

Aluminum Nitride by Microwave-Assisted Synthesis: Effect of Added Ammonium Chloride¹

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Abstract—Hexagonal aluminum nitride (AlN) crystals were synthesized by microwave method with ammonium chloride used as an additive. Starting mixtures consisted of Al powder, NH₄Cl, and urea as a fuel taken in a 1 : 3 : 1 ratio. The microwave oven operated at 630 W, the synthesis time was 10, 30, 60, and 120 min. The results showed that the pure AlN powder with regular and fine grains could be obtained in 30 min. The synthesized powders were characterized by TGA/DTA, XRD, FT-IR, UV-VIS, SEM, and TEM.

Key words: microwave-assisted synthesis, aluminum nitride, gas-solid reactions, ammonium chloride, urea

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1. INTRODUCTION

Metal nitrides possess very high thermal, mechanical, and chemical stability. Several nitrides are also characterized by low densities and are therefore of great technological interest for light-weight applications [1]. There has been considerable interest in the synthesis of new nitrides, because of their technological and fundamental importance [2]. The nitride groups are useful because of their hardness, although they are being increasingly used for their electrical properties in such applications as integrated circuitry [3]. These nitrides also show superconducting behavior with attractive properties for potential applications [4].

Aluminum nitride (AlN), also a popular product of SHS reactions, is considered as an important industrial material [5] because of unique combination of its properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, moderately low dielectric constant, and good thermal shock resistance [6, 7]. It has been considered for many applications such as substrates for power electronics, an insulating material for RF and microwave packages, an electrostatic chuck dielectric for semiconductor processing equipment, heat sinks of main frames for super-computers, high thermally conductive composite materials and hardware for containing or processing molten metals and salts [8, 9].

Nitride powders are synthesized commercially by either carbothermal reduction of Al₂O₃ [10] or direct nitridation [11] of metals. The synthesis of these important nitrides by the conventional procedures,

though, is often overwhelmed by extremely long reaction times (several hours to even days) caused by slow diffusion rates in solids and usually involve many burdensome steps. They often require the use of atomized metal powders (involving risk of explosions) [12], laser heating [13] at high pressures, numerous additives [1], etc.

Recently, the use of microwaves has been found to offer several advantages for the synthesis of many inorganic materials as compared to conventional methods [14–16]. The foremost of these advantages are the very short time periods involved in the synthesis, enhanced reaction kinetics, and the reactant selectivity during energy transfer from the microwave field [17]. In the conventional nitridation of a metal compact, the surface nitridation preface the bulk, which limits further diffusion of nitrogen into the metal. Then it was envisaged that this reaction limiting complication could be circumvented by the inverse temperature gradient (inside → out), a unique feature of the microwave method, leading to complete nitridation of the metal. In the microwave process, a more uniform volumetric heating takes place, and the ignition could be achieved at much lower power level. Compared to conventional processing, the microwave process favors a reduction in both processing time and temperature.

Ammonium chloride plays a crucial role because it produces hydrogen chloride which can be considered as an intermediate product. HCl promotes the vaporization of molten aluminum cores into unstable aluminum chloride species and facilitates the growth of nitridation through series of spontaneous chlorination and nitridation intermediate reactions [18]. Ammonium chloride in the reaction mixture successfully prevents the coalescence of aluminum metal particles

¹ The text was submitted by the author in English.

