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Hydrophobing of aluminium nitride powders

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The hydrophobing of AlN powders through adsorption of capric acid, stearic acid and cetyl alcohol on the particle surface was investigated by statistical analysis. Stearic acid as surface adsorbent and cyclohexane as solvent were identified as the best combination for achieving highly effective hydrophobicity of AlN. The adsorption data obtained for this combination indicated a Langmuir chemisorption isotherm. Even after 96 h leaching in water, no crystalline phase other than AlN could be detected by X-ray diffraction (XRD).

1. Introduction

AlN has interesting properties for a wide range of applications, such as high thermal conductivity and electrical resistivity, and good mechanical properties at high temperature. The fabrication of AlN-based ceramic parts commonly involves colloidal processing, which has to be carried out in non-aqueous solvents, because of the high reactivity of the AlN powder with water.

The mechanism and kinetics of the hydrolysis reaction of AlN have been extensively studied [1–5]. A simplified representation of the reactions taking place in neutral water is

$$AlN + 2H_2O \longrightarrow AlO(OH)_{amorphous} + NH_3 \quad (1)$$

As the NH_3 raises the pH according to

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2)$$

formation of crystalline bayerite, $Al(OH)_3$, becomes favourable at room temperature

$$AlO(OH)_{amorphous} + H_2O \xrightarrow{OH^-} Al(OH)_{3,\,crystalline} \quad (3)$$

The pH ultimately strives towards 12 as a result of the dissociation equilibrium of ammonium hydroxide [1]. Thus, the stability of the AlN powder with respect to hydrolysis in water can be evaluated by recording the ΔpH with time.

To suppress AlN hydrolysis, organic long-chain molecules, such as carboxylic acids, may be used as a surface-modifier not only to improve the hydrophobic nature of AlN powder, but also to improve the dispersive properties of powders in liquid suspensions [6–11]. The present contribution investigates the influence of surface treatment parameters (surfactant, solvent, and others) and colloidal processing parameters (pH, mixing time) on the hydrolysis of AlN in aqueous suspension. A statistical method is employed to determine the relative significance of these parameters in relation to AlN stability in water (ΔpH).

All the possible combinations of the various factors (full factorial design) cannot normally be overcome due to the number of experiments that would be necessary. Therefore, a one-by-one factor method is commonly used, in which one factor is varied while all the other factors are held constant. The drawback of this method is that the result of each experiment is only valid for fixed experimental conditions, and the prediction of experimental results for other conditions is uncertain. Therefore, a fractional factorial design method was used to reduce the number of experiments necessary to obtain unequivocal results for hydrophobing AlN powders.

Conducting fractional factorial design makes use of orthogonal arrays [12–15]. Data from all experiments in the set are analysed by means of standardized analysis of variance and the F-test to evaluate the significance of specific factors.

2. Materials and methods

2.1. Matrix experiments

Table I summarizes the parameters taken into account for the statistical analysis. For each parameter two different values (except for the type of surface modifier) were chosen to cover the range of reasonable processing conditions.

Components (solvents and surfactants) with different properties were chosen. A non-polar, cyclohexane (dielectric constant 2.015, at 25 °C [16]), as well as a polar solvent, acetone (dielectric constant 20.7, at 25 °C [16]), were used. Three different surfactants were employed: cetyl alcohol ($CH_3(CH_2)_{15}OH$), capric acid ($CH_3(CH_2)_8COOH$) and stearic acid ($CH_3(CH_2)_{16}COOH$), in order to analyse the influences of the functional groups (–OH, –COOH) and of the chain length. The remaining processing parameters were chosen according to standard procedures presented in the literature [6].

