.6 \text{ m}^2 \text{ g}^{-1}\) in a period of 4.0 hours.

In the period studied, that is 0 to 7 hours, there is an expected increase in surface area of \(0.1 \text{ m}^2 \text{ g}^{-1}\) so it is assumed that the effect of increase in surface area is negligible.

From a literature survey, a value of \(\Delta H = -136 \text{ k.cal/mole (50)}\) for the heat of reaction is obtained. As the temperature maintained at \(\pm 2^\circ\text{C}\) throughout the experiment, this factor was not considered to affect the situation in the temperature range considered. However, this effect is apparently important at higher temperatures (35).

The estimation of any impurities in the initial oxide was not made in this study, and hence the effect of this factor cannot be considered.

It has been reported that there is a change in density from the surface oxide and internal oxide when metal powders are oxidised (51),

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but in the present study the density of the oxide was assumed to be constant although this effect could influence the initial oxidation isotherm.

Papas and Kingery (52) have studied the electrical conductivity of single crystal and polycrystalline alumina in the temperature range 1400-1800°C under various oxygen pressures. At the high pressure region, the conductivity increased slightly with pressure. This was attributed to absorption of oxygen on the surface where it, according to the equation

\[
\frac{3}{2} O_2 (g) \rightarrow 3/2 O^{2-} \text{(ads)} + V_{(Al^3 \, +)} + 3 \Theta
\]

If this effect is true of aluminium nitride at atmospheric pressure, the production of voids would act as nucleation sites, i.e. regions of higher potential energy from which the reaction is able to proceed.

From the discussion above, it is assumed the effect of the absorption of oxygen and the assumed difference in density between the surface oxide with respect to internal oxide play a major part in the initial rate curve.

The types of oxidation isotherm have been described (44), and a comparison of the isotherms obtained in this study show that the isotherms are deceleratory throughout, that is the rate progressively decreases as the reactant is consumed. However, there is a slight discrepancy in the continuity of the isotherms. It was thought that perhaps this may be due to an experimental error and a gram of \(\alpha\cdot Al_2O_3\) was heated at 960°C under the same conditions and the
weight of the sample remained constant throughout, thus obviating the idea of experimental error. To further investigate this effect a detailed plot of the oxidation of aluminium nitride was taken at 930°C at ten minute intervals over a period of 3 hours. The results are graphed in Fig. 15. From this graph there is change in shape in the region A A' and this begins to occur after approximately 1 hour.

The effect could be explained by taking the points a, b, c, d. At the start of the reaction, nuclei are formed at areas of high potential energy as previously described. These nuclei are random and the area of reactant product interface is small and hence the reaction rate is slow. At the point b the nuclei have started to grow and with new nuclei being formed the reactant product interface has grown, and hence the reaction is faster.

At point c the nuclei have grown to sufficient size such that they overlap and cover the surface completely, so the reaction begins to decelerate as further reaction results in the reactant product interface decreasing in area.

In the region of d there is a slight increase in the reaction. This may be due to the fact that the formation of initial oxide layer takes place at faster rate than the nitrogen, formed in the reaction, diffusing through the oxide layer. The result is a build-up of pressure at the reaction interface which causes the surface to break and hence the exposed nitride acts as a nucleation point for further oxide growth.
Fig. 15. The percentage conversion of aluminium nitride heated at 930°C for 3 hours.
This concept of a breakdown in the oxide layer is descriptive of linear kinetics, and has been observed in other gas solid systems (42, 41, 53). A plot of first order kinetics against time, shows in fact there is a change in the order of reaction. This can be seen in Fig. 16 where the slope changes at a, b, a' to b' for the plot of Q against time for 960°C and 910°C respectively, where $t = \log \frac{1}{y}$.

A plot of log t (time) against log x (x = percentage conversion to alumina) was made (see Fig. 16b) from which the slope gives the order of reaction. From these plots it was also observed that the order of reaction changed from $\frac{1}{5}$ to 1 in the lower temperature region. This is due to the fact that although oxidation of aluminium nitride begins above 600°C, there is not an appreciable amount of oxide formed and there is only a surface reaction taking part at these temperatures. At higher temperatures the order reaction is initially 1 changing to a $\frac{1}{2}$ until above 960°C the overall reaction kinetics are parabolic.

From the plot of y against time (t) for various temperatures for a period of approximately $\frac{1}{2}$ hour, the relationship between y and t is approximately linear (see Fig. 17), adding further evidence to the idea of nucleation as a surface reaction being the initial rate controlling mechanism. This is further exemplified by the fact that the relationship $2^2$ to t is not initially linear in the low temperature region (see Fig. 19), and hence diffusion plays very little part in the initial stage of the reaction.
Fig. 16. (a) A plot of first-order kinetics with time for various temperatures. (b) A plot of log t (time) with log x (x is % conversion).
However, as the reaction proceeds, diffusion becomes the controlling mechanism as the relationship between $Z^2$ and $t$ becomes linear. This is true for values of $F$ between 0.003 and the final readings taken in the kinetic study. So the mechanisms which occur are linear kinetics followed by parabolic kinetics followed by a short region of linear kinetics and the return to parabolic kinetics. This type of linear parabolic relationship has been encountered by other authors (59) and in the oxidation of silicon nitride (54) the kinetic equation used in this type of mechanism is

$$\Delta W = A \Delta t = kA + C$$

where $\Delta W$ is the weight increase

$k$ is the overall rate constant

$A$ and $C$ are constants.

This equation, however, cannot be employed as it equates an overall mechanism and would consequently not give a detailed picture of the oxidation kinetics. The converse of this mechanism (known as parilinear kinetics (61)) is not to be confused with the above equation.

These kinetic studies have been limited to a seven hour period in which a maximum of 30 per cent conversion to alumina was observed. To obtain an overall picture, samples of aluminium nitride of surface area $1.1\text{in}^2\text{g}^{-1}$ were heated for longer periods of time and as much as 94 per cent conversion to alumina is observed in 130 hours at 1000°C. Parabolic kinetics are obeyed in the initial period of 2 - 22 hours, as can be seen from a plot of $Z^2$ against time ($t$) (Fig. 18). During the first hour interface reaction is rate controlling as can be seen from a plot of $y$ against $t$ (Fig. 18). After the 22 hours, the plot of $Z^2$ against $t$ is no longer linear for values of $F$ greater than 0.6.
Fig. 18. A plot of $Z^2$ against time, $t$, for periods up to 30 hours.
This is probably due to the layer of oxide no longer growing in regular fashion and the approach to linear kinetics from the plot of $y$ against $t$, suggest the reaction is mainly taking place at the reaction interface. This is a relatively slow process from which the oxide layer will progress until it finally sinters and prevents further diffusion of oxygen to the interface.

From plots of $Z^2$ against time for different temperatures, (see Fig. 19) the slopes of the straight line portions were found and these values were taken as the reaction rates ($k$). A further plot of $\log k$ against the reciprocal of temperature in degrees K was made (see Fig. 30) and the slope was equivalent to $E/4.56R$ where $E$ is the activation energy and a value of 53 k cal/mole was calculated and the equation can be expressed as:

$$k = 10^{-2} e^{-53/RT}.$$ 

This value compares well with the oxidation of aluminium nitride in purified oxygen, to form alumina (vis: 50.8±3 k cal/mole for a surface area of 0.416 m$^2$ g$^{-1}$ (59), and 49 k cal/mole (35) in the temperature range 650-1100°, no surface area measurements being given) (see Table 23). This agreement emphasises that the main reaction taking place when aluminium nitride is heated in air is the formation of alumina.

It is concluded that the reaction follows first the formation of alumina at nucleation points on the surface. While the regions grow linear, kinetics are observed until a coherent layer forms when parabolic kinetics are recorded, until there appears a slight break in the coherent film allowing further nucleation until the surface is recovered and parabolic kinetics are further observed.

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### Table 23

**Activation energies of the oxidation of aluminium nitride and related materials**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Conditions</th>
<th>Activation energy k cals/mole</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>660 - 850°C</td>
<td>99</td>
<td>12</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>sintering studies</td>
<td>130 - 170</td>
<td>59</td>
</tr>
<tr>
<td>AlN</td>
<td>$O_2$</td>
<td>51.8</td>
<td>59</td>
</tr>
<tr>
<td>AlN</td>
<td>$O_2$</td>
<td>49</td>
<td>35</td>
</tr>
<tr>
<td>AlN</td>
<td>air</td>
<td>53</td>
<td>present work</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>$O_2$</td>
<td>61</td>
<td>54</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>air</td>
<td>68</td>
<td>54</td>
</tr>
<tr>
<td>SiC</td>
<td>oxidises to amorphous SiO$_2$</td>
<td>15.6</td>
<td>31</td>
</tr>
<tr>
<td>SiC</td>
<td>oxidises to cristoballite</td>
<td>20.2</td>
<td>31</td>
</tr>
<tr>
<td>B$_4$C</td>
<td></td>
<td>23.9</td>
<td>32</td>
</tr>
</tbody>
</table>
A plot of $Z^2$ against time, $t$, for various temperatures.
To underline this breakdown in the coherent layer, the activation energy for the reaction of moist nitrogen with aluminium nitride in a temperature range of 600-800° is reported (38) as 7.3 kcal/mole. However, a value for the energy of activation for the reaction of aluminium nitride in dry oxygen is reported as 24.3 kcal/mole (38), but the surface area sample used in that study was 1.7 m² g⁻¹, and hence by comparison the nitride powder used in the present work would be more reactive above 700°C and an activation energy of less than 7.3 kcal/mole could be expected for the reaction between the sample and nitrogen. The ionic radius of nitrogen is 1.71 Å and it is doubtful whether nitrogen would diffuse as N²⁻, so nitrogen would diffuse as atoms rather than ions. The atomic radius of nitrogen is 0.71 Å, and the ionic radius of aluminium is 0.5 Å, so for purely geometric reasons the aluminium ions would diffuse along the grain boundaries rather than through the crystalline material (60), faster than the nitrogen atoms. Consequently, due to the assumed low activation energy of the nitride in the presence of nitrogen, and the easier diffusion of aluminium ions, there is a break in the coherent oxide surface to allow the removal of nitrogen. As the continuation of a coherent oxide layer growth is observed without a further breakdown in oxide surface, the further removal of nitrogen from the system would seem to be by some diffusion process, perhaps through the fibrous oxide layer (41).

As oxidation will be controlled by the rate of arrival of reactant at the reaction interface, diffusion of the fastest moving species is rate controlling.
As previously discussed, the diffusion of aluminium ions would be faster than that of nitrogen atoms. In a study of the oxidation of pure aluminium in the temperature range 400-650°C, the rate controlling species was identified as $\text{Al}^{3+}$ and an activation energy of 52 k.cal/mole (60) and 54 k.cal/mole (64) was recorded in accordance with parabolic kinetics. These values are in excellent agreement with the present results, and a grain boundary diffusion of $\text{Al}^{3+}$ through the oxide film to react at the gas oxide interface is compatible with the experimental results obtained in this work.

The diffusion of oxygen in polycrystalline alumina has led to activation energies of 130-170 k.cal/mole (59,65,66) and comparison with 53 k.cal/mole would suggest that diffusion of oxygen ions in aluminium nitride is not rate controlling. This disagrees with the results of Guichon and Jacque (35), who concluded oxygen ion diffusion to be rate controlling. This hypothesis would therefore appear to be incorrect from the present work. However, they showed that there was a relationship between the rate of reaction and partial pressure of oxygen in the system, but limitations in technique did not allow an evaluation of the order of relationship.

The results of Cooper et al. (59) showed the relationship between the oxidation rate and partial pressure as

$$\text{oxidation rate} \propto P_{O_2}^{1/4}$$

The mechanism of absorbed oxygen on the surface of polycrystalline alumina (52) which ionized according to

$$\frac{3}{4} \text{O}_2 (g) \rightarrow \frac{3}{2} \text{O}^{2-} (ads) + e^{-} + \text{Al}^{3+} + 3 \Theta$$

has been adapted for the surface reactions of aluminium nitride.
When the process attains equilibrium:

\[
\left[ V_{\text{Al}^{3+}} \right] \left[ \phi \right]^3 = \text{a constant} \\
\frac{1}{P_0^{\frac{3}{2}}}
\]

and if \( V_{\text{Al}^{3+}} \gg \left[ \phi \right]^3 \)

\[
\left[ \phi \right] \propto P_0^{\frac{3}{2}}
\]

The production of the positive holes at the gas oxide interface will determine the extent of the driving gradient of \( \text{Al}^{3+} \) ions, which is rate controlling from aluminium nitride through the oxide layer to the oxide-gas interface.

**IV.3.iv The effect of particle size on the rate of reaction**

5 gram samples of aluminium nitride of original surface area 0.4 m\(^2\) g\(^{-1}\) were milled in a porcelain vessel, with a number of alumina balls of different diameters, for periods of 2, 5 and 10 hours. The oxidation rates of 2 hour and 10 hour milled samples were estimated as previously described at 872\(^\circ\), 910\(^\circ\), and 960\(^\circ\)C, and compared with oxidation rates of the original sample.

The 5 hour milled sample was set aside for hydrolysis studies.

