Synthesis of AlN – presence and absence of additive

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Abstract. Direct nitridation of hexagonal aluminium nitride (AlN), using additive like NH_4Cl, was performed from Al metal powder. Different methods of AlN synthesis, viz. a) Al powder, b) Al and NH_4Cl, c) Al and NH_4Cl with urea, were carried out in continuous flowing of N_2 gas at 900 °C for 5 h. The synthesized powder was characterized by employing TGA/DTA, XRD, FTIR, SEM, UV-VIS Spectroscopy and CHNS analysis. The mechanism for the formation of AlN by the influence of additive and role of urea are discussed.

Key words: ceramics, AlN, direct nitridation, XRD, SEM, NH_4Cl, urea.

1. INTRODUCTION

Aluminium nitride (AlN), an industrial important material due to its gorgeous properties like high intrinsic thermal conductivity and thermal expansion coefficient, close to that of silicon, as well as apart from other appropriate electric and dielectric properties, has been favoured as substrate material in electronic devices [1–4]. Its chemical stability and high hardness render is useful in various structural and refractory composite applications [5]. It has been considered for many applications such as insulating material for RF and microwave packages, an electrostatic chuck dielectric for semiconductor processing equipment, heat sinks of mainframes for supercomputers and hardware for containing or processing molten metals and salts [6,7]. Probably, AlN would also be an ideal substrate material for GaN lasers and light emitting diodes [8].

Further, AlN is considered as one of the most effective materials for field emission device applications [9–11]. The recent intensification of advances in electronic devices with a high chip density requires a material with excellent

properties, especially thermal conductivity. Consequently, aluminium nitride is likely to become an alternative material to alumina (Al_2O_3) [12].

At present, commercial AlN powder is produced via carbothermal reduction of Al_2O_3 or direct nitridation of aluminium metal powder [13]. When compared to carbothermal reduction synthesis, direct nitridation has the recompense of simplicity and cost effectiveness but metallic aluminium tends to agglomerate due to its lower melting point (660 °C) than the nitridation temperature [12,14,15]. Also, a consistent nitride skin is usually formed on the surface of Al particles [16–18]. Both upshots prevent continuous good nitrogen access and consciousness of complete nitridation. Recent developments on direct nitridation include incorporating some additives like NH_4Cl to the starting Al powder to accelerate the nitridation process [16,17]. It has been reported that the direct nitridation reaction of Al in presence of NH_4Cl greatly assists the growth of AlN whiskers [19].

In the present study, three kinds of AlN powders were produced by direct nitridation viz., a) Al metal powder (System 1), b) NH_4Cl in addition with aluminium (System 2), c) NH_4Cl and urea in incorporation with aluminium (System 3), in the presence of continuous flowing of nitrogen gas at 900 °C for 5 h. Crystal structure of all the systems is hexagonal. Furthermore, an attempt has been made to show that the synergic effect of additives like NH_4Cl and urea are able to improve the nitridation and compare with other systems for the formation of AlN.

2. EXPERIMENTAL

A technical grade aluminium metal powder (99% purity), a chemical grade ammonium chloride powder (minimum assay 99%) and urea (minimum assay 99%) were used as reactants. Oxygen free nitrogen gas (>99% purity) was used as a nitriding agent.

To prepare the samples, approximately 25 g of a homogeneous mixture of aluminium powder, ammonium chloride and urea were thoroughly mixed in the range 1:3:1. The mixture was well ground using a pestle and mortar. Urea acts as a fuel to propel the reaction to form the desired compound and an alternative source of nitrogen. An inexpensive and easily available alumina crucible having a high melting point, strong hardness and good chemical stability was chosen for this study. The mixture was taken in the crucible and placed in an electrical heated furnace (100 mm ID, 200 mm ht). The furnace was heated up to 900 °C under a flow of nitrogen gas at the rate of 500 ml/min and this temperature was maintained up to 5 h. Then the furnace was cooled down to room temperature under the nitrogen atmosphere. The synthesized nitride products were characterized by different analytical techniques. Differential Thermal Analysis and Thermo Gravimetric Analysis (TGA/DTA) of the samples were done using Rigaku Thermal – Plus TG 8120. The phase formation and the structural details