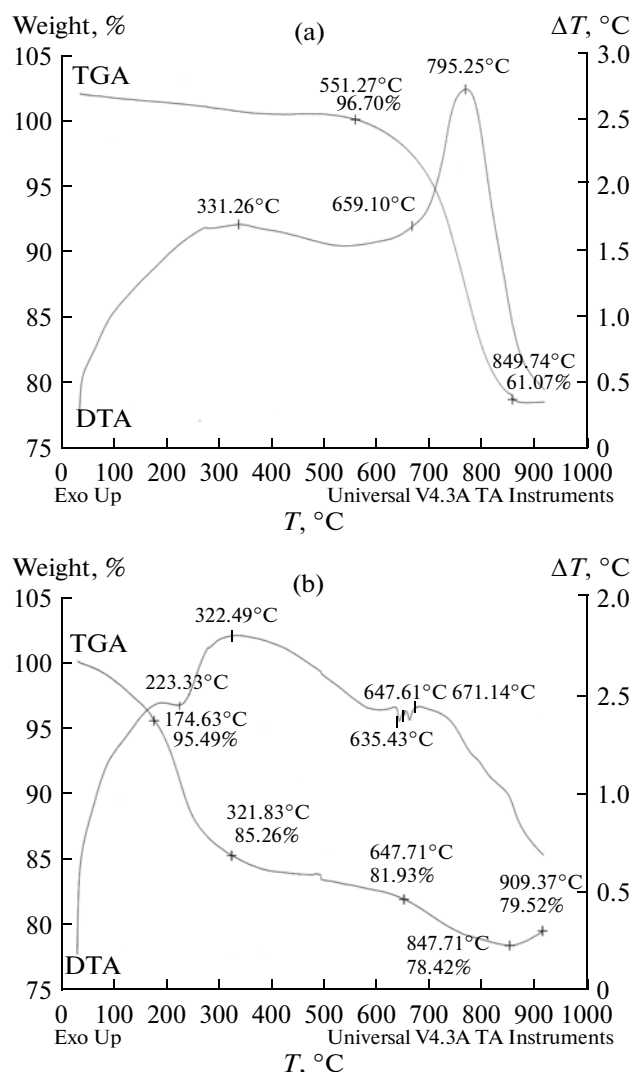


Fig. 1. TGA/DTA curve for a) Sample 1 ($\tau = 10$ min), b) Sample 2 ($\tau = 30$ min).

prior to nitridation [1]. Thus, a small amount of NH_4Cl was found to promote the nitridation [19]. The urea molecules construct a coordination sphere around the metal atom and form a stable structure.

In this work, we developed a novel, simple, and fast microwave-assisted technique for preparation of AlN . The ability of additive to prevent the Al particles from coalescing was examined and the influence of the additive on the characteristics of as-prepared AlN powder was studied, and the reaction mechanism was discussed.

2. EXPERIMENTAL

The microwave setup consists of a modified commercial microwave oven producing microwaves at 2.45 GHz, and the sample temperature was monitored using a dual wavelength pyrometer. Al metal powder was used as a source aluminum. NH_4Cl was used as an

additive and urea as a fuel. Each 10-g batch was prepared using $\text{Al-NH}_4\text{Cl-urea}$ mixtures taken in a 1 : 3 : 1 ratio. The reaction mixture was placed in a high alumina crucible which was used as a holding vessel. The nitridation reactions were performed in flowing N_2 gas at a flow rate of 500 mL/min. The microwave oven operated at 630 W. The synthesis time τ was 10, 30, 60, and 120 min and the synthesized samples will be hereinafter indicated as Sample 1, Sample 2, Sample 3, and Sample 4, respectively.

The as-prepared samples were characterized by differential thermal analysis and thermogravimetry (DTA/TG, Rigaku Thermal-plus, TG 8120) to study the phase transition. A heating rate of $10^\circ\text{C}/\text{min}$ was used for the measurements from room temperature to 1000°C in nitrogen. The phase identification by X-ray powder diffraction (XRD) patterns using $\text{Cu-K}\alpha$ ($\alpha = 1.541 \text{ \AA}$) radiation with 2θ values ranging from 10 to 90° was done using a JEOL 8030 X-ray diffractometer.

