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Surface chemistry and hydrolysis of a hydrophobic-treated aluminium nitride powder

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Abstract

The surface chemistry of a hydrophobic-treated and an untreated AlN powder has been studied using XPS, FTIR and zeta potential measurements. Whilst the surface-treatment provided significant hydrophobic behaviour, experiments revealed that the powder could not completely resist hydrolysis without the additional use of ≥ 1 wt.% of an appropriate surfactant. The latter also improved the water-resistance of the untreated powder, though to a far lesser extent. The active hydrolysis protection mechanism for the treated powder is believed to be the creation of a molecular shell that was formed as a result of the surfactant adsorbing onto the hydrophobically treated surface.

Keywords: B. Surfaces; C. Chemical properties; AlN; Hydrolysis

1. Introduction

Aluminium nitride (AlN) has received considerable attention in recent years for a range of industrial applications. Both the thermal conductivity and electrical resistivity are better than those of alumina and as a consequence AlN ceramics are being increasingly used as substrate materials for electronic packaging and as refractories, amongst other applications [1–5]. Although AlN can be consolidated by hot pressing or hot isostatic pressing, pressureless sintering at temperatures of 1600–2000 °C is increasingly being used [6–8]. Common green fabrication processes for pressureless sintering are injection moulding, slip casting and tape casting. These techniques rely on the formation of dispersed suspensions and this offers advantages for dispersing small quantities of sintering aids, such as SiO_2, Y_2O_3 and Al_2O_3, homogeneously [9–11]. However, due to economic and environmental concerns, the processing of AlN powders into components via the use of aqueous, rather than organic, based suspensions is attracting increasing interest. Unfortunately, as shown by a range of studies based on X-ray photoelectron spectroscopy (XPS) [12–14], auger electron spectroscopy [15] and diffuse-reflectance Fourier transform infrared (FTIR) spectroscopy [16], the surfaces of AlN powders are easily hydrolyzed by water to form γ-AlOOH, $Al(OH)_3$ or γ-Al_2O_3 species [17,18]. Hence, in order to process AlN powders by aqueous colloidal routes, modification of their surfaces with either inorganic [19–21] or organic [22–25] chemicals is usually performed to make them hydrophobic. A dispersant is then required to allow the treated powders to be formed into an aqueous suspension.

In this paper, the surface chemistry and hydrolysis behaviour of a commercial hydrophobic-treated AlN powder and a second, untreated AlN powder were studied in conjunction with an appropriate dispersant. As a result, the mechanism by which the hydrophobic treatment depresses the hydrolysis process is suggested.

2. Experimental procedure

Two AlN powders were investigated, the first (Advanced Refractory Technologies (ART), USA) was hydrophobically

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treated whilst the second (Aldrich Chemical Company, USA) was untreated; both were produced by carbothermal reduction. The surfactant used during the work was a polyoxyalkylated aldylaryl phosphate ester sodium salt (Emphos 1316, ART, USA) whilst the other chemicals, all analytical grade, were $Al(OH)_3$, KBr, KNO_3 powders, NaOH and HCl solutions (Aldrich Chemicals, Ltd., UK).

The surface chemistry of the as-received AlN powders was investigated using XPS (X-ray Photoemission Spectroscopy, VG Scientific Ltd., UK). The measurements were performed using 15 kV, Mg radiation, an anode power of 300 W and a typical pass energy of 25 eV. The core level binding energies of the different peaks were normalized by setting the bonding energy for the C–C bond (C_{1s}) to be 285.0 eV [26].

Two separate series of suspensions were produced by dispersing 0.5 g of each of the AlN powders into 100 g deionised water containing surfactant concentrations of 0, 0.5, 0.7, 1.0, 2.0, 3.0 and 4.0 wt.% by mass of the AlN powders. The treated AlN powder required the use of an ultrasonic probe (300 kW, Kerry Ultrasonic Ltd., UK) to obtain a dispersion when no surfactant was used. The reactivity of the powders was measured by recording the suspension pH (Jenway 4040, Jenway Ltd., UK) as a function of hydrolysis time. The dried, hydrolyzed products were then characterized using FTIR (5DXB, Nicolet Instrument Corporation, USA) and XRD (D500, Siemens GmbH, Germany).

