SYNTHESIS OF ALN AT LOW TEMPERATURE - THE ROLE OF NH_4CL

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ABSTRACT:

Aluminium nitride powders were synthesized from γ-Al_2O_3 in the presence of NH_4Cl via the gas-phase reaction of system at differences temperature and difference NH_4Cl/Al_2O_3 ratios. The synthesized AlN was characterized by XRD and from that the yield of AlN was estimated. The yield of AIN is found to increase as the mole ratio of NH_4Cl/Al_2O_3 increased. Also, the nitridation yield increased as the reaction temperature increased, and it reaches 91% at a temperature of 1050°C. It demonstrated that the nitridation to form AlN could be performed at low temperature in the presence of NH_4Cl.

Keywords: Aluminium nitride, nitridation, ammonium chloride.

1. Introduction

Aluminum Nitride (AlN) is known for its excellent thermal conductivity, electrical insulation, and mechanical properties, making it valuable for various applications in electronics, optoelectronics, and thermal management. AlN can be synthesized through different methods, such as direct nitridation of aluminum [1-4], ammonolysis of aluminum compounds, carbothermal reduction [5,6], sol-gel method [7,8], and chemical vapor deposition (CVD) [9,10].

In direct nitridation method, it involves heating aluminum metal in a nitrogen or ammonia atmosphere. The reaction typically takes place at temperatures ranging from 1000 to 1300°C. Aluminum reacts with nitrogen to form aluminum nitride. The reaction is exothermic, and it releases a considerable amount of energy. This method is known for producing high-purity AlN, but it requires careful control of reaction conditions to prevent the formation of unexpected aluminum oxide impurities. On the other hand, in the ammonolysis approach, aluminum compounds, such as aluminum chloride ($AlCl_3$) or aluminum oxide (Al_2O_3), can react with ammonia gas (NH_3) to produce AlN. This reaction occurs at low temperatures compared to direct nitridation, making it a more energy-efficient process. By controlling the reaction conditions, the formation of impurities can be minimized.

Another approach, that is carbothermal reduction, a mixture of aluminum oxide (Al_2O_3) and a carbon source (e.g., graphite) were heating in a nitrogen atmosphere. Carbon reacts with the oxygen in the aluminum oxide, leaving behind aluminum metal. The aluminum metal then reacts with nitrogen to form AlN. This method is cost-effective and is capable of producing AlN powder on a larger scale. However, the process requires high temperatures, *i.e.*, typically above 1600°C and can lead to the incorporation of carbon impurities in the final product. However, in the sol-gel method, aluminum alkoxides are hydrolyzed to form a gel precursor. The gel is then dried and heated to form AlN. This method allows for precise control over composition and morphology. By manipulating the reaction parameters and additives, researchers can tailor the particle size, shape, and porosity of the resulting AlN. The sol-gel process is versatile but can be more complex than other methods.

CVD is an approach relating to a thin-film deposition technique used to produce AlN films. It involves the reaction of volatile aluminum and nitrogen precursors in a high-temperature environment. The precursors were decomposed, and the resulting species react on the substrate surface to form a thin film of AlN. CVD offers well control of film thickness, uniformity, and composition. It is commonly used for coating substrates with AlN layers for various applications.

In a previous study, the synthesis of aluminum nitride (AlN) is carried out using a process that involves the formation of aluminum chloride ($AlCl_3$) as an intermediate. The reaction mechanism includes the utilization of ammonium chloride (NH_4Cl) as one of the reactants. The process can be summarized as follows. First, NH_4Cl vaporizes without melting at 340°C to form equal volumes of ammonia and hydrogen chloride: $NH_4Cl \rightarrow NH_3 + HCl$ (1). Then, the second reaction is carried out as follows: $6HCl + Al_2O_3 \rightarrow 2AlCl_3 + 3H_2O$ (2). The aluminum chloride ($AlCl_3$) as intermediate then undergoes a reaction with ammonia gas (NH_3) to form aluminum nitride (AlN). This reaction can be represented as: $AlCl_3 + NH_3 \rightarrow AlN + 3HCl$ (3). In this reaction, the conditions could exhibit significant influence on the rate of the reaction and purity of the product. Some factors that need to be considered such as temperature, pressure, reactant proportion, purity of reactants, reaction time, catalyst. The reaction is typically conducted at elevated temperatures, often in the range of 800 to 1200°C. Higher temperatures help facilitate the chemical conversion and the formation of aluminum nitride.

