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Vapour Phase Synthesis of AlN Using a Transferred Arc Plasma System

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Department of Chemical Engineering McGill University, Montreal December 1993

Under the Supervision of Prof. R. J. Munz

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of Doctor of Philosophy

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Abstract

This work introduces a new concept for the synthesis of ultrafine aluminum nitride powder. A transferred arc plasma torch of 6.5 kW was used as a heat source to vaporize an aluminum ingot as a source of aluminum vapour for the synthesis of aluminum nitride outside the plasma chamber. The aluminum vapour produced in the plasma chamber was carried by the argon plasma gas to a tubular synthesis reactor where it reacted with ammonia injected radially. The effects of arc current, arc length and argon flow rate on the aluminum evaporation rate and the gas temperature reached in the mixing zone were studied. The results show that long arcs, high currents and high argon flow rates were best to maximize the temperature in the mixing zone and short arcs, high current and high argon flow rate were best for high evaporation rates. Experiments were performed to study the effect of arc length, nitriding agent used, ammonia jet momentum, ammonia flow rate, residence time and temperature on the conversion to aluminum nitride. Conversions up to 100% were achieved. The aluminum nitride produced had an average particle size of approximately 20 nm and specific surface area of about 90 m²/g. A numerical model, describing the aerosol particle size evolution, developed by Proulx and Bilodeau was successfully applied to the system.

Résumé

Un nouveau concept pour la synthèse de poudres ultrafine de nitrure d'aluminium est présenté. Une torche à plasma à arc transféré d'une puissance de 6,5 kW a été utilisée pour vaporiser une pastille d'aluminium comme source de vapeur d'aluminium pour la synthèse de nitrure d'aluminum à l'extérieur de l'enceinte où est contenu le plasma. Les vapeurs d'aluminium produites dans l'enceinte du plasma étaient charriées par le gas plasmagène (argon) vers un réacteur de synthèse tubulaire où elles se combinaient à l'ammoniac injecté de manière radiale. L'influence du courant d'arc, de la longueur d'arc et du débit d'argon sur l'évaporation d'aluminium et sur la température des gaz dans la zone où ces derniers se mélangent a été étudiée. Les résultats montrent que de longue colonnes d'arc, de hauts courants et un haut débit d'argon optimisaient la température dans la zone où les gaz se mélangent et de courtes colonnes d'arc, de hauts courants et un haut débit d'argon optimisaient le débit des vapeurs d'aluminium. Des expériences ont été menées pour étudier l'influence de la longueur d'arc, des différentes sources d'azote utilisées, du flux et du débit d'ammoniac, du temps de résidence et de la température sur le taux de conversion de l'aluminium en nitrure d'aluminium. Des taux de conversion de 100 p.cent on été observés. Les particules de nitrure d'aluminium produite avaient une taille moyenne de 20 nm et une aire spécifique de 90 m²/g. Un modèle numérique de la taille des particule aérosoles, développé par Proulx et Bilodeau, étaient en accord avec les résultats expérimentaux.

To my twin soul, my wife Norma with all my love.

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1 Introduction

As technology advances, the search for new materials with very specific mechanical, chemical and physical characteristics, has become a great challenge of the modern world. Among these materials, ceramics have received particular attention from researchers over the last decade. Due to their remarkable qualities, when properly made, ceramics have been successfully utilized in areas where common sense dictated that their use should not be possible.

There are two good definitions for ceramics. The first one states that ceramics are "Minerals of variable composition and rather doubtful purity (that) are subjected to an unmeasurable thermal treatment for a period of time just long enough to allow unknown reactions to take place incompletely, yielding the heterogeneous, non-stoichiometric material known by the name ceramics". This definition from Professor Gugel is a rather curious one. However those working in this field know that there is some truth to it. A lot of improvements have been made over the last decades, but a lot of studies are yet to be done in order to render this definition total!y erroneous. The second definition states that "Ceramics are inorganic nonmetallic solids with ionic and covalent bonding. These bond types give rise to the properties of ceramics (hardness, inertness, high melting temperature, ionic conductivity, electrical resistivity, ferroelectricity, piezoelectricity, thermal conductivity, thermal expansion etc.) and undesirable ones (brittleness, difficulty to fabricate to theoretical density, etc.)" [Nicholson 1988]. The main objectives of this work were:

- to design and built a new kind of synthesis reactor where the vapour synthesis phase reaction was carried out outside the plasma chamber,
- to investigate the use of this reactor for production of aluminum nitride and to study the effect of some relevant variables of the process, and
- to apply suitable models to improve the general understanding of the mechanisms of particle nucleation and growth.

The text which consists of six chapters is divided into two main parts. The first part comprises Chapters 1 to 4 and consists of introduction, literature review, theoretical background and experimental apparatus, and procedures. This part gives the necessary background to the project including the state of the knowledge, discussion about thermodynamic, an overview of the model describing the aerosol particle evolution, and detailed description of the experimental apparatus and procedures as well as the techniques used to characterize the powder produced. The second part comprises Chapters 5 and 6 and consists of results and discussion, and conclusion.

2 Literature review

High technology applications require more and more stringent physical and chemical requirements on the starting powders. Table 2.1 lists some relevant ceramic powder properties and techniques of analysis utilized for evaluating them.

Myriad of qualities and possible applications for ceramics can be enumerated, but manufacturing problems still persist and have to be solved. Unfortunately, there is also a myriad of problems, not only related to the sintering processes, but also related to powder quality, yield, accuracy of the test data of the sintered parts, etc.

In order to obtain a ceramic material with properties as close as possible to the desirable properties, it is necessary to use the most adequate sintering process and to work with high quality powders. Using powders with high quality is one of the most important requirements for obtaining a ceramic material with reliability.

Accurate test data are very important for dimensioning parts of equipment. Besides the fact that accurate data are difficult and expensive to obtain, mechanical tests usually result in non-reproducible data that cannot be easily related to the actual performance of the ceramic material [Lewis Nov. 1988].

It is well known that the powder preparation route determines the degree of sintering because that process controls the particle morphology, purity, chemical homogeneity, degree of crystallization, particle size and particle size distribution

Despite these problems, ceramics offer enormous potential advantages that support expending research on them.

2.1 Chemical Property Requirements

The crystalline structure of the powder is the first property to be considered. To obtain the appropriate crystal structure is very often the main purpose of the synthesis process. Many ceramic materials can be in present more than one crystal structure, for example α and β Si₃N₄. Many compounds exist as low-temperature crystal structures after synthesis but are transformed into a more ordered crystal structure at the high temperature environment typically found during sintering processes. This transformation may play an important role in the densification process which makes control of the crystal structure composition and content an important requirement.

X-ray diffraction is most frequently used to determine crystal structure composition and concentration. Comparison with calibration curves of either the peak heights or areas under peaks provides a reliable measurement of the amount of each crystal structure present. Infrared and Raman spectrometry are also used but take longer and do not provide as much information about other substances. However, Raman spectroscopy can identify small fractions of crystal structures that cannot be detected with X-ray diffraction [Lewis Jan. 1988].

Chemical purity seems to be the most costly feature of advanced ceramic powders given the high level of difficulty and the costs involved in removing the final ppm's of impurity. Depending on the application, the final ppm's are very important because they can affect sinterability, grain growth and final property of the sintered parts. For example, oxygen lowers the thermal conductivity in aluminum nitride ceramic. There are three types of impurities: - cation impurities often have limited solid solubility in the major crystal structure and form second crystal structures during heating processes. Second crystal structures often are deleterious to such properties as strength, optical transmittance, chemical resistance, electrical behaviour, high-temperature creep resistance and thermal conductivity.

- anion impurities may play an important role during the sintering processes. Oxygen is the most important anion impurity. It can be present as an oxide or oxinitride layer on the surface of the particles and may react with sintering aids to form low-melting point crystal structures.

- particulate impurities, of organic or inorganic nature, left within the powder are difficult to detect. Many impurity analysis techniques rely on milligram-sized samples, which have a high probability of completely missing the impure particle. A good sampling methodology becomes very important to allow a reliable analysis [Rhodes 1989].

Chemical composition is often determined by classical chemical techniques. However, when the objective is to detect impurities, there are a number of techniques that can be used. Some of these techniques are listed in table 2.1.

Property	Technique		
Morphology, particle size and particle size distribution	Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray and electron diffraction.		
Specific surface area	Brunner-Emmett-Teller (BET) method.		
Crystal structure composition and concentration	Quantitative X-ray diffraction (XRD) and infrared (IR).		
Chemical composition	Wet chemical analysis, atomic absorption, emission spectroscopy, mass spectroscopy and plasma emission spectroscopy.		

Table 2.1 Ceramic Powder Property and Analysis Techniques

Cation impurities are often identified using emission spectroscopy, atomic absorption, mass spectrometry and plasma emission spectrometry. Anion impurities are identified using mass spectrometry, neutron activation and combustion. Particulate impurities are identified using optical and electron microscopy, X-ray diffraction and chemical analysis.

2.2 Physical Property Requirements

Ceramics are refractory materials, which means that the ceramic parts must be formed by sintering processes and not by melting and casting. Ceramic parts are brittle which means that the microstructure cannot be substantially changed after sintering. Therefore the sintering process must produce the final desirable structure. The fundamental requirement of a ceramic powder is its sinterability; it must reach full density when heated below its melting point. The sintering driving force is proportional to the thermodynamic surface energy per unit area, which is constant, and to the variation of surface area. Hence the requirement for high surface area powders, which is obtained from very fine powders. Also important for sinterability is the number of particle to particle contacts per unit volume of powder compact. Hence, the importance of the particle size distribution of powder. The particle size distribution must be as narrow as possible. High green densities can be achieve by mixing powders with very well known particle sizes. Powder segregation and agglomeration must be controlled because they can limit the attainable green density and lead to local inhomogeneous mixing causing problems to the final sintered microstructure. Agglomerates are probably the most difficult powder property to control [Ring 1990]. Many methods are employed for determining morphology, particle size and particle size distribution. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the most widely used techniques available to evaluate all these properties. Light scattering is an easy and fast technique to perform particle size evaluation. It uses a light beam passing through a slurry and the scattering is correlated to the particle size. Other methods include measurements of air permeability, Brunner-Emmett-Teller (BET) (surface area) method and X-ray diffraction peak broadening.

The most widely used method to evaluate specific surface area is the BET method. Sinterable powders require surface areas in the range of 10 to 50 m^2/cm^3 which are accurately measurable by the BET method [Kendall 1989].

There are two interesting features of ceramic powders that are rarely measured: surface energy and composition. The surface energy of a powder appears in the equation describing sintering and agglomeration. Surface composition of powders may be an important feature. Many powders are known to react on their surface to produce surface films of different properties.

2.3 Ceramic Powders Market

The U. S. market for advanced ceramic powders according to applications and material types is shown in Tables 2.2 and 2.3, respectively. Electronic components form a large part of the present market for advanced ceramics. The largest growth is expected to be in structural

components. Among the different types of ceramic powders, the largest growth is expected to be in the combined nitride market.

Application	1989		1990		1995		AAGR
	(%)	(\$M)	(%)	(\$M)	(%)	(\$M)	(%/yr.) 1990-95
Electronic	81.6	340.5	81.2	374.1	80.8	561.0	8.5
Structural	13.3	55.6	14.0	64.2	15.3	105.9	10.5
Coatings	5.1	21.3	4.8	22.2	3.9	27.0	4.0
Total	100.0	417.4	100.0	460.5	100.0	693.9	8.5

Table 2.2 The U. S. Market for Advance Ceramic Powders According to Applications

Source: Business Communications Co.

Table 2.3 The U. S. Market for Advanced Ceramic Powders According to Material Types

Material	1989		1990		1995		AAGR
Туре	(%)	(\$M)	(%)	(\$M)	· (%)	(\$M)	(%/yr.) 1990-95
Oxides	88.2	368.0	87.7	404.0	87.8	608.9	8.5
Carbides	9.8	41.0	10.0	46.0	9.4	65.0	7.1
Nitrides	2.0	8.4	2.3	10.5	2.8	20.0	13.8
Total	100.0	417.4	100.0	460.5	100.0	693.9	8.5

Source: Business Communications Co.

Aluminum nitride (AlN) has received a lot of attention from the electronics industry in recent years. AlN has many attractive properties for electronic applications.

2.4 Applications of Aluminum Nitride

Aluminum nitride is characterized by the presence of covalent bonding in its structure: it has high thermal conductivity and high electrical resistivity. The major applications in electronics include ignition modules, RF microwave packages, hybrid power-switching packages, laser diode heat spreaders, etc.

The thermal conductivity of aluminum nitride measured on single crystals, is 320 W/m.K which is comparable to that of copper (400 W/m.K). However, measurements indicate that residual impurities in commercial AIN, particularly oxygen, are responsible for lowering the thermal conductivity. It is reported in the literature [David 1990] that the thermal conductivity for commercial AIN products can vary between 30-320 W/m.K depending on the level of impurities. Therefore, AIN is an attractive material to be employed in the solution of heat dissipation problems in semiconductor devices operating at or above room temperature. One method of heat removal is to bond the semiconductor to a non metallic substrate of high thermal conductivity.

Structural parts of AlN can exhibit a high performance due to its mechanical, chemical and thermal stability. Sintered parts manufactured from AlN have been used for nozzles, thermocouple protecting tubes, crucibles, boats, cutting tools, filters for polymer and glass compounds, etc.

AlN can also be made translucent or transparent if it is of high density and high purity, which, when combined with its wear resistance, make AlN attractive for some electrooptics applications.

2.5 Conventional Synthesis of Aluminum Nitride

Aluminum nitride has been synthesized in industry mainly by carbothermal nitridation of alumina [Bachelard 1989]. This process is characterized by a solid-solid reaction between carbon and alumina as the first step of the global reaction. This seems to be the rate determining step. Gas-solid reaction also takes place due to the presence of carbon monoxide generated in the first step. The AlN particle size obtained is similar to the starting alumina. As a result the starting material must be very fine in order to generate AlN powders with a particle size distribution required for advanced ceramics.

A carbothermal nitridation process using colloidal oxide precursors trapped in a polymer matrix has been developed [Silverman 1988]. In this process, the polymer acts both to isolate the particles during reduction (limiting growth and agglomeration) and to serve as the carbon source for reduction. The first step in the synthesis is the trapping of colloidal alumina particles in the polymer. Following polymerization, the alumina poly composite (furfuryl alcohol) is reduced in nitrogen atmosphere at 1575°C.

AlN powders can also be prepared from alkoxide by carbothermal reduction and nitridation [Mitomo 1987]. In this process aluminum hydroxide powder is precipitated by the hydrolysis of aluminum isopropoxide solution. The precipitate is formed on fine carbon powder dispersed in alkoxide or alkoxide solution. This mixture is heated in flowing nitrogen or ammonia. During heating, the AlOOH precipitate decomposes thermally to Al_2O_3 . At high temperature ($\pm 1300^{\circ}C$), the carbothermal and nitridation reactions take place to form AlN.

