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PROCESSING AND MECHANICAL PROPERTIES OF SILICON NITRIDE FORMED BY ROBOCASTING AQUEOUS SLURRIES

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ABSTRACT

Robocasting is a new freeform fabrication technique for dense ceramics. It uses robotics to control deposition of ceramic slurries through an orifice. The optimization of concentrated aqueous Si_3N_4 slurry properties to achieve high green density robocast bodies and subsequent high sintered densities was investigated. The effects of pH, electrolyte, additives and solids loading on the dispersion and rheological properties of Si_3N_4 slurries were determined. The mechanical behavior of sintered robocast bars was determined and compared to conventionally produced silicon nitride ceramics.

INTRODUCTION

Silicon nitride ceramics exhibit high potential for various high-temperature/high-stress applications. The demand and manufacturability for improved performance of Si_3N_4 ceramics in advanced engines and gas turbines have continually increased. Colloidal processing has shown its potential to improve the strength and reliability of high-performance ceramics. Although colloidal processing techniques such as slip casting[1-2], gel casting[3] or coagulation casting[4] have been used to consolidate silicon nitride ceramic components, these techniques require long processing time and more organic chemicals. Robocasting[5] is a new technique for freeform fabrication of dense ceramics using slurry deposition. 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. In addition, robocasting is moldless and binderless, and ceramic parts can be formed,

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dried, and sintered within 24 h.[6] 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 colloidal techniques. Hence, the aim of the present work is to investigate the robocasting of Si_3N_4 aqueous slurries. Fundamental aspects about the dispersion and rheology of Si_3N_4 aqueous slurry are discussed in order to obtain the optimal robocasting conditions. Finally, the mechanical properties and microstructure of sintered robocast bars are described.

EXPERIMENTAL PROCEDURE

High-purity α-Si_3N_4 powder (GS-44, Allied Signal Inc, 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. Darvan 821A (with 40 wt% of ammonium polyacrylate of molecular weight about 3500) obtained from R.T.Vanderbilt company was used as a dispersant. 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 12h. The pH was adjusted to a desired value and the resultant suspension was poured into graduated tubes, and allowed to stand for 5 days at room temperature. The states of dispension and final sedimentation cake heights were recorded.

Viscosity was measured using a Brookfield cone-plate rotary viscometer (Brookfield Model LVT, Stoughton, MA). An external bath circulator maintained the sample temperature at 22 ±0.1°C. The bar samples were robocast from 52 vol% GS-44 aqueous slurry at Sandia National Labs. The robocast bars were dried overnight at room temperature and sintered by pressure sintering in a N_2 atmosphere from 1600°C to 1800°C for 1~2 h. Sintered density was determined by water immersion (standard method ASTM C20). The flexural strength was measured using a four-point bending configuration 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). The Vickers microhardness was determined by the indentation method with an applied load of 1 kg for 15s (LECO M-400 Microhardness Tester, Leco Corp., St. Joseph, MI). These fracture surfaces were examined using scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Rheology of Aqueous Si_3N_4 Slurries

Fig. 1 shows the results of the sedimentation tests on the dispersive effect of Darvan 821A. The zero point of charge (ZPC) of GS-44 powder, which corresponds to the highest sedimentation height for non-polyelectrolyte aqueous suspensions, was at about pH 6.0. It means that the number of positive sites equals the number of negative sites and the net charge equals zero at ZPC. The GS-44 powder could be dispersed only at pH ≥ 9.6 in the absence of dispersants by electrostatic repulsion between the negatively charged surface sites.

With the addition of Darvan 821A from 0.5 wt% to 3 wt%, the pH range at which the Si_3N_4 powder can be dispersed is enlarged and tends to low pH values, such as pH = 6.5 (thick line in Fig. 1). Dissociation of Darvan 821A ($RCOONH_4$) depends on the pH in the suspension. The $RCOO^-$ groups can be adsorbed on positive sites of the Si_3N_4 powder surface. At pH ≥ 6.5, GS-44 powders are dispersed due to both electrostatic and electrosteric interactions between particles.

