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Si_3N_4 POWDERS APPLIED FOR WATER-BASED DCT

Ola Lyckfeldt
Swedish Ceramic Institute
P.O. Box 5403
SE-402 29 Göteborg
Sweden

Kent Rundgren
Permascand AB
P.O. Box 42
SE-840 10 Ljungaverk
Sweden

ABSTRACT

Two Si_3N_4 powders, one direct-nitrided, (P95L, Permascand AB) and one imide derived, high grade (SN-E10, UBE Industries, Japan) have been processed and evaluated to meet the demands in water-based Direct Casting Techniques (DCT).

Pre-dispersing followed by freeze granulation/freeze drying of SN-E10 was shown to significantly improve the possibilities of reaching high solids loading without critical slip dilatancy. Generally, pure electrostatic stabilization by a pH adjustment to 10, *in-situ* with P95L or with NH_4OH, was shown to be the more efficient dispersing concept. The use of polyacrylates gave considerably higher viscosity but a lower degree of dilatancy at extreme solids loading. Together with pre-milling/freeze granulation/freeze drying a solids loading of 54 vol% P95L (including 6 wt% Y_2O_3 and 2 wt% Al_2O_3 as sintering aids) could be reached using small amounts of polyelectrolyte.

Applied in DCT, e.g. protein forming (PF) and starch consolidation (SC), the addition of protein or starch resulted in increased viscosity but reduced dilatancy. Combined with a polyelectrolyte, pre-agglomeration of the protein took place, which gave less good sintering of the shaped Si_3N_4 specimens owing to a coarser microstructure. For SC the polyelectrolyte appeared to improve the dispersing of the starch granules which favored the sintering performance. With a pH adjustment to 10, protein-formed specimens sintered to near full density with gas pressure sintering whereas starch-consolidated specimens showed residual porosity originating from the starch granules.

INTRODUCTION

Silicon nitride (Si_3N_4) is today a structural ceramic that has an established market in engineering applications[1–2]. Several producers of Si_3N_4 powders and

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Si_3N_4 components, including RBSN (reaction bonded Si_3N_4) with silicon powder as raw material, exist worldwide. The prospective of Si_3N_4 is also considered to be favorable with a growing market, not only for structural applications but also as functional materials. The manufacture of Si_3N_4 components requires careful control of each processing step from the raw powder properties, colloidal processing, shaping to sintering to achieve the required material properties. The raw powder properties in terms of purity, phase composition, surface silica (surface-chemical properties) and particle size distribution very much depend upon the specific manufacturing route (imide decomposition, carbothermal reduction, direct nitridation etc)[3–4]. The choice of powder is a matter for consideration in terms of cost, processing route (type of shaping and sintering) and material requirements. As there has been a growing pressure on cost reduction in the manufacture of Si_3N_4 components attention has focused on cheaper (direct-nitrided) powders, water processing and low pressure sintering. This often requires pre-processing to obtain a powder that is easy to disperse to high solids loaded suspensions at the same time as it gives adequate sintering performance.

Several research groups have studied dispersing of various silicon nitride powders in water over the last 15–20 years[5–7]. It is typical that commercial Si_3N_4 powders consist of various amounts of silica on the particle surfaces, which has a significant impact on the surface-chemical properties. The degree of surface silica influences the charging behavior at a specific pH, the isoelectric point (iep) and the degree of adsorption of dispersants. Depending on the powder-manufacturing route the formation of silica can bind particles into tight agglomerates[8]. These agglomerates entrap water, immobilize milling media, and can make it difficult to reach high solids loaded suspensions. One way to overcome this problem is to pre-disperse (de-agglomerate) at moderate solids loading, freeze and freeze dry to avoid re-agglomeration[9]. When re-dispersing, the powder shows less water binding capacity through the absence of tight agglomerates. Combined with an efficient stabilizing concept (dispersant or pH adjustment) higher solids loadings can therefore be reached.

A complicating factor when processing Si_3N_4 materials is the need of substantial amounts of sintering aids, often various oxides. Typical is yttria (Y_2O_3) that cannot be processed in water unless high pH is applied owing to a critical solubility that causes slip destabilization. Several successful attempts to inhibit solubility of yttria and silica on the Si_3N_4 particles by surface modifications have been made. One example is the use of silanes that has been shown to reduce the solubility significantly[10–11]. However, the processing appears complicated and inconvenient, especially when very high particle concentrations are to be reached.

