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ROBOCASTING AND MECHANICAL TESTING OF AQUEOUS SILICON NITRIDE SLURRIES

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ABSTRACT

Aqueous slurries of silicon nitride were freeform fabricated using a novel technique termed robocasting. The process utilizes high solids loading slurries of 52 vol% which is within 10% of maximum consolidated density, while using no binder and less than 2 wt% organics in the form of polyelectrolyte dispersants. The combined effects of polyelectrolyte, pH, and solids loading were optimized to produce slurries with a shear thinning rheology suitable for the robocasting process. Through the layer-wise process, silicon nitride ceramic parts were fabricated without molds and subsequently fired to > 99% theoretical density. Four point bend testing yielded an average strength of 737 MPa using ASTM standard C-1161.

INTRODUCTION

Colloidal processing has shown its potential to improve the strength and reliability of high-performance ceramic components with complex shapes [1,2]. Although colloidal processing techniques such as slip casting [1,3], gel casting [4] or coagulation casting [5] have been used to consolidate silicon nitride ceramic components, these techniques require long processing times and more organic chemicals. Other freeform fabrication processes such as fused deposition modeling [6] use large amounts of binders which require lengthy and careful drying and firing processes. Robocasting [7] is a novel technique for freeform fabrication of dense ceramics using high solids loading, no binder, and less than 2 wt% organics in the form of dispersants which allows ceramic parts to be formed, dried and sintered in less than 24 hours. Ceramic components with simple or complex shapes can be rapidly produced from a computer-aided-design (CAD) drawing directly to a finished component that requires little or no machining after fabrication. Proper control of slurry rheology, build parameters and drying conditions allows part fabrication without molds. The key to successful robocasting is a thorough understanding of the rheology or fluid characteristics of the colloidal ceramic system. Si_3N_4 is a non-oxide material and generally is quite difficult to process via aqueous colloidal techniques. Therefore, the principal objective of this research was to determine aqueous slurry conditions appropriate for robocasting. These conditions require a shear thinning rheology at a solids loading close to the maximum consolidated density. Fundamental aspects about the dispersion and rheology of aqueous Si_3N_4 slurry are discussed in order to obtain the optimal robocasting conditions. Finally, the mechanical properties and microstructure of sintered robocast bars are described.

DISCLAIMER

DISCLAIMER

EXPERIMENT

GS-44 Si_3N_4 powder (AlliedSignal Inc., Torrance, CA) was used in the experiment. The average particle diameter measured by an x-ray absorption/sedimentation technique was 0.77 μm. The specific surface area measured by standard BET N_2 adsorption was 7.7 m^2/g. A commercially dispersant, Darvan 821A (R.T.Vanderbilt Company Inc., CT), which was 40 wt% ammonium polyacrylate in solution and has a molecular weight of approximately 3500, was used for the preparation of the aqueous slurries. The pH was adjusted with analytical grade nitric acid (1N) and ammonium hydroxide solutions (40%). Deionized water was used throughout this study.

Sedimentation tests were conducted using 5 vol% Si_3N_4 aqueous suspensions. Various amounts of Darvan 821A were added to the suspensions which were then ball-milled for at least 12 hours. The pH was adjusted to the desired value and the resulting suspension was poured into graduated tubes, and allowed to settle, covered, for 5 days at room temperature. The states of dispersion and final sedimentation cake heights were recorded.

Effect of pH and wt% dispersant on viscosity was determined using a Brookfield cone and plate rotary viscometer (Brookfield Model LVT, Stoughton, MA). Billets of Si_3N_4 were robocast from a 52 vol% GS-44 aqueous slurry at Sandia National Labs. The robocast billets were sintered at AlliedSignal Inc. (Torrance, CA). Sintered density was determined by water immersion method (ASTM standard C20). Sintered GS-44 bars were machined into Type A MOR bars. The flexural strength was measured using four-point bend testing (ASTM standard C-1161) with a crosshead speed of 5 mm/min, and inner and outer spans of 10 and 20 mm respectively (INSTRON 5565, Instron Corp., Canton, MA). These fracture surfaces were examined using a scanning electron microscope (SEM) (Stereoscan 90, Cambridge Instruments).