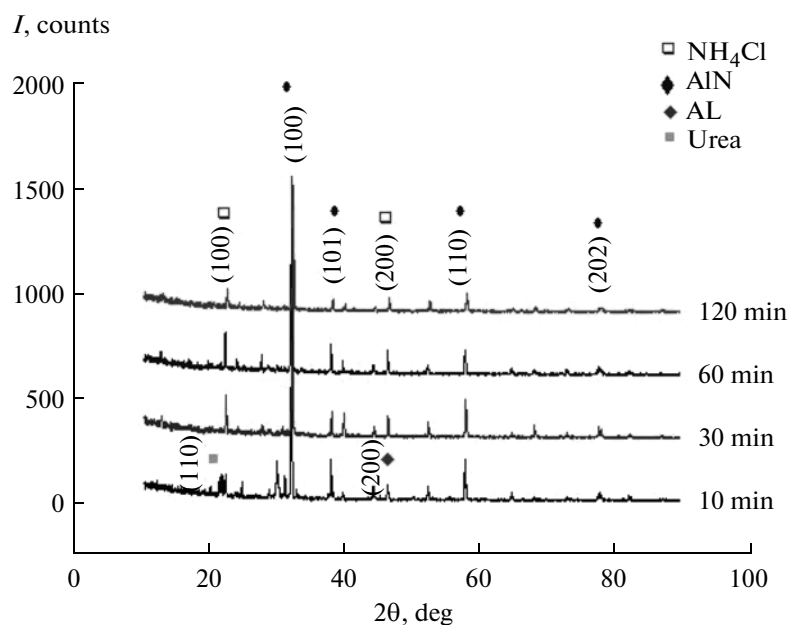


Fig. 2. Diffraction patterns of synthesized AlN samples.

The Fourier-transform infrared (FT-IR) spectra were recorded over the range 400–4000 cm^{-1} using a Perkin Elmer UK Paragon-500 spectrometer. The morphology of the samples was examined by SEM (JEOL JSM-3.5 CF, Japan). UV-VIS reflectance measurements were carried out using a JASCO Model 7800 UV-VIS spectrophotometer. TEM measurements were performed using a 200 keV TECNAI 20-G2 microscope.

3. RESULTS AND DISCUSSION

TGA/DTA curves of Samples 1 and 2 are shown in Figs. 1a, 1b, respectively. In the TGA curve in Fig. 1a, a sharp weight loss was observed up to 427°C at about 8.8 wt % (may be desorption of water) followed by a slight decrease in weight loss approx. 1 wt % up to 612°C, considerably due to the removal of small amount of volatile organic compounds. The broad exothermic peak in the DTA curve centered at 282°C, accompanied by a gradual weight loss, was because of the decomposition of NH_4Cl (or urea) [20, 21]. Two smaller endotherms (635°C, 688°C) and one small exotherm at 715°C in the DTA curve correspond to melting of Al and the nitridation of Al, respectively. The weight gain increased up to 908°C at about 5.53 wt %. The weight gain means that the extent of oxidation gives a proper identification of the stoichiometric nitride product. Similar trend was discussed by Vaidhyanathan et al. [1].

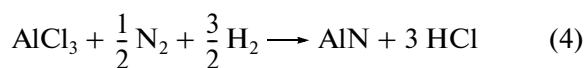
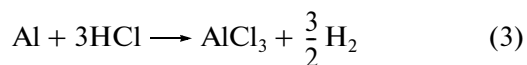
In the TGA curve in Fig. 1b, a sharp weight loss was observed up to 383°C at about 7 wt % (may be desorption of water) followed by a slight decrease in weight

loss approx. 0.8 wt % up to 660°C, considerably due to the removal of small amount of volatile organic compounds. The broad exothermic peak in the DTA curve centered at 335°C, accompanied by a gradual weight loss, was because of the decomposition of NH_4Cl (or urea) [20, 21]. The unreacted Al metal melted at 660°C and then oxidation occurred up to 907°C, accompanied by a weight gain at about 5.85 wt %. The weight gain clearly indicates the formation of nitride product [22].

