

Influence of the deagglomeration procedure on aqueous dispersion, slip casting and sintering of Si_3N_4 -based ceramics

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Abstract

The influence of the deagglomeration procedure on the rheological behaviour of Si_3N_4 -based aqueous suspensions, the slip casting performance and the final properties after sintering were investigated. Ball milling and planetary milling performed deagglomeration of powders. The experimental results showed that the time required to obtain the same degree of deagglomeration was considerably shorter in the case of planetary milling. The decrease in viscosity during the milling procedure enabled well dispersed and relatively high-concentrated (55-vol.%), suspensions to be obtained by adding successive 5-vol.% increments of solids to an initial 45-vol.% suspension. The time required to achieve complete deagglomeration of the starting suspension or after adding each 5-vol.% solids' increments was of 4 h for planetary mill and varied from 24 to 48 h for ball mill, with increasing solids loading, reaching total deagglomeration times of 12 and 96 h, respectively. The results have shown that, for a given solids volume fraction, both the degree of deagglomeration and the time required to achieve it, i.e. the duration of the contact between the powders and the dispersing aqueous solution, are key factors for achieving dense and homogeneous green microstructures, and for improving the densification behaviour and final properties of sintered bodies. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Milling; Sintering; Si_3N_4 ; Slip casting; Suspensions

1. Introduction

Due to its high covalent bonding character, silicon nitride particles are known to be very hard and have a low sintering activity, which is usually overcome by adding sintering additives to obtain dense Si_3N_4 -based microstructures.^{1–3} The achievement of dense multi-phase microstructures requires the use of appropriate methods to eliminate or destroy the powder agglomerates and obtaining a homogeneous mixing of all the components in the starting formulation.^{3–7} Some successful methods to improve the densification of Si_3N_4 -based ceramics and yield uniform microstructures involved the coating of the Si_3N_4 particles with precursors of the sintering additives.^{8–13} It was already shown that the coating method and the slip casting process improved the sintering ability of silicon nitride over the mechanical mixing method and dry pressing route.¹³ Further, the

minimisation of powder agglomeration in the green bodies achieved by slip casting revealed to be more determinant to the sintering behaviour than the homogeneous distribution of the sintering additives around the Si_3N_4 offered by coating.¹³ Recently, it was demonstrated that silicon nitride-based suspensions, with solids loading as high as 60-vol.%, could be prepared from mechanically mixed pre-treated powders following a slow process of increasing the solids volume fraction in steps of 5-vol.%, starting from 45-vol%.¹⁴ After each increment of solids, ball milling was conducted for periods of 24 h, which then increased up to 48 h with solids loading increase. This means that a long deagglomeration time would be required to obtain high concentrated and well-dispersed suspensions. During such long periods of contact between the aqueous solution and the powders, oxidation and hydrolysis will occur on the surface of the particles, improving the dispersing ability and, at the same time, the amount of oxygen at the interface.^{6,7,14,15}

The present work aims at the preparation of highly concentrated and well-dispersed silicon nitride-based

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suspensions while reducing the deagglomeration time by using high-energy planetary milling. The higher shear stresses generated by this milling method are expected to be more efficient on breaking agglomerates in order to reduce the suspension viscosity and obtain a complete sub-micrometer particle size distribution.^{5,16} The effects of deagglomeration procedure on rheology of the suspensions, slip casting performance, green packing density and sintering ability of the consolidated bodies will be evaluated.

2. Experimental procedure

2.1. Materials and powders' pre-treatments

The composition used was 90-wt.% α - Si_3N_4 (Grade M11, H.C. Starck, UK), 5-wt.% Y_2O_3 (Grade C, H.C. Starck, UK) and 5-wt.% Al_2O_3 (Grade A16SG, Alcoa Chemicals, USA). A synthetic high-molecular-weight polyelectrolyte, Dolapix PC33, having carboxylic functional groups was used as dispersant (pH=9.5 at 20 °C, Zschimmer and Schwarz, DE), which is very efficient in dispersing silicon nitride.¹⁷