Another route for synthesizing aluminum nitride is the direct nitridation of aluminum [Belau 1988 and Kimura 1989]. This method is important because it can be easily used continuously by the nitridation of aluminum particles floating in a stream of nitrogen (N_2) and ammonia (NH_3) gas. In this process aluminum powder is agitated mechanically and a nitrogen stream blows the aluminum up inside the reactor which is heated by a resistance furnace. A N_2/NH_3 gas mixture is then injected inside the reactor. Since ammonia gas is more reactive than nitrogen, AlN can be synthesized at a lower temperature.

AlN can be synthesized via pyrolysis of a precursor, for example $Al(NH_2)_3$. The precursor in this case, can be prepared by reacting $AlBr_3$ with KNH_2 in liquid ammonia [Maya 1986, Seibold 1989 and Peters 1990].

Synthesis of ceramic powders from vapour phase generates finer powders. It is well known that obtaining fine powders with a narrow particle size distribution is one of the most important requirements for making advanced ceramic parts.

AlN powders can be synthesized by a vapour phase reaction between AlCl₃ and NH₃ at about 1200°C [Kimura 1988 and Nickel 1989], a reaction that produces highly corrosive byproducts. The costs involved are high since reactors have to be manufactured with corrosion resistant materials and the gas effluent must be treated. On the other hand, the advantages of this process are:

- the production of finer powders and

- the attractiveness of possibly working continuously.

2.6 Thermal Plasmas and Ceramic Powder Synthesis

The thermal plasma synthesis method offers an attractive and chemically unspecific route for ceramic powder synthesis. Recently, there has been an increasing interest in the use of this technique. This method is distinguished by its complete flexibility in the choice of reactants. It is advantageous in forming fine powders because the reactions take place at high temperatures with subsequent high quenching rates of gases at the exit. This is necessary in avoiding decomposition of products and excessive growth of the particles [Kong 1989 and Meyer 1987].

Thermal plasmas for synthesis can be produced by:

- high frequency discharges,

- high intensity alternate current (A.C.) arcs and

- direct current (D.C.) arcs.

2.6.1 Radio Frequency Plasma

The radio frequency (R.F.) inductively coupled plasma is often used for ceramic powder research. The main advantage of the R.F. plasma technique arises from the fact that the absence of electrodes gives rise to a clean process which generates reaction products with higher purity. R.F. plasmas generate a large diameter and low velocity plasma which is ideal for studying and carrying out chemical reactions. However, both the low energy utilization efficiency, known to be about 50% (or less) of the power input, and sensitivity from outside interferences are problems to be overcome. The discharges always become unsteady when reactive materials are

added to the discharge region. This seems to have prevented this technique from being rapidly developed and applied [Zhu 1985 and Kameyama 1987]. Some attempts, such as the development of a hybrid D.C./R.F. plasma torch, have been made to solve this problem. Unfortunately, the electrodeless feature is then lost [Yoshida 1985].

2.6.2 Direct Current Plasma Torch

In the case of high intensity arcs, DC arcs are commonly utilized in plasma synthesis research. Both non-transferred and transferred arcs have been used to promote chemical reactions. Non-transferred arcs can be operated at low voltages (20-150 V) and are characterized by their ability to sustain the arc at relatively low flow rates and high exit gas enthalpies; these conditions are ideal for material synthesis. However, the device will operate at higher current which leads to significant electrode erosion, increase in costs and higher levels of contaminants in the reaction products.

There are two types of transferred arcs:

- the arc is transferred from the cathode to a workpiece;

- the transferred arc is terminated on a secondary electrode.

Transferred arcs attain the highest efficiency when the anode is the workpiece, because the energy losses are then essentially from the cathode.

Each plasma generator has its distinct advantages and limitations and only future research, including the effects of scale-up, will lead to a choice of the optimum technology for structural ceramic powder synthesis.

2.7 Synthesis of Aluminum Nitride in Thermal Plasmas

2.7.1 Synthesis of AlN in DC Arcs

Etemadi (1991) investigated the synthesis of aluminum nitride by evaporation of an aluminum anode in a free-burning atmospheric-pressure nitrogen arc. The plasma chamber was evacuated at a pressure of around 0.13 Pa. The arc parameters were the following:

- 100 Amperes and 20 Volts;

- gas flow rate of 18 L/min;

- arc length was kept at 1 cm.

In this process the aluminum vapour reacts with nitrogen resulting in AlN. About 40% of the product was collected in the form of highly oriented polycrystalline aluminum nitride. The rest was deposited on the plasma chamber walls as an ultrafine Al + AlN powder with an average particle diameter of 300 Å (30 nm). A typical result was a deposition rate around 100 g/h at an arc power level of 2.2 kW. It was also observed that the oxygen content of the deposited powder diminished when only a small percentage of NH₃ was injected into the chamber. This was probably due to the reaction between oxygen, hydrogen and the radicals produced in plasma from the dissociation of ammonia.

The following effects on crystal growth were observed:

- no crystal growth was observed when synthesizing AlN by evaporation of an impure aluminum anode at currents higher than 100 A,

a stronger plasma flow prevented the formation of AlN crystals, an increase in the flow rate of the gas injected around the cathode tip into the plasma slowed down the crystal growth and
the crystal growth decreased when introducing NH₃ or H₂ into the reactor.

Godin et al (1991) studied the effects of arc length, current intensity and the nature of the nitridation gas on the synthesis reaction of AlN using a transferred arc plasma torch. The arc power of the pilot plant ranged from 200 to 350 kW (450 to 650 A) and arc length from 15 to 30 cm. The plasma generated between a thoriated tungsten cathode and an aluminum anode was stabilized by a shrouding nitrogen or ammonia gas. The aluminum evaporated from the anode reacted with nitrogen bearing gas to form AlN. It was observed that the arc length and arc current were minor factors for the evaluation of the chemical composition of AlN. Ammonia gave a total nitridation of aluminum at ratios up to 10 for stoichiometric products, whereas, pure nitrogen gave a non-stoichiometric material whatever the gas flow rate was applied. The powders collected on the chamber walls and from a filter located outside the furnace had the same characteristics. The AlN was found to be hexagonal using X-ray diffraction. It was found, using TEM, that the individual particle size was below 0.2 µm but that particles agglomerated in clusters with an average diameter of about 0.7 µm. The particles had spherical or hexagonal shapes. Elemental chemical analysis revealed an oxygen content less than 1.5%.

Ishizaki et al (1989) investigated the production of ultra-fine nitride (Si₃N₄ and AlN) and carbide (SiC, TiC and WC/W₂C) powders using a plasma arc in a controlled atmosphere (with ammonia or methane gas). The metallic specimens were placed on a water-cooled copper anode plate in an atmosphere-controlled chamber. The arc was generated between the tungsten cathode and the anode sample by a tungsten inert gas (TIG) welding machine. Before each experiment

the chamber was evacuated to about 100 Pa several times and the air purged off by argon. Aluminum nitride ultrafine powders were produced in an ammonia atmosphere. The possibility of producing AlN with a good yield using only argon as plasma gas and ammonia as nitriding agent, demonstrated that the main nitridation reaction occurs immediately outside of the plasma area. A TEM observation of the powder showed that AlN was composed of rounded shapes 20 to 50 nm in diameter.

Baronnet et al. (1990) studied the synthesis of aluminum nitride by a transferred plasma arc system. The arc was struck between a thoriated tungsten cathode and an aluminum ingot (99.9%) inserted in a graphite crucible held on the anode. Nitrogen or a mixture of nitrogen and hydrogen was used as plasma gas. Ammonia was used as a jacket plasma gas. Typical operating conditions were:

- 200 A, 90 V;

- arc length around 110 mm;

- 20 NL/min of nitrogen and 15 NL/min of hydrogen.

TEM analysis indicated that the particle size varied from 10 to 100 nm, the particle morphology was hexagonal and the crystalline structure was a closed-packed hexagonal structure. The most important chemical impurity was aluminum condensed from of the vapour phase. The authors also observed the formation of a "mushroom" on the aluminum ingot. The presence of AlN and Al was identified in this mushroom by X-ray diffraction.

Ageorges et al. (1991) studied two different devices to synthesize ultrafine powder of aluminum nitride. The first device and results were described and discussed by Baronnet et al (1990). In the second, the cathode (thoriated tungsten) and the anode (copper) were coupled above Al (99.9%) held by a graphite crucible. The cathode arc was nitrogen and the anode arc was argon. The angles of the arcs were established in order to allow the nitrogen tail flame to impinge directly on the aluminum. An ammonia stream was directed on the aluminum surface. The results for this second device were: specific surface area of the order of 12 to 16 m²/g and particle size diameter around 135 nm. Using N₂ as a nitrogen source the powder product was constituted of 40% of AlN and 60% of aluminum. The supplying of ammonia increases the aluminum nitride content in the product up to 90%. Using a nitrogen anode arc, the aluminum content had been increased up to 99.3%. In this case, an excessive crosion of the copper anode had occurred.

Lu and Pfender (1989) studied the synthesis of aluminum nitride using a lab scale triple torch plasma reactor (TTPR) operating in the non-transferred mode. In this device the argon or argon and nitrogen plasma jets from three identical plasma torches form a converging plasma volume with a temperature valley in the center. The operating conditions were as follows:

- 300 A and 60 V,

- plasma gas flow rate was 6 L/min of argon and 7 L/min of nitrogen

- the nitrogen carrier gas flow rate was 3.5 L/min and

- sheath nitrogen gas flow rate of the powder feeding tube was 5 L/min.

The reactor vessel was evacuated to 1.3 Pa and refilled with argon before starting the plasma torches. The reaction was performed at atmospheric pressure. Nitrogen was used as carrier and sheath gas for introducing the aluminum powder (1 to 2 μ m) into the plasma. The vaporized aluminum reacted with nitrogen to form aluminum nitride. X-ray diffraction analyses indicated that the crystal structures in the final product, collected at 15 cm downstream from the

converging point of the plasma jet, were hexagonal and cubic. It was also observed that only very little aluminum remained unreacted. In the samples collected 5 cm downstream from the converging point, the amorphus structure was greatly reduced. Hotter surfaces also reduced the formation of the cubic crystal structure of AlN due to the reduced quenching rate.

Vissokov et al. (1983) studied the synthesis of ultrafine aluminum nitride by interaction of aluminum and nitrogen in a electric-arc plasma. High purity aluminum powder was injected into the end of the active part of the arc using a vibratory feeder. Nitrogen was used as carrier gas and nitrating agent. Argon and mixtures of argon and nitrogen were used as plasma gas. In this process aluminum was evaporated and synthesized to aluminum nitride in the gaseous phase and by diffusion on the phase boundary. The authors found that the rate determining step of the process is the evaporation of the aluminum powder. A nearly 100% pure aluminum nitride powder was produced. The diameter of its spherical particles was less than 60 nm and the specific surface varied from 60 to 100 m²/g. It was also observed that the fine dispersion determined the chemical reactivity of the powder. With continuous exposure to an atmosphere with 100% relative humidity, the aluminum powder was completely hydrolysed to hydroxide and ammonia.

Long and Foster (1959) looking for a ceramic material that could resist aluminum attack in the temperature range 1800 to 2000°C, they studied aluminum nitride synthesis by ctriking a DC arc between two high-purity consumable aluminum electrodes in a nitrogen atmosphere. The aluminum vaporized in the arc reacted with nitrogen to form a hard lump of aluminum nitride between the two electrodes. The growth of the lump extinguished the arc. About 80% of the product was recovered as highly sintered lumps and about 20% was deposited on cold wall of the reactor as fine powder. By chemical analysis the lump of aluminum nitride was 92 to 94% AlN. The fine powder was about 25% AlN. They had to grind the lumps in order to get the fine powder required for sintering process. After ball milling for 72 hours in commercial methanol containing traces of water the powder obtained was 57.5% AlN. The aluminum was reactive to moisture, particularly during grinding when fresh surfaces were exposed. Dry milling was not practical because the material was extremely abrasive.

2.7.2 Synthesis of AlN in RF Induction Plasma

Baba et al. (1987) studied the synthesis of aluminum nitride using an RF induction plasma. The chamber was evacuated at about 1.3 Pa and filled with argon gas at 101.3 kPa. Then, the plasma gas (42 L/min argon and 18 L/min nitrogen mixture) was introduced from the top to the copper coil connected to an RF generator (13.56 MHz, 20 kW input power). Pure aluminum metallic cubes were lifted up into the plasma flame. Nitridation gas, ammonia (5 to 20 L/min), was introduced at the plasma tail flame just above the aluminum bath. The production rate of ultrafine powder was about 100 g/hr. Some of the properties of the ultrafine powder, such as specific surface area, atomic ratio and impurities were investigated. The specific surface area, measured by BET method, was about 50 to 80 m²/g. Particle sizes were estimated as being 230 to 370 Å. The atomic ratio N/Al was determined by chemical analysis as being 0.91 to 0.93. It was pointed out that this deficiency of nitrogen atoms was related to a Al(OH)₃ layer on the surface of the powder. Using radio analysis, it was observed that the oxygen impurity in the powder was about 5 wt%. Infrared spectra was measured to clarify the presence of oxygen in the powder. It was observed that a peak due to OH bonds and a weak absorption peak due to H_2O existed. This observation suggested that the H_2O from the air was absorbed on the powder surface, and afterwards, reacted with AlN forming Al(OH)₃. It was also observed that the oxygen content was roughly proportional to the specific surface area.

Wehling et al. (1991) investigated the synthesis of silicon nitride and aluminum nitride in an inductively coupled plasma. The metal powders were injected into plasma flame generated by a 48 kW high frequency generator. They observed that the major part of the powder was white with a spherical particle morphology. They found 7.4 wt% of oxygen in the powder obtained. They pointed out that some improvements of the process must be made in order to lower this content. Baba pointed out that the fine AlN powder is very reactive and it can reacts with the H₂O of the air. Some improvements on the handling of the powder after synthesis must be made. The specific surface area for AlN powder was 115 m²/g with an average particle size of 30 nm. They also observed that AlN powder obtained can be sintered to full density at 1530°C without additives at atmospheric pressure of nitrogen.

David et al (1990) investigated the synthesis of aluminum nitride powder and thin films in a parallel-plate RF plasma reactor by reacting trimethylaluminum (TMA) and ammonia. The powder produced was amorphous, had a particle size varing from 10 to 20 nm, and specific surface area of about 85 m²/g. The FTIR spectrum of the deposited powders showed the characteristic Al-N, O-H, N-H and Al-H bonds. The authors concluded that the peak centered around 3400 cm⁻¹, characteristic of O-H or N-H bonds was attributed to N-H bonding since oxygen readily converts from aluminum nitride to aluminum oxide and Al-O bond was not present after heat treatment of the powder.

3 Theoretical Background

This Chapter will be divided into two sections. In the first section, thermodynamic considerations for aluminum vaporization, and the aluminum nitride synthesis reaction will be discussed. A model for particle nucleation and growth will be presented in the second section.

3.1 Thermodynamic Considerations

Thermodynamic is a very useful tool in developing a new process or even for evaluating the possibility of optimizing existing processes. Thermodynamic calculations can establish the equilibrium conversion and composition for different conditions of temperature, pressure, type of reactants and reactant concentrations. The operating conditions needed to reach conversions at the desirable levels can be determined from these calculations. The reaction to be studied here is the vapour phase nitridation of aluminum to form solid aluminum nitride. Before going any further the reactants involved in the nitridation reaction will be analyzed.