Efficiently de-agglomerated and highly concentrated powder suspensions are favorable in most ceramic processing. This is crucial not least when using the so-

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called Direct Casting Techniques (DCT). In DCT (gel casting, direct coagulation casting (DCC), hydrolysis-assisted solidification (HAS) etc.)[12] shaping is conducted in non-porous molds by transforming a ceramic powder suspension into rigidity without compaction or removal of liquid. Consequently, the solids loading of a prepared suspension corresponds directly to the shaped density. One advantage of DCTs over other shaping techniques is the fact that consolidation takes place in a well-dispersed and homogeneous state. This promotes sintering, symmetric shrinkage and the ultimate material properties. Furthermore, components with complicated shapes and sections with varied thickness are possible to manufacture. Today, there are DCTs available that potentially will make it possible to combine non-hazardous and environmentally friendly processing with economic efficiency and high material demands. Protein forming (PF)[13] and starch consolidation (SC)[14] are two examples of water-based DCTs that utilize non-hazardous processing aids, such as globular proteins and starch. In PF the rigidity of a ceramic suspension relies on the gel formation of a globular protein (albumin, whey proteins etc) whereas the water absorption and the swelling of starch are responsible for the consolidation in SC. In PF, the nanosized, spherically configured protein molecules and a fine-stranded gel network normally provide full densification of shaped ceramics using low pressure sintering. SC, on the other hand, requires hot (isostatic) pressing in order to reach complete densification owing to the involvement of large starch granules (5–100 μm) that leave pores of the corresponding size after debinding.

In this study two Si_3N_4 powders, a medium-cost, direct-nitrided powder (SicoNide P95 L, Permascand AB) and a high-grade, imide-derived powder (SN-E10, Ube Industries Ltd), were evaluated and processed to meet the demands in DCT. The powders were used both in the as-received and in the pre-treated states for dispersing and forming studies. Utilizing DCT, exemplified by protein forming (PF) and starch consolidation (SC), material specimens were shaped and pressureless sintered or gas pressure sintered (GPS).

MATERIALS AND EXPERIMENTALS

Materials and Powder Pre-Treatments

The manufacturers' data on the Si_3N_4 powders used in this study are presented in Table I. Pre-treatment of P95L was conducted by milling for 48 h in water at 40 vol% without dispersant followed by freezing and freeze drying (Lyovac GT2, Leybold AB, Sweden). The freezing was carried out by spraying the suspension into liquid nitrogen, i.e. freeze granulation (LS-2, PowderPro HB, Sweden). Pre-treatment of SN-E10 was conducted by dispersing in water at 35 vol% with a pH adjustment to 10 with NH_4OH and subsequently freeze-granulating and freeze-drying. Dispersing was conducted by planetary milling (PM 400, Retsch,

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Germany), using Si_3N_4 liners and balls, at 200 rpm for 60 min whereas 100 rpm was used for the milling.

Table I. Specifications for as-received SicoNide P95L and UBE SN-E10

Powder	α/(α+β) (wt%)	Si (wt%)	Fe (wt%)	Al (wt%)	Ca (wt%)	C (wt%)	O (wt%)	BET area (m^2/g)
P95L	93/7	0.2	0.04	0.06	0.01	0.30	0.46	6.3
SN-E10	99.5	-	<0.01	<0.005	<0.005	-	1.33	11.0

Other ceramic powders used as sintering additives were Al_2O_3 (AKP-30, Sumitomo Corp., Japan) and Y_2O_3 (Grade C, HC Starck GmbH, Germany).

Dispersants (polyelectrolytes) or pH adjustment to 10 with NH_4OH were used as dispersing concepts. The utilized polyelectrolytes, Duramax D-3021 from Rohm & Haas and Dolapix PC75 from Zschimmer & Schwarz, are assumed to be polyacrylates, a type of dispersant commonly used for water-based processing of Si_3N_4. In the case of P95L, the natural pH adjustment to about 10 by the powder itself made it unnecessary to use NH_4OH.

As consolidators, a globular protein (Bovine Serum Albumin (BSA), A5401, Sigma Chemicals Ltd) and a potato starch (Mikrolys 54, Lyckebystärkelsen AB, Sweden) were utilized.