The total degrees of freedom f that gives the minimum number of experiments that must be performed to investigate the control factors is given in Table II. One degree of freedom is always associated with the overall mean regardless of the number of factors to be

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TABLE I Control factors and their levels

Factors	Levels		
	1	2	3
M (surface-modifier)	Capric acid	Stearic acid	Cetyl alcohol
D (predehydration)	No	Yes	
P (powder)	AlN	AlN + 6 wt % CaF_2	
S (solvent)	Cyclohexane	Acetone	
R (molar ratio $M:P$)	1:1	1:2	
X (mixing time)	3 h	5 h	
F (filtering/washing)	2 times	4 times	
E (drying environment)	Air	Vacuum	
T (drying temperature)	120 °C	250 °C	
Y (drying time)	3 h	6 h	

TABLE II Calculation of degrees of freedom

Factor	Degrees of freedom f
Overall mean	1
M	$1 \times (3 - 1) = 2$
$D, P, S, R, X, F, E, T, Y$	$9 \times (2 - 1) = 9$
Total	12

TABLE III Matrix experiment

Experiment No.	Column number and factor assigned									
	1 + 2	3	4	5	6	7	8	9	10	11
	M	D	P	S	R	X	F	E	T	Y
1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2
3	1	2	2	2	1	1	1	2	2	2
4	2	1	2	2	1	2	2	1	1	2
5	2	2	1	2	2	1	2	1	2	1
6	2	2	2	1	2	2	1	2	1	1
7	3	2	2	1	1	2	2	1	2	1
8	3	2	1	2	2	2	1	1	1	2
9	3	1	2	2	2	1	2	2	1	1
10	3	2	1	1	1	1	2	2	1	2
11	3	1	2	1	2	1	1	1	2	2
12	3	1	1	2	1	2	1	2	2	1

TABLE IV AlN powders used

Powder	Composition (wt %)				BET ($m^2 g^{-1}$)	d_{50} (μm)
	O	N	C	Fe		
AlN Grade B (H. C. Starck)	1.60	34.0	0.070	0.005	3.2	1.3
AlN GP5 (Bayer)	0.91	32.6	0.051	0.002	8.0	0.4

studied. In addition, the number of degrees of freedom related to a factor is equal to one less than the number of levels for that factor. Thus, twelve experiments are sufficient to estimate the effect of each factor.

The orthogonal array L_{12} (Table III) [17], which consists of twelve individual experiments corresponding to the twelve rows (equal to the degrees of freedom required for the case study), was chosen. The ten columns of the matrix represent the ten parameters as indicated in the Table. The first and second columns of the original L_{12} orthogonal array were combined in order to offer three settings for the factor M (surface modifier). The entries in the matrix represent the levels of the parameters. For example, experiment 1 was conducted with each parameter at the first level.

2.2. Materials and processing

AlN powders supplied by H. C. Starck (nitrided aluminium) and Bayer (gas phase synthesised [18]) were used, and their characteristics are summarized in Table IV. In addition, CaF_2 powder (> 99.9%), capric acid (> 98%), stearic acid (> 97%), cetyl alcohol (> 97%), cyclohexane (> 99%) and acetone (> 99.5%, dry) were used. CaF_2 was taken as a sintering additive to promote liquid-phase sintering of AlN at low oxygen levels [18].

One half of the AlN powder was dehydrated in vacuum at 360 °C for 3 h. The other half was taken as received. The surface-modifiers were mixed with a solvent in two different quantities in relation to the powder to be treated (either a molar ratio 1:1 or 0.5:1). Subsequently, the AlN powder (with or without 6 wt %CaF_2) was added to the solution. The suspensions were mixed under a light argon flow in a three-neck reaction flask with a magnetic stirrer, at a temperature 20 °C higher than the boiling point of the solvent. The AlN powder was filtered under vacuum and washed with 100 ml solvent. The mixing time and the number of washings were varied. The drying treatment was carried out under different conditions, shown in Table I (temperature, time, atmosphere).

2.3. Measurement of AlN stability in water

The measurement of pH was made at room temperature with a digital pH meter (pH 90, WTW, Weilheim, Germany) in aqueous suspensions of surface-modified AlN powder as well as of pure AlN powder. A concentration of 0.5 wt % powder was always used (0.15 g powder 30 g^{-1} powder + water). In two of four measurements, mixing was carried out for 1 h in an ultrasonic horn (RK51OH, Bandelin, Berlin, Germany) at a frequency of 35 kHz. The initial pH of the aqueous suspensions was also varied (either 5.1 other 6.0).

