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Last Advances in Aqueous Processing of Aluminium Nitride (AlN) - A Review

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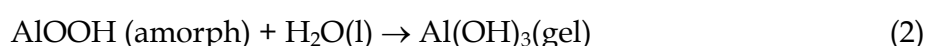
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1. Introduction

Aluminium nitride (AlN) is a ceramic material that has been intensively studied in the last years due to its good thermal conductivity (319 W/mK, theoretical value), low dielectric losses (8.8), small dielectric consumption ($\approx 4 \times 10^4$), a thermal expansion coefficient matching that of silicon, together with other physical properties that make AlN to be the most interesting substrate material for highly integrated microelectronic units (Greil et al., 1994; Iwase et al., 1994; Knudsen, 1995; Prohaska and Miller, 1990; Sheppard, 1990). The most recent breakthroughs were achieved in the processing science field of the AlN, namely on: (i) replacing of the traditionally used organic solvents by water; and (ii) decreasing the sintering temperatures AlN powder compacts through appropriately selecting the sintering additives and process optimization.

Aqueous colloidal processing has been pursued by many authors along the most recent years as an alternative to alcoholic or other flammable and costly dispersion media. The advantages of aqueous processing are the healthier and more environmentally friend production at lower and more competitive costs, which enables to increase and diversify the applications for the nitride-based ceramics. However, nitride powders are susceptible to hydrolysis, what is particularly true in the case of aluminium nitride (AlN) (Bellosi et al., 1993; Osborne & Norton, 1998; Reetz et al., 1992). In fact, when AlN powder is hydrolysed by water, undesirable aluminium hydroxydes are formed on the surface of particles, with a concomitant increase of the oxygen content and the production and release of ammonia. Accordingly, an amorphous layer composed by AlOOH is initially formed at the surface of AlN particles, which then transforms to bayerite, $\text{Al}(\text{OH})_3$, according to the following reactions:



The resultant hydroxyl ions (OH^-) tend to raise the pH of the suspension. The increasing rate of pH is dependent on temperature and initial pH value. Under strong acidic conditions ($\text{pH} \leq 3$), some authors have even reported the need of a certain incubation time for hydrolysis to start, while accelerated hydrolysis can be expected for $\text{pH} > 7$ (Fukumoto et al., 2000; Krnel et al. 2000; Oliveira et al., 2003; Reetz et al., 1992; Shan et al, 1999). According to this, recently Kocjan (Kocjan et al., 2011) presented a detailed study about the reactivity of AlN powder in diluted aqueous suspensions in the temperature range 22–90 °C in order to better understand and control the process of hydrolysis. The authors conclude that hydrolysis rate significantly increased with higher starting temperatures of the suspension, but was independent of the starting pH value; however, the pH value of 10 caused the disappearance of the induction period. Furthermore, the authors shown that the chemical reaction at the product-layer/un-reacted-core interface was the rate-controlling step for the second stage of the hydrolysis in the temperature range 22–70 °C, for which the calculated activation energy is 101 kJ/mol; whereas at 90 °C, the diffusion through the product layer became the rate-controlling step. Since there is a continuous formation of ammonia during the hydrolysis, the as created basic conditions approach the isoelectric point (pH_{iep}) of the aluminium hydroxides rich surfaces promoting flocculation. Finally, gelling of the $\text{Al}(\text{OH})_3$ reaction product gives rise to a rigid network. Therefore, for a successful aqueous processing one must overcome the hydrolysis of powders' surface that degrades the nitrides by forming hydroxides and releasing ammonia gas bubbles in the suspension and increase the pH of the dispersing media. The gas bubbles trapped in the suspension and in the green bodies act like strength-degradation flaw populations, reducing the density and the general properties of the ultimate products. Other consequences of hydrolysis reactions include an increase of pH and the destabilization of the suspensions leading to structural and compositional inhomogenities.

On the other hand, the natural enrichment of the surface of nitride particles in oxides may be deleterious for sintering ability and, consequently, for their most characteristic properties, such as the thermal conductivity of AlN. Considering these difficulties, the processing of nitride-based ceramics traditionally involves a previous homogenization of the powders in organic media, followed by consolidation of the green parts via uniaxial and/or isostatic pressing, which have strong limitations in terms of the ability to form complex shapes and achieving a high degree of homogeneity of particle packing. Contrarily, colloidal shaping techniques have the capability to reduce the strength-limiting defects when comparing with dry pressing technologies (Lewis, 2000). Besides traditional processing methods, such as slip casting, tape casting, pressure casting and injection moulding, some new colloidal forming technologies have been developed in the past decade for the near-net-shape forming of complex ceramic parts, including gel-casting, freeze forming, hydrolysis assisted solidification, direct coagulation casting, temperature induced forming, etc. The possibility of application of such performing techniques on the processing of AlN ceramics would broaden their field of application, while keeping ceramics quality higher than those produced by the traditional pressing techniques, turning the materials more commercially competitive. The key controlling factor for the production of reliable ceramic components through colloidal processing is the obtaining of high concentrated and low viscous suspensions. Thus, the work here presented was focused on the preparation of these proper suspensions facing the solid/liquid interfacial reactions and the mutual interactions between the dispersed particles in the suspending aqueous media. The suspensions obtained could then be used for the consolidation of complex-shaped bodies by different

techniques, which could be pressureless sintered at relatively low temperatures. The main goals achieved were the obtaining of standard nitride-based aqueous suspensions that could be used to consolidate homogeneous and high dense green bodies by colloidal techniques, such as slip casting, tape casting, gel casting or to produce high packing ability granulated powders for dry pressing technologies. This enabled obtaining high density ceramic bodies using simpler and less expensive procedures while keeping the high standard valued for the desired final properties. Such achievements are expected to have a tremendous positive impact at both scientific and technological levels, enabling to replace the organic based solvents used in colloidal processing, which are much more volatile and require the control of emissions to the atmosphere, by the incombustible and non-toxic water. Therefore, many efforts have been made to protect AlN powder against hydrolysis, in order to facilitate storage and to make it possible to process and consolidate green bodies from aqueous suspensions (Egashira et al., 1991; Ehashira et al., 1994; Fukumoto et al., 2000; Kosmac et al., 1999; Krnel et al., 2000, Krnel et al., 2001; Shimizu et al., 1995; Uenishi et al., 1990). Most treatment processes involve coating the surface of AlN particles with long chain organic molecules, such as carboxylic acids, particularly stearic acid, or through use of cetyl alcohol, n-decanoic acid, dodecylamine acid and so on (Egashira et al., 1991; Ehashira et al., 1994). These organic substances are characteristically hydrophobic and thus prevent water from coming into contact with the surface of the protected particles, therefore hindering a good dispersion in water to be achieved even in the presence of organic or inorganic wetting agents, which cause the suspensions to foam. Another disadvantage of this process is that it involves the use of organic solvents that are flammable and dangerous to health, therefore, just transferring the use of this kind of solvents to an earlier step of the processing. Therefore, it is not surprising that more attractive approaches have been attempted to protect AlN surface powders by chemisorbing hydrophilic anions from acidic species such as phosphoric, H_3PO_4 , or silicic acids from aqueous media (Kosmac et al., 1999; Oliveira et al., 2003; Uenishi et al., 1990). The efficiency of H_3PO_4 in protecting aluminium from corrosion through anodization was already known to result on impermeable and low soluble phosphate complexes, preventing the reaction. H_3PO_4 also revealed to be very effective in protecting AlN powders dispersed in aqueous solutions for periods of days or even weeks (i.e., long incubation times for hydrolysis to occur). However, besides hydrolysis suppression, another important condition for successfully processing AlN ceramics from aqueous suspensions is the achievement of a high dispersion degree to enable the preparation of stable and highly concentrated suspensions. Such suspensions can then be used to consolidate AlN-based ceramics by different processing techniques such as tape casting and slip casting, or to granulate powders by freezing or spray drying for dry pressing technologies. A proper colloidal processing is essential for enhancing the reliability of the final components and decreasing their production costs.

It is known that the covalent bonds in AlN confer to the material a low diffusivity, which, in turn, demands for high sintering temperatures (1900-2000°C). The use of sintering aids is a common approach to enhance AlN densification at relatively lower temperatures (Baranda et al., 1994; Boey et al., 2001; Buhr & Mueller, 1993; Hundere & Einarsrud, 1996; Hundere & Einarsrud, 1997; Khan & Labbe, 1997; Qiao et al., 2003a; Qiao et al., 2003b; Virkar et al., 1989; Watari et al., 1999; Yu et al., 2002). Y_2O_3 and CaO are the most frequently used sintering additives for aluminium nitride, which provide low-melting point liquids on reacting with Al_2O_3 existing on the surface of AlN particles. These liquids crystallize on cooling to calcium aluminates for CaO or CaC_2 additives and yttrium aluminates for the Y_2O_3 additive.

However, considering the deleterious effects of oxygen on sintering ability and on the thermal conductivity of AlN, many efforts have been made towards finding alternative oxygen-free sintering aids. Moreover, other sintering conditions such as atmosphere, furnace, sintering schedule are also of crucial importance. The appropriate manipulation of these factors could eliminate major structural defects and, consequently, improve the thermal conductivity, which is the more important property of this material. In fact, the thermal conductivities of aluminium nitride often differ extremely from the theoretical value, because structural defects, such as pores and grain boundary segregations, as well as point defects within the AlN lattice all cause a considerable decrease of the thermal conductivity.

This chapter is a review of the last advances on processing AlN-based ceramics in aqueous media, which includes the methodologies for surface coating of the powder against hydrolysis, the preparation of high concentrated suspensions, the consolidation of ceramic parts by different colloidal shaping techniques, the characterization of the green samples and their sintering ability as a function of sintering aids under different atmospheres, including the analysis of the thermo dynamical aspects, and the characterization of the sintered samples.

2. Stability of AlN powders against hydrolysis

The hydrophobic treatment processes firstly used to protect the surface of the AlN particles prevent water from coming into contact with the surface of the protected particles (Binner et al., 2005; Egashira et al., 1991; Ehashira et al., 1994; Fukumoto et al., 2000; Zhang, 2002). However, such approaches present serious disadvantages as follows: (i) they involve the use of organic solvents that are flammable and dangerous to one's health; (ii) the protected hydrophobic powder cannot be dispersed in water without adding organic or inorganic wetting agents, which cause suspensions to foam; (iii) finally, the effectiveness of hydrolysis suppression was shown to depend on the thickness and solubility of the induced protection layer. Low concentrations of some weak to poorly dissociated acids, such as phosphoric, H_3PO_4 , or silicic acids in aqueous media, are known to result in a high protection efficiency of the surface of AlN powders for some days or even weeks (i.e., long incubation times) (Koh et al., 2000; Kosmac et al., 1999; Uenichi et al., 1990). In the particular case of H_3PO_4 , aluminium protection through anodisation is known to result on impermeable and low soluble phosphate complexes, preventing the reaction. However, this protection of the AlN is not stable for a long time and the powder does not stand water resistant after an energetic milling procedure or even under relatively high temperatures. In order to overcome these disadvantages another kind of pre-treatments involving a stronger temperature-induced chemical bond between the AlN surface and the phosphate species is most promising. A process for protecting AlN powders against hydrolysis reported by Krnel and Kosmac (Krnel & Kosmac, 2001) appeared to be very promising for these purposes. This protection process involves the use of aluminium phosphate groups to coat the surface of the AlN particles. The protection efficiency of phosphoric acid, acetic acid and a thermochemical treatment with aluminium dihydrogenophosphate solutions in shielding AlN particles from hydrolysis could be described by the evolution of the pH of the AlN aqueous suspensions, as well as, by the crystallinity of AlN particles after hydrolysis, as presented in Figure 1 (Oliveira et al., 2003; Olhero et al., 2004).

