

Influence of powder pre-treatments on dispersion ability of aqueous silicon nitride-based suspensions

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Abstract

The rheological properties and the dispersion stability of highly concentrated aqueous silicon nitride powder suspensions in the presence of an anionic polyelectrolyte dispersant have been investigated. Silicon nitride-based suspensions with solids loading as high as 60 vol.% could be prepared following a slow process of increasing the solids volume fraction in steps of 5 vol.%, starting from 45 vol.%. After each increment of solids, ball milling was conducted for periods of 24 h, which then increased up to 48 h with solids loading increasing. Slips were prepared either from the as received or the pre-treated powders. Zeta potential measurements were conducted on Si₃N₄, Al₂O₃ and Y₂O₃ powders submitted to different pre-treatments, in absence and in the presence of dispersant, to evaluate the influence of these experimental variables on surface-charge properties of the particles. It was concluded that both aqueous ball milling and calcining enhance the repulsive interaction forces between particles, like the presence of the dispersant. On the other hand, rheological and particle size analysis revealed that ball milling and the ageing time enhance the dispersing ability of the powders and decrease the viscosity (for a given solids loading) and the shear-thinning character of the suspensions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aqueous suspensions; Electrophoresis; Rheology; Si₃N₄; Suspensions

1. Introduction

Dense silicon nitride ceramics are well known by their relative high-strength and high-temperature resistance. However, the covalent bonding character confers to the Si₃N₄ a poor sinterability. The attainment of a high degree of densification requires the use of oxide additives, such as yttria, alumina and magnesia, which allow sintering to proceed via a transient liquid phase.^{1,2}

The traditional processing of Si₃N₄-based ceramics involves previous powders preparation and consolidation by uniaxial and/or isostatic pressing before sintering. Many variants have been introduced in all processing steps in order to diminish some process limiting-characteristics such as the poor ability to form complex shapes or to achieve high degrees of homogeneity of particle packing.^{3–5} For complex shapes other consolidation techniques such as slip casting, pressure casting or gel-casting are preferred. These processing methods also enable

the control and manipulation of the forces between particles within a liquid and improve the homogeneity of the green compacts,⁴ which is essential for the sintering behaviour and the ultimate material properties.⁵ A successful processing requires the use of well deagglomerated and relatively high concentrated suspensions. For obtaining such suspensions, the complex interfacial reactions between solvent media, dispersant, powders and additives must be taken into account. These reactions can be related with inherent oxidation, heteroflocculation, and/or evaporation processes, which might lead to structural inhomogeneities. Such structural inhomogeneities will act as strength-degradation flaw populations and, consequently, will reduce the density and the thermo-mechanical properties of the ultimate products.^{2,5}

Silicon nitride-based compositions are usually difficult to disperse in aqueous media, with the suspensions achieving only low or moderate solids concentrations.^{6–9} A solids volume fraction as low as 27.8 vol.% was reported⁶ for a non pre-treated Si₃N₄-based powders mixture dispersed with the same dispersant used in the present work. Other authors^{7–9} were able to prepare moderate concentrated suspensions (47.5⁷, 43⁸ and 42 vol.%⁹) by

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Table 1
Powder characteristics as provided by the suppliers or measured by the authors

Material	Grade	Supplier	Density (g/cm ³)	Sp. S. area (m ² /g)	Particle size ^b (μm)		
					D ₉₀ ^b	D ₅₀	D ₁₀
Si ₃ N ₄	M11	H.C.Starck,UK	3.2	— ^a	1.29	0.38	0.12
Y ₂ O ₃	C (Fine)	H.C.Starck,UK	5.03	—	2.32	0.75	0.36
Al ₂ O ₃	A16SG	AlcoaChemicals,USA	3.98	11	1.64	0.38	0.20

^a Not given.

^b Particle size data acquired by the authors.

using pre-oxidised powders at 550–600°C. Therefore, pre-oxidation improves the dispersing ability of these compositions in water. On the other hand, it is known that the surface of nitride particles processed in aqueous media undergo oxidation and/or hydrolysis. The enrichment of the surface particles in SiO₂ can be detrimental for the sintering behaviour and for the high temperature resistance of the ceramic materials.^{1,2} For this reason, some authors removed the surface oxide layer by chemical etching.⁵ Other approaches to improve the dispersing ability of Si₃N₄-based compositions and the homogeneity of the mixtures involve the coating of the Si₃N₄ powders with the sintering oxide additives.^{4,10}

On the other hand, pressureless sintering has clear advantages for the fabrication of ceramic products having large sizes and irregular or complex shapes. Therefore, a successful processing of such materials requires an appropriate amount of the sintering additives, their homogeneous distribution and the understanding of all interfacial interactions between powders solvents and dispersants, as well as the effects of powder pre-treatments.

