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A non-aqueous processing route for phosphate-protection of AlN powder against hydrolysis

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Abstract

A commercial AlN powder was treated in an ethanol with H_3PO_4 and $Al(H_2PO_4)_3$ to passivate its surface against hydrolysis. The treated powder was quite stable in water for >72 h as confirmed by pH measurement, X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and energy dispersive analysis with X-rays. The coating layer was stable up to 1200 °C as confirmed by thermogravimetry and differential thermal analysis. The aqueous processing ability of treated AlN powder was tested in aqueous gelcasting of β-SiAlON reaction precursor mixtures for fabricating dense ceramic bodies and 500 mL thin wall crucibles. The sintered gelcast β-SiAlON exhibited the following properties: bulk density of 3.07 g/cm^3, apparent porosity of 0.13%, water absorption capacity of 0.04%, linear shrinkage of <16%, β-SiAlON content of >90%, hardness of 14 GPa and fracture toughness of 3.95 MPa m$^{1/2}$.
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Keywords: AlN powder; Phosphate coating; $AL(H_2PO_4)_3$; H_3PO_4; Y_2O_3

1. Introduction

Recently, polycrystalline AlN ceramics have received a considerable attention owing to their attractive properties like high thermal conductivity, low thermal expansion, high electrical resistivity, and excellent resistant to attack by molten metals.[1] They are employed in heat engines, as crucibles for molten aluminium and gallium arsenide, as air-borne ballistic armor materials,[2] etc. These products are normally made by conventional dry-powder pressing techniques followed by sintering at elevated temperatures to achieve full density, and then by extensive and expensive machining to obtain the final desired shape. However, this conventional processing route is not suitable for fabricating certain products with high relative density and high uniformity, and thus, high reliability of performance. Colloidal processing routes were found to be suitable for fabricating such products.[2] Despite of many advantages, the major limitation associated with AlN is its poor resistant to hydrolysis which causes difficulty in aqueous colloidal processing of AlN products.[3–8] Even during storage, AlN powder surface reacts with water vapour according to Eqs. (1)–(3):

$$AlN + 2H_2O \rightarrow AlOOH_{amorph} + NH_3 \tag{1}$$

$$NH_3 + H_2O \leftrightarrow NH_4{}^+ + OH^- \tag{2}$$

$$AlOOH_{amorph} + H_2O \rightarrow Al(OH)_3 \tag{3}$$

A great variety of techniques have been tried to passivate AlN powder surface against hydrolysis mostly using hydrophobic coating agents.[2–5] Such treatment processes usually involve coating the surface of the AlN particles with long chain organic molecules, such as carboxylic acids, particularly stearic acid, or cetyl alcohol, *n*-decanoic acid, dodecylamine acid and so on. The disadvantages of these processes is the use of dangerous organic solvents, and the difficulty of dispersing the coated powders in water without adding wetting agents, which cause the suspensions to foam. In a previous study, Shimizu et al.,[3] used a dicarboxylic acid (sebacic acid) in an attempt to protect AlN powder from hydrolysis and keep the hydrophilic carboxylic groups on the powder surface to facilitate the powder dispersion in water. Binner and Zhang[6] studied the hydrolysis and dispersion behaviour of a commercial AlN powder pro-

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tected against hydrolysis by silicon-based organic acid/ester hydrophobic coatings and an un-protected AlN powder using a commercial dispersing agent.[7,8] The interactions between the long hydrocarbon chain and the underlying surface were regarded as the driving force for surfactant adsorption,[7,9] with the lateral interactions between adsorbed molecules becoming increasingly important as adsorption density increased covering the hydrophilic sites.[8] However, the maximum achievable solids loading in aqueous suspensions using hydrophobised powders was found to be unsatisfactory.[2] Therefore, there was still an open quest for finding suitable hydrophilic coating agents and treatment processes, which help dispersing the protected AlN powder in the aqueous medium and achieve satisfactory solids loading (~50 vol.%) for colloidal processing.

The chemisorption of anions from poorly dissociated acids, such as phosphoric or silicic acids from aqueous environments, has been reported to result in a high protection efficiency of AlN powders.[10–13] Krnel and Kosmac[11,12] studied the hydrolysis behaviour of AlN at pH ~1 and ~3 by using several inorganic acids, which include HF, HCl, HNO_3, H_2SO_4, H_3PO_4, and $Al(H_2PO_4)_3$. At pH ~1 an efficient stability against hydrolysis of AlN was observed regardless of the acid used. However, at pH 3, the stability was found dependent on the nature of the acid used. The same authors also reported that $Al(H_2PO_4)_3$ provided very effective protective coating against hydrolysis.[12] However, the use of acid solutions at $pH < 2$ for treating large amounts of AlN powder is not advisable at least from the environment point of view, and the resulting the amount of phosphate species in the coating surface layer was relatively high.