of the synthesized compounds were characterized by X-ray powder diffraction (XRD) using CuKα ($\lambda = 1.541$ Å) radiation with 2 θ value range of 20° to 90° using PAnalytical X'pert powder diffractometer. The Fourier Transform Infrared (FTIR) spectra were recorded in the range of 400 to 4000 cm^{-1} using Perkin Elmer UK Paragon – 500 spectrometer. Scanning Electron Microscopy (SEM) was employed for the morphological studies using JEOL JSM 3.5 CF Japan make model. UV Visible Spectrophotometer was employed for the absorbance study using JASCO Model 7800 UV Visible Spectrophotometer. Elemental analysis was done using CHNS Elemental Analyzer elementar Model Vario EL III.

3. RESULTS AND DISCUSSION

The TGA/DTA curve obtained for system 1 is shown in Fig. 1a. It can be seen that gradual weight loss occurred up to 363 °C which was only 2 wt%, corresponding to the exotherm peak at 338 °C in DTA. The weight loss was gradual up to 419 °C for system 2 (Fig. 1b) and the corresponding exotherm existed at 328 °C. But for system 3 (Fig. 1c), the gradual weight loss up to 312 °C was 2 wt%, and up to 979 °C, the weight change was only 1 wt%. The exotherm peak observed at 328 °C might be due to the decomposition of urea. The weight gain (extent of oxidation) at 671 °C clearly indicates (Fig. 1a) the formation of AlN product. A minor exothermic peak at 674 °C corresponds to the formation of AlN [20].

In Fig. 1b for system 2, the weight gain was observed up to 985 °C, corresponding to large endotherm in DTA. This envisages that large amount of heat was removed due to the endothermic decomposition of ammonium chloride. Further, HCl was released by the decomposition reaction and NH_3 reacted with the nitrogen to form ammonium azide (~1/3 of the product), which precluded further nitridation even if ammonium azide is one of the nitrogen agents. The weight gain in TGA might be due to the formation of ammonium azide. XRD results also confirmed that the compound consisted of 27% ammonium azide.

From the DTA curve in Fig. 1c, no reaction was observed up to 1000 °C for system 3. The weight changes, observed in Fig. 1c, might have occurred due to the slow diffusion of nitrogen gas into the metallic aluminium, which was difficult in the presence of Al_2O_3, forming a thin film on the Al surface (particles). A broad endothermic peak was pragmatic up to 1000 °C in TGA, perhaps, due to the formation of ammonium azide during the decomposition of ammonium chloride and urea. The XRD data coincided with this result and the product has been found to contain 34% ammonium azide.

Ammonium chloride plays a decisive role and also acts as a parting agent concurrently by generating voids in Al powder when it decomposes. Also, HCl, produced during the decomposition of NH_4Cl, is to be considered as an intermediate product. HCl promoted the vaporization of molten aluminium cores into
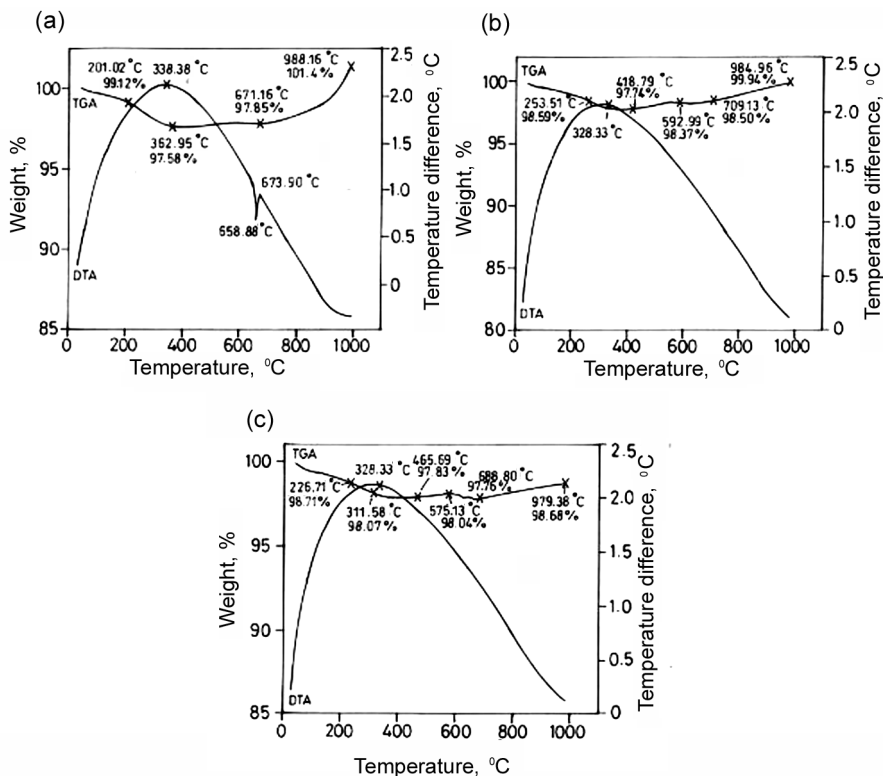
Fig. 1. TGA/DTA curves for AlN: (a) Al+N$_2$; (b) Al+NH$_4$Cl+N$_2$ (1:3); (c) Al+NH$_4$Cl+Urea+N$_2$ (1:3:1).