The received powders were milled in isopropanol, followed by drying, sieving and calcination at 600 °C for 4 h according to a procedure followed in a previous report,¹⁴ which proved that this pre-treatment enhances homogeneity and the electrostatic stabilisation of silicon nitride powder in aqueous solution. The beneficial effect of calcination on the dispersing ability of silicon nitride powders has been also referred to by other authors.^{18,19}

The additives, Al_2O_3 and Y_2O_3 , were mixed in equal amounts to yield a 10-wt.% sintering aid for silicon nitride, since this is a typical industrial Si_3N_4 -based composition. The contamination brought by the milling media and milling jars was controlled by weighing them before and after the deagglomeration step.

2.2. Slips preparation and characterisation

Aqueous slips of the pre-treated powders were initially prepared at 45-vol.% solids in the presence of 0.5-wt.% dispersant. Ball milling (BM) and planetary milling (PM) were carried out to deagglomerate particles. The BM was performed in a polyethylene jar with Al_2O_3 balls, for at least 24 h before incremental amounts of 5-wt.% solids have been added, up to final concentrations of 55-vol.%. The new incremental additions of 5-wt.% solids were always accompanied by the corresponding amount of deflocculant in order to keep a constant ratio between the powders and the dispersant. For the PM, Al_2O_3 jars and Al_2O_3 and Si_3N_4 balls were used and the same incremental procedure was followed to prepare the slips. The proportion between milling media and the powders in the starting suspension was fixed at about

300:100 g, without further adjustments with solids loading increasing. In the PM, the deagglomeration of the starting suspension and after adding each new 5-vol.% increments was conducted for 2, 3 and 4 h periods. At the end of each deagglomeration period and before adding a new increment of solids, viscosity and particle size distribution were measured using a rheometer (Carri-med, CSL500, UK) and a Coulter LS230 particle size analyser (Coulter, UK), respectively. The rheological characterisation of BM slips was carried out using a concentric-cylinder measurement device, in the shear rate range of about 0.1–550 s^{-1} . The set of rheological tests performed on the PM deagglomerated slips was carried out using a cone and plate system, on the shear rate of 0.1–1300 s^{-1} because, for practical reasons, the concentric-cylinder measurement device was temporarily unavailable. All the rheological tests were carried out at 20 °C.

2.3. Consolidation and characterisation of green bodies

The final suspensions were degassed before pouring into plastic rings placed on a plaster plate. The slip cast bodies were slowly dried at room temperature for 24 h. After demoulding, the samples were placed in an oven at 110 °C for complete drying. The green density was geometrically calculated according to the weight and dimensions of the bodies.

2.4. Sintering and final characterisation

The green samples were embedded in a 1:1 weight ratio of Si_3N_4 and BN powders bed inside a graphite crucible. Samples obtained from BM suspensions were previously calcined at 500 °C, for burning of impurities resulting from the internal consuming of the polyethylene jar. Pressureless sintering of all samples took place at 1750 °C for 2 h in a nitrogen atmosphere. The final densities of the sintered bodies were measured by the immersion method in ethylenglykol, following the Archimedes' principle. Crystalline phases formed during sintering were determined by X-ray diffraction analysis in a X-ray diffractometer (D/MAX-C, Rigaku, Japan), using CuK_α radiation.

3. Results and discussion

3.1. Influence of milling procedure on deagglomeration of powders

The presence of agglomerates in the as-received and pre-treated powders has limited the concentration of starting suspensions to 45-vol.% of solids. The larger size and the irregular shapes of agglomerates, compared to the primary particles, and the fraction of liquid trapped

intra- and inter-agglomerates confer to the starting suspensions high values of viscosity limiting the maximum solids volume fraction that can be incorporated. The gradual destruction of agglomerates during milling decreased the viscosity and enabled further incremental additions of 5-vol.% solids, each one mediated by a new deagglomeration period, up to a final concentration of 55-vol.%. It seems reasonable to accept that the duration of milling period of the starting suspension, and after each incremental amount of 5-vol.% solids has been added, should be long enough to promote an appropriate deagglomeration degree and a reduction in viscosity compatible with that increment, which in turn, would depend on the efficiency of the milling procedure.

