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Hydrolysis control of alumina and AlN mixture for aqueous colloidal processing of aluminum oxynitride

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Abstract

AlN powder, surface modified by phosphoric acid treatment was employed for the aqueous colloidal processing of Aluminum Oxynitride (AlON). The hydrolysis of AlN leads to the formation of $Al(OH)_3$ and NH_3. On mixing of alumina to the phosphoric acid treated AlN in aqueous medium this reaction reoccurred. The phosphoric acid shield around AlN particles is ruptured by alumina addition thus exposing AlN surface to hydrolysis reactions. Hence hydrolysis can be effectively controlled by providing a phosphoric acid treatment to the alumina, prior to its addition to AlN. AlON precursor mixture thus obtained can be successfully shaped by an aqueous slip casting process and sintered to phase pure AlON at 1925 °C for 2 h. Viscosity, pH, SEM, FTIR, and XRD measurements are employed to elucidate the effect of Al_2O_3 addition on surface modified AlN for colloidal processing of AlON.

Keywords: Aluminum Nitride; Hydrolysis; Aluminum Oxynitride; Surface modification

1. Introduction

Combinations of AlN and alumina are widely used for the syntheses of various compounds such as Aluminum Oxynitride [1–11], MgAlON [12–14], SiAlON [15–17], and their composites [18–30]. The synthesis route generally employs organic solvents as the dispersing medium due to the tendency of AlN to undergo hydrolysis reaction in aqueous medium, which results in the formation of AlOOH followed by $Al(OH)_3$ and NH_3 [31–35] according to the following reactions:

$$AlN + 2H_2O \rightarrow AlOOH + NH_3 \quad (a)$$

$$NH_3 + H_2O \leftrightarrow NH_4{}^+ + OH^- \quad (b)$$

$$AlOOH + H_2O \rightarrow Al(OH)_3 \quad (c)$$

It is therefore difficult to maintain the molar ratio between Al_2O_3 and AlN in order to obtain the required phase stoichiometry of the final product. Moreover, aqueous colloidal shaping processes require slurries with high solid loading content. In such processes that involve AlN powder, the hydrolysis reaction of AlN consumes the water from the slurry and transforms it into a high viscous paste, unsuitable for casting. Employing organic solvents as a processing medium and compaction as a shaping technique generally alleviates the said problems. The colloidal processing route, by virtue of its advantages provides defect free products with complex shaping made simple. This is also a cost effective technique for the fabrication of ceramic materials.

The hydrolysis of AlN was effectively used by Kosmac and co-workers. They used this to develop the colloidal based consolidation technique known as hydrolysis assisted solidification [34,36,37]. This technique has further been used for the fabrication of dense β-SiAlON by employing a mixture of treated and untreated AlN powders [38]. Miller and Kaplan added AlN powder into aqueous alumina slurry and limited their milling time for 2 h after the addition of AlN to avoid its hydrolysis reaction [9], for the synthesis of AlON.

The hydrolysis of AlN has been effectively controlled or the incubation period of AlN in water has been prolonged by treating AlN with various surface modifiers such as butyl acid phosphate, ammonium phosphate, poly phosphoric acid, aluminum dihydrogen phosphate, ortho phosphoric acid, citric acid, sebacic acid and stearic acid etc. [10,39–45]. The passivated powders thus obtained were further made to slurries

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of >76% solid loading in aqueous medium and the samples were casted and sintered successfully.

In the present work, the effect of addition of alumina on surface modified AlN in aqueous medium for the colloidal processing of AlON has been investigated. Samples of AlON were casted using this process, sintered and characterized for its phase and micro structural properties. The effectiveness of phosphoric acid treatment of AlN for surface passivation is examined in the presence of alumina and modified techniques are presented to retain the surface passivation of AlN, in order to enable the aqueous colloidal processing of AlON.

2. Experimental procedure

High purity alumina (SM8, Baikowski Chemie, France, d_{50} – 0.4 μ, BET surface area – 14 m^2/g) and AlN powders (Grade-C, H.C. Starck, Germany, d_{50} – 1.12 μ, BET surface area – 4.06 m^2/g) were used for the entire process.

2.1. Hydrolysis of AlN

As received AlN powder was dispersed in distilled water with 60 wt% solid loading using 1 wt% Darvan 821A (R.T.Vanderbilt Co., Inc., Norwalk, CT, USA) as a dispersant. Dispersion was carried out in a magnetic stirrer at ambient temperatures. The slurry was checked for pH and the viscosity was measured (MCR 51, Anton Paar GmbH, Austria) at 30 min interval until the slurry turned into a high viscous paste. The paste was dried at 50–60 °C and the powder was characterized for its micro structure by SEM (Hitachi, FEG SEM, Japan) and for the phase analysis by XRD (D8, Bruker, Germany). FTIR analysis (Spectrum GX, Perkin Elmer, U.S.A) was also carried out to elucidate the bond characteristics. For this characterization, 10 mm diameter and 0.1–0.2 mm thick pellets were compacted uniaxially at 10 tons load using a mixture of 200 mg KBr and 2 mg hydrolyzed AlN powders.

2.2. Surface modification of AlN

AlN was dispersed in distilled water containing 1–2 wt% ortho phosphoric acid (98% H_3PO_4, Qualigens, India) using Darvan 821A as a dispersant. Dispersion was carried out in a magnetic stirrer at 60–70 °C for 15 min. The excess water was filtered out from the slurry after the dispersion and the filtrate was dried at 50–60 °C for 24 h in air. The dried powder was characterized for its morphology by SEM. The dried powder was then made into slurry, with 60 wt% solid loading in water using Darvan 821A as a dispersant. The slurry was checked for its pH and the corresponding viscosity was measured every 30 min. The dried powder was further analyzed for phases by XRD and for functional groups by FTIR.

2.3. Addition of alumina in surface modified AlN

65–70 mol% of alumina that corresponded to the AlON ($Al_{23}O_{27}N_5$) composition was added to the surface modified AlN for all the done experiments. Aqueous slurry of alumina and AlN with 60 wt% solid content was prepared using Darvan 821A as a dispersant. The slurry was stirred in a magnetic stirrer for 5 h and the pH and viscosity was measured at every 30 min. The slurry was further dried at 50–60 °C and subjected to micro structural, FTIR and phase analyses.