The mass change of treated AlN powders was measured after heating in air at 500 °C for 1 h. These measurements were converted to adsorption density, in moles of surface modifier/grams of aluminium nitride. Crystalline phases of surface-modified, leached and dried AlN powders (according to Table I) were analysed by X-ray powder diffraction (XRD) (PW 1729, Philips, Eindhoven, Netherlands), using monochromatic CuK_{α} radiation. Infrared (IR) spectra were obtained (Perkin Elmer 783, Eden Prairie, MN, USA) from samples which were ground with an excess of KBr (200 times the mass of sample, i.e. 1.5 mg of AlN).

3. Results and discussion

3.1. Analysis of variance

An analysis of variance was performed on the ΔpH after 24 h leaching in water of the AlN powder samples (Table V). *f* is degrees of freedom (see Table II), Σ is the sum of squares for the factor, *V* is the variance, i.e., the sum of squares for the factor divided by the degrees of freedom in that factor, and *F* represents the results of the Fisher significance test. The *F* value corresponds to the variance of each factor divided by the error variance. Single asterisks denote that the factor was significant at a 95% confidence level and double at 99%. Some variances of control factors, which seem to have no relative significance, has been pooled into an estimate of error. The final column (ρ) indicates the percentage contribution to the variance by each factor.

The factors *M* (surface modifier) and *S* (solvent) ($F = 13.62$ and 6.79, respectively) are the most important in terms of ΔpH. Similar analyses were made for other times (1 and 96 h), confirming the factors *M* and *S* to be the most significant. Figs 1 and 2 show mean values of pH along the leaching time in water for the AlN powders treated with different surface-modifiers or solvents, i.e. the two most significant factors, according to the analysis of variance. From these figures it can be seen that the AlN powders treated with stearic acid as surface-modifier and cyclohexane as solvent present the most pronounced hydrophobic character. Other factors have a less significant influence on the results; therefore, the most economic levels of these factors should be used.

Fig. 3 illustrates the ΔpH after 24 h leaching in water of the coated AlN powders in relation to the adsorption density. All possible combinations of surfactant and solvent and a point corresponding to the as-received AlN powder are shown. Excluding experiments 1 and 11, in which an overdeposition of surfactant took place (there was probably a solidification of the surfactants during filtration/washing), the adsorption density is relatively low. Experiments 2, 4, 5 and 6 yield the highest hydrophobicity. Three of these four points are related to the powders that have stearic acid as surface-modifier. The combination of stearic acid and cyclohexane corresponds to the lowest ΔpH value (considering to a mean value of experiments 4 and 5, both using stearic acid and acetone).

The XRD data collected on non-coated AlN powders after 0, 24, and 96 h leaching in water (Fig. 4) showed gradual formation of bayerite, $Al(OH)_3$ [2]. The AlN powder coated with stearic acid in cyclohexane solution showed no crystalline phase other than AlN in the time interval measured (Fig. 5), indicating the protective effect of the hydrophobic coating.

3.2. Surface adsorption of stearic acid

Two different AlN powders (with a surface area of 8.0 and 3.2 $m^2 g^{-1}$) were added to varying concentrations of stearic acid (from 1 to 10 wt % with respect to AlN + surfactant) solution in cyclohexane. The mass change of surface-modified and dried powders was

TABLE V Analysis of variance for mean ΔpH of treated AlN powders after 24 h leaching in water

Factor	*f*	Σ	*V*	*F*	ρ (%)
M (surface-modifier)	2	21.84	10.92	13.62**	30.81
D (predehydration)	1	0.01	0.01 o		
P (powder)	1	0.93	0.93 o		
S (solvent)	1	5.45	5.45	6.79*	7.07
R (molar ratio *M*:*P*)	1	2.15	2.15	2.69	2.06
X (mixing time)	1	0.00	0.00 o		
F (filtering/washing)	1	0.84	0.84 o		
E (drying environment)	1	2.57	2.57	3.21	2.69
T (drying temperature)	1	1.55	1.55 o		
Y (drying time)	1	0.00	0.00 o		
Reproducibility error	36	30.35	0.84 o		
Pooled error	42	33.68	0.80		
Total	47	65.69			

o Pooled factor into error.
* Significant at 95% confidence. $F(1,42) = 4.07$, $F(2,42) = 3.22$.
** Significant at 99% confidence. $F(1,42) = 7.27$, $F(2,42) = 5.15$.

