



Synthesis of aluminium nitride nanopowder

DARIUSZ SMOLEN^{1*}, PAWEŁ DOMINIK², KAROL TROCEWICZ², SŁAWOMIR PODSIADŁO², ANDRZEJ OSTROWSKI²,
WOJCIECH PASZKOWICZ³, KAMIL SOBCZAK³, PIOTR DLUZEWSKI³, CEZARIUSZ JASTRZEBSKI⁴, JAROSŁAW JUDEK⁴

¹ Polish Academy of Science, Institute of High Pressure Physics, Sokolowska 29/37, 01-142 Warsaw

² Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw

³ Polish Academy of Sciences, Institute of Physics, Al. Lotników 32/46, 02-668 Warsaw

⁴ Warsaw University of Technology, Faculty of Physics, Koszykowa 75, 00-662 Warsaw

*e-mail: smolendarek@gmail.com

Abstract

Aluminium nitride (AlN) nanopowder was successfully synthesized from aluminium oxide via a single-step reaction with ammonia as a source of nitrogen. The process was carried out in a horizontal mullite tube reactor located in an electric furnace in the ranges of temperature, time and gas flow rate of 1050-1350 °C, 1-5 h and 100-150 l/h, respectively. Nanopowders of γ -Al₂O₃ and α -Al₂O₃ were used as starting materials. Influence of temperature, time, gas flow rate and type of aluminium oxide on reaction productivity, powder morphology and product phase composition was investigated. Dynamic light scattering (DLS), Raman spectroscopy, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and specific surface area measurements by the BET isotherm technique were used to characterize the obtained materials.

Aluminium nitride prepared under optimal reaction conditions, comprising the reaction time of 5 h, the temperature of 1250 °C, and the gas flow rate of 150 l/h, was found to be nanocrystalline powder with a mean crystallite size of about 60 nm in the synthesis from gamma aluminium oxide and 65 nm in case of alpha aluminium oxide as a starting material. The productivity of nitridation reaction in such conditions was close to 99%, basing on gravimetric measurements. In case of the synthesis from gamma oxide, PXRD analysis indicated the pure hexagonal aluminium nitride structure which was confirmed by TEM analysis. In case of alpha aluminium oxide nitridation, the obtained aluminium nitride contained the unreacted oxide. Additionally, the investigation of average agglomerate sizes in the water suspension conducted by DLS showed that aluminium nitride obtained from γ -Al₂O₃ had an average particle size of 282 nm, and in the case of α -Al₂O₃ used as a starting material it was 2219 nm.

Keywords: Nanopowder, AlN, Al₂O₃, Synthesis

SYNTEZA NANOPROSZKU AZOTKU GLINU

Nanoproszek azotku glinu (AlN) zsyntezowano z powodzeniem, wykorzystując tlenek glinu i jednoetapową reakcję z amoniakiem jako źródłem azotu. Proces przeprowadzono w poziomym, mullitowym reaktorze rurowym umieszczonym w piecu elektrycznym, stosując temperaturę z zakresu 1050-1350 °C, czas wynoszący 1-5 h i przepływ gazu - 100-150 l/h. Nanoproszki γ -Al₂O₃ i α -Al₂O₃ użyto jako materiały wyjściowe. Zbadano wpływ temperatury, czasu, przepływu gazu i rodzaju użytego tlenku glinu na wydajność reakcji oraz morfologię i skład fazowy wytworzonego proszku. Wykorzystano metodę dynamicznego rozpraszania światła (DLS), spektroskopię Rammana, dyfrakcję rentgenowską na próbkach proszkowych (PXRD), skaningową (SEM) i transmisyjną (TEM) mikroskopie elektronowe oraz pomiary powierzchni właściwej metodą BET w celu scharakteryzowania właściwości otrzymanych materiałów.