2.4. Addition of surface modified alumina in surface modified AlN

Alumina was also subjected to surface modification as per the procedure followed for AlN and the AlON precursor slurries with 60 wt% solid loading was prepared using the surface modified AlN and alumina powders using Darvan 821 A as dispersant. The slurry was stirred in a magnetic stirrer for 5 h with periodic measurements of pH and viscosity. The slurry was further dried at 50–60 °C in air and subjected to SEM, FTIR and XRD analyses.

2.5. Shaping by slip casting

Aqueous suspensions of surface modified alumina and AlN were prepared with 76–80 wt% solid loading using Darvan 821A as a dispersant. The slurry was casted in a porous alumina mould and dried at ambient conditions for 24 h followed by drying at 80 °C for 24 h. Dried samples were then subjected to heat treatment at 500 °C for 2 h in air and further sintered at1925 °C in nitrogen atmosphere for 2 h. Sintered samples were characterized for their density by Archimedes principle and phase analysis by XRD.

3. Results and discussion

Fig. 1a and b shows the morphology of alumina and AlN respectively used for the processing. Alumina particles have size distribution in a narrow range and the average particle size is in the range of 200–400 nm while AlN particles were found to have a wider distribution of sizes ranging from 500 nm to 3 μm.

3.1. Hydrolysis of AlN

Fig. 2 shows the plot of pH and viscosity with time. The pH values of untreated AlN slurry started changing within the first 30 min confirming the vigorous tendency of AlN to hydrolysis forming AlOOH followed by $Al(OH)_3$ and NH_3. It was observed that the pH of initial slurry rises to 10.3 from 8.5 within 5 h due to the evolution of NH_3 from the hydrolysis reaction. The viscosity of the slurry also increased reaching a value of 10.6 mPa s from 2 mPa s. An abrupt change in viscosity was observed after 2 h. The change in viscosity is due to the consumption of water by AlN from the slurry for its hydrolysis to form AlOOH followed by $Al(OH)_3$.

Fig. 1c shows the microstructure of AlN that had undergone hydrolysis reaction and clearly indicates the presence of needle like boehmite particles on the surface. Most of the particles were covered with hydroxide whereas some particles remained unaffected.

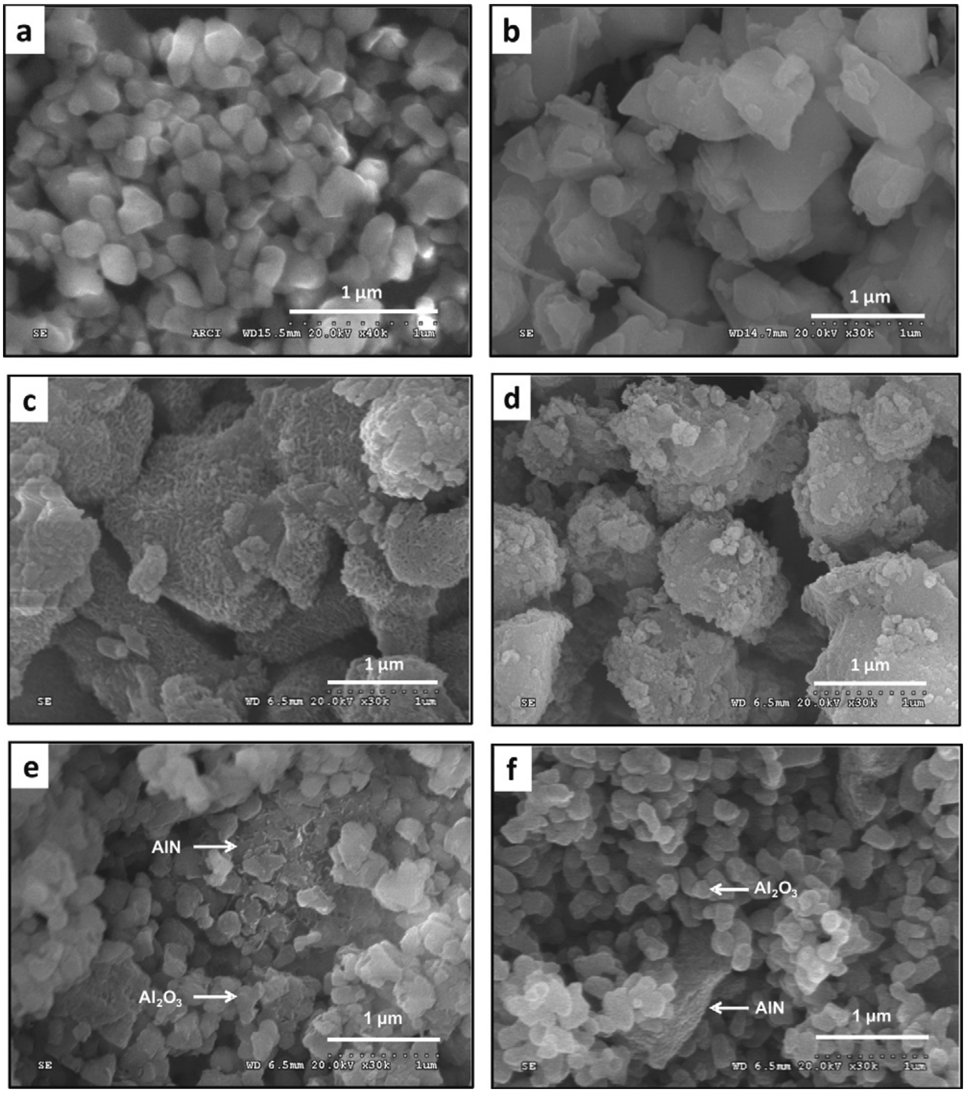

Fig. 1. Powder morphology of a) alumina – as received, b) AlN powder – as received, c) AlN – after hydrolysis, d) AlN – after surface modification, e) treated AlN with untreated alumina, f) treated AlN with treated alumina.