Powder Characterizations

Zeta (ζ) potential measurements in the range of pH 3–11 with as-received and pre-treated Si_3N_4 powders were done with an Acoustosizer (Matec Applied Sciences). For this, 5 vol% suspensions were prepared with a background electrolyte concentration of 0.01 M KCl.

The effect of the milling of P95L upon the physical properties was characterized by measurements of BET specific surface area (FlowSorb II 2300, Micromeritics, USA) and particle size distributions (Sedigraph 5100, Micromeritics, USA).

Dispersing and Consolidation Experiments

Powder suspensions at various solids loadings of as-received and milled/ freeze-granulated/freeze-dried Si_3N_4 powders were prepared by planetary milling at 200 rpm for 60–120 min. Higher solids loading was reached by adding the powder in portions which required the longer total milling time. In the case of P95L, 6 wt% Y_2O_3 and 2 wt% Y_2O_3 as sintering aids were included in all suspensions in order to evaluate a realistic powder composition. After milling, all slips were conditioned for 16 h in slowly rotating plastic containers without balls before rheological evaluations took place.

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Either 10 wt% protein (BSA) or 3 vol% starch based on water was added to slips with higher solids loadings of P95L. The slips were impeller stirred for 2 h prior to rheological evaluations.

Rheological Measurements

Rheological studies (viscosity and viscoelasticity) were carried out with a rotational controlled-stress rheometer (StressTech, ReoLogical Instruments AB, Sweden) using a concentric cylinder measurement device (Ø = 25 mm) with a 1 mm gap. Steady-shear measurements (equilibrium viscosity) of the suspensions were conducted in the shear rate range of 1–700 s^{-1}. To achieve equal rheological history, all suspensions were exposed to a pre-shearing at 400 s^{-1} for 1 min, followed by a rest for 1 min prior to measurement. The characterization of the consolidation, the protein gelling and the starch-swelling processes, was carried out by oscillatory shear measurements at a constant frequency (1 Hz) and strain (10^{-3}) while the temperature was increased by 2°C/min from 25°C to 70°C or 80°C (15 min dwell time).

Shaping and Sintering

A few drops of defoamer (Contraspum, Zschimmer & Schwarz GmbH) were added to the P95L slips with protein or starch, and the slips were vacuum-treated (at about 100 Pa) for a short period of time until, visually determined, the air bubbles were removed. Shaping of specimens (∅ = 10–25 mm, h = 10 mm) was carried out in covered plastic rings placed on a Teflon surface. To achieve consolidation, the molds were treated at 70°C (SC) or 80°C (PF) for 60 min. After cooling to ambient temperature demolding took place and drying at ambient conditions was conducted. Removal of the remaining water and organic additives (starch or protein) was carried out either in a nitrogen atmosphere or in air with 1°C/min up to 500°C and 60 min dwell. Using a graphite resistance furnace (Balzer/Pfeiffer, Germany) specimens were pressureless sintered, placed inside a Si_3N_4 powder bed in a graphite crucible, at 1800°C at 0.1 MPa nitrogen pressure for 3 h. Some specimens were gas pressure sintered (FPW 250/300, FCT, Germany) placed inside a Si_3N_4 powder bed in a Si_3N_4 crucible. In this case a two-step sintering cycle, 3 h and 1 MPa at 1800°C followed by 3 h and 3 MPa at 1900°C, was utilized. The densities of sintered specimens were measured using Archimedes' principle (the water intrusion method).

RESULTS and DISCUSSIONS

Effects of Powder Pre-Treatments

The results from the ζ potential measurements with the SN-E10 powder versions are presented in Figure 1. For the as-received powder the isoelectric point (pH_{iep}) was defined to about 5.4. Pre-dispersing of SN-E10 resulted in a

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slight increase of pH_{iep} to about 5.8 and a decrease of the ζ potential at high pH. This indicates that a certain removal (leaching) of surface silica occurred during the pre-dispersing procedure. It has to be noted that the dwell time for the powder in water was in fact longer (2–3 h) than the specific dispersing (milling) step prior to the freeze-granulation operation. The reduced number of silanol groups, which is responsible for the negative charge sites on the surfaces, is also expected to reduce the zeta potential at high pH levels.

