Near-net shaping of silicon nitride via aqueous room-temperature injection molding and pressureless sintering

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ABSTRACT

Silicon nitride (Si_3N_4) is of interest because of its high inherent fracture toughness due to interlocking and elongated β-Si_3N_4 grains, but it is difficult to economically produce into near-net and complex shapes. In this study, the difficulties were overcome with the use of a novel injection molding process where highly loaded (up to 45 vol%) suspensions were loaded into a syringe and injected at a controlled rate into a mold of a desired shape. The suspensions have carefully tailored yield-pseudoplastic rheology such that they can be injection molded at room temperature and low pressures (< 150 kPa). Four suspensions were studied; two different commercially available concrete water-reducing admixtures (WRAs) were used as dispersants with and without a polymer binder (Polyvinylprolidone, PVP) added for rheological modification and improved green body strength. Test bars formed via this process were sintered to high densities (up to 97% TD) without the use of external pressure, and had complete conversion to the desirable β-Si_3N_4 phase with high flexural strengths up to 700 MPa. The specimen sets with the smallest average pore size on the fracture surface (77 μm) had the highest average flexural strengths of 573 MPa. The hardness of all specimens was approximately 16 GPa. The ease and low cost of processing of these water-based suspensions, and the robust mechanical properties reported, demonstrate this as a viable process for the economical and environmentally friendly production of Si_3N_4 parts.

1. Introduction

Of special interest is the fracture toughness of Si_3N_4, which has been reported to be nearly twice that of any other monolithic ceramic due to unique interlocking elongated β-Si_3N_4 grains that promote crack deflection and crack bridging in the material [1–3]. Si_3N_4 is an attractive material for high-temperature turbine engine parts, as well as other numerous structural applications, based on high flexural strength and hardness, superior wear resistance, and substantial creep resistance up to 1350 °C [4]. However, the use of Si_3N_4 in these high-temperature, high-stress applications is severely limited by production costs and the difficulty of forming the necessary complex shapes [5,6]. Due to these issues, the commercial use of Si_3N_4 has been limited to simple shapes like ball bearings and cutting tools produced via hot pressing [5,7]. The use of a more cost-effective and near-net shaping technique (one that does not require post forming processing), paired with pressureless sintering, can enable the expansion of this material into advanced technology areas including aerospace, automotive, and biomedical implants [8].

One method to overcome these typical problems associated with processing advanced ceramics is through a traditional powder injection molding (PIM) process [9]. This technique is based on mixing of ceramic powders with a polymer binder mixture to create a feedstock, which is then injected at high pressures and temperatures due to the high feedstock viscosity [9]. PIM has been applied successfully to many advanced ceramic systems, including silicon nitride, and is a promising ceramic processing method due to the ability to produce near-net and complex shapes with high precision at high production rates [9–12]. Some major problems have been identified with this process, though, including extended binder burnout processes (large parts can have cycles up to a week in length) which lead to slumping and crack formation [9,13,14]. Thicker cross sections (~1 cm) often require binder burnout cycles of 20 h to one week in length, making it difficult, if not impossible, to use traditional PIM to produce parts with thick cross sections [9,14]. The long binder burn-out times, along with high tooling costs, still limit the commercial use of PIM for ceramic production [14]. Binder burnout issues can be mitigated through significant decreases in polymer additives used, while tooling costs can be reduced through reducing the pressures and temperatures needed for molding.

Silicon nitride has been produced through a modified PIM approach from Millán et al. with use of aqueous Si_3N_4 suspensions and

agarose added as a gelling agent [15]. Rheological tailoring, through the addition of strong bases and temperature modifications, of the ~40 vol% solids loading suspensions was used to decrease the pressure and temperatures needed during injection molding to 0.4 MPa and 60 – 65 °C, respectively [15]. Expensive PIM tooling was still used for the forming experiments, and somewhat low densities (~90%TD) were obtained with no mechanical behavior reported [15].

This current work proposes the use of highly-loaded (up to 45 vol%) aqueous Si_3N_4 suspensions, along with a room-temperature and low-pressure injection molding process, as an alternate processing method to effectively and economically produce near-net shaped Si_3N_4 parts without the use of harsh cross-linking or curing agents or further chemical processes. Our previous research found a novel route of using comb-polymer water reducing admixtures (WRAs), commercially produced for the concrete industry, as a dispersant for Si_3N_4 powders in water [16]. These comb-polymers offer steric stabilization in the system through adsorption of the charged polyacrylic acid (PAA) based backbone of the polymer on the ceramic particle surface, while the uncharged polyethylene oxide (PEO) side chains extend into solution and repels other particles [16]. The suspensions have been well stabilized through these comb-polymer dispersants so no temperature increases or strong acids or bases are needed to lower their viscosity. These suspensions have yield-psuedoplastic flow behavior desirable for this process; they are highly shear thinning with flowable viscosities at room temperature and their characteristic yield stress helps a part retain shape after injection molding so that no gelation additives are needed.