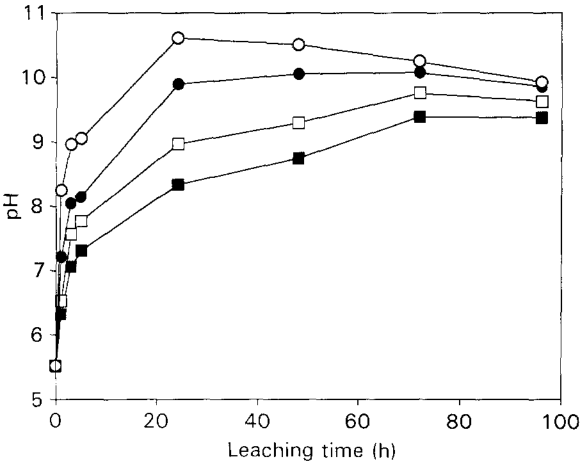

Figure 1 Mean values of pH for AlN powders treated with different surface modifiers after leaching in water. (○) non-coated powder; (●) cetyl alcohol; (□) capric acid; (■) stearic acid.

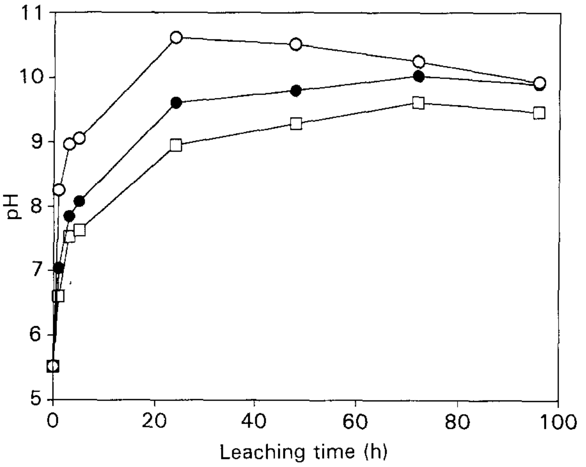

Figure 2 Mean values of pH for AlN powders treated with different solvents after leaching in water. (○) non-coated powder; (●) acetone; (□) cyclohexane.

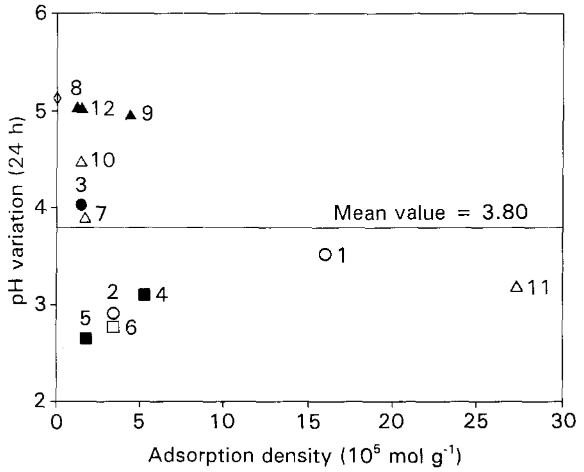

Figure 3 Mean values of ΔpH for surface-treated AlN powders, after 24 h leaching in water, in relation to the adsorption density (numbers indicate test, Table III).

determined. The adsorption data (Fig. 6) fitted a Langmuir-type curve very well [19, 20]

$$\Gamma = \Gamma_{\max} KC_A/(1 + KC_A) \qquad (4)$$

with a correlation coefficient of 0.9990 and 0.9933 for the powders with 8.0 and 3.2 $m^2 g^{-1}$, respectively. Γ is