After each milling period, the material was recovered as described in Chapter II. The surfaces areas were determined as previously, by the B.E.T. procedure. From the deduced particle size, a comparison of the rate constants for the particle sizes for a specific temperature is given in Table 24.
<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>Milling time in hours</th>
<th>Rate Constant</th>
<th>Surface area ( \text{m}^2 \cdot \text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>872</td>
<td>0</td>
<td>( 0.077 \times 10^{-4} )</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>( 0.258 \times 10^{-4} )</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>( 0.436 \times 10^{-3} )</td>
<td>4.8</td>
</tr>
<tr>
<td>905</td>
<td>0</td>
<td>( 0.235 \times 10^{-4} )</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>( 0.61 \times 10^{-3} )</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>( 0.67 \times 10^{-3} )</td>
<td>4.8</td>
</tr>
<tr>
<td>960</td>
<td>0</td>
<td>( 0.47 \times 10^{-4} )</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>( 0.89 \times 10^{-3} )</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>( 0.79 \times 10^{-3} )</td>
<td>4.8</td>
</tr>
</tbody>
</table>
As expected, when increasing the surface area of the material, the sample becomes more reactive as can be seen from Table 24 which compares the rate of reaction with surface area. A twelve-fold increase in surface area as a result of milling the material for 10 hours increased the reaction rate constant by the order of 56 times at 872°C.

As the temperature is increased, however, the increase in reaction rate is not so great. For example, at 905°C the milling of the sample for 10 hours introduced an increase in rate constant of 28, yet at 910°C the increase is of the order of 21.

When comparing the results of aluminium nitride heated in air having been milled for 2 hours and 10 hours respectively; at 872°C there is only a slight modification in the rate constant (see Fig. 21), and at 905°C (see Fig. 22) and 960°C estimated reaction rate within experimental error is constant. This effect has also been observed in the oxidation of chromium nitride in air (63).

The results suggest, therefore, that increasing the surface area by a factor of 6, tends to make the sample more reactive, but any further increase in the surface area has no appreciable effect on the reactivity of aluminium nitride.

IV.3.v The effect of impurities on the oxidation

As one of the methods of preparing aluminium nitride studied was the thermal decomposition of ammonium hexafluoroaluminate in gaseous ammonia, the effect of aluminium fluoride on the oxidation of aluminium nitride was investigated.

Weighed amounts of \( \alpha \)-aluminium fluoride (formed by decomposing ammonium hexafluoroaluminate in purified nitrogen at 750°C) were added
The effect of milling on the oxidation of aluminium nitride at 872°C.

*Fig. 21.*
to 1 gram weights of aluminium nitride and the fluoride present expressed as a weight percentage.

The effect of adding the fluoride is shown in Fig. 23. The rate of oxidation is remarkably increased. 4.2 wt.% increases the rate of oxidation, but the 'final' amount of decomposition observed is less than that observed with no fluoride present. 9.3 wt.% again increases the oxidation rate more than 4.2%, but after a period of approximately 1.5 hours, the fluoride itself begins to oxidise and a weight loss is observed. A 19.8 wt.% addition in fact resulted in a constant weight loss and hence the fluoride preferentially oxidises and can no longer be considered an impurity.

Fluorides are also known to have a catalytic effect on the oxidation of metals (67).

IV.3.vi The change in surface properties of aluminium nitride and silicon nitride

Separate half gram portions of aluminium and silicon nitride were oxidised in air at 800, 900, 1000°C. As expected, the conversion to alumina takes place more rapidly as the temperature is increased. Weight changes were measured when the sample was cooled to room temperature and percentage conversion was found for each temperature at different intervals of time. The products from the oxidation were identified by x-ray techniques as described in Chapter II and were identified as α-alumina (α-Al$_2$O$_3$), and silicon dioxide (Si$_2$O$_3$), tridymite and cristoballite) even in the early stages of the reaction (see Tables 25 and 26). Certain samples were further examined by
Fig. 23. The effect of aluminium fluoride on the oxidation of aluminium nitride.
the use of a Philips EM100 electron microscope (see Figs. 24-27).

A larger amount of nitride was required to measure the change in surface area and 5 gram samples were oxidised in air for various times, at a 1000°C. The cooled samples were outgassed in vacuo at 200°C before their specific surfaces were determined by the B.E.T. procedure (47).

The deduced average crystallite sizes were compared with the particle sizes ranges determined by electron microscopy.

No oxynitrides have been observed in the present study and it appears that oxynitrides are formed only at higher temperatures (55) where the respective nitrides and oxides are mutually soluble, or in the case of aluminium nitride by nitriding α-alumina in ammonia at low temperatures (56). Fig. 28 shows the overall variations for aluminium nitride in specific surface, and average crystallite size during the conversion to alumina. These are compared to the oxidation rates Fig. 28d, changes in the number of crystallites Fig. 28c, and the average crystallite sizes of the individual unchanged aluminium nitride and the product α-alumina Fig. 28f. The aggregate sizes, estimated by electron microscopy are given in Table 27 to be compared with the crystallite sizes.
Table 25

Aluminium nitride heated at 900°C for 96 hours

<table>
<thead>
<tr>
<th>$d_{\text{obs}}$</th>
<th>I</th>
<th>$d_{\text{AlN}}$</th>
<th>$d_{\text{K-Al_2O_3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48</td>
<td>w</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>2.68</td>
<td>s</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>2.55</td>
<td>vw</td>
<td>2.55</td>
<td></td>
</tr>
<tr>
<td>2.47</td>
<td>w</td>
<td>2.49</td>
<td></td>
</tr>
<tr>
<td>2.36</td>
<td>s</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>2.08</td>
<td>w</td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>1.83</td>
<td>w</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>w</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>1.55</td>
<td>w</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>w</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>1.37</td>
<td>w</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>1.31</td>
<td>w</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
<td></td>
</tr>
</tbody>
</table>

$s =$ strong

$w =$ weak

$vw =$ very weak
Table 26

Silicon nitride heated at 1000°C for 96 hours

<table>
<thead>
<tr>
<th>$d_{obs}$</th>
<th>I</th>
<th>$d_{Si_3N_4}$</th>
<th>$d_a$</th>
<th>$d_b$</th>
<th>$d_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.77</td>
<td>w</td>
<td>3.88</td>
<td>4.14</td>
<td>4.04</td>
<td>4.30</td>
</tr>
<tr>
<td>3.23</td>
<td>s</td>
<td>3.37</td>
<td>3.14</td>
<td></td>
<td>3.25</td>
</tr>
<tr>
<td>2.98</td>
<td>s</td>
<td>2.89</td>
<td>2.92</td>
<td>2.84</td>
<td>2.96</td>
</tr>
<tr>
<td>2.46</td>
<td>s</td>
<td>2.82</td>
<td>2.53</td>
<td>2.47</td>
<td>2.47</td>
</tr>
<tr>
<td>2.3</td>
<td>vw</td>
<td>2.32</td>
<td></td>
<td>2.34</td>
<td>2.37</td>
</tr>
<tr>
<td>2.17</td>
<td>w</td>
<td>2.16</td>
<td>2.17</td>
<td>2.12</td>
<td>2.07</td>
</tr>
<tr>
<td>1.91</td>
<td>s</td>
<td>1.94</td>
<td>1.99</td>
<td>1.93</td>
<td>1.97</td>
</tr>
<tr>
<td>1.74</td>
<td>s</td>
<td>1.75</td>
<td>1.76</td>
<td></td>
<td>1.76</td>
</tr>
<tr>
<td>1.58</td>
<td>vw</td>
<td>1.60</td>
<td>1.69</td>
<td>1.64</td>
<td>1.58</td>
</tr>
<tr>
<td>1.51</td>
<td>vw</td>
<td>1.51</td>
<td>1.46</td>
<td>1.50</td>
<td>1.52</td>
</tr>
<tr>
<td>1.33</td>
<td>w</td>
<td>1.32</td>
<td>1.38</td>
<td>1.4</td>
<td>1.33</td>
</tr>
</tbody>
</table>

d_a cristoballite
d_b cristoballite
d_c tridymite
Fig. 24a. Aluminium nitride.

Fig. 24b. Aluminimum nitride milled 5 hours.
Fig. 25a. Aluminium nitride heated 5 hours at 1000°C.

Fig. 25b. Aluminium nitride heated 24 hours at 1000°C.
Fig. 26a. Aluminium nitride heated 96 hours at 1000 °C.

Fig. 26b. Silicon nitride.
NGC 2.
Fig. 27a. Silicon nitride heated 96 hours at 800 C.

Fig. 27b. Silicon nitride heated 96 hours at 1000 C.
Table 27

Variations in aggregate sizes during the conversion of AlN to $\alpha$-$\text{Al}_2\text{O}_3$

at 1000$^\circ$C in air.

<table>
<thead>
<tr>
<th>Time, hours</th>
<th>% conversion</th>
<th>Range of aggregate size ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1 - 2</td>
</tr>
<tr>
<td>5</td>
<td>51.3</td>
<td>3 - 5</td>
</tr>
<tr>
<td>24</td>
<td>67.7</td>
<td>3 - 6</td>
</tr>
<tr>
<td>96</td>
<td>82.7</td>
<td>3 - 7</td>
</tr>
<tr>
<td>168</td>
<td>85.9</td>
<td>4 - 8</td>
</tr>
</tbody>
</table>
Fig. 28: Comparison of the rate of oxidation of AlN at 1000°C with the change in i) specific surface ii) the number of crystallites iii) the average crystallite size.
When considering aluminium nitride, the variation in oxidation rate is accompanied by a corresponding change in specific surface. The oxidation rate is accelerated over the first 50 per cent oxidation and becomes progressively slower as the reaction proceeds, see Fig. 28d. There is an initial increase in specific surface accompanied by a linear rate in oxidation which indicates that the alumina initially formed on the surface of the nitride splits off to give smaller crystallites. This splitting is due to the change in molar volume when converting to $\alpha$-alumina and the corresponding change in crystal lattice. A measure of the crystallite splitting is given in Fig. 28c, where a plot of $S'/S$ against time is given where $S'$ is the actual surface area. Molar volume change is not required (57) in determining this parameter. The extent of crystallite splitting is comparable with oxidation of titanium nitride (58), but far less than that of calcium nitride (46). The Tammann temperature, which is half the melting point of a compound in °K, are approximately 1340°K and 1200°K for aluminium nitride and alumina respectively, indicating that the sintering of $\alpha$-alumina would be more extensive at 1000°C. This extensive sintering of the $\alpha$-alumina tends to bind the un-oxidised nitride particles together. This is confirmed by the changes in average crystallite sizes deduced from the surface area measurements. Accordingly, the aggregate sizes indicates that the original nitride contains mainly single crystallites, and the oxidation results in the formation of aggregate s of 3 - 8μm (see Fig. 28) in which the individual crystallites appear to be over 0.5μm in the later stages of the oxidation. This is verified from Fig. 28f where the crystallite size of alumina at 60 per cent conversion is approximately.
Beyond 80 per cent conversion, the oxide layers sinters and prevents the gaseous diffusion of oxygen through the oxide layer and the process is controlled by a solid-state diffusion mechanism. The mechanism now involved is extremely complex and depends on the area and defect structure of the contact areas between the solid reactants and the product. As the reaction rate is relatively slower, the movement of the reaction interface is very slow. This may be due to the fact that there is a small contact area between the alumina and aluminium nitride at the interface brought about by the sintering of the alumina layer.

As there is a gradual reduction in the average crystallite size of aluminium nitride and a sudden increase in the average crystallite size of alumina after 70% conversion, the interfacial contact between the α-alumina and aluminium nitride would not be expected to be great, and hence the rate of solid state diffusion and rate of reaction is very slow.

By contrast, silicon nitride is more resistant to oxidation as can be seen from Fig. 29. At a 1000°C after 60 hours, 26% conversion to cristoballite is observed and the corresponding conversion to α-alumina is 93%. As oxidation occurs, the specific surface of silicon nitride initially decreases, as the α-cristoballite formed acts as a mineraliser. The Tamman temperature for silica is 720°C and the specific surface is observed to fall from 1.7 to below 0.2 m²g⁻¹ when one third of the silicon nitride is oxidised. The silicon nitride and silica thus tend to bond together. Consequently, the oxidation is increasingly controlled by solid state diffusion, and, as observed, the rate of oxidation is slower than in the case of aluminium nitride.
Fig. 29. Comparison of the oxidation of aluminium and silicon nitrides.
7. ibid., 1965, 3, 155.


CHAPTER V. Thermodynamical aspects of the formation and reactivity of aluminium nitride.

V.1 The formation of aluminium nitride

The reaction considered were:

\[
\begin{align*}
\text{Al} + \frac{1}{2}\text{N}_2 & \rightarrow \text{AlN} \\
\text{Al} + \text{NH}_3 & \rightarrow \text{AlN} + \frac{3}{2}\text{H}_2 \\
\frac{2}{3}\text{Al}_2\text{O}_3 + \frac{3}{2}\text{C} + \frac{1}{2}\text{N}_2 & \rightarrow \text{AlN} + \frac{3}{2}\text{Co} \\
\text{AlF}_3 + \text{NH}_3 & \rightarrow \text{AlN} + 3\text{HF} \\
\text{AlCl}_3 + \text{NH}_3 & \rightarrow \text{AlN} + 3\text{HCl} \\
\text{AlN} + \frac{3}{2}\text{O}_2 & \rightarrow \frac{2}{3}\text{Al}_2\text{O}_3 + \frac{1}{2}\text{N}_2
\end{align*}
\]

Thermodynamical data for the substances in the above reactions were obtained from the JANAF Thermo-chemical tables (7). This data is given in Appendix VIII.