3.1.1 Aluminum Vapour

The aluminum vaporized in the plasma chamber must reach the reaction zone in the vapour phase. Given the short residence time of the reactants (about 0.15 seconds) in the reactor used in this study, only gas phase reactions can reach complete conversion. The equilibrium

vapour pressure of aluminum at 1500 K is 1.73 Pa [Barin, Knake and Kubaschewski 1977]. It is possible to avoid aluminum condensation by keeping the aluminum partial pressures below the critical supersaturation pressure, which is about 1.7 10⁴ Pa at 1500 K. The latter assumes that aluminum has a critical supersaturation ratio of approximately 10⁴. According to Hecht, West, and Norton (1980) and Chang and Pfender (1987), inorganic solids, such as iron or potassium, with surface energy of the order of one J/m² can have supersaturation ratios as high as 10⁵. The supersaturation ratio (S) is defined by the ratio between the actual vapour pressure and the equilibrium vapour pressure. The supersaturation ratio for different aluminum molar concentrations as a function of temperature is shown in Figure 3.1.



Figure 3.1 Supersaturation Ratio vs. Temperature
Three distinct regions can be identified in Figure 3.1: subsaturation, supersaturation and critical supersaturation regions. The horizontal solid line represents the equilibrium (S=1), when the actual aluminum vapour pressure is equal to the equilibrium vapour pressure. The horizontal dashed line is the critical supersaturation ratio. A typical value for inorganic solids is 10^4 . It can be seen that the supersaturation ratio increases with the increasing of the concentration of aluminum. The critical supersaturation ratio plays an important role on nucleation. Below the critical supersaturation rate is significant. According to Chang, Young and Pfender (1987) nucleation occurs in a relatively short period of time (10^{-6} seconds). The aluminum molar concentration during the experiments performed during the present study was about 0.01. The gas temperatures must then be kept higher than 1400 K before reaching the reaction zone.

3.1.2 Nitriding Reactants

Ammonia and nitrogen gases are the most common nitrogen sources for the production of aluminum nitride powders. The equilibrium diagrams were calculated using the computer program, Facility for the Analysis of Chemical Thermodynamics ($F^*A^*C^*T$), developed by Bale, Pelton and Thompson (1979). Figures 3.2 and 3.3 show the equilibrium composition as a function of temperature for the Al/0.5N₂/75Ar and Al/NH₃/75Ar molar ratio mixtures, respectively. The molar ratios used in the calculations are approximately the same as values used in the experiments. According to these diagrams, under atmospheric pressure, complete conversion is possible below 1800 K for both nitrogen and ammonia. Based only on these thermodynamic calculations, it is not possible to determine clearly which reactant is the best nitriding agent.



Figure 3.2 Equilibrium Diagram of the Reaction Al $+ 0.5N_2 + 75Ar$

Figure 3.4 Shows the predominance diagram at 1073 K for the system Al-N-H-O. This diagram shows the predominance areas of aluminum compounds for different partial pressures of nitrogen or ammonia and different partial pressures of oxygen. The lines describe the equilibrium between two condensed phases. It can be observed that the predominance area of aluminum nitride is greater when using ammonia as the nitriding agent.



Figure 3.3 Equilibrium Diagram of the Reaction Al + NH₃ + 75Ar

This suggests that aluminum nitride can be synthesized at lower partial pressures of ammonia and higher partial pressures of oxygen. Ammonia appears to be an excellent nitriding agent, not only due to its reactivity [Godin, Chevallier, Amouroux and Morvan 1991] but also because aluminum nitride can be synthesized at higher partial pressures of oxygen due to the reducing atmosphere provided by ammonia. The equilibrium diagram for ammonia decomposition is shown in Figure 3.5. It can be seen in this diagram that ammonia starts to dissociate into nitrogen and hydrogen gases at temperatures above 300 K.



Figure 3.4 Predominance Diagram at 1073 K for the System Al-N-H-O

According to experimental kinetics results [Holzrichter and Wagner 1981] the decomposition is usually not fast enough to allow equilibrium to be achieved, particularly considering the residence time used to carry out the nitridation reaction in the experimental study. This will be further discussed in Section 5.4.1.



Figure 3.5 Equilibrium Diagram for Ammonia Decomposition

3.1.3 Effect of Ammonia Ratio

The effect of ammonia molar ratio on the AlN equilibrium composition can be observed in Figures 3.3 and 3.6. The equilibrium diagrams show the results for $Al/NH_3/75Ar$ and $Al/10NH_3/75Ar$ molar ratio mixtures. According to these figures no significant effect on AlN equilibrium composition was observed when the ammonia mole ratio was increased. From the kinetic point of view, however, it is justifiable to use an excess of ammonia in the experiments.



Figure 3.6 Equilibrium Diagram of the Reaction Al + 10NH₃ + 75Ar

3.1.4 Effect of Oxygen

The effect of the oxygen concentration on AlN stability is shown in Figure 3.7. This equilibrium diagram shows the equilibrium composition as a function of partial pressure of oxygen under atmospheric pressure at 1000 K. Even low partial pressures of oxygen in the

system lead to the formation of alumina (Al_2O_3) at the expense of AlN. According to this diagram at about 879 Pa, the stoichiometric ratio Al/O_2 , all the aluminum is converted to Al_2O_3 .



Figure 3.7 Equilibrium Diagram of the Reaction Al + 10NH₃ + 75Ar + XO₂

After synthesis, or even after sintering, the presence of oxygen can oxidize the AlN powders or AlN substrate. A recent study showed that the oxide on AlN forms a protective coating which inhibits further oxidation. This makes the particle size an important parameter when oxidation is considered. The presence of oxygen as Al_2O_3 in the aluminum nitride powder is responsible for lowering the thermal conductivity in the final sintered ceramic. Suryanarayana (1990) showed that the oxide layer on AlN substrate can be useful for improving the adhesive bonding on copper films.

3.2 Particle Nucleation and Growth Modelling

As mentioned before, particle size is one of the most important powder properties for a successful sintering. Thermal plasma systems have been used for the production of ultrafine particles mainly at a laboratory scale. According to the literature, determining the relationship between particle size and process parameters is primarily empirical due to the complexity of plasma systems [Girshick, Chiu and McMurry 1987]. At the present stage, mathematical modelling is being used as a tool to improve the general understanding of the mechanisms of particle nucleation and growth. The models being developed can, in the future, aid in the evaluation and planning of pilot scale trials and scale-up.

In the following sections, the two-dimensional model developed by P. Proulx and J-F. Bilodeau, which simulates the aerosol particle size evolution in a cylindrical reactor, will be described. This model is subject of a PhD thesis by J-F. Bilodeau at the Université de Sherbrooke. In the first section, an overview of the governing equations will be presented. In the subsequent section, the aerosol size evolution will be discussed. Some details about homogeneous nucleation, particle growth (coagulation and condensation) and the moments method will be also discussed in this section.

3.2.1 Flow, Temperature, and Concentration Fields

In this work, ultrafine particles (UFP) are formed in the region between the ammonia distributor and nitrogen distributor. In this zone, the gas-phase reaction between aluminum vapour and ammonia takes place, and the contact with ammonia cools the gases considerably. The vapour pressure of the condensable species drops and hence the supersaturation ratio increases triggering homogeneous nucleation. Figure 3.8 shows the region considered in the model. Since the synthesis reaction occurs outside the plasma chamber, the plasma flame itself is not considered in this study.



Figure 3.8 Synthesis Reactor and the Region Considered in the Model

3.2.1.1 Assumptions

The choice of assumptions is one of the most important steps in modelling. Since each assumption can cause the model to deviate from reality, the assumptions must be examined critically to maximize the ability of the model to make reliable predictions. The following assumptions were made to solve the equations describing the fluid dynamics and heat transfer of the reactor:

- steady state is achieved,

- the flow is considered laminar and axisymetric, and

- the ultrafine particles have no effect on the flow and temperature fields.

The steady state cannot be truly achieved in this system, because of the long time necessary to heat the refractory materials. In order to minimize the effects of this assumption on the predict ability of the model, samples were taken after eight minutes of reaction when the reactor approached steady state. After this point, the temperature varies only slightly with time (Figure 4.5). The flow is laminar with Reynolds number equal to 272. The 24 evenly spaced jets of ammonia around the circumference and the distance of 10 cm between the plasma chamber and the synthesis reactor support the assumption of axisymetric flow. The assumption that the particles have no effect on the flow and temperature fields is reasonable when nanosized particles at low concentrations are involved; this was the case in the experimental phase of the present study.

The fluid dynamics, heat and mass transfer are then determined by solving the continuity, momentum, energy, and mass conservation equations.

$$\nabla (\rho u) = 0 \tag{3.1}$$

$$\nabla(\rho u u) = -\nabla P + \nabla(\mu \nabla u) \tag{3.2}$$

$$\nabla(\rho u h) = \nabla(\frac{k}{C_p} \nabla h)$$
(3.3)

$$\nabla (\rho u \omega_A) = \nabla (\rho D_{AB} \nabla \omega_A) + R_A \tag{3.4}$$

Where u is the velocity vector, which has two components $(u_x \text{ and } u_y)$ [m/s],

- ρ is the gas density [kg/m³],
- P is the pressure [Pa],
- μ is the gas viscosity [kg/m·s],
- h is the enthalpy [J/kg],
- C_p is the heat capacity at constant pressure [J/kg-K],
- k is the thermal conductivity $[W/m \cdot K]$,
- ω_A is the mass fraction of the species A,
- D_{AB} is the diffusion coefficient for A and B diffusion [m²/s], and
- $R_{\rm A}$ is the rate of production of A by gas-phase reaction [kg/m³·s].

The diffusion coefficient is determined assuming the Schmidt number equal to one.

3.2.1.2 Boundary Conditions

The boundary conditions used to solve the governing equations are:

- the velocity and temperature profiles are assumed to be parabolic at the entrance,
- the gradients at the exit are specified equal to zero,
- the centerline is the axis of symmetry, then the gradients are equal to zero, and
- the wall temperature is calculated by energy balance.

3.2.2 Aerosol Size Evolution

The model to be presented is an improvement over the earlier models proposed by Proulx and Bilodeau (1991 and 1992). The present model considers:

- the stable nuclei generation is evaluated by the homogeneous nucleation rate expression proposed by Girshick and Chiu (1990),
- the surface phenomena of condensation and evaporation are treated simultaneously with the coagulation contribution,
- the gas-phase chemical reaction is coupled to the aerosol dynamics, and
- two-dimensional particle concentration coupled to vapour concentration fields.

The two-dimensional model describing the aerosol particle size evolution was applied to the production of aluminum nitride powder, using the following assumptions:

- AIN condenses directly into the solid phase,

- the particles are assumed spherical, in the free molecular regime and the coefficient of coalescence is equal to unity,
- vapour condensation of the particles is considered for $K_{\pi} > 0.2$,
- the mean particle flow deviates from the gas streamlines by the thermophoretic force,
- particle Brownian diffusion is considered, and
- particles are assumed to be at the gas temperature.

In the following sections, the homogeneous nucleation and particle growth (coagulation and condensation) will be discussed.

3.2.2.1 Homogeneous Nucleation

The homogeneous nucleation rate expression of stable nuclei proposed by Girshick and Chiu (1990) will be described below. The authors consider all the classical theory assumptions, except that regarding the equilibrium state to which the evaporation should be referred. The assumptions of the classical theory are:

- surface tension is size-independent (capillarity approximation),
- mass accommodation equal to unity,
- the clusters are spherical and charge neutral,
- the London Van der Waals force is neglected, and
- the system is sufficiently dilute that evaporation coefficients depend only on cluster properties and on temperature.

The proposed new expression for the rate of homogeneous nucleation from an ideal supersaturated vapour $(I_{km}, m^{-3} s^{-1})$ is presented in Equation 3.5.

$$I_{km} = v_1 \left(\frac{2\sigma}{\pi m_1}\right)^{1/2} n_s^2 S \exp\left[\Theta - \frac{4\Theta^3}{27(\ln S)^2}\right]$$
(3.5)

Where v_1 is monomer volume [m³],

 σ is surface tension [N/m],

 m_1 is mass of a monomer [kg],

 n_s represents the equilibrium monomer concentration for a saturated vapour $[m^{-3}]$,

S is the supersaturation ratio,

 Θ is a dimensionless surface energy (σ -s₁/(k_B-T)),

T is the temperature [K],

 s_i is the surface area of a monomer $[m^2]$, and

 $k_{\rm B}$ is Boltzmann's constant [J/K].

3.2.2.2 Particle Growth

Stable aerosol particles formed by homogeneous nucleation, subsequently grow by coagulation and condensation.

Coagulation occurs by the collision between two particles that generate a third particle with mass equal to the total mass of the initial particles (the probability of collision among three or more particles is neglected). Assuming that all collisions result in coalescence, the evolution of the aerosol by coagulation is described by the balance Equation 3.6 (n_j is the concentration of particles containing j atoms or molecules per mass of gas, kg⁻¹):

$$\frac{\partial n_j}{\partial t} = \frac{\rho^2}{2} \int_{s^*}^{j} \beta_{j-i,i} n_{j-i} n_i di = \rho^2 n_j \int_{s^*}^{\infty} \beta_{j,i} n_i di$$
(3.6)

In the free molecular regime, the Brownian coagulation coefficient between particles of sizes i and j is given by Equation 3.7.

$$\beta_{ij} = \left(\frac{3\nu_1}{4\pi}\right)^{\frac{1}{2}} \sqrt{\frac{6k_BT}{\rho_p}} \left(\frac{1}{i} + \frac{1}{j}\right) \left(i^{\frac{1}{2}} + k^{\frac{1}{2}}\right)^2$$
(3.7)

Where ρ_p is the particle density [kg/m³].

The condensation phenomenon is based on the collision between monomers (atoms or molecules) and stable particles. In the free molecular regime, and neglecting the size of the monomer compared to the stable particle, the growth by condensation (or decay by evaporation) for a particle of size j is given by equation 3.8.

$$\frac{dv_j}{dt} = B_1 v_1 v_j^3 (S-1)$$
(3.8)

 B_1 is the condensation coefficient, given by Equation 3.9.

$$B_{1} = (36\pi)^{\frac{1}{2}} v_{1}^{\frac{1}{2}} n_{s} \sqrt{\frac{k_{B}T}{2\pi m_{1}}}$$
(3.9)

3.2.2.3 The Balance Equation

The conservation law applied to the density concentration of particles of each size is represented by equation 3.10.

$$\frac{\partial(\rho n_j)}{\partial t} + \nabla \cdot (\rho u_e n_j) = Ig^* \delta_{(j-s\gamma)} + \rho \frac{\partial(n_j u_j)}{\partial j} -$$

$$\nabla \cdot (\rho D_j \nabla n_j) + \frac{\rho^2}{2} \int_{\mathbf{s}^*}^{j} \beta_{j-i,i} n_{j-i} n_i di - \rho^2 n_j \int_{\mathbf{s}^*}^{\infty} \beta_{j,i} n_i di \qquad (3.10)$$

Where I is nucleation rate of critical nucleus,

 g^* is the number of monomers in a critical nucleus,

 $\delta_{(j \cdot g^*)}$ is the delta function, equal to one if $j = g^*$,

 u_e is the particle velocity including the thermophoretic deviation [m/s]; particles smaller

than 1µm have thermophoretic coefficient size-independent equal to 0.55,

u_j is the velocity of condensation [mol/s], and

 D_i is the diffusion coefficient of particles of size j [m²/s].

