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# pH controlled dispersion and slip casting of $Si_3N_4$ in aqueous media

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**Abstract. The dispersion characteristics of commercial $Si_3N_4$ powder in aqueous media (deionized water) was studied as a function of pH in the range 2–11. The slip was characterized for its dispersion quality by various experimental techniques like particle size analysis, sedimentation phenomena, viscosity and flow behaviour and zeta potential analysis. The optimum dispersion was found to be in the pH region 9–11 wherein the slurry displayed minimum sedimentation height, minimum viscosity, near Newtonian flow behaviour and maximum zeta potential. The slip is highly agglomerated in the pH range 2–8 as manifested by higher sedimentation height, higher viscosity, lower zeta potential and thixotropic non-Newtonian flow behaviour. The 72 wt% (44 vol.%) $Si_3N_4$ slips made at pH = 10 resulted in green bodies having 53–59% of theoretical density after casting into plaster molds.**

**Keywords. Dispersion; slip casting; $Si_3N_4$ slips.**

## 1. Introduction

The advanced ceramic materials which are used in the vast variety of applications today, have some times to perform under very severe and stringent conditions with their best possible properties coupled with highest reliability as required for their use in advanced ceramic components. This necessitates utmost care in the choice of starting materials or in methods of their synthesis as well as in the methods of their processing and forming or fabrication (Sōmiya 1984). Their performances as structural ceramics depend mainly on their mechanical properties which are degraded by the presence of flaws such as voids, pores, agglomerates, inclusions or microstructural inhomogeneities (introduced during various stages of processing and fabrication) (Lange 1983; Alford *et al* 1986). Hence these flaws have to be eliminated or at least minimized.

The key step in processing of advanced ceramics is the control of the microstructure of the green bodies with minimized defects so that dense, high strength and reliable products are obtained on sintering (Brook 1985; Kendall 1992). Optimization is required at every stage of processing in order to achieve the desired microstructure and thereby the anticipated properties and resultant performances (Sheppard 1989).

It has been well established that the agglomerates present in the green compacts are difficult to eliminate through the conventional dry powder consolidation process as like uniaxial pressing (Alford *et al* 1986). Consequently, the wet processing route involving a colloidal dispersion of the fine powder particles in a liquid medium and their consolidation into a homogeneous dense green body with minimum defects (both in number and size) has gained wide acceptance (Freedman and Millard 1986; Dutta 1988; Roosen and Bowen 1988; Lange 1989). The colloidal consolidation technique involves the deflocculation and stabilization of micron/sub-micron sized ceramic powders dispersed in an aqueous or non-aqueous liquid medium before their consolidation. The spontaneously formed soft agglomerates due to van der Waals attractive forces between the powder particles are broken down into individual particles and dispersed by promoting interparticle repulsion by any or both of the following methods: (i) through the control of surface charges either by adjustment of pH of the medium or by adsorption of dispersants (electrolytes) on to the surface of powder particles (electrostatic stabilization) and (ii) through steric separation of individual particles by adsorption of neutral or charged large chain polymers on to the particle surface (steric or electrosteric stabilization) (Persson *et al* 1987; Lange 1989; Fries and Rand 1996; Hirata 1997; Ramachandra Rao *et al* 1999a,b,c; Ramachandra Rao and Kannan 2000).

In the present study the dispersability of a commercial $Si_3N_4$ powder in deionized water was examined as a function of pH using various experimental techniques like sedimentation, viscosity, rheology and zeta potential measurements. The results are compared and correlated in order to arrive at the pH condition of optimum dispersion required for the slip casting of $Si_3N_4$.

