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Reaction Study of Aluminium Chloride with Ammonia and Mechanisms Leading to Aluminium Nitride

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Abstract

The compound formed between $AlCl_3$ and NH_3 at room temperature and low temperature, characterized by different analysis methods, corresponds to the formula $AlCl_3{\cdot}6NH_3$. This intermediate was heated to 900°C under an ammonia stream to obtain aluminium nitride in low yield; as by-product NH_4Cl was formed during the thermolysis. In order to explain the decomposition mechanisms, two new pyrolysis were realized, under nitrogen and under reduced pressure. These showed formation of $Al(NH_2)NH$ in addition to NH_4Cl during the thermal decomposition. $Al(NH_2)NH$ can react with HCl, which results from the dissociation of NH_4Cl, to form AlClNH volatile combination. This is carried out by the gaseous stream during the thermolysis, thereby accounting for the low synthesis yield.

1 Introduction

The synthesis of aluminium nitride in powder or film form has been often realized from $AlCl_3$ precursor. The halide is generally heated to its sublimation temperature and then carried by a carrier gas (nitrogen, hydrogen, argon) to a reactor where ammonia is introduced. The reaction is performed at temperatures between 600 and 1400°C.[1–4] When aluminium nitride is obtained by this synthesis route, the decomposition mechanisms are difficult to describe. During the pyrolysis, a great amount of NH_4Cl is formed as a by-product. In order to explain the intermediate steps, the process used in this work is different from those proposed earlier. The reaction between $AlCl_3$ and NH_3 was first realized at room and low temperature, in order to establish its nature. This reaction results in the production of $AlCl_3{\cdot}6NH_3$.[5,6] Next $AlCl_3{\cdot}6NH_3$ was subjected to heat treatments under different atmospheres (ammonia, nitrogen or reduced pressure), and the decomposition products analysed by infra-red spectroscopy and X-ray diffraction. Comparison of the different results enabled the mechanism of aluminium nitride synthesis to be elucidated.

2 Experimental Procedures

2.1 Reactants

Aluminium chloride (bidistilled, from Atochem) was a fine, homogeneous, soft yellow and very hygroscopic powder (impurities: iron 500 ppm, Zn < 2 ppm). The ammonia used had a purity of 99·995%, its chemical composition being given by the following characteristics: $H_2O < 10$ ppm, $O_2 <$ 2 ppm, $N_2 < 10$ ppm, $CO + CO_2 < 5$ ppm. The nitrogen used had a purity of 99·998%, its chemical composition being given by the following characteristics: $H_2O < 2$ ppm, $O_2 < 3$ ppm, $C_nH_m < 0{\cdot}2$ ppm, $CO < 2$ ppm, $CO_2 < 1$ ppm.

2.2 Experimental assembly

The airtight assembly (Fig. 1) was developed for use at different temperatures (for high temperature use, a furnace is put around the quartz tube) under static conditions or under a gaseous stream.

2.3 Reaction at room temperature of $AlCl_3$ with NH_3

A definite mass (500 mg) of aluminium chloride was introduced into the quartz tube. Vacuum was realized in the assembly, then the reactor (1) was isolated. A known amount of ammonia was introduced into the rest of the assembly. The tap R_1 separating the two parts was opened, allowing ammonia gas to come into contact with the solid halide. After 24 h, when the pressure was stable, its value enabled the number of moles of ammonia still present in the assembly to be determined, and, by difference, the amount of ammonia consumed.

2.4 Reaction at low temperature of $AlCl_3$ with NH_3

The quartz tube was plunged into a dewar of ethanol at –50°C. Ammonia was introduced, which condensed on the aluminium chloride, and the reaction was left for ~24 h. The dewar was removed from the tube, so that the excess ammonia distils. The difference between the initial volume of gaseous ammonia and the removed volume allows calculation of the number of moles of ammonia consumed.

