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Additive manufacturing of boron carbide via continuous filament direct ink writing of aqueous ceramic suspensions

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ABSTRACT

Direct ink writing, a type of additive manufacturing, has been used to fabricate near-net shaped boron carbide (B_4C) specimens at room temperature with aqueous suspensions. Suspensions with B_4C solids loading of 48–56 vol.% were dispersed with polyethlenimine (PEI, 25,000 and 750,000 g/mol) and exhibited yield-pseudoplastic behavior. Specimens with filament layer shape retention were produced with suspensions with 50–56 vol.% B_4C and yield stresses ≥43 Pa and equilibrium storage moduli ≥700 Pa. No residual porosity or cracking between deposited layers was observed in any samples. However, warpage was observed in some green body specimens and was minimized through use of a low molecular weight polymer and reduction of the B_4C solids loading. Optimal specimens with high filament layer shape retention and no warpage were produced with suspensions containing 54 vol.% B_4C and 25k g/mol PEI.

1. Introduction

Boron carbide (B_4C) possesses a low density (2.52 g/cm^3), a high melting point (~2450 °C), low chemical reactivity, and high hardness, making it an ideal material for extreme environment applications [1,2]. Common applications for B_4C include: high wear components, control rods for fast-breeder nuclear reactors, and light-weight armor applications [1]. To achieve these favorable properties, however, B_4C must be sintered to full density. B_4C has historically been sintered using externally applied pressure, via hot pressing or hot isostatic pressing, due to the challenges associated with densification [2–5]. Hot pressing limits the geometries of the final pieces to simple shapes such as pellets, plates, disks, and rods [6]. Hot isostatic pressing (HIP), on the other hand, allows for the sintering of more complex shapes formed through processes such as slip, tape, or gel casting [7,8]. However, it must also be noted that there are limitations associated with these types of forming processes when used with B_4C and other ceramics [9]. Slip and tape casting have the ability to form cost effective near-net shapes but are limited to simple structures and require complex secondary machining to add intricate features [7,10]. While, gel casting has the ability to produce complex-shaped parts it typically requires suspensions with harsh crosslinking polymers or curing agents, and is limited by the complexity of the mold [7,9]. Ultimately, there is a need to develop forming methods that will allow for the cost-effective production of near-net and complex-shaped parts of B_4C.

Additive manufacturing techniques are rapidly gaining interest among the academic and industrial communities due to the ability to form complex shapes of materials that are difficult to cast or machine [11–15]. Direct ink writing is a form of additive manufacturing that uses a computer controlled system to deposited ceramic inks in a controlled fashion. This forming process can be divided into two main categories: droplet or filament based [14,16]. Droplet-based direct ink writing techniques deposit formed droplets of the binding material in a desired pattern to generate a layer-by-layer configuration [16]. Filament direct ink writing is an extrusion-based additive manufacturing process that deposits aqueous colloidal suspensions of ceramic powders in a continuous layer-by-layer fashion to produce complex-shaped dense ceramic parts [15,16]. Inks used in filament direct writing processes are typically composed of ceramic powders, a water-soluble polymer dispersant, and water and do not require crosslinking polymer or curing agents [14–17]. The rheological properties of the suspensions are designed to have a yield stress. Once the applied shear stress exceeds the yield stress, the suspension flows and parts can be constructed by rastering the extrudate

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in a controlled fashion, building up the part layer by layer. Upon removal of the shear stress the yield stress of the suspension quickly develops again, prohibiting the formed part from slumping due to either gravity or its own weight [9,15,17–19]. Suspensions are typically designed with high solids loading for two reasons. First, increased powder loading tends to increase the yield stress of the suspension, necessary for building parts with multiple stacked layers to avoid slumping. Second, increasing the powders loading increases the green body density, thus there is less porosity to remove during sintering [6,16,17].

Using continuous filament direct ink writing as an additive manufacturing technique has allowed the production of complex-shaped parts of many different ceramic systems including mullite, alumina, stabilized zirconia, and silicon nitride at solids loading greater than 50 vol.% [12,15,16,19,20]. Even with this strong interest to form complex ceramic structures, there has yet to be any significant development with producing B_4C shapes through the use of additive manufacturing primarily due to problems associated with forming aqueous suspensions with high solids loading. To continuously direct write B_4C, stable aqueous ceramic suspensions with the desired rheological properties have to be developed.

Previous research on aqueous colloidal processing of B_4C has been limited to slip and tape casting processes [6,7,10,21,22]. Leo et al. [6] reported that aqueous slip casting slurries of B_4C were only stable up to 40 vol.% when using 2.6 μm powders and Darvan C-N, an ammonium salt of poly(methacrylic acid) (PMAA), as a dispersant. As stated previously, higher solids loading must be used in a direct writing approach to achieve the desired rheological properties and higher green body packing densities [6,17]. Furthermore, other studies have reported that suspensions with higher solids loading minimize drying-induced crack formation and phase segregation while promoting higher sintered densities [6,12,17]. It is possible that the low molecular weight of Darvan C-N (10,000–16,000 g/mol) used by Leo et al. [6], was not enough to stabilize the B_4C particles, as larger molecular weight polymers have been shown in previous studies to offer higher dispersion via steric stabilization [20,23]. Higher solids loadings (>50 vol.%) of B_4C were achieved by Li et al. [10], but were only possible using acid-treated powders dispersed with tetramethylammonium hydroxide (TMAH) an ammonium salt and a mixture of water-borne epoxy emulsions and urethanes emulsions as the green body binder [7,10]. The suspensions formed in the study performed by Li et al. [10], are suitable for gel and tape casting but would lack the required viscoelastic properties as well as the drying dynamics that are required of direct ink writing. Therefore, it is necessary to develop highly loaded aqueous B_4C suspensions dispersed with a high molecular weight polymer while having the desired viscoelastic and rheological properties to facilitate the direct ink writing process.