volatile aluminium chloride species and facilitated the progress of nitridation through a sequence of spontaneous chlorination and intermediate nitridation reactions. Thus, a small amount of NH$_4$Cl is enough to promote the nitridation. But, in our system, NH$_3$ did not decompose into nitrogen and hydrogen before it reached the surface of Al powder [16]. Instead of promoting the nitridation by NH$_3$, it favoured the formation of NH$_4$N$_3$. The modelling of aluminium nitride by direct nitridation is also presented in Fig. 7.

The XRD pattern of AlN by direct nitridation method is shown in Fig. 2. Hexagonal würtzite structure of AlN can be observed about 14%, 13% and 15% for systems 1, 2 and 3, respectively. The identified peaks are equivalent to the AlN phases at (100), (002), (101), (102), (110), (103) and (202). The lattice constant values were compared with the standard value a = 3.114 Å, c = 4.986 Å (JCPDS number 08 - 0262) and are also presented in Table 1. The calculated lattice parameter value, X-ray density and crystalline size are also presented in Table 1. These values conform to the prescribed standard values. From the full width half maximum (FWHM) of the diffraction peaks, the average crystalline size of the aluminium nitride product was estimated, according to the Debye–Sherrer formula, to be 59, 41 and 58 nm for the systems 1, 2 and 3, respectively.

Table 2 provides the percentage of impurities and the resultant product of all the three systems.

Figure 3 shows the FTIR spectra of AlN by direct nitridation method for systems 1, 2 and 3. The weak band at 650.4 cm^{-1} for system 3 is attributed to the stretching frequency of hexagonal Al-N [21,22].

A broad O–H stretching band was observed in the range of 2600 to 3800 cm^{-1} for all the three systems. A C–H stretching band from surface organic impurities
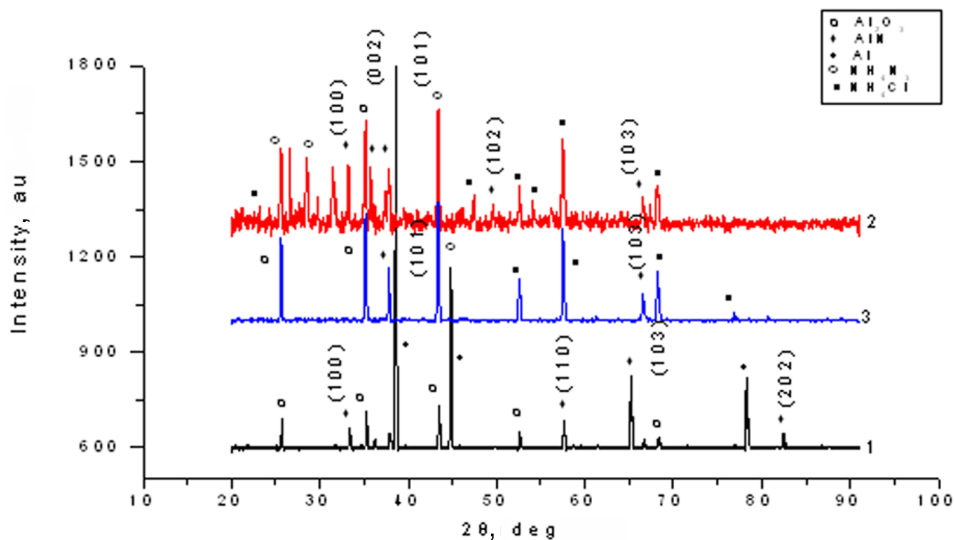

Fig. 2. XRD pattern of systems 1 (Al+N$_2$), 2 (Al+NH$_4$Cl+N$_2$) and 3 (Al+NH$_4$Cl+Urea+N$_2$).