The aim of the present work is to study the effects of different pre-treatments such as previous dispersal of the powders in non-aqueous or aqueous media, followed or not by a calcination step, on the electrophoretic behaviour and dispersing ability of the particles and on the rheological characteristics of concentrated suspensions. How the presence of a polyelectrolyte as dispersant, the ageing time, or the duration of the ball-milling period affect these behaviours will be also evaluated.

2. Experimental procedure

2.1. Materials and powders pre-treatments

The characteristics of the powders used, as provided by the suppliers, are presented in Table 1. A synthetic high-molecular-weight polyelectrolyte, Dolapix PC33, having carboxylic functional groups was used as the dispersant (pH = 9.5 at 20°C—Zschimmer and Schwarz, DE), which is very efficient in dispersing silicon nitride.¹¹

For the electrophoretic characterisation, powders were used as received, and after different pre-treatments

(Table 2): (i) ball-milling in water for 24 h (*W*); (ii) ball-milling in isopropanol for 24 h (*A*); (iii) the same as in (ii), followed by drying, sieving and calcination at 600°C for 4 h (*AC*). It is believed that this last pre-treatment would enhance homogeneity¹² and the electrostatic stabilisation of silicon nitride powder in aqueous solution.^{7–9}

Ball milling was carried out to deagglomerate particles. When carried out in aqueous media, ball milling is also expected to promote hydration and oxidation of the particles' surface. Calcination will lead to some surface oxidation and aggregation of the particles.

For the rheological characterisation of the suspensions, only the two extreme cases, the as received powders and the *AC* pre-treated powders were used. The additives, Al₂O₃ and Y₂O₃, were mixed in equal amounts to yield a 10 wt.% sintering aid for silicon nitride, since this is a typical industrial Si₃N₄-based composition. For the *AC* mixtures, batches of 100 g of the powders-mixture were added to 85 ml of isopropanol in a polyethylene jar with alumina balls for 24 h. Slurries so obtained were then slowly dried at 50°C, sieved (80 μm) and calcined at 600°C for 4 h.

2.2. Zeta potential measurements

The surface charge characteristics of the different powders were determined separately in the absence and in the presence of the dispersant, using a Doppler electrophoretic light scattering analyser (DELSA 440SX—Coulter, UK). Stock-suspensions containing 1 wt.% solids in deionised water were first prepared and let to equilibrate for 24 h. When the dispersant was used, an amount of 1 wt.% relative to the mass of solids was added. For electrophoretic measurements, each stock-suspension was first ultrasonicated for 5 min to destroy

Table 2
Powders submitted to different pre-treatments

Sample code	Ball milling	Calcination
As received	—	—
<i>W</i>	Water — 24 h	—
<i>A</i>	Isopropanol — 24 h	—
<i>AC</i>	Isopropanol — 24 h	600°C 4 h

the agglomerates. Then 0.5 ml of the stock-suspension was added to 200 ml of 0.001 M KCl to insure a constant ionic strength. Each working-suspension was divided in two equal parts for increasing and decreasing pH runs, and the pH values were adjusted by using either 0.1 M HNO₃ or KOH solutions, respectively.

2.3. Slips preparation and characterisation

Aqueous slips of the AC pre-treated powders were initially prepared at 45 vol.% solids. In the case of the as received powders, the starting solids loading could not exceed 30 vol.% due to a more accentuated viscous character of these suspensions. In both cases, 0.5 wt.% of dispersant was added. The slips were ball-milled for at least 24h before incremental amounts of 5 wt.% solids have been added, up to final concentrations of 60 vol.% for the AC pre-treated powders, or 35 vol.% for the as received powders. Before adding each new 5 vol.% increments, viscosity and PSD were measured using a rheometer (Carri-med, CSL500, UK) and a Coulter LS230 particles size analyser (Coulter, UK), respectively. All suspensions presented a natural pH value of about 8.

Rheological tests were also performed on a 45 vol.% suspension to evaluate the influence of ageing time on viscosity. All these rheological tests were carried out at 20°C using a coaxial-cylinder measurement device, in the shear rate range of about 0.1–550 s⁻¹. The correlation between the experimental results and different rheological models was tested, and the model that better fits the experimental results was selected.