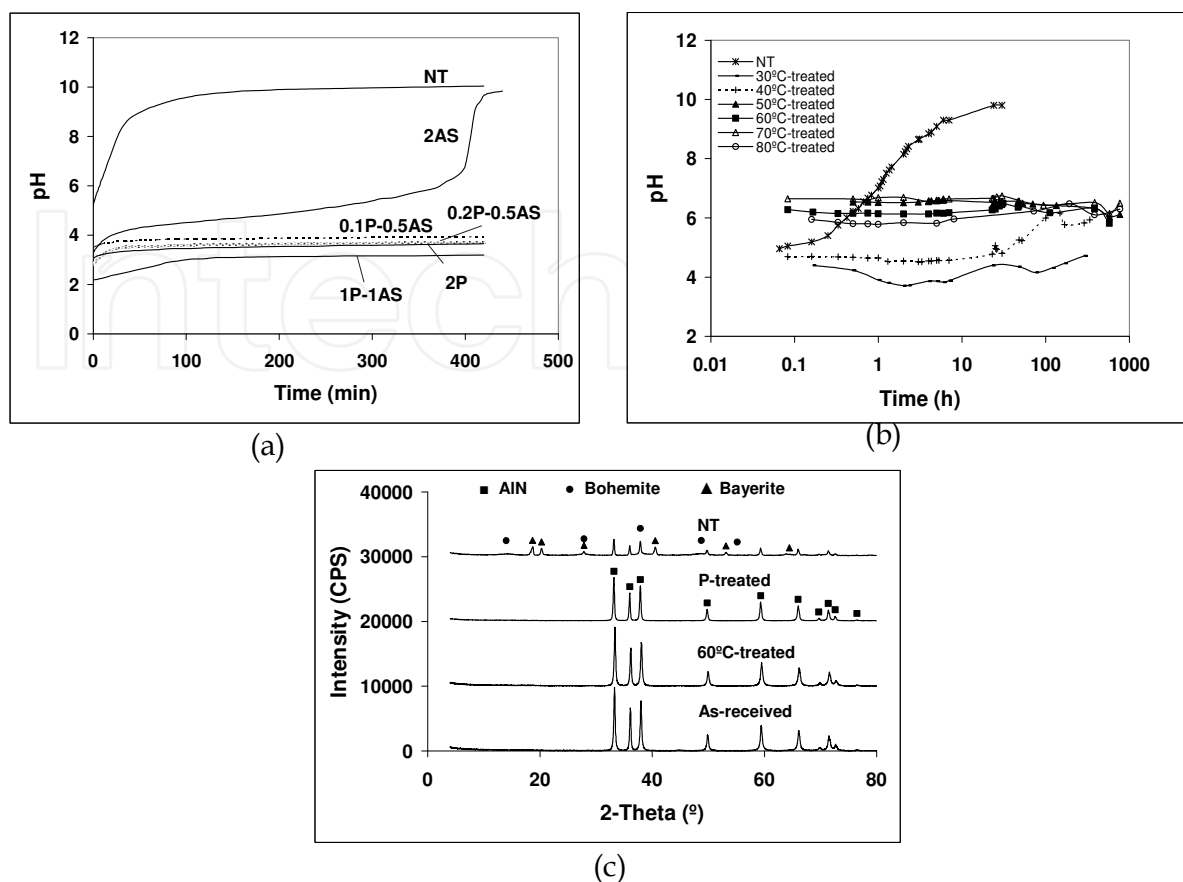


Fig. 1. Evolution of the pH as a function of time for 5-wt.% AlN aqueous suspensions after pre-treatment with: (a) H_3PO_4 and $\text{CH}_3\text{CO}_2\text{H}$ (NT, non-treated; P, H_3PO_4 -treated; AS- $\text{CH}_3\text{CO}_2\text{H}$ -treated); (b) $\text{Al}(\text{H}_2\text{PO}_4)_3$, varying the treatment temperature, (c) XRD patterns of AlN powders (as-received and protected by the different described methods) after hydrolysis tests.

In the case of aluminium dihydrogenophosphate, the influence of the treatment temperature is also presented in Fig. 1(b). The suspension prepared from a non-treated AlN powder, NT, suffered a fast pH increase with time (Fig. 1a), concomitant with a strong interfacial reaction leading to the formation of bayerite and amorphous boehmite as shown in Fig. 1(c). The protection of AlN surface with acetic, AS, and phosphoric, P, acids, resulted differently. Adding acetic acid was seen to retard the AlN hydrolysis reaction of the powder, but it did not efficiently avoid the reaction between particles' surface and water and pH steeply increased after about 6 and half hours. Adding H_3PO_4 alone resulted in good protection of the AlN powder particles toward water, as confirmed by the AlN-P-treated spectra that shows pure crystalline AlN. Although a good protection of the surface of the AlN particles could be assured by H_3PO_4 alone, the combination of H_3PO_4 and $\text{CH}_3\text{CO}_2\text{H}$ enhanced the dispersing behaviour of the protected powders, as will be shown in the next section. The effect of $\text{Al}(\text{H}_2\text{PO}_4)_3$ on protecting the AlN particles surface was quite similar to that of H_3PO_4 and $\text{CH}_3\text{CO}_2\text{H}$, regarding the low pH of the suspension (Fig. 1b) and the resulting pure crystalline AlN powders (Fig. 1c). A treatment temperature as low as 60°C was seen to result on a stronger bonding of the phosphate groups to the particles' surface, enabling

reliable protection over time. Above this temperature phosphate groups are more weakly bonded to the surface of the AlN particles and, as a result, their partial release into the solution will increase the ionic strength of the dispersing media, therefore decreasing the zeta potential. Due to that, 60°C was the temperature used to thermochemically treat the AlN powder for further investigation.

In order to better understand the interaction between the AlN powder and both H_3PO_4 and $\text{Al}(\text{H}_2\text{PO}_4)_3$ species the fully dried powders were analyzed by FT-IR in the 400–4000 cm^{-1} range (Fig. 2).

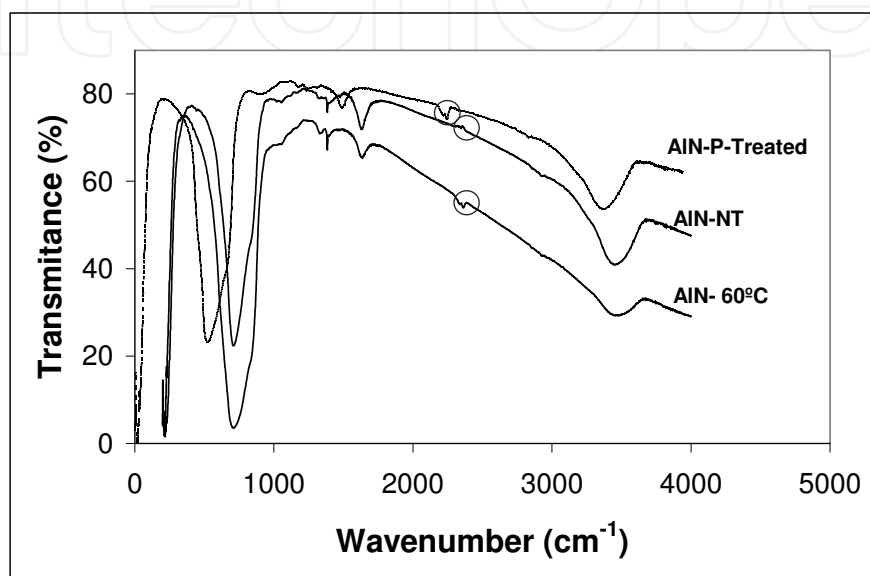


Fig. 2. FT-IR spectra of the AlN powder non-treated (NT), treated with H_3PO_4 (P-treated) and treated with $\text{Al}(\text{H}_2\text{PO}_4)_3$ at 60°C (AlN-60°C).

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 (Nyquist et al., 1997). The peaks observed in the spectra at the wave numbers of 1652 and 3485 cm^{-1} are known to be related with the C-O and H-O bonds vibration due to the surface adsorption of CO_2 and water vapour from the atmosphere, respectively. 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 intense band at 2000–3200 cm^{-1} due to different vibrations of phosphate molecule. Further, the spectrum of the AlN-non treated powder (AlN-NT) shows a transmittance peak located at 2366 cm^{-1} . This peak is characteristic of both Al-N and Al-O bond vibrations (Nyquist et al., 1997). Curiously, the H_3PO_4 -treated and $\text{Al}(\text{H}_2\text{PO}_4)_3$ -treated powder presents an absorption peak at the same wave number. This absorption peak is characteristic of the aluminum metaphosphate $[\text{Al}(\text{PO}_3)_3]_x$ (Richard et al., 1997). All of these results support the hypothesis that phosphate ions have been adsorbed at the AlN powder surface, although the chemical bonds involved cannot be stated unambiguously.

Since FT-IR was not conclusive and in order to check if $\text{Al}(\text{H}_2\text{PO}_4)_3$ is strongly attached than phosphoric acid, NMR and was evaluated. Figure 3 shows ^{31}P MAS NMR spectra obtained from H_3PO_4 -treated and $\text{Al}(\text{H}_2\text{PO}_4)_3$ -treated AlN powders. ^{31}P MAS NMR spectra displayed

a peak at *ca.* -10.7 ppm, consistent with the presence of P-O-Al environments, for example of the type P(OAl)(OH)₃ and, thus, supporting the covalent bonding of phosphate species to the AlN particles surface. The large full-width-at-half-maximum of this peak may arise due to the dispersion of other types of local ³¹P environments, for example P(OAl)₂(OH)₂ or even P(OAl)(OP)(OH)₂. The shorter dislocation of the large peak to more negative ppm values and the smoothness of the line spectra (less noisy) observed for the thermo-chemically AlN-Al(H₂PO₄)₃ treated powder suggests that stronger Al-O-P bonding has occurred, probably involving a higher amount of phosphates species attached at the AlN surface, such as P(OAl)₃(OH) or P(OAl)₄. This enhanced the stability of the AlN powder treated with Al(H₂PO₄)₃, in comparison to the H₃PO₄-treated one.

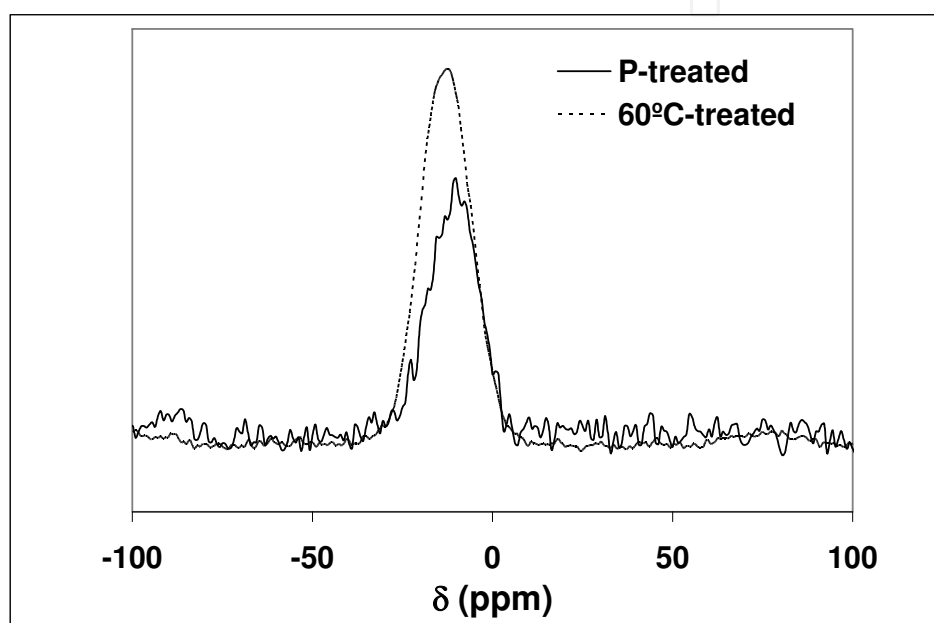
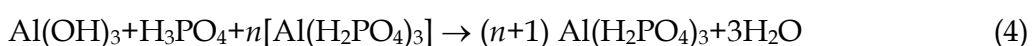


Fig. 3. ³¹P MAS NMR spectra obtained from the H₃PO₄ (P-treated) and Al(H₂PO₄)₃-treated (60°C-treated) AlN powders.

Based on these results, Ganesh (Ganesh et al., 2008) used the combination of H₃PO₄ and Al(H₂PO₄)₃ to passivate AlN powder against hydrolysis. The authors reported that the surface hydroxyl groups play a vital role in the formation of a protective layer against hydrolysis when the AlN powder is treated with H₃PO₄ and Al(H₂PO₄)₃. The reaction of an AlN surface with H₃PO₄ was expressed as follows:



In fact, the reaction occurs between Al(OH)₃ and H₃PO₄, and the Al(H₂PO₄)₃ is expected to perform a seeding action as Al(OH)₃ ultimately converts into Al(H₂PO₄)₃ by reacting with H₃PO₄ under the mild reaction conditions employed. It has been reported that approximately 1.1 mg of H₂PO₄⁻ is required to form a continuous single unimolecular monolayer on a square meter surface of AlN powder (Ganesh et al., 2008). Based on the results obtained a schematic representation of the monolayer coverage of H₂PO₄⁻ on the surface of an AlN particle was drawn and shown in Fig. 4.

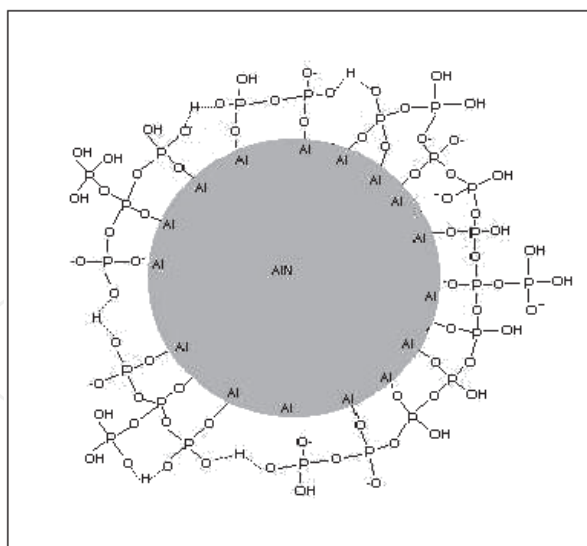


Fig. 4. Schematic representation of the phosphate layer chemisorbed onto the surface of an AlN powder particle.

