SYNTHESIS OF ULTRAFINE ALUMINUM NITRIDE
POWDERS IN A FLOW REACTOR

A Thesis presented to
The faculty of the College of Engineering and Technology
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In partial Fulfilment
of the Requirements for the Degree
Master of Science

by
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Chapter 1

INTRODUCTION

Originally, the word ceramic was used mainly for porcelain, brick and other traditional products made from clay, feldspar and silica. Currently, however, the term Ceramics includes abrasives, dielectrics, glasses, non-metallic magnetic materials, and refractories. Basically, ceramics are inorganic compounds of metallic & non-metallic elements.

Historical Background

It has been proved by archeological excavations that the making of clay pottery is as old as man himself. Therefore the ceramics are not new to mankind (Jayatilka, 1979). In order to satisfy one of man's most important need, hunger, the utensils and containers took second place only to the hunting weapons. In the early stages, prehistoric man used bark, wood and animal skin as container and utensils. This lead to the development of crude pottery which later expanded and developed into a
form of art.

During the Neolithic age, 6000 BC, unsuccessful attempts were made to achieve higher strengths in clay pottery by firing. These attempts failed because of the open hearths. When pottery was later fired in a covered system, it successfully achieved the desired result. The use of vertical kilns during 4000 BC proved even more successful in achieving this goal. Turning wheels were invented in Mesopotamia, during the same period, which allowed the potter use of both hands freely in molding and shaping clay. During the Bronze Age, in Greece, the use of colors in potteries was developed. A greater variety of ceramic materials came into use as civilization developed. High temperatures and glazing techniques were skillfully used, particularly in the Eastern World.

China, perhaps, is the most important in this respect. China-ware and porcelain making techniques in that country dates back to the Han (206 BC), Tang (618 AD), Sung (960 AD), and the famous Ming dynasties (1368 AD). Chinese people invented the highly skilled techniques of glazing at high temperatures, in the range of 1330 °C. The control of refined materials, molding techniques and fabrication procedures, and the coordinated use of temperatures lead to a breakthrough in scientific understanding of ceramic materials. China-ware was first introduced into the Middle East and then to the west by
Marco Polo, during the Italian Renaissance. The complicated techniques of making Chinese pottery, which were kept secret, were rediscovered by the west in the eighteenth century. This material progressed in many stages and today it has developed into a major industry based on sound scientific technology.

**Advanced Ceramics**

As stated earlier, the term ceramic grew to include clay or general ceramic as well as technical ceramics. Ceramic materials may be divided into traditional and advanced or technical ceramics. Technical ceramics are pure carbides, nitrides, oxides and other similar compounds. Technical or advanced ceramic materials are made for special applications by control of their microstructure to optimize certain properties. High temperature ceramics of this type are generally called Refractories.

**Classes of Refractory Materials**

The following grouping of refractory materials into Class A, B, C, and D, was suggested by J. T. Norton (Hove, 1965).

In Class A, non-metallic refractories made up of elements surrounding group IV are placed. These ceramics are graphite, silicon carbide, boron nitride, aluminum
nitride, beryllium oxide, magnesium oxide and calcium oxide.

Class B consists of the refractory transition metals. This consists of 3 rows in the periodic table starting with Sc in first row and ending with Pt in third row. In all these metals, the d band is being filled progressively.

Intermetallic compounds of transition metals with boron, carbon and nitrogen are categorized in class C. These have some of the highest known melting points. It has been observed for this class that melting points increase as the atomic mass increases and peaks when a metal is from group IV.

Class D consists of dioxides of group IV metals, mainly zirconia, hafnia, ceria and thoria. This class is further split into two with Ti, Zr, Hf and Th in one subclass and Si, Ge, Sn and Pb in second. It was observed that the later set is not very refractory.

Finally the miscellaneous category encompasses such materials as compounds of rare earths and actinides, boron carbide, beryllium carbide, beryllium boride, alkaline earth phosphides etc.

Considering refractories in class A, it may be observed that they center around group IV elements and they all have an average electron-to-atom ratio of four. These electrons all arise from s and p energy levels.
It is further observed that the melting temperatures are higher for covalent bonds and as the degree of ionic bonds is increased the melting points decrease too. This is evident from the class A refractories. It should be borne in mind that there are exceptions to this rule.

Aluminum nitride is a Group A ceramic. A study of the synthesis and characterization of this ceramic is described in the following chapters. Chapter 2 describes the background of the current research. Subsequent chapters include the experimental details and results of the present study.
CERAMICS AND ALUMINUM NITRIDE

Review of Fundamentals

Matter is bonded by energy. Some recognizable forms of energy are (1) Electrodynamic (2) Electromagnetic (3) Electrostatic (4) Gravitational (5) Inertial (6) Magnetic (7) Thermal (8) Vibrational. These forms of energy can react together and give rise to different kinds of chemical or physical forces.

The structure of the Atom

In a simple model, the atom is assumed to be made of three particles, Electron, with negative charge and negligible mass, proton, with positive charge and neutron having no charge, but mass equal to proton. Neutron and proton are grouped together at the nucleus (center) of the atom while electrons orbit around the nucleus. While orbiting around the nucleus, the electrons spin around their own axis. According to wave mechanics, the electrons should vibrate in stable vibration modes in certain discrete levels of energy called quanta. Zones of vibration for each quantum are called Principal Quantum Number or Principal Shell. 1 indicates the lowest energy
level and 7 is reserved for the highest level. Further, only four stable vibration modes are possible in each Shell and only 2 electrons can possess these modes. Modes are identified by letters s,p,d and f,in the increasing order of complexity.

Electrons in the outer most shell or the maximum normal energy level exert almost exclusive influence on the physical and chemical properties of the particular atom. If the outer-energy-level orbit is not completely filled by the electrons, then the atom is non-inert, and it is more likely to interact with adjacent atoms. The electrons of the incompletely filled outer shells are called the valence electrons, and that is why they determine the physical and chemical properties. The number of electrons that can exist in a quantum state is given in Figure 1.

**Material Characteristics**

The characteristics of a material are governed by the nature of its individual atom, and by the geometric pattern in which these atoms are placed. In order to understand these characteristics one must study the following atomic and structural phenomena:

1. Types of bond
2. Heterogeneity of bonding
Fig. 1. Representation of Energy levels of Principal Quantum Number (top) and Maximum possible number of Electrons in each Quantum state. (bottom).
Types of Bond

The linking of atoms together is called bonding. Atoms do not follow any one simple mechanism of bonding. Alternative bonds are always possible and invariably at least two types will operate simultaneously. There are three main types of bonds which are strong ones and there is a second group of three weaker bonds. The primary or strong bonds are (1) ionic bonds (2) covalent bonds and (3) metallic bonds. The weaker bonds are (4) molecular polarization bonds (5) electron dispersion bonds and (6) hydrogen bridge bonds. As stated earlier no one type of bond operates alone, and the different types of bonds will operate under different conditions.

Non-crystalline solids are formed by aggregations of basic stable groups of atoms called molecules, and a molecule itself is made of a fixed number of atoms having its own characteristic position. This configuration is a characteristic of material. Some crystalline materials are also molecular in nature if they are made up of molecules. Size, shape and bonding of molecules vary in
each substance and so does their behavior patterns when in aggregate, therefore it is necessary to understand these patterns in order to understand the bulk properties of any substance.