RESULTS AND DISCUSSION

Effects of Polyelectrolyte, pH and Solids Loading on Rheology of Aqueous Si_3N_4 Slurries

Figure 1 shows the effect of Darvan 821A and pH on settling. The isoelectric point (IEP) of GS-44 Si_3N_4 powder, which corresponds to the highest sedimentation height without polyelectrolyte, was about pH 6.0. At the IEP, the number of positive sites equals the number of negative sites on the particle and the net charge equals zero. In the absence of polymer and above the IEP sedimentation heights decreased with increasing pH. The minimum sedimentation height indicates repulsive forces are high, the particles are deflocculated and are able to achieve a relatively dense packing structure [8]. Highly charged negative surfaces above pH 9.6 create large electrostatic repulsive forces, allowing particle dispersion without polyelectrolyte.

Darvan 821A is a carbon chain polymer with carboxylic acid functional groups (COOH) along the backbone. At pH values ≤ 2, the functional groups remain as COOH and the polyelectrolyte behave as a neutral polymer. As the pH increases, H^+ ions dissociate from the polymer, leaving charged COO^- groups along the chain to help provide dispersion. Further increasing the pH promotes H^+ dissociation until pH ≥ 7 where the polyelectrolyte is nearly fully dissociated. Based on this knowledge of the polyelectrolyte, it would make sense to create basic pH slurry conditions where the polyelectrolyte is most effective. However, basic conditions are greater than the IEP of the particles (pH 6) and therefore the particle surface charge becomes increasingly negative. Because the polyelectrolyte head group is negatively charged, at pH values appreciably higher than the IEP, polymer adsorption decreases. These effects can be seen in the setting data from Figure 1. At pH > 6, only 1 wt% Darvan 821A is needed to deflocculate the particles. Less than pH 6, dispersant levels up to 3 wt% are not able to provide adequate repulsion. Results from these sedimentation tests are in agreement with Albano [3] and Liu [9] who used other experimental methods.

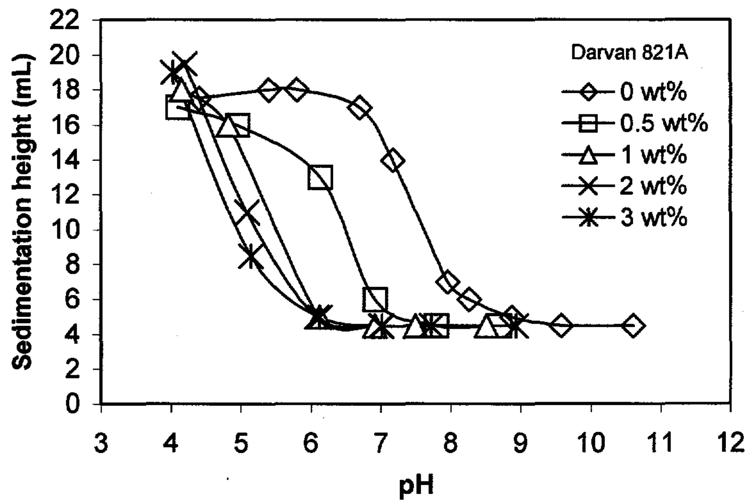


Figure 1. The relationship between pH, Darvan 821A and sedimentation height (5 vol% GS-44 Si_3N_4).

Figure 2 shows the effect of pH on viscosity and rheology for stabilized 20 vol% GS-44 Si_3N_4 slurries containing 1 wt% Darvan 821A. The viscosity of slurries decreased with an increase in pH and the rheological behavior changed from shear thinning to near Newtonian. For pH 4, the polyelectrolyte is not fully dissociated, however, its adsorption behavior on Si_3N_4 particles is of the high-affinity type. High viscosities and strong shear thinning behavior at pH 4 result due from aggregation caused by the formation of a relatively hydrophobic adsorbed layer of weakly charged polyelectrolyte on the particle surface. At pH 6, the polyelectrolyte chains become more dissociated. With more dissociation, the adsorbed polyelectrolyte has a larger number of negatively charged functional groups than at pH 4, which extend into solution and therefore increase the electrosteric repulsive barrier between particles, promoting lower viscosities [10]. At pH 8, the particles of Si_3N_4 are more negatively charged and the polyelectrolyte is fully dissociated. The low viscosity can be attributed to the enhanced electrostatic repulsion between particles, and, to a lesser extent, electrosteric repulsion due to lower polyelectrolyte adsorption.