To determine the effect of the surfactant on the surface charge behaviour, the zeta potentials of both powders were measured as a function of pH and surfactant concentration (ZetaSizer 4, Malvern Instruments Ltd., UK). Both powders were initially dispersed into deionised water to form 0.5 wt.% suspensions. 0.5 ml aliquots were then diluted further by addition to 0.001 M KNO_3 solution, the latter being used as an electrolyte to control the ionic strength. The pH of these very dilute suspensions was controlled in the range 2–11 using HCl and NaOH solutions.

3. Results and discussions

3.1. Surface analysis of the treated AlN powder

The C_{1s} spectrum (Fig. 1a) shows two separate peaks at binding energies of 285.0 and 286.4 eV. Because both C–C and C–H bonds, no matter what hybridization, yield an XPS peak positioned at 285.0 eV, it could be from any one of several atomic structures, e.g. C, CH, CH_2 or CH_3. The second, weaker peak at the higher binding energy is probably attributable to the C–O bond as the oxygen usually induces a shift to a higher energy by ~1.5 eV [26]. The N_{1s} spectrum (Fig. 1b) shows a single nitrogen peak at 397.6 eV that can be attributed to the Al–N bond in crystalline AlN and agrees well with other data, viz. 396.5 eV [13] and 398.6 eV [14]. The Al_{2p} spectrum (Fig. 1c) suggests the presence of AlOOH, Al_2O_3 or $Al(OH)_3$ species on the surface of the treated AlN powder [13]. The O_{1s} spectrum consists of three peaks positioned at 531.4, 532.7 and 534.2 eV (Fig. 1d). The first could be assigned to the Al–O bond in any of the compounds AlOOH, Al_2O_3 or $Al(OH)_3$ since they all occur at approximately 531 eV [13,26]. The strongest peak at 532.7 eV is best fitted to the Si–O bond in the polysiloxane structure, ~532 eV [26]. The peak at 534.2 eV is close to the binding energy for oxygen in carboxyl groups, which is known to have values of 533.5 eV [26]. Finally, the Si_{2p} spectrum (Fig. 1e), indicates three peaks positioned at 98.1, 100.3 and 102.6 eV. An $Si_{2p(3/2)}$ peak occurs at 101.8 eV in a type of silicone poly(dimethylsiloxane) [27], however the peaks at the lower binding energies have not been identified.

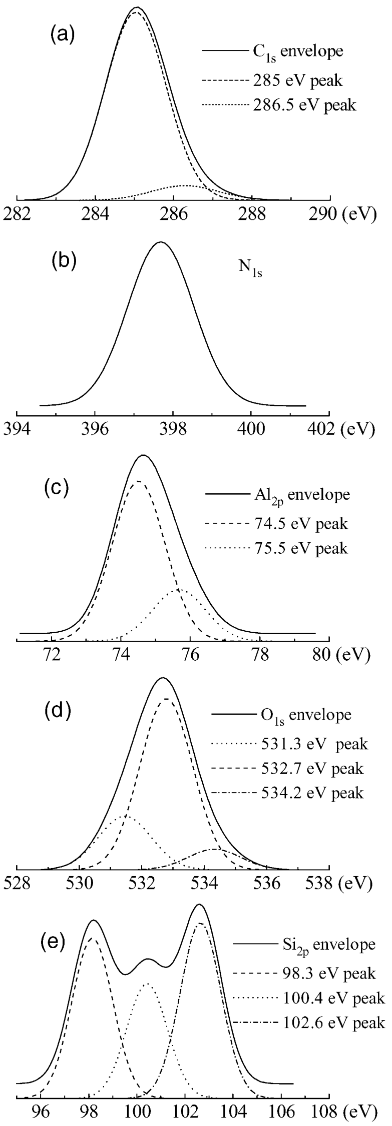

Fig. 1. XPS spectra for treated AlN powder. (a) C_{1s} spectrum, (b) N_{1s} spectrum, (c) Al_{2p} spectrum, (d) O_{1s} spectrum, and (e) Si_{2p} spectrum.