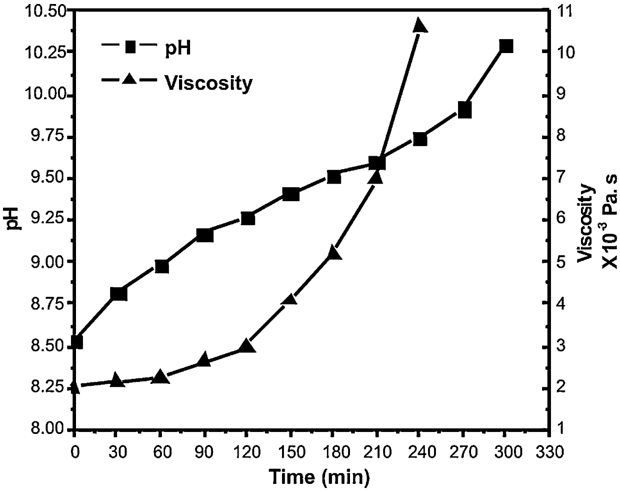

Fig. 2. Effect of hydrolysis of AlN on pH and Viscosity in aqueous slurry.

Fig. 3a schematically represents the hydrolysis reaction of AlN resulting in the formation of AlOOH and Al $(OH)_3$ compounds, and release of NH_3. The reaction is initiated at the surface of AlN and proceeds towards the core of the particle. The extension of the reaction mainly depends on the amount of water available and the exposure period.

3.2. *Surface modification of AlN*

The phosphoric acid treatment on AlN particles primarily results in the formation of phosphate bonds at the AlN surface. This phosphate bond provides complete surface coverage passivating the AlN particle from hydrolysis.

Fig. 4a compares the change in pH of slurries made of treated and untreated AlN powders with 60% solid loading. As mentioned earlier, the pH of received AlN increased rapidly and reached 10.3 in 5 h whereas the pH of the surface modified AlN remained constant within 7.5–7.8 even after 30 h of residence period in water. Viscosity results (Fig. 4b) also show similar

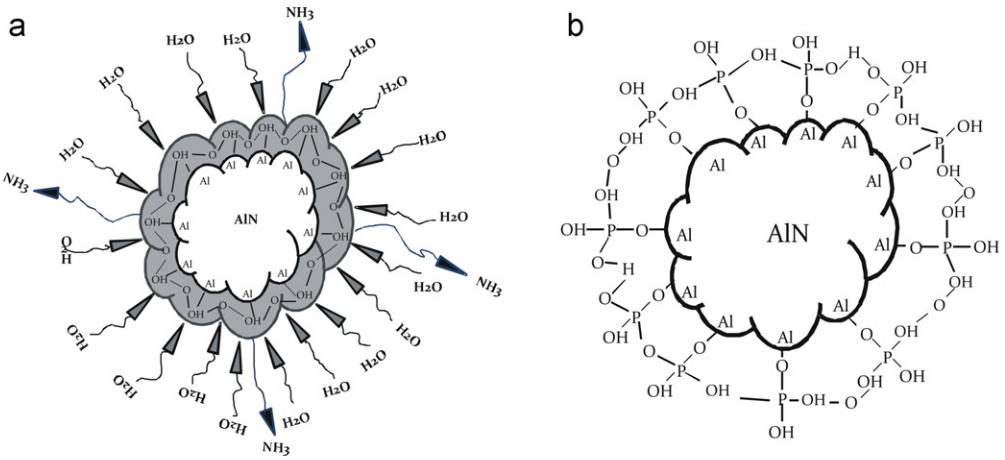

Fig. 3. Schematic of AlN particle a) during hydrolysis and b) after surface modification.

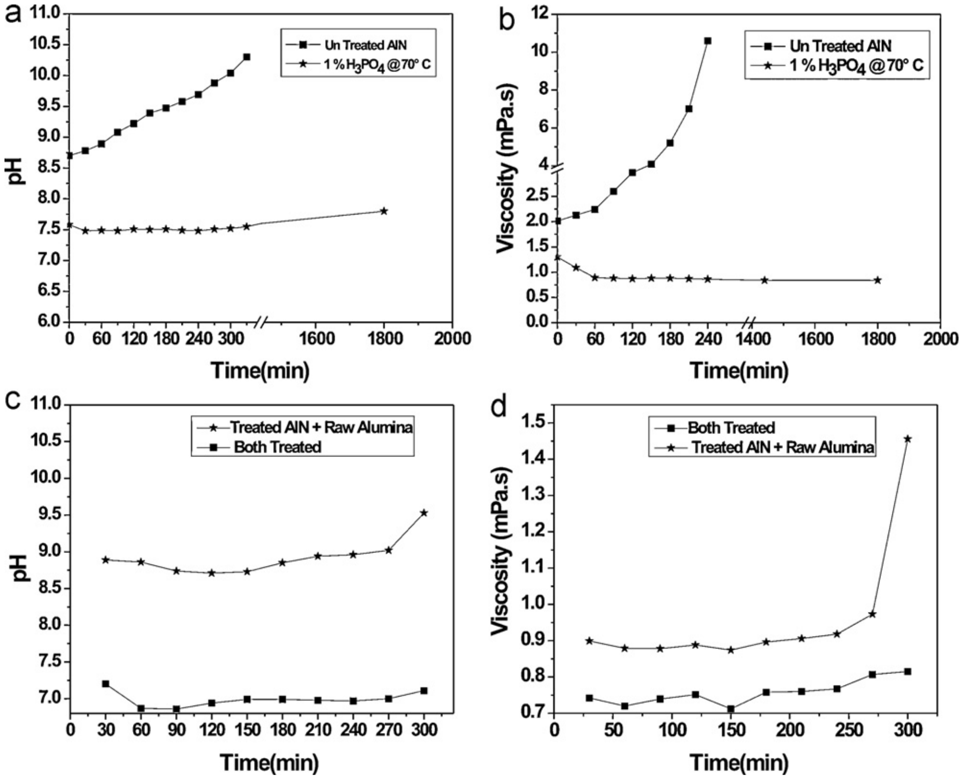

Fig. 4. Effect on pH (a) and viscosity (b) of a slurry containing as received and surface modified AlN and the effect on pH and the effect on pH (c) and viscosity (d) of a slurry of AlON composition containing treated AlN and untreated/ treated alumina.

trend to that of pH, where a rapid increase is observed on untreated powders while the viscosity remained constant for 30 h for the surface modified AlN powders indicating its resistance to hydrolysis. The morphology of AlN agglomerates as observed in SEM (Fig. 1d) indicates no evidence of needle shaped particles. This confirms the efficiency of the surface modification process.