Besides FT-IR and NMR, the authors (Ganesh et al., 2008) used XPS technique to confirm the presence of the protecting phosphate layer on the surface of AlN treated powder. The authors used four different powders to compare: A-AlN, AlN powder without treatment; T-AlN, AlN powder treated with H_3PO_4 and $\text{Al}(\text{H}_2\text{PO}_4)_3$; A-AlN-72h, AlN powder without treatment after 72 h immersion in water and T-AlN-72h, AlN powder with treatment after 72 h immersion in water. Figures 5 (a, b, c and d) shows the XPS photoelectron peaks of O 1s, N 1s, Al 2p, and P 2p, respectively, and the corresponding binding energy (BE) values are presented in Table 1. All these Figures and Table 1 clearly indicate that XPS bands are highly influenced by the powder surface treatment history, and the observed binding energy value for each element is in agreement with the literature reports (Perrem et al., 1997; Vassileva et al., 2004; Wang & Sherwood, 2002). The O 1s profiles (Figure 5a), are due to the surface hydroxyl groups in the case of the non treated powder (A-AlN) and to the overlapping contribution of oxygen from $\text{H}_2\text{PO}_4^{1-}$ in the case of treated powder (T-AlN) and treated after 72 h immersion in water (T-AlN-72 h) or of the hydroxyl groups from $\text{Al}(\text{OH})_3$ in the case of the non treated AlN powder immersed in water (A-AlN-72 h). Very interestingly, among all the powders investigated, the A-AlN powder exhibits the lowest oxygen concentration, whereas the A-AlN-72 h powder revealed the highest one. The increase in oxygen concentration for the T-AlN and T-AlN-72 h powders is due to the coating $\text{H}_2\text{PO}_4^{1-}$ layers and partial hydrolysis upon prolonged (72 h) contact with water. The highest oxygen concentration of A-AlN-72 h powder is the result of AlN hydrolysis with the formation of aluminium hydroxide.

Table 1 and Fig. 5 (b) show the binding energy of N 1 s photoelectron peaks for A-AlN, T-AlN, and T-AlN-72 h at 396.9, 397.1, and 397.1 eV, respectively, which agree well with the values reported in the literature (Perrem et al., 1997). The following trend is observed for the N surface concentration: T-AlN > T-AlN-72h > A-AlN > A-AlN-72 h. The amount of N detected in the A-AlN-72 h powder is negligible. This is due to the occurrence of extensive hydrolysis and to the fact that the soft X-rays (1–3 keV) used in the XPS analysis do not penetrate more than a 30 Å depth from the surface of the sample. Because of the high thickness of the aluminium hydroxide layer formed on the surface of AlN particles, the soft

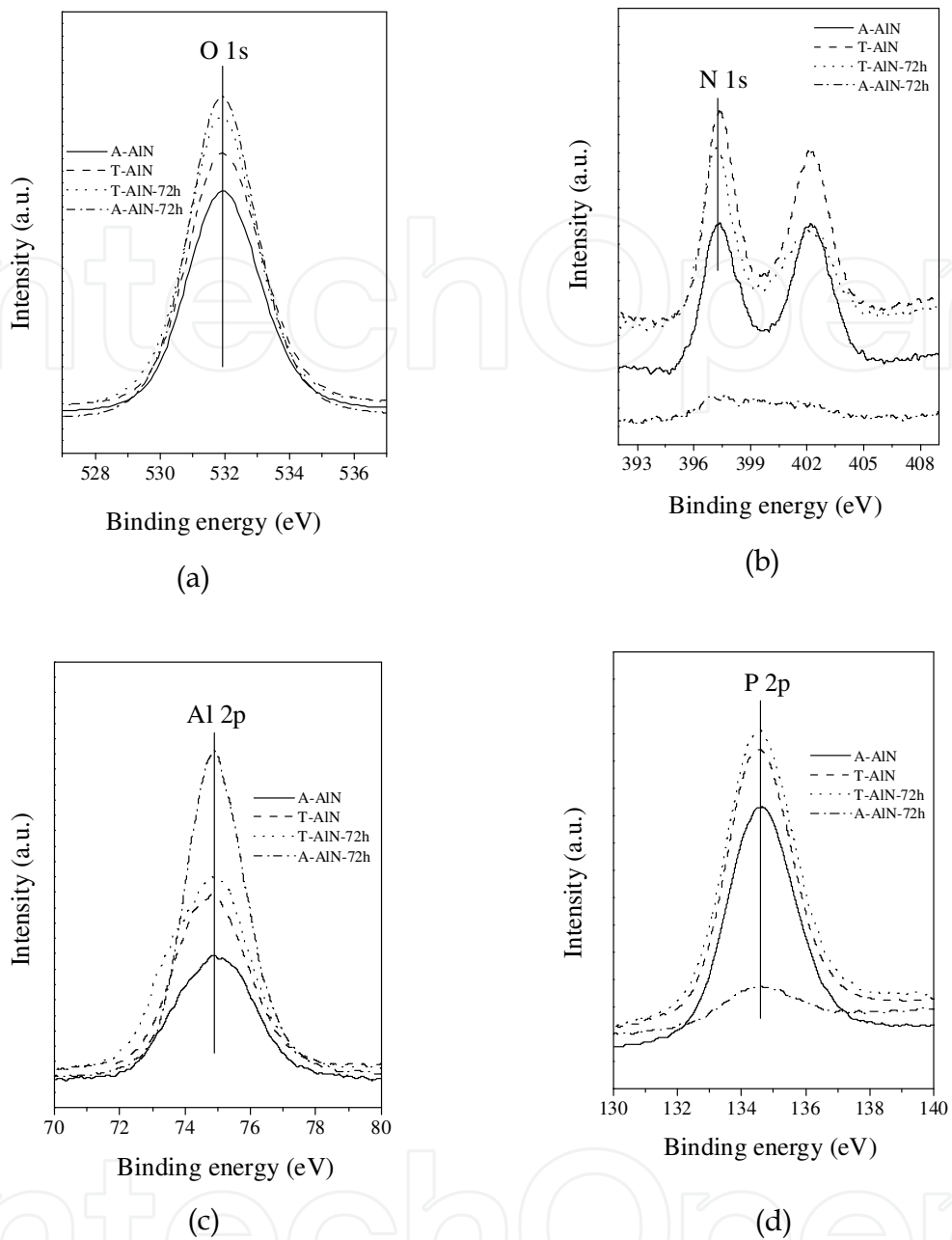


Fig. 5. XPS of the (a) O 1s, (b) N 1s, (c) Al 2p and (d) P 2p binding energy regions for various AlN powder samples: A-AlN (non treated), T-AlN (treated), T-AlN-72h (AlN treated after 72 h in aqueous media), A-AlN-72h (non-treated AlN powder after 72h in aqueous media).

X-rays could not reach the core of AlN particles, whereas hard X-rays used in the XRD study could detect some remaining AlN crystals. Figure 5 (c) and Table 1 shows also XPS peaks and BE values of Al 2p core levels belonging to four AlN powders. No appreciable chemical shifts could be seen in the BE values of Al for all analyzed powders, and the values match very well with those reported in the literature (Wang & Sherwood, 2002). The absence of noticeable chemical shifts in the BE of Al atoms is not surprising since all of them possess a +3 oxidation state. The small differences in the BE values reported in Table 1 are within the allowed range and could be due to the minor changes in the experimental conditions. The

concentration of Al detected in different powders is as follows: A-AlN-72 h > T-AlN-72 h > T-AlN > A-AlN. As a result of the formation of Al(OH)₃ upon hydrolysis of AlN, the surface concentrations of Al and O increase at the expenses of nitrogen, which escapes as NH₃ gas. Very interestingly, the A-AlN powder exhibited the lowest Al concentration and highest N concentration among the four powders. This indicates that the A-AlN powder has relatively low oxygen concentration, in good agreement with the technical data sheet from the supplier. Fig. 5 (d) shows the P 2p photoelectron peaks of four different AlN powders and the BE values recorded (Table 1) are according to the literature reports (Perrem et al., 1997; Wang & Sherwood, 2002). In the case of P also, no chemical shift is seen in BE values because of the availability of only a +3 oxidation state for the P atom. As expected, T-AlN and T-AlN-72 h reveal higher P concentrations than the other two powders, confirming the adsorption of a phosphate layer onto the surface of treated AlN particles. Surprisingly, even the A-AlN powder exhibits a small amount of P that can be regarded as an impurity.

Sample	Binding energy (±0.3 eV)				Peak range (eV)			
	O 1s	N 1s	Al 2p	P 2p	O 1s	N 1s	Al 2p	P 2p
A-AlN	532.5	396.9	74.9	134.6	527.0 to 538.9	393.8 to 407.0	68.0 to 80.6	128.0 to 141.1
T-AlN	532.4	397.1	74.8	134.6	527.0 to 538.9	393.8 to 407.0	68.0 to 80.6	128.0 to 141.1
T-AlN-72h	532.6	397.1	75.0	134.8	527.0 to 538.9	393.8 to 407.0	68.0 to 80.6	128.0 to 141.1
A-AlN-72h	531.9	-	74.9	134.6	527.0 to 538.9	393.8 to 407.0	68.0 to 80.6	128.0 to 141.1

Table 1. Binding Energies and Peak Range and XPS Intensity Ratios of Different Powders.

3. Optimisation of aqueous suspensions of pre-treated AlN powders for slip casting

Although several studies present the passivation of AlN powder against hydrolysis, the preparation of high concentrated suspensions using the treated powders is not strongly reported. Some authors present some attempts, however the solids loading achieved is to low to obtain good green and sintered samples (Groat & Mroz, 1994, Shimizu et al., 1995; Xiao et al., 2004; Wildhack et al., 2005). In fact, dispersing ability is negatively affected by the state of powders agglomeration, which needs to be minimised in order to obtain high degrees of green packing density and homogeneity and enhanced sintering behaviour. Using H₃PO₄ mixed with CH₃CO₂H (Oliveira et al., 2003) it was found that relatively fluid suspensions containing a solids volume fraction as high as 50-vol.% could be prepared by adding a suitable combination both, namely 0.2-wt.% and 0.5-wt.%, respectively. The flow curves presented in Fig. 6 reveal the starting suspension exhibits a strong shear thickening behaviour, which then tends to decrease as deagglomeration time increases, presenting a near Newtonian behaviour up to about 300 s⁻¹ after 120 min of ball-milling. The presence of coarser agglomerates/particles population and the predominance of the electrostatic stabilization mechanism were believed to be the main responsible factors for the accentuated shear thickening behaviour of the starting or the poorly deagglomerated suspensions. From these suspensions, AlN compacts with a green density as high as 71% of the theoretical density, could be obtained. However, the obtaining of well deagglomerated suspensions (Fig. 6) required a careful milling procedure with additional increments of H₃PO₄ at each 30min. milling time, in order to keep the coating integrity or to reform it onto

the new exposed surfaces resulting from deagglomeration. Therefore, this procedure to prepare the suspensions might not be so reliable in terms of surface protection and may originate unpredictable and non-reproducible suspensions characteristics. Conversely, the stronger bonding of phosphate species to the surface of AlN particles achieved by the thermo-induced phosphate protection of AlN powders seems more promising and the more resistant protection layer should better outstanding the milling stresses during the deagglomeration step.

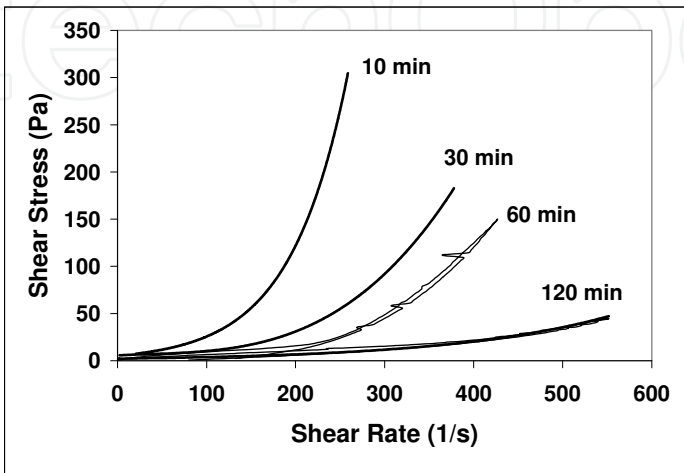


Fig. 6. Flow behaviour of the H_3PO_4 -treated AlN aqueous suspension with 50-vol.% solids concentration after different ball-milling times.

Fig. 7 shows the electrophoretic characterization of the thermo-chemical treated AlN powders at 60°C , in absence and in the presence of different dispersants. The aim was to gather useful data for selecting the most efficient dispersion conditions to stabilize the particles. The amounts used were previously selected as the most proper.