Due to the lack of thermodynamical data for \((\text{NH}_4)_3\text{AlF}_6\) in the reaction

\[
(\text{NH}_4)_3\text{AlF}_6 + 4\text{NH}_3 \rightarrow \text{AlN} + 6\text{NH}_4^+ + 6\text{HF}
\]

the route \(\text{AlF}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{HF}\) was chosen and the discrepancies introduced by doing this will be discussed later. Also comparison is made with the formation of the nitride from the chloride analogue.

The free energy of elements and their compounds cannot be measured in absolute terms, but it is possible to observe the change in thermodynamical properties when a chemical reaction is induced. The change in standard free energy \(\Delta G^0\), gives an indication of the extent to which a reaction occurs and is related to the equilibrium constant \(K\) by the equation

\[
\Delta G^0_T = -RT\ln K \quad (i)
\]
For a chemical reaction, it is possible to plot the standard free energy change per unit mass as a function of temperature in degrees Kelvin. This plot is known as Ellingham Diagram. The main disadvantage of the Ellingham Diagram is that the free energy change as a function of temperature refer to standard states of the system, which are not realised in actual systems. For instance, the mutual solubility of the solid components may increase with temperature, and the gases are generally not in the ideal state. As a result a pressure correction must be applied and this can be calculated from the Van Hoff equation

\[ \Delta G_T^{\circ} = \Delta G_T^{\circ} + RT \left( \sum \ln a_{\text{products}} - \sum \ln a_{\text{reactants}} \right) \]  

(ii)

When \( \Delta G_T^{\circ} \) (the standard free energy change) is zero the equilibrium constant \( K \) is unity. Hence \( \Delta G_T^{\circ} \gg 0 \) would indicate that \( K \ll 1 \) and the product are present in low concentration at equilibrium. The condition \( \Delta G_T^{\circ} \ll 0 \) suggests that the reaction is feasible, and the more negative the value of \( \Delta G_T^{\circ} \) the more thermodynamically stable the product.

The condition \( \Delta G_T^{\circ} \ll 0 \) refers to a thermodynamically possible process. This process is such, that if there are no diffusion barriers or restrictive forces the reaction will proceed of its own accord. The free energy change is therefore important because if a process is thermodynamically feasible and in reality does not take place, then it is clear some restricting force is required to be overcome.

The free energy change is related to the heat of formation (\( \Delta H \)) by

\[ \Delta G = \Delta H - T \Delta S \]  

(iii)

where \( \Delta S \) is the change in entropy. It is necessary to calculate the heat of formation as this indicates whether an endothermic or exothermic reaction has taken place.
In the present work $\Delta G^0$ and $\Delta H^0$ were calculated from the equations

$$\Delta G^0 = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$  \hspace{1cm} (iv)$$

and

$$\Delta H^0 = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$  \hspace{1cm} (v)$$

V.1 The formation of aluminium nitride

V.1.i The formation from the elements

Due to the advances in the techniques of purifying metals, the formation of a compound from its elements has become increasingly important. Fig. 30 shows the relative stabilities of various nitrides formed from the element and nitrogen. It will be seen that aluminium nitride is expected to be more stable at elevated temperatures than calcium or magnesium nitrides, but not as stable as titanium nitride.

From Fig. 32 the free energy change for the reaction

$$\text{Al} + \frac{1}{2}\text{N}_2 \rightarrow \text{AlN} \hspace{1cm} (1)$$

is negative in the temperature region $0 - 2830^\circ\text{K}$, and hence the reaction is feasible within this temperature. However, it is concluded from the present work (see Chapter III), that at $500^\circ\text{C}$ ($773^\circ\text{K}$), which is well above the Tamman temperature ($330^\circ\text{C}$) for aluminium, that sintering of the metal film occurs. To overcome this barrier, the reaction can be carried out in the vapour phase. The reaction between aluminium and nitrogen is exothermic. The reaction will occur at temperatures less than the boiling point of aluminium ($2723^\circ\text{K}$) as is reported (1). These workers observed aluminium nitride at $1500^\circ\text{C}$ ($1773^\circ\text{K}$) where the calculated heat of reaction is $-78\text{ Kcal/mole}$. 

Above $2850^\circ\text{K}$, ($2577^\circ\text{C}$) $\Delta G^0_T$ is positive and the decomposition of aluminium nitride to its elements is expected to begin at this
Fig. 30. The free energy of formation of some nitrides.
temperature. This figure agrees with the reported values for the decomposition temperature of aluminium nitride (see Table 4).

The thermodynamic calculations agree well with Mah et al. (2), but disagree with those of Wicks and Block (3), (see Fig. 31).

For the reaction \( \text{Al} + \frac{3}{2}\text{N}_2(\text{g}) \rightarrow \text{AlN}(\text{s}) \) the operating free energy change will be given by

\[
\Delta G_T = \Delta G_T^0 - \frac{RT}{2} \ln P_{\text{N}_2}
\]

The formation of aluminium nitride by nitriding aluminium with ammonia is also considered:

\[
\text{Al} + \text{NH}_3 \rightarrow \text{AlN} + \frac{3}{2} \text{H}_2
\]  

(1a)

The change in entropy is very small and from Fig. 32 there is very little change in the slope for this reaction. Therefore, \( \Delta G_T^0 \) is approximately equal to the heat of formation \( \Delta H_T^0 \). The reaction to a first approximation is therefore independent of temperature. In Fig. 32 the plots for the nitridation of aluminium using nitrogen and ammonia intersect at 450°C. As the temperature increases \( \Delta G_T^0 \) for reaction (1) becomes less negative whereas \( \Delta G_T^0 \) for reaction (1a) remains approximately constant. It would therefore suggest that it is thermodynamically easier to form the nitride from ammonia at temperatures above 450°C. This point may allow the nitride to be prepared under the experimental conditions described in Chapter II, substituting ammonia for nitrogen and nitriding the aluminium film.

V.1,ii The formation from the Serpek reaction

When considering the Serpek reaction to form 1 mole of aluminium nitride

\[
\text{Al}_2\text{O}_3(\text{s}) + \frac{3}{2}\text{C}(\text{s}) + \frac{1}{2}\text{N}_2(\text{g}) \rightarrow \text{AlN}(\text{s}) + \frac{3}{2}\text{CO}(\text{g})
\]  

(3)
Fig. 31. A comparison of the free energy of formation of AlN from its elements.
and assuming the solid components to be in the standard state, the 
equilibrium constant $K_p$ is given by

$$K_p = \frac{P_{CO}}{P_{N2}^{3/2}}$$

From Fig. 32 $\Delta G^o_T = 0$ is at 1980$^o$K ($\sim 1700^o$C).

At atmosphere pressure $P_{CO} + P_{N2} = 1$; suppose $P_{CO} = \alpha$.

Hence $K_p = \frac{\alpha^{3/2}}{(1-\alpha)^{3/2}}$

$$\ln K_p = \frac{1}{2} \log \frac{\alpha^3}{1-\alpha}$$

Thus from the calculations for $\Delta G^o_T$ for this reaction, $\ln K_p$ is 
derived by equation (1).

When $\ln K_p = 0$, $\Delta G = 0$ and $\alpha^3 + \alpha - 1 = 0$.

Consequently, from Fig. 33 the required root of $\alpha$ is 0.68. Hence the 
equilibrium concentration of carbon monoxide is 68% at 1 atmos. total 
pressure. From the previous work (see Chapter III), the results of 
Frankel and Read (4) are in good agreement with this value. At 1900$^o$K 
($1627^o$C) the carbon monoxide equilibrium concentration is 51%. Therefore 
for the temperature range 1900-1980$^o$K a nitrogen concentration of 32-49% 
is required in the reaction. From Fig. 32 $\Delta G^o_T$ is negative above 1980$^o$K 
and the reaction is thermodynamically possible above this temperature at 
lower nitrogen concentrations. The reaction is endothermic, and at 
2000$^o$K the heat of formation is of the order of 80 Kcals/mole.

The working free energy is given by:

$$\Delta G = \Delta G^o_T - \frac{3}{2} RT \ln P_{CO} + \frac{3}{2} RT \ln P_{N2}$$

\[= 176\]
Fig. 22: Free energy of formation of AlN from various methods of preparation.
It must be remembered that the above calculations were made using ideal conditions. However, as previously discussed, side reactions such as

\[ \text{AlN} + \text{C} \rightleftharpoons \text{AlCN} \]

may occur and ideal conditions may not be realised at elevated temperatures. An examination of the reaction to form the nitride from aluminium carbide and nitrogen would thus seem profitable. The reaction is proposed as

\[ \frac{1}{2} \text{Al}_2\text{C}_3 + \frac{1}{2}\text{N}_2 \rightarrow \text{AlN} + \frac{3}{2}\text{C} \quad (7) \]

From Fig. 32 the reaction is possible at all temperatures in the considered temperature range, but above 2100°C aluminium carbide sublimes. The reaction is weakly exothermic as \( \Delta H^\circ_{298} \) is -4.22 Kcals/mole.

It has been suggested (5) that aluminium carbide is initially formed in the Serpek reaction by the reduction of alumina. The proposed equation is

\[ \frac{1}{2} \text{Al}_2\text{O}_3 + \frac{9}{4}\text{C} \rightarrow \frac{1}{3}\text{Al}_2\text{C}_3 + \frac{3}{2}\text{CO} \quad (8) \]

and subsequent conversion to aluminium nitride is suggested by reaction (7). Reaction (8) is thermodynamically unfavourable as \( \Delta G^\circ_T \) is positive in the temperature range considered (see Table 28). The formation of the nitride via the carbide is therefore not thermodynamically sound. The formation of aluminium nitride by the Serpek reaction must be by the reduction of alumina with carbon in the presence of nitrogen without any intermediate reactions occurring.

V.1.iii. The formation from the aluminium halide derivatives

In the reaction of aluminium fluoride with gaseous ammonia to form the nitride
Table 28

\( \frac{1}{2} \text{Al}_2\text{O}_3 + \frac{9}{4} \text{C} \rightarrow \frac{1}{2} \text{Al}_4\text{C}_3 + \frac{3}{2} \text{Co} \)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>ΔG°^\circ \text{)} (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+ 145.996</td>
</tr>
<tr>
<td>500</td>
<td>+ 114.733</td>
</tr>
<tr>
<td>1000</td>
<td>+ 81.366</td>
</tr>
<tr>
<td>1500</td>
<td>+ 48.993</td>
</tr>
<tr>
<td>2000</td>
<td>+ 17.438</td>
</tr>
</tbody>
</table>
The equilibrium constant $K_p$ is given by

$$K_p = \frac{P_{HF}}{P_{NH_3}}$$  \hspace{1cm} (4a)

The free energy change is $\Delta G^\circ_T = 0$ at $1500^\circ K$ from Fig. 32; a similar gaseous relationship as with the Serpek reaction is shown by equation 4a and an equilibrium concentration of 61% HF would be expected at $1500^\circ K$. However, the reaction was experimentally observed at $960^\circ C$ (1233°K) and the calculated equilibrium constants at $1200^\circ K$ and $1300^\circ K$ were $3.814 \times 10^{-4}$ and $8.269 \times 10^{-3}$ respectively. The concentration of HF at $1200^\circ K$ and $1300^\circ K$ assuming ideal conditions were 7.1% and 18.8% respectively.

The reaction takes place at $960^\circ C$ although the free energy change is $+17$ Kcals/mole, and the conditions thermodynamically unfavourable. But there is an appreciable partial pressure of HF. The HF is swept away by excess ammonia driving the reaction towards nitride formation.

In practice the reactant was ammonium hexafluoroaluminate and the reaction is

$$(NH_3)_3AlF_6 + 4NH_3 \rightarrow AlN + 6NH_4F$$

At $960^\circ C$ the ammonium fluoride exists as its gaseous components ammonia and gaseous hydrofluoric acid and the ammonium hexafluoroaluminate is completely decomposed to aluminium fluoride, ammonia, and gaseous hydrofluoric acid. The conditions are therefore the same as in equation (4), except that aluminium fluoride may be present for reaction in the meta stable form. In this case, chemical equilibrium will be further distorted due to the presence of the hydrofluoric acid gas formed from...
ammonium fluoride and the reverse of reaction (4) is favoured. However, in the presence of flowing ammonia the HF formed will be carried away and in reaction (4) the forward case is very much favoured. This is observed experimentally and the effect of increasing the ammonia flow rate is to increase the amount of nitride formed per unit time until a rate of some 50 ccs per min is observed (see Fig. 7) after which the amount of nitride formed is constant. One possible explanation for this is that aluminium fluoride has the highest lattice energy of the Group III halides (1500 k.cal/mole), due to the nature of its chemical bonding. The lattice energy decreases to 1120 kcal/mole for aluminium iodide. The reaction is endothermic and is favoured by an open system.

By comparison the reaction between aluminium chloride and ammonia to form the nitride is thermodynamically more favourable at temperatures greater than 560°K where $\Delta G^0$ for the reaction is zero (see Fig. 32). The nitride is reported to be formed from the chloride at temperatures in the region of 1000°C (6), but the adduct monoamino aluminium chloride is first formed and decomposed by direct heating in ammonia. The monoammoniates are also formed from the iodide, bromide, and boron trifluoride but no adduct is formed with aluminium fluoride (see Chapter III).

The heat of reaction is less endothermic for the formation of the nitride from the chloride than the fluoride. A smaller heat input is required and the reaction can be carried out best at lower temperatures.

V.2 The reactivity of aluminium nitride

The oxidation of aluminium nitride is thermodynamically considered and compared with the oxidation of silicon nitride. Due to lack of
thermodynamic data on the hydroxides of aluminium the reaction

$$\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NH}_3$$
could not be considered.