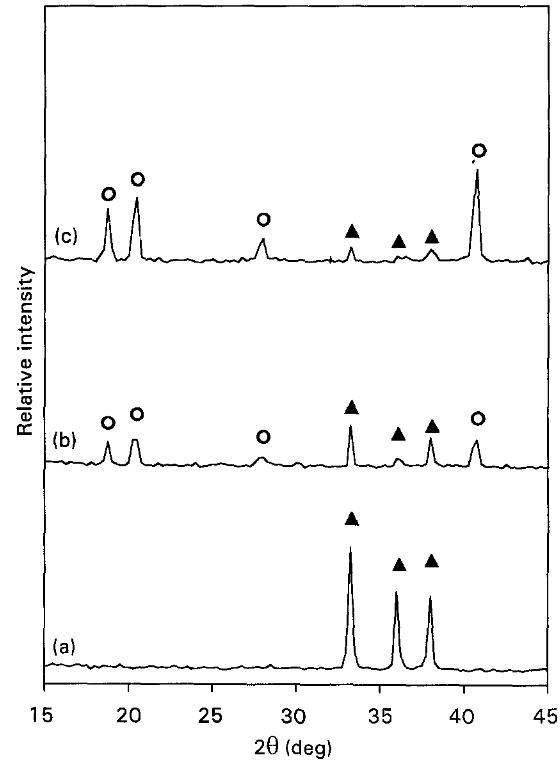

Figure 4 XRD of non-coated AlN powders after leaching in water. (○) Bayerite $Al(OH)_3$; (▲) AlN.

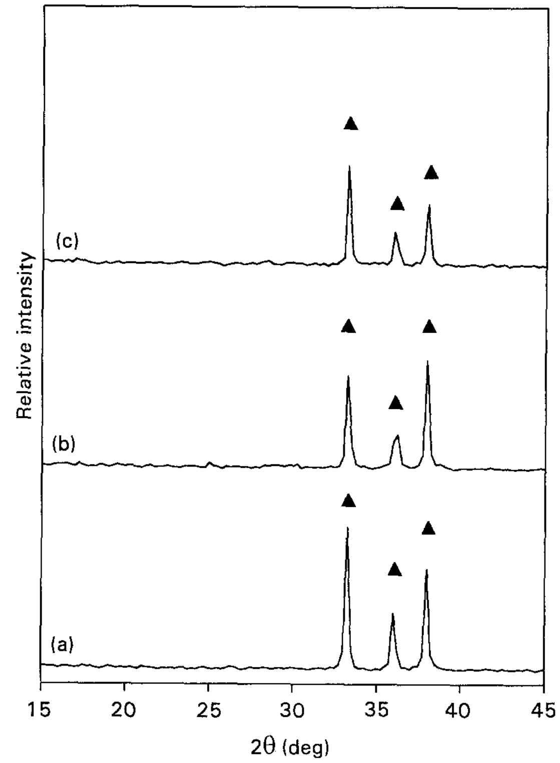

Figure 5 XRD of stearic acid-coated AlN powders after leaching in water. (▲) AlN.

the adsorption density, $\Gamma_{\max}$ is the maximum adsorption density, both in mol g^{-1} solid, K is the adsorption constant, in l mol^{-1}, and C_A is the added stearic acid concentration, in mol l^{-1}. The calculated values in this case were $\Gamma_{\max} = 2.70 \times 10^{-5}$ mol g^{-1}, and $K = 2.99 \times 10^{-3}$ l mol^{-1}, for the powder with the