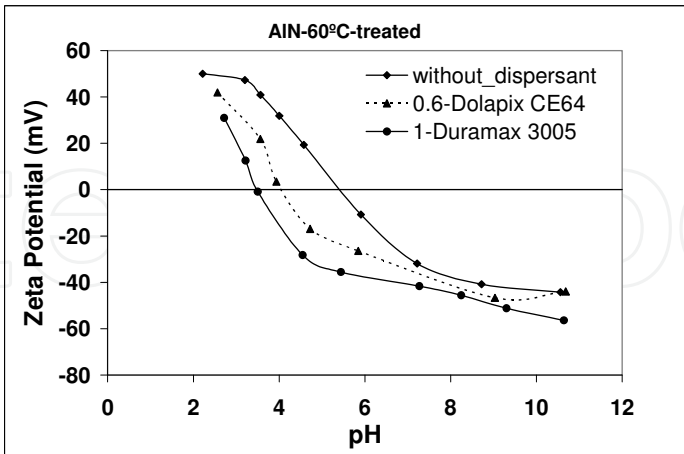


Fig. 7. Electrophoresis curves of thermochemically treated AlN at 60°C in the absence and in the presence of 0.6-wt.% of Dolapix CE 64 or 1-wt.% Duramax 3005.

From these results it can be concluded that Duramax 3005 is better suited to shift the pH_{iep} of the thermo-chemically treated AlN particles at 60°C towards the acidic direction, and to increase the negative zeta-potential values in the pH range of interest (near neutral or

slightly alkaline). Moreover, the results of electrophoresis measurements suggest that the stabilization mechanism might be predominantly of an electrostatic nature. It is important to note that in the presence of the Duramax 3005, a good dispersion could be achieved in the pH range from 8 to 9. Thus, for the preparation of well stabilised AlN-based suspensions, Duramax 3005 seems to be the most suitable dispersant. The evolution of rheological behaviour along deagglomeration time of concentrated suspensions containing 50-vol.% of solids loading dispersed with the selected type and amount of dispersant, 1%-wt Duramax 3005, is presented in Fig. 8.

All the suspensions exhibited a shear thinning behaviour within the lower shear rate ($\dot{\gamma}$) range (up to $\approx 200 \dot{\gamma} \text{ s}^{-1}$), followed by near-Newtonian plateau, ending with an apparent shear thickening trend for the highest $\dot{\gamma}$ values. The presence of some coarser particles and/or agglomerates, which would cause a higher resistance to flow, or the relatively large interaction size of the dispersed particles that one would expect when the electrostatic stabilisation mechanism predominates, might account for the shear thickening effect in the highest shear rate range.

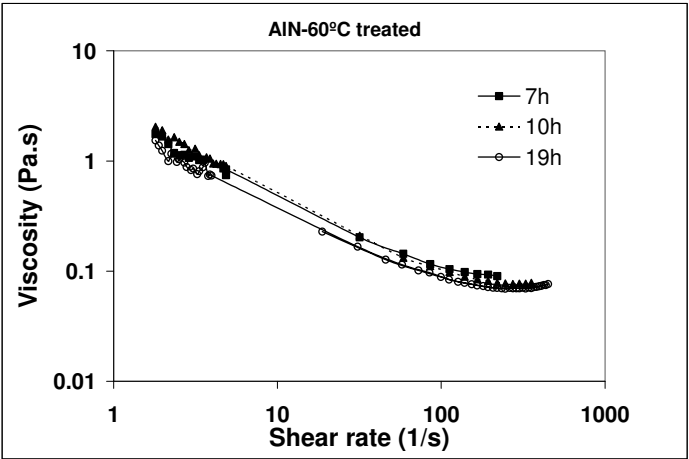


Fig. 8. Evolution of the flow behaviour along deagglomeration time of an aqueous AlN suspension containing 50-vol.% of solids.

Using this well deagglomerated AlN suspension in aqueous media it was possible to prepare green samples with green densities around 59% (percentage of theoretical density (TD) after 19 h deagglomeration time, as it can be seen in Table 2. Using the thermochemical treatment with aluminium phosphate species, the suspension is stable during all the time necessary for deagglomeration and casting, confirming the strong connection of these species to the AlN surface powder, investigated before.

50-vol.% solids	Green density (% TD)	
	10 h	19 h
AlN sample	57.7±0.07	59.1±0.2

Table 2. Green densities of slip-cast samples, obtained from 50-vol.% solids-loaded suspensions after deagglomeration for two different periods (10 and 19 h).

Examples of several crucibles obtained by the same suspension are also presented in Fig. 9.



Fig. 9. AlN crucibles obtained by slip casting with an aqueous suspension containing 50-vol.% solids.

3.1 Densification studies of slip casted AlN samples

The quality of ceramic processing based on powder technology, including many steps from preparation of raw materials to sintering of shaped components is a key point. Each step is, in different ways, crucial for the ultimate material properties. The quality of the starting powders, particle size, particle size distribution and particle shape are crucial factors which in an integrated way influence the final material properties (Komeya et al., 1969). Using the green slip casted samples obtained above with aqueous treated AlN suspensions with 50-vol.% solids, full dense aluminium nitride (AlN) ceramics were obtained after sintering for 2 h at 1750°C and characterised for Vickers hardness (1000 Hv), flexural strength (200 MPa), and thermal conductivity (115 W/mK) (Olhero et al., 2006a). YF₃ and CaF₂ were used as sintering additives in total amounts ranging from 5 to 7-wt.%, in ratios of 1.25; 1.5 and 2. The sintering additive compositions seem to affect the mechanical properties, density and thermal conductivity through the amount of intergranular phases formed, the volume fraction of porosity, the grain size and grain size distribution, as Table 3 and Fig. 10 suggest. The codes, A, B, C, D, E and F refers the different amounts of sintering aids used as follows: **A**- 5-wt% CaF₂; **B**- 3-wt.% YF₃; **C**- 2-wt.% YF₃ + 1-wt.% CaF₂; **D**- 3-wt.% YF₃ + 3-wt.% CaF₂; **E**- 4-wt.% YF₃ + 2-wt.% CaF₂ and **F**- 4-wt.% YF₃ + 3-wt.% CaF₂.

Samples	Sintered density (%TD)	Thermal conductivity W m ⁻¹ K ⁻¹	Hardness (Vickers)	Mechanical Strength (MPa)
A	99.01± 0.74	93.7 ± 4.68	962.3 ± 28.16	128.5 ± 15.9
B	99.6 ± 0.76	75.0 ± 3.75	1062.1 ± 64.03	135.5 ± 14.0
C	99.8 ± 0.56	77.9 ± 3.89	1100.1 ± 51.37	157.5 ± 20.9
D	100.1 ± 0.08	113.0 ± 5.65	971.3 ± 38.90	178.7 ± 22.8
E	99.9 ± 0.21	115.0 ± 5.75	950.2 ± 27.30	218.8 ± 18.7
F	99.5 ± 0.18	108.0 ± 5.40	908.9 ± 47.18	203.1 ± 21.3
Without additives	99.01± 0.74	93.7 ± 4.68	962.3 ± 28.16	128.5 ± 15.9

Table 3. Final properties (sintered density, thermal conductivity, hardness, and flexural strength) of the AlN samples.

Except the pure AlN samples that presented a relatively low sintered density ($\cong 80\%$) and the sample with added 5-wt.% CaF_2 (composition A, $\cong 97\%$), all the other compositions exhibit high densification levels ($>99.5\%$ TD), which tend to increase with an increase in the total amount of sintering additives. Nearly fully dense materials were obtained for compositions with higher total amounts of sintering aids (D and E). However, compositions B and C with the lowest total amount of sintering additives (3-wt.%) are denser ($>99.5\%$ TD) than composition A (99% TD) with 5-wt.%, the same total amount as in the fully dense composition D (100% TD). For composition F with the highest amount of sintering additives, the sintering density decreased (99.5 wt% TD), probably caused by an excess of secondary phases. In the system $\text{CaF}_2\text{-YF}_3$, the latter component is clearly the most effective one. Incomplete densification might be caused by the incomplete oxygen consumption at the grain boundaries and an insufficient amount of liquid phase formed. The increasing amount of intergranular phases and the concomitant increase in sintered density enhanced the flexural strength of the AlN. This is according to the microstructural observations on fracture surfaces (Figure 10) that clearly showed a number of transgranularly fractured

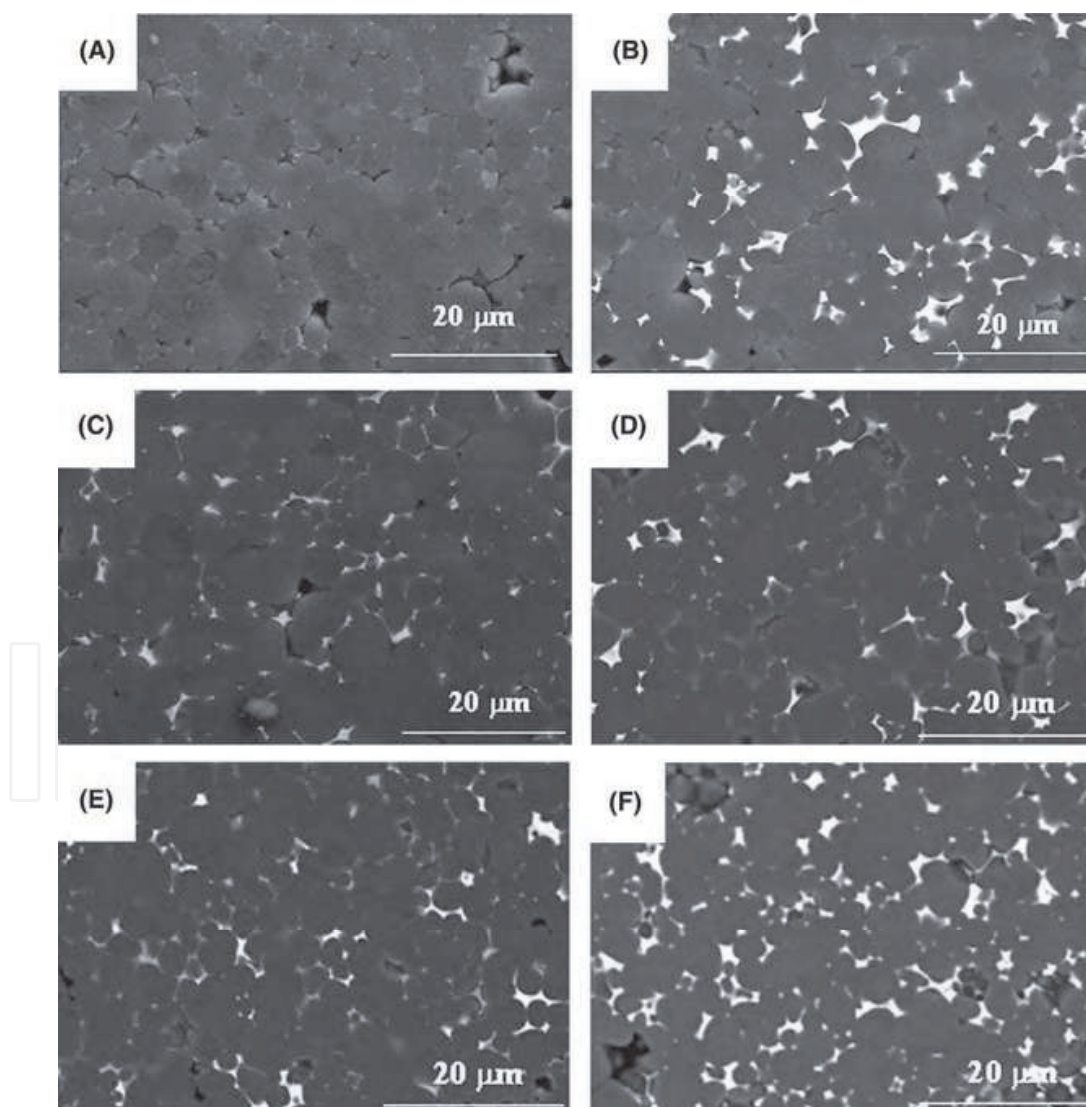


Fig. 10. Backscattering images of the polished AlN samples (A, B, C, D, E, and F) after sintering at 1750°C for 2 h.

grains, indicating strong bonding and high strength of the intergranular phase. The increase in the amount of sintering additives resulted in a decrease of microhardness due to the lower hardness of the secondary phases between AlN grains in comparison to that of crystalline AlN grains (Olhero et al., 2006a).

Therefore, the amount and ratio of the sintering additives play important roles in the microstructural development and in determining the final physical properties of the sintered bodies. These results were explained afterwards, as it will be shown in the next sections.