A crystal is formed from atoms or molecules arranged in a simple three dimensional geometric pattern such that each one of them is surrounded by exactly the same relative orientation and spacing of immediate neighbors as every other atom or molecule within the crystal structure. A crystal does not have a fixed size or shape.

Crystalline materials often possess particular properties because of the order of the crystalline form and for this reason the strongest materials are likely to be crystalline.

Heterogeneity of structure and composition is caused by impurities present in a substance, and this may cause undesirable properties. However in electronic materials the impurities are added intentionally so that certain properties can be improved and is called doping.

Bonds in ceramic materials are generally ionic and covalent ones. The difference between electrical and optical characteristics of crystalline metals, semiconductors and insulators can be qualitatively explained by an electron energy band model (Figure 2). It
has already been discussed that the energy an electron may possess is limited to certain ranges or bands, which are separated by forbidden energy levels.

Many states may exist in any given band depending on the momentum of the electrons. Again according to quantum mechanics only two electrons can occupy such a state. So if enough electrons occupy all the states, the band becomes completely filled and cannot accommodate any more of them. In such a case these electrons do not make any contribution to the electrical conduction. With reference to Figure 1, case 1 relates to an insulator where the lower band is completely filled with electrons and the upper empty band is well separated from it. As in the case of semiconductor materials, if this separation becomes small then, the thermal energy of the solid is sufficient to excite some electrons to move to the upper band resulting in some electrical conduction. Finally, if the empty band actually overlaps the filled band, as in the case of metals, the result is a partially filled single band capable of conducting electrical energy.

**Aluminum Nitride**

Aluminum Nitride possess certain physical, chemical and electrical properties, which make it a very attractive candidate for industrial applications. Due to its physical and electrical properties, it may be suitable for
Fig 2: Energy Band Configuration

(1) Insulator
(2) Semiconductor
(3) Metal
use as an active and passive component in semiconductor devices and for the fabrication of surface wave acoustic devices (Pauleau et al., 1980). Because of its high thermal conductivity (approx. $150 \text{ W m}^{-1} \text{ K}^{-1}$) and low electrical conductivity (less than $10^{-9} \text{ Ohm}^{-1} \text{ m}^{-1}$), it is being used as a substrate for microchips. It is also a primary ingredient in manufacturing of sheet steel. It has a density of approximately 3.26 gm/cc and a melting point of above 2200 °C.

**Material Criteria**

Advanced Ceramics in powder form should meet the following criteria if they are to be used for part fabrication in order to produce a good quality high strength part. (1) Powder should be roughly spherical, (2) It should be approximately equiaxed, (3) Should have high purity, and, (4) be within a narrow particle size range preferably in submicron range and be largely in an unagglomerated state (Bowen, 1980).

**Review of Past Studies**

Commercially, nitride ceramic powders are available in varying degrees of purity, and size ranges, but they are not available in ultrafine particle size range.

Pauleau et al. (1980) produced Aluminum Nitride
powder by Chemical Vapor Deposition. The deposition of Aluminum Nitride films by chemical reaction in AlBr₃-NH₃-H₂ gas flow system was carried out in a horizontal reaction tube. Silicon, nickel and vitreous carbon plates were used as substrates which were supported by a silicon carbide coated graphite susceptor heated by an RF generator. The total gas flow rate was maintained at 12 LPM. Aluminum bromide vapors were carried from the evaporator by hydrogen gas at the rate of 50 cc/min. The molar flow rate of aluminum tribromide in the reaction tube was between 0.00004 to 0.0001mole per min. Figure 3 shows deposition domains of AlN. Films were deposited at substrate temperatures between 500 °C to 900 °C. Above 900 °C the deposition rates were low and thickness was not uniform. Surface profiles of AlN films obtained by Pauleau et al. is shown in Figure 4.

Pauleau et al. (1980) also calculated the thermodynamics and kinetics of the system. Chemical compounds considered in thermodynamic computations are shown in Figure 5. The yields of AlN and aluminum halides vs trihalide vapor pressure or NH₃ pressure is shown in Figure 6.

Thermodynamic analysis had shown that the yield of aluminum nitride at equilibrium increased with increasing temperatures; this yield was higher than 98 % at 1200 K with the initial gas composition located in rectangle ABCD.
Fig. 3. Deposition domains of aluminum nitride in the initial gas phase composition diagram with the AlCl₃-NH₃-H₂ and AlBr₃-NH₃-H₂ systems. Solid lines, $T = 1200^\circ$K; dashed lines, $T = 1400^\circ$K.
Fig. 4. Surface profiles of aluminum nitride films. Films deposited at (A) 550°C, (B) 750°C, and (C) 850°C with a 2:1 ammonia-hydrogen mixture and an aluminum bromide vapor pressure of $8 \times 10^{-5}$ atm. Films deposited at (D) 550°C, (E) 750°C, and (F) 850°C with a 2:1 ammonia-hydrogen mixture and an aluminum bromide vapor pressure of $2.3 \times 10^{-4}$ atm. Films deposited at 650°C with an aluminum bromide vapor pressure of $8 \times 10^{-5}$ atm and an ammonia-hydrogen composition of (G) 1:9, (H) 2:1, and (F) 9:1.
### Fig. 5. Names of compounds considered in Thermodynamic analysis (Pauleau et al. 1980)

<table>
<thead>
<tr>
<th>AlCl₂-NH₃-H₂</th>
<th>AlBr₂-NH₃-H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>AlN</td>
</tr>
<tr>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>H₂</td>
<td>H₂</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₃</td>
</tr>
<tr>
<td>AlCl₂</td>
<td>AlBr₂</td>
</tr>
<tr>
<td>Al₂Cl₆</td>
<td>Al₂Br₆</td>
</tr>
<tr>
<td>AlCl₆</td>
<td>—</td>
</tr>
<tr>
<td>AlCl</td>
<td>AlBr</td>
</tr>
<tr>
<td>HCl</td>
<td>HBr</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Br₂</td>
</tr>
<tr>
<td>Cl</td>
<td>Br</td>
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<td>N₂</td>
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</tr>
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</tr>
<tr>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>AlN</td>
<td>AlN</td>
</tr>
<tr>
<td>AlH</td>
<td>AlH</td>
</tr>
</tbody>
</table>
Fig. 6. Aluminum Nitride yields for Aluminum trihalide, Aluminum trihalide or ammonia vapor pressure. (Pauleau et al., 1980)
(Figure 3). The decrease in deposition rates at higher temperatures was attributed to the kinetic characteristics of the deposition process which suggested a homogenous reaction in the gaseous phase (Figures 7, 8).