2.4. XPS measurements

XPS spectra were obtained from the surface of as-received Si₃N₄ powders and from the pre-treated AC Si₃N₄ powders before and after ageing in water for 120 h. The analyses were performed with an ESCALAB 200a electron spectrometer using Mg-K_α radiation. The analyser operated with pass energy of 50 eV using a step size of 1 eV. One survey spectrum was obtained for each sample, where N1s, O1s, C1s and Si2p regions (and Si1s, when relevant to the analysis) were found to be the most relevant peaks. Atomic percentages were calculated from the fitting of the region spectra to the peak envelopes provided by the data system.

3. Results and discussion

3.1. Electrophoretic characterisation

The surface chemistry of powders dispersed in aqueous media can be modified in order to produce repulsive inter-particle forces that promote dispersion. In the case of Si₃N₄, two strategies are usually adopted to

improve its dispersion ability: (i) change the ratio between acidic silanol (≡Si-OH) and basic amine (≡Si-NH) surface groups which, although powder-specific, can vary with some pre-oxidation-treatment;^{8,9} (ii) add an electrolyte that could reinforce the electrostatic interactions and, at the same time, introduce a steric contribution to stabilization.^{8,11,13,14} These effects can work isolated or simultaneously. Their combination is important especially in the case of high solids concentrations where the average inter-particle distance is short.

For oxides such as alumina and yttria, the properties of the cation and the hydration state of the solid phase are also thought to influence the inter-particle potential and consequently the dispersion in water.¹⁵

3.1.1. Effects of powders' pre-treatments on surface charge characteristics of Si₃N₄

Fig. 1 reports the influence of different pre-treatments on zeta potential of Si₃N₄ powder. It can be seen that the pH of the isoelectric point (pH_{iep}) of the powder deagglomerated in isopropanol is located at about pH 5.5, in close agreement with the results reported by Luther.¹⁶ This pre-treatment is believed to be the one that less interferes with the surface charge properties. Conversely, calcination accentuated the surface acidity of Si₃N₄ powder shifting the pH_{iep} from pH 5.5 to 3.6. This result is in agreement with the work of Albano and Garrido⁸ who have reported a dislocation of the pH_{iep} of about two pH units towards the acid region after calcination for 6 h. They suggested that calcination would be responsible for an increase of the silanol surface groups, enhancing a more negative potential and, consequently, the repulsion between particles. This interpretation is also supported by the observations of Nagel et al.⁷ who reported that oxidation for 8 h at 550°C in air resulted in an oxygen pick-up of 0.9 wt.%,

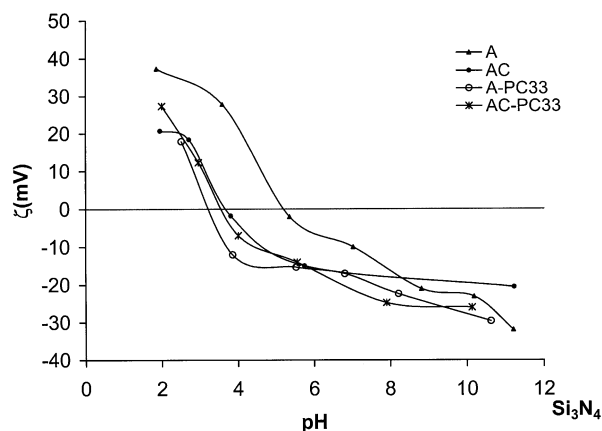


Fig. 1. Influence of pre-treatments and added dispersant on zeta-potential of Si₃N₄. A-deagglomeration in isopropanol-24 h; AC-deagglomeration in isopropanol-24 h+calcination at 600°C for 4 h; A-PC33 the same as A, but in the presence of 1 wt.% Dolapix PC33; AC-PC33-the same as AC, but in the presence of 1-wt.% Dolapix PC33.

and that this oxide layer resulted in a significant increase of the absolute value of zeta-potential. Moreover, aqueous suspensions prepared from the oxidised powder presented a drastic decrease of the yield stress compared to those prepared from untreated Si_3N_4 powders.

Addition of the dispersant to the suspension of powder *A* (*A-PC33*) caused a shift of the pH_{iep} and of the whole electrophoretic curve similar to that promoted by calcining, attesting the anionic nature of the polyelectrolyte Dolapix PC33. However, only very small changes in the electrophoretic behaviour are observed when the dispersant is added to suspensions of calcined powders. This can be understood since carboxylic groups –COOH of the polyelectrolyte are completely dissociated only at $\text{pH} \geq 8.5$. For pH values lower than 4 the degree of dissociation of the functional carboxylic groups would be low.⁸ Its adsorption onto the surface of the silicon nitride powders occurs through the silanol surface sites.⁸ On the other hand, the more negative surface charge due to the increase of the silanol surface groups will work against adsorption of negatively charged species ($-\text{COO}^-$). The combination of these two factors explains the observed results. Above pH_{iep} , the particles become negatively charged and start to repel the dissociated groups of the polyelectrolyte chain. One would then expect that Dolapix PC33 is more weakly adsorbed onto a negatively charged surface, as in the case of calcined silicon nitride, having a greater influence on the as received powders, which presented an higher isoelectric point. In the alkaline region zeta potential is a little bit improved in the presence of a dispersant as expected, since the charge of the polyelectrolyte is added to the particles surface charge.