The first term on the LHS of the equation 3.10 refers to the accumulation of particles in the volume element, and the second is the convection term (considering the transport gas velocity and the thermophoretic deviation). The first term on the RHS is the contribution of nucleation and the second represents the vapour condensation on the particle surface. The last two terms define the contribution of Brownian diffusion and interparticle coagulation, respectively.

3.2.2.4 Method of Moments

Proulx and Bilodeau (1989) presented a comparative study between the discrete model and the moments model. The solution of the concentration of each individual particle size (discrete model) for a two-dimensional model is prohibitive when compared to the moments model. The method of moments is based on the description of the aerosol evolution of the particle size (based on particle volume) distribution function. The history of individual particles is ignored. The loss in information is compensated by a reduction in computational time. The application of the equation of conservation of particles to the definition of the moments gives the general equation for the conservation of the moments of order k of the distribution. In the present study, the equation 3.11 will be solved explicitly for the moments of order 0, 1 and 2.

$$\frac{\partial(\rho M_k)}{\partial t} + \nabla \cdot (\rho u_e M_k) = J(g^*)^k + k B_1 \rho (S-1) (M_{k-\frac{1}{3}} - A_1 M_k + A_2 M_{k+\frac{1}{3}}) +$$

$$K_{1} \nabla \cdot \rho \nabla (M_{k-\frac{1}{2}} + C_{1} M_{k-\frac{3}{2}}) + (k-1)(k+2) \frac{\rho^{2}}{4} < \beta > M_{\frac{1}{2}}^{2}$$
(3.11)

Where M_k is the moment of order k of the particle size distribution,

 A_i is the correction term for condensation (0.3626·dp₁/ λ), dp₁ is the monomer diameter [m], λ is the mean free path [m], A_2 is the correction term for condensation (0.0418·dp₁²/ λ^2), B_i is the condensation coefficient ((36 π)^{1/3}·v₁^{4/3}·n_s·(k_B·T/(2 π ·m₁))^{1/2}), C_i is the correction for moments diffusion (3.314/dp₁), K_i is the constant for mean moment diffusivity (k_B·T/3 π ·µ·dp₁), and < β > is the average coagulation coefficient, based on the population size distribution as proposed by Frenklach and Harris (1987).

The terms on the LHS refer to the accumulation and convection terms. The effect of nucleation appears on the first RHS term. The effect of condensation follows, defined by a correlation extending the free molecular rate expression up to $K_n = 0.2$. The contribution of diffusion is as proposed by Phanse and Pratsinis (1989), and appears as a source term since it depends on other moments. The contribution of coagulation, defined in the same manner as in the work of Frenklach and Harris (1987) is the last RHS term.

The vapour concentration (equation 3.12) is coupled to the aerosol moments by the phenomena of nucleation and condensation, which act as sink terms in the conservation equation.

$$\frac{\partial(\rho n_1)}{\partial t} + \nabla \cdot (\rho u n_1) = -Jg * -B_1 \rho (S-1) (M_1 - A_1 M_1 + A_2 M_1) + \nabla \rho D_1 \nabla n_1 \quad (3.12)$$

Where
$$D_1$$
 is the monomer diffusion coefficient

The four equations described (vapour concentration, moments of order 0, 1 and 2), along with the equations describing the fluid flow, heat transfer and chemical mixture in the reactor are solved using the SIMPLER control volume algorithm developed by Patankar (1980).

4 Experimental Apparatus and Procedure

In this chapter the following items will be described: the experimental system used to carry out the nitridation reaction of aluminum, the experimental procedures adopted to perform the study, and the techniques used for the chemical and physical analysis of the powder produced.

4.1 Experimental Apparatus

The experimental apparatus used in this work, including all auxiliary equipment, is shown in Figures 4.1 and 4.2. It consisted of the following basic units:

- transferred-arc plasma system,

- auxiliary equipment,

- synthesis reactor and

- powder collection system.

A detailed description of each of these units is given in the following sections.

4.1.1 Transferred arc Plasma System

A transferred-arc plasma chamber has been adapted to vaporize aluminum ingots. As shown in Figures 4.3 and 4.4, the chamber, which was thermally insulated to increase the



Figure 4.1 Schematic Diagram of the Experimental Apparatus



Figure 4.2 Photograph of the Experimental Apparatus

aluminum vaporization rate, had double water-cooled stainless steel walls. The insulation consisted of a layer of alumina felt and a layer of graphite felt. A molybdenum liner separated the insulation from the vaporization chamber to avoid contamination from the insulation materials and to provide an easy to clean surface. The top flange contained a 67 mm diameter opening to accommodate the cathode assembly. The cylindrical body had a 205 mm inside diameter, was 350 mm high and contained a 75 mm diameter vertical opening for the connection of the tubular synthesis reactor. The bottom flange had a 100 mm diameter opening to accommodate the anode assembly. O-rings were used to seal each flange, the cathode and anode assembly.



Figure 4.3 Schematic Representation of the Plasma Chamber



Figure 4.4 Photograph of the Interior of the Plasma Chamber

4.1.1.1 Cathode Assembly

The cathode assembly can be seen in Figure 4.3. It consisted of a conical 2% thoriatedtungsten cathode tip cooled by water fed from the top and a water-cooled concentric sheath nozzle. This set was kept concentric and electrically insulated by two Teflon rings. The argon plasma gas was injected through the annulus between the cathode tip holder and the sheath. The lower Teflon ring was drilled along its circumference to work as a gas distributor. The section of the cathode sheath that contacts the molybdenum liner was electrically insulated by alumina cement to avoid arcing.

4.1.1.2 Anode Assembly and Crucible

The anode assembly can be seen in Figure 4.3. It consisted of a 160 mm diameter copper disk that was cooled by a water-cooling system placed below it. The set of cylindrical graphite crucibles was placed in the center of the chamber, on top of the anode. A schematic drawing of the crucible can also be seen in Figure 4.3. The crucible was designed to minimize heat losses by radiation, conduction and convection, and to maintain good electrical contact.

4.1.2 Auxiliary Equipment

The auxiliary equipment includes electrical devices, rotameters and a vacuum pump.

4.1.2.1 Power Supply

The power was supplied by a Thermal Dynamic 40 kW selenium rectifier, model TDC IA-40. The input voltage was 3-phase, 60 Hz, 575 V, while the output circuit could provide 80, 160 or 320 V. An open circuit voltage of 160 V was used for all experiments. The rectifier was connected to a control console.

4.1.2.2 Control Console and Ignition System

The control console was equipped with a high frequency generator, a current regulator to control the output power, an ammeter and a voltmeter. A water-cooled resistor (1.3 ohms) and an electrical switch were placed into the external circuit between the auxiliary anode (nozzle) and the power supply. The high frequency generator was used to start the arc between the cathode tip and the auxiliary anode, creating a DC plasma jet extending to the anode. This zone of ionized electrically-conducting gas allowed the formation of a transferred arc between the cathode tip and the anode. The switch was then opened to transfer the arc to the anode.

4.1.2.3 Electrical Measurement Equipment

The arc voltage was measured by a voltmeter attached to the control console and by a strip chart recorder. In order to protect the chart recorder, a voltage divider circuit was used to reduce the voltage by a factor of 16.

The arc current was measured by an ammeter attached to the control console and by a strip chart recorder connected to a shunt of 500 A and 50 mV in series with the arc.

4.1.2.4 Thermocouple and Readouts

A total of seven K-type thermocouples (wire=0.5 mm) and two readouts were used to measure the temperature at different places in the synthesis reactor. Four thermocouples with

exposed junctions were used to measure the gas temperature at the reactor inlet, outlet, after quenching and just before the filter. Three other thermocouples were used to measure the temperature of the reactor wall at the inlet, outlet and midway positions in the reactor.

4.1.2.5 Rotameter

Rotameters were calibrated and installed in the gas (argon, nitrogen and ammonia) lines to control and to measure flow rates. Industrial grade argon (minimum purity of 99.98%) was used as the plasma gas and for ammonia dilution. Industrial grade nitrogen (minimum purity of 99.98%) was used as a quenching gas in the synthesis reactor outlet. Ammonia (minimum purity of 99.99%) was used as a source of nitrogen for the nitridation reaction.

4.1.2.6 Vacuum Pump

Two vacuum pumps were used in this study. A dry vacuum pump was used to purge the system before each experiment, and a water-sealed vacuum pump with a variable bypass was used to control the pressure inside the system.

4.1.3 Synthesis Reactor

The synthesis reactor is shown in Figure 4.5. This reactor consisted of a stainless steel cylindrical tube 40 mm inside diameter and 600 mm long, and two gas distributors.



Figure 4.5 Schematic Representation of the Synthesis Reactor

The ammonia gas distributor is shown in Figure 4.6. It consisted of a hollow ring of 40 mm inside diameter with 24 radial holes of 0.8 mm diameter drilled through the inside face. The void contained two overlapping baffles to diffuse the flow. The nitrogen distributor consisted of a capped tube perforated on its circumference with 30 evenly spaced holes of 1mm diameter. This distributor was designed to move along the synthesis to allow evaluation of the effect of the reactor length (residence time). A thermocouple was placed in the center of the nitrogen distributor to measure the outlet temperature of the reactor. The synthesis reactor was heated using beaded resistance heaters in five different sections. This facilitated temperature control for different reactor lengths. A pressure gauge was installed to measure the pressure in the synthesis reactor.



Figure 4.6 Schematic Representation of the Ammonia Distributor

4.1.4 Powder Collection System

The stainless steel 10µm porous filter used to collect the powder is depicted in Figure 4.5. Valves placed at both ends of the filter holder prevent contact between the moisture of the air and the powder produced. One end was connected to the synthesis reactor and the other end was connected to the water-sealed vacuum pump. Since pressure drop through the filter increased as powder was deposited on the filter, a water-sealed vacuum pump was used to keep the pressure of the system at one atm during the powder collection. This vacuum pump had a bypass and a valve to control the amount of gas being exhausted.

4.2 Experimental Procedure

The experimental procedure to study the effects of plasma parameters on aluminum vaporization and the effects of reaction variables on aluminum nitride synthesis will be described in this section.

4.2.1 Aluminum Vaporization

Before each experiment, the system was thoroughly cleaned. The inner crucible and the aluminum ingot (30 mm diameter and 10 mm height) were weighed. The aluminum ingot was of 1100 Aluminum alloy. The crucible set was placed on top of the anode and the plasma chamber closed. The experimental system was evacuated to about 13kPa for 15 minutes and then purged with an argon flow rate of 15 L/min for 5 minutes. The vacuum pump was kept running during the purging operation to decrease the oxygen concentration in the system as much as possible.

The aluminum ingot (anode) was vaporized by the transferred arc plasma. The plasma parameters were initially varied to study the effect of arc current, arc length and argon flow rate on vaporization rate. The following conditions were used in this study:

- arc current of 220 and 260 amperes,

- arc length of 30 and 40 mm and

- argon plasma flow rate of 10 and 20 L/min.

The amount of aluminum vaporized was computed from the difference in weight of the inner crucible and aluminum ingot before and after an experiment. Each experiment lasted 10 minutes.

4.2.2 Synthesis of Aluminum Nitride

Before each experiment, the procedure from section 4.2.1 for purging oxygen out of the system was adopted. The weight of the inner crucible and the aluminum ingot was also recorded. The argon, nitrogen and ammonia flow rates were set to the desired levels, and the cooling water was turned on. The plasma was ignited by the high frequency generator and the switch was opened to transfer the arc to the anode (crucible and aluminum ingot). The aluminum vapour produced in the plasma chamber was carried by the argon plasma gas to the synthesis reactor. Part of the aluminum vapour condensed on the plasma chamber walls and cathode sheath. The aluminum vapour started to react with ammonia in the mixing zone (reactor inlet position) leading to the growth of the aluminum nitride particles along the reactor length.

The plasma parameters for all experiments were kept constant at 240 A, arc length of 40 mm and argon flow rate of 15 L/min, except for two experiments, which were done at an arc

length of 32 mm. The reaction conditions were varied to study the effect of nitriding agent used, ammonia flow rate, residence time (reactor length) and temperature. These experimental conditions were:

- nitrogen (as nitriding agent) flow rate of 6 L/min;
- ammonia flow rate from 0.5 to 6 L/min;
- reactor length around 50 to 300 mm;
- temperature around 840, 920 and 1060 K and
- nitrogen (as quenching gas) flow rate of 25 L/min.

Individual experiments lasted 14 minutes. Samples were taken only during the last six minutes when the reactor approached steady state. Figure 4.7 shows the gas temperature history during the experiment.



Figure 4.7 Typical Temperature History During Experiment

During sample collection, it was necessary to have the water-sealed vacuum pump running to avoid a pressure rise in the reactor due to the pressure drop through the cake on the filter. The powder collected on the filter was then chemically and physically characterized.

4.3 Powder Analysis Techniques

The concentration of aluminum nitride in the powders produced was obtained by quantitative x-ray diffraction analysis. The samples for which complete conversion was achieved were also characterized by Dynamic Light Scattering (particle size and size distribution), BET method (specific surface area), Scanning Electron Microscope, Atomic Force Microscope (morphology) and Fourier Transform Infrared (bonds).

4.3.1 X-ray Diffraction (XRD)

The powders produced were quantitatively analyzed using X-ray Diffraction analysis (Rigaku - Rotating Anode Diffractometer). The powders were exposed to filtered CuK α radiation at an accelerating voltage of 50 kV, and a beam current of 150 mA with a scanning rate of 0.02 deg/sec and exposure time in each step of 0.5 seconds. The intensity and 20 data were acquired and stored in a computer system. In order to evaluate the amount of aluminum in the powder produced, a calibration curve (relative intensity <u>vs</u>. wt% aluminum content) was generated. The diffraction peak angles (20) selected to compute the relative intensity were 49.8° for aluminum nitride and 44.7° for aluminum. This curve was generated by known mixtures

(from 0 to 100 wt% Al) of AlN (98+%) and Al (99.5%) at the same conditions used to analyze the powders produced. Figure 4.8 shows the calibration curve for the range of interest in this study (0 - 20 wt% Al). Appendix B shows some of the XRD patterns used in the calibration curve and some of the XRD patterns of the experimental results.



Figure 4.8 Calibration Curve (wt% Aluminum vs. Relative Intensity)

The particle size of some samples was measured using the X-ray diffraction peak broadening [Cullity 1978] to evaluate the reliability of Dynamic Light Scattering technique.