Table 1. XRD data for AlN, t = 5 h

System	Lattice constants, Å	Crystalline size, nm	Volume, 10^{-24} cm^3	Density, g/cm^3
Al+N$_2$	a = 3.13 c = 4.82	58.84	41.14	3.31
Al+NH$_4$Cl+N$_2$	a = 3.14 c = 4.97	40.77	42.58	3.19
Al+NH$_4$Cl+Urea+N$_2$	a = 3.13 c = 4.93	58.32	42.04	3.23

Table 2. Percentage of components

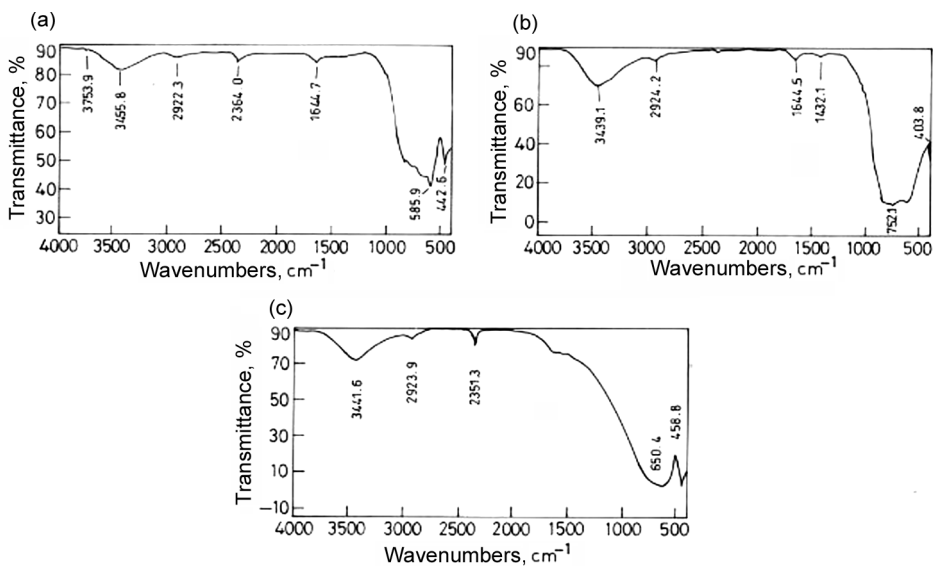| System	AlN	NH$_4$Cl	Al$_2$O$_3$	Al	NH$_4$N$_3$	Unidentified components
Al+N$_2$	13.78	–	8.1	78	–	0.12
Al+NH$_4$Cl+N$_2$	12.96	16.21	25.50	–	27.62	17.71
Al+NH$_4$Cl+Urea+N$_2$	15.30	26.50	24.13	–	34.04	0.03

Fig. 3. FTIR spectra of AlN: (a) Al+N_2; (b) Al+NH_4Cl+N_2 (1:3); (c) Al+NH_4Cl+Urea+N_2 (1:3:1).

was observed in the range of 2922 to 2924 cm^{-1} for all the systems. A sharp band at 1432.1 cm^{-1} for system 2 and at 1644 cm^{-1} for systems 1 and 2 corresponds to the absorbed water molecules and δ-NH_3, respectively. The bands at 2364 cm^{-1}, 2351.3 cm^{-1} for the systems 1 and 3 are attributed to stretching mode of CO_2 [23].

UV reflectance spectrum for AlN of system 1 is shown in Fig. 4. The absorption edge near 214 nm corresponds to the direct wide band gap of AlN. Other absorption edges found in the spectrum may correspond to the impurities in the matrix. Band gap value obtained from the spectra was equal (5.8 eV) for all the three systems.