The influence of the dispersing media on surface charge characteristics is shown in Fig. 2. The zeta-potential curves for the *A*- and *W*- Si_3N_4 powders are almost coincident especially in the acidic side of pH range. For pH values higher than ≈ 6 , the zeta potential of the *W*-powder appears more negative compared to

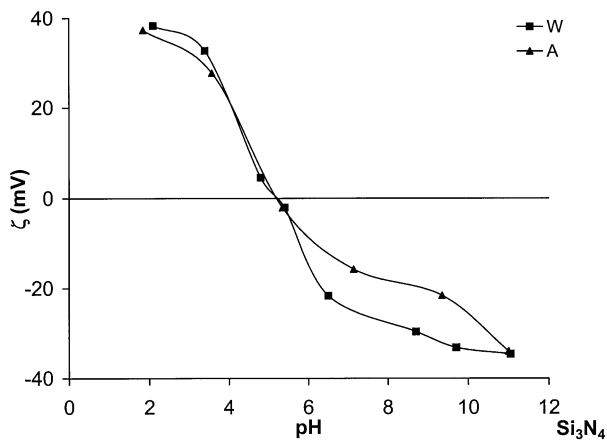


Fig. 2. Influence of the dispersion media for deagglomeration on the zeta-potential of Si_3N_4 powder. (W, water; A, isopropanol).

the *A*-powder. These results were expected since the exposure of the Si_3N_4 powder to water would promote a more negative surface-charge and an increase of the repulsive electrostatic inter-particle potentials, according to the reaction [1]¹⁷



3.1.2. Effects of powders' pre-treatments on surface charge characteristics of the oxide additives, Al_2O_3 and Y_2O_3

The effects of calcination and adding dispersant on the surface-charge properties of the Al_2O_3 and Y_2O_3 additives are shown in Figs. 3 and 4, respectively. It can be seen that powders *A* exhibit isoelectric points at about pH 9.3 (Al_2O_3) and pH 11 (Y_2O_3), which are in good agreement with other reported values for these

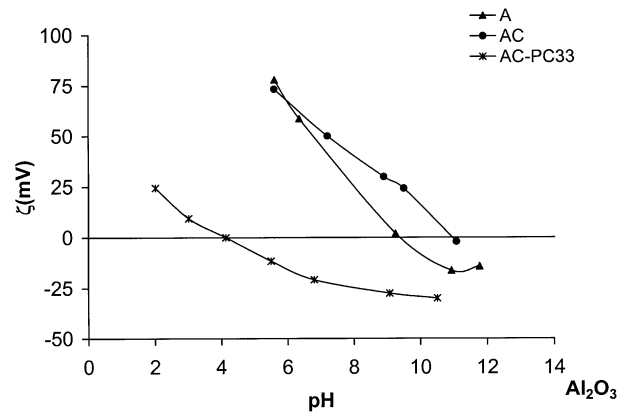


Fig. 3. Influence of pre-treatments and added dispersant on zeta-potential of Al_2O_3 . *A*-deagglomeration in isopropanol-24 h; *AC*-deagglomeration in isopropanol-24 h + calcination at 600°C for 4 h; *AC-PC33*-the same as *AC*, but in the presence of 1 wt.% Dolapix PC33.

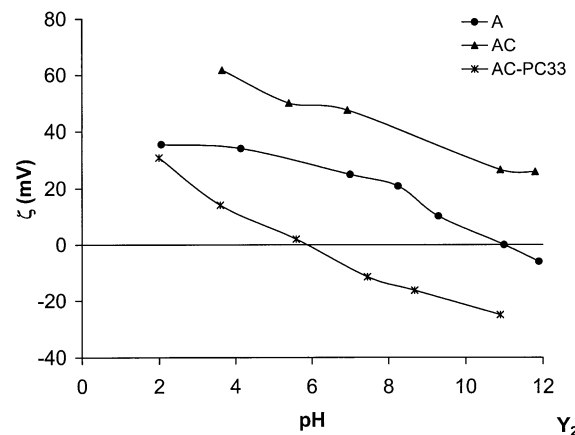


Fig. 4. Influence of pre-treatments and added dispersant on zeta-potential of Y_2O_3 . *A*-deagglomeration in isopropanol-24 h; *AC*-deagglomeration in isopropanol-24 h + calcination at 600°C for 4 h; *AC-PC33*-the same as *AC*, but in the presence of 1 wt.% Dolapix PC33.