The reactant proportions are also an important parameter for increasing the rate of reaction and the yield of the AlN product. Following the stoichiometry ratio in the balanced equation, 1 mole of aluminum chloride could react with 1 mole of ammonia gas to form AlN. In some cases, catalysts or additives may be used to enhance the reaction rate or control the crystal structure of the resulting aluminum nitride. Besides, the quality and purity of the reactants, particularly the aluminum chloride and ammonia, can significantly affect the yield of the reaction and the quality of the AlN. Finally, longer reaction times can help ensure complete conversion of reactants to products.

In the present work, ammonium chloride is used as a source of ammonia gas, which is an essential reactant in the formation of both aluminum chloride and aluminum nitride. The resulting aluminum nitride can be collected as the final product. This method offers the advantage of utilizing an intermediate compound (aluminum chloride) to facilitate the synthesis of aluminum nitride. The inclusion of ammonium chloride provides a convenient source of ammonia gas, which plays a key role in both reactions. The use of intermediate compounds in synthesis processes can help control reaction kinetics and improve the purity of the final product. It's worth noting that the choice of reactants, reaction conditions, and purification steps can significantly influence the yield, purity, and properties of the synthesized aluminum nitride. This synthesis route provides a tailored approach to producing AlN while taking advantage of the reactivity of ammonium chloride and aluminum oxide to generate intermediate compounds that lead to the desired end product.

2. Experimental

NH_4Cl (98%) is brought from Sigma-Aldrich. NH_3 (99%) is obtained from Duc-Giang Chemical company. The synthesized γ-Al_2O_3 with the surface area has 127 m^2/g was used as the starting material. The characteristic of γ-Al_2O_3 was shown in Figure 1a,1b.

Fig 1a. Isotherm of γ-Al_2O_3

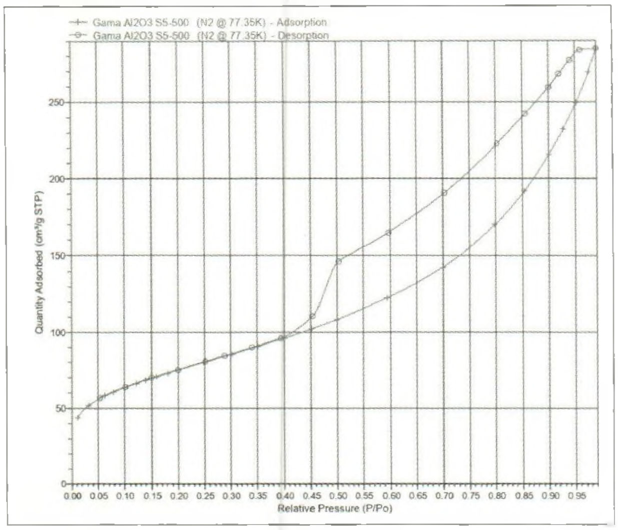
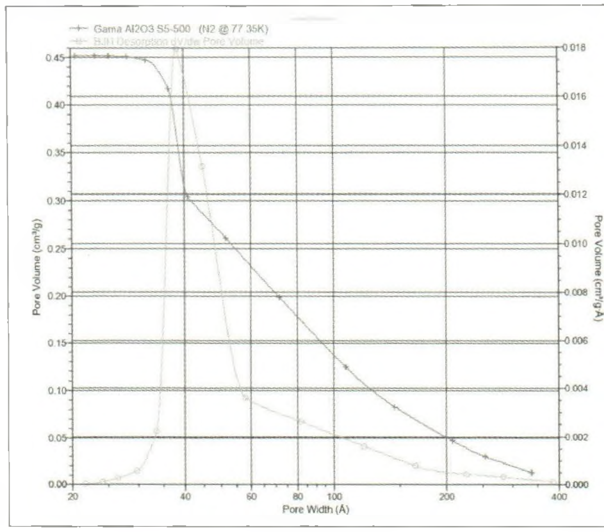