Hock & Nair (1979) prepared aluminum nitride powders by reduction-nitridation reaction. They obtained pure aluminum oxide powder by precipitating Al(OH)$_3$ from aluminum Isopropoxide, and reduced this alumina to aluminum nitride using ammonia. The major chemical reaction in their process was reported to be as follows:

\[
\begin{align*}
\text{Al(OC$_3$H$_7$)$_3$ + 3H}_2\text{O} & \rightarrow \text{Al(OH)$_3$ + 3C$_3$H$_7$OH} \\
\text{Al}_2\text{O}_3 + 2\text{NH}_3 & \rightarrow 2\text{AlN + 3H}_2\text{O}
\end{align*}
\]

Particles obtained were larger than 0.3 microns in size. Table 1 shows results obtained by Hock et al. (1979); however they did not report any chemical analysis of the AlN powder nor any particle size distribution.

Huseby (1983) reported synthesis of AlN powder from thermal decomposition of the intermediate compound \((\text{NH}_4)_3\text{AlF}_6\) to AlF$_3$ and then reduction of AlF$_3$ with high-purity ammonia. To obtain high purity \((\text{NH}_4)_3\text{AlF}_6\), high purity aluminum (99.9995 %) was cleaned with NaOH and washed with distilled water. It was then dissolved in HF. \(\text{H}_3\text{AlF}_6\) was then reacted to precipitate \((\text{NH}_4)_3\text{AlF}_6\). This dried powder was then placed in a current of electronic
Fig. 7. Variation of AlN deposition rate in the AlBr₃-NH₃-H₂ system vs. the deposition temperature.

Fig. 8. Variation of the decimal logarithm of aluminum nitride deposition rate vs. the reciprocal absolute temperature at an aluminum bromide vapor pressure of $2.3 \times 10^{-4}$ atm and an ammonia-hydrogen composition of (A) 1:9, (B) 2:1, and (C) 9:1.
Reduction-Nitridation of Amorphous Alumina by Ammonia Gas

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temp. (°C)</th>
<th>Powder density (g/cm³)</th>
<th>Composition of crystalline phases (wt.%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900 (24)</td>
<td>0.33</td>
<td>γ-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1000 (28)</td>
<td>0.34</td>
<td>50AlN, 50γ-Al₂O₃, trace α-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1100 (40)</td>
<td>0.45</td>
<td>50AlN, 30γ-Al₂O₃, 20α-Al₂O₃, trace θ-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1200 (24)</td>
<td>0.44</td>
<td>80AlN, 20α-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>1350 (18)</td>
<td>0.49</td>
<td>60AlN, 40α-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td>1350 (24)</td>
<td>0.44</td>
<td>50AlN, 50α-Al₂O₃</td>
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<tr>
<td>8c</td>
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<tr>
<td>10</td>
<td>1000 (24)</td>
<td></td>
<td>90α-Al₂O₃, 10γ-Al₂O₃, trace θ-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1350 (18)</td>
<td></td>
<td>AlN, trace α-Al₂O₃</td>
<td></td>
</tr>
</tbody>
</table>

Remarks:
- Numbers in parentheses indicate the time (in h) of heating at that temperature.
- Compositions were determined from the visual estimation of diffracted X-ray intensities.

Table 1 Results of Reduction-Nitridation in preparation of Aluminum Nitride by Hock et al. (1979)
## Reaction Conditions and Characterization of AlN Powder Synthesized From AlF₃ and NH₃

<table>
<thead>
<tr>
<th>Batch</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>NH₃ used (g)</th>
<th>(NH₃)AlF₃ used (g)</th>
<th>AlN formed (g)</th>
<th>Yield (%)</th>
<th>Specific surface area (m²/g)</th>
<th>Oxygen content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIN1</td>
<td>1000</td>
<td>14.3</td>
<td>553</td>
<td>NM</td>
<td>1.3</td>
<td>74.7</td>
<td>0.83</td>
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<tr>
<td>CIN2</td>
<td>900</td>
<td>46.5</td>
<td>1205</td>
<td>42.7</td>
<td>6.7</td>
<td>86.8</td>
<td>2.90</td>
<td>-</td>
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<tr>
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<td>800</td>
<td>45.6</td>
<td>4905</td>
<td>51.0</td>
<td>9.3</td>
<td>88.4</td>
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<td>24.8</td>
<td>2015</td>
<td>21.0</td>
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<td>80</td>
<td>2.62</td>
<td>-</td>
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<td>CIN5</td>
<td>850</td>
<td>41.0</td>
<td>4365</td>
<td>41.7</td>
<td>≈7</td>
<td>80</td>
<td>2.62</td>
<td>-</td>
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<td>CIN6</td>
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<td>18.3</td>
<td>1760</td>
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<td>63.8</td>
<td>2.25</td>
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<tr>
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<td>22.4</td>
<td>1930</td>
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<td>1600</td>
<td>NM</td>
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<tr>
<td>CIN9</td>
<td>950</td>
<td>6.5</td>
<td>765</td>
<td>44.1</td>
<td>Discontinued</td>
<td>-</td>
<td>0.24</td>
<td>-</td>
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<tr>
<td>CIN10</td>
<td>850</td>
<td>34.3</td>
<td>2830</td>
<td>43.4</td>
<td>7.5</td>
<td>82.3</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>CIN11</td>
<td>900</td>
<td>5.5</td>
<td>490</td>
<td>47.0</td>
<td>Discontinued</td>
<td>-</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>CIN12</td>
<td>800</td>
<td>18.0</td>
<td>1575</td>
<td>42.4</td>
<td>Discontinued</td>
<td>-</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>CIN13</td>
<td>800</td>
<td>39.5</td>
<td>4135</td>
<td>46</td>
<td>NM</td>
<td>74.7</td>
<td>0.49</td>
<td>-</td>
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<tr>
<td>CIN14</td>
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<td>32.4</td>
<td>2720</td>
<td>19.0</td>
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<td>65.1</td>
<td>0.49</td>
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<td>4475</td>
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<td>0.17</td>
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<td>CIN16</td>
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<td>4135</td>
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<td>5.0</td>
<td>80.1</td>
<td>0.76</td>
<td>0.25</td>
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<tr>
<td>CIN17</td>
<td>800</td>
<td>61.5</td>
<td>4410</td>
<td>25.2</td>
<td>4.0</td>
<td>75.5</td>
<td>0.53</td>
<td>-</td>
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<tr>
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<td>800</td>
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<td>29.8</td>
<td>4.2</td>
<td>77.5</td>
<td>0.34</td>
<td>-</td>
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<tr>
<td>CIN19</td>
<td>800</td>
<td>35.1</td>
<td>4320</td>
<td>27.0</td>
<td>4.4</td>
<td>77.6</td>
<td>0.26</td>
<td>0.30</td>
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<tr>
<td>CIN20</td>
<td>800</td>
<td>38.0</td>
<td>3313</td>
<td>27.2</td>
<td>4.4</td>
<td>77.0</td>
<td>1.01</td>
<td>-</td>
</tr>
</tbody>
</table>

* Yield=(x/y)×100%, where x=grams AlN and y=grams (NH₃)AlF₃, AlN, 'Measured by neutron activation. NM—not measured.

Table II. Reaction conditions and characterization of AlN powders. Results obtained by Huseby (1983).
grade ammonia under high temperature where it converted into AlN.

Powders with an oxygen content of <0.2 wt% were obtained. Most of the powder obtained was reported to be light tan, with some regions being white. Powders produced were rod shaped. Conversions were carried out at 1000, 900 and 850 °C (Table 2).