As shown in Fig. 1, GS-44 powder becomes dispersed (lowest sedimentation height) with polyacrylate additions from 0 to 1 wt% and a decrease in pH from 10 to 6.5. GS-44 remains dispersed with further additions of polyacrylate to 2.5 wt% at a nearly constant pH of 6.5. This indicates that the 1 wt% Darvan 821A is the most efficient concentration for dispersing the Si_3N_4 powder in aqueous suspensions. This implies that further addition of the dispersant beyond a certain level had no more measurable contribution to the interfacial charge of the powder because the adsorbed dispersant layers on powder surfaces are saturated. Results from these sedimentation tests are in agreement with Albano[2] and Liu[7] who used other experimental methods.

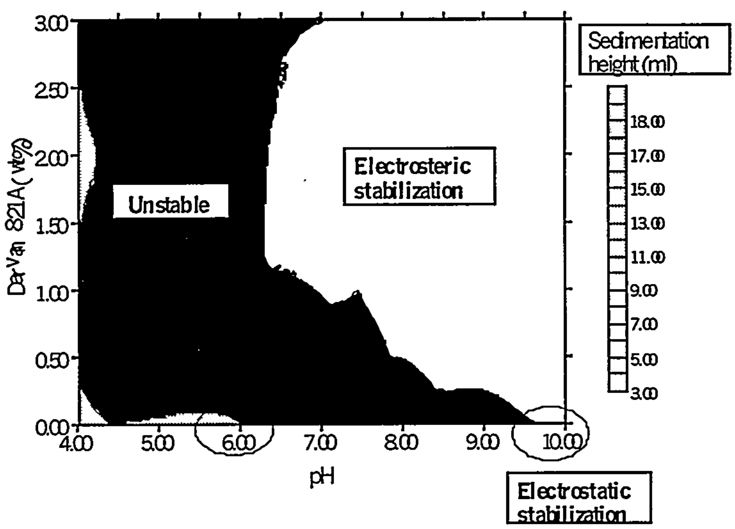


Fig.1. The relationship between pH, Darvan 821A and sedimentation height (5 vol% GS-44 Si_3N_4).

Fig. 2 shows the effect of pH on viscosity for stabilized 20 vol% GS-44 Si_3N_4 slurries containing 0~3 wt% Darvan 821A. The viscosity of slurries decreased with an increase in pH. In the absence of dispersants, the viscosity increased sharply at pH ≤ 9, but the viscosities increased sharply at pH ≤ 7 in the presence of dispersants. These increases are not shown in Fig. 2 because a different shear rate was required to make measurements within the viscometer's range. Increasing viscosity is related to a decrease in the negative charge characteristics of the absorbed polyelectrolyte and a decrease in the electrosteric repulsive barrier between particles. Relatively low viscosity occurred at pH 7~11. This pH range is in agreement with the sedimentation test where the GS-44 Si_3N_4 powder was well dispersed.

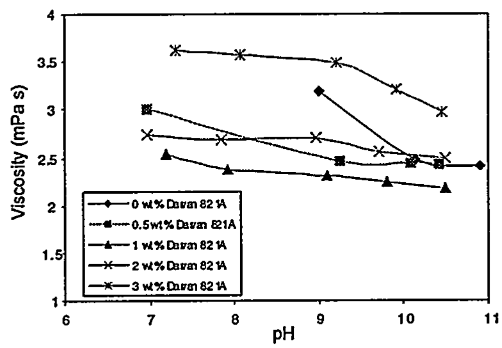


Fig. 2. Viscosity as a function of pH for 20 vol% GS-44 slurries with various amounts of Darvan 821A (shear rate 450 s^{-1})

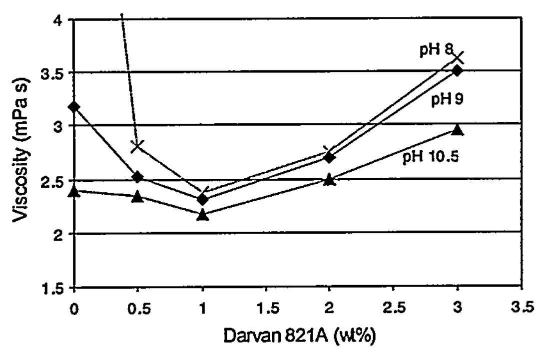


Fig. 3. Viscosity of 20 vol% GS-44 slurry versus amount of Darvan 821A added at different pH values.(shear rate 450 s^{-1})

Fig. 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) occurred at 1 wt% Darvan 821A. Further additions of polymer over 1 wt% increased the viscosity due to an excess of polymer in solution; i.e. the network developed by entanglement effects retards the sliding of Si_3N_4 particles past one another. For Darvan 821A additions $<$ 1 wt%, flocculation was due to incomplete adsorption which resulted in lower electrostatic repulsion between particles, thereby forcing particles together and increasing the viscosity.