Figs. 1–3 present the evolution of deagglomeration for the high-energy treated PM suspensions. The milling periods of the starting suspension and after each increment of 5-vol.% solids were, respectively, 2 h (2 h-PM), 3 h (3 h-PM) or 4 h (4 h-PM). Fig. 1 presents four dif-

ferent populations, while only three populations can be observed in Figs. 2 and 3. It is probable that the two sub-micrometric populations centred at $\cong 0.06$ and $\cong 0.4 \mu\text{m}$ are constituted by primary particles, while the other two can probably be attributed to the presence of agglomerates. From Fig. 1, it can be concluded that a milling time of 2 h between increments was impractical to obtain deagglomerated suspensions. In fact, the agglomerate populations on the final suspension are even more relevant than in the starting suspension. Increasing the milling period between increments to 3 h (Fig. 2), first improved the degree of deagglomeration, but with the continuous increase of solids volume fraction, the final deagglomeration degree was still unsatisfactory. Further enlarging of the milling periods to 4 h (Fig. 3) enabled to obtain a well-dispersed suspension in which only sub-micrometric particles could be detected.

Fig. 4 shows the evolution of deagglomeration performed by ball milling with increasing milling time and

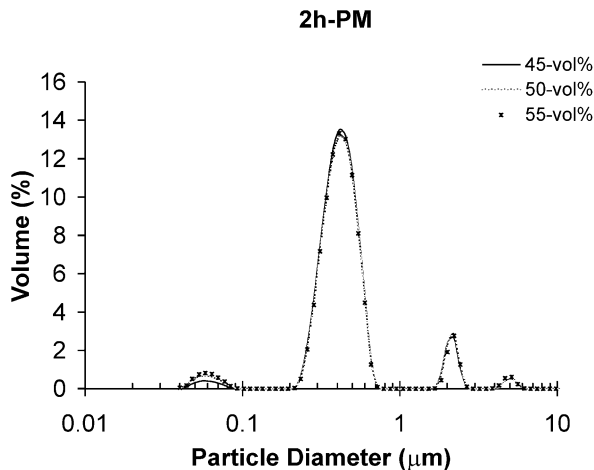


Fig. 1. Particle size distributions of planetary-milled suspensions with milling periods of 2 h before 5-vol.% solids increments.

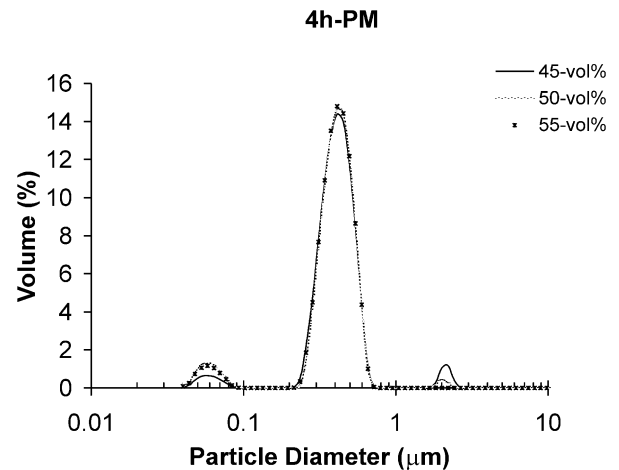


Fig. 3. Particle size distributions of planetary-milled suspensions with milling periods of 4 h before 5-vol.% solids increments.