oxides.¹⁵ Further, calcination worked differently in comparison with Si_3N_4 . In fact, for both oxides calcination shifted the isoelectric points towards the basic side reaching pH 11 for Al_2O_3 , and with a more significant increase in the case of the more basic Y_2O_3 powder, which pH_{iep} is outside of the pH range analysed.

Several authors mentioned by Parks¹⁵ proposed that, for oxide materials, any treatment likely to lead to bulk or surface dehydration would lead to a more acid isoelectric point compared with the hydrated materials. Particularly for Al_2O_3 , Robinson et al.¹⁸ have observed that heat-treatment decreased the isoelectric point from pH 9.2 (at equilibrium with water) to pH 6.7. These statements are in contrast with our results. It is conceivable that dehydration of oxides would occur through H^+ desorption and the consequent release of gaseous H_2O molecules, increasing the basic character of these powders. In the case of Y_2O_3 , hydration can lead to the formation of some positively charged species, which can be adsorbed at particles surface contributing to the observed shift in pH_{iep} . In the case of Si_3N_4 -based powders mixtures, the positively charged species derived from hydration of oxide additives can be adsorbed at the surface of Si_3N_4 particles as positive counter-ions, which will screen the negative surface charge, causing a decrease of zeta potential as suggested by Senturk.⁶

The comparison between Fig. 1 and Figs. 3 and 4 shows that the presence of the anionic polyelectrolyte surfactant Dolapix PC33 has a much stronger effect on the surface charge characteristics of the oxides than in the case of silicon nitride. This difference can be understood since adsorption of the negatively charged polyelectrolyte chains is enhanced when the adsorbate is positively charged. In fact, the Dolapix PC33 chains will be completely dissociated for $\text{pH} \geq 8.5$, while both calcined oxides exhibit relatively high positive values of zeta potential at $\text{pH}=8.5$. Therefore, the shift in the isoelectric point of about 7 pH units for Al_2O_3 powder is not surprising. Obviously, the shift in the isoelectric point is still higher in the case of Y_2O_3 as can be depicted from the Fig. 4. On the other hand, the amount of an anionic dispersant adsorbed decreases as pH increases due to the electrostatic interactions with the surface of particles but at a given pH it would be always higher in the case of Y_2O_3 .

3.1.3. Influence of ageing time on zeta potential of Si_3N_4 and Al_2O_3 powders

The effect of 120 h ageing time in aqueous media (the time needed to obtain a AC-PC33-60 vol.% deagglomerated suspension) on zeta potential is reported in Fig. 5 for AC-PC33 treated powders (Si_3N_4 and Al_2O_3). For comparison, the curve for the non-aged Y_2O_3 is also shown. It can be seen that ageing further slightly dislocates the isoelectric points towards the acid direction.

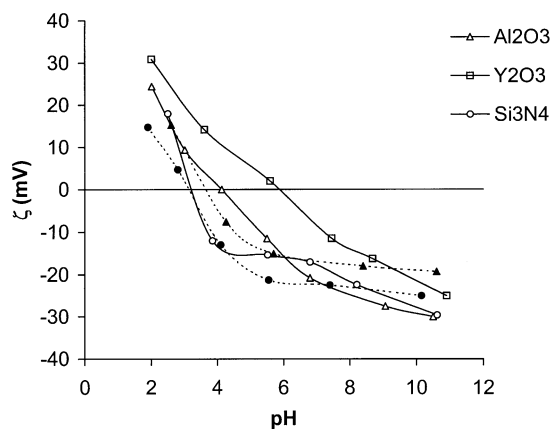


Fig. 5. Influence of 120 h ageing on the zeta-potential of the AC-PC33 Si_3N_4 and Al_2O_3 powders.

This shift is consistent with an increasing hydration degree of the surface of particles, which becomes more acidic.⁶ The enhancement of the acidic nature of the surface of particles with ageing might impose a decrease of the affinity between the surface and the anionic dispersant, which would be responsible for the apparent small decrease of zeta potential in the alkaline pH region.