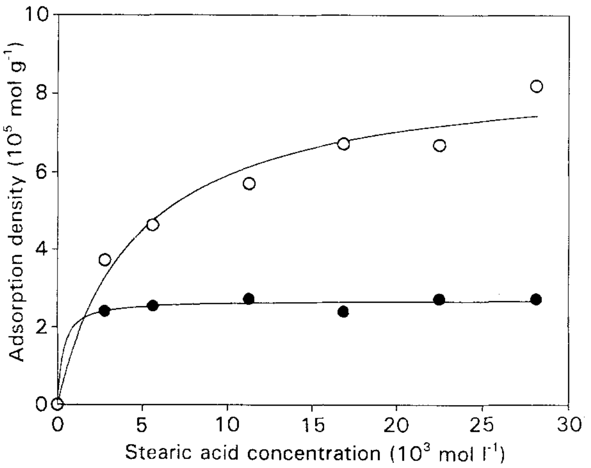

Figure 6. Adsorption isotherm of stearic acid-coated AlN powders. (○) 8.0 m^2 g^{-1}; (●) 3.2 m^2 g^{-1}.

lower surface area, and $\Gamma_{\max} = 8.6 \times 10^{-5}$ mol g^{-1}, and $K = 0.22 \times 10^{-3}$ l mol^{-1}, for the powder with the higher surface area. As expected, the maximum adsorption density was proportional to the surface area of the powder.

IR spectra of AlN powders are presented in Fig. 7. The presence of –OH groups in the AlN starting powder is clearly seen in the strong, broad bands characteristic of the O–H stretching fundamentals centred at ~3500 cm^{-1} (Fig. 7(a)), which correlates with a small hydrated oxide content [2]. A very strong, broad Al–N stretching fundamental centred at ~700 cm^{-1} (not shown) could be seen along with a group of features around 1400 cm^{-1}; the strongest of them at 1330 cm^{-1} is attributed to an overtone of this fundamental [4]. In Fig. 7b a softening of the O–H band is discernible, indicating that the primary –OH groups at the surface of the AlN powders had partially disappeared. New sharp bands can be observed just below 3000 cm^{-1}, corresponding to a C–H stretching band of an aliphatic chain, the strongest peak of added stearic acid [21]. Peaks corresponding to a stearate formation cannot be seen, because they are too weak in comparison to C–H peaks. In Fig. 7c surface-treated AlN powder after 96 h leaching in water shows a decrease of the bands at 1330 and ~3000 cm^{-1}. These observations are characteristic of the formation of non-crystalline AlO(OH) (see Equation 1) and of the absence of aliphatic chain. For the same range, XRD analyses of hydrophobized AlN powders (see Fig. 5) showed no crystalline phase other than AlN, suggesting the existence of an amorphous oxide hydrate phase [3, 4], which should be the subject of further investigations.

The mechanisms involved in the process of adsorption from liquid solution have been discussed previously [11, 22, 23]. Those experimental results [11, 23, 24] suggested that the polarities of adsorbent (solid surface), liquid medium (solvent) and adsorbate (solute) molecules play an important role. In the present case the adsorbate molecules are amphiphilic, i.e. they contain both a hydrophobic non-polar part (aliphatic chain) and a hydrophilic polar ionic carboxyl group. Depending on the relative magnitude of the hydrophobic or hydrophilic part and the polarity or non-polarity of the solid surface and of the solvent, these solutes may become adsorbed primarily either by the hydrophobic effect (repulsion between aliphatic chain and a polar molecule) or by the electrostatic or coordinative interaction (attraction between functional groups of solute and solid surface) [25, 26].