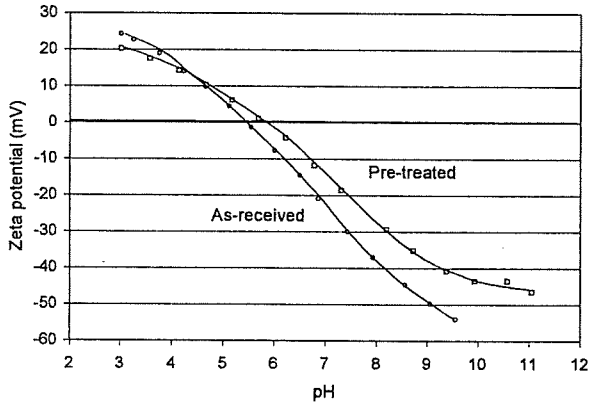

Figure 1. Measurement of ζ potential vs pH for as-received and pre-treated UBE SN-E10. Adapted from[9].

In contrast, the pH_{iep} decreased from about 5.3 to 4.8, and the charge at high pH increased for the P95L powder through the milling procedure (see Figure 2). In this case (new) Si_3N_4 surfaces were produced and, when exposed to hydrolysis reactions, an overall increase of the silica content could be expected. With small additions of the polyelectrolyte PC75 a clear shift of the pH_{iep} downwards can be seen. This is most likely a result of polymer adsorption at lower pH. However, at high pH the level of charging is similar to that without dispersant indicating that no or limited polymer adsorption took place. This is in agreement with the findings of others[15–16] regarding adsorption of polyacrylic acids on Si_3N_4.

Besides the change in surface charge properties the milling of P95L resulted in an increase of the BET surface area from 6.3 to 10.1 m^2/g and a reduction of the mean particle size (d_{50}) from 1.3 to 0.7 μm (Sedigraph 5100, Micromeritics, USA). The finer and narrower particle size distribution was expected to promote the sintering unless the indicated increase of silica unfavorably changed the sintering aid composition.

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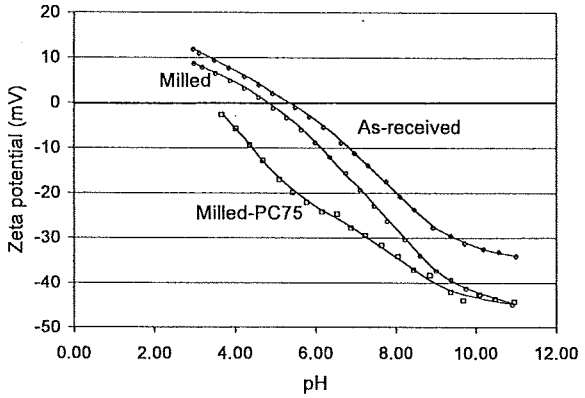

Figure 2. Measurement of ζ potential vs pH for as-received and pre-treated P95L, the latter with and without dispersant (0.05 wt% PC75).

Dispersing Study

Figure 3 shows the low-shear viscosity of Si_3N_4 slips based on as-received SN-E10 and P95L with various amounts of dispersant. The zero-point levels of polymer addition represent a pH adjustment to 10, occurring naturally with P95L and through the addition of a base with SN-E10. The difference in solids loadings should be noted along with the fact that the P95L suspensions included sintering aids. P95L caused a natural pH adjustment to >10 by a significant hydrolysis with a release of NH_3 that is far from being as pronounced as when using SN-E10. Furthermore, both dispersants adjust the pH to a similar level, also given in the figure.

In both cases the addition of the polyelectrolyte gave rise to a continuous viscosity increase, stronger for the SN-E10 than for the P95L system. Since the adsorption of polyelectrolytes, such as polyacrylic acids (PAA), on Si_3N_4 is poor at high pH levels, the influence of free and highly dissociated polymers must be the reason for these results.