2.4.1 Extractions with liquid ammonia

This technique was used to show the possible presence of ammonium chloride (NH_4Cl) in the reaction compound. If $AlCl_3$ undergoes an ammonolysis in liquid ammonia, the resultant product will not comprise a single compound but a melt including NH_4Cl.[7–9]

A quantity of ammonia (the order of 50 ml) was condensed on $AlCl_3$ in the reactor. The Pyrex tube (2), under vacuum and isolated from the rest of the assembly, was plunged into a dewar of liquid nitrogen in order to acquire a lower temperature than the reactor temperature; the latter was heated at the same time. Upon opening of tap R_2, the pressure difference created between the two tubes permitted the liquid to decant through the filter into the Pyrex tube. Any dissolved ammonium chloride precipitates on the Pyrex tube which is allowed to warm to room temperature while ammonia distils. This procedure was repeated about 20 times. NH_4Cl formed was quantified by titration (gravimetric technique).

2.5 Thermal decomposition

2.5.1 Under ammonia stream

After reaction, the assembly was filled with ammonia in order to maintain a gaseous stream. Heating rate, temperatures and stage times were programmed.

2.5.2 Under nitrogen stream

After reaction the assembly was filled with nitrogen, the stream obtained carrying away any gaseous products formed during the thermal decomposition. The assembly was connected via tap R_3 (Fig. 1) to a flexible tube which bubbled the nitrogen stream through hydrochloric acid solution. Thereafter, the gaseous products were determined by titration.

2.5.3 Under reduced pressure

Once the reaction between $AlCl_3$ and NH_3 was over, vacuum was realized in the assembly, and the subsequent pyrolysis followed by continuously monitoring the pressure. The volumes pressures and temperatures are known, so it is possible to determine the number of moles of gaseous products evolved. So, gaseous escape is quantified.

3 Formulation and Nature of Compound Formed Between $AlCl_3$ and NH_3

3.1 Reaction of $AlCl_3$ with NH_3

3.1.1 Room temperature

The reaction which occurs between ammonia gas and $AlCl_3$ solid is very fast and exothermic. A liquid phase transition is observed; then, very quickly, a solid layer forms and grows. Ammonia absorption, very important at the beginning of the reaction, decreases progressively and is most probably limited by the formation of the solid layer; after 24 h this absorption is over. A white fine powder is obtained which is stable under vacuum at room temperature and sensitive to the slightest moisture.

3.1.2 Low temperature

At low temperature (–50°C), the precursor saturates

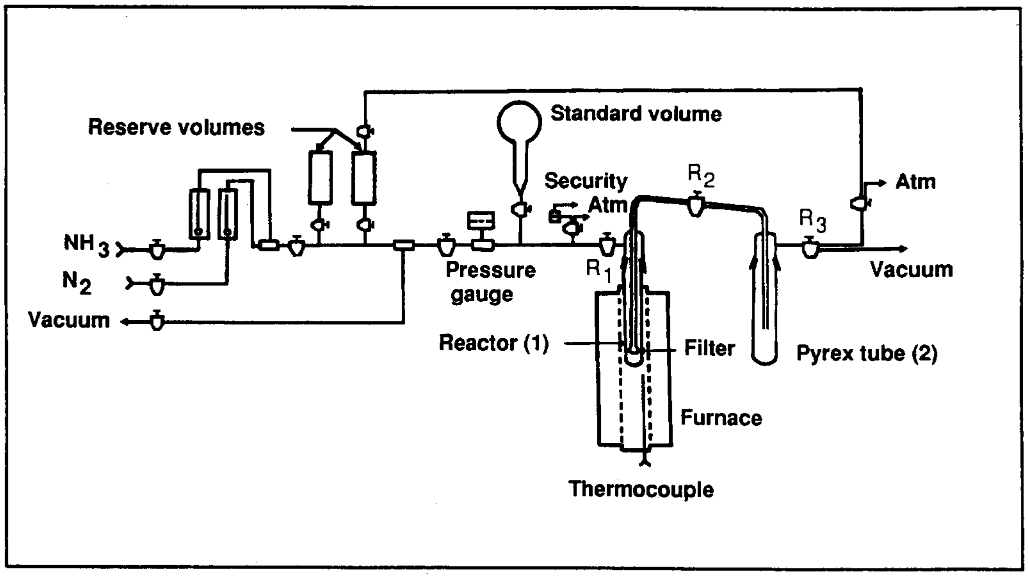


Fig. 1. Schematic illustration of the reactor assembly.