Fig 1b. BJH Desorption Cumulative Pore Volume of γ-Al_2O_3



The reaction process is carried out in a continuous flow reaction scheme. The reactant mixture consisting of Al_2O_3 and NH_4Cl is blended in varying proportions and then introduced into the reaction tube made of ceramic. The reaction temperature is controlled using an electrical furnace through a control unit with a temperature error of <1%. The range of the mass flow controller is 0-200 ml/min. Excess unreacted NH_3 gas is neutralized using a 35% wt. of HCl solution.

The reaction experiments were conducted under atmospheric pressure conditions with a NH_3 gas flow rate of 300 ml/min for 6 h reaction time.

A series of reaction experiments were conducted to assess the impact of temperatures on the reaction efficiency.

The nitridation yield was obtained from the intensity of XRD results as shown in the following equation [11].

$$\frac{I_{AlN(100)}}{I_{AlN(100)} + I_{\alpha\text{-}Al_2O_3(113)} + I_{\theta\text{-}Al_2O_3(403)} + I_{\delta\text{-}Al_2O_3(4012)}}$$

Where $I_{AlN(100)}$ is an integrated intensity of a AlN main peak at $2\theta = 33.17°$, $I_{\alpha\text{-}Al_2O_3(113)}$ is an integrated intensity of a α-Al_2O_3 (113) main peak at $2\theta = 43.34°$, $I_{\theta\text{-}Al_2O_3(403)}$ is an integrated intensity of a θ-Al_2O_3(511) main peak at $2\theta = 36.61°$ and $I_{\delta\text{-}Al_2O_3(4012)}$ is an integrated intensity of a δ-Al_2O_3 main peak at $2\theta = 67.31°$, respectively.

3. Results and discussion

The role of NH_4Cl in nitridation reaction of AlN.

To assess the role of NH4Cl in the reaction, reaction experiments were conducted with different NH4Cl/Al_2O_3 ratios. The reaction temperature was set at 1150°C. A total of 1 g of Al_2O_3 was used as the input material for each reaction.

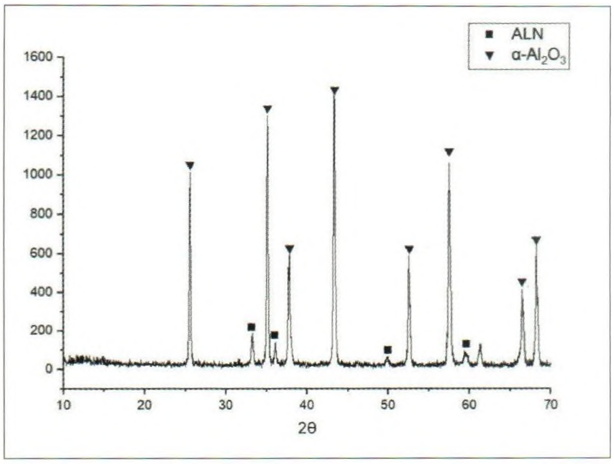
From the XRD spectrum in Figure 2a, it is evident the clear formation of the AlN phase along with the strong presence of the α-Al_2O_3. The calculated results indicate that the nitridation ratio for the formation of AlN is 16%, and the remaining portion is α-Al_2O_3 phase. No observable formation of the θ-Al_2O_3 is seen in this pattern.

The results in Figure 2b showed that the nitridation yield has increased to 46%, and there is a clear evidence of the θ-Al_2O_3 formation. Also, the intensity of the α-Al_2O_3 decreases rapidly.