The present study aims to produce near-net shaped B_4C green-bodies using direct ink writing of highly loaded aqueous suspensions. Our approach to fabricate suspensions with maximum solids loading and ideal yield stresses and viscoelastic properties for direct writing, was to use a cationic polyelectrolyte dispersant (polyethlenimine or PEI) with a high molecular weight to afford greater particle stability via steric repulsion. PEI was chosen due to its large electrostatic potential with B_4C [24], as previous research has shown that a high electrostatic potential will allow for the stabilization of ceramic powders and suspensions with desirable flow properties [25]. The suspensions formulated for the current study are a mixture of 48–56 vol.% B_4C, 5 vol.% (PEI) polymer dispersant, 5 vol.% hydrochloric acid (HCl), and a balance of water. This study will assess the effects of PEI molecular weight and B_4C solids loading on the rheology and quality of final specimens produced via direct ink writing.

2. Experimental procedures

2.1. Boron carbide suspension preparation

One hundred grams of grade HS boron carbide (H.C. Starck, Germany) were suspended in 150 mL of 200 proof ethanol and were attrition milled at 50 RPM with 1 kg of 3.2 mm diameter WC milling media (Union Process, Akron, OH) for 2 h [26,27]. After attrition milling, the ethanol was evaporated at 150 °C for 24 h. The mass of the milling media was weighed before and after attrition milling to evaluate the amount of WC that was introduced into the system. Each batch of attrition milled powders had roughly 2.7 vol.% residual WC. A Beckman Coulter LS 230 particle size analyzer (Brea, CA) was used to determine the average B_4C particle size before and after attrition milling. A particle size of 3.73 ± 1.27 μm and 1.72 ± 0.35 μm was obtained for pre- and post-attrition milled B_4C powders, respectively with the residual WC having an average particle size of 0.15 ± 0.06 μm.

Preliminary zeta potential analysis [24] using a ZetaSizer Nano Z (Malvern Instruments Ltd, Worcestershire, UK) revealed that attrition milled B_4C in a polyethylenimine (PEI, Sigma–Aldrich, St. Louis, MO) and reverse osmosis (RO) water solution had a maximum potential of ±70 mV at a wide pH range (5–8). The pH of the suspensions was lowered with 5 vol.% hydrochloric acid (37% HCl, Sigma–Aldrich, St. Louis, MO) solution in order to achieve suspensions in the optimum range as it is considered that zeta potential values greater than 30 mV afford moderate colloidal stability [28]. The pH of the final suspensions was measured using an Oakton pH 5 m (Vernon Hills, IL), which was calibrated with electrolytic buffer solutions of pH 4 and 10. The pH values of the final suspensions were all in the range of 5.35–5.91. PEI average molecular weights of 25,000 (25k) g/mol and 750,000 (750k) g/mol were used in this study. The large molecular weight of either PEI molecules allows it to act both as an electrosteric dispersant and green body binder.

Attrition milled B_4C powders were incrementally added to the PEI and (RO) water solution in a 250 mL Nalgene bottle to produce highly-loaded aqueous suspensions. These suspensions were mixed with four 12.7 mm diameter WC milling media (Union Process, Akron, OH) in a Dual Asymmetric Centrifuge (DAC 450, Flacktek, Landrum, SC). Powders were mixed at 800 RPM for 60 s and 1200 RPM for 60 s until all the B_4C was added and sufficiently dispersed. The suspensions were then ball milled for 24 h to achieve complete uniformity. The B_4C solids loading and water content were systematically altered to determine the optimal rheological properties for forming and are shown in Table 1. All suspensions had nominally 5 vol.% PEI and 5 vol.% HCl added.

2.2. Rheological characterization

The rheological and viscoelastic properties of the B_4C suspensions were measured using a Malvern Bohlin Gemini HR rheometer (Malvern Instruments Ltd., Worcestershire, UK) with a 25 mm cup and bob geometry fixture with a gap of 150 μm. Roughly 13 mL of the suspension was used in each analysis. To minimize premature evaporation of the suspension, a water trap was attached to the system during the test.

Flow curves were obtained for each suspension by measuring the shear response for controlled shear rates increased logarithmically from 0.01 to 35 s^{-1}. Each curve was fitted to the Herschel-Bulkley model for yield-pseudoplastic materials [29], displayed in the following equation:

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

where σ is the shear stress, σ_y is the yield stress for the material, k is the consistency index, $\dot{\gamma}$ is the applied shear rate on the suspension,