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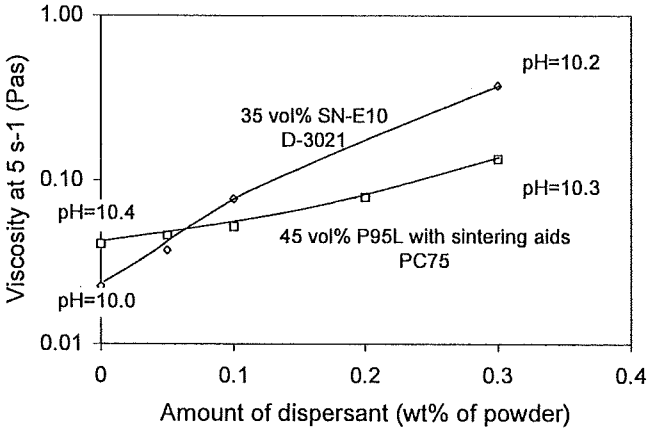

Figure 3. Steady shear viscosity at low shear rates vs amount of polyelectrolyte added to Si_3N_4 slips based on SN-E10 and P95L (with sintering aids).

The viscosity increase could be due to interactions between free polymer molecules and a general increase of the water-phase viscosity. However, the destabilizing phenomena caused by an increased electrolyte concentration and charge-screening effects are also likely to be significant. The negative consequences of adding polyelectrolyte appeared to be less serious with the P95L system. But in this case we could expect a certain polymer adsorption on the sintering aids (Al_2O_3 and Y_2O_3) that reduced the amount of free polymer and contributed to a stabilization of the oxide particles. In general, the P95L powder is a more easily processed powder that can be deagglomerated with less energy input than SN-E10. Together with a wider particle size distribution, higher solids loadings can therefore be reached with P95L, and this is reflected by the viscosity data in Figure 3. In DCT it is desirable to maximize the solids loading to achieve high shaped density. However, in view of the processing requirements, the viscosity level as such but more often a critical slip dilatancy is the limiting factor. Dilatancy is a common phenomenon with highly concentrated and well-stabilized powder suspensions. For the Si_3N_4 powders used in this study, dilatancy appeared at different levels of solids loading as illustrated in Figure 4 and 5. Regarding the as-received powders, electrostatically stabilized at high pH levels, dilatancy appeared at about 50 vol% P95L and about 42 vol% SN-E10. This situation was changed when the pre-treated powder versions were used, especially for SN-E10. Apart from a significant viscosity decrease, dilatancy with the pre-dispersed SN-E10 did not become pronounced until a solids loading of about 46 vol% was reached. Figure 4 shows that the viscosity profile still expresses a pure shear thinning behavior at 44 vol% solids.

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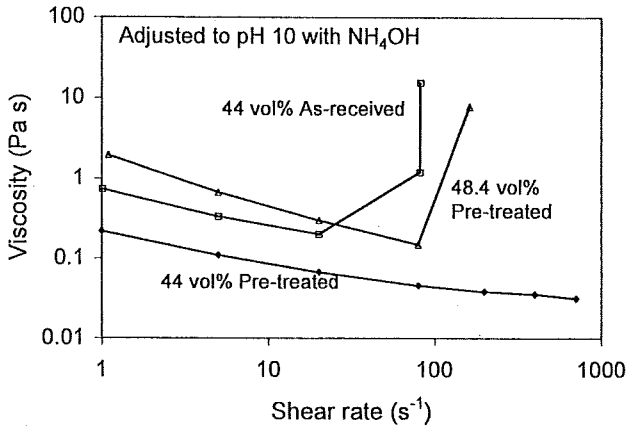

Figure 4. Steady shear viscosity vs shear rate of electrostatically stabilized Si_3N_4 slips based on UBE SN-E10. Adapted from[9].

Since the SN-E10 powder became easier to deagglomerate by the pre-treatment we could also expect a substantial difference in the dispersing process as the solids loading became high. In a situation with the same powder concentration, another addition of the tight agglomerates of as-received powder would rapidly entrap water and immobilize milling media. The consequence would be a significant increase of viscosity and dilatancy that would limit or even inhibit further deagglomeration. The dilatancy in itself would be a factor that immobilizes the milling media under high-speed conditions.