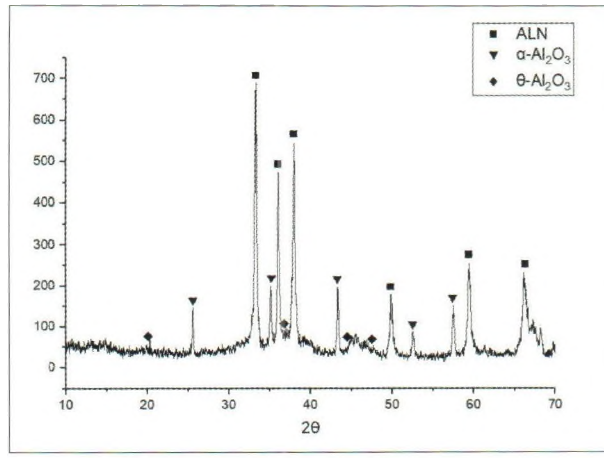
A high nitridation yield indicated that the reaction process has occurred through reactions 1 and 2. Al_2O_3 transforms into $AlCl_3$ at around 400-600°C according to reaction (1) and (2), and then AlCl3 reacts with NH3 to form AlN at 700-1000°C [12]. The formation of AlCl3 from reaction (2) minimizes the phase transition from gamma to α-Al_2O_3 at high temperatures. (13).

At the high nitridation yield, no XRD signals corresponding to the θ-Al_2O_3 and NH4Cl phase as

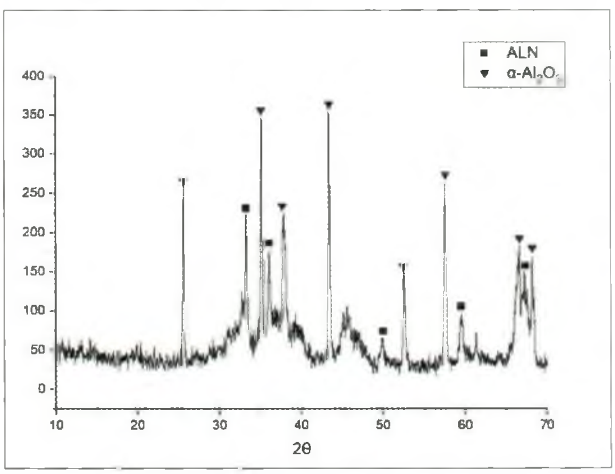
Fig 2. X-Ray Diffraction pattern diagram of products after reation.



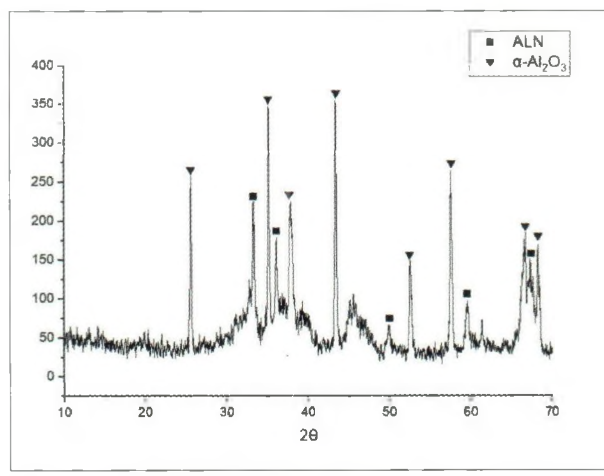
(a) NH_4Cl/Al_2O_3 mol ratio of 0/1



(b) NH_4Cl/Al_2O_3 mol ratio of 3/1

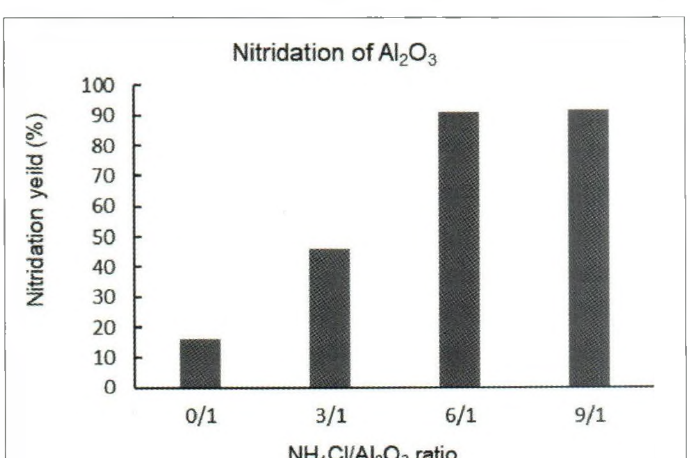


(c) NH_4Cl/Al_2O_3 mol ratio of 6/1



(d) NH_4Cl/Al_2O_3 mol ratio of 9/1

Fig 3: Nitridatio ratio of products obtained from with different NH4Cl/Al_2O_3 at 1150°C for 6h



shown in Figures 2(c) and 2(d). This indicates that the θ-Al_2O_3 has been nitrided to form AlN. A small signal of the α-Al_2O_3 phase also existed. According to previous work [11], the α-Al_2O_3 structure is very stable, and it is difficult to transform into AlN.