The protection mechanism of AlN from hydrolysis by using phosphoric species is based on the reactions between these species and the surface hydroxyl groups, as schematically described by Eqs. (4) and (5) for Al surface sites with two bonds, or with a single bond, to the bulk particle, respectively.[4,5,11,12]

$$=\mathrm{Al(OH)} + \mathrm{H_3PO_4} + n[\mathrm{Al(H_2PO_4)_3}] \rightarrow \mathrm{Al(H_2PO_4)} + n[\mathrm{Al(H_2PO_4)_3}] + \mathrm{H_2O} \quad (4)$$

$$-\mathrm{Al(OH)_2} + 2\mathrm{H_3PO_4} + n[\mathrm{Al(H_2PO_4)_3}] \rightarrow \mathrm{Al(H_2PO_4)_2} + n[\mathrm{Al(H_2PO_4)_3}] + 2\mathrm{H_2O} \quad (5)$$

These equations suggest that 1–2 bulky phosphate anions bond to each single surface aluminium atom, thus uniformly coating the surface of the particles and letting little chance for AlN to react with water molecules that interact preferentially the hydroxyl of phosphate anions *via* hydrogen bonding.

The hydrolysis resistance of AlN can also be improved by simple calcination process at about 600–800 °C at which a stable Al_2O_3 coating forms on the surface of each particle. However, the stability of the powder obtained by this route was insufficient to turn viable the aqueous processing.[13] Morisada et al.[14] reported a process in which SiO coating was provided on AlN powder in vacuum at 1150–1450 °C to protect it from hydrolysis. However, all of these techniques involve either lengthy/cumbersome experimental procedures or capital-intensive equipment.

In this paper, we report a simple non-aqueous processing route for protecting AlN powder from hydrolysis. In this study, H_3PO_4 and $Al(H_2PO_4)_3$ were utilized for providing the protective phosphate layer. The main advantage of this process is the formation of a single uni-molecular phosphate monolayer provided that the exact amount (or even some excess) of coating agents is used. The excess (un-reacted) coating agents can be eventually washed away by simply washing with ethanol from the powder surface. The ethanol used for washing purpose can be separated from coating agents by a conventional distillation process and can be re-used several times for the same purpose. This differs from the aqueous acidic solution processing route that requires an excess of H_3PO_4 or $Al(H_2PO_4)_3$ which will remain on the powder surface.

The as-purchased (A-AlN) and the as-treated and washed (TW-AlN) powders were characterized by various techniques before, and after being suspended in water for 72 h, samples (A-AlN-72 h) and (TW-AlN-72 h), respectively. The aim was to evaluate the efficiency of the non-aqueous processing route in protecting the AlN powder from hydrolysis. Finally, a powder mixture consisting of the treated and washed AlN (TW-AlN) powder, α-Si_3N_4, α-Al_2O_3 and Y_2O_3 was dispersed in an aqueous pre-mix solution to obtain a slurry with 50 vol.% solids loading, which was consolidated in different shapes (including a 500 mL thin-wall crucible) by gelcasting, and sintered at 1675 °C for 4 h to obtain dense β-$Si_4Al_2O_2N_6$.

2. Experimental procedure

2.1. Raw materials and reagents

The starting raw materials included powders of AlN (Grade AT, H.C. Stark, Germany), α-Si_3N_4 (P95H, VESTA Ceramics AB, Sweden), α-Al_2O_3 (HP, ACC India Limited, India), and Y_2O_3 (Rhodia Inc., Phoenix, Arizona). The specific surface areas (m^2/g) and average particle sizes (μm) of these powders as given by the suppliers are 1.24, 6.51, 6.72 and 3.41, and 1.39, 17.77, 7.62, and 3.23, respectively. Absolute ethanol (99.9%, Les Alcools De Commerce Inc., Ontario) was used as dispersing medium to coat the AlN particles. Ortho-phosphoric acid, H_3PO_4 (85% assay, AR Grade, Qualigens, India) and aluminium di-hydrogen phosphate, $Al(H_2PO_4)_3$ (assay $\geq$ 97.0%, Fluka, Germany) were used as coating agents.

2.2. Surface treatment of aluminum nitride powder

In a typical experiment, ~245 g of AlN powder was suspended in an absolute ethanol to obtain ~250 mL of a slurry with 30 vol.% solids loading in a 500-mL volume three neck round bottom (RB) flask. The RB flask was fitted with an equalization funnel and valve to pass dry-nitrogen gas and was placed into a thermostatic oil bath (150 mm diameter and 75 mm height, Thermol-100, Biolabs, India, −50 to +250 °C). In a separate flask, ~2 g $Al(H_2PO_4)_3$ was dissolved in ~5 mL of hot H_3PO_4. This solution was then mixed with ~50 mL ethanol and added drop-by-drop to the above alcohol-based AlN suspension with the help of an equalization funnel. The RB flask was then continuously refluxed at 80 °C for 24 h while passing N_2 at the rate of 100 mL/min. The content of the RB was agitated with a magnetic stirrer (5MLH-DX, Remi, India). The treated AlN slurry was filtered off and washed with fresh ethanol several times in order to remove un-reacted/excess H_3PO_4 and $Al(H_2PO_4)_3$. After distillation, the ethanol was re-used for washing the treated powder.