Table 1 shows the percentages of the different elements present within the surface layer, and the ratios of Al to N and

Table 1
Calculated percentages for the different elements present in the surface layer and relevant ratios

	Elements					Atomic ratio	
	Al	Si	O	N	C	Al:N	O:Si
Sensitivity	0.18	0.25	0.66	0.42	0.25	1.6:1	3.1:1
Percentage	16	11	34	10	29		

Si to O, obtained from the XPS spectra using the approach of Briggs and Seah [26]. The results show significant amounts of oxygen and carbon in the surface layer; these can be primarily attributed to the organic species used for the surface modification. The excess Al indicated by the higher than expected atomic ratio of 1.6 Al to 1.0 N may be assumed to represent a nitrogen deficiency caused by either oxidation or hydrolysis of the surface layer. Similarly, the excess oxygen represented by the 3.1 O to 1.0 Si ratio is believed to arise from the presence of the Al hydroxide or oxide and the modifying organic species.

3.2. Hydrolysis behaviour of the AlN powders

The hydrolysis of AlN powders occurs according to the thermodynamically favourable reactions [28]:

$$\mathrm{AlN} + 2\mathrm{H_2O} \rightarrow \mathrm{AlOOH_{amorph}} + \mathrm{NH_3} \quad (1)$$

$$\mathrm{NH_3} + \mathrm{H_2O} \leftrightarrow \mathrm{NH_4^+} + \mathrm{OH^-} \quad (2)$$

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

the transformation from the amorphous monohydroxide, AlOOH, to the crystalline bayerite, $\mathrm{Al(OH)_3}$, being generally believed to be a dissolution-recrystallisation process [12,29]. The presence of these species is thus indicative of the hydrolysis of AlN.

The result shown in Fig. 2 confirmed that the treated AlN powder could not resist the hydrolysis process on its own indicating the existence of hydrophilic sites on the particle surfaces. Without the presence of the surfactant, the pH of the suspension increased rapidly before reaching saturation (the initial slight decrease in pH was probably due to the dissolution of the organic acid used in the surface-treatment of the powder), whilst when the surfactant was used it can be seen that only 1.0 wt.% was sufficient to suppress the hydrolysis reaction.

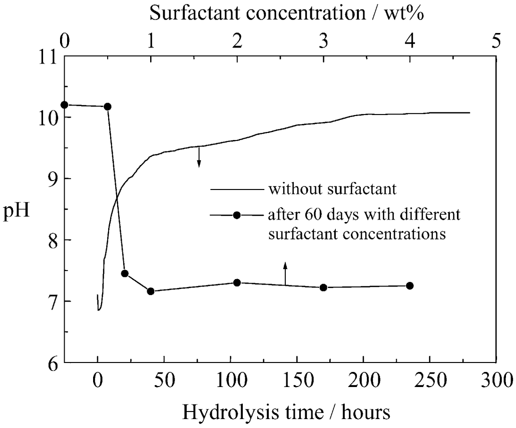

Fig. 2. Change in pH with time for an aqueous suspension of the treated AlN powder without surfactant and the pH after 60 days for suspensions prepared with the surfactant, as a function of surfactant concentration.