## 2. Experimental

A commercial $Si_3N_4$ powder (Type S1, M/s Hermann Stark, HCST, Germany) was characterized for phase

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purity by X-ray diffraction (XRD) (X-ray diffractometer, PM 9002, M/s Phillips, Holland) method. The powder was dispersed in deionized water using magnetic stirring and the pH was adjusted to different values ranging from 2 to 11 using $HNO_3$ for acidic and $NH_4OH$ for basic ranges respectively. The particle/floc size distribution of the powder was determined using a slurry with 5 wt% solid loading, as a function of pH by X-ray sedimentation technique (Sedigraph 5100, M/s Micromeritics, USA). The sedimentation behaviour of the 20 wt% solid loaded slurries maintained at different pH values (2–11) was studied to arrive at the condition for best dispersion. The height of the sedimented solid was measured from the bottom of the test tube as a function of time and plotted as a function of pH. The viscosity and shear stress measurements were made for a 44 wt%/20 vol.% solid loaded $Si_3N_4$ slurry maintained at different pH values as a function of shear rates using a rotational viscometer (Viscotester, VT-500, M/s Haake, Germany). The electrophoretic mobility and hence the zeta potential of $Si_3N_4$ particles in 20 wt% solid loaded slurry was measured as a function of pH using a mass transport apparatus (Zeta Potential Analyser, 1202, M/s Micromeritics, USA).

Aqueous slurry of $Si_3N_4$ prepared with solid loading of 67–71 wt% at the optimum pH of 10–10·3 was milled for about 20 h in a polythene jar using alumina balls as milling media and the resultant slip was cast into plaster molds to obtain green bodies in the form of rectangular bars ($50 \times 9 \times 9$ mm$^3$) and discs (25 mm φ × 10 mm). Similar slip casting was also performed with $Si_3N_4$ slips containing $Y_2O_3$ and $Al_2O_3$ as sintering additives. The green samples were characterized for bulk density by weight and dimensional measurements.

## 3. Results and discussion

### 3.1 *$Si_3N_4$ slurry characterization*

The XRD analysis of the $Si_3N_4$ powder shows that it is a mixture of 92% *a*-$Si_3N_4$ and 8% *b*-$Si_3N_4$. The particle size distribution (PSD) of $Si_3N_4$ powder dispersed in deionized water measured as a function of pH is presented in figure 1. The results clearly reveal the effect of pH on the extent of dispersion of $Si_3N_4$ particles in deionized water. At pH values of 2 and 6, PSD curves indicate the presence of high levels of agglomeration of fine particles since the curves show a narrow particle size distribution on the coarser side. At pH value of 8·5 the curve is shifted to the right indicating the deflocculation effect, but with retention of some amount of agglomerates in the suspension. On the contrary at pH = 10·5 the best dispersion is observed by shifting the PSD curve towards finer ranges with wider size distribution. The PSD analysis therefore shows the great influence of the pH of the medium on the dispersability of $Si_3N_4$ powder in deionized water even at a very low solid loading (5 wt%).

The simple experiments on sedimentation behaviour of $Si_3N_4$ as a function of pH and of time provide more spectacular revelation of the changing states of dispersion as a function of the above variables. The sedimentation heights measured after different time intervals plotted as a function of pH for $Si_3N_4$ presented in figure 2 show that highly agglomerated conditions which prevail in the acidic range of pH = 2–6, gets gradually broken down in the pH range 6–7 and more sharply in the pH range 7–8·5 beyond which the slurry continues to be well dispersed. The minimum in sedimentation heights for the pH values in the range 9–11 is a result of optimum dispersion of the particles and the pH values in the range 8–9 could be considered to result in an intermediate state of dispersion, thus complimenting the particle size analysis results. These results compare well with the sedimentation behaviour observed for $Si_3N_4$ whiskers as a function of pH of the slurry (Hirata *et al* 1990). However, sedimentation studies on $Si_3N_4$ powders by Torre and Bigay (1986) show minimum sedimentation heights in two pH windows of 3·5–7 and 9·5–12. These behaviours could be attributed to the difference in surface chemistry of the powders.

The $Si_3N_4$ slurries were further subjected to the viscosity and zeta potential measurements. The viscosity of $Si_3N_4$ slurry measured as a function of pH at two different shear rates is presented in figure 3, while the zeta potential versus pH curve is plotted in figure 4. The flow (rheological) behaviour of $Si_3N_4$ slurry as a function of pH is depicted in figures 5 and 6.