4. Application of the AlN aqueous suspensions in other colloidal processing techniques

From the technological point-of-view, the inhibition of hydrolysis at the AlN particles surface, a good dispersion of the protected powders and the control of the rheological behaviour of highly concentrated AlN-based suspensions, are the key factors to extend the application of aqueous AlN suspensions to other fields of ceramic processing. Examples include the use of other colloidal shaping techniques such as tape casting, gel casting and so on, or the production of granulated powders (freeze granulation) for the dry pressing technologies. As stated above, from the rheological point-of-view, a shear thinning behaviour is desirable for the highly concentrated aqueous suspensions of the protected AlN powder, especially if the suspensions have to undergo relatively high shear rates in a given processing step. Such requirements are therefore of major importance in the particular cases of tape casting or freeze granulation due to the high shear rates achieved when the suspension passes under the blade or through the spray nozzle. The compatibility between dispersants, binders and plasticizers and their specific interactions with the AlN protected-surface and water must be also taken into account, since they affect the sintering density and the final properties of the AlN-based ceramics, such as the required excellent thermal conductivity.

4.1 Freeze granulation

Granulation is a size enlargement operation by which a fine powder is agglomerated into larger granules to generate a specific size and shape to improve flowability and appearance and, in general produce a powder with specific properties such as granule strength, apparent bulk density and compacting ability. Compared to the conventional powder granulation technique by spray drying, freeze granulation has the advantage of obtaining granules without inner cavities and with a higher degree of homogeneity, due to the absence of binder segregation during drying or the migration small particles (Nyberg et al., 1993; Nyberg et al., 1994). The density and other physical properties of the freeze dried granules can be controlled by varying the solids content of the slip, the particle size distribution and a proper combination of processing additives to confer the suspension the desired shear thinning behaviour and avoiding pumping difficulties and/or clogging of the spray nozzle that divides the suspension into small droplets. The presence of the binder and plasticizer is essential for confer to the forming granules the required physical properties and the compacting ability, therefore eliminating the possibility of using suspensions without processing additives. Fig. 11 shows general microstructural aspects as well as details of the granules obtained after spraying and freezing suspensions with 50-vol.% solids containing 5-wt.% binder + 2.5-wt.% plasticizer (P200). The high homogeneity of the

binder and plasticizer in the starting suspensions was determinant for the reproducibility of granules characteristics after spraying and freezing, namely: (i) granules size ($\approx 100\text{--}800\ \mu\text{m}$), (ii) wide granule size distribution, and (iii) perfectly round shaped and smooth granule surface. Varying the amounts of binder and plasticizer the aspect of the granules is similar although higher binder amounts affect the compacting ability of the granules in dry pressing. In fact, the increased plasticity of the granules containing the highest content on the polymeric additives binder and plasticizes would account for the higher density values in the greens obtained after uniaxial pressing.

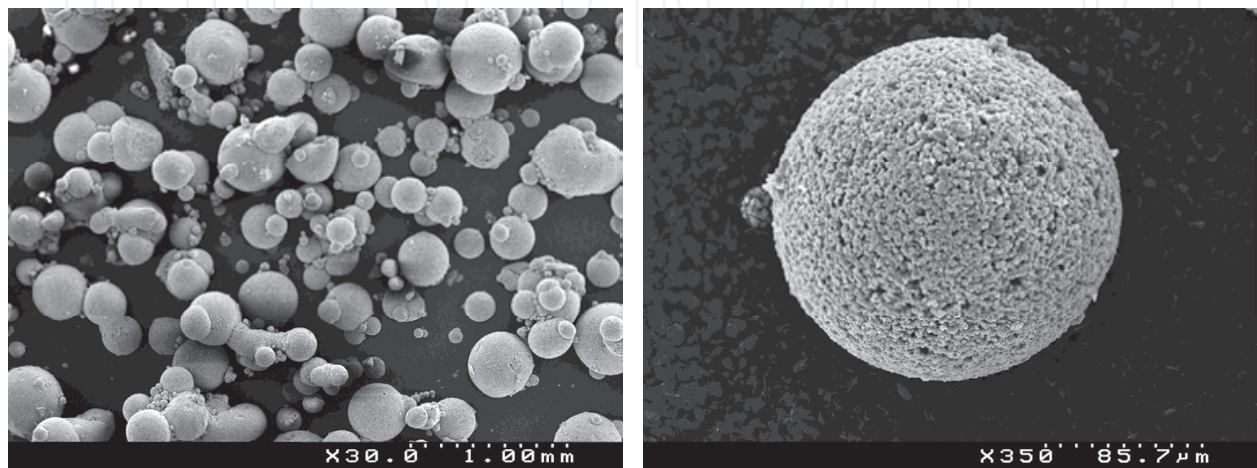


Fig. 11. Size, size distribution and microstructure of the granules obtained by freeze granulation from AlN aqueous suspensions containing 50-vol.% solids and 3-wt% binder + 1.5-wt% plasticizer (P200).

4.2 Tape casting

Oppositely to freeze granulation, tape casting process using AlN suspensions in aqueous media was already reported by other authors (Chartier et al., 1992; Hotza & Greil, 1995; Xiao et al., 2004). As in other forming methods, the arrangement and packing of the AlN particles in the green body influences the sintering behaviour and the final properties. The green microstructure depends on the system to be consolidated and the forming technique employed. Assuming well-dispersed starting slurry, the microstructure of the casting tapes will be determined by two key processing factors: (i) particles' arrangement during the casting process and the shrinkage during drying; (ii) the shear stress generated when the slurry passes under the blade. Due to all of these reasons, the rheological behaviour of the suspensions is of paramount importance in the tape casting process. The rheology determines the flow behaviour in the casting unit, which is dependent on the type and concentration of powder, binder, solvent and other organic additives such as dispersants and wetting agents. In order to obtain aqueous AlN-based suspensions with suitable viscosity for tape casting, and tapes with good mechanical properties (strength and flexibility) the same processing additives used for freeze granulation were also added but in larger amounts: 10- and 15-wt.% of binder and 5- and 10-wt.% of P200 (Streicher et al., 1990a). In same formulations the plasticizer P200 was replaced by a higher molecular weight one, P400, added in the same proportions. All the viscosity curves presented a first shear thinning that is a desired behaviour for the tape casting process, enabling structural

decomposition when the suspension passes under the blade and its level out, as well as, the structural regeneration after passing the blade, avoiding particles segregation and unwanted post-casting flows. Therefore, it is important to mention that no evident incompatibility between binder and plasticizers was observed. From all the suspensions tested, it was possible to obtain un-cracked green tapes, presenting smooth and uniform surfaces, as those shown in Figure 12 (Olhero & Ferreira, 2005). The minimum amount of binder required to produce flexible tapes with a thickness value as high as 1.5 mm was seen to be 15-wt.%. Thicker tapes could be obtained by increasing the solids loading in suspensions through partial evaporation of the excessive water introduced with the emulsion binder.



Fig. 12. Green tapes obtained by tape casting from the aqueous AlN-based suspensions.

5. Influence of de-waxing atmosphere on the AlN properties

High-performance advanced electronic packaging for high-density circuits and high-power transistors needs to have high thermal conductivity to dissipate the heat generated during functioning in order to have lower operational temperatures and improved reliability and performance. In the last 10 years, AlN ceramics have been intensively studied for substrates applications due to the high thermal conductivity, non-toxicity and low dielectric constant among other properties (Collange et al., 1997; Enloe et al., 1991; Jackson et al., 1997; Raether et al., 2001). The thermal conductivity was found to depend on several factors, namely intrinsic and extrinsic. The intrinsic ones are material dependent such as the oxygen content (total and lattice dissolved), the microstructure, lattice defects among others, while the extrinsic ones are sintering conditions (atmosphere, furnace), sintering temperature, time and sintering additives. Hence, to achieve excellent properties of AlN, namely high thermal conductivity, it is important to know how to optimize the extrinsic factors, which in turn influence the intrinsic ones. One factor that promotes deleterious sintering is the presence of oxygen at the grain boundaries. In fact, along the sintering period, impurities such as oxygen are solid-dissolved in AlN crystal lattices or form a composite oxide, such as Al-ON, which hinders the propagation of the thermal oscillations of the lattice. During firing, these impurities are incorporated into the AlN lattice by substitutional solution in the nitrogen site, creating aluminium vacancies, according to the following reaction (5):



where $[\cdot]\text{Al}$ denotes an aluminium vacancy.

Mass and strain misfits caused by the vacant aluminium site increase the scattering cross section of phonons, which decreases the phonon mean free path, thereby lowering the thermal conductivity. Taking into account the reasons exposed above, numerous efforts have been done aimed at lowering the oxygen content within the AlN grains and grain boundaries to decrease the temperature of densification and consequently to reduce the costs of the AlN substrates (Jarrige et al., 1993; Liu et al., 1999; Qiao et al., 2003b; Streicher et al., 1990b; Thomas et al., 1989). The use of sintering aids has been the approach more extensively studied to enhance AlN densification and thermal conductivity (Baranda et al., 1994; Boey et al., 2001; Buhr & Mueller, 1993; Hundere & Einarsrud, 1996; Hundere & Einarsrud, 1997; Khan & Labbe, 1997; Qiao et al., 2003a; Qiao et al., 2003b; Virkar et al., 1989; Watari et al., 1999; Yu et al., 2002). If oxygen impurities in raw powders react with sintering aids to form stable alumina compounds at the grain boundaries of sintered AlN, oxygen impurities do not diffuse into AlN lattice and crystal defects are not produced (Hyouun-Ee & Moorhead, 1994). The thermodynamics and kinetics of oxygen removal by the sintering aids determine both the microstructure and the impurity level of AlN ceramics. Therefore, besides adequate selection of sintering aids, suitable sintering conditions are very important to prevent further increase in the oxygen content of the AlN powder (Lavrenko & Alexeev, 1983; Wang et al., 2003). A higher thermal conductivity is achieved if the grain boundaries are clean from sintering additives and the system is free of oxygen. This is accomplished by heat treatments that lead to liquid removal by evaporation or migration to concentrate at grain-boundary triple points. Recently, Lin (Lin et al., 2008) studied the effect of reduction atmosphere and the addition of nano carbon powder to enhance deoxidation of AlN parts.

The viability of using aqueous media for processing AlN at industrial level is strongly dependent on the final properties, namely thermal conductivity and mechanical properties. The achievement of comparable properties using water to disperse the powders (AlN + sintering aids) and aqueous suspensions to consolidate green bodies by colloidal shaping techniques or to granulate powders for dry pressing, will have enormous benefits in terms of health, economical and environmental impacts. Further benefits will be obtained if the AlN ceramics processed from aqueous suspensions can be sintered at lower temperatures than those usually used ($>1850^{\circ}\text{C}$) to densify AlN ceramics processed in organic media without jeopardizing the final properties (high thermal conductivity, mechanical strength, etc.). As exposed above, aqueous processing of AlN needs a surface protection of the particles to avoid hydrolysis, turning the system more complex. Therefore, transposing the findings of sintering studies using AlN samples prepared in organic media to samples processed in aqueous media is not straightforward. The coating layer composed of oxygen and phosphorous might turn the sintering behaviour ambiguous, and further studies were necessary. In fact, the surface layer used to protect the AlN particles could be a trouble for the sintering process, due to the rising amount of oxygen content at the surface of AlN particles supplied by the protection layer (Olhero et al., 2004). Moreover, when binders and plasticizers are used as processing additives, such as in tape casting or powder granulation, it is necessary to remove these organic species prior to densification. Due to the easy oxidation of aluminium nitride in presence of oxygen and the residual carbon supplied by the organic species during burnout, the de-waxing atmosphere is a critical parameter (Olhero et al., 2006b).

Table 4 presents the amounts of carbon, oxygen, phosphorous, aluminium and nitrogen measured for the different AlN powders, without treatment (AlN), after thermochemical treatment (AlN-T), and for the samples A, B and C after de-waxing under different atmospheres (air or N₂). A, B, and C are samples that presents different amounts of sintering aids and binders as follows: **A**: 3-wt.% YF₃ + 2-wt.% CaF₂ and 4.5-wt.% organic binders; **B**: 4-wt.% YF₃ + 2-wt.% CaF₂ and 4.5-wt.% organic binders; **C**: 4-wt.% YF₃ + 3-wt.% CaF₂ and 4.5-wt.% organic binders. The ratios between the different elements, O/Al, N/Al and C/Al are also shown. Comparing the results for AlN and AlN-T powders, it is clear that there was an important surface enrichment in oxygen (≈9–10 wt.%) and P (≈8 wt.%) elements attributed to the phosphate species of the protective layer against hydrolysis, and a concomitant depletion of N and Al elements, confirming the results of the earlier report (Olhero et al., 2004). The decrease of the amount of aluminium at the surface of the AlN-T might also be partially due to a possible reaction between the oxygen and the aluminium to form aluminium oxide and oxynitride (Bellosi et al., 1993; Ichinose, 1995; Osborne & Norton, 1998).

Elements	Content (at %)							
	AlN	AlN-T	Sample A		Sample B		Sample C	
			O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
C (1s)	12.61	12.91	13.79	20.96	12.81	21.63	13.96	21.68
N (1s)	16.99	9.35	6.05	6.21	6.19	6.54	6.14	6.38
O (1s)	35.75	44.97	45.86	40.84	45.91	40.84	45.98	40.68
Al (2p)	34.65	24.97	26.06	23.79	26.52	23.44	25.73	23.08
P (2p)	---	7.80	8.24	8.20	8.58	7.55	8.18	8.19

Table 4. Comparison of surface composition measured by XPS of the AlN powder without treatment and AlN treated powder (AlN-T) before and after de-waxing under different atmospheres (air or nitrogen).