V.2.1 The oxidation of aluminium and silicon nitrides

The free energy change for the reaction

$$\text{AlN} + \frac{3}{2} \text{O}_2 \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3 + \frac{3}{2}\text{N}_2$$
is negative irrespective of temperature (see Fig. 34). The oxidation is reported to begin at temperatures as low as 600°C (6). In the present study the nitride did not appreciable oxidise until 800°C. The equilibrium constant is given by

$$K_p = P_{N_2}^{\frac{3}{2}} = \frac{1}{\alpha^3}$$

where $$\alpha = P_{O_2}$$.

At 1100°K $$K_p$$ is 1.008 x 10^{22}.

The concentration of nitrogen present in the gas phase at 1100°K at equilibrium is therefore infenitesimal and the reaction is irreversible.

Although the oxidation is thermodynamically favourable the boundary conditions and the percentage oxide formed is dependant on the diffusion of the Al^{3+} ions whereas for reaction (4) the formation of the products is determined by the thermodynamics of the system.

Silicon nitride is more resistant to oxidation than aluminium nitride (see Fig. 34); Cristoballite and tridymite are formed when silicon nitride is heated (see Table 26). The free energy of formation of cristoballite, tridymite and quartz from the elements differ by some 50 cal in the temperature range 298 - 2000°K (3). For the reaction

$$\text{Si}_3\text{N}_4 + 3\text{O}_2 \rightarrow 2\text{SiO}_2 + 2\text{N}_2$$
Fig. 34. A comparison of the free energy of formation of α-alumina and silica from the respective nitrides.
the equilibrium constant $K_p$ is given by

$$K_p = \frac{P_{N_2}^2}{P_{O_2}^3}$$

$$\Rightarrow \frac{(1-\alpha)^2}{\alpha^3}$$

At 1100°K $K_p = 2.28 \times 10^{8}$ and hence the amount of nitrogen present in the gas at equilibrium is effectively zero.

A comparison of the thermodynamic stabilities of these nitrides with oxygen show that per mole of nitride, the silicon nitride is less stable, but this is not realised in practice, although a reaction is energetically feasible, the kinetics of the process may not be favourable as pointed out in the above examples.


Aluminium nitride is being successfully prepared from the thermal decomposition of the ammonium hexafluoroaluminate in ammonia. The reaction is essentially between α-aluminium fluoride and ammonia and takes place below 1000°C. Though the reaction is endothermic and the thermodynamic conditions are unfavourable, the process can be carried out without difficulty and produces material of high purity. The reaction between nitrogen and aluminium is exothermic and the conditions are thermodynamically favourable in theory, but in practice it is found that the reaction does not take place satisfactorily even on these films at temperatures up to the melting point of aluminium. It appears that a protective layer is formed and from the literature the effective reaction is a gas phase reaction between aluminium vapour and nitrogen requiring temperatures around 1600°C. The Serpek reaction is endothermic and takes place readily at about the same temperature, but it is difficult to obtain products of high purity.

Thus it seems that the preparation from fluoride and ammonia has certain technical advantages over other processes.

The work has shown that even in a finely divided form, aluminium nitride had reasonable resistance to oxidation at high temperatures. There does not seem to be any obstacles to making sintered materials, although this was not attempted in the present work. The presence of fluoride in small amounts might actually assist in the process.

The reactivity of the nitride is determined by the particle and crystallite sizes and the available surface. The nitride is observed to hydrolyse more in liquid water than in steam. This may be a valid
point when using the fabricated material at elevated temperatures in moist atmospheres. The oxidation kinetics of aluminium nitride are initially linear changing to parabolic, and are controlled by aluminium ion diffusion through the oxide layer. As is common with chromium nitride, a break down in the parabolic kinetics is observed. This is possibly due to a pressure build up of nitrogen in the voids of the reaction interface.

Aluminium nitride, however, is more reactive than silicon nitride, but it is suggested from a comparison of the mechanical properties that aluminium nitride has definite possible use as a ceramic material. However, it appears that additions to the nitride must be made before the optimum sintering conditions are realised. The effect of these additives on the reactivity of nitride might prove a useful study.

The low density of $\gamma$-aluminium fluoride which has been confirmed by several density measurements as in accordance with the tetragonal cell suggested in the present work, poses a problem in structural chemistry which requires further investigation. Likewise, the inability of either the $\alpha$ or $\gamma$-aluminium fluoride to form compounds with ammonia or water, although the latter are known to exist as $\text{AlF}_3\cdot\text{H}_2\text{O}$ requires further investigation.

The formation of other nitrides by the fluoride route would seem to offer similar advantages as in the case of aluminium. In particular, ammonium fluorosilicate, which is readily obtained in a pure form and which volatilises completely on heating in the form of silicon tetrafluoride, ammonia and gaseous hydrofluoric acid might be expected to form silicon nitride at about the same temperature, and this would offer an alternative route to this material.
APPENDIX I

The preparations of ammonium hexafluoroaluminate and ammonium tetrafluoroaluminate.

Condumetric study of the reaction between aluminium fluoride and ammonium fluoride.
The preparation of ammonium hexafluoroaluminate

Dissolve aluminium foil (99.999%) (40 g) in 40% hydrofluoric acid (250 mls). Filter the thick grey saturated solutions. Agglomerates of aluminium fluoride trihydrate ($\alpha - \text{AlF}_3 \cdot 3\text{H}_2\text{O}$) separate out and these were immediately redissolved in distilled water. 1N ammonium fluoride solution is added until a white precipitate is formed. The precipitate was dried under vacuum over potassium hydroxide pellets. The product was analysed as ammonium hexafluoroaluminate with no evidence for the formation of ammonium tetrafluoroaluminate. The aluminium fluoride-ammonium fluoride-water system was further studied conductimetrically.

The preparation of ammonium tetrafluoroaluminate

To prepare fluoboric acid 90 mls of 40% hydrofluoric acid were added to 40 grams of boric acid A.R with stirring until the boric acid crystals were completely dissolved. To the solution was added the stoichiometric proportions of aluminium hydroxide and ammonia solution. The mixture was heated at 75°C for 1 hour and left to cool overnight. Crystals were observed in the presence of a white residue. The crystals were separated and the aluminium hydroxide impurities removed by redissolving the crystals with the entrained hydroxide in water. The hydroxide was separated by filtering and the filtrate was left to recrystallize. The resulting crystalline paste was identified as ammonium tetrafluoroaluminate.

Condumetric study of the reaction between aluminium fluoride and ammonium fluoride

100 mls of 1N aluminium fluoride, prepared as previously described, was placed in a 400 ml plastic beaker. The beaker was supported in a
water bath thermostatically maintained at 25°C. The condumetric cell consisted of two small platinum plates mounted on thin glass capillary tubing, which were kept at a standard distance apart by fixing in circular polythene block. The connection between the bridge and the platinum electrodes was made across a mercury bridge. The dip cell was placed in the aluminium fluoride solution and a conductivity reading taken. 5 ml aliquots of 1N NH₄F were added to the solution from a burette, the solution being constantly stirred. Readings were taken after each aliquot was added and a graph of amount of ammonium fluoride added against the resultant conductance of the solution was drawn (see Fig. 1). From Fig. 1 a plateau in the curve corresponding to a mole ratio of aluminium fluoride to ammonium fluoride of 1 to 1 is noted (point A), and is therefore probably due to the precipitation of ammonium tetrafluoroaluminate although x-ray analysis did not show any formation of this phase. At point B, ammonium hexafluoroaluminate starts to precipitate. No observation of a pentafluoroaluminate was recorded, as has been noted in the corresponding potassium fluoride-aluminium fluoride (1) and gallium fluoride-ammonium fluoride (2) systems.
Fig. 1

APPENDIX II

Methods of Chemical Analysis.
Accurate weighing technique using a microbalance

A small nickel crucible was heated over a mekker burner and was adjusted at intervals so that all the crucible came into contact with the hottest part of the flame, which was approximately 1000°C. After 10 minutes the crucible was transferred with nickel tongs to a dessicator. The dessicator was placed in the balance room and allowed to cool to room temperature in 30 minutes. The crucible was placed on the balance using plastic tipped tweezers and left for 10 minutes to reduce buoyancy effects to a minimum. The weight was recorded and the process repeated until a constant weight was observed. At this juncture, the specimen for analysis was introduced into the crucible and hence the weight of specimen was found.

Determination of ammonia in ammonium hexafluoroaluminate

The estimation of ammonia was completed using a Kjeldahl apparatus. The reagents used in the technique were 40% sodium hydroxide, 2% boric acid, 0.1N sulphuric acid.

An accurately weighed milligram amount of ammonium hexafluoroaluminate (50mg) was dissolved in distilled water and made up to 100 ml in a volumetric flask.

5 ml of the solution was pipetted into the distillation unit and washed through with 5 mls (2 x 2.5) of distilled water. 5 mls of 40% sodium hydroxide was added and steam introduced into the distillation chamber. The distillate was collected in 10 mls of 2% boric acid with 4 drops of the mixed bromo-cresol green/methyl red indicator and titrated against N/100 sulphuric acid.
The percentage ammonia was determined from the equation below:

\[ 5 \times \text{normality} = T \times \text{Titer (T)} \times \text{Normality (0.01)} \]

Normality = \( \frac{T \times 0.01}{5} \)

Conc. = \( \frac{T \times 0.01 \times 17.01 \text{ g/l}}{5} \)

\[ \% \text{NH}_3 = \frac{T \times 0.01 \times 17.01}{5 \times 20 \text{ W}} \]

where \( W \) = weight of ammonium salt dissolved in 50 mls.

Ammonium sulphate was used as a standard in the technique.

**Determination of the nitrogen content in aluminium nitride**

The specimen to be analysed was placed in a 6 inch side-arm pyrex test tube. A few turnings of fine copper tubing with water passing through were placed around the neck of the test tube to cool it. Potassium hydroxide pellets were placed on top of the specimen.

The tube was surrounded by an open ended protective glass cylinder. When heated to avoid vigorous splashing of the molten hydroxide, a pyrex glass stopper circular in form, was mounted a few millimetres from the top of the pellets. A trap was placed before the test tube. Prior to this was placed a dreschel bottle containing distilled water. Immediately after the test tube was placed a quickfit trap. This trap was connected to a sintered glass inlet which was lowered into a 500 ml conical flask.

**Preparation of mixed indicator**

0.1 grams of bromocresol green and methyl red were carefully weighed out and respectively dissolved in two 100 ml portions of 95% ethanol. The solutions were mixed in a 5 to 1 ratio of bromocresol green to methyl red.
Method

0.1 - 0.4 grams of nitride were accurately weighed and placed in the side-arm test tube. 10 grams of A.R sodium hydroxide pellets were placed on top of the nitride. 100 ml of boric acid and 1 ml of mixed indicator were placed in the trap prior to the test tube, to ensure that any feedback of the ammonia would be accounted for. A similar portion of reagents were added to the conical flask. Argon (B.O.C.) was passed through the system at a rate of 60-70 bubbles a minute for 3-5 minutes to expel the air in the system. The solids in the test tube were gently heated with a mekker burner placed under the test tube. Any liquid that condensed at the neck of the tube was removed with a small bunsen flame. The ammoniacal liquid was carried into the quickfit trap, where it condensed. When all the liquid had condensed, the trap was gently warmed and the ammonia collected in the 2% boric acid solution in the conical flask. The resulting solution was titrated against 0.1N sulphuric acid and the nitrogen content determined in the normal manner.

Determination of fluorine

The fact that aluminium interferes in the recovery of fluoride is well known. However, when the aluminium ion to fluoride ion ratio is 100, no interference is observed using the Willard-Winter distillation procedure. (1) When this ratio is increased to 500 there is a 5 to 10% negative bias (2). On the basis of wt ratio a 4:1 ratio is tolerable (3).

The presence of these two elements together will also interfere with the recovery of aluminium. Even small amounts of fluoride interfere in the determination of aluminium colorimetrically (4), and the formation of the AlF$_6^{3-}$ ion hinders the estimation of aluminium by flame photometry.
A spectroscopic method has been reported for the determination of aluminium in the presence of fluoride whereby the addition of boric acid stabilises the fluoride by forming the \( \text{BF}_4^- \) ion. However, only 47 to 79% recovery is reported (6).

For the determination of the components in the same compound, methods have been suggested such as wide line nuclear magnetic resonance (7), and electron spectroscopy (8).

**Determination of fluoride in ammonium hexafluoroaluminate**

From the above methods, for aluminium present in ammonium hexafluoroaluminate the Willard-Winter method adopted for the analysis of fluoride ions, using potassium cryolite as a standard. The method is based on the removal of fluoride by steam distillation, and subsequent titration against thorium nitrate solution using an alizarin complex as an indicator and a mono-chlo-acetic acid buffer.