Table 1. Chemical analysis[a] of reaction compound

	Element (wt%)			
	N	*Cl*	*Al*	*H*
$AlCl_3$ + NH_3 reaction	35·4	44·0	11·8	6·8
$AlCl_3{\cdot}6NH_3$ theoretical	35·9	45·2	11·5	7·6

[a] N determined by Kjeldahl titration, Cl by gravimetric titration, Al by chelatometric titration and H by C–H–N titration.

with ammonia. A white fine powder is obtained in liquid ammonia. After 24 h, the whole is allowed to warm to room temperature and excess ammonia distils. The resultant product is the same that synthesized at room temperature during direct reaction.

3.1.3 Reaction compounds

Whatever the reaction conditions used, the compound obtained corresponds to the absorption of six ammonia molecules by one aluminium chloride molecule. The $AlCl_3{\cdot}6NH_3$ formula, which is confirmed by chemical analysis (Table 1), is established by the difference between the number of moles of ammonia introduced and remaining in the assembly.

3.2 Nature of the $AlCl_3{\cdot}6NH_3$ compound

Two assumptions have been set down: either $AlCl_3{\cdot}6NH_3$ is an adduct compound like $[Al(NH_3)_6]^{3+}$ $3Cl^-$ (Refs 5, 10 and 11) or the $AlCl_3{\cdot}6NH_3$ formulation is the result of an ammonolysis leading to a melt such as $AlCl_{3-x}(NH_2)_x$, $(6 - 2x)NH_3$ + xNH_4Cl by analogy with other compounds.[7–9] In this last case, it is easy to show the presence of NH_4Cl by liquid ammonia extractions.

3.2.1 $AlCl_3{\cdot}6NH_3$ treated by liquid ammonia

After extraction with liquid ammonia for two weeks, the amount of chlorine removed was determined to be 4% of the theoretical chlorine content related to $AlCl_3{\cdot}6NH_3$. This low amount of chlorine indicates that the reaction between $AlCl_3$ and NH_3 is not an ammonolysis, but the resultant compound is an ammoniate adduct compound like $[Al(NH_3)_6]^{3+}$ $3Cl^-$.[12,13]

3.2.2 Physicochemical characterizations of $AlCl_3{\cdot}6NH_3$

Analysis by X-ray diffraction. As $AlCl_3{\cdot}6NH_3$ is very hygroscopic, the most airtight possible sample case has to be used. We employed a beryllium window which is transparent to X-rays and thus can form a cap isolating the powder from ambient atmosphere. The sample case has some disadvantages: it diffracts and gives two strong lines. The thickness of the beryllium window means that the sample case is not exactly in the radiation plane, leading to a low gap between the lines observed.

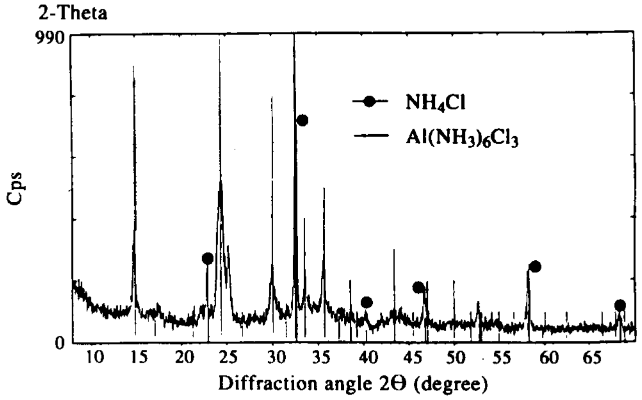


Fig. 2. X-ray diffraction pattern of the $AlCl_3{\cdot}6NH_3$ powder.

The powder is not well crystallized (Fig. 2). The X-ray diffraction pattern shows lines that can be attributed (by means of the ASTM card) to the $Al(NH_3)_6Cl_3$ compound.[10] The presence of NH_4Cl characteristic lines is observed, some of which are shared with $Al(NH_3)_6Cl_3$. The formation of a low amount of NH_4Cl during the reaction between $AlCl_3$ and NH_3 can be accepted, as 4% of chlorine was removed during the washings. The presence of NH_4Cl can also arise by partial hydrolysis of the powder during preparation or analysis.