3.2. Influence of pre-treatments and deagglomeration time on rheology

The effects of solids loading and deagglomeration time on the rheological characteristics of suspensions prepared from the as received and AC-treated powder-mixtures dispersed with Dolapix PC33 are reported in Fig. 6. The maxima solids concentrations achieved, 35 vol.% for the as received powders and 60 vol.% and for the AC-treated powders are related to the highest acceptable viscosity for casting operations. This difference is significant and reveals that the as received powders are more difficult to disperse than the AC-treated

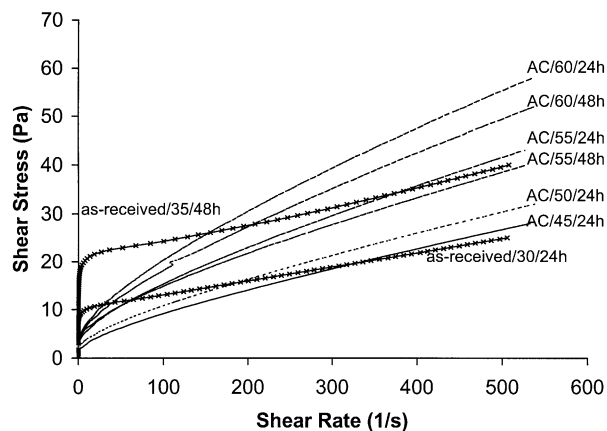


Fig. 6. Influence of solids loading and milling time on the viscosity of AC- and as-received powder-mixtures (Si_3N_4 - Y_2O_3 - Al_2O_3) suspensions.

ones, as expected from the above discussion. Besides the considerably lower maximum solids loading achieved with the as received powders, the suspensions so obtained exhibit a plastic behaviour and well defined yield stresses, which closely approaches the Bingham model. This means that particles in suspension are structured in such a way that the flow is initiated only after a given stress has been achieved (≈ 10 Pa for 30 vol.%, and ≈ 20 Pa for 35 vol.%). On the other hand, the suspensions of the AC-treated powders behave as pseudo-plastic fluids. The shear-thinning character increases with increasing solids loading and, for a given solids volume fraction, decreases with increasing deagglomeration time. The increase of deagglomeration time from 24 to 48 h was conducted only at the higher solids loading (35 vol.% for the *as received* powders, and 55 and 60 vol.% for the AC-treated powders) in an attempt to improve the fluidity of the suspensions. It can be observed that, even after deagglomeration for 48 h, the as received 35 vol.% suspension requires higher shear stresses to flow along all shear rate range than the AC 55 vol.% suspension.

The rheological behaviour of the as received powders suspensions would be mainly determined by the surface characteristics of the Si_3N_4 component, namely, by the co-existence of acid silanol groups and basic amine groups.¹⁶ When in suspension, the acid surface sites will be attracted by the basic ones leading to particles structuration. Calcining would lead to a loss of amine groups and to an enrichment of the surface in silanol groups, therefore improving the dispersing ability of the main component in the mixture. This interpretation is in agreement with the report of Nagel,⁷ who observed significant yield stresses and typical plastic behaviours for the suspensions of non-calcined Si_3N_4 powders.

The suspensions prepared from the calcined powders presented a shear-thinning behaviour, with no yield stress but with a gradual rupture on the suspension structure with increasing shear rate, characteristic of fine particles suspensions with moderate concentrations.

Fig. 7 shows the effect of milling time on PSDs of the as received and AC-powders suspensions. The as received and AC-45-0h (before milling) powders present two populations, one centred at about $0.3 \mu\text{m}$ corresponding essentially to the size of individual particles (average size), and another less intense centred at about $1.1 \mu\text{m}$ due to particle agglomerates. Ball-milling the AC-45-vol.% suspension for 24 h caused a reduction in the number of agglomerates and a consequent increase in the number of the average sized particles, as well as the appearance of a low intense third population centred at about $0.09 \mu\text{m}$. It can be also observed that the as received powder seems much more difficult to deagglomerate compared to the AC-powder. In fact, 24 h of milling did not produce visible changes in PSD of the 30 vol.% suspension, which is almost coincident with that of the AC-45 vol.% before milling. This can

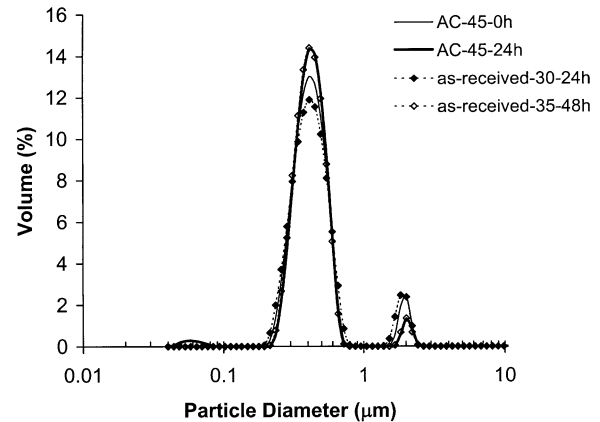


Fig. 7. Comparison of the deagglomeration level achieved on AC- and as-received-powder-mixture suspensions as a function of solids loading and milling time.