Comparing the results for AlN-T and the compositions A, B and C after de-waxing in air atmosphere, it can be concluded that the surface of AlN particles becomes about 1-wt.% rich in oxygen after the burnout step. On the other hand, de-waxing in N₂ atmosphere results in significant decrease of the amount of oxygen (≈4 wt.%) and a concomitant increase in the carbon content (≈8–9 wt.%). The analysis of the atomic ratios between the different elements reveals that O/Al ranges from 1.73 to 1.79 for the samples de-waxed in air, and between 1.72 and 1.76 for the specimens de-waxed in N₂. On the other hand, the N/Al is 0.23–0.24 for the first set and 0.26–0.28 for the latter one. However, differences in the C/Al atomic ratio are the largest: 0.48–0.54 in air, and 0.88–0.94 in N₂. These results are in good agreement with the findings of other authors (Nakamatsu et al., 1999; Yan et al., 1993). Therefore, the binder burnout process left a significant amount of residual carbon on the AlN surface, which is larger in the case of the samples heat treated in nitrogen. By analysing the C1s peak, Yan (Yan et al., 1993) concluded that the first layer of carbon is bound to oxygen atoms at the AlN surface while additional carbon is bound to carbon itself, forming amorphous graphitoid carbon clusters which covered the powder surface uniformly. In spite of carbon increasing after binder burnout, oxygen content seems to be the most abundant element at

the surface of all AlN powders. Therefore, the use of proper amounts of sintering aids is of crucial importance to help releasing the excess of oxygen. Recently, Robinson and co-workers found that oxygen distribution was not continuous along thickness direction of the oxidized AlN (Robinson & Dieckmann, 1994; Robinson et al., 1994). They suggested that additives enhancing densification may be critically important to the oxidation kinetics of AlN polycrystals and the oxidized structure as well. Wenjea Tseng (Wenjea et al., 2004) also supported this proposition by showing that the additive chemistry and the doping level both play crucial roles in determining the oxidation behaviour of fully sintered AlN. Using different amounts and proportions of sintering additives did not affect the surface chemistry of AlN particles after de-waxing, but influenced the thermal properties after sintering. The results of density and thermal conductivity of the different AlN-based compositions after de-waxing (in air or nitrogen) and sintering at 1750°C for 2 h are reported in Table 5. Considering that the standard deviation of sintered density is $\pm 0.1\%$, one can conclude that full densification was obtained for all the compositions tested, independently of the de-waxing atmosphere used. The values of thermal conductivity are also reported in Table 5, with a standard deviation of $\pm 5\%$. Since all samples reached full density, the observed differences in thermal conductivity cannot be attributed to the densification degree. The nature and concentration of sintering aids and the de-waxing atmosphere are the most relevant factors determining thermal conductivity, which in turn depends on the microstructural features and on the crystalline phases formed. Significant differences (increases of 22%) in thermal conductivity are observed when comparing the data of samples sintered in air and in nitrogen. These differences might be related to the secondary intergranular crystalline phases. Yttrium aluminium monoclinic (YAM- $Y_4Al_2O_9$) is present when nitrogen atmosphere was used, while yttrium aluminium perovskite (YAP- $YAlO_3$) or $YCaAl_3O_7$ were formed when de-waxing was made in air.

Samples	Sintered densities (%TD)		Thermal conductivity (W/m.K)	
	De-waxing in air (O ₂)	De-waxing in N ₂	De-waxing in air (O ₂)	De-waxing in N ₂
A	100	100	111	125
B	100	100	111	136
C	99.8	99.9	119	136

Table 5. Density and thermal conductivity values of the sintered AlN samples

The origin of these secondary crystalline phases in the sintered samples is postulated to be as follows. The surface of AlN treated powder contains significant amounts of oxygen and phosphorous coming from the protective layer against hydrolysis. XPS analysis revealed that the phosphorous element still present at the surface of AlN powders after de-waxing at 500°C (Table 4) could no more be detected after heat treating the samples at temperatures $\geq 1400^\circ\text{C}$ (temperature of liquids). This means that P element volatilizes upon heating up to 1400°C. The formation of liquid phase is expected to occur at $\approx 1400^\circ\text{C}$, according to the phase diagram (Roth et al., 1983). The oxygen remaining at particles' surface reacts with the sintering additives (YF_3 and CaF_2) to form a low melting point eutectic phase. This liquid phase assists the densification process and gives rise to crystalline phases, such as YAM or

YAP, either precipitated during sintering or on solidification. It is worthwhile to note that the yttrium-rich second phases were formed when the de-waxing was made in nitrogen atmosphere. Therefore, a correlation between the C/O atomic ratio at the AlN powder surface and the Al/Y/Ca in the second phase of the sintered material can be found. In fact, secondary intergranular phases became yttrium-rich ($\text{Y}_4\text{Al}_2\text{O}_9$) as surface C/O ratio increases, consequently enhancing the thermal conductivity. The change of the secondary intergranular phases from aluminium-rich to yttrium-rich can be understood based on carbon de-oxidation during sintering, which removes oxygen impurities from the grain boundaries according to the following chemical reaction:



The above results are in good agreement with those reported by other authors who defended that when $\text{Y}_4\text{Al}_2\text{O}_9$ is formed in AlN- Y_2O_3 ceramics instead of $\text{Y}_3\text{Al}_5\text{O}_{12}$ or YAlO_3 , the highest thermal conductivity can be achieved (Nakano et al., 2003; Virkar et al., 1989). The distribution of the secondary phases in the samples, which may contribute to the increase in thermal conductivity, was also found to be dependent on C/O ratio (Yan et al., 1993). The effect of de-waxing atmosphere on microstructural features of fracture surfaces of sintered samples A and C can be observed in Figure 13 and Fig. 14, for the samples de-waxed in air and nitrogen, respectively. It can be seen that AlN grains are separated by grain-boundary films, the thickness of which depend on the type of de-waxing atmosphere. The results of EDS analysis of the inter-granular films revealed that they consist of different proportions of Y, O, Al and N, being more yttrium-rich when de-waxing was in N_2 . In samples A and C de-waxed in air, the inter-granular films extend along the whole grain boundaries showing good wetting properties. The presence of these grain boundaries films disrupts the connections between grains and consequently decreases the thermal conductivity. Contrarily, the inter-granular film in sample A and C de-waxed in N_2 atmosphere is thinner and the secondary phases are apparently less abundant and appear preferentially located at the triple points. These differences can be related to the surface composition of the AlN grains. The higher C/Al atomic ratios (see Table 4) of the samples sintered in N_2 atmosphere will decrease the ratio between the grain-boundary energy (γ_{ss}) and the solid-liquid interfacial energy (γ_{sl}), $\gamma_{\text{ss}}/\gamma_{\text{sl}}$, leading to the isolated structure of the second phase observed in these specimens and increasing the thermal conductivity.

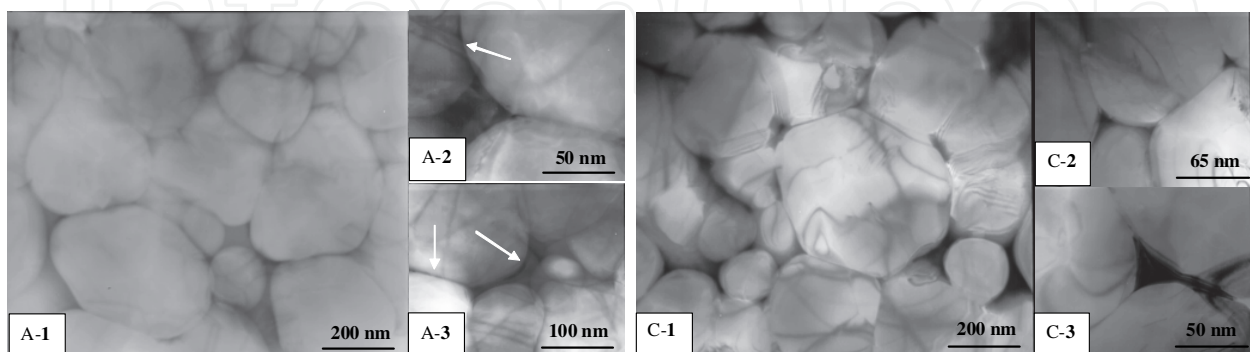


Fig. 13. TEM images of samples A (3-wt.% YF_3 + 2-wt.% CaF_2 and 4.5-wt.% organic binders) and C (4-wt.% YF_3 + 3-wt.% CaF_2 and 4.5-wt.% organic binders) sintered at 1750°C for 2h after de-waxing in Air.

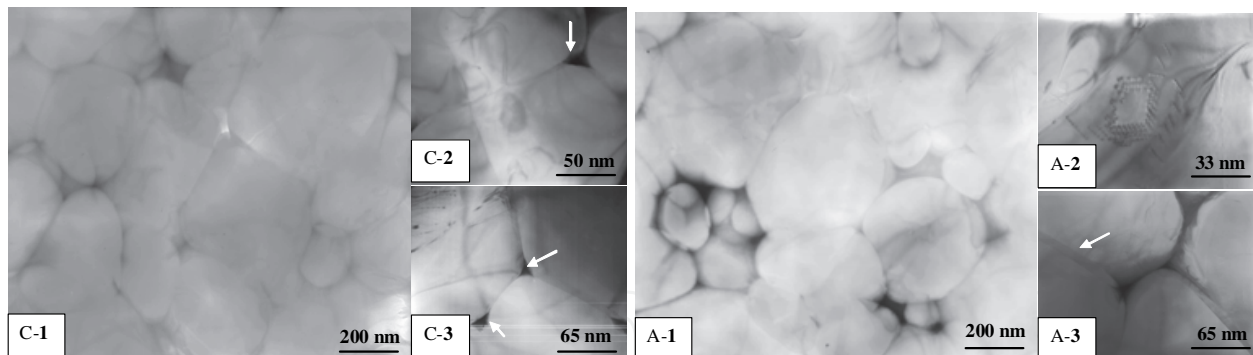


Fig. 14. TEM images of samples A (3-wt.% YF_3 + 2-wt.% CaF_2 and 4.5-wt.% organic binders) and C (4-wt.% YF_3 + 3-wt.% CaF_2 and 4.5-wt.% organic binders) sintered at 1750°C for 2 h after de-waxing in Nitrogen.

Table 5 shows that increasing the total amount of sintering additives and the YF_3/CaF_2 ratio enhances thermal conductivity. It is suggested that the formation of Y-rich secondary phases de-wets the grain boundaries and segregates the intergranular phases preferentially to the triple points leading to a more effective AlN–AlN grain-boundary contact.

Practically full dense AlN ceramics having thermal conductivities varying from 110 to 140 W/mK have been successfully produced from granulated powders processed in aqueous media. De-waxing atmospheres, sintering aids and firing conditions were identified as key processing parameters in controlling density and thermal conductivity. The burnout of organic additives in N_2 atmosphere left a significant amount of residual carbon at the AlN powder surface that partially removes the excess oxygen. The reaction between the remaining excess oxygen and the sintering additives (CaF_2 and YF_3) leads to the formation of yttrium-richer ($\text{Y}_4\text{Al}_2\text{O}_9$) secondary phases preferentially located at the triple points that enhance thermal conductivity. Contrarily, de-waxing in air favours the formation of more abundant alumina-richer yttrium aluminates that better wet the AlN grains and spread along the whole grain boundaries, increasing the density of structural defects, such as dislocations, therefore decreasing thermal conductivity.

6. Thermodynamic studies on the AlN sintering powders treated with phosphate species

Because AlN is a covalently bonded material, pressureless sintering of low oxygen-containing AlN is usually carried out by liquid-phase sintering, where the liquid provides rapid mass transport and therefore rapid densification at low temperatures (Jarrige et al., 1993; Khan & Labbe, 1997; Liu et al., 1999; Streicher et al., 1990b; Thomas & Nicholson, 1989). Chemical reactions between the ceramic powder, sintering aid, and the atmosphere during firing are important for successful sintering. The key elements are those that form volatile species, either directly or by reactions with the atmosphere (Sonntag et al., 2003). The additives typically used to promote the sintering of AlN are alkaline-earth oxides, rare-earth oxides, or mixtures of oxides and carbides (Boey et al., 2001; Buhr & Muller, 1993; Hundere & Einarsrud, 1997; Kurokawa et al., 1988; Qiao et al., 2003a; Molisani et al., 2006; Terao et al., 2002; VanDamme et al., 1989; Watari et al., 1999; Wang et al., 2001; Yu et al., 2002). The sintering aids of the CaF_2 – YF_3 system are interesting due to the absence of oxygen

and the low liquidus temperatures. The eutectic points in the $\text{CaF}_2\text{-YF}_3$ system occur at 60 and 91 mol% CaF_2 at 1120° and 1106°C, respectively (Seiranian et al., 1974). The studies on the thermodynamics taking place during sintering of AlN have been reported for AlN samples processed in organic media, therefore involving a residual amount of alumina at the surface of the AlN particles and the sintering additives (Buhr et al., 1991; Gross et al., 1998; Hagen et al., 2002; Hundere & Einarsrud, 1996; Medraj et al., 2005; Virkar et al., 1999). For samples processed in aqueous media, the presence of a protecting surface layer against hydrolysis makes the system more complex. If the surface layer adds extra oxygen to the surface of the AlN particles as it is demonstrated above, it might have a negative impact on sintering. Therefore, the contribution of this surface layer, phosphate based, to the AlN sintering needs to be investigated in order to choose the best conditions (sintering temperature, amount of sintering additives, etc.) to improve the final properties of AlN ceramics. Therefore, the aim of this part is to make a review of the kinetic effects of the phosphate-based surface layer used to protect AlN powder against hydrolysis on the sintering behaviour of AlN in the presence of YF_3 and CaF_2 as sintering aids, and consequently on the final properties of the samples processed in aqueous media. For that, AlN samples with different amount of sintering aids, in absence or in presence of binders and plasticizers (organic species) were analysed. Table 6 presents the compositions of the samples tested and the respective codes.