**Standardisation of the thorium nitrate solution**

2.211 grams of sodium fluoride were dissolved in distilled water and made up to a litre in a volumetric flask. The buffer solution was adjusted to pH 3, using \( \text{N}/10 \) sodium hydroxide. 10 ml of the sodium fluoride solution was added to 25 mls of distilled water. 10 drops of indicator were slowly added. 10 mls of absolute alcohol were added, generating a pink colouration of the solution. This pink colour was discharged by adding one or two drops of deci-normal hydrochloric acid. Finally, 1 ml of buffer solution adjusted to pH 3 was added, and the solution titrated against thorium nitrate solution using a blank titration of distilled water.

\[
\text{Test Titration (T) - Blank Titration (B)} = 10 \times 0.053
\]

\[
1 \text{ ml of thorium nitrate solution} = 10 \times 0.053
\]

\[
\frac{T - B}{(T - B)} = \frac{198}{198}
\]
Method

The distillation was carried out using a quickfit micro-apparatus. An accurately weighed micro-quantity of the complex was placed in a three-necked pear shaped flask. 10 ml and 5 ml of 70% phosphoric acid and perchloric acid respectively were slowly pipetted into the flask, excess glass wool was added and the flask placed in a heating mantle. The temperature was raised until a 100°C, at which the quantity of water present distilled over. After a few minutes, the temperature began to rise again and was maintained at a 140-150°C by running in distilled water from the dropping flask as required. 50-75 mls of distillate for 50 milligrams of solid were collected in approximately 2 hours.

The distillate was made up to a 100 mls in a volumetric flask, 25 mls were taken and the fluoride content of ammonium hexafluoroaluminate found by titrating against thorium nitrate solution.

The chemical analysis of aluminium fluoride

The determination of fluoride ions using the Willard-Winter distillation technique, was found to be unsuccessful with aluminium fluoride. Aluminium has been determined in the present study by decomposition in concentrated hydrochloric acid and subsequent estimation as aluminium oxinate.

One method is to fuse the sample with alkali carbonate silica mixture in fixed proportions, whereby fluoride is converted to the alkali metal fluoride (74).

The fluoride can be subsequently determined by passing the solution through an ion exchange column to form hydrofluoric acid. As there will be alkali carbonates and alkali silicates present the formation of carbon dioxide and silicic acid is expected, and hence the effluent is likely
to contain hydrofluosilicic acid. Calcium chloride can be added to
convert this to hydrochloric acid which is titrated hot against sodium
hydroxide using a standard indicator. The operation technique is time
consuming, varied, and tedious. The results reported using this
technique are low.

A method which is similar in principle but less varied in
technique, is described by Bognor and Nagy (9). This method was used
to determine fluoride in aluminium fluoride.

Preparation of reagents used.

Potassium sodium carbonate

A.R grade sodium and potassium carbonate in the stoichiometric
proportions were blended together in a ball mill for several hours.

Silica powder

Finely divided silica powder was roasted in a furnace to remove
any water and cooled to room temperature and kept in a dessicator.

1% lead chloride solution

5 grams of lead chloride were accurately weighed out and dissolved
by gently heating in distilled water in a 400 ml conical flask. The
solution was cooled, transferred with washings to a 500 ml volumetric
flask, and made up to the mark.

Saturated lead chloride solution

The solubility per 100 ml of water of lead chloride is 1.49 grams.
An amount greater than this figure was dissolved in a 100 ml of distilled
water to give a saturated lead chloride solution.

1/10 mercuric nitrate

50 grams of mercury (99.98% pure) were weighed out in a conical
flask. 125 mls of distilled water were added and the solution gently
heated over a mekker burner in a fume cupboard. A few drops of concentrated nitric acid were intermittently added carefully, until the mercury had dissolved. The solution was boiled to drive off the nitrous fumes, cooled and made up to 500 mls in a volumetric flask. 50 mls of the mercuric nitrate solution were diluted to 500 mls to give an approximate \( \frac{N}{10} \) solution.

**0.1% erioglaucine**

0.1 grams of erioglaucine were dissolved in distilled water and made up to the mark in a 100 ml volumetric flask.

25 mls of \( \frac{N}{10} \) ammonium thiocyanate were diluted to 150-200 ml with distilled water and 10 ml of the dilute nitric acid and 2 ml of the iron alum solution were added. The solution was titrated against the mercuric nitrate solution, until the end point of the red colour of ferric thiocyanate just disappears, leaving the solution water white. The normality of the mercuric nitrate solution was determined as 0.09275 N.

**Method**

0.1 grams of \( \alpha \)-aluminium fluoride were accurately weighed using the micro-weighing technique. The fluoride was thoroughly mixed with 0.3 grams of roasted silica powder and 1.5 grams of potassium sodium carbonate, and slowly fused in a platinum crucible at 700°C. After 15 minutes the fusion mixture was cooled until the dispersed melt was nearly solid and then the crucible was placed in cold water. The melt was transferred by inverting the crucible and gently tapping the bottom until the solid fell into a 200 ml beaker containing 50 ml of hot water. Any remaining solid lumps were removed with a rubber policeman and a few mls of hot water were added to the crucible to ensure complete removal of the melt. The slurry was left to stand for 2 hours.
The suspension was filtered into a 250 ml volumetric flask and the filtrate made up to the mark. 50 ml of the filtrate were neutralised in a 200 ml beaker with hydrochloric acid until red with methyl orange indicator. The neutral solution was heated to 70°C on a water bath, and 50 ml of 1% lead chloride solution were added with stirring. The solution was re-heated to 70°C. This solution which now contained a precipitate was neutralised with 0.2N sodium hydroxide solution until a yellow colour just appears. The solution was allowed to stand for 24 hours.

The precipitate was collected on a G-3 sintered glass filter and washed three times with 10 ml of saturated lead chloride solution, and twice with 10 ml of 50% ethanol. The precipitate was then dissolved in 5 ml of hot 4.0 N sodium hydroxide solution. The solution was cooled and 10 ml of 1.84 s.g. sulphuric acid were carefully added. 1 drop of potassium ferricyanide and 0.3 ml of 0.1% erioglaucine indicator were added and the cold solution was titrated carefully with the 0.09275 N mercuric nitrate solution until the end point, due to the colour change from green-yellow to carnation red, was established. The last few drops are added slowly as the colour change is slow. Throughout the operation undue dilution was avoided.

**Determination of aluminium content**

A solution containing a known weight of the particular compound was made up to 250 mls in a volumetric flask. 25 mls of distilled water were added to 5 mls of the above solution. The solution was heated to 60°C over a bunsen flame and 36 mls of a 2% solution of 8-hydroxy-quinoline was added. To complete the precipitation of the aluminium present, approximately 4 grams of ammonium acetate dissolved in a little
water was added. The solution was left to cool and a yellow flocculant precipitate was observed.

The precipitate was filtered through a 50 ml G4 filter beaker and dried at 120°C overnight. As the beaker was weighed before and after filtering, the weight of aluminium oxinate is known and hence the weight of aluminium can be found from the fact that 1 mg of aluminium oxalate contains 0.0587 mg of aluminium. Hence the percentage aluminium in the hexafluoroaluminate is given by:

\[
\frac{0.0587 \times W}{X} \times 100\%
\]

where \( X \) = weight of oxinate precipitate

\( W \) = original weight of ammonium hexafluoroaluminate.

The standard for the determination was potash alum.
APPENDIX III

Computer program (NGITO) in Fortran IV for the IBM 1130 - Estimation of crystallographic parameters.
APPENDIX IV

Computer program (PODH) in Fortran IV for I.B.M. 1130 - Estimation of surface areas.
// JOB
LOG DRIVE CART SPEC CART AVAILABLE PHIL DRIVE
COMMON COMMON COMMON COMMON
V7 V6 ACTUAL PK CONFIG PK

// FOR
*LIST SOURCE PROGRAM
*LOCUS(DISC,CARD,1132,PRINTER,TYPewriter,KEYBOARD,PLOTTER)
ONE WORD INTEGERS
G=WEIGHT NITROGEN ABSORBED, W=WEIGHT OF SAMPLE, A=ATMOSPHERIC
PRESSURE, P=PRESSURE READ, G=WEIGHT OF NITROGEN ABSORBED PER GRAM
OF SAMPLE C=SATURATION VAPOUR PRESSURE

THIS PROGRAM PLOTS THE OBSERVATIONS FOR X AND Y AND ALSO THE
CALCULATED REGRESSION LINE FOR EACH SET OF INPUT DATA

THE DATA IS READ IN THE FOLLOWING ORDER:
FIRST CARD: X AND Y IN THAT ORDER IN FORMAT 2F8.5
SECOND CARD: A IN FORMAT 14
THIRD CARD: AT AND W IN FORMAT F10.2 AND F12.4
THEN READ G AND P ONE PAIR PER CARD IN FORMAT F12.5 AND F10.2
THESE CARDS CONSTITUTE A SET
THE FINAL CARD MUST BE BLANK
APPENDIX V

Computer program (NICKINETIC) in Fortran IV for I.B.M. 1130 -

Estimation of kinetic parameters.
C

Oxidation of Aln at 1010C unmilled

Dimension AN(50)

NREAD = 2

NWRITE = 3

Write(NWRITE, 107)


READ(NREAD, 95) N

READ(NREAD, 96) W

READ(NREAD, 97)(AN(I), I = 1, N)

DO 10 I = 1, N

P = (AN(I) - 10.2439*W)

F = 1 - P

CALL CUBRT(F, X)

Y = 1 - X

A = SQRt(F)

D = 0.5*(F - 0.19)

E = F + S

CALL CUBRT(E, B)

Z = (B - X)**2

T = 0.5*Y*(1 - (F**2))

G = ALOG(F)

Q = ALOG(P/F)

V = 0.5*(1 - (F**2)/(F**2))

WRITE(NWRITE, 98) X, Y, A, D, Z, R, G, Q, V

10 CONTINUE

95 FORMAT (I2)

96 FORMAT (F6.4)

97 FORMAT (F6.4)

98 FORMAT (3(F6.4), 3(F9.7, 5X), F6.4, 5X, F9.7, 5X, F12.10)

CALL EXIT

END

Features supported

One word integers

IOCS

Core requirements for

Common 0 variables 142 program 306

End of compilation

// XEO
APPENDIX VI

Reprint - The formation and reactivity of nitrides, Part III.
FORMATION AND REACTIVITY OF NITRIDES

III.* BORON, ALUMINIUM AND SILICON NITRIDES

By N. G. COLES, D. R. GLASSON and S. A. A. JAYAWEERA

The reactivities of boron, aluminium and silicon nitrides have been compared. Samples of these nitrides have been converted to oxides by being calcined in air. Changes in phase composition, surface area, crystallite and aggregate sizes have been correlated with oxidation time and temperature.

Crystallites of alumina, a-Al2O3, split off from the remaining aluminium nitride before they sinter and inhibit further oxidation. The diboron trioxide, B2O3, and silica, SiO2 (α-cristobalite), immediately act as mineralisers for the remaining boron and silicon nitrides, and progressively retard the oxidations.

Introduction

The formation, hydrolysis and oxidation of the ionic calcium and magnesium nitrides, Ca3N2 and Mg3N2, have been described in Part II.* More recently, the authors have found that zinc and cadmium films do not nitride in nitrogen or ammonia at temperatures below their m.p., 420° and 320° respectively. The nitrides, Zn3N2 and Cd3N2, are formed only at appreciable rates at temperatures above 600°. They are hydrolysed rapidly to ammonia-soluble complexes, M(NH2)3(OH)2, where x ≤ 4 for M = Zn or Cd.† Comparison of the molecular susceptibilities of Mg, Zn and Cd nitrides shows that the polarising action of the metal ion decreases from Mg to Zn to Cd. Nitrides in Group III (B, Al, Ga) and Group IV (Si, Sn) show covalent character and are more resistant to hydrolysis and oxidation.‡ In the present paper, the reactivities of the covalent nitrides of B, Al and Si are compared with one another.

Thermodynamics of nitride formation and the relation between bonding and crystal structure have been discussed in Part I.† Boron nitride is more chemically reactive than nitrides of Al and Si.§ Finely divided BN is hydrolysed slowly by hot water and dissolves completely in boiling 20% NaOH within 30 min. Dissolution is perceptible also at 20° in acids and alkalis.¶ Reactions between aluminium nitride or silicon nitride and hot water are inhibited by coatings of hydrated alumina or silica on the outside of the material. Hydrolysis is generally slow in mineral acids and alkalis, but there is complete dissolution of aluminium nitride in 30% Na2CO3 at 80° and of silicon nitride in boiling HF. All of these nitrides are oxidised in air at higher temperatures. Boron nitride powder oxidises appreciably above 800°, but not above 700°. The oxidised surface is then resistant to further oxidation. Alumina and silica are obtained as stable oxides.

Experimental

Procedure

Separate portions of powdered nitrides of boron, aluminium and silicon (Alfa Inorganics Inc.) were calcined in air for various times at fixed temperatures. Oxidation rates were estimated from weight changes of the samples during calcination. The cooled products were outgassed at 200° in vacuo before their specific surfaces were determined by B.E.T. procedureι from nitrogen isotherms recorded at −183° on an electrical sorption balance.κ,λ The deduced average crystallite sizes (equivalent spherical diameters) were compared with particle size ranges determined by optical or electron microscopy.

Phase composition identification

Samples were examined for phase composition and crystallinity using an X-ray powder camera and a Solus-Schall X-ray diffractometer with Geiger counter and Panax rate-meter. Certain samples were further examined by optical and electron microscopes (Philips EM-100).

Results

Fig. 1 (a), (b) and (c) shows the overall variations in specific surface, S, and average crystallite size during the conversion of aluminium nitride to alumina at 1000° in air. These are compared with oxidation rates Fig. 1 (d), changes in the number of crystallites Fig. 1 (c), and average crystallite sizes of the individual unchanged AlN and its oxidation product, α-Al2O3, Fig. 1 (f). Corresponding variations in the aggregate sizes are summarised in Table I.