The impurity analysis of all the three systems is presented in Table 3. Nitrogen, hydrogen and sulphur were not present in the product of system 2. This result contradicted to XRD data for system 2 where the phase formation of AlN was only 13%. Higher nitrogen content was present in the system 1 when compared to other two systems. This result also contradicted the corresponding XRD data which may have occurred due to the oxidation of samples during preparation.

The SEM images of the product of systems 2 and 3 are shown in Fig. 5. The product is very dense with unreacted Al particles with little AlN whisker formation (Fig. 5a). The grain diameter increases from 2 to 15 μm for system 3 (Fig. 5b). Oxygen was the main impurity present during the nitridation reactions. This could be due to the oxidation of unreacted Al particles and also insufficient nitrogen diffusion. Usually, NH_4Cl decomposes and produce NH_3 and HCl. However, here NH_3 reacted with nitrogen to form ammonium azide (NH_4N_3), which did not promote the nitridation reaction.
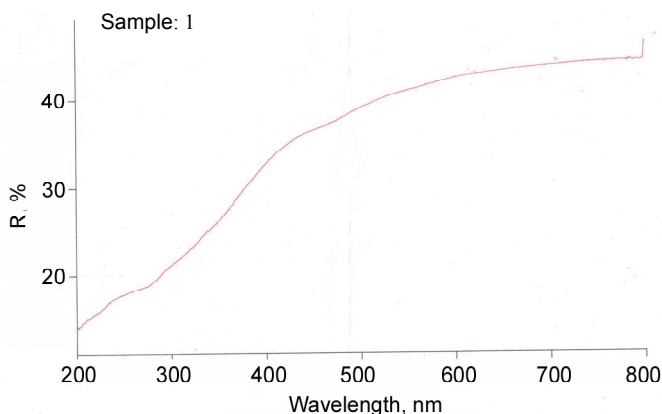
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Fig. 4. UV–VIS-spectra of AlN for Al+N_2.

Table 3. Percentage of C, H, N, S content

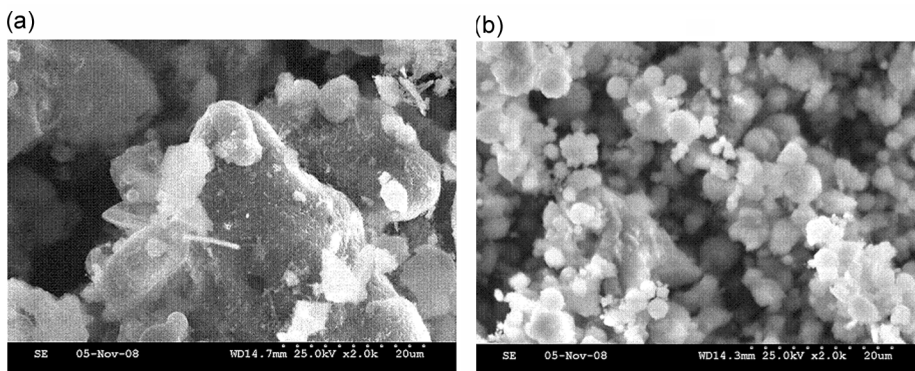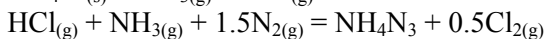| Samples	Nitrogen	Carbon	Sulphur	Hydrogen
Al+N_2	0.831	0.058	0.000	0.000
Al+NH_4Cl+N_2	0.000	0.145	0.000	0.000
Al+NH_4Cl+Urea+N_2	0.256	0.219	0.000	0.000

Fig. 5. SEM micrographs of AlN: (a) Al+NH_4Cl+N_2 (1:3); (b) Al+NH_4Cl+Urea+N_2 (1:3:1).

Figure 5b shows the morphology of the product AlN for the system 3. In this microstructure, the access of further nitrogen gas to unreacted Al particles is withdrawn and retarded the development of nitridation to completion [24]. The particles were dense in nature and agglomerated due to the clumsiness of the starting Al powder. In this system, the NH_4Cl decomposed to produce NH_3 and HCl as before and instead of aiding the growth of AlN, the NH_3 reacted with nitrogen to form NH_4N_3, which did not promote the complete nitridation. The

unreacted Al particles get oxidized and retarded further nitridation. The urea also did not encourage the nitridation reaction.