Stwierdzono, że azotek glinu przygotowany w optymalnych warunkach reakcji, obejmujących czas reakcji wynoszący 5 h, temperaturę - 1250°C i przepływ gazu - 150l/h, był nanokrystalicznym proszkiem o średnim rozmiarze krystalitu wynoszącym około 60 nm w przypadku syntezy wykorzystującej jako materiał wyjściowy odmianę gamma tlenku glinu i 65 nm w przypadku odmiany alfa tego tlenku. Wydajność reakcji azotowania wyniosła w tych warunkach 99%, jak pokazały pomiary grawimetryczne. W przypadku syntezy z odmiany gamma tlenku glinu analiza PXRD wskazała na wyłącznie heksagonalną strukturę azotku glinu, co potwierdziły też obserwacje TEM. W przypadku odmiany alfa, otrzymany azotek glinu zawierał nie przereagowany tlenek glinu. Dodatkowo, oznaczenia średniego rozmiaru aglomeratów w zawiesinie wodnej przeprowadzone za pomocą metody DLS pokazały, że azotek glinu otrzymany z γ -Al₂O₃ miał średni rozmiar cząstki wynoszący 282 nm, podczas gdy w przypadku α -Al₂O₃ - 2219 nm.

Słowa kluczowe: nanoproszek, AlN, Al₂O₃, synteza

1. Introduction

Nowadays aluminium nitride is becoming an attractive material, especially in the nanopowder form. It is an important material for electronics and for optoelectronic devices. It has got the largest band gap in the group III nitrides (6.2 eV

and very low dielectric constant (8.6) [1]. Owing to such properties, AlN is the ideal material for the use as an electronic substrate and integrated circuit packaging materials [2]. Additionally, aluminium nitride has a low coefficient of thermal expansion ($4.3 \cdot 10^{-6} \text{ K}^{-1}$) which makes it a potential solution for the problems with thermal matching between the

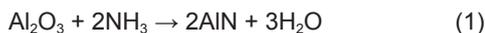
substrate and the semiconductor, and problems with cooling of high power electronic devices caused by the integration and micromation [3]. Other important applications of this material include surface acoustic wave devices and buffer layers for group III nitride thin film epitaxy [4]. Nowadays, there is also an interest in creating a new source of light based on a composite of semiconductive nanopowder like aluminium nitride and conductive polymers, which in comparison to the current solution will offer low energy consumption and high efficiency [5].

Commercial AlN powders are mostly synthesized by direct nitridation of aluminium [6] or by carbothermal reduction and nitridation of aluminium oxide [7]. The second method, the carbothermal reduction process, requires a high temperature to remove carbon from the obtained product, which usually in comparison to other methods increases rapidly the size of grains and causes high powder agglomeration [7]. Other papers present the production of AlN powder by a vapour phase reaction between ammonia and aluminium chloride using nitrogen as a carrier gas [8]. This method gives a possibility of producing AlN powder directly from the vapour phase, avoiding an additional step of grinding, but usually the obtained material contains ammonium chloride as a by-product. Aluminium nitride can be also synthesized in the reaction between aluminium and urea which was the subject of works published by the authors of this paper [9, 10]. In literature, there are also many works reporting processes such as ion evaporation or DC arc plasma [11] that require complex equipments and force aluminium to react with ammonia or nitrogen gas under extreme conditions [12]. These methods provide good results, but due to the cost reason, are not used for mass production of aluminium nitride nanopowders.

The main purpose of this paper was to develop a method for obtaining a pure and fine AlN nanopowder with an average grain size lower than 100 nm and agglomerate size below 500 nm via a simple and cost effective technique of synthesis. The paper also presents differences between nitridation of alfa and gamma aluminium oxides during aluminium nitride synthesis.