4.3.2 Particle Sizer

The particle sizes and size distributions of the fully converted AIN powders were measured using the Dynamic Laser Light scattering NICOMP 370 (Pacific Scientific Instrument Division). The instrument is capable of measuring particle diameters in the nanometer range. A small amount of AIN powder was dispersed in isopropanol and the soft agglomerated particles were broken down with an ultrasonic probe. A small amount of dispersion was injected into the instrument. Light from a laser (5 mW HeNe) was focused into a glass tube containing the dilute suspension of particles. Each of the particles illuminated by the incident laser beam scatters the incident light. The intensity of the light scattered by a single isolated particle depends on its molecular weight, size and shape. By measuring the intensity of the scattered light, the mean spherical diameter of the particles can be calculated. The Dynamic Light Scattering technique is described in more detail below.

4.3.2.1 Dynamic Light Scattering (DLS)

The light generated by a HeNe laser is focused into a glass tube containing a dilute suspension of particles in a fluid, usually water. In this study isopropanol was used due to the great reactivity between aluminum nitride and water. The suspended particles are continually bombarded on all sides by the molecules of the solvent causing a random movement, known as Brownian Motion. The optical path lengths of the scattered light waves vary according to the position of the particles. This variation determines if the scattered wave will reach the photomultiplier in phase (constructive interference), or in the other extreme, out of phase (destructive interference). As a consequence, the scattered waves arriving at the photomultiplier detector will cause the net intensity at the detector to fluctuate randomly in time like a typical noise signal. The time scale intensity fluctuations depend on the particle diffusivity and hence on the particle size. Small particles move relatively rapidly, resulting in a rapidly fluctuating intensity signal. By contrast, large particles move slowly, resulting in a slowly varying intensity. These signals are mathematically treated by the autocorrelation function (C(t')), Equation 4.1, to evaluate the correlation between the value of the intensity of the scattered light (I_s) at a given time, t, and the value of I_s at an earlier time, t-t'. This comparison is then made for many different values of t in order to obtain a good statistical average for C(t').

$$C(t') = \sum_{t} I_{s}(t) \cdot I_{s}(t-t')$$
(4.1)

This value is an exponentially decaying function of t'. A rapid decay suggests that the particles is moving very rapidly, high diffusivity, and then are small, while slow decay suggests larger particles.

An ideal case of uniform particle sizes will be discussed to make easier to understand the calculation procedures. The exponential decay of C(t') is well described by Equation 4.2.

$$C(t') = A \cdot \exp(-t'/\tau) + B \tag{4.2}$$
Where A is $\sum I_s^2(t) - [\sum I_s(t)]^2$ and

B is the limiting value (baseline) $[\sum I_s(t)]^2$ and

 τ is the characteristic decay time constant of the exponential function (decay speed).

The diffusion coefficient D of the particles from the decay constant τ is given by Equation 4.3.

$$D = \frac{1}{2 \cdot K^2} \cdot \frac{1}{\tau} \tag{4.3}$$

Where K is a calibration constant [$(4 \cdot \pi \cdot n/\lambda) \cdot \sin \theta/2$],

n is the index of refraction of the solvent (1.385 for isopropanol),

 λ is the HeNe laser wavelength (632.8-10⁻⁹ m), and

 θ is the angle at which the scattered light is intercepted by the photomultiplier detector

The particle size radius R can finally be evaluated (assuming a sphere) using the Stokes-Einstein relation, Equation 4.4, .

$$D = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot R} \tag{4.4}$$

Where k is the Boltzmann's constant (1.38-10⁻¹⁶ erg/K),

T is temperature [K] and

٠÷.

 η is shear viscosity of the solvent (2.10 cp for isopropanol at room temperature).

Obviously, real samples contains a range of particle sizes inducing an autocorrelation function which is no longer a simple decaying exponential function, i.e. having a single well defined decay time constant τ . The existence of different decay time constant τ_i leads to a particular diffusivity D_i and, hence, to a particle radius R_i . The deviations of autocorrelation function can give a range of different distributions. The distribution might be simple, consisting of a smooth symmetric single peak (unimodal distribution) or might be qualitatively more complex, such as two discrete peaks (bimodal distribution) or even more complicated shape. In the first case, the autocorrelation results are then well fitted to a Gaussian distribution. In the second case, such as bimodal, the results are completely misinterpretated by the Gaussian analysis, for this case the NICOMP distribution analysis, based on inversion of the Laplace transform, provide an alternative method for analyzing the autocorrelation function.

4.3.2.2 DLS Result Interpretation

It is very difficult to measure particle size of an order of magnitude of 100 nm. SEM visual analysis for this order of magnitude shows some limitations when working with DLS analysis some problems also appear. Agglomeration is a hard problem to overcome. Chemical reactions can also become a problem for such high specific surface area ($\approx 100 \text{ m}^2/\text{g}$). Then, the interpretation of the DLS technique data is very difficult. In order to establish a procedure to interpret the data collected, some preliminary runs were planned to evaluate the agglomeration and/or chemical reaction effects. Figure 4.9 shows the mean diameter results as function of time for three runs of the same dispersion.

In the first run, a fresh batch of the dispersion was injected. In the second run, a batch of the same dispersion was injected without any previous treatment. In the third run, another batch of the same dispersion was injected with a previous treatment with a ultrasonic probe to break the soft agglomerates.



Figure 4.9 Mean Diameter vs. Time for Three Different Runs

The results shown in Figure 4.9 reveal a great instability in the five first minutes of the 1st run because too little data had been acquired. After this time the mean diameter results fall to a stable value (true value). After some time, the mean diameter starts to slightly increase suggesting that the particles agglomerate or even that unexpected reactions are taking place. After the second batch is injected (2nd run). It can be seen that after stabilizing the data acquisition the particles are larger and still growing. After the third batch is injected, and after stabilization of data acquisition, the particles are slightly smaller than the last evaluated particle size of the 2nd run, but are also still growing. This fact suggests that the agglomeration and/or chemical reactions form hard agglomerates during the analysis.

Based on these observations, the true value for particle size was assumed to be the smallest mean diameter measured, i. e. in the earliest time after injection and with the best statistical fit.

4.3.3 BET Method

Brunner-Emmett-Teller (BET) method was used to measure the specific surface area of the fully converted powders. The aluminum nitride powder samples were loaded in a Pyrex glass sample holder and then heated to 300°C for 30 minutes to remove absorbed water. After heating, N₂/He gas flows through the sample holder and then the powder is cooled with liquid nitrogen. The volume of nitrogen absorbed is a function of the specific surface area of the powder. The process of absorption and desorption are monitored by measuring the change in thermal conductivity of the gas mixture. Equivalent spherical sizes can be evaluated from the specific surface area. The particle size of some samples was measured using this approach to evaluate the reliability of DLS technique. The average particle diameter (d_{ev} , m) was obtained using the Equation 4.5.

$$d_{av} = \frac{6}{\rho_p \cdot S_A} \tag{4.5}$$

Where ρ_p is the true density of aluminum nitride [g/m³] and

 S_A is the specific surface area [m²/g].

4.3.4 Scanning Electron Microscope

The morphology of aluminum nitride and particle size of the powders was examined by scanning electron microscopy (SEM), JEOL JSM840A. The powder samples were prepared by dispersing a small amount of AlN powder in acetone. The soft agglomerates were then broken down using ultrasound. The dispersed powders were placed on aluminum sample holders, dried and gold coated, and then examined.

4.3.5 Atomic Force Microscope

• -

The morphology and the particle size of the aluminum nitride powder was also examined by Atomic Force Microscope (AFM) (Digital Instruments, Nanoscope III). The AFM measures the force variations between the sample and the probe at the atomic level in order to generate a image of the sample surface. These force variations are determined by measuring the deflection of a spring cantilever using a laser beam and a photodetector. The sample was prepared by uniaxial die pressing into a cylindrical pellet without any additives or further coating. The pellet was then placed on a sample holder and examined.

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4.3.6 Chemical Composition

The chemical analysis was performed by ELKEM Metals CO. in Niagara Falls (NY). The nitrogen and oxygen contents were obtained using a TC136 LECO EF100 electrode furnace and associated analyzer. The oxygen present in the sample, under high temperature (~3000°C), reacts with carbon previously mixed with the AlN powder to form carbon monoxide (CO). The gases are then analyzed by an Infrared (IR) analyzer. Following this, the gases are then separated, leaving only the nitrogen and helium used as a carrier gas. This mixture passes though a thermal conductivity cell where the nitrogen produces a variation in the output signal due to its lower thermal conductivity compared with pure helium. The time integral of this signal is then interpreted as the nitrogen content of the sample. The carbon is analyzed in a very similar method.

4.3.7 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) (Bomem - Michelson 100) Spectroscopy was used primarily to determine the presence of oxygen as O-H bond in the aluminum nitride powder produced. The samples analyzed consisted of 2 wt% finely ground KBr mixed with the AlN powder produced. The transmittance was determined by the detector using pure KBr as a reference material.

5 Results and Discussion

The experimental results and discussion will be presented in this chapter. The text is divided into six main sections: - effects of plasma parameters on aluminum vaporization, - effect of arc length (plasma parameter) on AlN conversion, - effect of reaction parameters on AlN conversion, - powder characterization, and - a comparison of the powder produced with other authors and commercial powder.

5.1 Effects of Plasma Parameters on Aluminum Vaporization

During the present study, several experiments were carried out to investigate the effects of argon gas flow rate, arc current and arc length on the amount of aluminum vaporized and gas temperature in the mixing zone. Each experiment lasted 10 minutes. The amount of aluminum vaporized was calculated by the weight difference of the inner crucible and aluminum ingot before and after experiment. The temperatures reported are those read after 10 minutes of experiment, i. e. near steady state.

The plasma parameters and the experimental results are listed in Table 5.1. A factorial analysis computer program [Kohler 1989] was used to correlate the plasma parameters and the experimental results. The eight treatment combinations using the factors a (arc current), b (arc length) and c (argon flow rate) at two levels are listed in Table 5.1. The minimum level is represented by letter I. The treatment designated as A means the factor a (current) at the maximum level and the others two factors at the minimum level; for AB, the factors a and b at the maximum level and factor c at the minimum level and so on.

Treatment	Current [A]	Arc Length [mm]	Ar Flow Rate [L/min]	Gas Temperature [K]	Aluminum Vaporized [mg]
1	240	30	10	776	1330
Α	260	30	10	824	1990
В	240	40	10	958	1260
С	240	30	20	853	1720
AB	260	40	10	993	1520
AC	260	30	20	906	2660
BC	240	40	20	994	1450
ABC	260	40	20	1090	230

Table 5.1 Plasma Parameters and Experimental Results

5.1.1 Gas Temperature at the Mixing Zone

The results presented here are particularly relevant because temperature plays an important role in aluminum nitride synthesis. The thermocouple temperature errors are estimated in Appendix A. The rate of the synthesis reaction, nucleation and growth of the particles depend strongly on the supersaturation ratio of the metal vapour. It is important that the aluminum reach the reaction zone in the vapour phase. The residence time in the reaction zone is a fraction of a second. For this order of residence time, only gas phase reactions can reach complete conversion. Table 5.2 shows the results of the statistical treatment of the influence of the plasma parameters on the maximum temperature reached in the mixing zone. It can be observed in Table

5.2 that the arc length (factor b) is the most important plasma parameter to maximize the temperature. As can be seen in the second column of Table 5.2 (*effect*), the average increase in temperature (taking into account the other plasma parameters) when the arc length is increased from 30 to 40 mm is 169°C. It can also be observed that the combined effect of arc length and argon flow rate has a negative effect on the temperature reached in the mixing zone. All three plasma parameters have a significant effect with 99% probability level on the temperature reached in the mixing zone. The coefficients of the empirical equation generated by this statistical treatment are listed in the third column of Table 5.2. The correlation coefficient between the gas temperature observed and calculated using the empirical equation is 0.997.

Treatment	Effect (K)	Coeff. of the Equation	Probability F (%)	Temperature observed (K)	Temperature calculated (K)
1	-	432	-	776	783
A	58.0	-2.20	99.18	824	817
В	169.0	0.100	99.99	958	951
С	73.0	-29.4	99.64	853	846
AB	7.5	0.075	-	993	1000
AC	16.5	0.165	-	906	913
BC	-6.5	-0.130	-	994	1001
ABC	14	-	-	1090	1083

 Table 5.2 Factorial Analysis Results for Gas Temperature

The empirical Equation 5.1, temperature [K] (T) as a function of arc current [A] (I), argon plasma gas flow rate [NL/min] (Q_{Ar}) and arc length [mm] (L) was generated by the statistical treatment and the coefficients are shown in Table 5.2. Figures 5.1 and 5.2 were plotted using the empirical Equation 5.1.

$$T = 705 - 2.2 \cdot I + 0.1 \cdot L - 29.4 \cdot Q_{Ar} + 0.075 \cdot I \cdot L + 0.165 \cdot I \cdot Q_{Ar} - 0.13 \cdot L \cdot Q_{Ar}$$
(5.1)



Argon Flow Rate = 10 L/min

Figure 5.1 Gas Temperature vs. Arc Current and Arc Length for 10 NL/min of Argon



Figure 5.2 Gas Temperature vs. Arc Current and Arc Length for 20 NL/min of Argon

These figures show the gas temperature after 10 minutes of experiment as a function of current and arc length for 10 and 20 NL/min of argon, respectively. The gas temperature increases with the increase of all three variables. An increase in current provides more power to be transferred from the arc; an increase in arc length provides more effective radiation to the

chamber walls; and an increase in argon flow rate causes the heat transfer from the chamber to the synthesis reactor to also increase.

5.1.2 Aluminum Vaporization

The aluminum vaporization results were also statistically treated to evaluate the influence of the plasma parameters on the amount of aluminum vaporized. These results are presented in Table 5.3.

T	7.00	0	D. 1.1.11		A 1
Treatment	Enect	Coeff. of	Probability		Aluminum Non Smal
		me	F	vap. [mg]	vap. [mg]
		Equation	(%)	(observed)	(calculated)
1	-	-9226	-	1330	1369
A	677.5	44,13	99.33	1990	1951
В	-292.5	283.8	91.04	1260	1221
С	507.5	-477.3	98.20	1720	1681
AB	-122.5	-1.225	-	1520	1559
AC	217.5	2.175	-	2660	2699
BC	-22.50	-0.450	-	1450	1489
ABC	77.50	-	-	2300	2261

Table 5.3 Factorial Analysis Results for Aluminum Vaporization

From Table 5.3 it can be observed that the current (factor a) and argon flow rate (factor c) are the most important plasma parameters to maximize the aluminum vaporization.

Both current and argon flow rate have a significant effect at the 98% probability level. It can also be observed that the effect of arc length (factor b), and its combined effect with arc current (AB) and argon flow rate (BC) are deleterious on the amount of aluminum vaporized. Arc length has a significant negative effect at the 90% probability level on aluminum vaporization. The coefficients of the empirical equation generated by this statistical treatment are also listed in Table 5.3. The correlation coefficient between the amount of aluminum vaporized, observed and calculated, using the empirical equation is 0.997.