As the mole yield increases, the nitridation ratio of AlN goes up and becomes almost constant above the ratio of 6/1. At this point the nitridation ratio reaches more than 90% as it was shown in Figure 3. According to equations (1) and (2), the theoretical NH_4Cl/Al_2O_3 ratio is 6/1. However, when increasing the ratio to

9/1, the reaction efficiency does not increase. The reason is that NH_4Cl decomposes into NH_3 and HCl at 390°C, followed by the reaction between HCl and Al_2O_3 to form $AlCl_3$. However, due to the poor diffusion of the Al_2O_3 molecules caused by deeply embedded within the block, Al_2O_3 does not react to form AlCl3. As the temperature increases, the formation of the α-Al_2O_3 structure occurs. Therefore, the efficiency of AlN formation does not continue to increase to its maximum value.

The influence of reaction temperatures on the nitridation yield

The Figure 4 show the nitridation yield of AlN as funtion of the reaction temperatures at the NH_4Cl/Al_2O_3 ratio of 0/1 and 6/1. At the NH_4Cl/Al_2O_3 ratio of 0/1, the nitridation yield is very low. Within the temperature range of 900°C to 1250°C, all experiments show that AlN yield below 20%.

The XRD pattern at the Figure 5 indicated that the α-Al_2O_3 phase predominates in the structure of the product, while the AlN phase is present in low amounts with a nitridation ratio of 16%. This result can be explained by the fact that at high temperatures, a significant amount of Al_2O_3 undergoes the phase transition to produce the α-Al_2O_3 phase, and this α-Al_2O_3 phase is very difficult to be nitrided to form AlN as reported in previous work [14].

Fig 4. The nitridation yield of AlN versus reaction temperatures at NH_4Cl/Al_2O_3 ratio of 0/1 (●) and 6/1 (■)

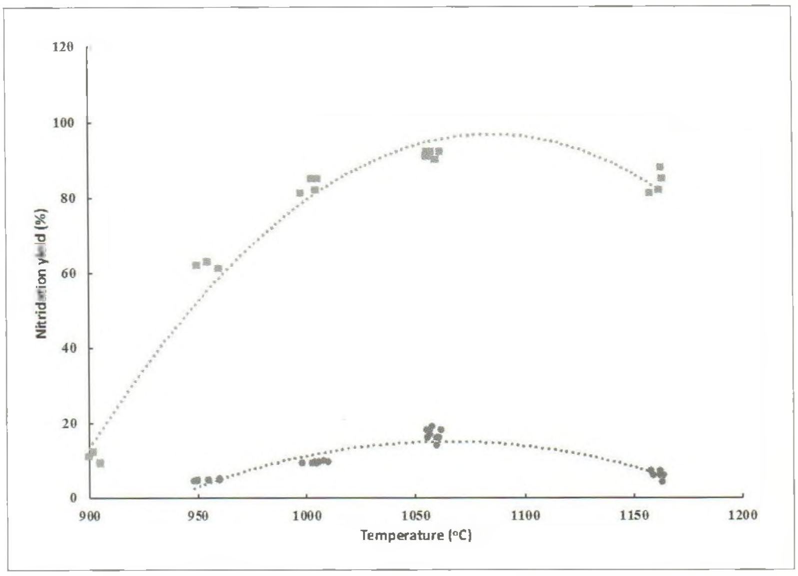
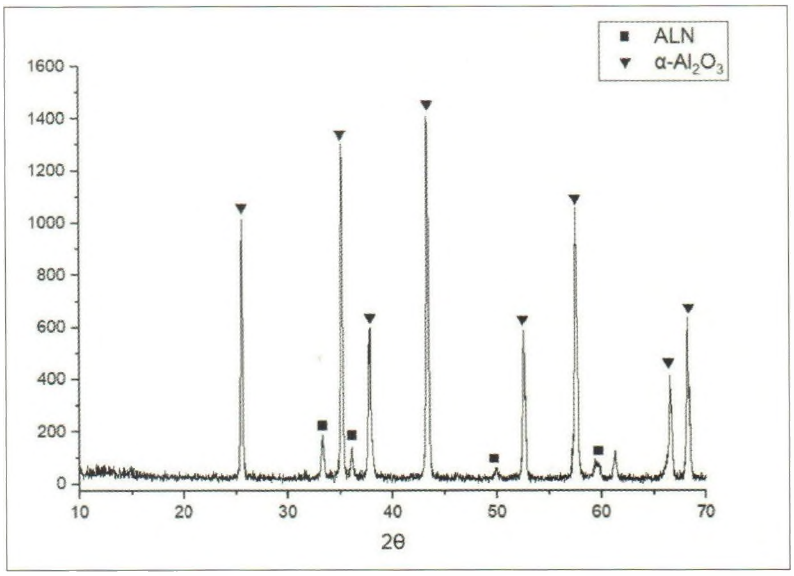