2.3. Preparation of β-$Si_4Al_2O_2N_6$ ceramics

β-$Si_4Al_2O_2N_6$ ceramics were obtained from a precursor mixture consisting ~9.37 wt.% of treated and washed AlN (TW-AlN), ~64.33 wt.% of α-Si_3N_4, ~23.36 wt.% α-Al_2O_3, and ~7 wt.% Y_2O_3. The powder mixture was dispersed in an aqueous pre-mix solution to obtain a slurry with 50 vol.% solids and then consolidated by gelcasting according to the process developed by Janney et al.[15] For this purpose, the premix solution was first prepared by dissolving 20 wt.% MAM (methacrylamide), MBAM (methylenebisacrylamide) and NVP (*n*-vinylpyrrolidinone) in 3:1:3 ratio in de-ionized water.[16] Dolapix A88 (an amino alcohol cationic dispersant) procured from Zchimmer & Schwarz, Berlin, Germany was used at the ratio of 25 μL/g of powder mixture to improve the fluidity of the suspension. After deagglomerating the powder in a 1000 mL polypropylene bottle placed on a rotary pot mill with the help of alumina balls having 12 mm diameter (charge to balls ratio was 1:3) for 16 h, the slurries were degassed for ~5 min under partial vacuum. The suspension was once again degassed for ~2 min after adding a polymerization initiator (10 wt.% aqueous solution of ammonium persulfate (APS)) and a catalyst (tetramethylethylenediammine (TEMED)) at the ratio of 4 and 2 μL per gram of slurry, respectively. The as-obtained slurry was then cast into non-porous white petroleum jelly coated split-type aluminium moulds (60 mm × 30 mm × 30 mm) and allowed to set under ambient conditions till the completion of the gelling process.[17] Five hundred milliliters of volume thin-wall crucibles were also consolidated by gelcasting. The green bodies were de-moulded and dried in a controlled humidity oven (Model: LHL-113; Espec Corporation, Japan) to avoid cracking and non-uniform shrinkage due to rapid drying and then sintered for 4 h at 1675 °C to obtain dense β-$Si_4Al_2O_2N_6$.[18,19]

2.4. Material characterization

XRD patterns were recorded on a Bruker (Karlsruhe, Germany) D8 advanced system using a diffracted beam monochromated Cu Kα (0.15418 nm) radiation source.[20] Crystalline phases were identified by comparison with PDF-4 reference data from International Centre for Diffraction Data (ICDD). Relative phase compositions of samples were calculated from the peak height measurements of the respective peaks. For this, the most intense peak of each individual phase was taken into consideration.[20] The peak heights of all the phases were summed up and the percentage concentration of a particular phase was estimated from the ratio of the strongest peak of that phase to the sum of various phases present in a given system.[20] The thermal behaviour of the different powders was analyzed in argon atmosphere in the temperature range between 30 and 1200 °C using a TG/DTA (NETZCH Luxx STA 409 PC) instrument, using α-Al_2O_3 as the reference material, and a heating rate of 10 °C/min. The FT-IR spectra were recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions, using KBr disks, with a normal resolution of 4 cm^{-1} and averaging 100 spectra. The values of bulk density (BD), apparent porosity (AP) and water absorption (WA) capacity of sintered ceramics were measured according to Archimedes principle (ASTM C372) using Mettler balance and the attachment (AG 245, Mettler Toledo, Switzerland). For this purpose, about 2–3 sintered bars were crushed into 3–5 mm sized grains and ~20 g of each sample was taken for measuring sintered properties (BD, AP and WA capacity). On average three measurements were performed on each sample.[21] The SEM micrographs of the powders were recorded on a Hitachi, S-3400N, Scanning Electron Microscope, Japan with an energy dispersive scanning attachment for qualitative and quantitative microanalysis.