2. Experimental methods

Aluminium nitride nanopowder was obtained in a horizontal mullite tube reactor located in an electric furnace by using the following reaction:



Commercially available nanopowders of gamma and alfa aluminium oxides (Alfa Aesar, USA), both of average grain size below 50 nm, were used as the starting materials. Gaseous ammonia was used as a source of nitrogen. A weighed sample was placed in a mullite boat and set in the mullite tube furnace of 41 mm in inner diameter. The reactor was heated to the required reaction temperature at a rate of 18-25 °C/min with a gaseous ammonia flow rate of 100-150 l/h. The process was carried out for 1-5 h at 1050-1350 °C. After the predetermined time of reaction, the furnace was cooled at approximately 18-30 °C/min in the ammonia atmosphere.

The effect of temperature, time, gas flow rate and regimes of heating and cooling on nitridation extent was systemati-

cally tested. A gravimetric method was used to measure the productivity of the process determined as a percentage weight decrease caused by the substitution of oxygen atoms with nitrogen atoms. For the case of the 100% productivity for the nitridation of one mole of aluminium oxide, the theoretical weight decrease was assumed to be 19.98 g. The phase composition of the reaction products was analyzed by powder X-ray diffraction (PXRD), using a Model HZG-4 diffractometer, (Seifert GmbH) and CuK α radiation operated at 40 kV and 40 mA. The Scherrer equation was used for the determination of crystallite sizes from powder diffraction line profiles. Specific surface area of the powders was measured by the Brunauer-Emmett-Teller (BET) method (Gemini 2360, Micromeritics Instruments). The morphology of the nanopowder samples was examined with scanning (ZEISS LEO 1530) and transmission electron (JEOL JEM2000EX) microscopes. Transmission electron microscopy investigations were carried out using the microscope with spherical aberration coefficient $C_s = 1.3$ mm operating at 200 kV. The specimens for the TEM observations were prepared by crushing the powders in an agate mortar and ultrasonic dispersing into methanol. A drop of the particle suspension was placed on a holey carbon film supported on a 300 mesh copper grid. High-resolution TEM (HRTEM) images were observed at the axial illumination condition with the use of an objective aperture of 6 nm⁻¹ in diameter. The dynamic light scattering method was used to estimate the size of agglomerates (DLS, Zetasizer 3000, Malvern). The water suspension was formed by adding 20 mg of tested sample to 4 ml of water and sonicated for 15 s in a laboratory ultrasound bath. The DLS measure was conducted just after the suspension formation to minimize the influence of aluminium hydrolysis effects on the obtained results. Raman spectroscopy measurements with the resolution of a spectrometer of about 1 cm⁻¹ were also used (Dilor XY-800 micro-Raman spectrometer). The laser excitation line 459.7 nm had a power of few mW and it was focused on the samples due to 50 \times objectives.

3. Results and discussion

As a source of aluminium, α -Al₂O₃ and γ -Al₂O₃ nanopowders were used, both with crystallite sizes in the range 40-50 nm. Alfa aluminium oxide had a tendency to form few-micrometer agglomerates, when the gamma nanopowder kept the agglomerates size below 500 nm. The specific surface areas were 42 m²/g and 36 m²/g for gamma and alfa oxides, respectively. Dynamic light scattering measurements showed that the average particle sizes in the water suspension were 212 nm and 702 nm for γ -Al₂O₃ and α -Al₂O₃, respectively. The study of zeta potential as a function of pH for the gamma and alfa aluminium oxide suspensions showed the isoelectric points occurring at different pH values: 8.7 and 10.3 for γ -Al₂O₃ and α -Al₂O₃, respectively.