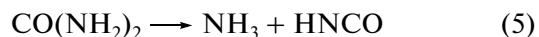
The exothermic reaction may be represented by the following scheme:



NH_4Cl dissociated into HCl and NH_3 vapors, thus giving rise to the following thermodynamically spontaneous reactions:



The decomposition reaction of urea can be represented as



The formation of HNCO enhances the surface reaction and increases the nitridation. The complete conversion was obtained at a relatively low tempera-

Table 1. XRD data for synthesized AlN samples

	τ , min	Crystal structure	Lattice constants	Crystal size, nm	ρ , g/cm ³
Sample 1	10	hexagonal	$a = 3.15 \text{ \AA}$ $c = 4.73 \text{ \AA}$	43.24	3.42
Sample 2	30	hexagonal	$a = 3.12 \text{ \AA}$ $c = 4.982 \text{ \AA}$	29.18	3.11
Sample 3	60	hexagonal	$a = 3.16 \text{ \AA}$ $c = 4.56 \text{ \AA}$	32.58	3.45
Sample 4	120	hexagonal	$a = 3.13 \text{ \AA}$ $c = 4.92 \text{ \AA}$	41.26	3.22

ture (<1200°C) because urea used as a fuel, which is most extensively used because of its cheapness, produces high temperature, and generates a lower volume of gases [23]. The gases evolved due to the sublimation or decomposition of NH_4Cl produce numerous pores which prevents the Al particles coalescing after melting and allows better nitrogen access into the burden [18].

The XRD patterns of all synthesized AlN samples are shown in Fig. 2. From the XRD data it follows that the hexagonal wurtzite-type AlN is present in Sample 2 at about 74%. The theoretical lattice constants— $a = 3.114 \text{ \AA}$, $c = 4.986 \text{ \AA}$ (JCPDS no. 25-1133)—are comparable with the values derived from XRD data: $a = 3.12 \text{ \AA}$, $c = 4.982 \text{ \AA}$. The calculated lattice parameters, X-ray density, and crystal size are presented in Table. 1. From the full-width half-maximum of the diffraction peaks of AlN, the crystallite size d can be estimated using the Debye-Scherrer formula: it was found to have a value of about 29 nm.

The XRD data for Sample 4 with d values and respective peak intensities are collected in Table 2.

The FT-IR spectra of all AlN samples are shown in Fig 3. A weak band at 635 cm^{-1} was attributed to the Al–N– stretching vibrational frequency in the hexagonal structure [24, 25]. Other sharp bands at 1404–1406 and 1644–1648 cm^{-1} correspond to water molecules and δNH_3 , respectively. The band at 2365 cm^{-1} corresponds to the stretching mode of carbon dioxide [26].

Figures 4a–4d show the UV-VIS reflectance spectra for all four AlN samples. The absorption edge near 220 nm corresponds to the direct wide-band gap of AlN. The other absorption edges found in the spectra may correspond to the impurities in the matrix. Band-gap values ($\sim 5.8 \text{ eV}$) derived from the spectra indicate the formation of a homogeneous compound.

The impurities present in synthesized samples are characterized in Table 3. In Sample 2 the nitrogen

Table 2. d values and their corresponding intensity for Sample 4

d , $\text{\AA}$	I , %
6.55612	3.56
5.03630	0.88
3.85740	14.67
3.114807	3.19
3.03802	1.03
2.73080	100.00
2.33131	9.04
2.23195	8.43
2.02005	3.76
1.93504	7.48
1.73054	4.67
1.57972	13.31
1.43025	1.08
1.36916	4.64
1.22237	2.10

Table 3. Impurity analysis of synthesized AlN

	τ , min	N	C	S	H
Sample 1	10	0.256	0.219	0.000	0.000
Sample 2	30	0.831	0.058	0.000	0.000
Sample 3	60	0.337	0.250	0.000	0.000
Sample 4	120	0.000	0.145	0.000	0.000

content is higher compared to other three samples. This is consistent with the XRD data showing a 74% AlN content of Sample 2. All the samples contained no sulfur and hydrogen impurities. Carbon content is