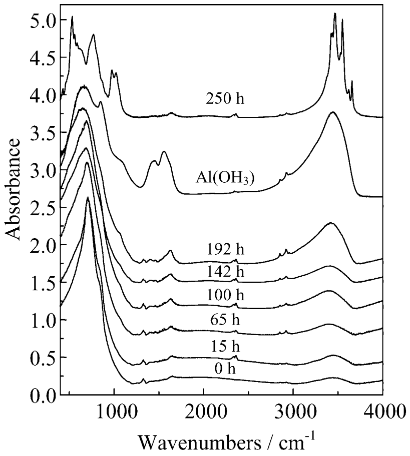

Fig. 3. FTIR spectra for treated AlN powder, without addition of surfactant, after hydrolysis for varying time periods and a reference spectrum for powdered $\mathrm{Al(OH)_3}$.

The FTIR analysis of the hydrolyzed products for the treated powder without surfactant is shown in Fig. 3. The peaks centred at 710 and 1326 $\mathrm{cm^{-1}}$ have been assigned to the vibration of the AlN bond [30] whilst the increasing presence of physisorbed molecular water was confirmed by the peaks at 1398, 1457 and 1635 $\mathrm{cm^{-1}}$ and the shoulder feature at about 1580 $\mathrm{cm^{-1}}$ [31]. The absorption bands at 1398 and 1580 $\mathrm{cm^{-1}}$ are attributable to water molecules bound to tetrahedral and octahedral coordination Al ions respectively, whilst the band at 1457 $\mathrm{cm^{-1}}$ arises from water molecules that bridge between these sites. The 1635 $\mathrm{cm^{-1}}$ peak originates from the bending vibration for molecular water that is not coordinately bonded to an AlN ion [32]. The broad peak at around 3400 $\mathrm{cm^{-1}}$ that increases with hydrolysis time has been attributed to the O–H stretching vibration of AlOH species that undergo hydrogen bonding with neighbouring hydroxyl groups. In addition, the O–H stretching vibration of molecular $\mathrm{H_2O}$ may also contribute to this band. Whilst the gradual change in the location and intensity of the peaks with hydrolysis time up to 192 h increasingly matches the referenced amorphous $\mathrm{Al(OH)_3}$, by 250 h the spectrum is much closer to that of crystalline bayerite ($\mathrm{Al(OH)_3}$) [29].

The FTIR spectra for the treated powder after hydrolysis for 60 h with different levels of surfactant (Fig. 4) showed no significant changes in the patterns when the concentration was $\geq$1.0 wt.%, and the sample containing 0.7 wt.% showed only very slight changes, however that containing 0.5 wt.% showed total conversion to crystalline bayerite. This result confirms the earlier results (Fig. 2) that as little as 1.0 wt.% addition was sufficient to completely suppress the hydrolysis reaction.

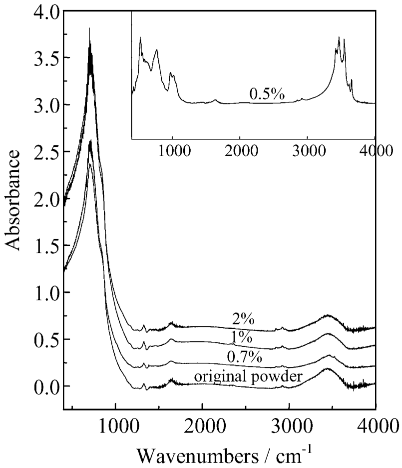

Fig. 4. FTIR spectra for treated AlN powders after contact with water containing various levels of surfactant for 60 days.

The presence of the surfactant also slowed down the hydrolysis process for untreated AlN powder, albeit only slightly (Fig. 5). Fig. 6a indicates that without the surfactant present the peak intensity of the AlN was reduced greatly after only 10 h of hydrolysis and crystalline bayerite was observed after 21 h. However, with the addition of 1 wt.% surfactant the AlN peaks were still very strong after 21 h of hydrolysis (Fig. 6b). Despite this, after 40 h severe hydrolysis occurred with or without the presence of the surfactant, even up to concentrations as high as 4 wt.%.