Sample codes	Phosphate species (wt.%)	Binder and plasticizer (wt.%)	YF_3 (wt.%)	CaF_2 (wt.%)
AlN-P	2	---	---	---
AlN-P-B	2	4.5	---	---
AlN-P-B-Y	2	4.5	3	---
AlN-P-Ca	2	---	---	5
AlN-P-B-YCa (3/2)	2	4.5	3	2
AlN-P-2B-YCa (3/2)	2	6.0	3	2
AlN-P-2B-YCa (4/2)	2	6.0	4	2

Table 6. Sample codes and the respective compositions of the AlN samples tested.

Firstly the samples were submitted to thermal analysis from room temperature to 1600°C in order to analyse the weight loss. Figs. 15 (a) and (b) show the weight loss of the AlN samples in presence of the phosphate surface layer and with different amounts and ratios of sintering additives (Table 6), obtained at two different heating rates, 2°C /min and 10°C /min, respectively. Table 7 summarizes the percentage of weight loss of the Aluminium Nitride (AlN) samples measured within certain temperature ranges at a heating rate of 2°C/min.

	Weight loss (%)					
Sample codes	25-300	300-400	980-1030	1025-1100	1250-1600	Total
AlN-P	0.87	-0.44	0.08	----	-0.81	-0.30
AlN-P-B	2.80	1.06	----	0.51	----	4.37
AlN-P-B-Y	2.51	1.11	0.31	----		3.93
AlN-P-B-Ca	0.70	-0.41	0.17	----	3.70	4.16
AlN-P-B-YCa (3/2)	2.71	1.07	0.36	----	2.43	6.57
AlN-P-2B-YCa (3/2)	2.71	2.42	----	0.43	2.56	8.12
	•Water evaporation •Binder burnout (short chains)	•Binder burnout (long chains)			• Calcium evaporation	

Table 7. Percentage of Weight Loss of the Aluminium Nitride (AlN) samples measured within certain temperature ranges at a heating rate of 2°C/min.

The AlN powder coated with the phosphate species (AlN-P) showed a slight weight decrease up to 300°C, from where a small weight increase was observed up to 1300°C. Above 1300°C, a second weight gain was observed. The addition of the processing aids (binder and plasticizer) to the phosphate-treated AlN powder (AlN-P-B) resulted in significant differences in the weight loss. A first weight loss of about 3.9 wt.% was observed in the temperature range from room temperature up to $\cong$ 400°C due to the burnout of the organic species, while a second weight loss of about 0.7 wt.% was observed between 1030° and 1060°C, followed by a small weight increase above 1200°–1300°C. The weight loss of the phosphate-treated AlN samples in the presence of the sintering aids (AlN-P-B-Y, AlN-P-B-Ca, AlN-P-B-YCa (3/2)) was practically the same from room temperature till 1300°C. Above this temperature, the samples containing CaF₂ (AlN-P-Ca and AlN-P-B-YCa (3/2)) showed a significant weight loss, while the sample with YF₃ (AlN-P-B-Y) showed a slight weight increase as in the samples with phosphates only (AlN-P and AlN-P-B). In order to investigate the effects of carbon residuals on the weight loss during sintering, TG analysis of the sample with a mixture of the two sintering additives, with two different amounts of binder and plasticizer, was carried out (AlN-P-B-YCa (3/2) and AlN-P-2B-YCa (3/2)). The TG curves presented the same behaviour along the entire temperature range, however, with higher percentages of weight loss (about 2% more) for the sample with a larger amount of binder, as expected. On the other hand, the mass loss observed at around 1000°C started at a lower temperature for the powder with a larger amount of binder (AlN-P-2B-YCa (3/2)). Moreover, the weight loss around this temperature was more gradual in the AlN-P-2B-YCa (3/2) powder, occurring more abruptly in the presence of lower amounts of processing aids (i.e., less amounts of residual carbon).

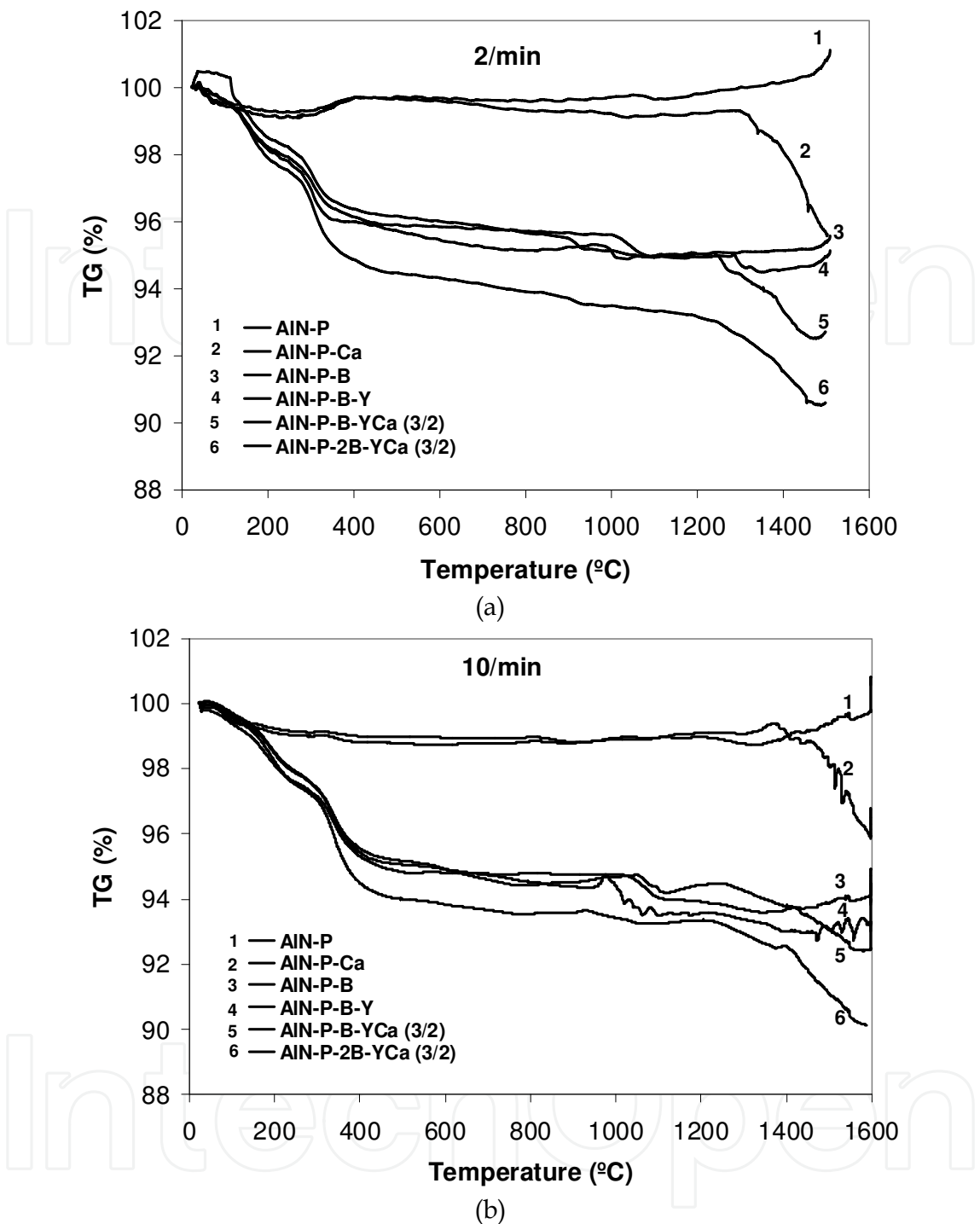
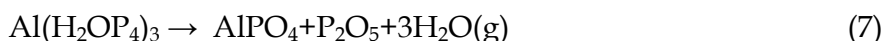
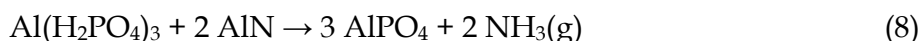


Fig. 15. Thermogravimetric curves of the AlN samples in the absence or in the presence of phosphates species with different added amounts of sintering aids and organic species (binders and plasticizer): (a) obtained at a heating rate of 2°C/min; (b) obtained at a heating rate of 10°C/min.

During heating of the protected AlN powders with a dihydrogenphosphate surface layer (AlN-P), the small mass loss measured within the temperature range of 100°-150°C, could be attributed to the water evaporation and release of adsorbed gases on the powder surface, according to the following reaction:



The water vapour produced by reaction (7) may also react with AlN, leading to the following reaction:



which only predicts weight loss due to evaporation of ammonia at low temperatures instead of water. Reaction (8) leads to higher relative oxygen content in the powder mixture. The removal of oxygen from the AlN lattice during sintering is beneficial for enhancing thermal conductivity (Buhr et al., 1991; Gorzawski et al., 1995; Hundere & Einarsrud, 1996; Rang-Rong Lee, 1991; Virkar et al., 1999;). However, oxygen should not be removed during an early stage of the sintering process because Al_2O_3 is needed in the formation of a liquid phase. The weight gain observed for the same sample (AlN-P) at $\approx 250^\circ\text{C}$ at a slow heating rate ($2^\circ\text{C}/\text{min}$) could be attributed to the formation of alumina due to the hydrolysis of AlN, according to:

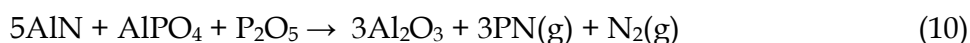


The weight gain at $\approx 250^\circ\text{C}$ was only observed for the samples AlN-P and AlN-P-Ca without addition of processing aids.

However, this reaction could also occur in the presence of the processing aids, but the corresponding weight gain due to hydrolysis is masked by the high weight loss derived from the burnout of the organic species. The weight loss corresponding to the burnout of the organic species is divided into two stages: one from 100° to 300°C , corresponding to the burnout of the organic species with shorter chains, and another one from 300° until $\approx 400^\circ\text{C}$, derived from the burnout of the organic species with longer chains. Thermodynamic calculations using Factsage program (Bale et al., 2002) were carried out in order to predict the changes in the phase composition of the powder mixture during sintering and after the removal of water. The program calculates the chemical equilibrium in a closed system as a function of temperature and pressure. The input to the program is the chemical composition and we provided equilibrium calculations in the temperature range of 1200° – 1800°C at constant total pressure 1 bar using the following initial compositions:

- i. $10\text{AlN} + 0.1\text{AlPO}_4 + 0.01(\text{P}_2\text{O}_5)_2 + 10\text{N}_2$
- ii. $10\text{AlN} + \text{YF}_3 + \text{CaF}_2 + 0.1\text{AlPO}_4 + 0.05(\text{P}_2\text{O}_5)_2 + 10\text{N}_2$
- iii. $10\text{AlN} + 0.1\text{YF}_3 + 0.1 \text{CaF}_2 + 0.01\text{AlPO}_4 + 0.005 (\text{P}_2\text{O}_5)_2 + 0.2\text{Al}_2\text{O}_3 + 10\text{N}_2$
- iv. $10\text{AlN} + 0.1 \text{YF}_3 + 0.1\text{CaF}_2 + 0.1\text{Al}_2\text{O}_3 + 10\text{N}_2$

The surface coating, $\text{Al}(\text{H}_2\text{PO}_4)_3$, was represented by AlPO_4 and P_2O_5 in the calculations because the loss of water, reaction (7), is expected to occur before the initial stage of sintering. Fig. 16 (a & b) present the minority condensed phases ($a=1$, AlN not present) between 1200° and 1800°C , and the dominating volatile species within the same temperature range for the system in the absence of phosphate species: $10 \text{AlN} + 0.1 \text{CaF}_2 + 0.1 \text{YF}_3 + 0.1 \text{Al}_2\text{O}_3 + 10 \text{N}_2$, respectively. The presence of phosphate species did not change the minority volatile phases presented in Fig. 16 (a & b). These species, in the presence of AlN, are unstable and will react to form alumina, $\text{PN}(\text{g})$, and $\text{N}_2(\text{g})$ even at low temperatures. The reaction between AlN and phosphate species can be written as follows:



Reaction (10) could not be confirmed by thermogravimetry. However no phosphate species could be detected in the sintered samples and supporting the evaporation of phosphorous. The reducing condition in the graphite furnace as discussed further below will contribute to the thermodynamic instability of the phosphate species.