Formation of AlN by decomposition of aluminum amide-imide was reported by Maya (1986). Several routes aimed at obtaining the target compound were explored. Figure 9 shows infrared spectra depicting conversion of aluminum amide-imide into aluminum nitride. It can be seen that the depressions in the curves at wavenumbers 1545 and 1505 shows bands due to the vibrations of NH$_2$ and NH groups. At 600 °C these have vanished indicating conversion to aluminum nitride. Particle size was large in the range of 10 to 20 microns.

Preparation of AlN powders from alkoxide-derived oxides, similar to the process of Hock et al. (1979) was attempted by Mamoru et al. (1987). They used nitrogen instead of ammonia to reduce alumina into AlN in the presence of carbon. Powders so obtained were of sub-micron size distribution and purity levels were 70 to 95%. The reactions were carried out between 1430 to 1500 °C. They reported degree of reaction to be:
Fig. 9. Infrared spectra showing conversion of aluminum amide-imide into aluminum nitride.
Degree of Reaction = \( \frac{\text{AlN}}{\text{AlN} + \text{Al}_2\text{O}_3} = \frac{2x}{1+x} \)

where \( x \) is the stoichiometric amount of \( \text{N}_2 \). Figure 10 depicts the results obtained by Mitomo et al. Figure 10 also shows the plot of degree of reaction vs. % weight loss.

None of the methods described above were carried out in a flow reactor. It was observed that it is extremely difficult to obtain high levels of purity with any of the previous methods.

Alam and Flagan (1986) discuss the development of a flow (aerosol) reactor for production of silicon. They applied theory of simultaneous nucleation and aerosol growth to design a flow reactor. They observed that particle formation and growth from a vapor are initially controlled by: (i) homogenous nucleation, and, (ii) heterogenous condensation or reaction on particle surfaces. Particle growth by coagulation was also examined, which they found to be too slow for particles to grow out of submicron size range.

Wu (1986) simulated the aerosol reactor processes and compared the results of simulation with the experimental data obtained from production of silicon and titanium oxide powders. It was observed that coagulation dominated the production of refractory powders, which lead
Table II. Weight Loss after Heating the Al₂O₃ and Carbon Mixture at 1430° or 1500°C and Chemical Compositions in Powders

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heating time (h)</th>
<th>Weight loss (%)</th>
<th>Composition in powder (wt%)</th>
<th>Calculated α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>N</td>
</tr>
<tr>
<td>1430</td>
<td>4</td>
<td>25.6</td>
<td>52.8</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>33.2</td>
<td>57.4</td>
<td>23.3</td>
</tr>
<tr>
<td>1500</td>
<td>6</td>
<td>34.8</td>
<td>60.3</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>39.1</td>
<td>63.3</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. Plot of degree of reaction vs weight loss and chemical composition of AlN powders obtained by Mitomo et al. (1987)
to a broad size range distribution and which does not vary significantly in shape from one system to another. Also, if reaction is initiated at a slow rate and then accelerated gradually, growth by vapor and cluster deposition can be made to dominate over coagulation thereby producing particles in a much narrower size range than that in a coagulating system. Wu used a flow reactor with a five stage heating so that a better temperature control can be exercised. She verified the theory that the properties of the powders produced in a flow reactor can be controlled by changing the temperature profile, initial vapor concentration, and seed particle conditions. There was a consistency in both the simulation results and experimental data.
Chapter 3

EXPERIMENTAL STUDIES

A number of methods are being currently used to obtain ceramic powders having a uniform submicron particles with spherical shape, high purity and free from agglomerates. Powders produced in solution synthesis can be extremely uniform, but this method is limited in application. Other methods of obtaining ceramic powders are based on thermally induced gas phase reactions. Thermal energy can be supplied by either one of the following (1) Lasers (2) Plasma (3) Flames or (3) Heating furnaces. Present study utilizes the furnace heating in a flow reactor to induce reactions.

In the present study, AlN ultrafine powders were produced in a flow reactor by direct decomposition of aluminum isopropoxide (Al[OCH(CH₃)₂]₃), presumably into Al₂O₃, followed by reduction of alumina with high purity nitrogen or ammonia in the presence of very fine carbon particles. It is believed that the reactions might have proceeded as follows:

\[
\begin{align*}
\text{Al[OCH(CH₃)₂]₃} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 36\text{C} + 3\text{H}_2 \\
\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 & \rightarrow 2\text{AlN} + 3\text{CO}
\end{align*}
\]
The carbon particles were obtained as a by product of reduction of aluminum isopropoxide. The reaction quoted above was also suggested by Mitomo (1987). Presence of carbon particles was confirmed by noticing the deposits on the reactor walls and detecting carbon monoxide in the exhaust gases. Decomposition of alkoxide was carried out at 600 °C and reduction of alumina was carried out at between 750 to 800 °C. Schematic of the experimental setup is shown in Figure 11.

**Vapor Generation and Delivery**

As generally observed in CVD processes, the aim was to obtain comparatively pure aluminum or its compound. This could be done easily if a suitable aluminum compound is found which can be vaporized without much difficulty. Many materials were studied as possible candidates for this process. These included halides of aluminum and other organometallic compounds containing aluminum. It was observed that the majority of the compounds were either difficult to vaporize at low temperatures, or they were difficult to handle. For example, all aluminum halides have tendency to react violently with water, causing explosive reactions. Finally, aluminum isopropoxide was chosen as it was the only compound which was relatively safe to handle with a low boiling point.

Aluminum isopropoxide was obtained from Aldrich
Fig 11: Schematic of system for synthesis of Aluminum Nitride using a Flow Reactor
Chemical Company, in a 1 kg. packages. It had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>[(CH_3)_2CHO]_3Al</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>204.25</td>
</tr>
<tr>
<td>Melting Point</td>
<td>128-132 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.035</td>
</tr>
<tr>
<td>Purity</td>
<td>98 +%</td>
</tr>
</tbody>
</table>

A Pyrex glass gas washing bubbler with a capacity of 500 ml. was used as a vapor generator. The bubbler containing Aluminum Isopropoxide was kept in a constant temperature bath kept at 150 °C. The main difficulty with using the glass bubbler was that it would be impossible to open the caps after it is cools down. Another major difficulty was that the aluminum isopropoxide would decompose into alumina when washed with water, and these particles would block the fine pores on the fritted end of the stem. The third major problem was the lack of sealing and connection with the metallic tubing. This would limit the capacity to pressurize the system when purging it. In view of the above difficulties, a 316 stainless steel bubbler was fabricated, which could easily be connected to the system and withstand high pressures. One precaution that has to be taken is that a non-return valve has to be put on the inlet side of the bubbler in order to avoid the backflow of liquid isopropoxide during
purging. This arrangement, shown in Figure 12, was satisfactory.

Vapors generated in the bubbler were then delivered to the top of the flow reactor. Care was taken to heat the delivery line so that no condensation of vapors occurred. Temperature of the delivery line was kept at about 175 °C.