The empirical Equation 5.2, mass of aluminum vaporized [mg] $(Al_{v,p})$ as a function of arc current [A] (I), argon plasma gas flow rate [NL/min] (Q_{Av}) and arc length [mm] (L) was generated by the statistical treatment and the coefficients are shown in Table 5.3. Figures 5.3 and 5.4 were plotted using the empirical equation 5.2.

$$Al_{yrp} = -9226 + 44.1 \cdot I + 284 \cdot L - 477 \cdot Q_{Ar} - 1.2 \cdot I \cdot L + 2.2 \cdot I \cdot Q_{Ar} - 0.5 \cdot L \cdot Q_{Ar}$$
(5.2)

These figures show the amount of aluminum vaporized as a function of current and arc length for 10 and 20 NL/min of argon. The amount of aluminum vaporized increases as both current and argon flow rate increase. The current has the major effect on the vaporization of aluminum. The power being transferred to the anode increases as current increases, leading to an increase of the surface temperature of the aluminum bath, which in turn promotes higher vaporization rates. Mass transfer near the aluminum bath surface increases for higher argon flow rate, contributing to higher vaporization rates. The arc length has a negative influence on aluminum vaporization. An intense cathode jet impinging on the anode surface pushes hot plasma against the anode increasing the evaporation rate. The influence of the cathode jet on the anode decreases as the arc length increases.



Figure 5.3 Aluminum Vaporized vs. Arc Current and Arc Length for 10 NL/min of Argon

The plasma parameters were very important to reach the ideal conditions to carry out the gas phase reaction. The results show that long arcs, high currents and high argon flow rates were best to maximize the temperature in the mixing zone. Short arcs, high currents and high argon flow rates were best for vaporization rates. It is thus clear that a compromise must be made to both adequate gas temperature and sufficiently high vaporization rates.



Figure 5.4 Aluminum Vaporized vs. Arc Current and Arc Length for 20 NL/min of Argon

5.2 Effect of Arc Length (Plasma Parameter) on AlN Conversion

As discussed in Section 5.1, the plasma parameters play an important role in the gas phase synthesis of aluminum nitride. The arc current, arc length and argon plasma gas flow rate determine the aluminum vaporization rate and the temperature of the gases leaving the plasma chamber.

The gas temperature is a critical parameter since the temperature has to be kept high enough to avoid aluminum condensation before entering the synthesis reactor. Only gas phase reaction can take place in a such short residence time, since the residence time of the reactants in the tubular reactor used in this study is not long enough to carry out gas liquid or gas solid reactions. To support this point, experiments were performed to study the effect of arc length, which is the most important parameter to maximize the temperature of the gases leaving the plasma chamber, on AlN conversion. The AlN conversion was evaluated by the AlN content in the final powder collected on the filter. In these experiments, all plasma parameters except arc length were kept constant. The reactor temperature was kept constant at about 976 K using beaded heaters.

Figure 5.5 shows the effect of arc length on AlN conversion for arc lengths of 32 mm and 40 mm. For arc lengths of 32 mm, the gas temperature upstream of the ammonia injection position was not high enough and it is highly probable that aluminum condensation took place. The condensed aluminum would not react and complete conversion was not achieved. For arc lengths of 40 mm, the gases leaving the plasma chamber reached higher temperatures and vaporization rate was lower; as can be seen in Figure 3.1 these effects combined to reduce the



Figure 5.5 AlN Conversion vs. Arc Length

5.3 Effect of Reaction Parameters on AlN Conversion

The study of the effect of reaction parameters, such as nitriding agent used, ammonia jet momentum, residence time, ammonia flow rate and temperature, on AlN conversion will be presented in this section. The plasma parameters were kept constant for all experiments. The arc current and arc voltage were 240 A and 27 \dot{V} , respectively. The arc length was 40 mm and the argon plasma gas flow rate was 15 NL/min. Each experiment lasted 14 minutes, but the samples were taken only during the last six minutes when the reactor approached steady state.

5.3.1 Effect of Nitriding Agent

As analyzed in the section 3.1.2, both nitrogen and ammonia could be used as a nitriding agent. From the thermodynamic point of view, the reaction between aluminum gas and nitrogen can reach complete AIN conversion. The question here is: how much time does this reaction need to achieve equilibrium? Vissokov and Brakalov (1983) and Etemadi (1990) demonstrated that when the reaction is carried out inside the plasma chamber, nitrogen can be used as a nitriding agent. It can be suggested that, for such high temperature, the nitrogen decomposed becoming more active, which allowed the reaction to reach high AIN conversions in a short period of time. Etemadi (1990) also studied the effect ammonia addition in the nitrogen flow on the content of AIN in the synthesized powder. It was demonstrated that the addition of ammonia increased the content of AIN and diminished the content of oxygen in the powder produced.

Figure 5.6 shows the effect of nitriding agent on AlN conversion. The nitriding agents (ammonia or nitrogen) were injected at a gas flow rate of about 6 NL/min. It can be seen that nitrogen gas is inert at these conditions of low temperature and short residence time. At the same conditions, the reaction between aluminum and ammonia reaches complete conversion.



Figure 5.6 Conversion vs. Nitriding Agent

5.3.2 Some Preliminary and Puzzling Results

In these preliminary experiments, the nitridation reaction was carried out using pure ammonia flow rates of 2, 4 and 6 NL/min. These experiments were planned to study the effects of ammonia concentration and residence time. Some unexpected results were obtained suggesting that another parameter might be affecting the results. The experimental results are summarized in Figures 5.7, 5.8 and 5.9.



Figure 5.7 AlN Conversion vs. Ammonia Flow Rate for 0.14 s of Residence Time

It can be seen in Figures 5.7 and 5.8 that the increase in ammonia flow rate from 2 to 4 NL/min does not show a clear trend on AlN conversion. Complete conversion was achieved only at flow rate of 6 NL/min. Poor distribution of reactants over the cross section of the reactor is one of the most common causes of low conversion. The momentum of the ammonia jets may not have been sufficiently high to reach the center of the reactor resulting in a central channel of poor mixing. Efficient radial mixing assures optimum concentration and temperature profiles in this reactor.



Figure 5.8 AlN Conversion vs. Ammonia Flow Rate for 0.41 s of Residence Time

Figure 5.9 shows the apparent effect of residence time on AlN conversion. The nitrogen distributor was moved towards the rear of the reactor increasing the reactor length and consequently increasing the residence time. For a residence time close to 0.14 seconds the



Figure 5.9 AlN Conversion vs. Residence Time for NH, Flow Rate of 2 NL/min

It can be observed that the AlN conversion decreased slightly as the residence time increased. This fact supports the hypothesis that mixing is a critical parameter. For short residence times (shorter reactor lengths), the nitrogen injection creates some turbulence in the mixing zone improving the mixing of the reactants. For longer reactor lengths, the nitrogen distributor is far from the mixing zone, causing no such turbulence effect. The possible cooling effect of the nitrogen when injected near the reaction zone (100 mm of reactor length) did not lower the AIN conversion, suggesting that the reaction is carried out in the front part of the reactor.

It was clear from the preliminary results that these experiments did not allow the effects of ammonia concentration and residence time on the conversion of aluminum to aluminum nitride to be determined. A new set of experiments was planned to investigate the influence of mixing on AlN conversion.

5.3.3 Effect of the Ammonia Jet Momentum

In an attempt to separate the effects of mixing and ammonia concentration on AIN conversion, a series of experiments was performed using the radial injection of mixtures of ammonia and argon.

The ammonia flow rate was kept constant at 2 NL/min and the argon flow rate in the mixture was varied to increase the momentum of the gas jets in the ammonia distributor. Figure 5.10 shows the effect of ammonia/argon jet momentum on AlN conversion. In the first two experiments in which the ammonia jet momentum was kept equal to 0.0038 kg·m/s (Figure 5.10), ammonia was injected pure. In the last two experiments, i.e. with momenta of 0.035 and 0.066 kg·m/s, respectively, mixtures of ammonia and argon were injected. In these experiments argon was injected at flow rates of approximately 2.6 and 4 NL/min, respectively. It can be seen that the AlN conversion increases with an increase in gas jet momentum and reaches complete conversion for a gas jet momentum equal to 0.035 kg·m/s (argon flow rate of 2.6 NL/min). It is interesting to note that the momentum of pure ammonia jets for 6 NL/min, at which complete

conversion was achieved, was calculated to be approximately 0.035 kg-m/s. This order of momentum provided a good mixing, allowing complete AIN conversion to be achieved for lower ammonia concentration. This observation reinforces the hypothesis that mixing is an important parameter to improve AlN conversion.



Figure 5.10 AlN Conversion vs. Ammonia Jets Momentum

5.3.4 Effect of Ammonia Flow Rate

For the experimental results in the following sections, different flow rates of argon were injected with ammonia to keep the momentum of the mixture (ammonia and argon) in the ammonia distributor constant, thus giving a constant mixing pattern. Table 5.4 shows the ammonia and argon flow rate in the mixture necessary to keep the momentum at approximately 0.035 kg·m/s.

The influence of ammonia flow rate on AlN conversion was measured from 0.5 to 2.5 L/min. Figure 5.11 shows the effect of ammonia flow rates on AlN conversion.



Figure 5.11 AlN Conversion vs. Ammonia Flow Rate

As expected, the increase of ammonia flow rate, as indicated in Figure 5.11, promoted an increase in AlN conversion. Complete conversion was reached for an ammonia flow rate of 2 NL/min or an ammonia/aluminum molar ratio equal to 12.4. In the present study, 24 jets of ammonia were used in the distributor. In a recent study, Njah et al (1993) showed that faster mixing is achieved with a smaller number of jets (2 or 4). This suggests that the NH₃/Al molar ratio to give complete conversion may be further reduced by using less jets.

Table 5.4 Ammonia and Argon Flow Rates to Keep the Momentum at 0.035 kg a

Ammonia Flow Rate [NL/min]	Argon Flow Rate [NL/min]
0.5	3.6
1.0	3.2
1.5	2.9
2.0	2.6
2.5	2.2

5.3.5 Effect of Residence Time

Initially, three different reactor lengths were studied, 100, 200 and 300 mm. This resulted in residence times of approximately 0.15, 0.27 and 0.41 seconds, respectively. Figure 5.12 shows the effect of residence time on AlN conversion.

Within the scatter of the results presented in Figure 5.12, no clear trend in AlN conversion vs. residence time was observed. This suggests that the very fast nitridation reaction is essentially completed even at the shortest time.

In order to further investigate the residence time required to carry out the nitridation reaction, reactor lengths of 50 and 100 mm were used. This resulted in residence times of 0.06 and 0.15 seconds, respectively. Ammonia was injected at 2.5 L/min to allow the reaction to reach complete conversion. Figure 5.13 summarizes these results.

It can be seen that the residence time has a slight effect on AlN conversion. The reaction reached approximately >8% conversion for a reactor length of 50 mm and reached complete conversion for a reactor length of 100 mm.



Figure 5.12 AlN Conversion vs. Residence Time for 0.5 NL/min of Ammonia



Figure 5.13 AlN Conversion vs. Residence Time for 2.5 NL/min of Ammonia

5.3.6 Effect of Temperature on AIN Conversion

The influence of inlet temperature on AlN conversion was measured from 920 to 1100 K. These experiments were performed at an ammonia flow rate of 0.5 NL/min and a residence time of 0.15 seconds. Figure 5.14 summarizes the effect of temperature on AlN conversion. It can be seen within the scatter of the data that temperature has a slight effect on AlN conversion, i.e.



Figure 5.14 AlN Conversion vs. Temperature

Since two competing phenomena, aluminum condensation and the nitridation reaction of the aluminum vapour, are occurring at the same time, the influence of temperature may not have a direct effect on the nitridation reaction itself, but primarily on aluminum condensation. If aluminum condensation takes place, the condensed aluminum would not react, lowering the AlN conversion.

5.4 Kinetic Analysis of Aluminum Nitridation

Thermodynamic calculations can establish the maximum conversion or equilibrium conversion, but cannot supply any information about the reaction mechanisms and at which velocity the equilibrium is reached. This latter information is very important in investigating the feasibility of the process. The variables of the process affecting the reaction rate, such as type of reactants involved, concentrations and temperature, need to be evaluated quantitatively to generate useful information for future scale up study, or even for further, more advanced, studies at laboratory scale. Ultimately, it is desirable to develop a rate equation from the interpretation of these data collected in a laboratory scale reactor.

The rate equation parameters, reaction rate constant k and the order of the reaction α can be evaluated by measuring the effects of concentrations at constant temperature on reaction rate. Subsequent experiments at different temperatures can establish the activation energy E_A and the frequency factor A. Since it is difficult to measure velocities and concentration within a reactor, normally the data are collected on the feed and effluent streams, the complete information about the rate equation is seldom obtained in a real reactor. The apparatus used in this study is not perfect to produce kinetic data due to limitations imposed by the complexity of the plasma system used to vaporize aluminum. Nonetheless, the kinetic data obtained were analyzed to provide an interpretation of the conversion experiments and guidance for further work in this type of reactor system.

5.4.1 Ammonia Decomposition

Based on the kinetic data presented by Holzrichter and Wagner (1981) the decomposition of ammonia can be evaluated for the experimental conditions studied here. Table 5.5 presents the kinetic parameters for the rate reaction equation of ammonia decomposition. It can be seen that the range of temperature indicated in Table 5.5 is much higher than the range used in the present study. It was thus necessary to extrapolate the rate equation to a lower temperature range to make the calculations. Figure 5.15 shows the calculation results for ammonia decomposition.

Table 5.5 Kinetic Parameters for Ammonia Decomposition Reaction

Kinetic Parameter	Values for $T = 2200 - 3300$ K and $P = 2.03 - 495$ kPa
Frequency Factor	5.5 · 10 ¹⁵ 1/s
Activation Energy	451 kJ/mol
Reaction Order	Unimolecular

The results show that the ammonia decomposition is very sensitive to temperature and the decomposition does not take place at the range of temperature (922 - 1088 K) used in the present study. Based on these results the nitridation reaction of aluminum vapour can be written in the following form:

$$Al(g) + NH_3(g) \rightarrow AlN(s) + 3/2 H_2(g)$$



Figure 5.15 Ammonia Decomposition Results ([NH₃] vs. Reactor Length)

5.4.2 Determination of the Reaction Rate Equation for aluminum nitridation

Once the reactants involved in the reaction are defined, the determination of the concentration (or partial pressure) and temperature terms of the rate equation is possible. The starting point for evaluating the rate equation is the study of the effect of concentrations at constant temperature on the reaction rate.

The average rate of consumption of aluminum or ammonia, or production of aluminum

nitride [mol/s·m³] can be calculated by Equation 5.3.

$$-r_{Al} = -r_{NH_2} = r_{AlN} = \frac{\chi \cdot F_{Alb}}{V_R}$$
(5.3)

Where χ is the AIN conversion,

 F_{Alo} is the aluminum vaporization rate [mol/s] and

 V_R is the reactor volume [m³].