As the solids loading increases, the magnitude of viscosity also increases. It has been found that when the solids content of silicon nitride slurries exceeded about 47 vol%, the slurry becomes extremely dilatant and ceases to flow.[8] Hence, conventional silicon nitride slurries for slip-casting typically utilize a solids content of less than 47 vol%. As the volume percent of solids increases, the viscosity also increases. Fig. 4 illustrates the rheological behavior of a dispersed GS44 Si_3N_4 powder slurry. 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%, interparticle interactions and interparticle collisions become dominant; viscosity begins to increase appreciably, and the rheological behavior becomes highly shear-thinning. At approximately 52 vol% percent solids, particle mobility becomes restricted, and the slurry locks up into a dilatant mass. For optimal robocasting, it is desirable to robocast with slurries that have solids loading close to the dilatant transition[5]. In order to change the rheology of GS-44 Si_3N_4 slurry from dilatant to pseudoplastic at high solids loading, additions of aluminum nitrate or aluminum chloride can be used.

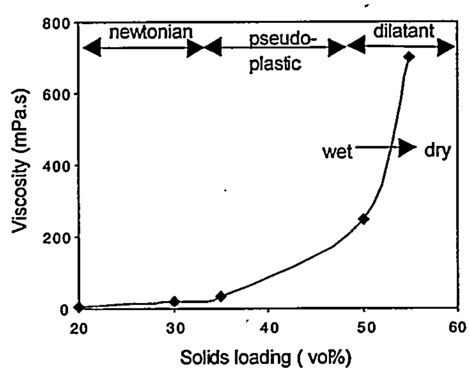
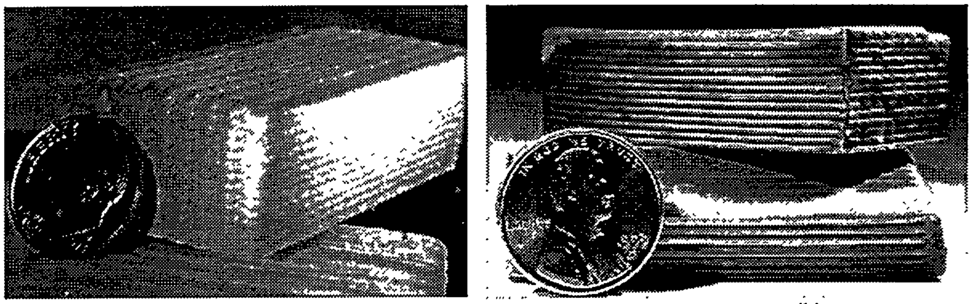


Fig. 4. Viscosity versus solids loading behavior for dispersed GS-44 slurries at 1 wt% Darvan 821A and pH 8 shear rate 24 s^{-1}).

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. The optimal conditions for robocasting were 52 vol% GS-44 Si_3N_4 with 1 wt% Darvan 821A and 0.4 wt% aluminum nitrate at pH 7.8~8.5 based on rheological studies of GS-44 slurry. No meshing, warping and cracking were observed during forming and drying (Fig. 5 a). 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 3.22 g/cm^3 (or 99.3% of theoretical). Visually there was no apparent cracking and the overall color is fairly uniform (Fig. 5 b).



(a) (b)

Fig. 5. Robocast bars, (a) green ; (b) sintered

Mechanical Properties and Microstructure

Sintered GS-44 bars were machined into MOR bars. The average flexural strength and hardness of robocast samples are shown in Table I and they are comparable to the standard properties of slip cast GS-44 products.