**Flow Reactor**

The flow reactor was made from a 1" diameter, 6 feet long quartz tube, which was placed vertically inside of heating furnaces. The top of the reactor was connected to the vapor delivery system and to the reactant gas supply. The bottom of the reactor was connected to a particle collection system. The top section, also called secondary or seed particle reactor, extended 12" and was heated by a Lindberg Electrical Furnace (Figure 13). Its specifications are:

- **Furnace I.D.:** Seed or Secondary
- **Model:** 55031
- **Maximum Temperature:** 1200 °C
- **Voltage:** 120 Volts

Temperature control was achieved by a proportioning controller made by Love Controls. This section was kept
Figure 12: Vapor Generator
Fig 13: Secondary Furnace
at 600 °C and was used to decompose the Aluminum Isopropoxide vapors.

The second section of the flow reactor, comprised of 40" long section heated by Lindberg electric furnace was the primary or main furnace. In this furnace heating was accomplished by passing a current through Silicon Carbide elements, which were arranged in rows of two on either side of the reactor tube. The Quartz tube and the heating elements were all arranged inside the walls which were made of refractory bricks. The specifications of this are as follows (Figure 14).

<table>
<thead>
<tr>
<th>Furnace I.D.</th>
<th>Primary or Main</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Lindberg</td>
</tr>
<tr>
<td>Model</td>
<td>54453-V</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>1500 °C</td>
</tr>
<tr>
<td>Power ratings</td>
<td>6857 Watts, 240 volts</td>
</tr>
<tr>
<td>Heating Elements</td>
<td>Silicon Carbide</td>
</tr>
</tbody>
</table>

Care was taken in introducing the quartz tube inside the reactor assembly so as not to strike or impact any of the SiC heating elements. These elements are very brittle and sensitive to any mechanical stresses, and break very easily. A breakage of any element would be indicated by the reduced current on the main temperature controller ammeter.
Fig: 14: Main Furnace
The temperature of the main furnace was kept between 750 to 800 °C. Control was achieved by a controller supplied by Lindberg and made by Eurotherm. Heating to 500 °C should be attained as soon as possible since the SiC elements have a tendency to oxidize if kept at lower temperatures. This can be achieved by passing the maximum current of 30 amps, without blowing the fuse. It should also be noted that once the SiC elements are heated above 500 °C, their resistance actually decreases, resulting in an increased current. Therefore, it becomes necessary to readjust the current parameter so as not to blow the fuse.

The connection between quartz reactor tube and the metal tubing is accomplished through use of o-ring joints. Care was taken not to overheat them and to keep the pressure in the system below 10 psi. Above 10 psi proper seal will not be achieved. The metal tubing system itself was joined together with the help of compression fittings which proved to be very satisfactory.

Temperature sensing was done with a type K thermocouple on the secondary furnace, whereas the main furnace had a built in Pt-Rh thermocouple.

**Particle Collection System**

The final product in the form of submicron
particles was collected at the bottom of the reactor, in a high efficiency filter assembly. The filter assembly consisted of a six inch diameter metallic high efficiency filter placed in a cylindrical holder with a tight seal. Sealing was accomplished with the help of rubber o-rings. The Filter holder had the dimensions of a 6 inch diameter with a 15 inch length. It was made from 316 stainless steel and had an inlet opening at the top for incoming reaction products from the reactor (Figure 15). A large cylindrical cavity inside the filter holder served as storage space during collection of the particles. The outlet of the filter holder had two connections; one to the exhaust, and the other was connected to a supply of inert gas. This was provided so that a backflow could be generated in case filter became clogged by the powder.

**Gas Cleaning and Drying System**

It was very essential that the reactant gases have very high purity so as to avoid inclusion of impurity in the final product. Commercially obtained gases such as Nitrogen, and Argon, although they were relatively pure, still had oxygen and water vapor in them. To remove these trace impurities, a cleaning and drying train was set up as shown in Figure 16. It consisted of a moisture absorbent filter containing Drierite (a hygroscopic
Fig. 15: Filter Unit
Fig. 16: Gas Drying & Cleaning system
chemical. This was followed by a reducing pass which consisted of copper fillings heated to 400 °C by flexible heating tape. The drying and cleaning train was regenerated by passing pure Hydrogen gas through it at about 300 °C. Caution was exercised in handling the Hydrogen gas. A limited amount of H₂ was used, since fractures would occur in the material of the oxygen purging unit due to reducing action of H₂.

**Determination of Flows**

Computations of flows were based on selected residence time in the reactor. It was estimated that a residence time of 10 seconds would be sufficient for completion of the reaction. Volume flow rate \( Q \) in the reactor is given by:

\[
Q = UA
\]

where \( U \) is the velocity in m/sec

\[
A \text{ is area in sq.m.}
\]

or, \( U = \frac{Q}{A} \) m/sec

The reactor in the present study, had a diameter of .0254 meters. The area is then approximately 0.0005 sq. meters.

Residence time for the reactor is given as,

\[
T = \frac{L}{U}
\]

where, \( L \) is the length of the reactor in meters.
The following parameters were then determined for the experiment,

\[ U = \frac{Q}{30} \text{ (approximately)} \]

\[ T = 10 \text{ seconds.} \]

\[ Q = 1.905 \text{ LPM.} \]

**Vapor Generation Rates**

Additional experiments were carried out to determine the generation rates for the vapors. A measured amount of carrier gas was passed through the vapor generator and the particles were collected at the end of the seed reactor on a standard 0.1 micron membrane filter. This filter was weighed before and after the particles were collected. Time was recorded for the period the vapors were generated. Table 3 shows the generation rates.

The difference in the last readings and the others in Table 3 can be explained by the fact that the third reading was obtained with a clean fritted stem.
<table>
<thead>
<tr>
<th>No.</th>
<th>Bubbler LPM</th>
<th>Mass Rate mg/min</th>
<th>Time Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4</td>
<td>1.35</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.16</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0.77</td>
<td>1.88</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>60.3</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table 3. Generation rates from bubbler.
Experiments with NH₃

For about 0.8 liters per minute flow through the vapor generator, 0.0017 grams/min of Al(OH)₃ particles are obtained. This was determined by weighing the mass of particles collected on a fine filter averaged over 10 hours.

Initially it was decided to use ammonia as nitriding agent, therefore the amount of ammonia required for the reaction was determined as follows.

Assuming, that the aluminum hydroxide reacts with ammonia to form AlN, the reaction would then proceed as follows:

\[
\text{Al(OH)}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{H}_2\text{O}
\]

\[
78.03 \quad 17.03 \quad 40.99 \quad 18.015
\]

Thus the stoichiometric amount of ammonia required is equivalent to 0.048 cc/min.

Based on the 10 minute residence time, it was decided that 0.722 cc/min of ammonia would be introduced into the system, 1.1 LPM of nitrogen would pass directly as a diluter and 0.8 LPM of Nitrogen would pass through the vapor generator. Thus the total flow becomes 2.0 LPM.
Experiments with Nitrogen

The first 6 runs were made with ammonia as reactant or reducing gas. It was abandoned since the powder obtained was grossly contaminated with oxides and other substances. Nitrogen was subsequently used as the reactant gas for all remaining runs.

In these experiments, the residence times were essentially kept same as in case of ammonia and amount of ammonia was replaced with nitrogen.
PROCEDURE

While conducting the experiments the following procedure was developed and followed to ensure proper performance of the equipment, safety and the highest possible quality of the material.