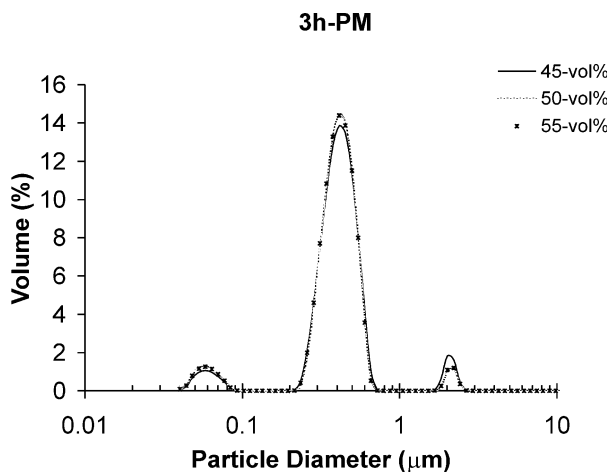


Fig. 2. Particle size distributions of planetary-milled suspensions with milling periods of 3 h before 5-vol.% solids increments.

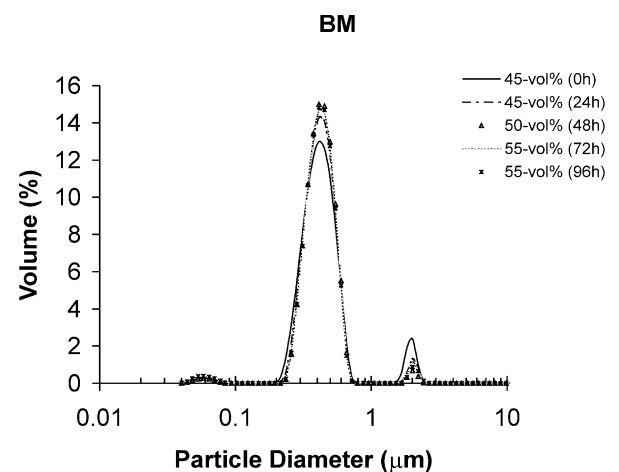


Fig. 4. Particle size distributions of ball-milled suspensions with milling periods of 24–48 h before 5-vol.% solids increments.

solids concentration. The particle size distribution of the undeagglomerated powders is also shown for comparison. It can be seen that the highest dispersion degree was achieved at 50-vol.% solids. Further increasing of the solids volume fraction to 55-vol.% resulted in a lower dispersing degree, even if the deagglomeration period between increments has been prolonged to 48 h.

Ball milling is a low-energy method, compared with the planetary milling. The lower values of shear stresses generated during BM make this procedure considerably less efficient than PM, thus requiring longer milling times to obtain the same dispersing effect. This clarifies the higher deagglomeration difficulties brought by the last increment to 55-vol.% solids. On the other hand, the better results observed at 50-vol.% suggest that there will be a defined solids concentration for each system at which milling efficiency is maximised. For lower concentrations than the optimal one, the probability for the agglomerates or even the coarser primary particles to be smashed between two milling elements decreases, while for higher concentrations than the optimal one, the concomitant increase in viscosity will decrease the dispersion efficiency.

In order to evidence the relationship between the solids loading and dispersion ability of the different milling procedures, the data obtained at 45 and 55-vol.% solids are compared in Figs. 5 and 6, respectively. It is interesting to note that the volume fraction of agglomerates (population centred at $\cong 2 \mu\text{m}$) present in the 2 h-PM suspension nearly doubles that one detected in the 4 h-PM suspension (Fig. 5). Moreover, similar degrees of dispersion seem to have been obtained in the 4 h-PM and 24 h-BM suspensions at this solids volume fraction. The population centred at $\cong 0.06 \mu\text{m}$ tends to increase probably due to the higher shear stress generated in the case of planetary milling. However, in neither case the population centred at $\cong 2 \mu\text{m}$ completely disappeared

under these experimental conditions. Fig. 5 also includes the PSD measured for the 12-PM suspension, which followed the expected trend of enhancing deagglomeration with increasing milling time, but a small population centred at $\cong 2 \mu\text{m}$ still remains at this solids loading.

On the other hand, although the generated shear stresses are not so strong under BM, other dispersing mechanisms like erosion of particle contacts and ageing phenomena can take place along the milling time. Song and Evans⁵ mentioned erosion and fracture as the two relevant deagglomeration mechanisms and suggested the relative strength between the applied shear stress and agglomerates' hardness as the dominant factor controlling mechanical dispersion. Erosion was defined as a very slow process by which particles were gradually washed away even under low shear stresses, while fracture would occur when the shear stress could reach agglomerates' strength. The effect of milling time on mechanical dispersion was considered insignificant at a fixed shear stress and solids content. However, as described in our previous work,¹⁴ long low-energy milling times could improve the dispersion through erosion or aging effects.