The investigation was started with the determination of maximum gas flow rate in the reactor. It was 150 l/h for both starting materials; faster gas flow was blowing out nanopowders from the reaction zone. The effect of gas flow rate on process productivity was similar for both oxides. It has been observed that an increase of ammonia flow rate from 100 l/h to 150 l/h almost doubled the productivity (from below 50% to 99%). The crystallite size analysis showed that, for the

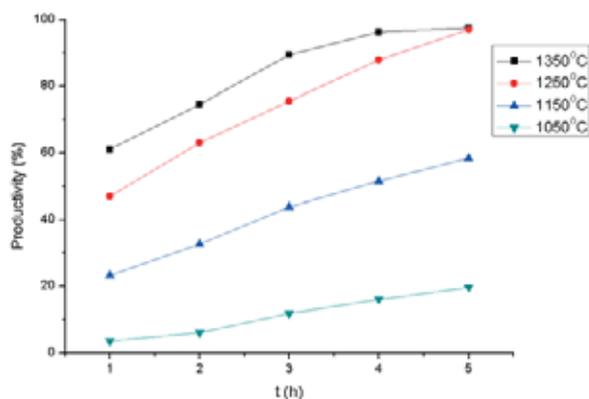


Fig. 1. Productivity of nitridation reaction as a function of temperature for $t = 5$ h and $V = 150$ l/h.

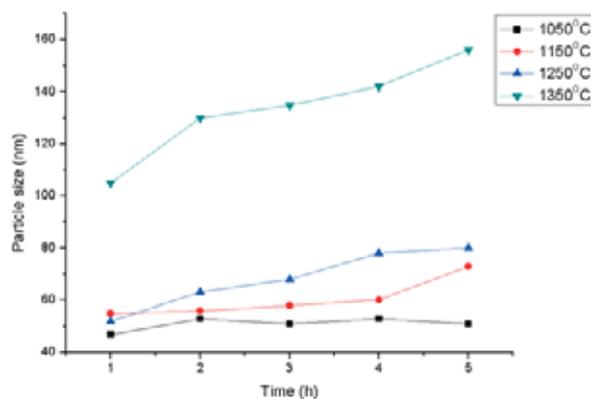


Fig. 2. Product grain size as a function of reaction temperature for $t = 5$ h and $V = 150$ l/h.

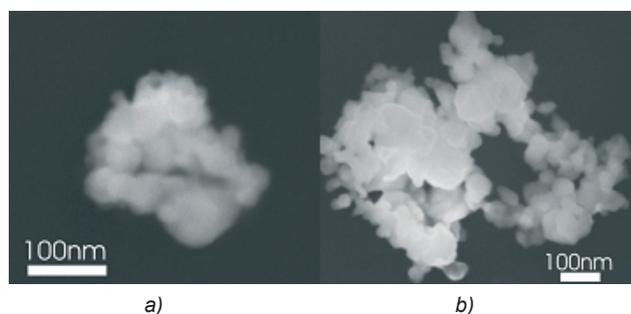


Fig. 3. SEM micrographs of product powders synthesized for 5 h at 1250 °C (a) and 1350 °C (b).

gas flow rate of 100 l/h, the crystallite size estimated with the Scherrer equation was 140 nm under the reaction conditions of $T = 1250$ °C and $t = 5$ h. Increasing the gas flow to 150 l/h resulted in a decrease of the average crystallite size to 70 nm for the same reaction conditions. It can be concluded that not only the temperature and the time of reaction have the important influence on product formation, but also the flow speed of ammonia can change strongly the yield and the crystallite size of the product.

Fig. 1 shows the productivity of the nitridation reaction as a function of temperature for the reaction time of $t = 5$ h and the ammonia flow rate of 150 l/h. In all the reactions, the time of heating and the time of cooling were identical and equal 1 h. As far as the effect of temperature on productivity is concerned, the results are similar for both oxides and the