Fig. 3b schematically shows the coverage of AlN by phosphate shield consisting of various possible compounds such as $P(OAl)(OH)_3$, $P(OAl)_2(OH)_2$, and $P(OAl)(OP)(OH)_2$ [39]. This hydrophilic layer surrounds the AlN surface and sufficiently prolongs the period of hydrolysis to enable aqueous slip casting process.

3.3. Effect of alumina on surface modification of AlN

The surface modified AlN powders were used for synthesis of AlON and precursor composition with 32 mol% AlN was made into aqueous slurry having 60% solid loading. The plot on pH vs. time as presented in Fig. 4c indicating an initial pH of 9.0 that remained constant for about 4 h. Beyond this period the pH of the slurry increased due to the evolution of ammonia from the hydrolysis reactions of surface modified AlN. This indicates that the protective shield around AlN has been ruptured after the addition of alumina leading to AlN hydrolysis. Viscosity measurements also indicated a similar trend as shown in Fig. 4d, confirming that the surface passivation of AlN is weakened after the addition of alumina. One plausible mechanism for this observation could be the affinity of alumina particles towards phosphate bonding. The precursor slurry of AlON was transformed to a paste due to the hydrolysis of surface modified AlN powder and made unsuitable for casting. In order to circumvent this problem, an attempt was made to modify the alumina particles using a similar phosphoric acid treatment prior to its addition with surface modified AlN powders. It can be observed that the pH and the viscosity remained constant after the addition of surface modified alumina with surface modified AlN showing the necessity of the surface treatment for alumina.

Fig. 1e shows the microstructure of AlON precursor powder containing treated AlN and untreated alumina and Fig. 1f shows the precursor powder containing treated AlN and treated alumina. The formation of needle shaped structures on the surface of treated AlN (Fig. 1e) proves that the surface modified AlN has under gone hydrolysis after the addition of alumina. But, the needle formation was not found (Fig. 1f) on the surface of treated AlN when the alumina was added after its surface treatment. This shows the requirement of surface treatment for alumina to protect the phosphate shield of AlN and to enable the aqueous processing of AlON precursor mixture.

Fig. 5 schematically represents the proposed mechanism of controlling the hydrolysis of surface modified AlN after the addition of alumina. Fig. 5a shows the rupture of AlN phosphate shield after the addition of alumina due to the affinity of latter towards phosphate bonds. This occurrence exposed the surface of AlN to water and leads it to hydrolysis. Therefore to prevent the rupture of AlN phosphate shield by alumina, it is necessary to arrest the inclination tendency of alumina towards phosphate bonding. This has been achieved by conducting