The impact of milling on the P95L slips became less pronounced (see Figure 5) than the pre-treatment of SN-E10 showed. Since the powder is easy to deagglomerate already in the as-received state the differences in rheological behavior are mainly related to the change in particle size distribution towards a finer and narrower size range. In practice, this will give an increase of the effective solids loading. The effective volume, including the electrostatic double-layer (the range of the electrostatic forces) of a smaller particle is always influenced more than that of a bigger one. Consequently, we could expect a general viscosity increase as is shown in Figure 5. More important for the processing properties, however, is the decrease in dilatancy by the milling operation. As indicated by the ζ potential measurements, an increased amount of surface silica also was assumed to result in an increased ion concentration. Like the solubility of common sintering aids such as Y_2O_3, soluble silica is an often-addressed ageing problem in slurry processing of Si_3N_4. However, at extreme solids loading an increased ion concentration through the presence of a larger amount of surface silica can contribute to decreased dilatancy by charge screening and a compressed electrostatic double-layer.

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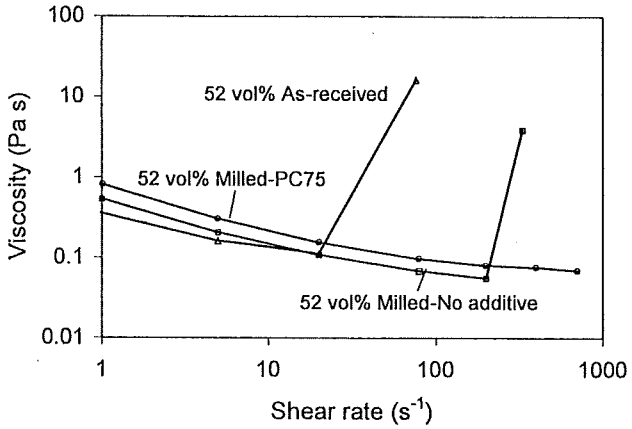

Figure 5. Steady shear viscosity vs shear rate of electrostatically stabilized Si_3N_4 slips based on P95L including sintering aids. Adapted from[17].

Since polyacrylates have shown poor adsorption onto Si_3N_4 at high pH, the main stabilizing factor must be of electrostatic origin through the pH-adjusting ability of the commonly used PAA. The reason for the results shown in Figure 5, where the addition of 0.05 wt% Dolapix PC75 gave a general viscosity increase but, at the same time, a clear decrease of the dilatancy, can therefore be related to ion-concentration effects. Rheological impact by free-polymer interactions is also possible but considered to be less important. At even higher solids loading (54 vol%) the rheological difference, with and without dispersant, was almost eliminated (see Figure 6). When approaching the maximum solids loading the ion concentration in the water phase will increase in general. A further contribution to the ion concentration by added polyelectrolyte would therefore have less impact.

Protein and Starch Additions

The addition of the globular protein (BSA) to highly concentrated Si_3N_4 suspensions pushes the viscosity further up as shown in Figure 6. This effect can be seen as a result of increased solids loading through the addition of spherically configured polymers. Depending on the specific system (dispersant, type and concentration of ions) the protein molecules have a tendency to agglomerate to a varying degree. In this case, the viscosity increase was more severe with the dispersant (PC75) present, which indicated an interaction between the free dispersant polymer and the protein molecules. However, as the viscosity increased, the degree of dilatancy decreased when adding BSA and even more in combination with the dispersant, which is a favorable result for the slip processing.

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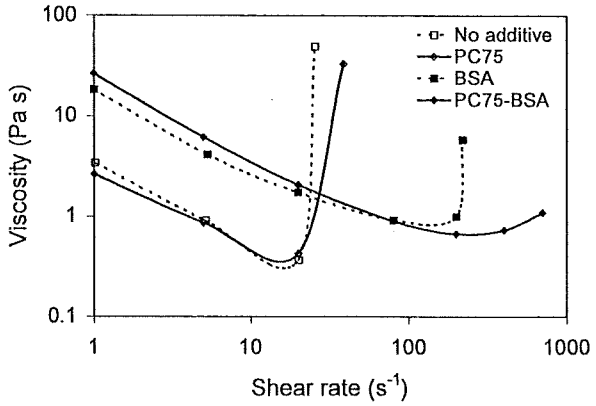

Figure 6. Steady shear viscosity for 54 vol% pre-milled P95L (including sintering aids) before and after addition of 10 wt% BSA based on water. Adapted from[17].