differences do not exceed 2% for the analogous processes. In our investigation, the course of the processes at four different temperatures of 1050, 1150, 1250 and 1350 °C was compared. The details of the effect of temperature on products crystallite size are presented in Fig. 2. The results show that the most appropriate temperature for nitridation is 1250 °C. The processes running at the highest tested temperature of 1350 °C gave only a slight increase in the reaction yield at the reaction times ranging from 1 h to 4 h in comparison to the analogous reactions conducted at 1250 °C, and, what is more important, the processes carried out for 5 h gave almost identical results for the both temperatures. The analysis of the results of crystallite size measurements for the products obtained at different temperatures enables to distinguish two groups of reactions. The crystallite size of the products obtained at 1050-1250 °C was in the range 45-75 nm. For identical reactions carried out at 1350 °C, the crystallite size was over twice bigger; this effect was more pronounced in reactions with alpha aluminium oxide. Fig. 3 shows SEM micrographs of the product powders obtained from γ - Al_2O_3 in the 5 h reaction at the temperatures of 1250 °C and 1350 °C.

Powder X-ray diffraction (data not shown) and TEM analyses used to determine the phase composition of the reaction products have shown that in case of the reactions with gamma aluminium oxide at the temperatures of 1250 °C and 1350 °C the only product is pure hexagonal aluminium nitride. Nevertheless, the gravimetric method doesn't indicate a 100% productivity but the values close to 99% (Fig. 1) probably caused by material losses, especially during loading and unloading operations. As the PXRD and TEM analyses indicated for the reaction at 1250 °C, there was no transformation of gamma into alpha oxide. The TEM investigations of the sample obtained from γ - Al_2O_3 in the reaction at $T = 1250$ °C, $t = 3$ h, and $V = 150$ l/h showed that it was composed mostly of hexagonal aluminium nitride nanocrystals; the ED pattern exhibited a rings pattern corresponding to the interplanar hexagonal type of the AlN structure. In addition, a ring at $d = 1.9868$ Å, that could be attributed to unreacted γ - Al_2O_3 has been found on the electron diffraction patterns (data not shown). For samples synthesised for 5 h at the same conditions ($T = 1250$ °C and $V = 150$ l/h), the TEM investigations (Fig. 4) showed that this structure was composed only of aluminium nitride nanocrystals of a mean particle diameter of 60 nm. No diffraction reflexes due to the gamma or alpha aluminium oxide structures were detected.



Fig. 4. TEM images of AlN powder obtained from γ - Al_2O_3 in reaction at $T = 1250$ °C, $t = 5$ h, and $V = 150$ l/h. In the insert a diffraction pattern connected to the hexagonal AlN structure is shown.

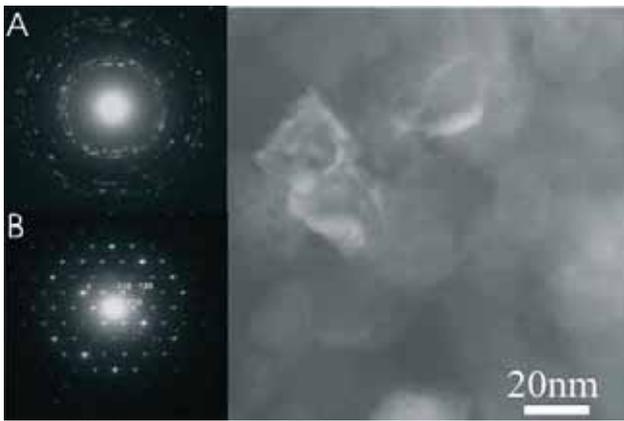


Fig. 5. TEM image of AlN powder obtained from α -Al₂O₃ in reaction at T = 1250 °C, t = 5 h, V = 150 l/h; in inserts: A - diffraction pattern corresponding to hexagonal AlN structure, B - diffraction pattern corresponding to hexagonal (Al₂O₃)_{5.333} structure and schematic indexing.

In the case of reactions with α -Al₂O₃, even for the samples heat treated at 1350 °C, the TEM investigations showed that the powders were composed mostly of the hexagonal AlN nanocrystals and the particles of another, foreign structure, as evidenced by two types of electron diffraction patterns observed. The first type was a ring-form ED pattern, corresponding to the hexagonal AlN structure (Fig. 5, insert A). The other type was a dot ED pattern, corresponding to hexagonal kappa aluminium oxide with a formula of (Al₂O₃)_{5.333} and the lattice parameters of a = 5.5440 Å and c = 9.0240 Å (Fig. 5, insert B). An average particle size of aluminium nitride nanocrystals was 65 nm.