According to Dalton's Law of partial pressures, the partial pressure of a component gas is given as the product of the molar fraction of the component gas and the total pressure of the gas mixture. Thus, the initial partial pressures of aluminum (P_{Ab}) and ammonia (p_{NH30}) are given by Equations 5.4 and 5.5.

$$p_{Alo} = \frac{F_{Alo}}{F_{lo}} \cdot P \tag{5.4}$$

$$p_{NH_{so}} = \frac{F_{NH_{so}}}{F_{so}} \cdot P \tag{(5.5)}$$

Where F_{Alo} is aluminum molar flow rate in the feed stream [mol/s],

 F_{NH30} is ammonia molar flow rate in the feed stream [mol/s], F_{10} is the total molar flow rate in the feed stream [mol/s],

P is the total pressure [1 atm],

Since temperature changes along the reactor were slight and the nitridation reaction reached 90% conversion or more in a fraction of a second (< 0.1 seconds) the temperature was assumed to be the reactor inlet temperature. The experimental conditions, AlN conversion, initial partial pressures and computed reaction rates are presented in Table 5.6.

Т [К]	Residence Time [s]	Xain	r _{∧t} [mol/m³·s]	F_{Ab} -10 ³ [mol/s]	F _{NH30} ·10 ³ [mol/s]	F _t ·10 ³ [mol/s]	$p_{Ab} \cdot 10^2$ [atm]	<i>р_{NH30}</i> ·10 ² [atm]
979	0.15	0.905	0.9901	0.1376	0.3408	13.16	1.046	2.590
984	0,15	0.882	0.9313	0.1327	0.3408	13.15	1.009	2.591
994	0.15	0.959	0.8407	0.1102	0.6816	13.20	0.8353	5.165
985	0.15	0.954	0.7966	0.1049	1.022	13.33	0.7874	7.671
987	0.15	0.968	0.9339	0.1213	1.022	13.34	0.9087	7.662
992	0.15	1.000	0.8346	0.1049	1.363	13.40	0.7834	10.18
991	0.15	1.000	0.9959	0.1252	1.704	13.55	0.9240	12.57

Table 5.6 Experimental Data

Assuming that the rate of disappearance of aluminum $(-r_{Al})$ during the reaction time is governed by the irreversible (equilibrium constant is large and one of the products is solid) reaction:

$$Al(g) + NH_3(g) \rightarrow AlN(s) + 3/2 H_2(g)$$

The rate equation can be written in terms of initial partial pressures of aluminum and ammonia as shown in Equation 5.6.

$$-r_{Al} = k \cdot p_{Alo}^{\alpha} \cdot p_{NH,o}^{\beta}$$
(5.6)

Where k is the reaction rate constant,

 α and β are the order of the reaction with respect to Al and NH₃, respectively, and p_{Alo} and p_{NH3o} are the average partial pressures of aluminum and ammonia, respectively.

Equation 5.7 is obtained after taking the natural logarithm of both sides in equation 5.6.

$$\ln(-r_{Al}) = \ln k + \alpha \cdot \ln p_{Alo} + \beta \cdot \ln p_{NH_{so}}$$
(5.7)

Using the experimental data presented in Table 5.6, the parameters $\ln k$, α and β can be calculated. Table 5.7 presents the values obtained with correlation coefficient of 0.99.

Parameters	Values		
$\ln k$	4.94		
$k [\mathrm{mol}/(\mathrm{atm}^{1.1}\cdot\mathrm{m}^3\cdot\mathrm{s})]$	140		
α	1.01		
β	0.09		

Table 5.7 Parameters of the Equation 5.7

Using the parameters presented in Table 5.7, the rate equation for the average temperature

of 987 K can be represented by Equation 5.8.

$$-r_{Al} = 140 \cdot p_{Alo}^{1.01} \cdot p_{NH,o}^{0.09}$$
(5.8)

So far, only the influence of the initial partial pressures on the reaction rate was considered when evaluating the partial pressure term in Equation 5.6. The reaction rate constant k includes the effect of all other variables, but the most important is temperature. The dependency of reaction rate constant on temperature may be assumed to follow the Arrhenius Law, Equation 5.9.

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}}$$
(5.9)

Where E_A is the activation energy [J/mol],

A is frequency factor [mol/(atm^{1.1}·m³·s)] and

R is the molar gas constant [J/mol·K].

Equation 5.10 was obtained after taking the natural logarithm of both sides in Equation 5.9.

$$lnk = lnA - \frac{E_A}{R} \cdot \frac{1}{T}$$
(5.10)
The calculated values of k using Equation 5.8 for different temperatures are presented in Table 5.8.

<i>T</i> [K]	Xain	r _{Al} [mol/m ³ -s]	$p_{_{NH3o}} \cdot 10^2$ [atm]	<i>р_{ль}-</i> 10 ² [atm]	k	ln k	1/T · 10 ⁴ [K ⁻¹]
922	0.844	0.708	2.598	0.8030	131.6	4.880	10.846
919	0.880	0.966	2.592	1.049	137.0	4.920	10.881
979	0.905	0.990	2.592	1.046	140.9	4.948	10.215
984	0.882	0.931	2.593	1.009	137.4	4.923	10.163
1101	0.879	0.947	2.593	1.009	139.8	4.940	9.083
1088	0.943	0.721	2.600	0.7330	147.1	4.991	9.191

Table 5.8 Values of k for Different Temperatures

The Arrhenius plot, $\ln k \underline{vs}$. 1/T, presented in Figure 5.16, yields a slope equal to $-E_A/R$ and a y-intercept equal to the frequency factor (A). The activation energy (E_A) equal to 2979 J/mol and a frequency factor (A) equal to 199 mol/(atm^{1.1}·m³·s) were obtained from the linear regression of Equation 5.10 using the data shown in Table 5.8 with correlation coefficient of 0.76. This correlation coefficient is significant at a probability level of 95%. Therefore, the reaction rate equation in terms of initial partial pressure and temperature which represents the experimental data for nitridation of aluminum vapour can be written in the following form:

$$-r_{Al} = 199 \cdot e^{-\frac{2979}{R \cdot T}} \cdot p_{Alo}^{1.01} \cdot p_{NH,o}^{0.09}$$
(5.11)



Figure 5.16 Arrhenius Plot ($\ln k vs. 1/T$)

These results show that the rate of aluminum vapour nitridation was a weak function of ammonia concentration (order of reaction equal to 0.09) and temperature (activation energy equal to 2979 J/mol). The very low dependency on ammonia partial pressure was undoubtedly due to the great excess of ammonia used. The magnitude of the temperature dependency suggests that chemical reaction is not the controlling step. These results, along with the fact that the ammonia concentration is very high in the ammonia jet zone and very low in the surroundings, suggest that another mechanism is controlling the reaction. This mechanism is probably related to heat

and mass transfer effects in the mixing zone. Further studies on this subject have to be done to clarify this hypothesis.

Even though a reasonable fit was obtained for the experimental data, the kinetic rate equation generated here cannot provide intrinsic reaction rates due to some problems that could not be overcome. The range of partial pressure of aluminum studied is not wide and it could not be accurately measured due to the complexity the plasma system used to vaporize aluminum. The temperature in the reaction zone could not be precisely measured because the reaction takes place by contact between aluminum vapour coming from the plasma chamber, i.e. at high temperature (≈ 2000 K) and the ammonia fed at room temperature. If the objective is to measure intrinsic kinetic rates, a different reactor system must be used.

5.5 Powder Characterization

The results of the characterization of the fully converted powders collected on the filter is presented in the following sections. Figure 5.17 shows a photograph of the aluminum nitride powder collected on the filter.

5.5.1 Morphology and Crystal Structure

The aluminum nitride powder was white. The particles were examined visually by a Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). Both SEM and AFM examinations showed a near spherical particle morphology. Figure 5.18 and 5.19 show the SEM and AFM photographs of the aluminum nitride powder run# 24. The crystalline structure was found to be hexagonal using X-ray Diffraction (XRD). Figure 5.20 shows a typical XRD pattern for run# 25; only the aluminum nitride peaks for the hexagonal crystal structure (JCDD index card 25 1133) can be seen.



Figure 5.17 AlN Powder Collected on the Filter



Figure 5.18 SEM Photograph of AlN Powder for Run# 24





Figure 5.19 AFM Photograph of AlN Powder for Run# 24

Figure 5.19 (a) and (b) shows the top view and 3D view of the sample surface. It can be seen that the particles are spheroidal. The calculation of mean diameter from BET technique based on the assumption of spherical particle is thus reasonably correct. Figure 5.19 (c) shows the surface profile along the indicated line.



Figure 5.20 Typical XRD Pattern for a Fully Converted Powder

5.5.2 Particle Size and Size Distribution

The particle sizes were measured by the Dynamic Light Scattering (DLS) technique. The particle size was also obtained using XRD peak broadening and Brunauer, Emmett and Teller (BET) techniques for some samples to evaluate the reliability of the DLS technique. Table 5.9 shows the particle size results using the techniques mentioned above for three similar samples. The specific surface area, which was evaluated using BET technique, varied from 80 to $100 \text{ m}^2/\text{g}$. The particle size was estimated from the values of specific surface area using the Equation 4.5.

Technique	Particle Size [nm] of Sample Run#					
	24	25	28			
DLS	22.8 ± 2.5	21.1 ± 2.5	18.8 ± 2.5			
XRD	13.5 ± 2.3	18.2 ± 2.3				
BET	18.4± 2.0		23.5 ± 2.0			

Table 5.9 Particle Sizes Measured by Different Techniques

It can be seen in Table 5.9 that, with the exception of XRD result for sample run# 24 (13.5 nm), the particle size measured by the different techniques overlap. Thus, Dynamic Laser Scattering seems to be a reliable technique. A typical particle size distribution result (run# 28) obtained using the DLS technique is shown in Figure 5.21.



Figure 5.21 Typical Particle Size Distribution Obtained from DLS Technique

A strong peak (98.08% in volume) with mean diameter of 18.8 nm and a very weak peak (1.92% in volume) with mean diameter of 148.1 nm can be seen. The latter peak may be attributed to the hard agglomerates which could not be broken by the ultrasonic probe when preparing the dispersion, or agglomerates formed by agglomeration and/or chemical reactions taking place during the measurements.

The particle size distributions of aluminum powder obtained without injection of ammonia were also measured. Figures 5.22 and 5.23 show the particle size distributions for two different reactor lengths, 100 and 200 mm, respectively.



Figure 5.22 Aluminum Particle Size Distribution for Reactor Length of 100 mm



Figure 5.23 Aluminum Particle Size Distribution for Reactor Length of 200 mm

A clearly bimodal distribution with mean diameters of 5.8 nm (54.47% in volume) and 21.0 nm (45.53% in volume) can be seen in Figure 5.22. In Figure 5.23, for longer reactor length, it can be seen that the first peak has disappeared. This suggests that for reactor length of 100 mm, the aluminum vapour did not have time to condense completely, i. e. part of the aluminum remained in the vapour phase, which condensed to a smaller particle size when the nitrogen quenching gas was injected. For the reactor length of 200 mm, the aluminum vapour

had enough time to condense and grow to a larger particle size. This occurrence is not observed for the case of aluminum nitride powders, because two factors contributed for a faster nucleation and growth; the ammonia injection behaved as a pre-quench and the aluminum nitride probably has a much lower critical supersaturation ratio.

Table 5.10 shows the particle size distribution for fully converted powder obtained for different residence times. Within the scatter of the results presented in Table 5.10, the residence time had no influence on particle size and size distribution, i. e. a clear trend was not observed. The standard deviations are high because this parameter is estimated taking into account the second peak with a much higher particle size. These results will be further discussed in Section 5.6.

Table 5.10 Particle Size and Size Distribution

Run#	24	25	26	27	28
Particle Size [nm]	22.8	19.5	20.9	21.1	18.8
Standard Deviation [nm]	27.5	29.1	20.1	14.6	18.3

5.5.3 Fourier Transform Infrared Spectroscopy Results

The results of the Fourier Transform Infrared (FTIR) spectroscopy for the aluminum nitride powder produced (run# 24) and commercial AlN are presented in Figure 5.24.



Figure 5.24 Infrared Spectra for AIN Powder Produced and Commercial AIN

The infrared spectra show a broad peak related to Al-N bond centered around 670 cm⁻¹ confirming the presence of aluminum nitride obtained by the XRD technique. Since ammonia was used as nitriding agent, and from the thermodynamic predictions, a small amount of AlH can be present at equilibrium, the peak appearing at 2200 cm⁻¹ might be attributed to the presence of the Al-H bond. The most important reason for the use of this technique is to determine the presence of oxygen in the powder. The broad peak centered around 3400 cm⁻¹ was

due to the presence of O-H or N-H bonds. Baba et al (1987) suggested that the high specific surface area of AlN powder might make it very reactive with the moisture in the air forming Al(OH)₃. This hypothesis is reasonable because no special precaution was taken to avoid contact with air. David et al (1990) claimed that the broad peak centered around 3400 cm⁻¹ could also be due to the presence of the N-H bond, since the peak decreased significantly after heat treatment. Al(OH)₃ under heat treatment would form Al₂O₃ and no strong Al-O peak was observed at 460 cm⁻¹ after heat treatment. Baba et al (1987) attributed the peaks around 1600 cm⁻¹ to the presence of absorbed water. The author suggested that the molecular water might be adsorbed on the Al(OH)₃ layer.

5.5.4 Comparison With Other Authors and Commercial AIN

Table 5.11 summarizes the results of the characterization of the powder produced in this work, the results obtained by other researchers and the commercial powder (Starck grade C) specifications (De Renzo 1987). Wehling et al (1991) produced aluminum nitride (AIN) powder by injecting aluminum powder into an inductively coupled plasma flame and reacting the aluminum vapour produced with ammonia inside the plasma chamber. Ageorges et al (1992) produced AlN powder by the evaporation of an aluminum ingot using a transferred arc plasma system and reacting the aluminum vapour produced with an ammonia/nitrogen mixture inside the plasma chamber. Baba et al (1987) produced AlN powder, reacting the aluminum vapour produced by evaporation of an aluminum ingot using an inductively plasma system with ammonia inside the plasma chamber.

		Run#24	Starck C	Wehling	Ageorges	Baba
Particle Size [nm]		23	800-1300	30	150	23-37
Standard Deviation [nm]		27.5	N/A	N/A	N/A	N/A
Specific Surface Area [m ² /g]		100	5-8	115	~7	50-80
	Al	60.04	min. 64	N/A	57.7	N/A
Chemical Composition	N	26.40	min. 29.5	N/A	22.5	N/A
[wt%]	0	11.88	max. 2.5	7.4	14	~5
	С	0.43	max0.08	N/A	6	N/A

Table 5.11 AlN Powders Produced from Different Method

It can be seen that the particle size of AlN powder produced using an inductively plasma system (Wehling and Baba) had a smaller particle size than the AlN powder produced by an transferred arc plasma system (Ageorges). The configuration of the equipment used may explain these results. It can be observed that the reactants residence time at high temperatures in the equipment used by Ageorges is longer than those used by Wehling and Baba. This longer residence time might be the cause of the larger particle size obtained by Ageorges. Based on this observation, the reaction between the aluminum vapour and ammonia was carried out outside of the plasma chamber in the present study. The results show that the particle size of the present powder was of same order as that obtained using an inductively plasma system.

All powders had oxygen content higher than the maximum specification of the commercial powder. This was probably due to contamination after removal from the reactor, since no special precaution was taken to avoid the contact between the powder and the moisture present in the air. The samples were stored in a dessicator but exposure to air prior to analysis

was unavoidable. The carbon content observed in run# 24 and that of Ageorges was from the graphite crucible.