Two comb-polymer WRA dispersants, ADVA CAST 575 and Glenium 7500, were identified as optimal and were explored along with suspensions containing Polyvinylprolidone (PVP), a non-toxic and water soluble linear polymer added for rheological tailoring and improved green body strength. These four suspensions (two dispersants, with and without polymer added) were used in this room-temperature and low-pressure injection molding process to identify suspensions which create the most dense and mechanically robust Si_3N_4 parts. The use of inexpensive and commercially available plastic syringes, along with rapidly produced polymer molds, makes this a more economical and environmentally friendly process that can be scaled for mass production. The low amount of polymer used (3– 7.5 vol%), can help avoid defects that traditionally come with the long binder-burnout cycles needed in traditional PIM.

2. Experimental approach

2.1. Suspension preparation and characterization

Alpha silicon nitride powders (SNE-10, UBE Industries, Japan), with company specified d_{50} of 0.50 μm and specific surface area (SSA) of 9–13 m^2/g, were used in this study. Powders from lot number A136828 were used with a SSA of 10.6 m^2/g (As measured by UBE). All experiments utilized 5 wt% aluminum oxide (Al_2O_3) and 5 wt% yttrium oxide (Y_2O_3) as sintering aids as they have been proven to facilitate liquid phase sintering in Si_3N_4 at low temperature (< 1800 °C) to

achieve high densities (> 95%TD) [17–21]. The Al_2O_3 had an average particle size of 0.50 μm and specific surface area of 7–12 m^2/g (grade A-16 SG, Almatis, Leetsdale, PA), while the Y_2O_3 (Sigma Aldrich, St. Louis, MO) had a company specified d_{50} of 2–10 μm. The sintering aids were mixed with Si_3N_4 powders, without milling media, using a dual-centrifugal speed mixer (DAC 400, Flacktek Inc, Landrum, SC) for 2 min at 850 RPM to ensure uniformity. This low rate was used to avoid particle size or morphology change during mixing.

Table 1 shows the name and composition of the suspensions used in this study. The commercially available concrete water reducing admixtures come as aqueous solution and were ADVA CAST 575 (W.R. Grace, Columbia, MD) and Glenium 7500 (BASF, Ludwigshafen, Germany) and will henceforth be referred to as dispersants. Our previous study using these dispersants found optimal loadings of 1.9 mg/m^2 and 2.9 mg/m^2 (with respect to the ceramic loading) for ADVA 575 and Glenium 7500, respectively [16]. PVP (1-ethenyl-2-pyrrolidinone homopolymer, 55,000 g/mol, Sigma-Aldrich, St. Louis, MO) was added in some suspensions for green body strength and rheological modification, and it will be referred to as a binder. Si_3N_4 suspensions were fabricated by mixing reverse osmosis (RO) water with the appropriate dispersant and binder content, followed by slowly mixing in the Si_3N_4 and sintering aid mixture in 10 g increments. The previously mentioned dual centrifugal mixer was used to thoroughly mix these highly-loaded suspensions. Mixing increments were done for 1–3 min starting at 800 RPM and increasing to up to 2000 RPM with increasing solids loading, with total mixing time taking less than 1 h. Suspensions were used for either rheology testing or injection molding approximately 24 h after mixing.

Rheological properties of the suspensions were determined using a Malvern Bohlin Gemini HR rheometer (Malvern Instruments Ltd, Worcestershire, UK) with a 25 mm cup and bob geometry fixture and a gap of 150 μm. Approximately 13 mL of each suspension was used for each test, and a water trap was used to prevent premature drying of the suspension during testing. Each suspension was pre-sheared for 60 s at a shear rate of 1 s^{-1} to ensure a uniform shear history. A shear rate from 0.005 to 30 s^{-1} (on a logarithmic scale) was applied to measure the low-shear viscosity and shear stress of the samples. The shear rate applied to the suspensions during room-temperature injection molding was estimated to be 1 s^{-1}, considering a syringe diameter of 8 mm and a compression rate of 5 mm/min applied by the MTS while forming. This approximate shear rate is much lower than the rates experienced during traditional PIM, typically on the order of 100–1000 s^{-1} and sometimes reaching 15,000 s^{-1} [11,15,22,23].

The shear stress measured as a function of applied shear rate for each sample was fitted to the Herschel-Bulkley model for yield-pseudoplastic fluids [24], using a method of least squares, defined as:

$$\sigma = \sigma_y + k\dot{\gamma}^n$$

where σ is the measured shear stress, σ_y is the yield stress, k is the consistency index, $\dot{\gamma}$ is the applied shear rate, and n is the flow index (with values ranging from 0 to 1). A given material is considered shear-thinning if the flow index is less than 1 [25]. Materials with flow index values greater than 1 are considered shear thickening and have

Table 1
Composition and rheological behavior of Si_3N_4 suspensions used in injection molding experiments.

Sample Name	Dispersant content (vol%) [mg/m^2]	PVP content (vol%)	Viscosity at 1 s^{-1} (Pa-s)[b]	Herschel-Bulkley Curve-fit Parameters		
				Yield Stress, σ_y (Pa)	k (Pa.s^n)	n
A575	3 [1.9]	0	43.6	24.0	17.3	0.54
A575-PVP[1]	3 [1.9]	2.5	166.6	128.7	35.1	0.50
G7500	5 [2.9]	0	66.7	54.5	11.8	0.69
G7500-PVP	5 [2.9]	2.5	122.0	101.7	17.9	0.77

[1] Critical shear rate of dilatant behavior ~ 4 s^{-1}.
[b] Estimated shear rate during injection molding.