Figure 3 shows the influence of the amount of Darvan 821A on the viscosity of 20 vol% GS-44 Si_3N_4 slurries at pH 8, 9 and 10.5. The minimum viscosity (greatest degree of dispersion) occurs at 1 wt% Darvan 821A. Further additions of polymer over 1 wt% increase the viscosity due to an excess of polymer in solution, that is, a network developed by polymer entanglement retards the sliding of Si_3N_4 particles past one another, increasing viscosity. For Darvan 821A additions less than 1 wt%, flocculation occurs due to insufficient adsorption which results in lower electrosteric repulsion between particles, thereby allowing particles to touch under shear, increasing the viscosity.

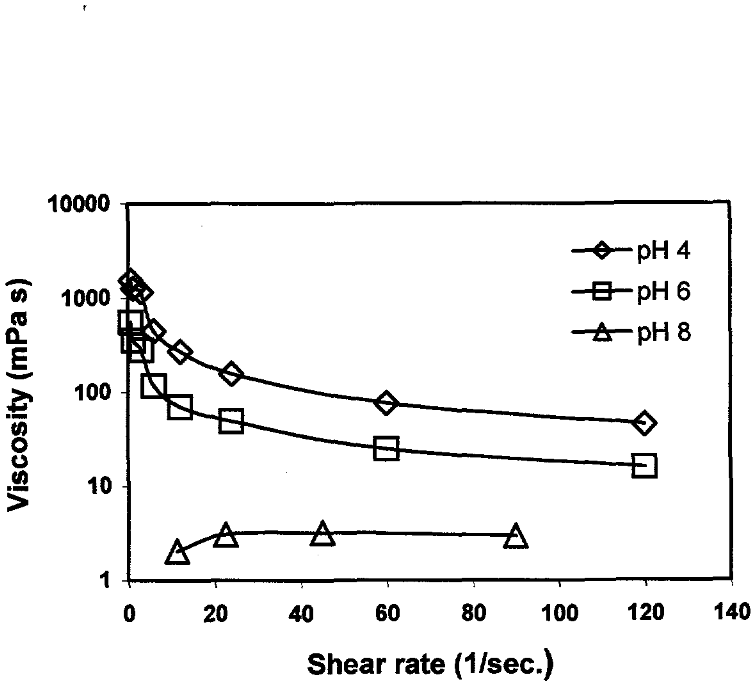


Figure 2. Viscosity as a function of shear rate at different pH values for 20 vol% GS-44 slurries with 1 wt% Darvan 821A.

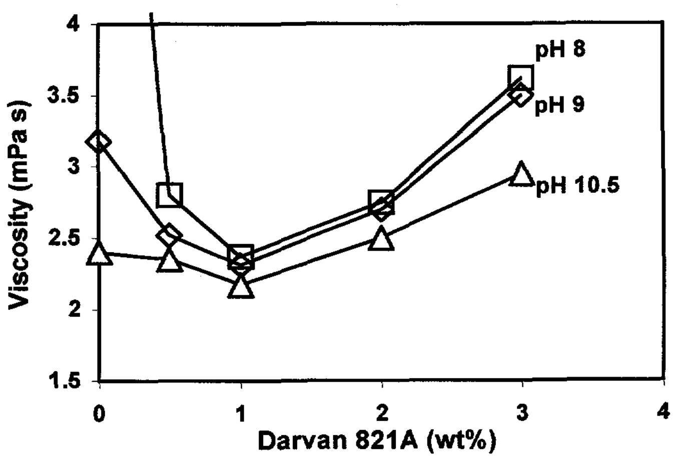


Figure 3. Viscosity of 20 vol% GS-44 slurry versus amount of Darvan 821A added at different pH values (shear rate 450 s^{-1}).

Figure 4 illustrates the rheologies of dispersed GS-44 Si_3N_4 powder slurries. As the solids loading increases, the magnitude of viscosity increases and rheological behavior also changes. At low solids loading, dispersed slurries exhibit very low viscosity and are rheologically Newtonian. Around 35 vol% solids, the slurries begin to show pseudoplastic (shear-thinning) behavior even though the viscosity is still relatively low. As the solids content approaches 50 vol%, particle collisions become prominent as the probability of interaction increases. Viscosity begins to increase appreciably, and the rheological behavior becomes highly pseudoplastic. At approximately 58 vol% percent solids, particle mobility becomes restricted, and the slurry locks up into a dilatant (shear-thickening) mass. For robocasting, it is desirable to use with slurries that have solids loading close to the dilatant transition so that upon minimal drying, the extruded bead will maintain shape [7]. It is also desirable that the highly loaded slurries exhibit an appreciable yield stress. Additions of $Al(NO_3)_3$ or $AlCl_3$ can be used to control the yield stress of the GS-44 Si_3N_4. These additives reduce the polyelectrolyte efficiency by complexing with the COO^- groups, allowing partial flocculation of the slurry, resulting in Bingham plastic (Newtonian with a yield stress) shown in Figure 5. The yield stress created by the partial flocculation was ~25 MPa. This yield stress helps maintain extruded bead shape until sufficient drying pushes the slurry into the dilatant regime.