When adding starch, the viscosity increased significantly. The main reason for this is the fact that starch granules absorb a certain amount of water already at room temperature. As in the case of protein, starch additions tended to decrease the degree of dilatancy. This, however, was less pronounced with dispersant present. The lower viscosity with PC75 indicated that the polyelectrolyte might have contributed to a more effective dispersing of the starch granules even though their highly hydrophilic character normally make them easy to disperse in water without dispersant. Another effect can of course be that dispersant adsorption on the starch granules inhibited water absorption or suppressed any attraction to Si_3N_4 particles and, therefore, limited the viscosity increase.

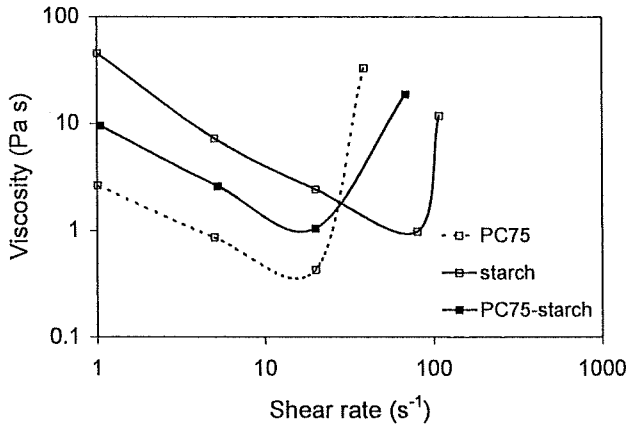

Figure 7. Steady shear viscosity for pre-milled P95L (including sintering aids) before and after addition of 3 vol% starch based on water. Adapted from[17].

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As illustrated in Figure 8, sudden and significant increases of the storage modulus (dynamic rigidity) during heating indicate gelling of protein (BSA) or swelling of the starch. In general, the consolidation was much stronger and took place at lower temperatures with starch than with BSA. The water absorption and the swelling of starch were not critically influenced by the specific system, i.e. dispersants or ions present. On the other hand, BSA showed more sensitivity to the slurry composition. This was expressed by different gelling behavior with or without dispersant.

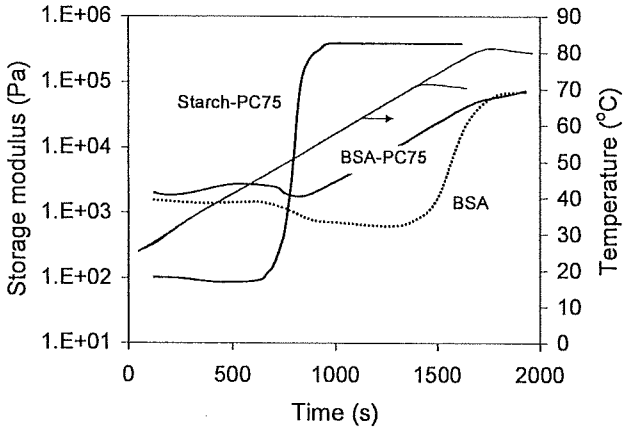

Figure 8. Storage modulus vs time and temperature for slips based on 54 vol% P95L (including sintering aids) with the addition of 3 vol% starch or 10 wt% BSA based on water. Adapted from[17].

With PC75 a prolonged gelling process took place, initiated at low temperatures by a pre-agglomeration. This might have resulted in a coarse gel structure. With no dispersant, the gelling occurred at a higher temperature but was more rapid which is assumed to result in a more fine-stranded gel network.

Evaluations of Shaped and Sintered Materials

The results from the sintering of selected shaped materials are summarized in Table II. The first obvious conclusion is that pressureless sintering was insufficient to reach full density. The main reason for this is related to the low shaped density, typical of all types of DCT. PF specimens showed a higher degree of densification owing to less influence on the microstructural homogeneity than with starch as consolidator. This fact was demonstrated more clearly when GPS was utilized, in which case PF materials reached near full density whereas the SC materials only reached 94% of theoretical density at best. To be able to sinter SC specimens of advanced ceramics to full density, hot isostatic pressing (HIP) is

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required. The main reason for this is the size of the starch granules (10–30 μm), which expand further by the water absorption. This results in large pores after debinding that remain after sintering. On the other hand, small protein molecules (some nm) can form networks within the water phase that normally keeps the homogeneity unaffected unless significant agglomeration occurs prior to gelling. However, higher initial slip viscosity and a prolonged gelling process when the polyelectrolyte (PC75) was present indicated such agglomeration. In turn, this gives rise to a coarser gel structure, less favorable shaped microstructure and, as shown in Table II, lower sintered density when PC75 was used. In contrast, the SC specimens in which PC75 had been used showed significantly higher sintered density than those without the polyelectrolyte. Again, the viscosity data indicated better dispersing of the starch and/or reduced water adsorption, factors that promoted sintering of shaped materials. Microstructural studies might give further confirmation of these results.