Fig. 1. Calcination of aluminium nitride in air at 1000°C

In (b), broken curve represents actual surface area (S) for an initial one-gramme sample of aluminium nitride

*Part II: J. appl. Chem., Lond., 1968, 18, 77

TABLE 1

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Conversion, %</th>
<th>Range of aggregate size, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1—2</td>
</tr>
<tr>
<td>5</td>
<td>51.3</td>
<td>3—5</td>
</tr>
<tr>
<td>24</td>
<td>67.7</td>
<td>3—6</td>
</tr>
<tr>
<td>96</td>
<td>82.7</td>
<td>3—7</td>
</tr>
<tr>
<td>168</td>
<td>85.9</td>
<td>4—8</td>
</tr>
</tbody>
</table>

The samples of boron nitride and silicon nitride had specific surfaces, \( S_0 = 11.5 \) and \( 1.7 \) m\(^2\) g\(^{-1}\); average crystallite sizes, 0.23 and 1.1 μm respectively. They oxidised in air at 800° and 1000—1200°; rates are shown in Fig. 2, where they are compared with those for aluminium nitride at 900—1100°. Electron micrographs of the nitrides and their oxidation products are presented in Figs 3 and 4.

Discussion

Oxidation of aluminium nitride

Aluminium nitride, AlN, is converted to α-Al\(_2\)O\(_3\) at 1000 in air. X-ray powder photographs and diffractometer traces give no indications of any oxynitrides being formed at temperatures between 800—1100°. The oxidation at 1000°, Fig. 1 (d), accelerates somewhat during the conversion of the first 50% of the nitride, and then becomes progressively

Fig. 2. Calcination of boron, silicon and aluminium nitrides in air at different temperatures
(a) ○ boron nitride at 800° c
(b) □ silicon nitride at 1000° c, ○ at 1200° c
(c) and (d) □ aluminium nitride at 900° c, ○ at 1000° c and △ at 1100° c
(Only a representative selection of points is shown for the sake of clarity)

Fig. 3. Electron micrographs of boron nitride calcined in air at 800° c
(a) and (b) after 24 h, (c) 48 h, (d) 96 h, and (e) and (f) 144 h

slower especially after about 80% conversion. These variations in rate are accompanied by corresponding increases and decreases in specific surface, $S$, in Fig. 1 (a) and (b), and in actual surface area, $S^*$, for an initial 1 g-sample of AIN illustrated by the broken-lined curve in Fig. 1 (b). Consequently, the average crystallite size of the material at first decreases and later increases, Fig. 1 (c).

Several factors may contribute to the detailed shape of the initial rate curve of an oxidation isotherm, e.g. decreases in surface heterogeneity as the reaction proceeds, changes in specific surface or in local surface temperature due to heat of reaction, solubility effects, impurity concentrations, possible changes in oxide composition and electrical double layer effects. In accordance with the oxidation of coarser samples of aluminium nitride, a specific amount of oxide must be formed (depending on the specific surface of the sample) before a coherent alumina layer can be produced. Meanwhile, the free nitride surfaces remain exposed to the gas phase, so that the kinetics approach linearity. When there is sufficient oxide of rational crystallite-size composition, it sinters to form surface films through which normal gaseous diffusion cannot easily occur. The reaction becomes controlled by solid-state diffusion, with the kinetics becoming parabolic and the surface area decreasing as observed after about 50% conversion in Fig. 1 (a), (b) and (d). Parabolic kinetics are characteristic also when the oxidation of aluminium produces better crystallised aluminas.

The increases in $S$ (and decreases in average crystallite size) during the acceleratory and approximately linear stages of the oxidation, Fig. 1 (a), (b) and (d), indicate that the alumina initially formed on the surface of the nitride splits off to give smaller crystallites. Any additional spalling at the nitride-oxide interface when the samples were cooled for surface area determination was negligible by comparison, since the reheated samples proceeded to give oxidation rates similar to those of samples which had been continuously heated. Thus, the extent of crystallite splitting depends generally on differences in molecular volume and type of crystal lattice compared with the original nitride (cf. Pilling-Bedworth rule for oxidised metals), and also on the rate of oxide sintering as discussed in Part 1. Although the conversion of AIN to $\alpha$-Al$_2$O$_3$ involves practically no fractional volume change, nevertheless the crystal lattice change is apparently sufficient to cause a limited amount of crystallite splitting. In this instance, $(S^*/S)^3$ directly represents the increases in the number of crystallites as oxidation proceeds, Fig. 1 (c), no allowance being required for molecular volume changes. The maximum increases of less than twenty-fold are comparable with those found for the oxidation of TiN described more fully in the next paper. They are much smaller than the increases during the oxidation and hydrolysis of Ca$_3$N$_2$, viz. $5 \times 10^{10}$ and $10^{12}$ respectively.

The m.p. of AIN ($> 2400$ °C) and Al$_2$O$_3$ (2050 °C) give Tammann temperatures (half m.p. in K) of > 1336 K, and 1160 K, indicating that sintering of alumina should be much more extensive than that of aluminium nitride at 1000 °C. In the latter stages of the oxidation, the alumina appears to act as a mineraliser for the remaining aluminium nitride particles, inhibiting their further oxidation, cf. Fig. 1 (d), and moulding together the material. Changes in the average crystallite size of the aluminium nitride (assuming no appreciable sintering) and the $\alpha$-Al$_2$O$_3$ are deduced from the surface-area data and shown in Fig. 1 (f). These confirm the ultimate sintering of the alumina, and the larger crystallite sizes given during the first half of the oxidation (above the broken-line) are caused probably by some of the newly-formed alumina not being detached from the nitride surface. Accordingly, the aggregate sizes of the materials (Table 1) indicate that the original nitride consists mainly of single crystallites. The alumina produced tends to promote formation of aggregates, mainly of 3—8 μm sizes, in which the individual crystallites appear to be over 0.5 μm in the later stages of the oxidation as also indicated in Fig. 1 (f). Similarly, 86% oxidation of aluminium nitride in 14 h at 1100 °C, Fig. 2 (d), gives alumina crystallites of 0.5—1 μm size, sintering at the higher temperature being restricted by the shorter oxidation time.

**Oxidation of nitrides of boron and silicon**

The boron nitride and silicon nitride oxidise at 800 and 1200 °C respectively, giving diboron trioxide, B,O$_3$, and silicon dioxide, SiO$_2$ ($\alpha$-cristobalite), even in the early stages. In contrast to the behaviour of aluminium nitride on oxidation, the specific surfaces of the materials initially decrease rapidly as the boric oxide (m.p. ~ 450 °C) and the silica (m.p. 1710 °C) act as mineralisers. Although the silica does not melt, it is well

---

**Fig. 4.** Electron micrographs of silicon nitride calcined in air at 1200 °C
(a) original sample, (b) after 5 h and (c) after 35 h
above its Tammann temperature (720°) and the specific surface, \( S \), falls from 1.7 to below 0.3 \( m^2 g^{-1} \) when one third of the silicon nitride has been oxidised. The products tend to bond together and shrink, cf. bonding and hot pressing of boron nitride with silica glass. Consequently, the rates decrease considerably for both nitrides as their oxidations become increasingly controlled by liquid- or solid-state diffusion, especially the latter, cf. Fig. 2 (a) and (b).

The original boron nitride has a flaky texture with rod-shaped and hexagonal plate-like particles. About 20% of the BN is converted to \( B_2O_3 \) after 24 h calcination at 800° in air, Fig. 2 (a), while the hexagonal plates become rounded and tend to form aggregates as in the electron micrographs in Fig. 3 (a) and (b). Further calcination continues this aggregation, cf. Fig. 3 (c) at 48 h, and after 96 h the rod-shaped particles become distorted by the newly-formed \( B_2O_3 \), cf. Fig. 3 (d). When over 80% of the BN has been oxidised after 144 h, there is sufficient \( B_2O_3 \) to crystallise out and change the appearance of the aggregates as in Fig. 3 (e) and (f). The silicon nitride particles, Fig. 4 (a), also form aggregates with rounded edges when only about 20% of the nitride has been converted to silica after 5 h calcination at 1200° in air as in Fig. 4(b). Further calcination (35 h) produces larger aggregates as in Fig. 4 (c).

Acknowledgment

The authors thank Mrs. M. A. Sheppard for her assistance in the analytical work; the University of London, Imperial Chemical Industries Ltd., and the Science Research Council for grants for apparatus and a S.R.C. Research Technicianship (for M.A.S.); the College Governors for a Research Assistantship (for N.G.C.).

John Graymore Chemistry Laboratories, College of Technology, Plymouth


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APPENDIX VII

Thermochemical Data.
ALUMINUM TRICHLORIDE (AlCl₃)  

(CRYSTAL)  

MOL. WT. = 133.351  

Heat of Formation:  

J. F. Coughlin, J. Phys. Chem. 62, 419 (1959) measured the heat of solution of crystalline aluminum chloride and aluminum at 303.15 K. In 4.360 M hydrochloric acid solution. Based on the data, \( \Delta H_{\text{fus}} \) of AlCl₃ was calculated as \( -51.67 \pm 0.14 \text{ kcal mole}^{-1} \) for the reaction  

\[
2\text{AlCl}_3(-180^\circ C) \rightarrow \text{Al}_2\text{Cl}_6(g)  
\]

Heat of Solution:  

-78.5 \pm 0.5 \text{ kcal mole}^{-1} for AlCl₃(c).  

Concentration of Solution:  

-79.45 \pm 0.5 \text{ kcal mole}^{-1} for AlCl₃(c).  

Heat of Solution:  

Heat capacity and entropy:  

The low temperature heat capacity, 15-200 K, and the high temperature heat capacity, 200-465 K, were determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, and R. A. McDonnell, Thermal Laboratory, The Dow Chemical Company, private communication, 1960, respectively. The two sets of data were joined smoothly at 298 K by a graphical method. Above 465 K, the C₃ values were estimated by graphical extrapolation. \( \Delta H_{\text{m}} \) was reported by P. L. Oetting, private communication, September 10, 1962, based on the C₃ data determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, loc. cit., using \( \Delta S \) (extrap.) = 0.094 cal deg.⁻¹ mole⁻¹. The high temperature heat capacities were also reported by W. Fischer, Z. anorg. allg. Chem. 258, 186 (1932) and H. Sivanova, Z. Elektroehem. 58, No. 4, 327 (1951), respectively. They were obtained by solution calorimetry and not used for similar reason.

Heat of Solution:  

Heat of sublimation:  

The heat of sublimation, 298-150 K, and the high temperature heat capacity, 200-465 K, were determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, and R. A. McDonnell, Thermal Laboratory, The Dow Chemical Company, private communication, 1960, respectively. The two sets of data were joined smoothly at 298 K by a graphical method. Above 465 K, the C₃ values were estimated by graphical extrapolation. \( \Delta H_{\text{m}} \) was reported by P. L. Oetting, private communication, September 10, 1962, based on the C₃ data determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, loc. cit., using \( \Delta S \) (extrap.) = 0.094 cal deg.⁻¹ mole⁻¹. The high temperature heat capacities were also reported by W. Fischer, Z. anorg. allg. Chem. 258, 186 (1932) and H. Sivanova, Z. Elektroehem. 58, No. 4, 327 (1951), respectively. They were obtained by solution calorimetry and not used for similar reason.

Molar heat capacity:  

Heat of sublimation:  

The heat of sublimation, 298-150 K, and the high temperature heat capacity, 200-465 K, were determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, and R. A. McDonnell, Thermal Laboratory, The Dow Chemical Company, private communication, 1960, respectively. The two sets of data were joined smoothly at 298 K by a graphical method. Above 465 K, the C₃ values were estimated by graphical extrapolation. \( \Delta H_{\text{m}} \) was reported by P. L. Oetting, private communication, September 10, 1962, based on the C₃ data determined by W. E. Hatton, G. C. Sinke, and D. R. Stull, loc. cit., using \( \Delta S \) (extrap.) = 0.094 cal deg.⁻¹ mole⁻¹. The high temperature heat capacities were also reported by W. Fischer, Z. anorg. allg. Chem. 258, 186 (1932) and H. Sivanova, Z. Elektroehem. 58, No. 4, 327 (1951), respectively. They were obtained by solution calorimetry and not used for similar reason.

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ALUMINUM TRIFLUORIDE (AlF₃)  

**CRYSTAL**

**MOL. WT.** 93.98

**Structure:**

The crystal structure of AlF₃ is known as a face-centered cubic unit cell. The space group is Fm-3m (No. 225). The lattice constants are as follows:

- *a* = 5.46 Å
- *b* = 5.46 Å
- *c* = 5.46 Å

**Electronic Structure:**

AlF₃ is an ionic compound with a high melting point of 1270°C. It is a soft material with a low thermal conductivity. The electrical conductivity of AlF₃ is low, but it increases with temperature.

**Chemical Properties:**

AlF₃ is soluble in water and reacts with water to form aluminum oxide and hydrofluoric acid. It is a strong Lewis acid and a Lewis base.

**Preparation:**

AlF₃ can be prepared by the reaction of aluminum with fluorine at high temperatures. It can also be synthesized by the reaction of aluminum metal with gaseous fluoride.

**Applications:**

AlF₃ is used in the production of aluminum and as a catalyst in various chemical processes. It is also used in the electronics industry as a etchant for aluminum and in the manufacturing of aluminum oxide.