The viscosity graphs show two regions of distinct minima in the pH ranges 2–3 and 9–10·5 indicating optimum dispersion at these pH values. The lowest viscosity values in the pH range 9–10·5 is in accord with the sedimentation results (figure 2) as well as higher zeta potential values depicted in figure 4. A very steep variation of viscosity in the pH range of 4–7 could be due to very high level of agglomeration and de-agglomeration of fine particles that set in around this pH range. In figure 4, a near

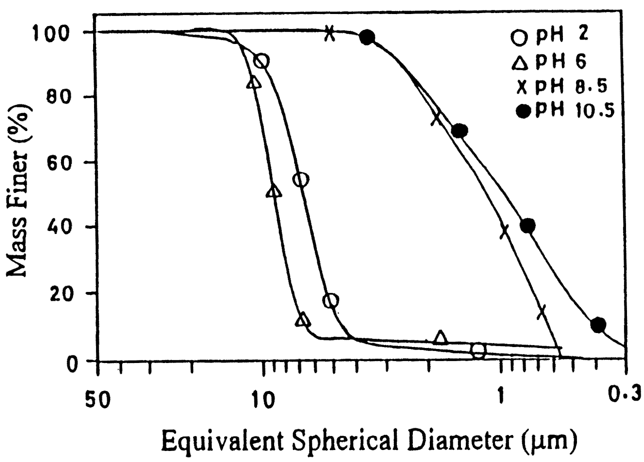


**Figure 1.** Particle size distribution of $Si_3N_4$ powder at different pH values.

zero value of zeta potential is seen around the iso-electric point (IEP) of 5·5. The IEP observed is in agreement with the values reported earlier (Hoffmann *et al* 1989; Peter Greil 1989; Bergstrom and Bostedt 1990; Galassi *et al* 1995, 2000).

The studies on surface chemistry (Bergstrom and Pugh 1989; Stadelmann and Petzow 1989; Bergstrom and Bostedt 1990; Li *et al* 1995) have shown that $Si_3N_4$ powder contains two types of surface groups viz. the amphoteric silanol (Si–OH) and basic silazane ($Si_2$–NH) and silylamine (Si–$NH_2$) on its surface. In aqueous solution, the silanol and amine groups undergo acid/base reactions depending on the pH of the medium and develop positive or negative surface charges depending upon the adsorption of either of the potential determining $OH^-$ or $H^+$ ions.

$$SiOH_2^+ \xleftarrow{H^+} SiOH \xrightarrow{OH^-} SiO^- + H_2O,$$

$$SiNH_2 \xrightarrow{H^+} SiNH_3^+,$$

$$Si_2NH \xrightarrow{H^+} Si_2NH_2^+.$$

Depending upon the relative site density of amphoteric silanol and basic amine groups, the IEP of $Si_3N_4$ may vary between 3 and 9 and hence their pH dependent dissociation behaviour (Galassi *et al* 2000).