The results in Table II also indicate a positive effect of debinding in air compared to debinding in nitrogen. This was most pronounced with the SC specimens. The main reason is believed to be a more efficient debinding rather than an influence on the oxygen content. However, more studies are required to define the influence of the debinding conditions on the carbon/oxygen content.

Table II. Results from pressureless sintering at 1800°C and GPS (in bracket) of PF and SC specimens based on 54 vol% milled P95L powder. Adapted from[17].

Dispersant	Shaping	Effective solids (vol%)	Debinding atmosphere	Sintered relative density (% of theoretical)
-	PF	51.4	N_2	88.0
			Air	90.2 (99.4)
PC75	PF	51.4	N_2	84.1
			Air	88.2 (98.4)
-	SC	53.2	N_2	78.4
			Air	79.4 (86.4)
PC75	SC	53.2	N_2	79.5
			Air	80.8 (94.0)

SUMMARY AND CONCLUSIONS

This study has shown that the processing of Si_3N_4 powders in water at extreme solids loadings can be supported by powder pre-treatments and basic knowledge of colloidal effects. A powder that is highly agglomerated and difficult to process, such as UBE E10, can be given more favorable properties by pre-agglomeration and freeze granulation. Higher solids loading without critical dilatancy can thus be reached, which is crucial when utilizing direct casting techniques (DCTs). With

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direct-nitrided powders, such as SicoNide P95L (Permascand AB), higher solids loading can generally be reached owing to wider particle size distributions and less severe agglomeration in the as-received state. Increase of ζ_{iep} indicated leaching and reduction of SiO_2 at short-term processing of SN-E10 whereas the opposite effect was found for long-term milling of P95L. Typical of the latter powder was also a significant hydrolysis with ammonia release that produced a self-dispersing effect through the adjustment of the pH to a high level. As in the case of adjusting the SN-E10 slips to pH 10 with NH_4OH, the pure electrostatic stabilization was shown to be the most efficient dispersing concept. In general high pH is also required to restrict solubility of commonly used sintering aids, such as Y_2O_3, that may cause flocculation of the Si_3N_4 slip.

Considering poor polymer adsorption at high pH of commonly used dispersants for Si_3N_4 such as polyacrylic acids (PAA), the major dispersing effect is the pH-regulating ability. In this study the addition of polyelectrolytes gave rise to higher viscosity but less slip dilatancy at extreme solids loading than pH adjustment to 10. The milling of P95L with the assumed increase of the SiO_2 content resulted in similar rheological effects. The main factor behind these effects was concluded to be an increase of the ion concentration by the polyelectrolyte or by soluble silica that reduced the electrostatic interactions between the Si_3N_4 particles. Although the stabilizing force was negatively affected, the decrease of dilatancy was considered to be more important for the processing performance in shaping operations. Small amounts of PAA are therefore suitable when highly concentrated Si_3N_4 is to be processed, as they also enable accurate dispersing of sintering aids.

In this study, other processing (consolidating) additives were used as well and they were shown to have significant rheological impact on the Si_3N_4 suspensions. Starch addition and even more protein (Bovine Serum Albumin) addition tended to increase the viscosity but decrease the degree of dilatancy. The gelling of the protein was negatively influenced by the polyelectrolyte present that caused pre-agglomeration, an assumed coarser gel-structure and less favorable sintering performance of shaped specimens. For starch consolidation, polyelectrolyte gave the opposite effect with assumed better dispersing of the starch granules and better sintering performance of shaped specimens. In general, starch consolidation showed less sensitivity to the additives present, higher consolidation force but less good sintering of shaped specimens than protein forming did. Based on milled P95L powder and sintering additives (6 wt% Y_2O_3 and 2 wt% Al_2O_3) protein-formed specimens were sintered to full density if gas pressure sintering was utilized.

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