Infrared spectroscopy. As $AlCl_3{\cdot}6NH_3$ is very hygroscopic, the preparation of pellets (a small amount of $AlCl_3{\cdot}6NH_3$ diluted in KBr) for infrared analysis was carried out in a glove box. On the other hand, during experimental measurements the samples were not protected from the air, so hydrolysis was possible.

The infra-red spectrum was recorded in the frequency range 4000–600 cm^{-1} (Fig. 3). A large but not very strong band was observed around 1600 cm^{-1} which corresponds to the antisymmetric deformation vibrations of NH_3 groups. The fine band centred around 1350 cm^{-1} is characteristic of the NH_4^+ ion. In the 800–750 cm^{-1} region the rather large band is assigned to the pendulum vibrations of NH_3 groups.

The $AlCl_3{\cdot}6NH_3$ compound can thus be described

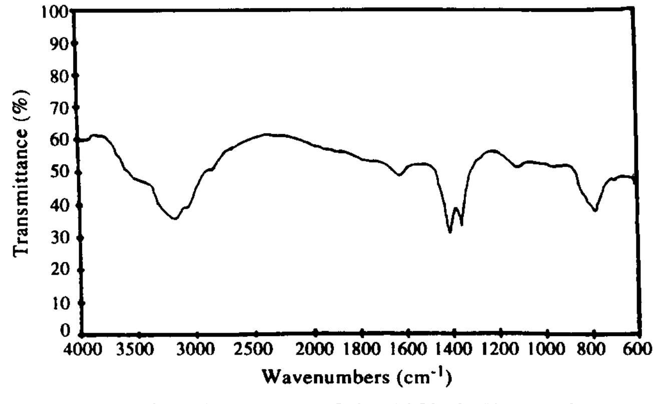


Fig. 3. Infrared spectrum of the $AlCl_3{\cdot}6NH_3$ powder.

as a complex $[Al(NH_3)_6]^{3+}$ $3Cl^-$,[10,11] with the NH_3 groups being regarded as ligands.

4 Thermal Decompositions of $AlCl_3 \cdot 6NH_3$

4.1 Under ammonia

4.1.1 Observations

A heating rate of 5°C min^{-1} was chosen, the stage temperature being 900°C (1 h). During the pyrolysis gaseous products were released from 300°C, then a fine white powder condensed on the cold areas of the assembly. At the end of the pyrolysis, a little powder remained at the bottom of the tube and a thin film which sticks strongly deposited on the reactor walls. The film and the powder were white, the powder having the appearance of transparent fine particles.

4.1.2 Characteristics of products formed

The crystalline powder that collected on the pipes was analysed by X-ray diffraction and found to have the same structure as NH_4Cl. An absorption band centred on 1400 cm^{-1}, characteristic of the $NH^+{}_4$ ion, was present in the infra-red spectrum.

The film analysed by X-ray diffraction seemed to be better crystallized than the powder collected at the bottom of the tube. The lines observed were assigned to aluminium nitride phase (Fig. 4). The maximum intensity line on the X-ray diffraction pattern and that of ASTM card No. 251133 are not the same; the nitride obtained is preferentially oriented in the (0, 0, 2) direction. The powder analysed by scanning electron microscopy (SEM) looks like big platelets: L = 150–200 μm; l = 300–350 μm; e = 15–20 μm (Fig. 5). These platelets are probably amorphous, as the crystallization occurs in part on a surface. Crystallites would be expected to form on the platelets' surface.[14] The film deposits on quartz seem to be more homogeneous (Fig. 5); the silica tube would constitute a good substrate for growth of aluminium nitride.[15]

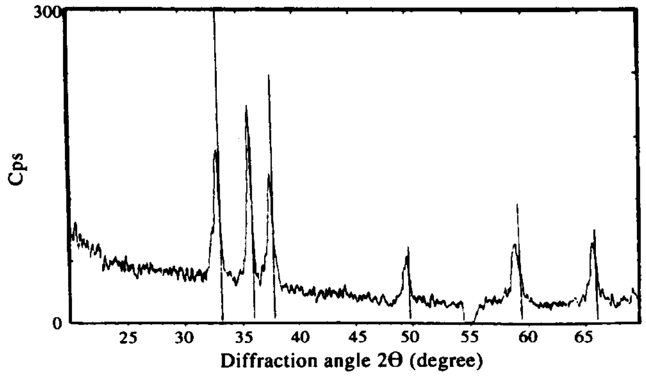


Fig. 4. X-ray diffraction pattern of the powder collected at the bottom of the tube.