The schemes of reactions are:

$$NH_4Cl_{(s)} = NH_{3(g)} + HCl_{(g)}$$
$$HCl_{(g)} + NH_{3(g)} + 1.5N_{2(g)} = NH_4N_3 + 0.5Cl_{2(g)}$$

The EDAX result (Fig. 6a) for the system 2 shows that the unreacted Al particles get oxidized and also reveals the existence of Al_2O_3 [25]. There was only 13% AlN present in the product. The nitrogen gas diffusion was very low during the reaction. The nitrogen gas reacted with ammonium chloride to form ammonium azide, which was a candidate material to hinder further nitridation. In
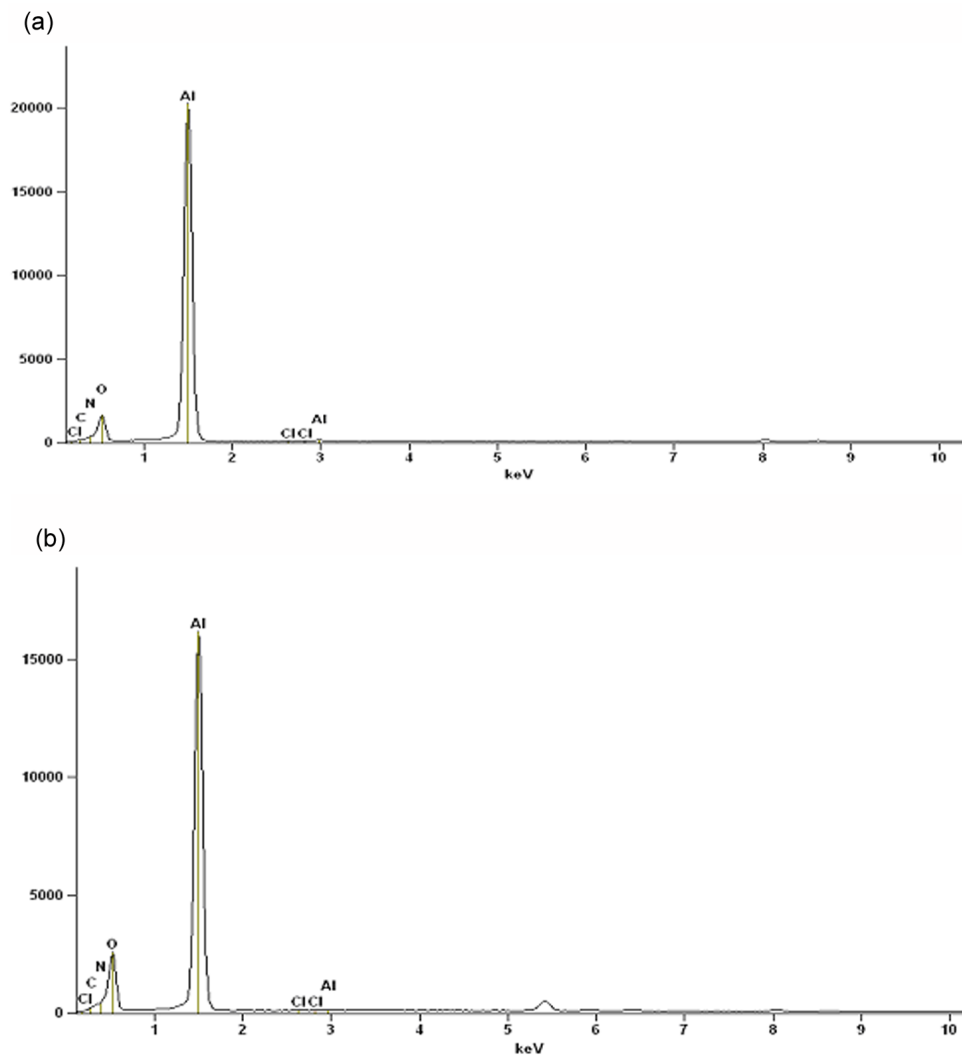