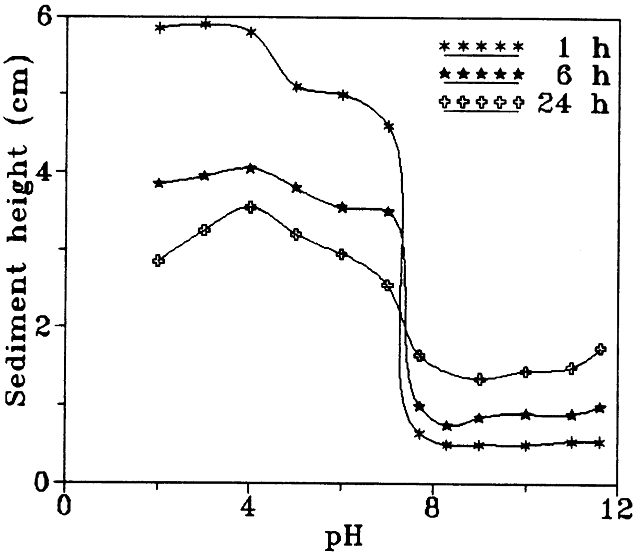


**Figure 2.** Sedimentation height as a function of pH for $Si_3N_4$ (20 wt%) at different time intervals.

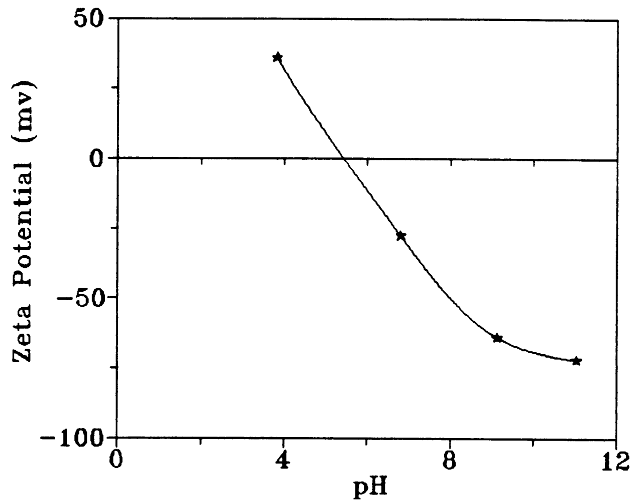


**Figure 4.** Zeta potential vs pH for $Si_3N_4$ powder in de-ionized water (20 wt%).

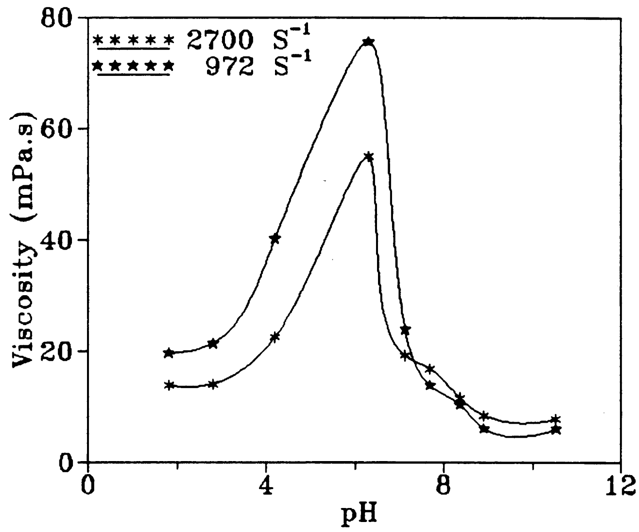


**Figure 3.** Viscosity as a function of pH for $Si_3N_4$ slurry (44 wt%) at different shear rates.

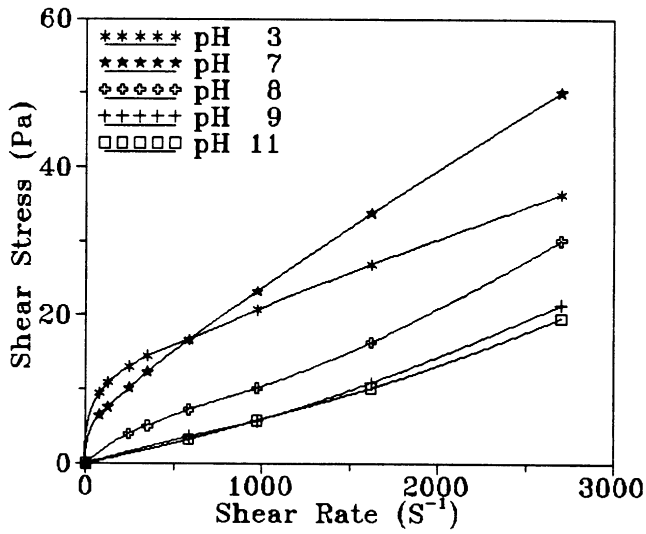


**Figure 5.** Shear stress vs shear rate flow curves for $Si_3N_4$ slurry (44 wt%) at different pH.

**Table 1.** Slip casting conditions of $Si_3N_4$ powder (type S1).

| Sl no. | Sintering additives (wt%) | | pH | Milling time (h) | Solid loading (wt%) | Samples | Green density (% theoretical)* |
|---|---|---|---|---|---|---|---|
| 1 | – | | 10·3 | 20 | 66·7 | Bars | 55·1 |
| | | | | | | Discs | 55·3 |
| | | | | | | Cup | 55·5 |
| 2 | – | | 10·1 | 20 | 71·4 | Bars | 59·2 |
| | | | | | | Discs | 59·4 |
| | | | | | | Cup | 57·9 |
| 3 | $Y_2O_3$ | 5 | 10·5 | 20 | 71·4 | Bars | 52·6 |
| | $Al_2O_3$ | 3 | | | | Discs | 51·2 |
| 4 | $Y_2O_3$ | 10 | 10·2 | 17 | 72·3 | Bars | 53·1 |
| | $Al_2O_3$ | 3 | | | | Discs | 53·1 |
| 5 | $Y_2O_3$ | 5 | 10·0 | 20 | 70·3 | Bars | 54·2 |
| | $Al_2O_3$ | 3 | | | | Discs | 54·2 |