3. Results and discussion

3.1. Characteristics of treated AlN powder

The surface of raw AlN powder is usually covered with a process-dependant alumina (i.e., θ- and γ-Al_2O_3) and/or a hydrated alumina layer (γ-AlOOH and $Al(OH)_3$).[3] Such layers are further developed during storage because of poor chemical stability against oxidation and hydrolysis. When the AlN powder is treated with H_3PO_4 and $Al(H_2PO_4)_3$, the surface hydroxyl groups play a vital role in the formation of a protective layer against hydrolysis. In the reactions of Al surface atoms with H_3PO_4 and $Al(H_2PO_4)_3$, Eqs. (4) and (5),[11,12] $Al(H_2PO_4)_3$ is expected to perform a seeding action, since under the reaction conditions employed $Al(OH)_3$ ultimately converts into $Al(H_2PO_4)_3$. It has been reported that ~1.1 mg $H_2PO_4^-$ is required to form a continuous single uni-molecular monolayer on a square meter surface of AlN.[12] However, in order to ensure the coating of all particles, ~5 mg of H_3PO_4 and ~3.7 mg of $Al(H_2PO_4)_3$ per square meter of AlN was added in the present work. Therefore, an excess of about 7 mg $H_2PO_4^-$ ions per square meter of AlN is available during reaction, ensuring the coating of all powder particles. The un-reacted phosphate ions were then removed by washing with absolute ethanol. The treated AlN powder was found to remain stable against hydrolysis while dispersed for 72 h in water and/or while exposed for 3 months to open air atmosphere.

The hydrolysis behaviours of as-purchased AlN (A-AlN) and of the as-treated (T-AlN) powder before and after being washed (TW-AlN) was studied by registering along a period of 72 h the pH evolution of aqueous suspensions containing 5 wt.% solids. Fig. 1 shows that the suspension's pH of A-AlN drastically increased from 6.7 to 9.7 within a few hours indicating a fast hydrolysis process. In contrast, the aqueous suspension of T-AlN was stable as its pH decreased very slowly due to dissolution of un-reacted $H_3PO_4/Al(H_2PO_4)_3$ adsorbed on the powder surface. Very interestingly, the suspension pH of (TW-AlN) is quite stable up to ~6 h, steadily decreasing afterwards to reach a value

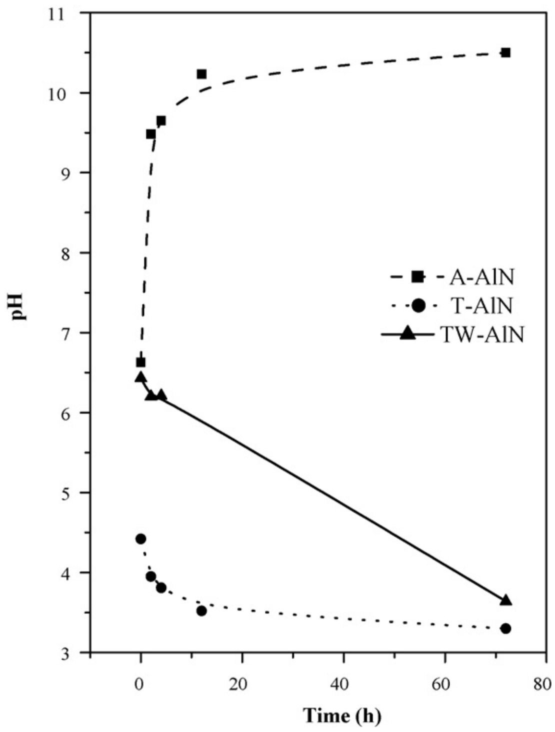

Fig. 1. Hydrolysis behaviour of as-purchased AlN (A-AlN), as-treated AlN (T-AlN) and treated and washed AlN (TW-AlN) powders.

of 3.7 after 72 h. A 6 h period is normally sufficient to perform gelcasting of the TW-AlN containing precursor mixtures.[15,16] It is important to note that the release of any un-reacted phosphate ions from the powder surface at this stage will neither affect the pH of the slurry, which has been already set to a value of less than pH 5 upon addition of the polymerization initiator (APS) solution, nor the gelling of organic monomers.[15,16]

The stability of the TW-AlN powder against hydrolysis was also confirmed by the XRD study. The X-ray diffraction patterns of A-AlN, TW-AlN, A-AlN-72 h and TW-AlN-72 h powders are presented in Fig. 2. The major diffraction lines of the A-AlN-72 h belong to $Al(OH)_3$ (ICDD File No.: 00-020-0011) and only minor peaks of AlN are observed. The A-AlN powder and the two treated powders only exhibit XRD lines belonging to AlN phase (ICDD File No.: 00-025-1133). This result clearly suggests that the phosphoric acid-treated AlN powder is stable in water at least for periods up to 72 h.