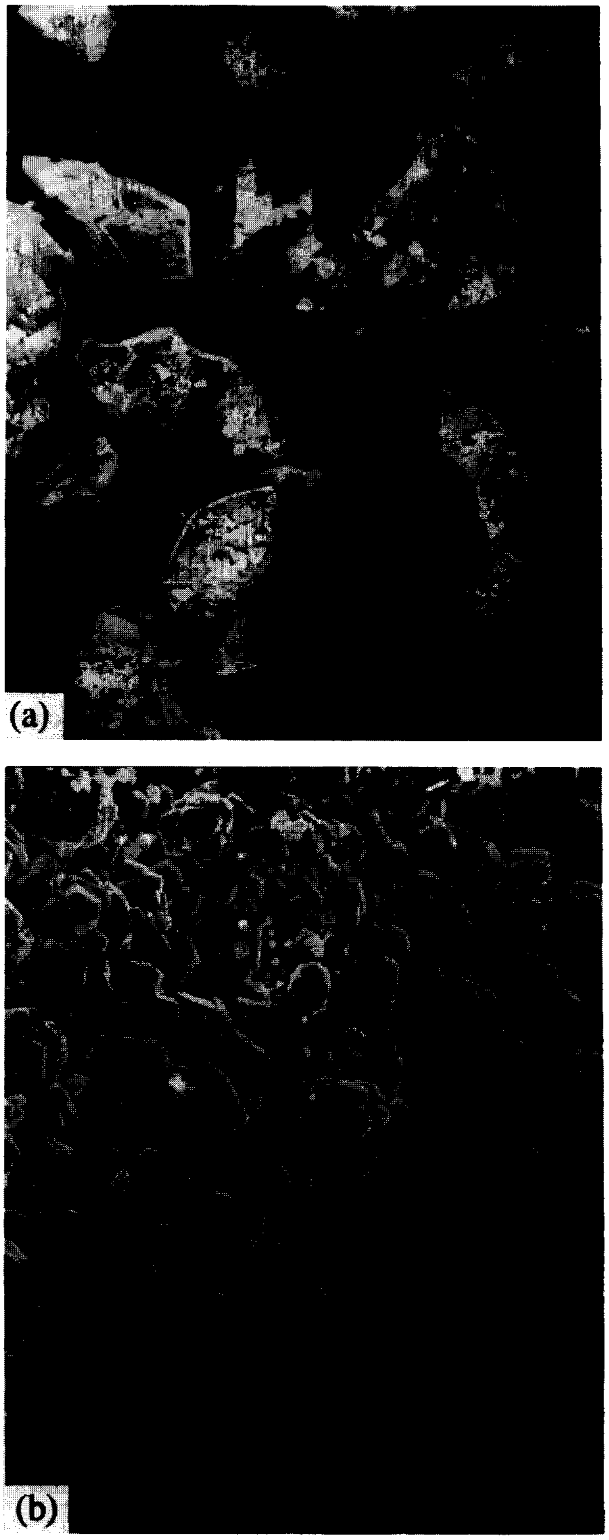


Fig. 5. Scanning electron micrographs of (a) the powder collected at the bottom of the tube (× 1000) and (b) the coated film on the silica tube (× 15000).

The specific area of the powder is of the order of 24 m^2 g^{-1}. The synthesis yield is about 10%.[12]

4.2 Under reduced pressure

4.2.1 Observations

A heating rate of 3°C min^{-1} was programmed with a stage of 900°C. A thin layer of white, rather dense deposits was observed on the tube walls. A

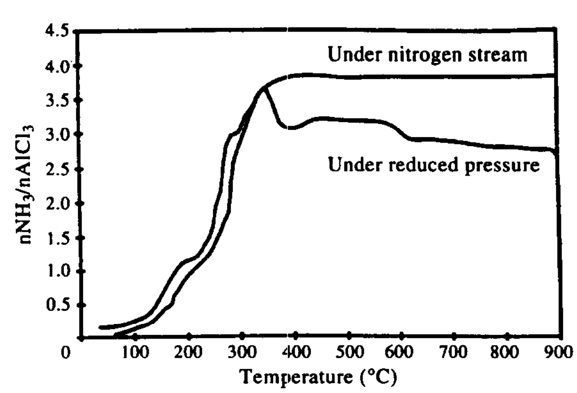


Fig. 6. Thermal decomposition curves of $AlCl_3{\cdot}6NH_3$ under reduced pressure and under a nitrogen stream.