3.3. Interactions between the surfactant and particle surface

The zeta potential data in Fig. 7a and b reveals information about the absorption of the surfactant onto the particle surfaces. Fig. 7a shows that the IEP was shifted from ~8.2 for the untreated powder, where the presence of the A1OOH species will have dominated, to ~2.8 for the treated powder as a result of the presence of the acidic hydrophilic species. This difference in the zeta potentials can also be seen at 0 wt.% surfactant addition in Fig. 7b. In both cases there was a rapid decrease in zeta potential as the surfactant attached in increasing quantities until ~1 wt.%, when there was a levelling off in the rate of change. For the treated powder, the zeta potential was almost constant above 1 wt.%, suggesting that saturation had been reached whilst for the untreated powder the zeta potential continued to decrease, albeit at a much slower rate, suggesting that attachment was still possible. This tied in well with the fact that in the case of the treated powder 1 wt.% of surfactant was sufficient to almost completely prevent hydrolysis. Thus, it appears that the combination of the hydrophobic treatment and the surfactant formed a kind of ‘shell’ that prevented the water molecules hydrolysing the powder. The following theory is based on the experimental observations recorded and the literature; photocorrelation spectroscopy, which was not possessed at the researchers’ laboratory, should reveal further information.

The adsorption of the surfactant onto the treated AlN is almost certainly the result of hydrophobic interaction [33,34]. As a result, the surfactant will have adsorbed

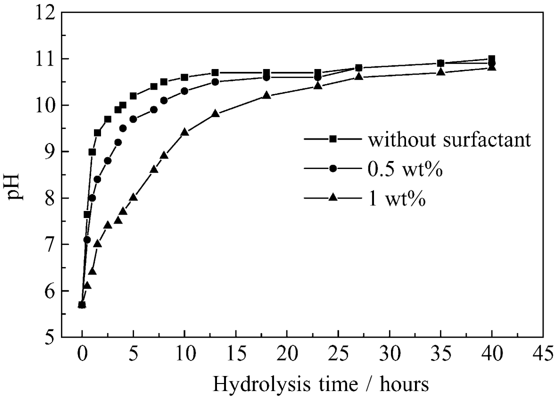

Fig. 5. Change in pH with time for an aqueous suspension of the untreated AlN powder as a function of surfactant concentration.

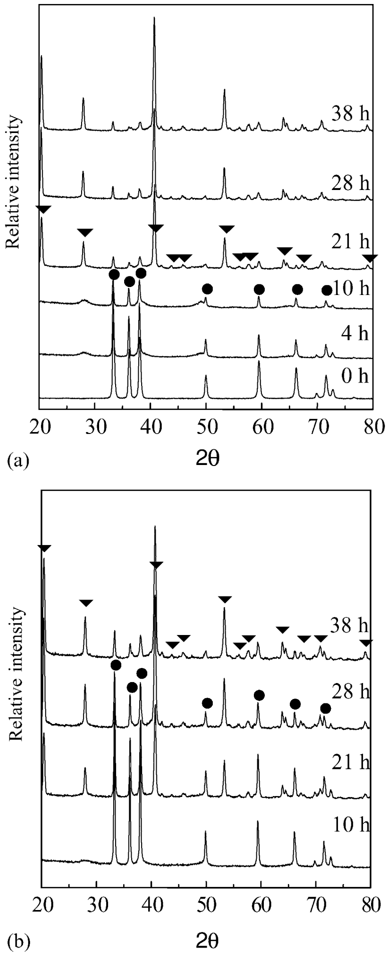

Fig. 6. XRD spectra of untreated AlN powder: (a) without addition of surfactant and (b) with addition of surfactant, after hydrolysis for varying time periods (●: AlN peaks, ▼: crystalline bayerite).