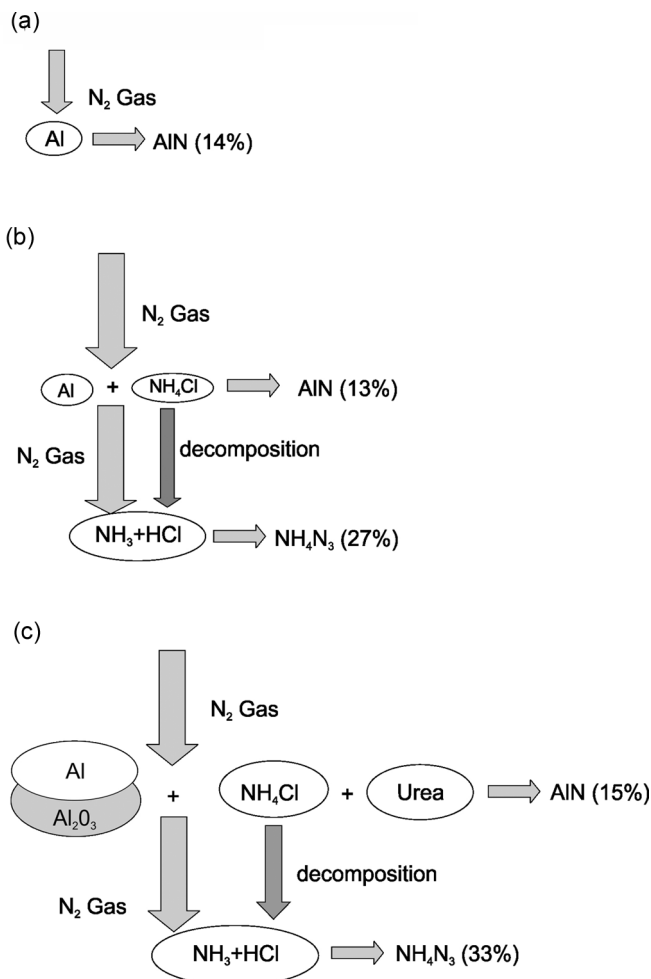**Fig. 6.** EDAX of AlN: (a) Al+NH$_4$Cl+N$_2$ (1 : 3); (b) Al+NH$_4$Cl+Urea+N$_2$ (1 : 3 : 1).

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Fig. 7. Modelling of AlN by direct nitridation in flowing N_2 gas for the systems: (a) $Al+N_2$; (b) $Al+NH_4Cl+N_2$; (c) $Al+NH_4Cl+Urea+N_2$.

system 3, the EDAX result (Fig. 6b) shows that the same trend as in the case of system 2, and also urea does not promote to complete the nitridation of the sample. Only 15% of AlN was present in this system. Figure 7 summarizes the whole reaction mechanism of aluminium nitride by direct nitridation schematically for all the three systems.

4. CONCLUSIONS

Aluminium nitride was synthesized by NH_4Cl assisted direct nitridation of Al metal powder and urea as a fuel in the presence of nitrogen gas at 900 °C for 5 h.

The synergic effect of NH_4Cl and urea are unable to promote the nitridation. In this system, the NH_4Cl decomposed to produce NH_3 and HCl as before and instead of aiding the growth of AlN, the NH_3 reacted with nitrogen to form NH_4N_3, which does not promote complete nitridation. The nitridation conversion of system 3 was only about 15% with crystallite size of 58 nm. The nitridation conversion for the other two systems is also only 14% and 13%. The band gap value for the AlN was 5.8 eV, which is very close to 6 eV (theoretical value). The main impurity during the nitridation reaction was oxygen and urea did not promote complete nitridation.

ACKNOWLEDGEMENTS

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AlN süntees lisandainete juuresolekul ja ilma nendeta

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Heksagonaalset alumiiniumnitriidi (AlN) sünteesiti alumiiniumipulbri vahetul nitreerimisel NH_4Cl-i juuresolekul. Katsetati meetodeid, kus lähteaineks oli: a) puhas Al-i pulber, b) Al-i ja NH_4Cl-i segu, c) Al-i, NH_4Cl-i ja uurea segu. Kõigil juhtudel kasutati pidevat N_2 voolu temperatuuril 900 °C viie tunni vältel. Saadud pulbreid iseloomustati TGA/DTA-, XRD-, FTIR-, SEM- ja UV-VIS-spektroskoopia ning CHNS-analüüsi meetoditega.

Artiklis on analüüsitud lisandite, eriti uurea mõju ja AlN-i tekkemehhanismi.