little powder remained at the bottom of the tube. The pressure was recorded continuously and transformation to the number of moles of gaseous products permits establishment of the curve $nNH_3/nAlCl_3 = f(T)$. The gaseous product evolved was ammonia.

4.2.2 Interpretation of the curve $nNH_3/nAlCl_3 = f(T)$
The curve obtained (Fig. 6) shows several transformation areas. The first, where pressure increases rather quickly, corresponds to the escape of one mole of ammonia per mole of precursor at 175°C. Then the slope of the curve increases, expressing the escape of two additional moles of ammonia. The emanation occurs more slowly and achieves a maximum of around 4 for $nNH_3/nAlCl_3$ ratio at 350°C. Subsequently ammonia reabsorption is observed until a composition of $AlCl_3{\cdot}3NH_3$, then pressure is stabilized.

4.2.3 Contents
The sublimate which deposits on the tube walls, analysed by X-ray diffraction, has the same structure as NH_4Cl. The powder collected at the bottom of the tube is amorphous, its analysis by infrared spectroscopy not revealing the characteristic absorption band of the Al–N bond.[16] Probably, the thermal decomposition of $AlCl_3{\cdot}6NH_3$ under reduced pressure ends the formation of an ammoniate melt.[17–19]

4.3 Under nitrogen

4.3.1 Observations
A heating rate of 3°C min^{-1} was programmed with a stage of 900°C. The gaseous escape during the pyrolysis was carried out by the nitrogen stream and analysed by titration. The gaseous product comprised ammonia, acid emanation was never observed. White vapours appeared from 200°C and then condensed on the cold areas of the assembly to form a fine white powder during the whole of the thermolysis. A sublimate deposited on the walls tube at the furnace exit. There was no compound at the bottom of the tube. The results of titrations allowed the curve $nNH_3/nAlCl_3 = f(T)$ to be established.

4.3.2 Interpretation of the curve $nNH_3/nAlCl_3 = f(T)$
The thermal decomposition curves under reduced pressure and nitrogen stream are rather similar (Fig. 6), with the same transformations being present. However, ammonia refixation is avoided under the nitrogen stream. The maximum ammonia escape corresponds to a $nNH_3/nAlCl_3$ ratio of around 4. The main difference between the two types of pyrolysis is the result of the violent sublimation of NH_4Cl and particularly the absence of pyrolysis residues at the bottom of the tube.

4.3.3 Contents
The great amount of fine powder collected on the pipes was essentially NH_4Cl (infrared, X-ray diffraction analysis). The absence of pyrolysis residues is attributed to the formation of volatile compounds during the thermal decomposition. These condense on cold areas of the assembly. Thus the sublimate formed contains an important chlorine content of the order of 55 wt%, and aluminium too (≈ 5%).

4.4 Conclusions

The thermal decomposition of $AlCl_3{\cdot}6NH_3$ under an ammonia stream from 900°C leads to the formation of crystalline aluminium nitride. The byproduct of the pyrolysis is NH_4Cl, which deposits on the cold areas of the assembly in great amounts and disturbs the synthesis. The presence of NH_4Cl—which can interact with aluminium compounds—results from the formation of volatile compounds that are carried out by the gaseous stream, thereby contributing to the yield decrease.

5 Decomposition Mechanisms from $AlCl_3{\cdot}6NH_3$ to AlN

From previous observations, all the reactions leading to AlN from $AlCl_3{\cdot}6NH_3$ are suggested here. These different mechanisms have been deduced from the observation of curves (Fig. 6) and the phenomena occurring during pyrolysis (ex: NH_4Cl formation perceptible).