The molar ratio of N:Al was calculated to be 0.85 for run# 24 and 0.89 for the commercial product. These results indicated a deficiency of nitrogen probably related to the presence of $Al(OH)_3$. If the hydrolysis of the sample by atmospheric moisture is ignored, the molar ratio of N:Al of the powder produced is 0.95.

5.6 Modelling Results of Particle Nucleation and Growth

A comparison of the modelling results with the experimental data will be presented in this section. The model will also be used to provide some information not obtained experimentally, such as the effects of aluminum concentrations on particle nucleation and growth.

The experimental results in terms of particle size of AlN powders collected for different residence times are presented in Figure 5.25. The results show that within the scatter of the data, the residence time had no effect on the nucleation and growth of aluminum nitride particles. This suggests that the gas phase reaction and subsequent nucleation and growth are very fast, and that the particles reached a stable size possibly in less than 0.1 second. The average AlN particle size was approximately 20 nm.

Simulations of the aerosol evolution in the synthesis reactor were made using the model presented in section 3.2. The reactor had an inside diameter of 40 mm and was 100 mm long. The reactants at the reactor inlet position were assumed to consist of 15 NL/min of argon

containing 1% aluminum by mass. Ammonia was injected at room temperature. The gas temperature at the inlet position is assumed to be 2000 K. The reactor wall temperature was calculated by energy balance.



Figure 5.25 Particle Size vs. Residence Time

The temperature fields estimated for 2, 4 and 8 NL/min of ammonia are shown in Figure 5.26. This figure shows the effect of ammonia flow rate on the isotherms along the reactor length. It can be seen that the ammonia injection position is a critical zone for the nucleation and

growth since the temperature gradients are extremely steep. Therefore, this zone must be very well represented in the numerical procedures. A grid of 80 axial by 50 radial points was used to simulate the AlN nucleation and growth.



(c) 8 NL/min of Ammonia



The temperature fields in Figure 5.26 show that, as the ammonia flow rate increases there is a steeper decrease in temperature at the point of ammonia injection. This also suggests a better mixing of the reactants, which is the ideal condition to carry out gas phase reactions. It is interesting to note here that experimental results showed incomplete conversion from Al to AlN for ammonia flow rate of 2 NL/min. The presence of a large central channel of poor mixing which may be the cause of incomplete conversion can be seen in Figure 5.26 (a).

It can also be seen that the region immediately downstream of the ammonia injection point is very cold and that the growth stops in this layer of cold gas surrounding the central hot core. This suggests that the nitrogen quench flow had no effect on AlN particle growth, since this occurred almost entirely in the ammonia injection zone.

The modelling results for nucleation and growth of aluminum nitride are presented in the following figures. Figure 5.27 shows the configuration used in the simulations. The position of ammonia injection are represented by z = 0 cm.



Figure 5.27 Position of the Radial Mass Mean Diameter Profiles

Figures 5.28 and 5.29 show the results of mass mean diameter of AlN particles plotted for different axial positions as a function of the reactor radius for ammonia flow rates of 2 and 8 NL/min, respectively. The lower four curves in Figures 5.28 and 5.29 were obtained at positions upstream of the nitrogen injection position. The curve z = 16 cm (upper curve) has a region of zero diameter which extends from 0 to 6 mm due to the presence of the nitrogen quench tube. Figure 5.28 shows the modelling results for an ammonia flow rate of 2 NL/min. It can be observed for curve z = 0 cm (ammonia injection position) that growth does not occur in the central channel due to the bad mixing.



Figure 5.28 Mass Mean Diameter vs. Reactor Radius for 2 NL/min of Ammonia

When the radius is increased to 5 mm the zone of better mixing has been reached and a particle growth can be observed. When analyzing the axial position at 1, 5, and 8 cm, some growth in the center of the reactor can be observed. These three curves are outside of the central channel of bad mixing.

Figure 5.29 shows the results for a higher flow rate of ammonia (6 NL/min). Under this condition, the ammonia was sufficient to promote a good mixing in all sections of the reactor. For this case the powder particle sizes are more uniform and slightly smaller than those showed in Figure 5.28.



Figure 5.29 Mass Mean Diameter vs. Reactor Radius for 6 NL/min of Ammonia

Figure 5.30 shows the simulation results for the final mass mean diameter as a function of aluminum mass concentration at the inlet position. As expected, the initial aluminum concentration has a strong effect on particle nucleation and growth. For 1% aluminum mass concentration, the mean AlN particle size at the exit of the reactor was about 27 nm. This particle size increases to 60 nm with an order of magnitude increase in the aluminum mass concentration. The aluminum mass concentration in the experiments can be estimated to be approximately 0.7%. It can be concluded that the model successfully predicted the experimental results.



Figure 5.30 Final Mass Mean Diameter vs. Aluminum Concentration

The experimental and simulations results show that the ammonia injection position is the critical zone for synthesis, nucleation and growth of AlN particles. As expected, when varying the aluminum mass concentration, the simulation results show that this parameter plays an important role on nucleation and growth of AlN particles.

6 Conclusions

A new type of plasma reactor system was designed, built and evaluated for production of ultrafine aluminum nitride. In this system, metal is evaporated in a transferred arc plasma chamber and then reacted in a separate tubular reactor.

White aluminum nitride powder with spheroidal shape and with hexagonal crystal structure was produced at essentially complete conversion in the new reactor. The mean particle size was approximately 20 nm with a standard deviation of approximately 22 nm. The specific surface area varied from 80 to 100 m²/g. FTIR analysis indicated the presence of O-H bond. If hydrolysis of the sample by atmospheric moisture after removal from the reactor is ignored, the molar ratio of N:Al in complete converted product was 0.95. To produce commercially acceptable powder, surface oxidation must be avoided by avoiding contact with the atmosphere before final parts are produced.

The results of the study of the effect of plasma parameters on aluminum vaporization and gas temperature in the mixing zone showed that long arc lengths, high arc currents and high argon flow rate were best to maximize the gas temperature and short arc lengths, high currents and high argon flow rate were best for high vaporization rates. It is thus clear that a compromise must be made for both adequate gas temperature and sufficiently high vaporization rates.

The arc length was a critical parameter since the temperature of the argon carrier gas must be kept high enough to avoid aluminum condensation before entering the synthesis reactor. For the order of residence time of the reactants in the tubular reactor used in this study only vapour phase reaction could occur. The results showed that the reaction with ammonia reached complete conversion for an ammonia/aluminum molar ratio of about 12 while nitrogen, under the same conditions, was inert.

The ammonia jet momentum was revealed to be an important parameter to improve the aluminum nitride conversion. For ammonia jet momentum less than 0.035 kg·m/s, the gas did not reach the center of the reactor creating a central channel of poor mixing and incomplete conversion.

A study of reactant residence times showed that the vapour phase nitridation reaction is very fast reaching complete conversion in less than 0.15 seconds. The reaction reached approximately 98% conversion for a residence time of the order of 0.06 seconds (reactor length of 50 mm). Thus, the reactor was essentially the mixing zone between the axial flow of aluminum and argon, and the radial injection of ammonia and argon.

The results of the effect of temperature on aluminum nitride conversion revealed a weak effect. The very low dependency of the reaction rate on temperature (activation energy equal to 2980 J/mol), suggested that chemical reaction was not the rate controlling step. The overall reaction rate was probably controlled by heat and mass transfer effects in the mixing zone.

A numerical model, describing the aerosol particle size evolution, developed by Proulx and Bilodeau was successfully applied to the system.

Contribution to Knowledge

- A new concept of experimental apparatus for production of ultrafine aluminum nitride powder was evaluated.
- The effect of plasma parameters on aluminum evaporation in a transferred arc plasma chamber was examined.
- The effect of operating parameters on conversion of aluminum vapour to aluminum nitride powder was studied.
- The aluminum nitride product was characterized using an atomic force microscope.
- The particle size and size distribution of the nanosized aluminum nitride powder were evaluated using the Dynamic Light Scattering technique. The reliability of this technique was evaluated.

Recommendations for Future Work

Ultrafine aluminum nitride powder can be produced by reacting aluminum vapour, produced in a transferred arc plasma system, with ammonia outside of the plasma chamber. Further studies will be useful for a better understanding and optimization of the process. Future work may be concentrated in the following areas:

- the ammonia and aluminum/argon mixing zone should be studied in more detail, both experimentally and by the use of models since this is the crucial area for scale up.
- the effect of a larger aluminum concentration range on particle nucleation and growth, and on AlN conversion should be studied to clarify the kinetic behaviour of the vapour phase nitridation reaction. The aluminum concentrations may be varied without affecting other variables of the process by cooling the anode (crucible) using different water cooling rates. This study should be done with a better temperature sensor in the mixing zone.
- the economic viability of the process should be evaluated.
- the experimental apparatus could be used for other ceramic material production.
- a continuous aluminum ingot feeding system should be developed.

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Appendix A Thermocouple Temperature Error

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The thermocouple temperature was a result of the total energy exchange between the thermocouple tip (exposed junction) and the surroundings. The thermocouple temperature can be substantially different from the gas temperature which is to be measured. The thermocouple loses energy mainly by radiation from the thermocouple tip.

The temperature of the thermocouple is T_v , the true temperature of the gas is T_g , and the temperature of the reactor wall is T_w . The difference between the true gas temperature and thermocouple temperature (T_g - T_w) can be evaluated by the following energy balance:

$$h \cdot A \cdot (T_g - T_i) = \sigma \cdot A \cdot \varepsilon \cdot (T_i^4 - T_w^4)$$

Where h is the convective heat transfer coefficient from the gas to the thermocouple

A is the thermocouple tip area assuming a sphere (A = $3.14 \cdot 10^{-6} \text{ m}^2$), σ is the Stefan-Boltzmann constant ($\sigma = 6.67 \cdot 10^{-11} \text{ kW/m}^2 \text{ K}^4$),

 ε is the surface emissivity of the thermocouple (chromium alloy, $\varepsilon = 0.29$), and

The difference between the true gas temperature and thermocouple temperature $(T_g - T_w)$ for the conditions used during the experiments (15 L/min of argon, and temperatures varying from 950 to 1050 K) was estimated to vary from 19 to 32 K.

Appendix B XRD Spectra

Calibration curve (10% of aluminum)



Calibration curve (20% of aluminum)



Experimental result run# W1


Experimental result run# A1



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Appendix C Experimental Results

Preliminary Experimental Results

Conditions: Argon Plasma Gas Flow Rate = 15 NL/min Arc Current = 240 A Arc Length = 40 mm Arc Voltage = 27 V

Run #	Ammonia [NL/min]	Temperature [K]	Residence Time [s]	Aluminum Vaporized	Conversion
1	2	1003	0.14	2.57	94.6
2	2	1011	0.14	3.07	92.2
3	2	1032	0.14	3.14	89.2
• 4	2	1065	0.13	3.09	86.2
5	2	1031	0.28	2.39	95.1
6	2	1034	0.26	2.85	90.5
7	2	1072	0.43	2.55	91.3
8	2	1003	0.41	2.49	83.4
9	2	1012	0.42	2.54	87.7
10	2	988	0.40	2.57	87.6
11	2	1091	0.41	2.78	94.0
12	4	1039	0.15	2.32	93.9
13	4	985	0.12	2.37	91.6
14	4	1124	0.13	2.82	95.0
15	4	1077	0.29	2.85	91.8

Preliminary Experimental Results (continued)

Conditions: Argon Plasma Gas Flow Rate = 15 NL/min Arc Current = 240 A Arc Length = 40 mm Arc Voltage = 27 V

Run #	Temperature [K]	Ammonia [NL/min]	Residence Time [s]	Aluminum Vaporized [g]	Conversion
16	992	4	0.29	2.58	89.3
17	1057	4	0.26	2.37	92.0
18	1048	4	0.27	2.43	91.8
19	988	4	0.44	2.80	88.6
20	984	4	0.42	2.79	84.6
· 21	989	4	0.38	3.33	84.3
22	1053	4	0.40	2.77	86.2
23	1080	4	0,34	2.65	86.6
24	976	6	0.15	2.34	100
25	1102	6	0.13	3.08	100
26	973	6	0.28	2.31	100
27	1047	6	0.26	2.73	100
28	961	6	0.43	3.09	100
29	1023	6	0,34	2,34	100
30	1072	6	0.39	2.65	100

Experimental Results

Conditions: Argon Plasma Gas Flow Rate = 15 NL/min Arc Current = 240 A Arc Length = 40 mm Arc Voltage = 27 V Ammonia Jet Momentum = 0.035 kg·m/s

Run #	Argon Mixture [NL/min]	Ammonia [NL/min]	Temperature [K]	Residence Time [s]	Aluminum Vaporized	Conversion [%]
					[g]	
L1*	0	6	973	0.14	3.06	91.5
L2	0	6	979	0.14	2.34	100
NI	0	6	1048	0.13	2.93	0
N2	0	6	976	0.13	2,34	100
AÏ	3.6	0.5	979	0.15	3.12	90.5
A2	3.6	0.5	984	0.15	3,01	88.2
A3	3.2	1	994	0,15	2,50	95.9
A4	2.9	1.5	985	0.15	2,38	95.4
A5	2.9	1.5	987	0.15	2.75	96.8
A6	2.6	2	992	0.15	2,38	100
A7	2.2	2.5	991	0.15	2.84	100
TI	3.6	0.5	922	0.15	2.39	84.4
T2	3,6	0.5	919	0.16	3.13	8.80
T3	3.6	0.5	979	0.15	3.12	90.5
T 4	3.6	0.5	984	0.15	3.01	88.2

* Arc Length = 32 mm

Experimental Results (continued)

Conditions: Argon Plasma Gas Flow Rate = 15 NL/min Arc Current = 240 A Arc Length = 40 mm Arc Voltage = 27 V Ammonia Jet Momentum = 0.035 kg-m/s

Run #	Argon Mixture	Ammonia	Temperature	Residence Time	Aluminum Vaporized	Conversion
				[S]		[%]
T5	3.6	0.5	1101	0.13	3.10	89.7
T6	3.6	0.5	1088	0.13	2.18	94.3
Rl	3.6	0.5	979	0.15	. 3.12	90.5
R2	3,6	0.5	984	0.15	3.01	88.2
R3 ⁻	3.6	0.5	993	0.28	2.40	92.9
R4	3.6	0.5	998	0.42	2.42	86.5
R5	3.6	0.5	1007	0.42	2.39	94.3
R6	3.6	0.5	967	0.42	2.29	94.6
	2.2	2.5	972	0.06	2.79	97.8
R8	2.2	2.5	991	0.15	2.84	100
MI"	0	2	1003	0.14	2.60	94.6
M2"	0	2	1011	0.14	3.07	92.2
M3	2.6	2	992	0.15	2.38	100
M4 ⁺	4	2	985	0.15	3.35	100
W1	0	0	985	0.16	2.82	0
W2	0	0	1008	0.34	2.67	0
W3	0	0	1003	0.34	2.55	0

Ammonia Jet Momentum = 0.0038 kg·m/s

Ammonia Jet Momentum = 0.066 kg-m/s