be attributed to the low efficiency of wet-milling when relatively low concentrated suspensions are used, and to the predominance of attractive interaction forces between the particles of the as received powder. Moreover, a PSD similar to that obtained for the AC-45 vol.% suspension ball-milled for 24 h was only achieved for the *as received* powder after an increment of 5 vol.% in solids volume fraction and a further deagglomeration for 48 h. This confirms the increased difficulties in dispersing the as received powders. For the AC-powder suspensions, Fig. 8 shows that the deagglomeration process continues with the solids loading increasing, although at a lower rate as expected, since suspensions become more viscous.

The influence of ageing time on rheology was analysed on the AC-45 vol.% suspension, which was left to roll in the ball-milling container without balls. The results presented in Fig. 9 show that viscosity first decreases with increasing ageing time reaching an equilibrium situation after 48 h ageing, in agreement with

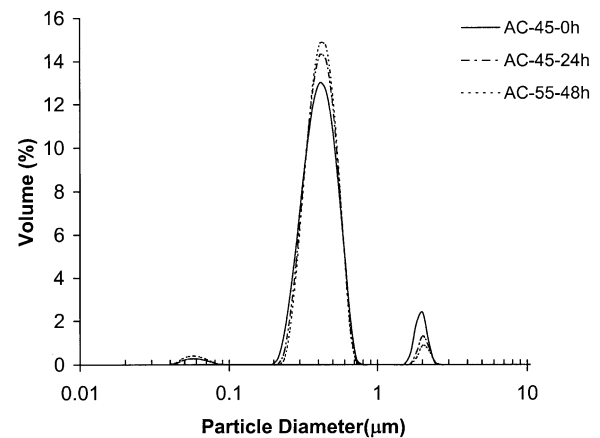


Fig. 8. Effects of milling time and solids loading on deagglomeration level for AC-powder-mixture suspensions.

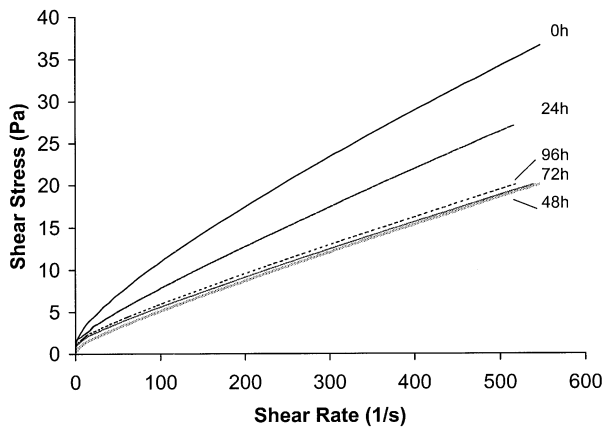


Fig. 9. Influence of ageing time on the viscosity of AC-45 vol.% powders-mixture suspension.

results reported in a previous work,¹⁷ followed by a slight increasing trend.

The results presented above show that deagglomeration is promoted by ball milling and by the increasing duration of the contact between solid and liquid phases (at least up to 48 h). These effects improve the dispersing ability of the silicon nitride-based compositions and enable the use of an incremental process to obtain highly concentrated (up to 60 vol.%) aqueous Si₃N₄-based suspensions. However, this is a long duration process and hydrolysis reactions of the Si₃N₄ powder in water may increase the amount of SiO₂ in the powder surface. A compromise between the enhanced dispersing ability of Si₃N₄ powders in aqueous media by the enrichment of the particles' surface in SiO₂ and the decrease in sintered density and high-temperature properties of the final compacts due to a non-proper amount of liquid phase is generally accepted.¹⁹

3.3. Effects of pre-treatments on surface composition of Si₃N₄

In an attempt to separate the contributions of the powders pre-treatments and the ageing effect of the suspensions on the surface oxidation of Si₃N₄ powders, XPS analyses were conducted on the following powders: as-received, and AC before and after ageing in water for 120 h (the time required to obtain a AC-PC33-60 vol.% deagglomerated suspension). The atomic ratios N/Si and O/Si at the powders' surface and their respective variations under different treatment conditions are presented in Table 3. It can be seen that both treatments lead to a decrease of the N/Si ratio and to a concomitant increase of the O/Si ratio at the powder surface. Calcination changed the O/Si ratio from 0.23 to 0.36. The surface of the calcined powder became further oxidised by ageing in water for 120 h with the final O/Si ratio being about double in comparison with the as-received powder. Both treatments, calcination and the