Fig. 6 clearly shows that the dispersing efficiency of the PM has been improved by increasing the solids volume fraction to 55-vol.%. At this solids content, the PM suspensions have accumulated deagglomeration times of 6, 9 and 12 h. Only for deagglomeration periods of 4 h after addition the initial or incremental powders the population centred at $\cong 2 \mu\text{m}$ completely disappeared at 55-vol.% solids under PM. Under these conditions, well-dispersed suspensions containing only sub-micrometric particles could be detected.

The dispersion degree achieved under the low-energy BM, for a longer (96 h-BM) deagglomeration period seems fairly good if we consider that the population centred at $\cong 0.4 \mu\text{m}$ has the same intensity as that

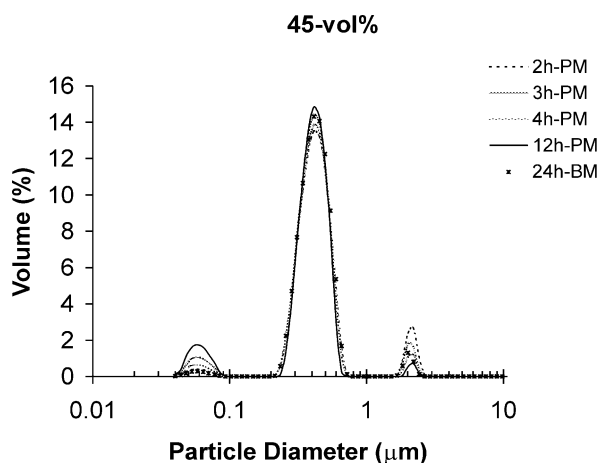


Fig. 5. Particle size distributions of 45-vol.% solids concentrated suspensions planetary-milled (PM) and ball-milled (BM) for different times.

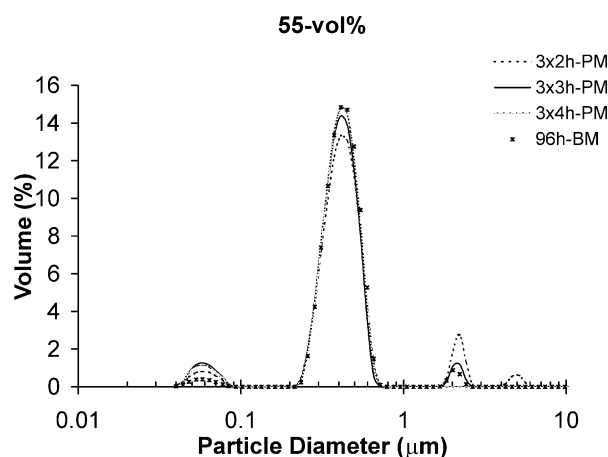


Fig. 6. Particle size distributions of 55-vol.% solids concentrated suspensions planetary-milled (PM) and ball-milled (BM) for different times.

detected for the 4 h-PM. However, there are still some agglomerates (population centred at $\cong 2 \mu\text{m}$) in the 96 h-BM suspension and the volume fraction of very fine particles (population centred at $\cong 0.06 \mu\text{m}$) is smaller than that observed for the 4 h-PM suspension. This finer fraction of particles produced during planetary milling can be related with the breaking of primary particles.

The results presented clearly show that planetary milling is the most efficient deagglomeration method and that optimal dispersing periods and solids loading should be adopted, which are different from one to another method.