**References:**

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**ALUMINUM NITRIDE (A1N)**

**CRYSTAL**

\[
K_F = 1000 \quad \text{at} \quad 1300 \, \text{K}
\]

**Heat of Formation**

The selected heat of formation is the average of two independent calorimetric determinations. The heat of formation was recently determined to be $-76.0 \pm 0.5$ kcal mol$^{-1}$ and $-75.6 \pm 0.4$ kcal mol$^{-1}$. The former value was reported by C. A. Neugebauer and J. L. Mankrogo, Z. Anorg. Allgem. Chem. 290, 67 (1957). The latter value was reported by A. D. Fan, E. O. King, W. K. Willard, and A. V. Christiansen, U. S. Bureau of Mines Report of Investigations 5716 (1961).

Vapor pressure measurements agree with the selected heat of formation. For instance, $\Delta H_{vap} = -75.6$ kcal mol$^{-1}$ for AlN was calculated from the heat for the reaction $\text{Al}(c) = \text{Al}(g) + \text{N}_2(g)$ and the heat of sublimation, 78.0 kcal mol$^{-1}$ for AlN. This heat of reaction was obtained from a direct observation calculation using JANAF values for the free energy functions and thermal diffusion pressure measurements by D. L. Hillebrand and L. F. Theard, Aerophysical Technical Report U-1497 (1961). Vapor pressure measurements with a microlance in a vacuum system by L. H. Dregger, V. V. Odepe, and J. L. Mankrogo, J. Phys. Chem. 65, 1566 (1961) agree with the selected heat of formation.

Earlier determinations of the heat of formation which apparently are in error are summarized by C. A. Neugebauer and J. L. Mankrogo (loc. cit.) and by L. H. Dregger et al. (loc. cit.).

**Heat Capacity and Entropy**

The heat capacity and entropy were reported by A. D. Fan et al. (loc. cit.). They measured the low temperature (51-298.15°K) and high temperature (298.15-1600°K) heat capacities and extrapolated the heat capacity from 0 to 51°K using the T^2 law. A smooth extrapolation of the heat capacity was made from 1600°K to 2783°K.

The heat content of AlN(c) was recently determined from 500 to 1000°K by R. Kuzaki. "Heat Contents of Inorganic Substances at High Temperatures," J. Phys. Soc. Japan 29, 1556 (1962) agree with the selected heat of formation. When recalculated with the sublimation coefficient ($\Delta H_{subl} = 21.2 \times 10^{-3}$) reported by Hillebrand and Theard, the heat of sublimation was calculated to be 75.6 kcal mol$^{-1}$ for AlN(c).

**Decomposition Data**

F. O. Contiero and W. C. Williams, Bull. Am. Phys. Soc. 11, 120 (1956) studied the vaporization of AlN with the mass spectrometer and detected only the gaseous species Al and N. The temperature at which the $\Delta F$ of AlN(c) and AlN(g) were equal, 2700°K, was taken as the temperature of decomposition.
SILICON GEELLE (A]PHA A12O3)

(CRYSTAL)

MOLE. WT. = 101.960

\[ \frac{\Delta H_f}{T} = -597.5 \pm 0.3 \text{ kcal} \cdot \text{mole}^{-1} \]

\[ \frac{\Delta S_f}{T} = 12.17 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1} \]

\[ \Delta G_f^0 = -400.1 \pm 0.5 \text{ kcal} \cdot \text{mole}^{-1} \]

\[ \Delta H_m = 26.30 \pm 0.55 \text{ kcal} \cdot \text{mole}^{-1} \]

Heat of Formation

The value of \( \Delta H_f \) derived from the direct combustion of pure aluminum in oxygen was taken from A. D. Kidder, J. Phys. Chem. 61, 1577 (1957). Other values for \( \Delta H_f \), obtained in the same way are: -359.04 ± 0.3 kcal. mole\(^{-1}\) reported by P. E. Angier and H. Seltz, J. Am. Chem. Soc. 77, 568 (1955); -400.4 ± 3 kcal. mole\(^{-1}\) reported by C. E. Malley, Jr., and S. J. Huber, Jr., J. Am. Chem. Soc. 73, 5277 (1951); and -402 ± 3 kcal. mole\(^{-1}\) reported by A. Schneider and O. Betlew, Z. Anorg. Chemic Chem. 277, 41 (1954).

Heat Capacity and Entropy


MELTING DATA

The melting data were obtained from the measurements of F. B. Kantor, L. N. Lazareva, V. V. Kaminer, and E. M. Postnov, loc. cit. S. J. Schneider "Compilation of the Melting Points of the Metal Oxides," HBS Monograph 68, p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°F.K.
$$\begin{array}{cccc}
T \text{ (K)} & C^2 & S^\prime \text{ (cal. mol}^{-1}) & H^\prime - H_0 \text{ (kcal mol}^{-1}) \\
\hline
0 & 0.000 & 0.000 & \text{INFINITE} \\
100 & 1.993 & 2.100 & 1.390 \\
200 & 1.792 & 1.790 & 1.390 \\
300 & 2.034 & 1.372 & 1.390 \\
400 & 2.831 & 2.076 & 1.390 \\
500 & 3.946 & 2.786 & 1.390 \\
600 & 4.441 & 3.071 & 1.390 \\
700 & 4.946 & 3.370 & 1.390 \\
800 & 5.457 & 3.661 & 1.390 \\
900 & 5.970 & 3.951 & 1.390 \\
1000 & 6.480 & 4.241 & 1.390 \\
\hline
1100 & 5.304 & 2.532 & 2.300 \\
1200 & 6.430 & 3.537 & 2.883 \\
1300 & 7.572 & 4.540 & 3.463 \\
1400 & 8.625 & 5.543 & 4.042 \\
1500 & 9.639 & 6.537 & 4.622 \\
1600 & 10.671 & 7.531 & 5.202 \\
1700 & 11.693 & 8.525 & 5.782 \\
1900 & 13.676 & 10.513 & 6.942 \\
2100 & 15.654 & 12.498 & 8.102 \\
2200 & 16.632 & 13.489 & 8.682 \\
2300 & 17.610 & 14.479 & 9.262 \\
2400 & 18.588 & 15.469 & 9.842 \\
2600 & 20.530 & 17.449 & 10.992 \\
2700 & 21.499 & 18.439 & 11.572 \\
2800 & 22.466 & 19.429 & 12.152 \\
2900 & 23.430 & 20.419 & 12.732 \\
3000 & 24.398 & 21.409 & 13.312 \\
3100 & 25.360 & 22.399 & 13.892 \\
3300 & 27.258 & 24.379 & 15.052 \\
3400 & 28.192 & 25.369 & 15.632 \\
3500 & 29.122 & 26.359 & 16.212 \\
3600 & 30.040 & 27.349 & 16.792 \\
3700 & 30.958 & 28.339 & 17.372 \\
3800 & 31.873 & 29.329 & 17.952 \\
3900 & 32.793 & 30.319 & 18.532 \\
4000 & 33.710 & 31.309 & 19.112 \\
4100 & 34.634 & 32.299 & 19.692 \\
4200 & 35.560 & 33.289 & 20.272 \\
4300 & 36.496 & 34.279 & 20.852 \\
4400 & 37.438 & 35.269 & 21.432 \\
4500 & 38.382 & 36.259 & 22.012 \\
4600 & 39.332 & 37.249 & 22.592 \\
4700 & 40.289 & 38.239 & 23.172 \\
4800 & 41.251 & 39.229 & 23.752 \\
4900 & 42.218 & 40.219 & 24.332 \\
5000 & 43.189 & 41.209 & 24.912 \\
5100 & 44.160 & 42.199 & 25.492 \\
5200 & 45.133 & 43.189 & 26.072 \\
5300 & 46.107 & 44.179 & 26.652 \\
5400 & 47.081 & 45.169 & 27.232 \\
5500 & 48.055 & 46.159 & 27.812 \\
5600 & 49.028 & 47.149 & 28.392 \\
5700 & 49.998 & 48.149 & 28.972 \\
5800 & 50.968 & 49.139 & 29.552 \\
5900 & 51.938 & 50.129 & 30.132 \\
6000 & 52.908 & 51.119 & 30.712 \\
\hline
\text{March 31, 1901}
\end{array}$$

**CARBON (C)**

(REFERENCE STATE - GRAPHITE)

**MOL. WT. = 12.011**

$$
\begin{align*}
C^2 + 298.15 & = 0 \\
C^2 + 298.15 & = 170.89 \times 0.5 \text{ kcal mol}^{-1} \\
C^2 + 298.15 & = 1.359 \text{ cal deg}^{-1} \text{ mol}^{-1}
\end{align*}
$$

Heat of Formation

Zero by definition.

Heat Capacity and Extrapolation

The low temperature $C_p$ measurements of P. H. Keeson and H. Pearlman (1° to 4°K and 10° to 20°K), Phys. Rev. 55, 1119 (1935), and of W. DeSorbo and O. E. Nicholls (1° to 20°K), Phys. Rev. 82, 384 (1951), were joined smoothly with the $C_p$ measurements of W. DeSorbo and W. W. Tyler (15° to 300°K), J. Chem. Phys. 21, 1160 (1953). $C_p$ values above 300°K were taken from National Bureau of Standards Report 8926, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds". July, 1960. Heat capacity above 1000°K were adjusted to give smooth results. Above 4000°K, the $C_p$ values are estimated. $\Delta S_5$ and $\Delta H_5$ were calculated to be 0.000565 cal deg$^{-1}$ mol$^{-1}$ and 0.0382 kcal mol$^{-1}$ respectively from smooth $C_p$ values using Wadding's rule.
### Table 1: Carbon Monoxide (CO)

<table>
<thead>
<tr>
<th>T. K.</th>
<th>C_2</th>
<th>S</th>
<th>(-\text{H}_\text{f}^\circ / \text{kJ} / \text{mol})</th>
<th>(\text{H}_\text{f}^\circ / \text{kJ} / \text{mol})</th>
<th>(\Delta \text{H} / \text{kJ} / \text{mol})</th>
<th>(\Delta \text{S} / \text{J} / \text{mol} \cdot \text{K})</th>
<th>(\text{Ln K}_\text{f})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>INFINITE</td>
<td>INFINITE</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>100</td>
<td>0.046</td>
<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>200</td>
<td>0.092</td>
<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>300</td>
<td>0.138</td>
<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>400</td>
<td>0.184</td>
<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>500</td>
<td>0.230</td>
<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
<td>INFINITE</td>
</tr>
<tr>
<td>600</td>
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<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
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</tr>
<tr>
<td>700</td>
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<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
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</tr>
<tr>
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<td>0.001</td>
<td>1.020</td>
<td>7.207</td>
<td>27.200</td>
<td>27.200</td>
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<tr>
<td>900</td>
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<td>27.200</td>
<td>27.200</td>
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</tr>
</tbody>
</table>

**Ground State Configuration** \(^3\Sigma^+\)

\[
\text{CO}_\text{g} \rightarrow 13.133 \text{ cm}^{-1}
\]

\[
\text{CO}_\text{g} \rightarrow 0.017 \text{ cm}^{-1}
\]

**Heat Capacities and Entropies**

The values given for the heat of combustion, equation I, by P. D. Rossini, J. Research Nat. Bur. Standards 72, 407 (1969) was changed to account for the presently accepted molecular weight of CO₂. The heat of formation is obtained by means of the following cycles:

1. \(\text{CO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g)\) - 67.5355 kcal mol\(^{-1}\)

2. \(\text{CO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g)\) - 67.5354 kcal mol\(^{-1}\)

For details of equation II see CO₂ Sheet.

### Heat Capacities and Entropies


Belzer et al used a lower value for the dissociation energy in their calculations. However, their summation converges rapidly and this introduces no sensible error in the functions.

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**March 31, 1961**
functions that are 0.5 kcal mole\(^{-1}\) lower above 5000 K.

Data concerning the dissociation energy and the monatomic hydrogen sheet.

Heat Capacity and Entropy

H. W. Woolley, R. B. Scott and P. O. Brickwedde, J. Research Nat. Bur. Standards 44, 379 (1949), calculated the thermodynamic functions by a method of direct summation for normal H\(_2\) (75% ortho and 25% para) using spectroscopic constants derived from an analysis of U. V. band spectra. These constants are preferable for use in a summation method than those obtained by G. Herzberg. Can. J. Res. 27B, 144 (1950) from the measured quadrupole transitions in the ground state which accurately describe the lower vibrational levels only. In any case the difference in the functions resulting from the two sets of data are less than 0.26.

Since the entropies of Woolley et al. contain a contribution from nuclear spin, a correction of 0.7 kcal was applied. However, the entropy due to the mixing of ortho and para hydrogen which is a consequence of nuclear spin is included in the total entropy since this results in correct equilibrium constants based upon third law calculations. Differences in the values of \( R \) and \( S \), were found to have a negligible effect upon the functions.

Similar calculations with a different method of estimating the higher rotational levels by R. B. Johnston, L. O. Svedoff, and J. Balzer, Technical Report No. 2, Project N-F-515, Ohio State Univ. (1949), result in functions that are 0.56 lower above 5000 K.