1. Started the ventilation fan to ensure proper ventilation.

2. The heater on the oxygen removal or purging system was put on and the temperature was set between 350 to 400 °C.

3. The system was pressurized with an inert gas preferably Helium, to a pressure of 10 psi.

4. It was checked for leaks with a gas leak detector, while setting the leak detector for highest sensitivity. Care was taken to probe the crevices between the joints and o-ring joints.

5. Leaks were fixed by tightening the joints or replacing them. It is very essential for the quality of the product and safety that those leaks were fixed.

6. To remove any oxygen or water vapors in the system, the air in the system was purged thoroughly by first evacuating and then filling with pure clean nitrogen gas. The vacuum developed in the system was about 30 mm HG. This process was repeated at
least three times. The purging process, in brief, is as follows: The vacuum pump was started while opening both the rotameter valves. When the system was completely evacuated, and the gage read 30 mm HG, the exhaust valve was shut off, and the system was filled with pure nitrogen to a pressure of 5 psi. Then it again it was purged by opening the exhaust valve.

7. The main furnace was turned on by switching the controller on. The temperature was set at 750 to 800 °C.

8. Heating on the constant temperature bath of the vapor generator and heating tape on the vapor delivery line was switched on. The temperatures were set at 150 and 175 °C respectively.

9. Since the secondary furnace was able to heat up the seed particle section of the reactor very rapidly, it was switched on only after the primary furnace reached within 100 °C of the setting. The secondary furnace was set for 600 °C.

10. Introduce the Aluminum Isopropoxide vapors by passing carrier gas through the vapor generator. The reaction will start immediately. This was indicated by the formation of film on the walls of the reactor tube at the bottom of the reactor.

11. Flow of nitrogen (reactant) 1.1 LPM was
introduced into the reactor. After five minutes, a flow of .8 LPM was introduced through vapor generator.

12. In case of a dust buildup on the filter, the pressure in the system would rise and would be indicated on the pressure gage at the top. The filter was cleaned by the backflow of the nitrogen.

**Reactor Temperature Profiles**

Temperatures were measured along the length of the reactor for two different temperature settings. Measurements were taken by inserting a long stem (type K) thermocouple in the reactor and recording the temperatures at every 10 cms. Table 4 shows the temperatures at various locations.
Table 4. Reactor Temperature Profile

<table>
<thead>
<tr>
<th>Position</th>
<th>mV</th>
<th>t °C</th>
<th>Position</th>
<th>mV</th>
<th>T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.5</td>
<td>308</td>
<td>80</td>
<td>37.1</td>
<td>919</td>
</tr>
<tr>
<td>10</td>
<td>14.2</td>
<td>372</td>
<td>90</td>
<td>35.9</td>
<td>889</td>
</tr>
<tr>
<td>20</td>
<td>15.8</td>
<td>410</td>
<td>100</td>
<td>34.6</td>
<td>857</td>
</tr>
<tr>
<td>30</td>
<td>17.0</td>
<td>440</td>
<td>110</td>
<td>32.8</td>
<td>813</td>
</tr>
<tr>
<td>40</td>
<td>26.0</td>
<td>626</td>
<td>120</td>
<td>26.4</td>
<td>659</td>
</tr>
<tr>
<td>50</td>
<td>29.6</td>
<td>735</td>
<td>130</td>
<td>3.6</td>
<td>112</td>
</tr>
<tr>
<td>60</td>
<td>37.4</td>
<td>902</td>
<td>140</td>
<td>3.40</td>
<td>35</td>
</tr>
<tr>
<td>70</td>
<td>38.15</td>
<td>921</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Transfer Of Product from Filter Unit

In order to avoid post reaction contamination and oxidation of the AlN, it is necessary to transfer or remove the powder from the filter unit to the desired container in an inert atmosphere. This was done in a glove box with the facilities to introduce inert gases. The filter unit along with the container was used to store the powder and necessary tools to open and empty the unit were placed inside the glove box prior to sealing it shut. The air present in the glove box was purged by inflating balloons filling them with pure nitrogen at about 10 psi. Two balloons were inflated at a time so that they most nearly covered the entire volume while exhausting the air by displacement. After closing the exhaust valves, the balloons were deflated. This procedure was repeated 3 times to ensure proper purging. During purging and material transfer, the glove box was kept at 10 psi at all times to ensure that no air entered the glove box.
Chapter 4

CHARACTERIZATION

The Materials Advisory Board of National Research Council has defined the characterization as (Hench & Gould, 1971);

"Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use and suffice for reproduction of the material."

Evidently, then, in order to characterize a material, it is necessary to evaluate its structure and composition. Figure 17 illustrates 5 major categories of characterization features. Fortunately however, all of these five can be quantitatively evaluated. Since instrumental methods quite often provide rapid, reproducible and relatively easier measurements, they are normally used.

Chemical Composition

Analytical chemistry has an overwhelming variety of tools and techniques at its disposal. Basically,
Fig. 17. The relationship between characterization features and products of the ceramics processing sequence. (By L.L. Hench)
relative amount in a sample is found by obtaining a numerical value of some property of the sample. Determination methods can be classified into two major classes. (i) Chemical Techniques, with two sub-classes of gravimetric and volumetric, and; (ii) Physicochemical techniques, which are by far the most preferred one. It consists of almost all the remaining techniques in the analytical chemistry. However, only three methods are of interest to us, and will be discussed in detail. The following is the brief description of the theory behind these physicochemical techniques, known as optical methods.

Optical methods are based on the phenomenon of emission and absorption of radiant or electromagnetic energy by matter. Figure 1\textsuperscript{9} depicts the electromagnetic spectrum. As was described in chapter 2, an electron in an outer shell can be excited to the next higher energy level by supplying it with enough energy. And again, when it returns to its former state, it emits a photon or a quanta of energy which depends on the levels of energy. This process of an electron being excited to a higher energy level and its return to a lower energy level is called resonance radiation. Furthermore it is also possible to raise some inner as well as outer orbit electrons to higher levels of orbits. When these electrons return to the original state, they pause at each
Figure 13: The electromagnetic spectrum. After Reilley and Sawyer
level on the way back emitting different quanta of energy. Clearly then, an atom can be excited to varying degrees resulting in several thousand discrete and reproducible wavelengths. Such emission on the atomic level is the basis of emission spectroscopy.

Similarly, if an electron is bombarded by a beam of high speed electrons or energetic x-rays, emission of x-rays occur. These rays have short wavelengths and very high frequencies. This is the basis of x-ray analysis and in such cases an inner level electron is excited.

A molecule, has energy levels of its own which correspond to the atomic energy levels. There is a total correspondence between atoms and molecules of a substance as far as different vibrational modes and rotational modes are concerned. Thus in case of a molecule, absorption of radiation passing through these various levels becomes important, since energy transitions do not always produce observable emissions. Transition of energy between vibrational levels in a molecule occurs near the infrared region, while transition due to rotation is absorbed in far infrared and microwave region.

**Infrared Analysis**

Although Aluminum Nitride itself is transparent to infrared rays, infrared was mainly used to detect the
presence of alumina, aluminum hydride and other impurities. Prior to analysis, the powder must be conditioned for analysis. This was done by mixing equal amounts of AlN and potassium bromide powders and compacting them together in a sample holder provided with the analyzer.