In order to better understand the interaction between the AlN powder and phosphoric acid, the fully dried (in vacuum at 120 °C) powders A-AlN, TW-AlN, A-AlN-72 h, and TW-AlN-72 h were analyzed by FT-IR in the 400–4000 cm^{-1} range (Fig. 3). Normally, AlN powder exhibits a large transmittance band at 400–1000 cm^{-1}, and two small transmittance bands at 1300–1350 cm^{-1} and 1400–1450 cm^{-1}, due to different stretching vibrations of AlN.[22] The A-AlN-72 h powder shows transmittance bands at 3485 cm^{-1}, due to H–O bond vibrations.[22] Strong bands associated with –OH stretching vibrations of water and surface hydroxyl groups occur between 3200 and 3700 cm^{-1}.[20] A sharp and strong absorption band in the region 3650–3700 cm^{-1} was also noted in A-AlN-72 h characterizing the presence of hydroxyl groups. Hydration can be easily distinguished from hydroxyl groups due to the presence of the H–O–H bending motion, which also produces a medium band in the region 1600–1650 cm^{-1}. Free water has a strong and broad absorption band centred in the region 3200–3400 cm^{-1}.[20,21] A close look at Fig. 3 clearly reveals that the treated powders exhibited transmittance bands similar to those of as-received powder. Pure H_3PO_4 normally reveals a small transmittance band at 500–550 cm^{-1}, a large transmittance band at 1500–1800 cm^{-1}, and a low intensity

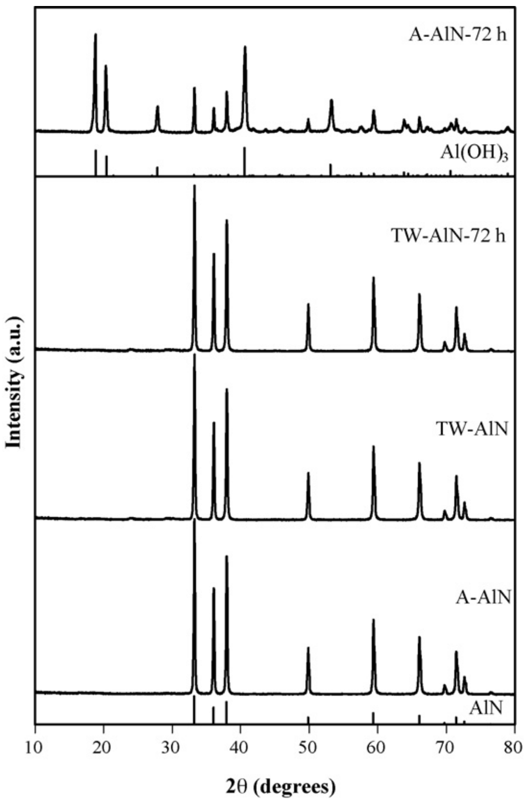

Fig. 2. XRD patterns of as-purchased AlN (A-AlN) powder, treated and washed AlN (TW-AlN) powder, as-purchased AlN powder suspended in water for 72 h (A-AlN-72 h) and treated and washed AlN powder suspended in water for 72 h (TW-AlN-72 h).

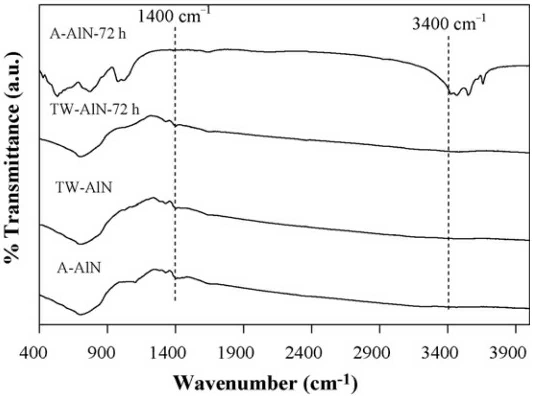

Fig. 3. FT-IR spectra of as-purchased AlN (A-AlN) powder, treated and washed AlN (TW-AlN) powder, as-purchased AlN powder suspended in water for 72 h (A-AlN-72 h) and treated and washed AlN powder suspended in water for 72 h (TW-AlN-72 h).

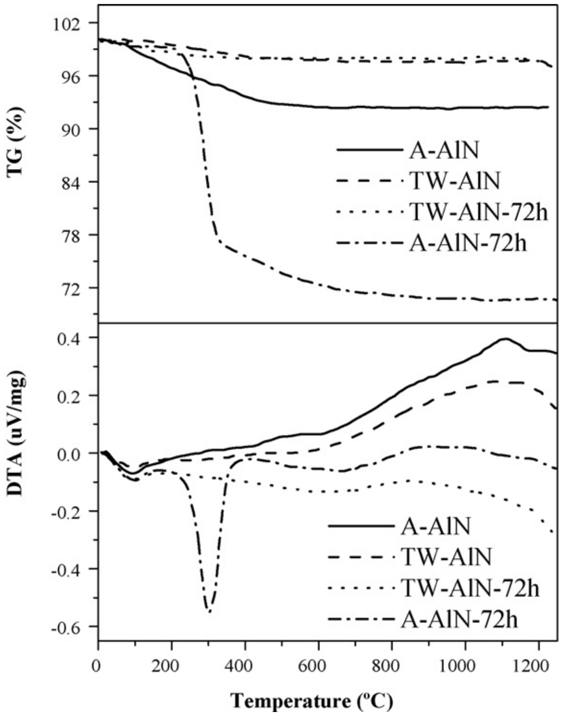

Fig. 4. TGA/DTA profiles of as-purchased AlN (A-AlN) powder, treated and washed AlN (TW-AlN) powder, as-purchased AlN powder suspended in water for 72 h (A-AlN-72 h), and treated and washed AlN powder suspended in water for 72 h (TW-AlN-72 h).