The sintering additives YF₃ and CaF₂ used melt between 1000 and 1200°C (Seiranian et al., 1974). Therefore, the reaction of the fluorides with alumina present in the AlN during sintering is important. Firstly, the reaction of YF₃ with the surface alumina is considered. Based on the XRD data YF₃ is converted to Y₂O₃, which reacts to ternary oxides such as YAP, YAM and YAG. During heating of the green bodies, Y₂O₃ was presumably formed according to reaction (11) as Y₂O₃ is formed according to Fig. 16(a):

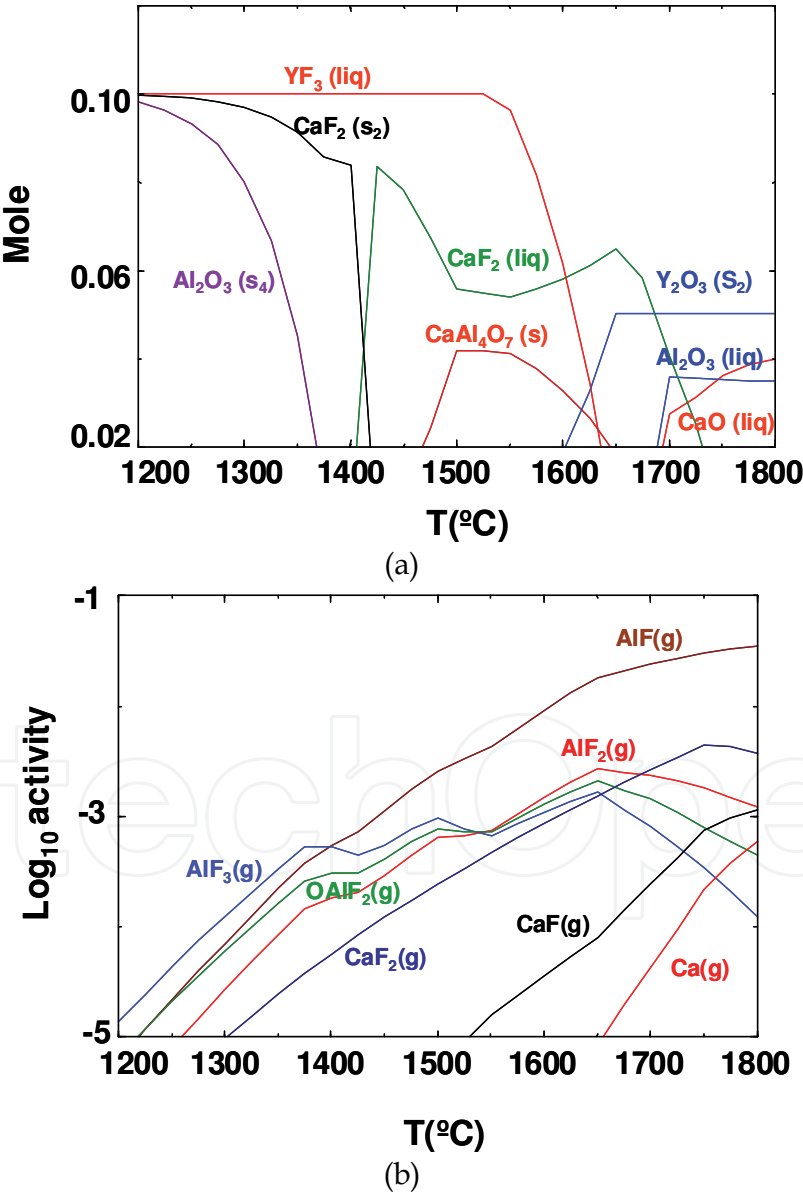
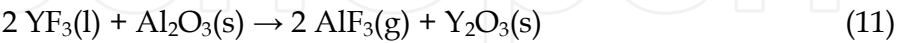


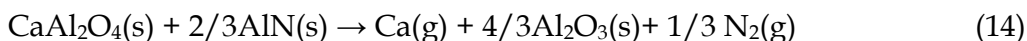
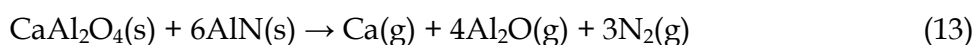
Fig. 16. (a) Minority condensed phases (a=1, AlN not present); (b) volatile species between 1200°C and 1800°C for the system 10 AlN + 0.1 CaF₂ + 0.1 YF₃ + 0.1 Al₂O₃ + 10 N₂.

Y_2O_3 is predicted to be formed in the thermodynamic calculations since the thermodynamic data for the ternary oxides is not included in the Factsage database. The melting point of YF_3 is reported to be 1155°C (Barin, 1989). Although some YF_3 might evaporate, most of YF_3 is assumed to react with Al_2O_3 and form $\text{AlF}_3(\text{g})$, which sublimates at temperatures higher than 1200°C , as can be observed in Fig. 16(b). CaF_2 can also react with alumina impurities present at the surface of the AlN, forming calcium aluminates (here simplified by CaO) and $\text{AlF}_3(\text{g})$, according to:

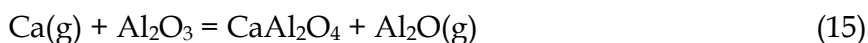


The presence of CaO containing species in the sintered materials using CaF_2 as sintering aid confirmed the conversion of CaF_2 to CaO . No fluoride species could be detected after sintering in agreement with the thermodynamic predictions.

Liquid phase sintering of AlN with CaF_2 at elevated temperatures ($>1300^\circ\text{C}$) results in a significant weight loss (Table 7) due to high vapour pressures generated by chemical reactions between AlN and the surface oxides as shown in equations (13) and (14) (Hagen et al., 2002).

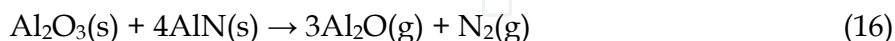


$\text{Ca}(\text{g})$ involved may react further with Al_2O_3 on the surface of AlN in the powder bed, for example, according to the following reaction:

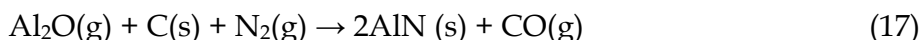


6.1 Effect of powder bed on densification, thermal conductivity and microstructure

The thermal conductivity, nature and amount of secondary phases were found to depend on powder bed composition and on the amount of processing aids, which probably introduce different amounts of carbon into the samples (Olhero et al., 2007). Two different compositions of powder bed were tested: 100-wt.% of AlN (100AlN) and 80-wt.% of AlN + 20-wt.% BN (80AlN/20BN). The weight loss of the AlN samples due to thermal decomposition of $\text{AlN}(\text{s})$ is considered to be negligible since the protecting embedding was used. However, the Al_2O_3 layer existing at the surface of AlN grains or further formed due to reaction with phosphates might react with AlN according to equation (16) resulting in a weight loss due to removal of oxygen (Hundere & Einarsrud, 1996):



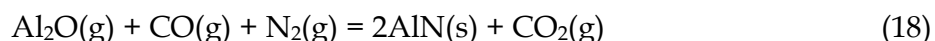
For this reaction to proceed, the $\text{Al}_2\text{O}(\text{g})$ formed has to diffuse through the protective powder bed and react with the carbon residue from the processing aids burn-out, the furnace itself or the outer graphite crucible to reform AlN according to reaction (17).



Hence, a more open powder bed will give the highest loss of $\text{Al}_2\text{O}(\text{g})$ species from the sample giving AlN ceramics with less oxygen content and therefore higher thermal conductivity (Hundere & Einarsrud, 1996). Since the 100AlN powder bed gave a material

with higher thermal conductivity in comparison to 80AlN/20BN, it might be suggested that the former powder bed has a more open structure.

When a sufficient CO(g) pressure is generated due to reaction (16), the Al₂O(g) might be nitrided inside the sample according to:



However, the CO₂ (g) formed in this reaction will further react with carbon in the surroundings forming more CO(g):



The change of the secondary phases from aluminium-rich to yttrium-rich using 80AlN/20BN or 100AlN as powder beds, respectively, can be understood based on the reactions given above, which remove alumina from the grain boundaries.

According to the results presented about influence of de-waxing atmosphere, a correlation observed between the C/O atomic ratio at the AlN powder surface and the Y/Ca in the sintering aids can be the reason for the differences in secondary phases. It was verified an important AlN surface enrichment in O₂ (≈ 9-10 at.%) and P (≈ 8 at.%) elements after treatment, attributed to the phosphate species of the protective layer against hydrolysis. Furthermore, the surface carbon amount in the AlN-treated samples is around 12-13 at% and increases about 8-9%, after binder burnout in N₂ atmosphere. In fact, based on the results obtained and according to Hundere (Hundere & Einarsrud, 1996) secondary intergranular phases became yttrium-richer (Y₄Al₂O₉) as surface C/O ratio increases, consequently enhancing the thermal conductivity. This explains the higher thermal conductivity values obtained for the AlN samples in the presence of larger amounts of processing aids when compared with the ones in presence of smaller amounts of binders and plasticizers. The smaller amounts of secondary phases present in the AlN sintered in 100AlN powder bed could also be explained by the higher weight loss measured for this sample.

According to the results obtained is possible to summarize that the phosphate species used to protect AlN from AlPO₄ and NH₃(g) during firing of the ceramics giving weight losses at temperatures lower than the liquid formation. Further, during liquid phase sintering with fluoride additives, chemical reactions take place between AlN and the sintering aid resulting in weight losses due to the formation of AlF₃ and Al₂O gas species. Evaporation of the Al₂O (g) reduces the oxygen content of the ceramics. The weight loss and the evaporation rate depend on the sintering temperature, the amount of the sintering aids and the embedding or surrounding atmosphere. The presence of reducing species (Carbon or CO(g)) further reduces the oxygen content of the AlN samples. Highest thermal conductivity was achieved using pure AlN as the powder bed and a large amount of processing aids giving carbon residue during firing (Olhero et al., 2007).

7. Conclusions

According to the main findings reported in the reviewed literature works on this subject it is possible to draw the following conclusions:

1. Soaking AlN powders in an aqueous solution of aluminium dihydrogenphosphate at temperatures around 60 °C offers the possibility of preparing water-resistant AlN

powders. Well-dispersed and high concentrated suspensions could be prepared from the protected AlN powder with added CaF_2 and YF_3 as sintering aids by using a commercial dispersant, Duramax 3005. The high degree of homogeneity obtained in the slip-cast green bodies made it possible to achieve relatively high sintered densities, similar to those usually obtained with organic-based suspensions after sintering at higher temperatures. The possibility to prepare high stable AlN suspensions in aqueous media opened the possibility to consolidate AlN samples by other colloidal shaping techniques, such as, freeze granulation and tape casting.

2. Fully dense and relatively high thermal conductive AlN ceramics can be consolidated by slip casting from aqueous suspensions and pressureless sintering at a temperature as low as 1750°C for a short time period of 2 h. This means that the organic solvents typically used to process this material can definitely be replaced by water. It was also shown that both the amount and ratio of the sintering additives play important roles in the microstructural development and in determining the final physical properties of the sintered bodies. The mixture of 4 wt.% YF_3 + 2 wt.% CaF_2 was the most appropriate combination to obtain AlN samples with relatively good properties.
3. Practically full dense AlN ceramics having thermal conductivities varying from 110 to 140 W/mK have been successfully produced from granulated powders processed in aqueous media. De-waxing atmospheres, sintering aids and firing conditions were identified as key processing parameters in controlling density and thermal conductivity. The burnout of organic additives in N_2 atmosphere left a significant amount of residual carbon at the AlN powder surface that partially removes the excess oxygen. The reaction between the remaining excess oxygen and the sintering additives (CaF_2 and YF_3) leads to the formation of yttrium-rich ($\text{Y}_4\text{Al}_2\text{O}_9$) secondary phases preferentially located at the triple points that enhance thermal conductivity. Contrarily, de-waxing in air favours the formation of more abundant alumina-rich yttrium aluminates that better wet the AlN grains and spread along the whole grain boundaries, increasing the density of structural defects, such as dislocations, therefore decreasing thermal conductivity.

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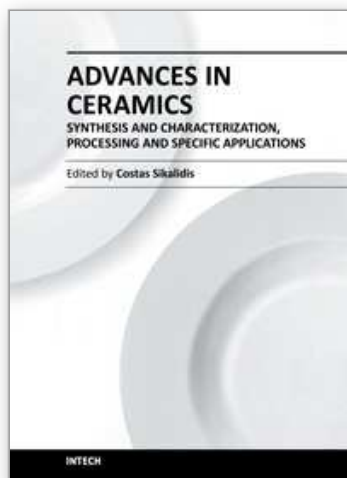
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