For details concerning the dissociation energy see the monatomic hydrogen sheet.
<table>
<thead>
<tr>
<th>T, K</th>
<th>G°C</th>
<th>G°K</th>
<th>(T-H°K)/T</th>
<th>H°K</th>
<th>A°H</th>
<th>A°S</th>
<th>Log Kp</th>
</tr>
</thead>
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<td>0</td>
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<td>0.01</td>
<td>Infinite</td>
<td>- 0.2255</td>
<td>- 0.2250</td>
<td>- 0.2254</td>
<td>Infinite</td>
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<tr>
<td>12</td>
<td>0.959</td>
<td>77.24</td>
<td>1.2493</td>
<td>- 0.2594</td>
<td>- 0.2593</td>
<td>- 0.2592</td>
<td>0.005</td>
</tr>
<tr>
<td>200</td>
<td>0.961</td>
<td>66.39</td>
<td>0.9082</td>
<td>- 0.2330</td>
<td>- 0.2329</td>
<td>- 0.2329</td>
<td>0.007</td>
</tr>
<tr>
<td>288</td>
<td>0.964</td>
<td>56.95</td>
<td>0.6645</td>
<td>- 0.2072</td>
<td>- 0.2072</td>
<td>- 0.2072</td>
<td>0.010</td>
</tr>
<tr>
<td>400</td>
<td>0.964</td>
<td>46.70</td>
<td>0.4444</td>
<td>- 0.1761</td>
<td>- 0.1761</td>
<td>- 0.1761</td>
<td>0.015</td>
</tr>
<tr>
<td>500</td>
<td>0.970</td>
<td>37.65</td>
<td>0.2513</td>
<td>- 0.1461</td>
<td>- 0.1461</td>
<td>- 0.1461</td>
<td>0.020</td>
</tr>
<tr>
<td>625</td>
<td>0.970</td>
<td>29.88</td>
<td>0.1196</td>
<td>- 0.1166</td>
<td>- 0.1166</td>
<td>- 0.1166</td>
<td>0.025</td>
</tr>
<tr>
<td>700</td>
<td>0.966</td>
<td>22.41</td>
<td>0.0796</td>
<td>- 0.0956</td>
<td>- 0.0956</td>
<td>- 0.0956</td>
<td>0.031</td>
</tr>
<tr>
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<td>0.0400</td>
<td>- 0.0558</td>
<td>- 0.0558</td>
<td>- 0.0558</td>
<td>0.055</td>
</tr>
</tbody>
</table>

**HOTELER'S CHLORIDE (HCl)**

| MOL. WT. | 36.465 |

**Note:** Values are given in molar mole units.

**Method:**

1. **Direct Method:**
   - Determination of HCl, HCl₂, and HCl₃ by all-solid calorimeter
2. **Indirect Method:**
   - Determination of HCl in an open calorimeter
   - Determination of HCl in a closed calorimeter

**References:**

1. **Tanaka, Acc. 1963**
2. **Lester, et al., 1943-52**
3. **Nehm, Acc. 1918**
4. **van Vartem, Acc. 1927**
5. **Richter, Acc. 1937**
6. **Hazen, Acc. 1927**
7. **Long, Acc. 1927**
8. **Richter, Acc. 1937**

**Additional Information:**

- The values are based on a variety of independent experiments.
- The standard deviations are given in the table.
- The value of 338.6 kcal/mol for the reaction HCl(g) + HCl(g) → HCl₂(g) is confirmed by a variety of independent methods.
- The enthalpy of formation of HCl(g) is determined to be 81.2 kcal/mol.

**Calorimetric Determination of HCl:**

- Determination of HCl in an open calorimeter
- Determination of HCl in a closed calorimeter
- Determination of HCl in a flow calorimeter

**Stoichiometry:**

- The reaction is a first-order reaction in HCl(g).
- The reaction is a second-order reaction in HCl(g).
- The reaction is a third-order reaction in HCl(g).

**Temperature Range:**

- The values are given in molar mole units.
- The values are given in molar mole units.
- The values are given in molar mole units.

**Heat Capacity and Entropy:**

- Spectroscopic constants for HCl³⁵ and HCl³⁷ were selected from the work of M. E. Flyer, M. J. Tidwell, and L. W. Friedman.

- The values were adjusted to 35.56 kcal/mol.
The heat of formation is a corrected value, calculated on the basis of the use of the reduction of the heat of formation of the elements. The value of the heat of formation is determined by the use of the heat of formation of the elements. The heat of formation is a corrected value, calculated on the basis of the use of the reduction of the heat of formation of the elements. The value of the heat of formation is determined by the use of the heat of formation of the elements.
<table>
<thead>
<tr>
<th>T, K</th>
<th>C_i</th>
<th>S'</th>
<th>(F-H)</th>
<th>H</th>
<th>ΔH</th>
<th>ΔS</th>
<th>Log K_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.000</td>
<td>INFINITE</td>
<td>-2.072</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>10</td>
<td>0.513</td>
<td>44.922</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>20</td>
<td>0.957</td>
<td>44.977</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>50</td>
<td>1.501</td>
<td>48.813</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>1.904</td>
<td>46.818</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>200</td>
<td>1.904</td>
<td>46.818</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
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<td>2.100</td>
<td>49.386</td>
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<td>0.000</td>
</tr>
<tr>
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<td>1.815</td>
<td>34.507</td>
<td>44.977</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Nitrogen (N₂)**

(IDL Gas - Reference State)

Vol. Mt. = 28.016

**Heat Capacity and Entropy**

B. F. Stoickeff, Can. J. Phys. 37, 630 (1959), determined the spectroscopic constants of N₂ by combining his measured rotational spectra with the results of band spectra given in the literature. These constants have been corrected to apply to the naturally occurring isotopic composition listed by D. Strooinge, J. H. Holland and D. T. Seberg, Rev. Mod. Phys., 30, 505 (1958).

L. Glatt, J. Belzer, and H. L. Johnston, Ohio State Univ. Res. Found. Prog. NCR, No. 1, 1955, calculated the functions for N₂ by a direct summation using spectroscopic data given by O. Hohmann, "Nuclear Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -ln 9 to remove the effects of nuclear spin included by Glatt, Belzer, and Johnston, and by 0.012 for the difference in spectroscopic constants.

J. A. Oft and S. O. White, Trans. Am. Soc. Mech. Engs., 77, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatt, Belzer, and Johnston is within 0.15.

See nitrogen constant sheet for details concerning the dissociation energy.
Heat of Reaction

The molecular constants for \( \text{HI} \) equilibrium are from a study of the vibration-rotation bands of \( \text{NH}_3 \) by K. Benedict and R. F. Flyler, Can. J. Phys. 25, 1955 (1957).

B. Overstreet and W. P. Giauque, J. Am. Chem. Soc. 55, 254 (1933) have determined the third law entropy of \( \text{NH}_3 \) (g) at its boiling point (259.68°C).

Their value compared to \( 259.68 \) interpolated from this table by the method of Lagrangean curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards 35, 151 (1945), is tabulated below.

\[ S \text{ in cal. deg}^{-1} \text{ mole}^{-1} \]

\begin{align*}
259.68 & \quad 44.15 \\
259.15 & \quad 44.17 \\
259.68 & \quad 44.06
\end{align*}


\( V_2 \) is the normal vibration of the deformation parallel type wherein the nitrogen atoms approach and recede from the plane of the three hydrogen atoms. Since the pyramid is comparatively flat the potential barrier to the inversion of nitrogen is low. Each state is characterized by the vibrational and rotational quantum numbers as well as by the symmetry number \( \sigma \) with respect to the inversion plane.

Attempts have been made to estimate the correction due to inversion doubling. See W. H. Noyes, J. Chem. Phys. 5, 126 (1955); K. H. F. Fillier, J. Chem. Phys. 37, 126 (1962); and C. C. Stephenson and N. D. Romanov, J. Am. Chem. Soc. 81, 457 (1959). In this case there are symmetrical electron spins in the potential. The correction is made by doubling the energy levels below the top of the potential barrier, these levels above the barrier are shifted upward. The summation of these levels for \( V_2 \) gives \( \text{NH}_3 \) greater electron density than for the Einstein functions where singly degenerate vibrational energy levels are employed.

The rotational correction is made by giving \( \sigma \) a value of 6. Since, if the inversion takes place, then each of the two positions of the molecule are equivalent, giving \( \text{NH}_3 \) less rotational entropy than when compared to the RRHO approximation with \( \sigma \ splice 6.

Einstein functions are employed for the \( V_1 \), \( V_2 \), and \( V_3 \) fundamentals, which implies no vibration-rotation interaction. But, for \( V_2 \) interaction is implied first by assuming inversion, then doubling \( \sigma \) and the levels, and then summing. However, these corrections are only canceling and approximating the RRHO.
Oxygen, Diatomic (O₂)

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>(C−H−H)/I</th>
<th>H−H</th>
<th>(\Delta H)</th>
<th>(\Delta F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5146</td>
<td>5141</td>
<td>1000.12</td>
<td>227.10</td>
<td>1000.12</td>
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<td>5141</td>
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<td>1000.12</td>
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<td>5141</td>
<td>1000.12</td>
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<td>5146</td>
<td>1000.12</td>
<td>227.10</td>
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<td>5141</td>
<td>5146</td>
<td>1000.12</td>
<td>227.10</td>
<td>1000.12</td>
</tr>
</tbody>
</table>

**Ground State Configuration**

\(\omega = 1500.246 \text{ cm}^{-1}\)

\(\omega = 12.071 \text{ cm}^{-1}\)

\(D_{0} = 1.456 \times 10^{-4} \text{ cm}^{-1}\)

**Heat Capacity and Entropy**

H. W. Wollaston, J. Research, Nat. Bur. Standards 44, 163 (1949), calculated the functions by a direct summation to 5000 K. The spectroscopic constants used are the same as those listed by H. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., 1950, except for \(D_{0}\), which differs by 2%. This difference has a negligible effect upon the thermodynamic functions. Raman measurements of rotation-vibration levels by A. Weber and R. A. McInnis, J. Mol. Spectrosc. 6, 105 (1960), support the constants selected by Herzberg which were changed to apply to the naturally occurring isotopic composition given by D. Strominger, J. W. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 583 (1958). These are listed above.

The entropies listed by Wollaston were reduced by 0.0063 cal. deg. −1 mole −1, since this amount was added by Wollaston to account for the difference in symmetry number between homo- and hetero-isotopic molecules. This correction is taken care of when isotopic mixing entropy is neglected, W. P. Bishop and H. Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

See anatomic oxygen sheet for details concerning the dissociation energy.
<table>
<thead>
<tr>
<th>T. K.</th>
<th>( \Delta G^\circ )</th>
<th>( S^\circ \text{ (mol deg}^{-1}) )</th>
<th>( H^\circ - H^\circ_{25} )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta F^\circ )</th>
<th>( \text{Log } K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
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</tr>
<tr>
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<tr>
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<td>249.379</td>
<td>104.015</td>
</tr>
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<td>219.000</td>
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<td>261.379</td>
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<td>263.379</td>
<td>80.355</td>
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<td>73.595</td>
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<td>211.000</td>
<td>268.379</td>
<td>269.379</td>
<td>70.215</td>
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</table>

**Heat of Formation:** \( \Delta H^\circ = -170.25 \text{ kJ mol}^{-1} \)

**Heat Capacity and Entropy:** \( C_p \) values above 900°K were estimated. \( \Delta C_p \) values were taken from K. K. Kelley, U. S. Bur. Mines Bull. 407 (1957).


**TRISILICON TETRAMONIDE (Si$_3$N$_4$)**

<table>
<thead>
<tr>
<th>T. K.</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta S^\circ )</th>
<th>( \Delta F^\circ )</th>
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</thead>
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<tr>
<td>140</td>
<td>-170.25</td>
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</table>

**Heat of Sublimation:** \( \Delta H^\circ = 22.6 \text{ cal deg}^{-1} \text{ mole}^{-1} \)

**Sublimation Temperature:** \( T_s = 2170^\circ K \).
<table>
<thead>
<tr>
<th>T. K.</th>
<th>C2</th>
<th>S</th>
<th>(H2O)</th>
<th>ΔH</th>
<th>ΔF</th>
<th>Log Kf</th>
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<td>0.06</td>
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<td>10.06</td>
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<td>0.06</td>
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<td>209.83</td>
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<td>10.00</td>
<td>0.06</td>
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<td>209.83</td>
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</table>

Silicon Dioxide, Quartz (SiO2) (Crystal)

Heat of Formation: The value taken was reported by W. D. Good, J. Phys. Chem. 85, 380 (1982). S. S. Wise, J. Pargave, H. K. Foder, and W. H. Hubbard reported a value of £Hf = 208.15 ± 0.2 kcal. mol^-1 in J. Phys. Chem. 66, 382 (1962). £Hf was measured by fluorine bomb calorimetry in both cases.

By oxygen bomb calorimetry, Humphrey and King, J. Am. Chem. Soc. 24, 2241 (1952) determined a value of £Hf = 208.15 ± 0.2 kcal. mol^-1.


£Hf was calculated from the low temperature heat capacities.

Transition Data: £Hf and £Hf reported by Feuer and Pitzer, J. Am. Chem. Soc. 65, 2546 (1943).

Molten Data: £Hf and £Hf reported by Rossman and Pitzer, J. Am. Chem. Soc. 84, 2546 (1943).

Sublimation Data: Porter, Chupka, and Ingren, J. Chem. Phys. 73, 218 (1955) reported vapor pressure data of SiO2(s) over SiO2(s) in the form of cristobalite. A table of the functions of cristobalite was calculated and £Hf was determined using the third law constants. The average of the results was 140.5 kcal. mol^-1. Using the heat of sublimation from The National Bureau of Standards Circular 500, it was found that £Hf for the reaction SiO2-->SiO2 cristobalite was 0.4 kcal. mol^-1. Correcting the calculated value of £Hf for quartz gave the reported value.
ΔG (Free energy of formation of reactions considered on Page 170)

<table>
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<th>Reaction T° K</th>
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AH (Heat of formation of reactions considered on Page 70)

<table>
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<th>4</th>
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