As results from Raman spectroscopy studies, all five main modes of aluminium nitride A₁(TO), E₂, E₁(TO), A₁(LO) and E₁(LO) were observed in all the samples. The position and the width (FWHM) were calculated using the Lorentzian function fitting. Raman spectra of AlN obtained from α -Al₂O₃ and γ -Al₂O₃ in reactions at T = 1250 °C, t = 5 h, V = 150 l/h, are presented in Fig. 6.

The specific surface area of obtained powders measured by the single-point BET method was decreasing with temperature and reaction time. In the case of AlN obtained from

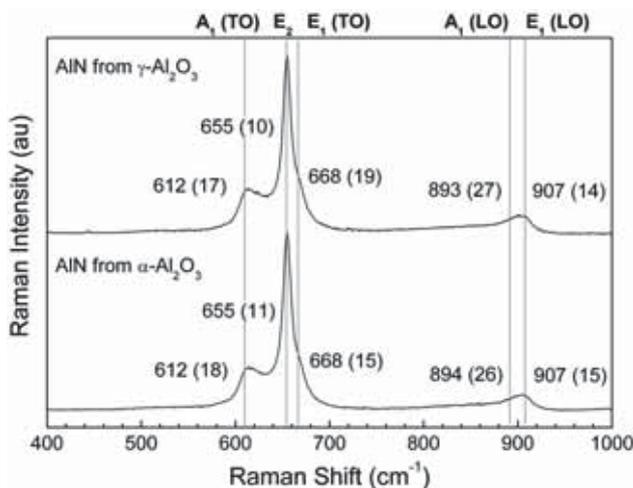


Fig. 6. Raman spectra of AlN nanoparticles obtained from different aluminium oxides. Peak positions and widths (in brackets) describe five main Raman modes of AlN.

γ -Al₂O₃, the specific surface area decreased from 42 m²/g in the starting material to 32 m²/g in the product of reaction at T = 1250 °C, t = 5 h and V = 150 l/h. For the identical reaction with α -Al₂O₃ as a starting material, the specific surface area decreased from 36 m²/g to 24 m²/g for the starting material and the product, respectively.

Dynamic light scattering measurements showed that agglomeration was increasing rapidly in reaction with the alfa oxide as a starting material. In case of the reaction at T = 1250 °C for t = 5 h, the average particle sizes of 282 nm and 2219 nm were measured for AlN obtained from γ -Al₂O₃ and α -Al₂O₃, respectively. The zeta potential studies indicated the isoelectric points at similar pH values for AlN obtained from γ -Al₂O₃ and α -Al₂O₃; the pH values were 9.68 and 9.74, respectively.

4. Conclusions

Presented work is a promising way for producing pure and fine AlN powder, even for commercial scale production. As compared with other techniques of synthesis described in literature [7-12], the developed method provides significant advantages in AlN nanopowder production. No mixing step or post-synthesis processing is necessary, and thus a high purity nanopowder can be produced in a single step process. The productivity of aluminium nitride in reaction under optimal parameters (T = 1250 °C, t = 5 h, V = 150 l/h) was over 99 mass %. Investigations proved significant differences between nitridation of γ -Al₂O₃ and α -Al₂O₃. TEM analysis showed that γ -Al₂O₃ is leading in nitridation reaction to pure AlN with average particle size 60 nm and agglomerates smaller than 300 nm. In case of reactions with α -Al₂O₃ as a starting material, for all temperatures TEM investigations showed that the product was composed of hexagonal AlN and hexagonal (Al₂O₃)_{5.333} structures with the average particle size of 65 nm, and agglomerates bigger than 2000 nm.

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