band at 2000–3200 cm^{-1}, due to different vibrations of phosphate molecule.[21] In an earlier study, Oliveira et al.[23] observed an absorption band at 2366 cm^{-1} due to the formation of $[Al(PO_3)_3]_x$ upon the reaction between hydroxyl groups of AlN and H_3PO_4. Although this band at 2366 cm^{-1} is not clearly seen, a sharp band at ∼3000–3200 cm^{-1} due to stretching vibrations of P–O bonds of phosphoric acid support the formation of phosphate layer on AlN surface. Fig. 3 clearly reveals the transmittance bands due to the presence of $Al(OH)_3$ indicating the decomposition of as-received AlN powder after suspending in water for 72 h.

The TGA/DTA profiles of different AlN powders can be seen in Fig. 4. Small endothermic peaks located at temperatures between 90 and 120 °C are caused by the evaporation of molecularly adsorbed moisture on the materials. The A-AlN-72 h exhibits completely different thermal events and weight losses as compared to other powders indicating that hydrolysis has occurred in a considerable extent in the un-coated powder. It was shown that boehmite, AlOOH, and bayerite, $Al(OH)_3$, were the successive solid reaction products derived from the gradual hydrolysis of AlN.[23] A major endothermic peak of the A-AlN-72 h powder, centred at 300 °C but stretching over the temperature range of 200–400 °C, is mainly due to de-hydroxylation of aluminium tri-hydroxide. This decomposition corresponds to a weight loss >24% up to 400 °C as can be seen from the TGA profile in Fig. 4. Considering that complete decomposition of pure $Al(OH)_3$ according to the reaction $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$[19] will result in a weight loss of 34.6%, it can be concluded that more than 70% of the starting A-AlN powder has been hydrolyzed after 72 h in water. Among the other powders, the un-treated one shows a larger weight loss in comparison to the TW-AlN and TW-AlN-72. This suggests that hydrolysis has already occurred to some extent in the A-AlN during storage by reacting with the water vapour from the atmosphere. Interestingly, the treated powders exhibit similar TGA profiles with relatively low weight loss, being stable up to 1200 °C. These results indicate that the moisture and the heating up to 1200 °C have little effects on the stability of treated AlN powder.

Table 1
EDAX analysis of the different powders

Sample code	Elemental analysis		
	O	Al	P
A-AlN	45.06	54.17	0.77
A-AlN-72 h	49.24	50.62	0.14
TW-AlN	27.20	71.56	1.23
TW-AlN-72 h	51.20	47.79	1.01

The morphology of all powders analyzed by SEM is shown in Fig. 5. As can be seen, A-AlN, TW-AlN and TW-AlN-72 h consist of relatively small particles/agglomerates (up to a maximum of ∼15 μm in size) in comparison to A-AlN72 powder, which has strong agglomerates with sizes as large as >75 μm. The formation of these large agglomerates further confirms the reaction of AlN in water, as it is due to conversion of AlN into a cementitious $Al(OH)_3$ phase.[24] These observations are also in line with other reported results by Krnel and Kosmac.[5,6,24]

Since the above characterization techniques (pH measurements, XRD, FT-IR, SEM and TGA/DTA analysis) did not enable to quantitatively estimate the amount of phosphorus adsorbed onto the surface of AlN particles, the four different types of AlN powders were also analyzed by EDAX. However, only the O, Al and P elements were taken into consideration to estimate the P contents, since when nitrogen is considered the amounts of P were hardly detected by the equipment. The results reported in Table 1 reveal that powders suspended in water (A-AlN-72 h and TW-AlN-72 h) contain relatively lower amounts of phosphorous than as-purchased (A-AlN) and –treated and washed (TW-AlN) powders. Furthermore, A-AlN-72 h has a higher oxygen concentration than nitrogen, in comparison to other three powders, confirming the hydrolysis of A-AlN upon suspending in water for 72 h. Interestingly, even the as-purchased powder (A-AlN) contains phosphorus as impurity (0.77%), while the amount of phosphorus detected in T-AlN powder is ∼1.23%.

3.2. *Use of the treated powder in gelcasting of* β-$Si_4Al_2O_2N_6$ *ceramics*

The suitability of treated and washed AlN (TW-AlN) powder for colloidal processing was assessed through consolidation of a β-$Si_4Al_2O_2N_6$ precursor mixture by aqueous gelcasting,[16,17,18] as mentioned in the experimental part. The material sintered for 4 h at 1675 °C presented the following properties: BD = of 3.07 g/cm^3, AP = 0.13% and WA = 0.04%.