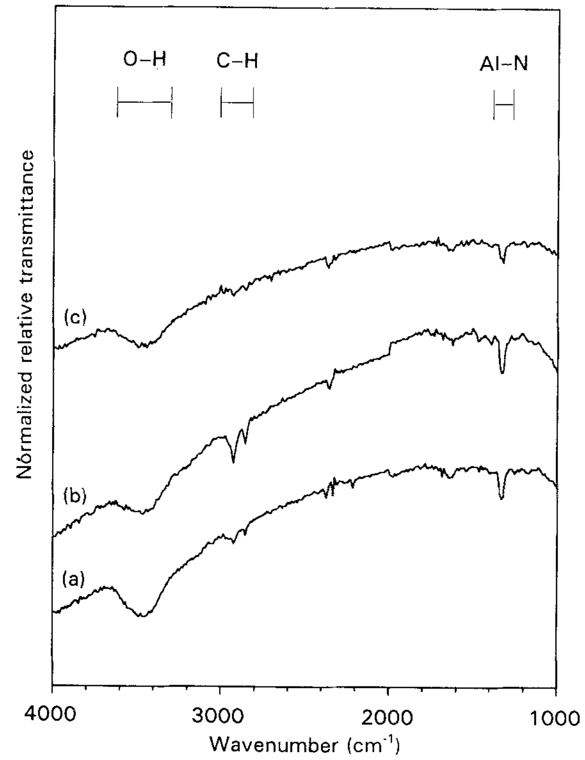

Figure 7 IR spectra of AlN powders: (a) as-received, (b) stearic acid-coated, and (c) stearic acid-coated after 96 h leaching in water.

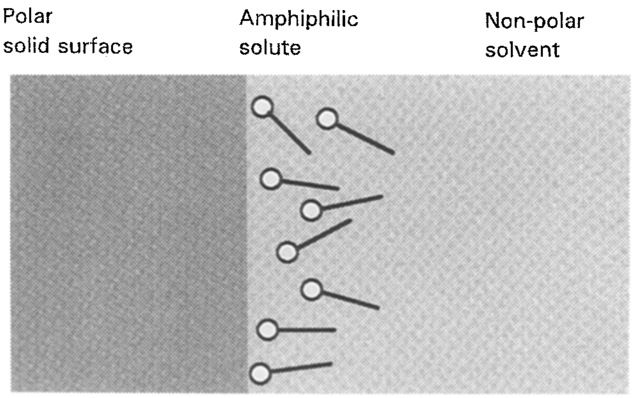

Figure 8 Stearic acid adsorption from cyclohexane.

The first step in the adsorption mechanism of stearic acid in cyclohexane on AlN is an orientation of the hydrophilic group of the surfactant (carboxyl group) towards the solid surface (Fig. 8). Using a non-polar solvent (cyclohexane) has produced a more effective covering of the AlN powder surface. Such behaviour has already been related to the adsorption of stearic acid on polar surfaces [27], and is in agreement with the chemisorption hypothesis.

The reaction of AlN with atmospheric moisture and/or oxygen showed the formation of an aluminium oxide or hydroxide film at room temperature [2, 3]. Hydrophilic surfaces are typical for oxides of Al and Si [28, 29]. Water molecules adsorb dissociatively onto an oxide to form surface –OH groups [29]. According to recent investigations [30], Al_2O_3 and AlN exhibited comparable surface characteristics and similar behaviour in the interaction with functional groups of organic additives. The formation of a covalent bond between surface hydroxyl groups of oxide surfaces and organic long-chain molecules, such as carboxylic acids, has been postulated [10, 24].

Thus, the chemical reaction of a carboxylic acid in contact with oxidized surfaces of AlN powders can be described to a first approximation by

$$>\mathrm{AlOH} + \mathrm{R{-}COOH} \rightleftharpoons\ >\mathrm{Al{-}OOC{-}R} + \mathrm{H_2O} \quad (5)$$

In this model, a carboxylic acid molecule should initially point its hydrophilic carboxyl group towards the hydroxyl groups present on the surface. After the reaction, the powder surface is covered with a monomolecular layer of aliphatic chain, which provides an effective protection of the powder surface against direct contact with water.

4. Conclusions

Based on statistical analysis the conditions for effective protection of AlN powder against hydrolysis reaction were evaluated. The hydrophobing of AlN powder was achieved by surface adsorption of stearic acid in non-polar solvent cyclohexane. The surface-treated AlN powder showed no formation of bayerite even after 96 h leaching in water. The adsorption of stearic acid on the AlN powder surface is attributed to a chemical reaction between the carboxylic groups and the hydroxyl groups present on the solid surface, resulting in a monomolecular surface coating, which protects the AlN powder from further hydrolysis reaction. Thus, hydrophobized AlN powder can be processed in aqueous medium (with the eventual addition of dispersants), which is of particular interest for environmental protection.

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