Calibration of the instrument was checked with the standard polystyrene sample. Then the prepared AlN sample was put in the proper place and infrared rays were allowed to pass through it. Both absorption and transmission spectra were recorded.

Size of Particles

These parameters are important from the point of view of processing the final properties of the AlN. For example, failure in ceramic materials occurs along the micro cracks, which are formed due to a variety of factors including porosity and impurities. Table 5 shows various methods of particle size analysis.

In the present study the particle size was determined by a Centrifugal Particle Size Analyzer (Horiba CAPA-300). It was capable of analyzing the particles down to 0.1 micron in size.

The principle of the operation of this instrument is based on the stokes theory of sedimentation and actions of
### Methods of Particle Size Analysis

<table>
<thead>
<tr>
<th>Type</th>
<th>Particle dimension measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedimentation</td>
<td>Stokes diameter; the diameter of a sphere having the same density and the same free falling speed as the particle in a fluid of the same density and viscosity (in the laminar flow region).</td>
</tr>
<tr>
<td>Sieving</td>
<td>Sieve diameter; the width of the minimum square aperture through which the particle will pass.</td>
</tr>
<tr>
<td>Elutriation</td>
<td>Drag diameter; the diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and at the same velocity.</td>
</tr>
<tr>
<td>Electronic</td>
<td>Volume diameter; the diameter of a sphere having the same volume as the particle.</td>
</tr>
<tr>
<td>Microscopic</td>
<td>A physical or statistical diameter or area.</td>
</tr>
</tbody>
</table>

Table 4. Methods of Particle Size Analysis and particle dimension each method measures. (L.L. Hench)
centrifugal forces on particles. Actually it measures the Stoke's diameter of the particle. According to the theory, the rate of fall \( (v) \) of a spherical particle is related to the diameter\( (d) \) of the particle by:

\[
d = \left( \frac{18nv}{(\rho - \rho_f)g} \right)^{1/2}
\]

where

- \( \rho \) is the particle density
- \( \rho_f \) is the fluid density
- \( g \) is the gravitational constant
- \( \eta \) is the viscosity of the fluid

The most common range for sedimentation analyses is 9.1 to 100 microns. This instrument uses sedimentation for particles above 10 microns and also uses centrifugal forces for particles below 10 microns.

Generally, particles tend to be in an agglomerated state. Hence to measure particle size accurately it is necessary to separate them. This was done by dispersing the particles in a soap solution by using ultrasonic vibrations. Before actual measurements, analyzer was calibrated by putting soap solution in both reference and sample cells. Then, after replacing the soap solution in the sample cell with the dispersed sample solution measurements were taken. It took nearly 30 minutes for each measurement since the particle size specified were in the submicron range.
Chapter 5

RESULTS

As indicated earlier, two sets of experiments were conducted. The first was with the ammonia gas as the reactant and the nitrogen as the vapor carrier gas. These experiments cover run numbers 1 to 6. The second set of experiments, including run numbers 7 to 15, were conducted with nitrogen both as the carrier and the reactant gas.

Table 6 depicts various reaction conditions. Run # 2, 10 and 11 were aborted because of the operational problems. No particle size data was collected for samples from runs, 2, 4, 10, & 11.

As indicated by the Table 6, temperatures varied from 1475 to 750 °C, and total flows were between 1.9 to 3.5 liters per minute. Table 7 shows aluminum Nitride powder characteristics.

Powders from run 3 & 13 looked similar (pale white). Run # 4, 5, 6, 10, 11, 15 were all white. Runs 7, 9 & 12 were yellowish white while run 8 was tan colored.

Samples from runs 3, 5, 7, 8, 9, 12, 13, & 15 were tested for particle size.

Runs 3, 12 & 13 had a range between 0.4 to 0.1 microns
### Table 6. Reaction Conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Main</th>
<th>Secondary</th>
<th>Bubbler</th>
<th>Reactant</th>
<th>Carrier</th>
</tr>
</thead>
<tbody>
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<td>150</td>
<td>NH$_3$</td>
<td>0.7</td>
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<td>150</td>
<td>NH$_3$</td>
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<td>150</td>
<td>NH$_3$</td>
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<td>150</td>
<td>NH$_3$</td>
<td>0.128</td>
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<td>550</td>
<td>150</td>
<td>NH$_3$</td>
<td>0.128</td>
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<tr>
<td>6</td>
<td>800</td>
<td>550</td>
<td>150</td>
<td>NH$_3$</td>
<td>0.128</td>
</tr>
<tr>
<td>7</td>
<td>800</td>
<td>600</td>
<td>175</td>
<td>N$_2$</td>
<td>0.54</td>
</tr>
<tr>
<td>8</td>
<td>850</td>
<td>600</td>
<td>175</td>
<td>N$_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>9</td>
<td>775</td>
<td>600</td>
<td>175</td>
<td>N$_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>775</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>775</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>12</td>
<td>775</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>0.5</td>
</tr>
<tr>
<td>13</td>
<td>800</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>0.5</td>
</tr>
<tr>
<td>14</td>
<td>775</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>1.375</td>
</tr>
<tr>
<td>15</td>
<td>750</td>
<td>600</td>
<td>150</td>
<td>N$_2$</td>
<td>0.25</td>
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</table>
Table 7. Powder Characteristics

<table>
<thead>
<tr>
<th>Run</th>
<th>Color</th>
<th>Particle Size (microns)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Max.  Min.  Peak</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Black</td>
<td></td>
<td>NH₃ thru Bubbler</td>
</tr>
<tr>
<td>3</td>
<td>Pale White</td>
<td>1.0  0.1  0.2</td>
<td>NH₃ at II stage.</td>
</tr>
<tr>
<td>4</td>
<td>White</td>
<td></td>
<td>NH₃ at top</td>
</tr>
<tr>
<td>5</td>
<td>White</td>
<td>1.0  0.2  0.4</td>
<td>(68 % between .3 to .6 microns)</td>
</tr>
<tr>
<td>6</td>
<td>White</td>
<td></td>
<td>Aborted</td>
</tr>
<tr>
<td>7</td>
<td>Yellowish</td>
<td>1.5  0.6  0.9</td>
<td>(70 % between 0.8 to 1.0) N₂ as Reactant</td>
</tr>
<tr>
<td>8</td>
<td>Tan</td>
<td>1.0  0.2  0.4</td>
<td>(66 % between .3 &amp; .5)</td>
</tr>
<tr>
<td>9</td>
<td>Yellowish</td>
<td>0.5  0.1  0.4</td>
<td>(89 % between .3 to .5)</td>
</tr>
<tr>
<td>10</td>
<td>White</td>
<td></td>
<td>Aborted due to leakages</td>
</tr>
<tr>
<td>11</td>
<td>White</td>
<td></td>
<td>Aborted</td>
</tr>
<tr>
<td>12</td>
<td>Yellowish</td>
<td>0.4  0.1  0.2</td>
<td>(90 % between .2 &amp; .3)</td>
</tr>
<tr>
<td>13</td>
<td>Pale</td>
<td>0.8  0.1  0.2</td>
<td>(skewed spread)</td>
</tr>
<tr>
<td>14</td>
<td>White</td>
<td></td>
<td>Aborted</td>
</tr>
<tr>
<td>15</td>
<td>White</td>
<td>0.1  0.2  0.6</td>
<td></td>
</tr>
</tbody>
</table>
with a large peak at 0.2 microns. Samples from runs 5, 8 and 9 all had large peaks at 0.4 microns with skewed spread around it.