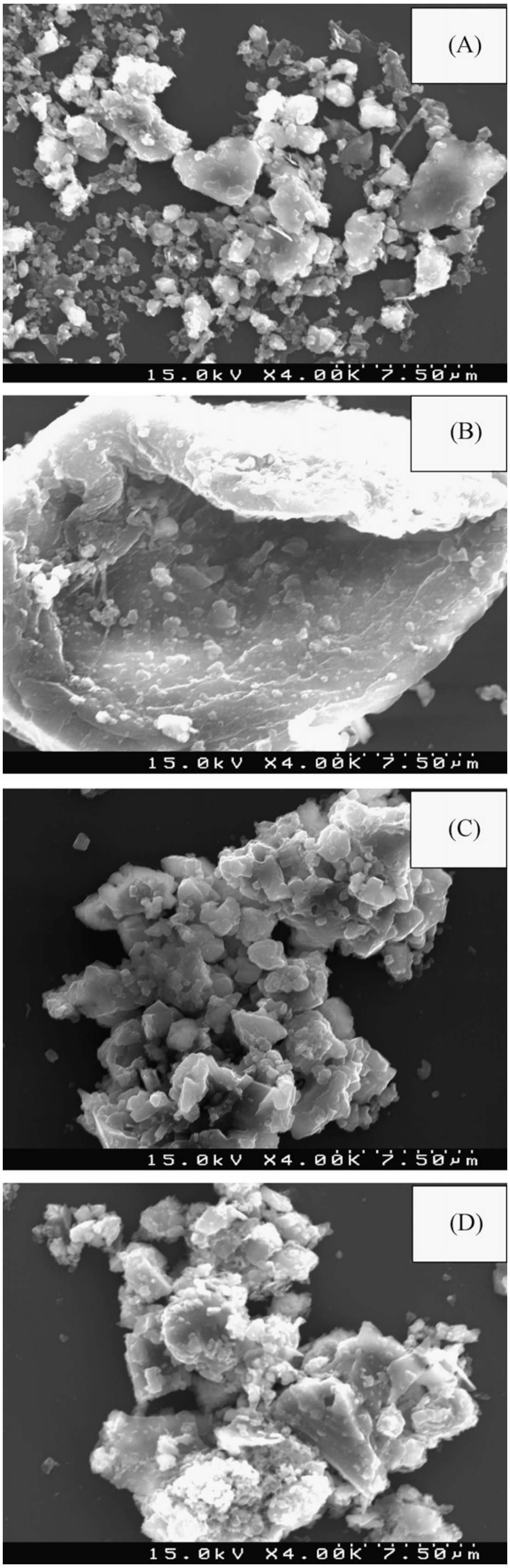

Fig. 5. SEM micrographs of (A) as-purchased AlN (A-AlN) powder, (B) as-purchased AlN powder suspended in water for 72 h (A-AlN-72 h), (C) treated and washed AlN (TW-AlN) powder, and (D) treated and washed AlN powder suspended in water for 72 h (TW-AlN-72 h).

β-$Si_4Al_2O_2N_6$ ceramics with a lower BD of 3.02 g/cm^3 have been considered suitable for random applications.[15] β-$Si_4Al_2O_2N_4$ exhibited BD > 3.02 g/cm^3, and a total linear shrinkage < 16%, which is within the acceptable range for making complex-shaped parts.[15,16] The higher BD obtained in the present work can be due to a 25 °C higher sintering temperature used and to eventual compositional differences (the amount of yttria is not referred to in the earlier reports).[15] During reactive sintering of β-$Si_4Al_2O_2N_6$ in the absence of sintering aids, a rapid liquid phase formation takes place at about 1600 °C, slightly above the binary Al_2O_3–SiO_2 eutectic temperature, which is 1587 °C. The SiO_2 comes from the surface oxidation of Si_3N_4, which is difficult to avoid.[16,25] This rather late liquid phase formation leads to a limited grain boundary mobility and hence, to a limited densification and high porosity.[25] However, in the presence of Y_2O_3, a ternary Y_2O_3–Al_2O_3–SiO_2 eutectic forms at 1350 °C. Since this temperature is much lower than the on-set temperature at which β-SiAlON phase formation starts, a glassy phase is easily formed during sintering and contributes to the densification through enhanced particle rearrangement.[26] This is the probable reason for the high BD achieved for the β-$Si_4Al_2O_2N_6$ ceramics in the present work. From the XRD pattern of the sintered material shown in Fig. 6 it can be seen that the main peaks belong to β-$Si_4Al_2O_2N_4$ (ICDD File No.: 00-48-1616) phase, which is representing more than 90%. The formation of Y_2SiAlO_5N (ICDD File No: 00-048-1627) was expected in this material due to the reactions between SiO_2, Al_2O_3 and Y_2O_3 at elevated temperature. However, no characteristic peaks of this phase are noticed, probably because the amount formed is below the detection limit of the XRD instrument or these oxides have entered in the intergranular amorphous glassy phase. Minor peaks of SiO_2 (ICDD File No: 00-085-0462) and $YO_{1.335}$ (ICDD File No: 00-039-1065) were also identified, which are intermediate phases for the formation of Y_2SiAlO_5N. These XRD results compare well with those reported by Janney et al.[15] Further, the as-obtained sialon ceramic exhibits a hardness of 14 GPa and fracture toughness of 3.95 MPa m$^{1/2}$, is also in good agreement with the values reported in literature.[25,26] A "green" crucible made of β-$Si_4Al_2O_2N_4$ precursor mixture containing treated AlN pow-