Fig 5. XRD pattern of product at reaction temperature 1050°C at NH_4Cl/Al_2O_3 ratio of 0/1.



As can be observed in Figure 4, the addition of NH_4Cl has a significant influence on the nitridation process. When NH_4Cl is present, Al_2O_3 undergoes the phase transition to form $AlCl_3$, which serves as an intermediate compound that could facilitate the conversion of Al_2O_3 to form AlN. At the lower temperature range of 900°C, the formation of AlN was detected with an efficiency of approximately 10%. As the temperature increased to 950°C, the nitridation rate reached 62%. This is a promising result for the nitridation process of producing AlN at low temperatures. When the reaction temperature increased to 1150°C, the nitridation reaction rate began to decrease. This can be explained that higher temperature has favored the formation of α-Al_2O_3 phase, which in turn hinders the nitridation process to form AlN.

4. Conclusion

In our study, the effect of NH4Cl on the nitridation of aluminum oxide powder was investigated. In the presence of NH4Cl, the nitridation process could be performed at lower temperatures, that is around 950°C, and the efficiency of the reaction of AlN could achieve a more than 91% at a temperature of 1050°C. At the same time, the formation of $AlCl_3$ intermediate could be promoted at lower temperatures, ranging from 400-600°C, thus inhibiting the formation of the α-Al_2O_3 phase. The formation of AlN, even at the low-temperature range of 950°C, could exhibit an efficiency of 62%. This demonstrated that the formation of AlN could be performed at much lower temperatures as well as achieving high efficiency of nitridation reaction ■

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VAI TRÒ CỦA NH_4CL TRONG TỔNG HỢP ALN Ở NHIỆT ĐỘ THẤP

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TÓM TẮT:

Nhôm nitrit được tổng hợp từ γ-Al_2O_3 NH_4Cl được tiến hành trong pha khí ở các nhiệt độ và tỷ lệ NH_4Cl/Al_2O_3 khác nhau. Sản phẩm AlN tổng hợp được đặc trưng bằng phổ nhiễu xạ tia X (XRD) và từ đó tính toán hiệu suất chuyển hóa tạo thành AlN. Kết quả cho thấy hiệu suất chuyển hóa tạo thành AlN tăng khi tỷ lệ mol NH_4Cl/Al_2O_3 tăng. Đồng thời, hiệu suất phản ứng nitrit hóa cũng tăng khi phản ứng tiến hành ở nhiệt độ cao, hiệu suất đạt 91% ở nhiệt độ 1050°C. Điều này chứng tỏ rằng, phản ứng nitrit hóa tạo ra AlN có thể tiến hành ở nhiệt độ thấp với sự có mặt của NH_4Cl.

Từ khóa: Aluminium nitride, nitrit hóa, ammonium chloride.