The first escape observed corresponds to one mole of ammonia; NH_4Cl is formed at the same time which involves the formation of the compound $Al(NH_2)NH$:[20]

$$AlCl_3{\cdot}6NH_3 \rightarrow AlCl_3{\cdot}5NH_3 + NH_3 \quad T = 25\text{–}175°C$$

$$AlCl_3{\cdot}6NH_3 \rightarrow Al(NH_2)NH + 3\ NH_4Cl + NH_3$$

At higher temperatures, NH_4Cl sublimes and breaks up into NH_3 and HCl, which explains the new ammonia escape observed. As for HCl, it fixes on $Al(NH_2)NH$ to form a volatile combination. The ammonium chloride which deposits on the cold areas is the result of the excess NH_3 and HCl recombination.

$$NH_4Cl \rightarrow NH_3\,(g) + HCl\,(g)$$

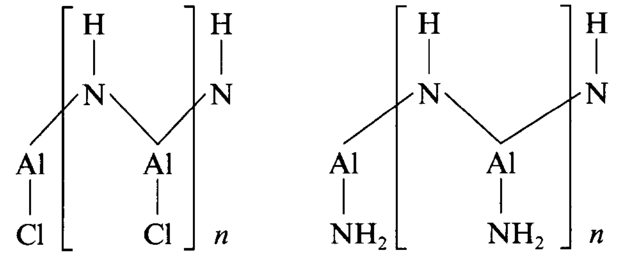
$$AlCl_3{\cdot}5NH_3 \xrightarrow{T = 225\text{–}300°C} AlCl_3{\cdot}3NH_3 + 2NH_3 \xrightarrow{T = 300\text{–}350°C} AlCl_3{\cdot}2NH_3 + 3NH_3$$

$$\begin{array}{l} Al(NH_2)NH + 3\,NH_3 + 3\,HCl \rightarrow \\ \qquad\qquad AlClNH + 3NH_3 + 2\,NH_4Cl \\ \qquad\qquad\qquad\qquad \downarrow \end{array}$$

volatile chlorinated nitrogen combination — recombination on the cold areas

The volatile combination is able to fix ammonia, but the refixation is avoided in the case of the pyrolysis under nitrogen stream. The assessment corresponds well to the maximum escape observed on the curves (Fig. 6).

As AlClNH and $Al(NH_2)NH$ compounds are volatile, they can be represented by polymerized forms:[3]



Aluminium nitride is obtained at the end of the thermolysis under ammonia whereas the thermal decomposition under nitrogen is characterized by the absence of pyrolysis residues. Under ammonia atmosphere, HCl fixation on $Al(NH_2)NH$ cannot take place in the same way:

$$\begin{array}{ccc} Al(NH_2)NH + 3\,NH_3 & + & 3\,HCl \\ \downarrow & & \downarrow \\ AlN + NH_3 & & 3\,NH_4Cl \end{array} \quad \text{recombination on cold areas}$$

The equilibrium is moved towards the formation of aluminium nitride. The chlorhydrate still forms during the ammonium chloride sublimation but in a more limited way. The chlorhydrate is a volatile species and is responsible for the low yield of aluminium nitride.

6 Conclusions

The compound of formula $AlCl_3{\cdot}6NH_3$, which is the result of the reaction between $AlCl_3$ and NH_3, looks like a fine white powder and is sensitive to moisture. It is an adduct compound: $[Al(NH_3)_6]^{3+}$ $3Cl^-$. $AlCl_3{\cdot}6NH_3$ leads to aluminium nitride after a thermal treatment at 900°C under ammonia, the aluminium nitride being obtained in powder or film form by this synthesis route. The crystalline AlN is oriented in a preferential direction. Several transformations occur during the thermal decomposition of $AlCl_3{\cdot}6NH_3$; release of ammonia not only takes place at one temperature but at different temperatures between 100 and 350°C. This indicates that there are different $AlCl_3$–NH_3 bonds in the $AlCl_3{\cdot}6NH_3$ compound, the strengths of which are not the same. Intermediates such as $Al(NH_2)NH$ form during the thermal decomposition. The presence of NH_4Cl, a by-product of the synthesis, involves the formation of volatile species. These are the result of the HCl fixation on $Al(NH_2)NH$, the HCl being produced during the dissociation of NH_4Cl. The low yield of the aluminium nitride is connected with the formation of these volatiles, which are carried out by the gaseous stream.

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