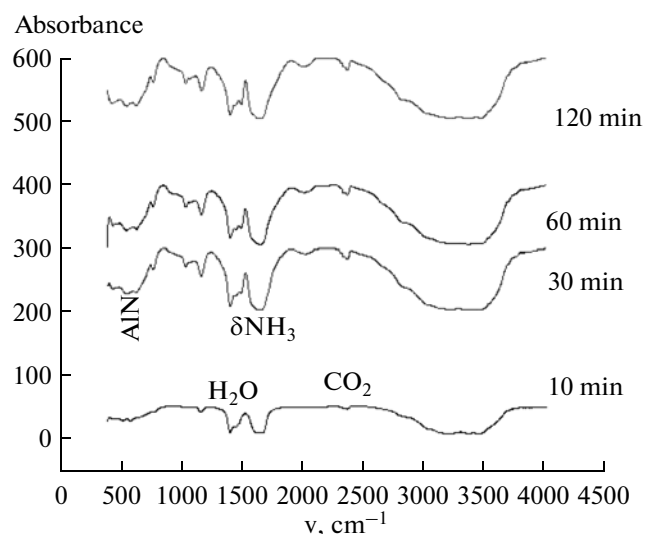


Fig. 3. FT-IR spectra of synthesized AlN samples.

low in Sample 2. In sample 4, the nitrogen content is zero, which is also confirms the absence of AlN in the XRD pattern.

The SEM images of all four AlN samples are presented in Fig. 5. No AlN crystals are seen in Fig. 5a, observed only coalesced Al particles which prevent the penetration of nitrogen source to the reactant. Figure 5b shows the formation of fine crystals. The surface of

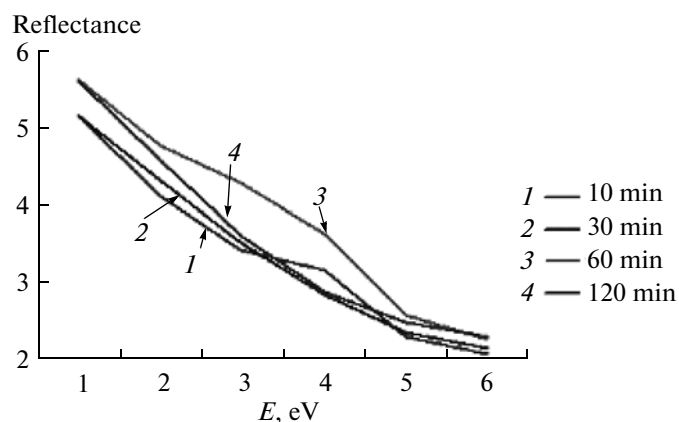


Fig. 4. UV-VIS reflectance spectra of Samples 1–4.

the aluminum particles begins to react with nitrogen to form aluminum nitride. The structural uniformity could be obtained using microwave processing [27]. Figure 5c clearly shows that NH_4Cl is completely volatilized before aluminum melting. Figure 5d shows numerous pores arising due to irregular vaporization inside the reactant mixture.

Figure 6 shows the TEM image of AlN nanoparticles in Sample 2. The average particle size is of 30 nm, which is also consistent with XRD data. The decomposition of NH_4Cl generates NH_3 and HCl , thus