3.2. Influence of deagglomeration method on rheology of suspensions

The shear stress versus shear rate curves of the suspensions 2 h-PM, 4 h-PM, and 96 h-BM, are presented in Figs. 7 and 8, respectively. It can be seen that all suspensions present a shear-thinning character, typical

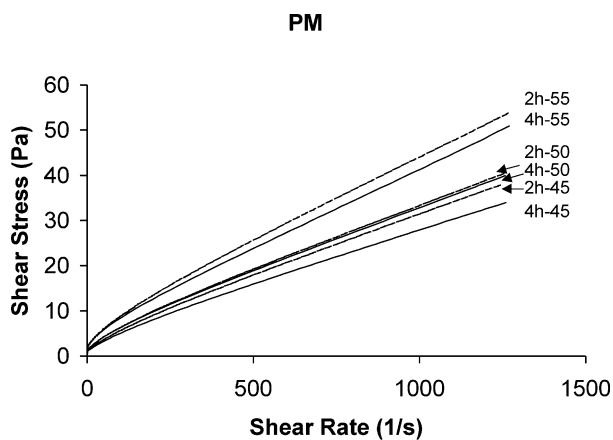


Fig. 7. Flow curves of planetary-milled suspensions (PM) during an incremental increase of solids loading for time intervals of 2 and 4 h.

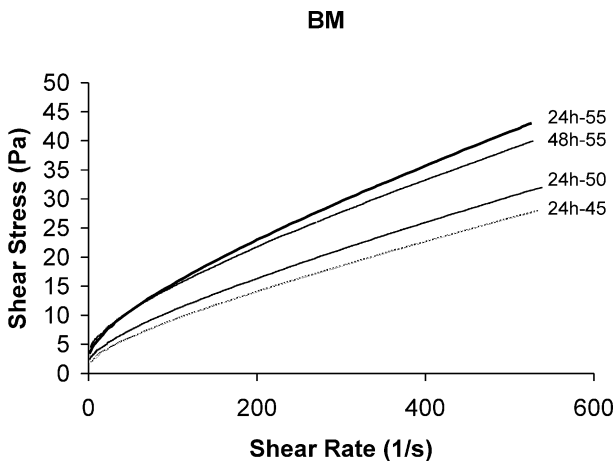


Fig. 8. Flow curves of ball-milled suspensions (BM) during an incremental increase of solids loading for time intervals of 24 and 48 h.

from concentrated suspensions of fine particles, which was seen to increase with solids loading. It can also be observed that the shear stress values at a given shear rate are strongly influenced by both the milling procedure and milling time. In fact, in both cases, the shear-thinning character has decreased with increasing milling time but, for a given solids concentration, the evolution is faster in the case of PM. Fig. 7 shows that fluidity of the suspensions is enhanced when the milling period mediating each consecutive increment of solids increases from 2 h (2 h-PM) to 4 h (4 h-PM). The same trend can be observed in Fig. 8, although for longer milling periods, as discussed above. These results are consistent with the observed evolution of the dispersion levels achieved for the suspensions. As suggested by Nagel et al.,¹⁸ the rheological behaviour of the suspensions is not only affected by the solids content but also by the particle–particle hydrodynamic interactions, which are greatly determined by the hydrodynamic particle radius, i.e. by the particle size distributions. The presence of a greater volume fraction of agglomerates in the poorly dispersed suspensions should be responsible for their higher flow resistance. The ball-milled suspensions presented a significant decrease of viscosity as the time of contact between solid and liquid phases increased, for all the solids concentrations tested. In this case, besides the particles deagglomeration, aging effects are also believed to contribute to the increase on suspensions fluidity.^{6,7,14}

3.3. Influence of milling conditions on green packing density, sintering ability and crystalline phase formation

The densification of Si_3N_4 -based materials occurs through a process of dissolution of $\alpha\text{-Si}_3\text{N}_4$, and its diffusion and precipitation into $\beta\text{-Si}_3\text{N}_4$, in the presence of a liquid phase formed by the reaction of SiO_2 , from Si_3N_4 particles' surface, with the sintering additives.^{20,21} For a defined sintering temperature and time, the densification degree achieved is determined by the amount and liquid phase composition, as by the proximity between particles.²¹

Table 1 presents the density values of the green and sintered slip-cast samples, and the linear shrinkage