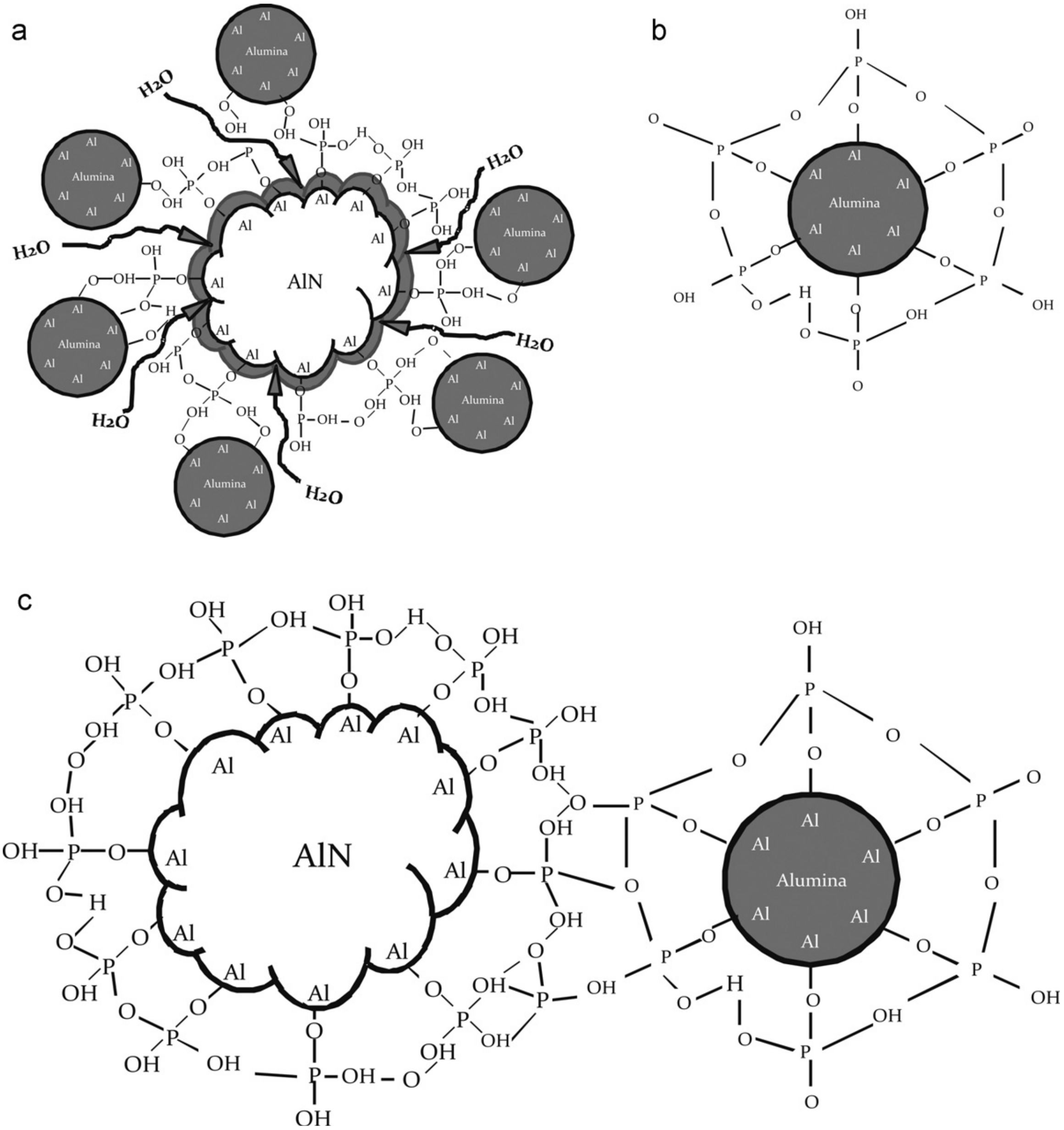

Fig. 5. (a) Rupture of AlN shield by alumina, (b) surface Modified alumina, (c) mixture of alumina and AlN after their surface modification.

another phosphoric acid treatment for alumina prior to its addition to treated AlN. The surface treatment of alumina saturates its surface with phosphate bonds (Fig. 5b) and arrests its inclination tendency towards the phosphate shield of AlN. The rupture of AlN phosphate shield by alumina was thus inhibited as shown schematically in Fig. 5c.

Fig. 6 compares the XRD patterns of received AlN (Fig. 6a), AlN after hydrolysis (Fig. 6b), surface modified AlN powder (Fig. 6c), AlON precursor mixture consisting surface modified AlN and raw alumina powders (Fig. 6d) and the AlON precursor mixture consisting surface modified AlN and surface modified alumina powders (Fig. 6e). Fig. 6b indicates the boehmite [AlOOH] and traces of bayerite [$Al(OH)_3$] compounds formed during the hydrolysis of AlN. The formation of boehmite and bayerite compounds depends on the exposure period of AlN to water and the amount of water used for the reaction. However, no such compounds were formed in surface modified AlN as shown in Fig. 6c and it can be observed that the peaks of surface modified AlN are exactly matching with the peaks correspond to the received AlN powder. This shows that the AlN has achieved the ability to survive against hydrolysis after phosphoric acid treatment. However, the ability was weakened when it was mixed with the received alumina powder during aqueous AlON processing. Fig. 6d corresponds to this mixture and shows the presence of boehmite and bayerite compounds indicating the disintegration of AlN due to hydrolysis and proves that the protection shield of AlN was not sustained after the addition of received alumina. The peaks corresponding to boehmite were not dominant which may due to its lower concentration with respect to alumina, but its existence was confirmed through FTIR investigations as discussed later on. Moreover, peaks corresponding to bayerite compounds can be seen in Fig. 6d which was formed due to the hydrolysis of AlN to an extent but the major parts of bayerite were presumably from the surface of the raw alumina [46]. And when the AlON precursor mixture is processed in aqueous medium using surface modified AlN and alumina powders, boehmite and bayerite compounds are not formed, as can be observed from Fig. 6e. The pattern showed only the peaks corresponding to alumina and AlN phases indicating the stability of AlN against hydrolysis.

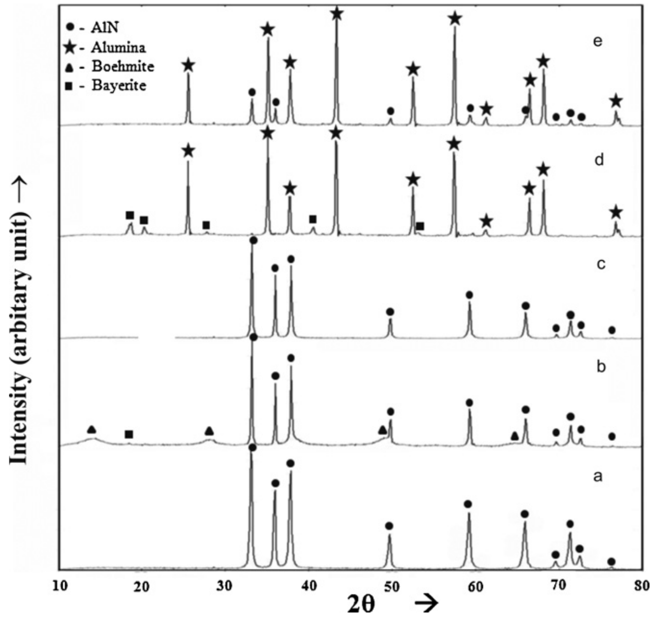

Fig. 6. XRD patterns of (a) as received AlN,(b) hydrolyzed AlN,(c) surface treated AlN,(d) treated AlN + raw alumina, (e) treated AlN + treated alumina.

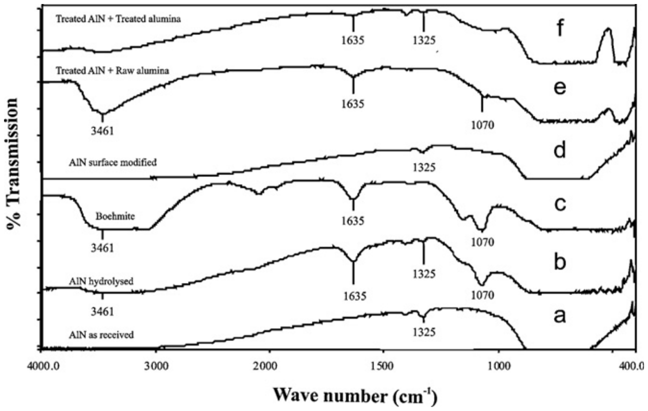

Fig. 7. FTIR patterns of (a) as received AlN, (b) hydrolyzed AlN, (c) surface treated AlN, (d) treated AlN + raw alumina, (e) treated AlN + treated alumina.