Table I. Comparison of mechanical properties between robocasting and conventional product

Property	GS-44 Robocasting	AlliedSignal Slipcast GS-44 SL[9]
Density	3.22 g/cm^3	3.2 g/cm^3
Hardness (Vickers)	14.74 GPa ± 0.51	14.31 GPa
Flexural Strength @ RT	737 MPa ± 38	759 MPa

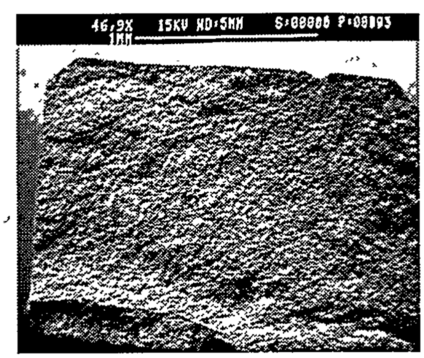


Fig. 6. Observation of fracture surface of GS-44 MOR bar at failure.

Fracture surfaces of MOR bars after measuring the flexural strength were examined using SEM. The surface flaws were found to be the origin of failure of sintered bars (Fig.6). Fig. 7 shows a lot of pullout β-Si_3N_4 fibers in the fracture surfaces. The regular hexagonal shapes of cross-section of β-Si_3N_4 fibers are clearly shown in Fig. 8. They are microstructural characteristics of typical dense Si_3N_4 ceramics and are believed to be responsible for the superior mechanical properties of Si_3N_4 ceramics.

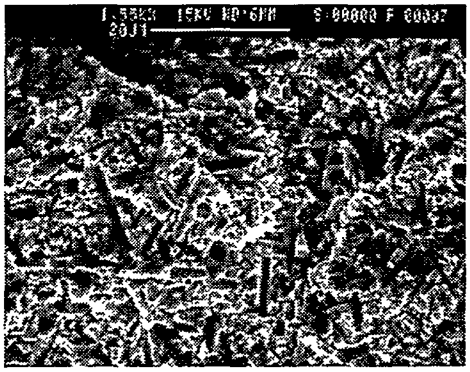


Fig. 7 Pullout β-Si_3N_4 fibers in the fracture surfaces of GS-44 sintered bars.

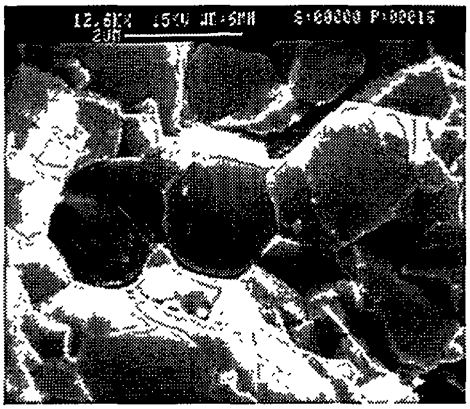


Fig. 8 Cross-section of β-Si_3N_4 fibers in Fig. 7.

CONCLUSIONS

(1) Rheology of GS-44 silicon nitride powder has been determined. The effects of pH, Darvan 821A, solids loading and other additives on the dispersion and rheological behavior of aqueous suspensions were determined. The ZPC of GS-44 powder was pH 6. GS-44 powder can be dispersed only at a pH ≥ 9.6 without dispersants. Well-dispersed GS-44 suspensions can be obtained at pH 6.5~11 range by addition of Darvan 821A. Viscosity of GS-44 slurry decreases with increasing pH and addition of Darvan 821A, with an optimum amount of 1 wt%.

The viscosity increases with increasing solids loading and rheological behavior is altered.
(2) GS-44 silicon nitride aqueous slurries have been successfully robocast and large bars have been obtained. Optimal conditions for robocasting have been determined.
(3) Pressure sintering of robocast GS-44 bars at N_2 atmosphere was studied. Higher than 99% of theoretical density was obtained.
(4) Mechanical properties and microstructure of robocast GS-44 were measured and compared favorably to products produced conventionally. Flexural strength at room temperature was 737 ±38 MPa and Vickers hardness was 14.74 ± 0.51 GPa. The fracture surface of sintered robocast GS-44 showed pullout β-Si_3N_4 fibers (hexagonal cross-section) and interlocking structure.

ACKNOWLEDGEMENT

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