Table 1

Density values measured before and after sintering and linear shrinkage of the samples obtained from suspensions 2 h-PM, 4 h-PM and 96 h-BM

Sample	Green density (%)	Density after sintering (%)	Linear shrinkage (%)
2 h-PM	63.2	97.4	12–13
4 h-PM	65.6	97.6	10.5–12
96 h-BM	66.0	98.0	10.5–11

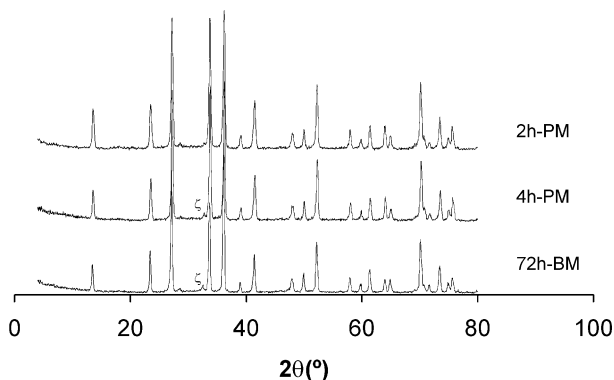


Fig. 9. X-ray diffraction patterns of sintered samples 2 h-PM, 4 h-PM and 96 h-BM (ζ - ζ - $\text{Si}_3\text{Al}_7\text{O}_3\text{N}_9$; all the remaining picks are from β - Si_3N_4).

suffered during thermal treatment. All the samples were obtained from suspensions containing 55-vol.% solids. It can be seen that the green packing density of the samples derived from the 4 h-PM suspension is higher than that of samples prepared from 2 h-PM suspension. This difference might be in the origin of the higher sintering density and lower linear shrinkage values observed for the 4 h-PM derived samples. It is conceivable that shorter inter-particle distances will give rise to a faster sintering. Moreover, the SiO_2 content at the Si_3N_4 particles' surface is expected to increase with the duration of the contact between powders and water,^{6,7,14,22} as confirmed previously through XPS analysis of particle surfaces.¹⁰ Thus, the highest final density of BM samples can be attributed to the higher SiO_2 content detected at the particles' surface due to hydrolysis.

The X-ray diffraction spectra of all sintered samples are displayed in Fig. 9. It can be observed that all the samples are mainly formed by β - Si_3N_4 . Traces of the crystalline phase ζ - $\text{Si}_3\text{Al}_7\text{O}_3\text{N}_9$ could be also detected, the amount of which increases with increasing the time of contact between the powders and the solvent media. The peak of this second phase is more intense for the 96 h-BM derived samples, not being detected in the samples prepared from 2 h-PM suspension. The presence of this second phase might be related with a more abundant liquid phase favoured by the presence of higher SiO_2 contents. The more abundant liquid phase expected in the samples 96 h-BM would be responsible for the more extensive transformation of α - Si_3N_4 into other phase besides β - Si_3N_4 . Furthermore, having a more dense atomic structure than β - Si_3N_4 , the significant presence of phase ζ - $\text{Si}_3\text{Al}_7\text{O}_3\text{N}_9$ in the 96 h-PM samples can also explain their higher final density and lower linear shrinkage values observed.

4. Conclusions

The experimental results presented and discussed on this work enable to draw the following conclusions:

1. High concentrated Si_3N_4 -based aqueous suspensions (up to 55-vol.%) could be prepared through the addition of consecutive solids increments of 5-vol.% to an initial 45-vol.% solids concentrated suspension, after deagglomeration by different time intervals.
2. Planetary milling revealed to be more efficient in deagglomerating the compositions used compared with ball milling, enabling a significant decrease of the milling period required to obtain full dispersion. The minimum duration of milling periods between consecutive increments was 4 h in the case of planetary milling and varied between 24 and 48 h in the case of ball milling, as solids concentration increased.
3. Higher dispersion levels revealed to be favourable to the fluidity of the suspensions, the green packing density and sintering ability of the slip cast samples.

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