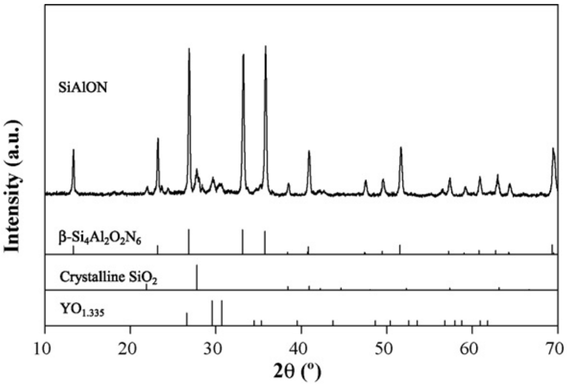

Fig. 6. XRD pattern of β-$Si_4Al_2O_2N_6$ sintered at 1675 °C for 4 h in nitrogen atmosphere of about 800 Torr pressure. The treated and washed AlN (WT-AlN) was used along with α-Al_2O_3, α-Si_3N_4, and Y_2O_3 as starting powders for synthesis of β-$Si_4Al_2O_2N_6$.

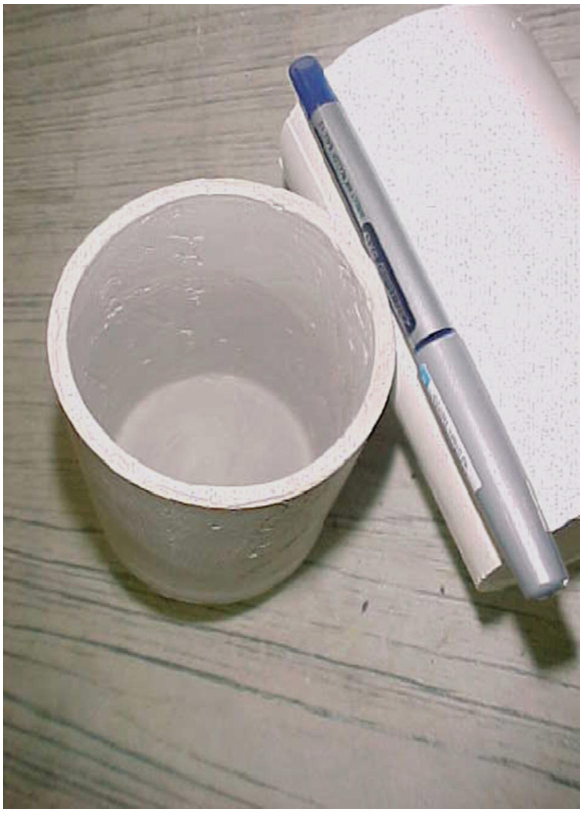

Fig. 7. A 500 mL thin-wall crucible consolidated by aqueous gelcasting from a slurry containing 50 vol.% of the β-$Si_4Al_2O_2N_6$ precursor mixture, including treated and washed AlN (TW-AlN) powder.

der consolidated by aqueous gelcasting of a slurry containing 50 vol.% solids loading is shown in Fig. 7.

4. Conclusions

The present study showed that the surface of a high purity commercial AlN could be passivated against hydrolysis by treating it in an ethanol solution containing ortho-phosphoric acid and aluminium di-hydrogen phosphate at 80 °C for 24 h. The passivation process involved the formation of a surface phosphate monolayer using the required amount of coating agents or an excess (which can be washed away from the powder surface with ethanol). The phosphoric acid treated AlN powder was found to be stable in water for more than 72 h, enabling the successful aqueous processing of a precursor β-$Si_4Al_2O_2N_6$ multicomponent (TW-AlN + α-Si_3N_4 + α-Al_2O_3 + Y_2O_3) powder mixture. Thin-wall components could be easily consolidated by aqueous gelcasting and sintered for 4 h at 1675 °C to obtain β-SiAlON ceramics with very interesting final properties (bulk density of 3.07 g/cm^3, apparent porosity of 0.13%, water absorption capacity of 0.04%, a linear shrinkage of <16%, β-SiAlON content of >90%, a hardness of 14 GPa and a fracture toughness of 3.95 MPa m$^{1/2}$).

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