The results were further confirmed through FTIR analysis. The characteristic spectra of the respective powders are shown in Fig. 7 and the wave numbers corresponding to main peaks are specified in Table 1. Fig. 7a exhibits the IR spectrum of received AlN powder with a broad peak in the region between 500 and 900 cm^{-1} and a small absorption peak at 1325 cm^{-1}. These peaks correspond to Al–N bonds [47]. Fig. 7b shows the pattern of AlN powder subjected to hydrolysis for 5 h. This pattern shows peaks at 1070 cm^{-1}, 1635 cm^{-1} and a broad band vibration in between 3050 and 3500 cm^{-1} in addition to the characteristic Al–N bonds. The peak at 1070 cm^{-1} corresponds to Al–OH bond and the peak at 1635 cm^{-1} corresponds to water. The peak corresponding to water proves the presence of another hydrate compound in the hydrolyzed AlN. The broad peak in between 3050 and 3500 cm^{-1} corresponds to $Al(OH)_3$ compounds [48]. To confirm the additional peaks that appear for hydrolyzed AlN corresponding to the group of Al–OH bonds, commercially available boehmite powder (Disperal, Sasol GmbH, Germany) was subjected to FTIR analysis (Fig. 7c). It can be observed that the additional peaks at 1070 cm^{-1}, 1635 cm^{-1} and in between 3050 and 3500 cm^{-1} for AlN after hydrolysis are matching with the characteristic boehmite peaks confirming that the additional peaks correspond to Al–OH bonds. But these additional peaks are absent in

Table 1
IR frequencies of alumina and AlN materials between 400 and 4000 cm^{-1} region.

Wave number (cm^{-1})	Species		Reference
500–900	Al–N	}	[47]
1325	Al–N		
1070	δA1–OH	}	[48]
1635	H_2O/OH of Boehmite		
3050–3500	$Al(OH)_3$		
3461	Bayerite	}	[46]

case of surface modified AlN as shown in Fig. 7d and is almost equivalent to the received AlN even after 30 h of dwell time in water. However, these additional peaks are reappearing (Fig. 7e) when the AlON composition is processed in aqueous medium. Though the composition was prepared with surface modified AlN to enable aqueous processing, the resistivity of AlN against hydrolysis was not sustained after the addition of raw alumina. The variation in pH (Fig. 4c), viscosity (Fig. 4d), microstructure of surface modified AlN (Fig. 1e) and the XRD pattern (Fig. 6d) confirm that the Al–OH formed after alumina addition (Fig. 7e) are due to the hydrolysis of surface modified AlN. There are no sharp peaks that correspond to boehmite and bayerite compounds for AlON composition containing surface modified alumina and AlN powders (Fig. 7f). This proves that the protection shield of AlN has not been collapsed after the addition of surface modified alumina. Also the presence of Al–N peak at 1329 cm^{-1} with less intensity owing to its reduced concentration proves the existence of aluminum nitride.

3.4. Processing of aluminum oxynitride

The surface modified powders of alumina and aluminum nitride were mixed in the molar ratio of 68:32 for the processing of AlON. The precursor mixture was made into slurry in water with solid loading up to 76 wt% and shaped by slip casting process. Fig. 8 shows the photograph of slip casted AlON sample.

The evolution of AlON phase formation in the slip casted samples with respect to their sintering temperature is shown in Fig. 9. It can be observed that the formation of AlON has already been started at 1725 °C showing more concentration compared to alumina and AlN. The approximate proportions of each phase and their variations based on the sintering temperatures are given in Fig. 9. When the sintering temperature is increased from 1725 °C to 1825 °C the AlON phase has enhanced to >96%. In addition, it can be observed that the alumina phase has been completely disappeared whereas the AlN phase is still exists for further reactions. This shows that the alumina has helped more in the formation of AlON than AlN at this temperature. At 1925 °C, the sample has attained 100% AlON formation and no peaks correspond to unreacted alumina and AlN are observed. The changes in densification of the casted samples with temperature are shown in Fig. 10. The samples had attained density above 96% of TD at 1725 °C and reached above 99% TD when they were sintered at 1925 °C for 2 h.

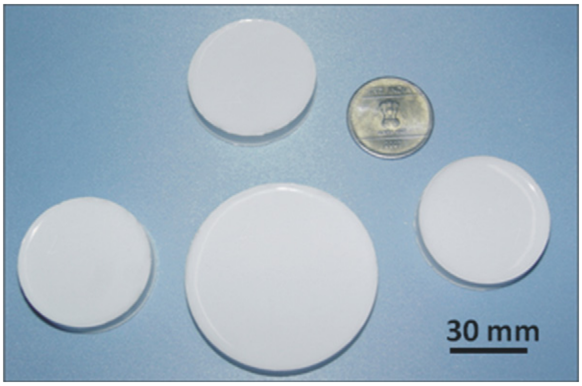

Fig. 8. Slip Casted AlON sample.

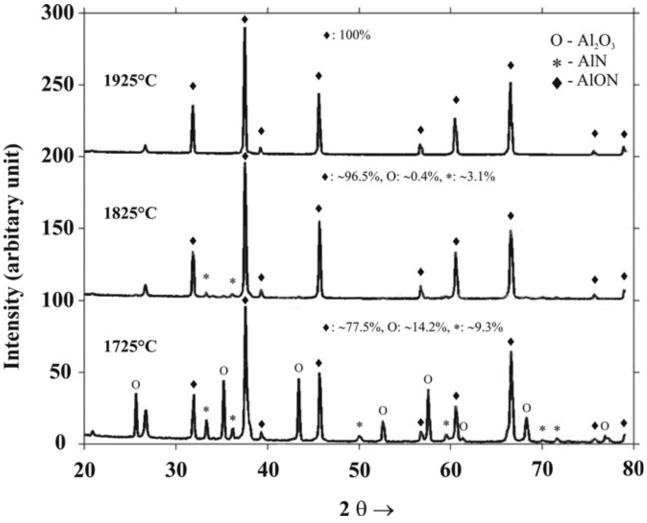

Fig. 9. XRD pattern of AlON sintered at 1725 °C, 1825 °C and 1925 °C 10. Fig. 9 microstructure of treated AlN surface after the addition of raw alumina (Fig. 9a) and surface modified alumina (Fig. 9b).