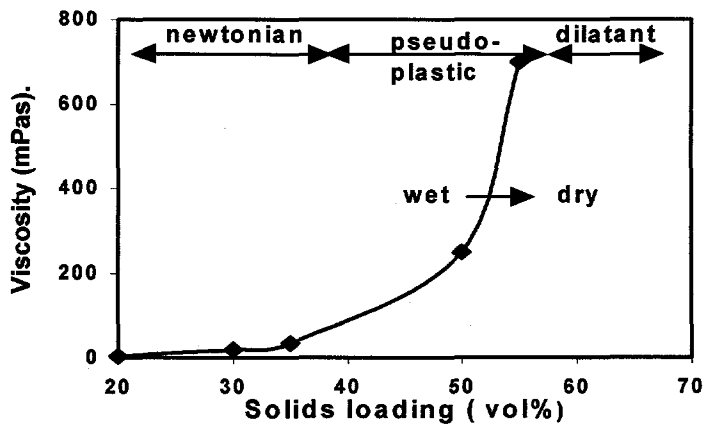


Figure 4. Viscosity versus solids loading behavior for dispersed GS-44 slurries at 1 wt% Darvan 821A and pH 8.5. (shear rate 24 s^{-1})

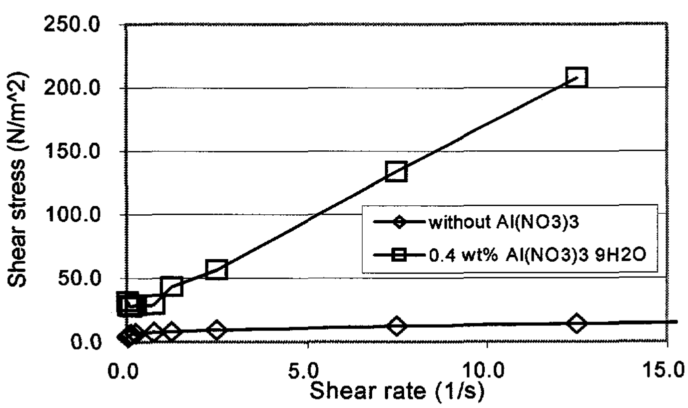
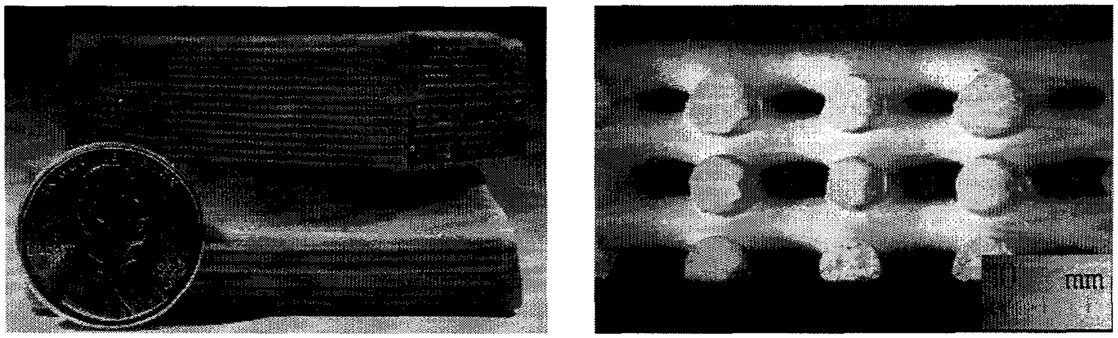


Figure 5. Rheology change from shear thinning to Bingham plastic with small additions of $Al(NO_3)_3$.