Table 3

Influence of the different treatment conditions on surface atomic ratios of silicon nitride (accuracy = ± 4%)

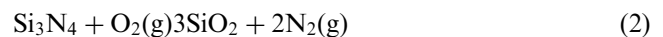
Si ₃ N ₄ powders	N/Si	ΔN/Si	O/Si	ΔO/Si
As-received	0.85	–	0.23	–
AC	0.81	(–) 0.04	0.36	(+) 0.12
AC-aged	0.79	(–) 0.03	0.49	(+) 0.13

further ageing of the aqueous suspension, seem to have similar contributions for the total oxidation of the surface of Si₃N₄-powders with ΔO/Si values of 0.12 and 0.13, respectively. These results are in good agreement with those reported by Castanho et al.,²⁰ who compared the contributions of different solvent media to the oxidation level of Si₃N₄. They found that the aqueous milling for 24 h produced a very high oxidation effect (ΔO/Si = 0.28) in absence of dispersant, while in the presence of dispersant the oxidation level was comparable to that achieved in alcohol (ΔO/Si = 0.053). They refer that dispersant would provide a protective screen to prevent further oxidation.

In the present work, the XPS results were obtained from pre-treated Si₃N₄ powders aged in aqueous environment for 120 h in the absence of the dispersant. Our results indicate that the increment in the oxidation degree, relative to the as-received powder, due to pre-oxidation and aqueous milling for 120 h is less than that obtained by Castanho et al.,²⁰ in 24 h of aqueous milling the as-received powder. It is conceivable that the oxidation reaction at the particles surface would tend to reach equilibrium, implying that the final oxidation degree would not be proportional to the duration of the contact between solid and liquid phases. The milling pre-treatment in an organic solvent is not expected to produce significant oxidation on silicon nitride particles.²⁰

Furthermore, calcination led to a first and the most significant decrease of N/Si ratio due, probably to a release of some amine groups and to the growing of the surface oxide layer. The ageing process promotes a further (less accentuated) decrease of the N/Si ratio. This second decrease is likely due to the continuous oxidation process of the particles' surface.

The contribution of calcination to the surface oxidation of Si₃N₄ is quite well understood.^{21–26} In fact, all the models already proposed to predict or simulate the oxidation kinetics on Si₃N₄-powders in different temperature ranges are based on the assumption that there is a weight gain dominated by adsorption or diffusion of O₂ and formation of SiO₂, according to the reaction (2):



It is generally accepted that, after an initial weight loss due to release of dissolved hydrogen or even adsorbed water, there is a weight gain, which is time

dependent and tends to deviate from a linear to a parabolic behaviour as temperature increases. As the temperature or time increases, nitrogen can be gradually substituted by oxygen. The oxidation kinetics, number of layers present and their thickness are thought to depend on powder characteristics, particularly on the synthesis process,^{2,21,26} possible presence of impurities and PSD.^{21,26}

4. Conclusions

The results presented in this work enable the following conclusions to be drawn:

1. The surface-charge characteristics of the Si₃N₄ powders namely, the relative concentrations of silanol and amine groups, and the adsorption of dispersant on the particles of sintering aids are the most relevant factors that control the dispersion ability of Si₃N₄-based suspensions.
2. Deagglomeration and calcination at 600°C for 4 h improved the positive ionic character of the surfaces of the sintering additive powders favouring the adsorption of the anionic dispersant. The same pre-treatment given to Si₃N₄ resulted in an increase of the silanol groups in detriment of the amine groups, shifting the isoelectric point to the acidic side, favouring the electrostatic stabilisation at pH 8.
3. Well-dispersed aqueous Si₃N₄-based suspensions with concentrations up to 60 vol.% could be prepared from the pre-treated powders by using a continuous deagglomeration and ageing process. The suspensions presented a shear-thinning behaviour characteristic of fine particles suspensions with relative high solids concentrations, but viscosity values low enough for casting operations.
4. The contribution of the aqueous processing to the oxidation degree of the silicon nitride powders is similar to that due to the pre-treatment usually given to nitride powders, even at the end of 120 h ageing. This clearly suggests that aqueous processing of Si₃N₄-based ceramics is suitable to prepare complex shapes for pressureless sintering at moderate temperatures.

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