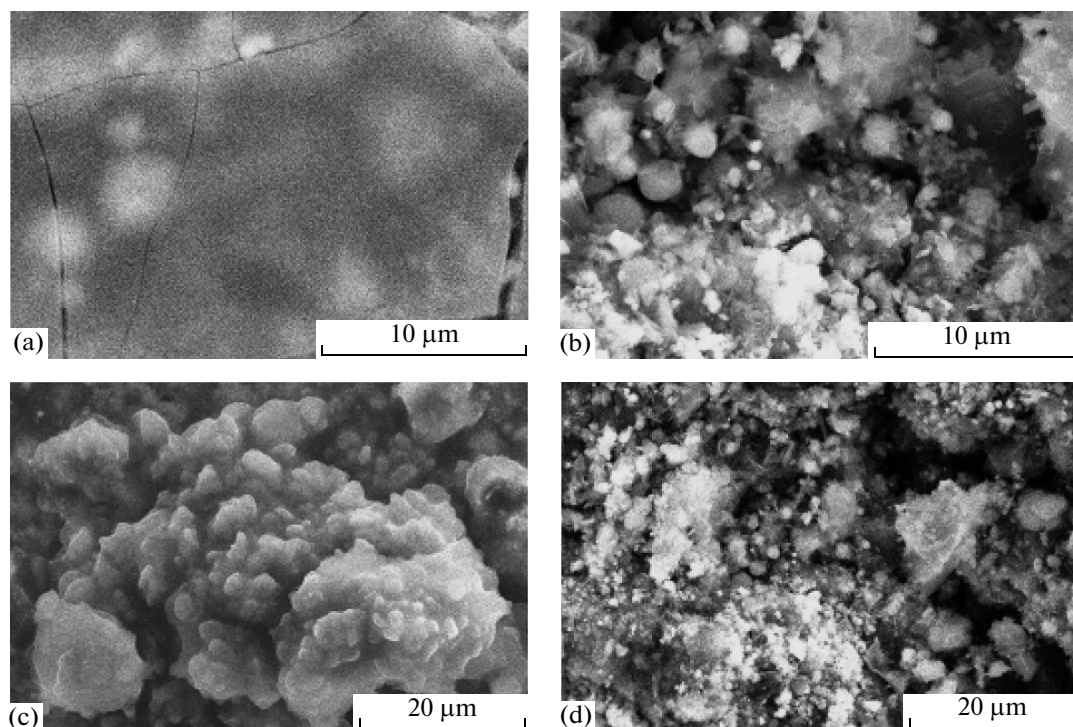


Fig. 5. SEM images of synthesized AlN samples: τ = 10 (a), 30 (b), 60 (c), and 120 min (d).

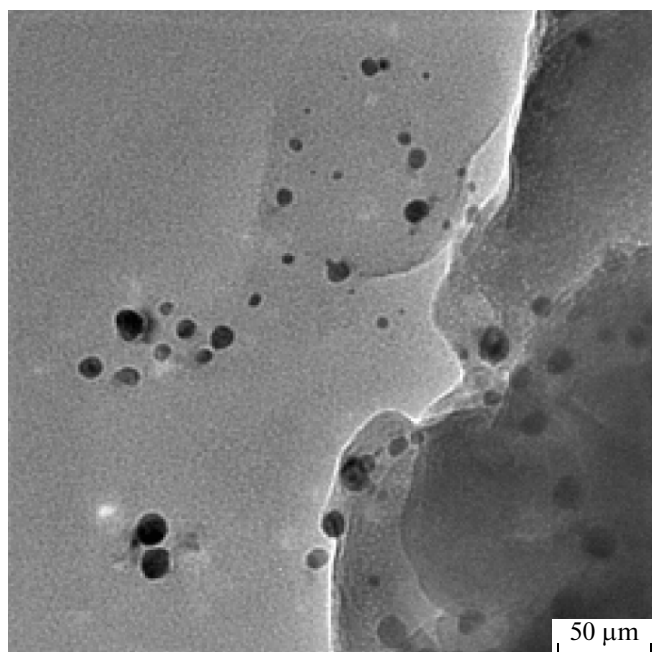


Fig. 6. TEM image of AlN nanoparticles in Sample 2.

enhancing the concentration of N_2 in the reacting mixture.

CONCLUSIONS

Hexagonal AlN crystals were synthesized by microwave method with ammonium chloride used as an additive. The results indicate that the fine and regular grains of AlN were obtained. The decomposition of NH_4Cl generates NH_3 and HCl , thus enhancing the concentration of N_2 in the reacting mixture. Small amount of added ammonium chloride was found to promote the nitridation reaction. In the presence of urea used as a fuel, the process yields nanosized AlN particles since the reaction is accompanied by controlled release of gases and dissipation of heat. The microwave-assisted technique has been demonstrated to be a simple, rapid, and efficient method for synthesis of aluminum nitride.

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