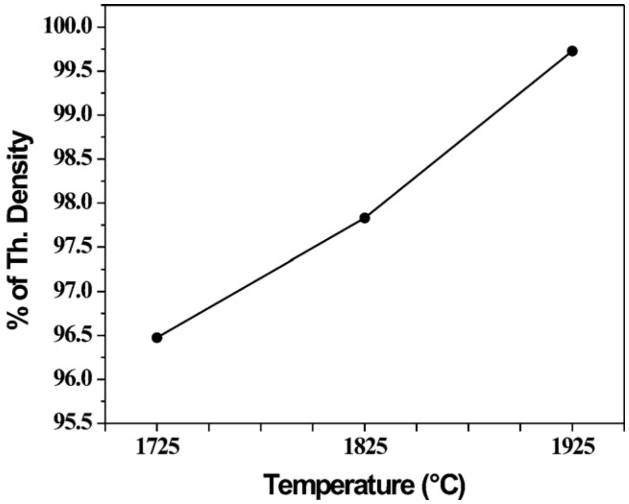

Fig. 10. Change in density of AlON vs. temperature.

4. Summary

The addition of alumina to phosphoric acid treated aluminum nitride powders resulted in the rupture of the passivating shield around AlN resulting in hydrolysis reactions leading to the formation of hydroxides. This has been effectively controlled by providing a phosphoric acid treatment for alumina powders prior to its addition to AlN. Viscosity and pH measurements confirmed the efficiency of process in preservation of the passivation shield. XRD and FTIR analysis confirmed the formation of hydrolysis products and their absence on surface modification. The treated raw materials were subjected to aqueous slip casting for the formation of phase pure and dense aluminum oxynitride.

References

[1] R. L. Gentilman, E.A. Maguire. L. E. Dolhert, Transparent Aluminum Oxynitride and Method of Manufacture, U.S. Pat. No. 4 720 362, Jan 19, 1988.

[2] J.W. McCauley, N.D. Corbin, Phase-relations and reaction sintering of transparent cubic aluminum oxynitride spinel (AlON), J. Am. Ceram. Soc. 62 (1979) 476–479.

[3] P. J. Patel, Processing and Characterization of Aluminum Oxynitride Ceramics, Ph.D dissertation, Johns Hopkins University, Baltimore, Maryland, USA (1999).

[4] G.A. Glide, P.J. Patel, J.C. Lasalvia, Method for Making Dense Polycrystalline Aluminum Oxynitride, U.S. Pat. No. 7 163 656 B1, Jan 16 (2007).

[5] P.J. Patel, G. Glide, J.W. McCauley, Transient Liquid Phase Sintering of Aluminum Oxynitride (AlON), U.S. Pat. No. 7 045 091 B1, May 16, 2006.

[6] R. Bachelard, J.P. Disson, B. Morlhon, Optically Transparent Gamma – Aluminum Oxynitride Powders and Ceramic Articles Shaped Therefrom, U.S. Pat. No. 5 688 730 Nov 18, 1997.

[7] W. Xidong, W. Fuming, L. Wenchao, Synthesis, microstructures and properties of γ-aluminium oxynitride, Mater. Sci. Eng. A 342 (2003) 245–250.

[8] S. Bandyopadhyay, G. Rixecker, F. Aldinger, S. Pal, K. Mukherjee, H.S. Maiti, Effect of Reaction Parameters on AlON Formation from Al_2O_3 and AlN, J. Am. Ceram. Soc. 85 (2002) 1010–1012.

[9] L. Miller, W.D. Kaplan, Water-based method for processing of aluminum oxynitride (AlON), Int. J. Appl. Ceram. Technol. 5 (2008) 641–648.

[10] R. Senthil Kumar, K. Rajeswari, B. Praveen, U.S. Hareesh, R. Johnson, Processing of aluminum oxynitride through aqueous colloidal forming techniques, J. Am. Ceram. Soc. 93 (2010) 429–435.

[11] N.D. Corbin, Aluminum oxynitride spinel: a review, J. Eur. Ceram. Soc. 5 (1989) 143–154.

[12] A. Granon, P. Goeuriot, F. Thevenot, J. Guyader, P. L' Haridon, Y. Laurent, Reactivity in the Al_2O_3–AlN–MgO System. The MgAlON spinel phase, J. Eur. Ceram. Soc. 13 (1994) 365–370.

[13] A. Granon, P. Goeuriot, F. Thevenot, Aluminum magnesium oxynitride: a new transparent spinel ceramic, J. Eur. Ceram. Soc. 15 (1995) 249–254.

[14] O. Morey, P. Goeuriot, MgAlON spinel structure: a new crystallographic model of solid solution as suggested by ^{27}Al solid state NMR, J. Eur. Ceram. Soc. 25 (2005) 501–507.

[15] N.C. Acikbas, E. Suvaci, H. Mandal, Fabrication of functionally graded SiAlON ceramics by tape casting, J. Am. Ceram. Soc. 89 (2006) 3255–3257.

[16] F. Ye, C. Liu, Y. Zhou, Q. Meng, Microstructure and properties of self-reinforced—α sialon ceramics doped with Lu_2O_3, Mater. Sci. Eng. A 496 (2008) 143–149.

[17] X. Xu, M.I.L.L. Oliveira, R. Fu, J.M.F. Ferreira, Effect of dispersant on the rheological properties and slip casting of concentrated sialon precursor suspensions, J. Eur. Ceram. Soc. 23 (2003) 1525–1530.

[18] Y.W. Kim, H.C. Park, Y.B. Lee, K.D. Oh, R. Stevens, Reaction sintering and micro structural development in the system Al_2O_3–AlN, J. Eur. Ceram. Soc. 21 (2001) 2383–2391.

[19] A. Maghsoudipour, M.A. Bahrevar, J.G. Heinrich, F. Moztarzadeh, Reaction sintering of AlN–AlON composites, J. Eur. Ceram. Soc. 21 (2005) 1067–1072.

[20] X. Wang, L. Gao, G. Li, W. Li, Synthesis of TiN/AlON composite ceramics, J. Univ. Sci. Technol. Beijing 10 (2003) 49–53.