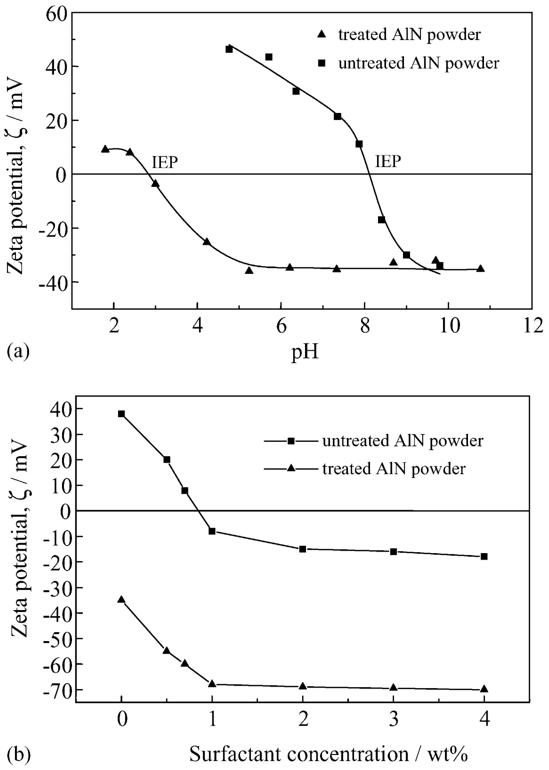

Fig. 7. Changes in zeta potential as a function of (a) pH and (b) surfactant concentration at pH 5.8, for the treated and untreated AlN powder in aqueous media, KNO_3 concentration 0.001 M.

along the particle surfaces, gaining energy from the interaction between the long hydrocarbon chain and the underlying surface [33]. As the adsorption density increased lateral interactions between the adsorbed molecules will have become increasingly important [35] leading to a dense layer of surfactant forming on the treated AlN particles surfaces, which will have gradually covered the hydrophilic sites. The experimental results are consistent in showing that above a critical surfactant concentration, in this case ~1.0 wt.%, the surface was fully covered and therefore the particle surfaces were protected from further attack by water molecules.

For the untreated powder, however, the surfactant will have attached onto the particle surfaces via electrostatic interaction between the charge on the particle surface and the charge on one end of the surfactant chain [35]. Since this attachment will have been in the form of point contacts, there will have been a lack of complete coverage and many hydrophilic sites will have remained uncovered to which the water molecules could adsorb leading to hydrolysis.

It therefore appears that the initial hydrophobic surface-treatment of the AlN powder had two functions, first to minimize contact between water molecules and the particle surfaces before the adsorption of the surfactant took place, and second to provide sites for the attachment of the surfactant that, in combination with the surface-treatment, effectively sealed the surfaces from hydrolytic attack.

4. Conclusions

The hydrophobic nature of the as-received treated AlN powder is believed to be the result of surface modification using a silicone-based organic acid or ester, however neither this nor the surfactant were sufficient on their own to protect the AlN from hydrolysis although it could be slightly depressed for a short period of time by either of them. However, when ≥1.0 wt.% of the surfactant was added to a suspension of the surface treated AlN powder the combination of the two was sufficient to prevent significant hydrolysis. It is believed that this occurred as a result of a continuous 'shell' being formed of the surfactant molecules bonded along the particle surfaces. This covered the hydrophilic sites and prevented the water molecules from gaining access to them. Whilst the surfactant was capable of bonding to the untreated AlN surfaces, probably via point contacts by electrostatic attachment, it was unable to form a dense enough layer to prevent hydrolysis.

Thus, the hydrophobic treatment of the powder appears to have had two effects. Firstly, it minimized the initial contact between water and particles whilst the adsorption of the surfactant onto the particle surfaces occurred. Secondly, it ensured that the AlN surfaces were mostly hydrophobic thus ensuring that there were an abundance of suitable sites to which the surfactant molecules could attach and that continuous coverage could be achieved.

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