Sample 15 was in the range of 0.1 to 1 micron with the bulk of the particles between 0.3 & 0.1 microns. Sample 7 had the largest particle size ranging from 1.5 to 0.6 peaking at 0.95 microns.

Powder particles were distributed over a narrow range of sizes, as can be seen from Table 7. Figures 19 through 26 show the particle size bar charts obtained from the analyzer. Samples from run # 1, 7, 8 & 9 were tested for chemical composition by infrared spectroscopy. Figures 27 through 32 show the IR spectra obtained for the above samples. It was observed that samples from run #1 showed presence of oxygen with either hydrogen or nitrogen and aluminum oxide (peaks at wave # 3500 & 1000). For sample # 7, the peak at 3500 has vanished therefore presence of N-H or O-H bond was not indicated. Only the peaks for oxides were present. For samples 8 and 9 IR spectra showed no indication of either oxygen, nitrogen nor any hydrogen in the typical bonds that may be expected in such material.

X-ray diffraction analysis (EDAX analysis), however showed presence of oxygen. This may have come from the raw material (since oxygen is present in the isopropoxide); and also as contamination from atmosphere
Figure 19: Aluminum Nitride Particle Size Distribution (run # 3) Temp; 1073 K, Color; Pale, Ammonia as reactant.
Figure 20: Aluminum Nitride Particle Size Distribution (run # 5) Temp; 1073 K, Color; Pale, Ammonia as reactant.
Figure 21: Aluminum Nitride Particle Size Distribution (run # 7) Temp: 1073 K, Color: Pale, Nitrogen as reactant.
Figure 22: Aluminum Nitride Particle Size Distribution (run # 8) Temp; 1123 K, Color; Tan, Nitrogen as reactant.
Figure 23: Aluminum Nitride Particle Size Distribution (run # 9) Temp; 1073 K, Color: Yellowish white, Nitrogen as reactant.
Figure 24: Aluminum Nitride Particle Size Distribution (run # 12) Temp: 1050 K, Color: Yellowish white, Nitrogen as reactant.
Figure 25: Aluminum Nitride Particle Size Distribution (Run # 13) Temp; 1073 k, Color; pale, Nitrogen as reactant.
Figure 26: Aluminum Nitride Particle Size Distribution (Run # 15) Temp; 1048 k, Color: yellow, Nitrogen as reactant
Fig. 27. Infrared Spectra for Aluminum Nitride (run # 1). Peaks at wavenumbers 3500 & 1000 correspond to N-H or O-H and -O group respectively.
Fig. 28. Infrared Spectra for Aluminum Nitride (run # 1). Peaks at wavenumbers 3500 & 1000 correspond to N-H or O-H and -O group respectively.
Fig. 29: Infrared Spectra for Aluminum Nitride (run # 7) Peak only at wavenumber 1000 is shown, indicating presence of -O group only.
Fig. 30: Infrared Spectra for Aluminum Nitride (run # 7A) Peak at wavenumber is smaller, indicating the reduction in -O group presence.
Fig. 31: Infrared Spectra for Aluminum Nitride (run #8) IR spectrograph shows no peaks indicating no N-H, O-H, or -O group.
Fig. 32. Infrared Spectra for Aluminum Nitride (run # 9) IR spectrograph shows no peaks indicating no N-H, O-H, or -O group.
since the powders were stored for a long time before analysis. The analysis also showed presence of aluminum and nitrogen in consistent ratios. The presence of oxygen indicates that the isopropoxide should not be preferred for manufacture of AlN in an aerosol reactor.

**Reactor Efficiency**

Based on run # 3, the amount of Al$_2$O$_3$ collected on a filter was 0.063 gms/minute. Therefore moles per minute correspondingly are, $\frac{0.0603}{101.964} = 0.000591$ moles/min. Now, using the reaction,

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

and the fact that 3.02 gms of AlN was obtained over a period of 51.5 minutes; the amount of Alumina converted to give this yield is, 0.0722 gms/min.

Similarly, the amount of Al. Isopropoxide evaporated was found out (by measuring the bubbler before and after experiment) to be 23.6 gms. 2 moles of Al-isopropoxide give one mole of Alumina. Therefore, the amount of alumina obtained from vapors is 0.1133 gms/min.

The overall conversion efficiency of the reactor in run #3 is then:

$$\text{Efficiency} = \frac{0.0722}{0.1133} = 0.637 = 63.7\%$$
Chapter 6

CONCLUSIONS AND DISCUSSIONS

Aluminum Nitride powders were prepared by direct thermal decomposition of vapors of aluminum isopropoxide and subsequent reduction by either nitrogen gas or ammonia gas. This method was significantly different from the methods used by other researchers.

It was possible to obtain a uniform sized submicron powder using a flow reactor. The difference in particle size for different runs can not be analyzed theoretically since the reaction kinetics were not determined. In order to understand this phenomenon, analysis of the process in the flow reactor might be undertaken.

As indicated by the IR spectrographs, it is possible to remove impurities by taking suitable precautions and further purifying the commercially available nitrogen and ammonia gases. The thermal decomposition and reduction reactions in the flow reactor are much faster than in the methods used by others. This process significantly reduces time involved in preparation by faster reaction, and elimination of intermediate steps of obtaining hydroxides, oxides and amides of aluminum.

It was observed that the product yield is very small
as compared to preparation from halides. This is due to
the fact that amount of aluminum contained in the parent
compound (aluminum isopropoxide) itself is only about 6 %
by weight. Yield might be improved if halides are used in
place of alkoxide (aluminum isopropoxide). In addition,
the elimination of oxygen from the products is extremely
difficult. Consequently, the use of halides is
recommended for such a process.

The best product obtained was between the
temperatures of 750 to 800 °C. If the temperatures were
raised above 900 °C, very fine carbon particles get
entrained in the gas stream and contaminate the product.
Black color observed in samples from runs 1 & 2 is
indicative of this. Perhaps, at this temperature above
900 °C carbon particles do not deposit at the walls of the
reactor and as a result find their way into stream (Carbon
particles have been found deposited on the walls of the
reactor).

Contrary to the expectations aluminum nitride
produced with ammonia was not of good quality as it
contained oxides and other impurities. Product with
nitrogen was better and devoid of impurities. Yet better
yields can be obtained by using Aluminum Halides as
starting materials with due care.

Difficulties that one faces with the use of flow
reactor are, (1) Preventing contamination, (2) vapor
generation and delivery,(3) Deposition on reactor walls.

Production of aluminum nitride in a flow reactor can be adopted for commercial production. This should be done only after analyzing the effect of operating parameters on the process. This can be a continuous operation as opposed to other methods. This process can achieve significant cost advantages because of the nature of process and fast production rates.
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