[21] N.H. Kim, Q.D. Fun, K. Komeya, T. Meguro, Phase relation and sintering behavior in the pseudo ternary system AlN–Y_2O_3–Al_2O_3, J. Am. Ceram. Soc. 79 (1996) 2645–2651.

[22] Y.W. Kim, Y.W. Oh, S.Y. Yoon, R. Stevens, H.C. Park, Thermal diffusivity of reaction—sintered AlON/Al_2O_3 particulate composites, Ceram. Int. 34 (2008) 1849–1855.

[23] P. Tabary, C. Servant, J.A. Alary, Microstructure and phase transformations in the AlN–Al_2O_3 pseudo–binary system, J. Eur. Ceram. Soc. 20 (2000) 913–926.

[24] I.L. Tangen, Y. Yu, T. Grande, R. Hoier, M.A. Einarsrud, Phase relation and microstructural development of aluminum nitride–aluminum nitride poly composites in the aluminum nitride–alumina–yttria system, J. Am. Ceram. Soc. 87 (2004) 1734–1740.

[25] P. Goeuriot, F.L. Fievez, D.G. Launay, F. Thevenot, Alumina–γ-AlON composites: chemical and microstructural effects of sintering Y_2O_3 addition, J. Eur. Ceram. Soc. 10 (1992) 405–413.

[26] F.Y.C. Boey, X.L. Song, Z.Y. Gu, A. Tok, AlON phase formation in a tape—cast Al_2O_3/AlN composites, J. Mater. Proc. Tech. 89–90 (1999) 478–480.

[27] D. Djenkal, D. Geouriot, F. Thevenot, SiC-reinforcement of an Al_2O_3–γ-AlON composite, J. Eur. Ceram. Soc. 20 (2000) 2585–2590.

[28] S.R. Jansen, H.T. Hintzen, R. Metselaar, Phase Relation in the BaO–Al_2O_3–AlN system: materials with the ß-alumina structure, J. Sol. Stat. Chem. 129 (1997) 66–73.

[29] F. Boey, L. Cao, K.A. Khor, A. Tok, Phase reaction and sintering behavior of a Al_2O_3–20 wt% AlN–5 wt% Y_2O_3 system, Acta. Mater. 49 (2001) 3117–3127.

[30] R.E. Leahman, A.P. Tomsia, Reactions of Ti and Zr with AlN and Al_2O_3, Acta. Metall. Mater. 40 (1992) S75–S83.

[31] P. Bowen, J.G. Highfield, A. Mocellin, T.A. Ring, Degradation of aluminum nitride powder in an aqueous environment, J. Am. Ceram. Soc. 73 (1990) 724–728.

[32] S. Fukumoto, T. Hookabe, H. Tsubakino, Hydrolysis behavior of aluminum nitride in various solutions, J. Mater. Sci. 35 (2000) 2743–2748.

[33] A. Kocjan, K. Krenel, T. Kosmac, The influence of temperature and time on the AlN powder hydrolysis reaction products, J. Eur. Ceram. Soc. 28 (2008) 1003–1008.

[34] S. Novak, T. Kosmac, Preparation of alumina ceramics from aqueous suspensions employing the hydrolysis of aluminum nitride, J. Mater. Res. 17 (2002) 445–450.

[35] K. Krnel, T. Kosmac, Reactivity of AlN powder in an aqueous environment, Eng. Mater. 264–268 (2004) 29–32.

[36] S. Novak, T. Kosmac, K. Krnel, G. Drazic, Principles of the hydrolysis assisted solidification (HAS) process for forming ceramic bodies from aqueous suspension, J. Eur. Ceram. Soc. 22 (2002) 289–295.

[37] S. Novak, T. Kosmac, Interactions in aqueous Al2O3–AlN suspensions during the HAS process, Mater. Sci. Eng. A256 (1998) 237–242.

[38] I. Ganesh, N. Thiyagarajan, D.C. Jana, P. Barick, G. Sundararajan, J.M. Ferreira, Dense-SiAlONs consoilidated by a modified hydrolysis-assisted solidification route, J. Eur. Ceram. Soc. 28 (2008) 879–885.

[39] M. Oliveira, S. Olhero, J. Rocha, J.M.F. Ferreira, Controlling hydrolysis and dispersion of AlN powders in aqueous media, J. Colloid Interface Sci. 261 (2003) 456–463.

[40] K. Krenel, T. Kosmac, Protection of AlN against hydrolysis using Aluminum dihydrogen phosphate, J. Eur. Ceram. Soc. 21 (2001) 2075–2079.

[41] M. Uenishi, Y. Hashizume, Yokote, Aluminum nitride powder having improved water resistance, U.S. Pat. No. 4 923 689, May 8, 1990.

[42] K. E. Horward, Method for aqueous processing of AlN and compositions therefrom, U.S. Pat. No. 5 234,676, August, 1993.

[43] K. Krnel, T. Kosmac, Reactivity of aluminum nitride powder in dilute inorganic acids, J. Am. Ceram. Soc. 83 (2000) 1375–1378.

[44] R. Metselaar, R. Reenis, M. Chen, H. Gorter, H.T. Hintzen, Surface characterization of chemically treated aluminium nitride powders, J. Eur. Ceram. Soc. 15 (1995) 1079–1085.

[45] I. Ganesh, N. Thiyagarajan, G. Sundararajan, S.M. Olhero, J.M.F. Ferreira, A non-aqueous processing route for phosphate-protection of AlN powder against hydrolysis, J. Eur. Ceram. Soc. 28 (2008) 2281–2288.

[46] D.H. Lee, R.A. Condrate Sr., An FTIR spectral investigation of the structural species found on alumina surfaces, Mater. Lett. 23 (1995) 241–246.

[47] E. Ponthieu, P. Grange, B. Delmon, L. Lonnoy, L. Leclercq, R. Bechara, J. Grirnblot, Proposal of a composition model for commercial A1N powders, J. Eur. Ceram. Soc. 8 (1991) 233–241.

[48] Ph. Colomban, Structure of oxide gels and glasses by infrared and Raman scattering, J. Mater. Sci. 24 (1989) 3002–3010.