Robocasting and Sintering of GS-44 Si_3N_4

GS-44 Si_3N_4 bars, up to 20x30x65 mm in size, have been robocast successfully at rates up to 0.05 mL/s. The optimal slurry characteristics for robocasting were 52 vol% GS-44 Si_3N_4 with 1 wt% Darvan 821A and 0.4 wt% aluminum nitrate at pH 7.8 to 8.5 based on rheological studies. Only very slight warping was observed during forming and drying. The green density was 1.8 g/cm^3 (or 56% of theoretical). After sintering, the bars showed a linear shrinkage of 16%. The average sintered density was 3.21 g/cm^3 (99.0% of theoretical - Table 1). Visually there is no apparent cracking and the overall color is fairly uniform (Figure 6a). A 52 vol% slurry at pH 10.8 which utilizes the large electrosteric effects of the highly charged particles (no polyelectrolyte needed) was used to create a 3 dimensional mesh (Figure 6b). The yield stress is sufficient to span the gaps in the part until sufficient drying occurs.



(a) (b)

Figure 6. Fired robocast billets (a) and 3-D mesh (b).

Mechanical Testing and Microstructure

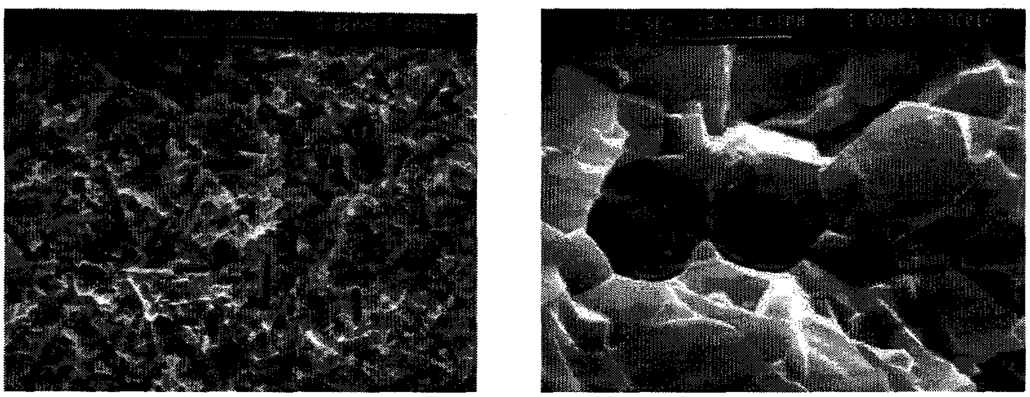
Strengths of 10 MOR bars shown in Table 1 yielding an average flexural strength of 737 MPa ± 38, which is comparable to the flexural strength of 759 MPa of slip cast GS-44 Si_3N_4 [11].

Table 1. Sintered density and strength of robocast GS-44 Si_3N_4 at room temperature.

Sample No.	Density (g/cm^3)	Density (% of theoretical)	Flexural strength at room temperature (MPa)
1	3.21	99.0	746
2	3.20	99.8	781
3	3.21	99.2	691
4	3.19	98.6	741
5	3.21	99.0	701
6*	3.21	98.9	368 (large defect)
7*	3.22	99.4	650 (lowest)
8	3.20	98.8	786
9*	3.22	99.4	831 (highest)
10	3.21	99.0	712
Average	3.21	99.0	737 ± 38

* not used in average calculations

Fracture surfaces of MOR bars were examined using SEM where surface flaws were found to be the origin of failure. Figure 6 (a) shows significant pullout β-Si_3N_4 fibers. The regular hexagonal cross-sections of β-Si_3N_4 fibers are clearly shown in Figure 6 (b). They are typical in dense Si_3N_4 ceramics and are believed to be responsible for the superior mechanical properties of Si_3N_4 ceramics.



(a) (b)

Figure 6. Pullout β-Si_3N_4 fibers in the fracture surfaces of sintered robocast GS-44 bars (a) and cross-sections of β-Si_3N_4 fibers (b).

CONCLUSIONS

The combined effects of Darvan 821A, pH, and solids loading on the dispersion and rheology of aqueous GS-44 Si_3N_4 suspensions were examined. Shear thinning slurries with a yield stress suitable for robocasting were created. Aqueous GS-44 Si_3N_4 slurries have been successfully robocast with fired densities greater than 99% of theoretical density obtained. Mechanical properties and microstructure of robocast GS-44 were measured and compared favorably conventionally produced Si_3N_4. Flexural strength at room temperature was 737 ± 38 MPa with fracture surfaces showing pullout of β-Si_3N_4 fibers and an interlocking structure.

ACKNOWLEDGMENTS

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