*Theoretical density of $Si_3N_4$ is 3·2 g·cm$^{-3}$.

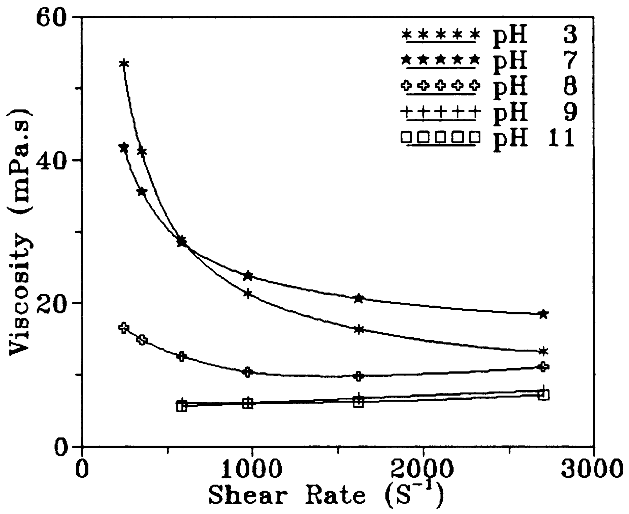


**Figure 6.** Viscosity vs shear rate flow curves for $Si_3N_4$ slurry (44 wt%) at different pH.

From the flow curves depicted in figures 5 and 6, it can be seen that the $Si_3N_4$ slurry shows near Newtonian flow behaviour at pH values of 9 and 11 indicating the pH range 9–11 as the condition of optimum dispersion which is in agreement with the higher zeta potentials observed in figure 4. The $Si_3N_4$ slurry shows a slight non-Newtonian behaviour at the pH value of 8 and a large shear thinning at pH values of 3 and 7 because of high degree of flocculation of the particles. The viscosity and rheological behaviour of the $Si_3N_4$ slurry is in agreement with those reported by earlier workers (Nagel and Petzow 1989; Sato *et al* 1995; Moreno *et al* 1998).

3.2 *Slip casting of $Si_3N_4$*

Based on the results of particle size distribution, sedimentation, viscosity, zeta potential and rheological behaviour as a function of pH, it is concluded that the pH range of 9–11 is optimal for dispersion of $Si_3N_4$ powders in aqueous media. A $Si_3N_4$ slurry adjusted to a pH value in the range 10–10·5 was used in slip casting experiments. The various casting conditions and the green density of slip cast samples are presented in table 1. The same pH value is expected to give good dispersion of $Y_2O_3$ and $Al_2O_3$ powders (sintering aids) in aqueous media since they show maximum zeta potential values at pH values above 10 according to a recent study by Moreno *et al* (1998). This is proved by the negligible effect of the addition of $Y_2O_3$ and $Al_2O_3$ on the green density of slip cast $Si_3N_4$ samples (table 1).

## 4. Conclusions

The results of the present study reveal that the dispersion behaviour of commercial $Si_3N_4$ powder in aqueous media can be controlled by changing the pH of the medium. By using various experimental techniques like particle size analysis, sedimentation, viscosity, rheology and zeta potential measurements for the $Si_3N_4$ slips in the pH range 2–11, the optimum condition of dispersion was found to be in the pH range 9–11. In this pH range, the slips showed a minimum in sedimentation height, a minimum in viscosity, a near Newtonian flow behaviour and a maximum of zeta potential. A 72 wt% solid loaded slip of $Si_3N_4$ prepared at the pH of around 10–10·5 with or without oxide sintering additives ($Y_2O_3$ and $Al_2O_3$) yielded green bodies having 53–59% theoretical density.

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