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Producing dense zirconium diboride components by room-temperature injection molding of aqueous ceramic suspensions

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Abstract

Aqueous suspensions of zirconium diboride (ZrB_2), boron carbide (B_4C) and tungsten carbide (WC) with dispersant and water-soluble polyvinylpyrrolidone (PVP) were investigated for processing by room-temperature injection molding, a novel, environmentally benign ceramic processing method. B_4C and WC were used as sintering aids, and the as-received powders were attrition milled to reduce particle size to promote full densification of ZrB_2 specimens by pressureless sintering. Zeta potential measurements of individual ZrB_2, B_4C and WC powders and of powder mixtures revealed that maximum stability was achieved in aqueous solutions of attrition milled powder mixtures dispersed using an ammonium polyacrylate dispersant. A maximum powder loading of 49 vol% with ≤ 5 vol% PVP was attained for $ZrB_2/B_4C/WC$ suspensions with dispersant. Although exhibiting a time-dependent rheological response determined by parallel-plate rheometry, suspensions containing 49 vol% powders and ≤ 3 vol% PVP, as well as suspensions of 46 vol% powders and ≤ 4 vol% PVP, were flowable under the conditions of the process. ZrB_2 rings prepared by room-temperature injection molding were machinable prior to binder removal and exhibited maximum brown densities of 56% true density (TD). Sintered densities were >98%TD with ~ 20% linear shrinkage. Scanning electron microscopy revealed an average grain size of 7.3 ± 2.8 μm, and chemical analysis confirmed that no undesirable oxide phases remained in the sintered ZrB_2 specimens. Aqueous ZrB_2-based suspensions containing B_4C and WC sintering aids and PVP were effectively processed via room-temperature injection molding to yield dense ZrB_2 rings after binder burnout and pressureless sintering.
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Keywords: Injection molding; Borides; Suspensions

1. Introduction

New technologies, particularly in aerospace, that involve design and manufacture of complex-shaped ceramic components have burgeoned in recent decades [1,2]. The development of advanced hypersonic and re-entry vehicles requires materials resistant to erosion and oxidation along with the ability to withstand operating temperatures well above 2000 °C that are routinely encountered in the severe re-entry environment [3]. Zirconium diboride (ZrB_2), an ultra-high temperature ceramic (UHTC), is an ideal candidate for these particular applications, due to its combination of high melting temperature (>3000 °C), high thermal conductivity, low density and exceptional strength [4,5]. The capability to form components with complex geometries is the next step in development of UHTCs for employment in aerospace and beyond.

Because ZrB_2 typically exhibits low volume and grain boundary diffusion rates, high temperatures are required to

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sinter parts to full density without sintering aids [6]. Dense ZrB_2 components have been traditionally prepared by hot-pressing at high temperatures ($>2000\ ^{\circ}C$) with moderate pressures (~ 30 MPa) or at lower temperatures (1800 °C) with very high pressures (>800 MPa) [7]. Although an effective and repeatable densification method, hot-pressing cannot effectively sinter ceramic components with complex geometries in a high-throughput manner suitable for widespread application [8]. Conventional densification methods for UHTCs, like hot pressing [9] or spark plasma sintering [10], cannot economically produce the complex-shaped components (i.e. highly curved leading wing-edges for hypersonic vehicles, rocket nozzle-inserts and re-entry vehicle nose cones) needed for aerospace applications without extensive machining [4].

With pressureless sintering, near-net shape production of complex-shaped parts and a reduction in post-processing costs are possible, making it a more appealing densification method for UHTCs. Pressureless sintering of UHTCs, including ZrB_2, has proven to be a challenge in the development and application of these advanced materials mainly due to unavoidable oxygen impurities that exist on the surface of starting powders [7]. These oxygen impurities manifest themselves in the form of boria (B_2O_3) and zirconia (ZrO_2) in the case of ZrB_2, and in their liquid and vapor form at relatively low temperatures ($\sim 1750\ ^{\circ}C$). Their presence enhances grain coarsening by increasing surface diffusion paths. As a result, these surface oxides further reduce the driving force to sinter in ZrB_2 samples, impeding full densification [11].

The effects of these surface impurities have been somewhat mitigated by incorporating a low-temperature heat treatment ($\sim 1340\ ^{\circ}C$) during the pressureless sintering procedure to remove by evaporation the boria phase, which limits grain growth. In order to remove the more complicated metal oxide, a successful approach to pressureless sinter ZrB_2 has involved adding a secondary phase to preferentially react with ZrO_2. Zhang et al. [12] and Fahrenholtz et al. [13] used attrition milling with tungsten carbide (WC) milling media to reduce ZrB_2 powder size to promote densification, as well as to introduce ~ 8 wt% WC into the system. 4 wt% boron carbide (B_4C) was also added to favorably react with ZrO_2 on the surface of ZrB_2 [12,13]. Consequently, these studies were able to achieve $>98\%$ dense ZrB_2 billets after pressureless sintering for only 1 h at 1850 °C [12] and $\sim 100\%$ relative density in ZrB_2 pellets after 2 h at 1850 °C [13], both in an argon atmosphere. Processing methods that employ sintering aids, namely tungsten carbide (WC) and boron carbide (B_4C) [12,13], have effectively reduced the pressureless sintering temperatures ($<2000\ ^{\circ}C$) required to densify ZrB_2 ceramics and composites without significant mechanical property losses [13].

These advances in pressureless sintering have paved the way for ZrB_2 production via colloidal near-net shaping methods, including extrusion, tape casting and gelcasting. Extrusion and tape casting by aqueous and non-aqueous routes have found relative success in producing dense ZrB_2 components; however, the geometries have been restricted by use of hot pressing or sintering at temperatures $>2000\ ^{\circ}C$ to achieve full densification [14,15]. These methods traditionally employ complex binders based on harsh chemical solvents, like toluene and methyl ethyl ketone, in combination with multiple plasticizers [15–17]. Although aqueous-based systems for tape casting and gelcasting of ZrB_2 have been studied recently, these processes require multicomponent binders and/or have not produced dense components without hot pressing or pressureless sintering at temperatures above 2000 °C [18–22].

An aqueous solution of 40% ammonium polyacrylate (PAA-NH_4) with low toxicity [23] has been observed to effectively disperse aqueous, highly loaded (≥ 45 vol%) ZrB_2-based suspensions [18,24]. Ammonium polyacrylate typically promotes stability of aqueous ceramic systems by PAA adsorbing to the surface of ceramic particles to enhance electrosteric stabilization [25]. The ionic dispersant has a molecular weight of 3500 g/mol and is highly soluble in water-based systems [26]. Polyvinylpyrrolidone (PVP) with varying average molecular weights, in combination with a dispersant of either ammonium polyacrylate [27] or of poly(methacrylic acid) ammonium salt (PMAA-NH_4) [28], has been observed to be an effective rheological modifier in aqueous alumina suspensions. Aqueous, PVP-based alumina suspensions dispersed with ammonium polyacrylate have been shown to enable room-temperature injection molding, which is a novel low-cost and low-toxicity ceramic process. This alternate processing method utilizes the flow properties of highly loaded ceramic suspensions to fabricate near-net shape ceramic components without the use of multicomponent binders, harsh crosslinking or curing agents or further chemical processes [27], as well as additive manufacturing [29]. In the current study, room-temperature injection molding was investigated as a water-based, alternative process to effectively produce dense near-net shape zirconium diboride parts.

2. Experimental approach

2.1. Materials

The ceramic powders used to prepare ZrB_2-based suspensions were ZrB_2 powder (Grade B, H.C. Starck, Newton, MA) and B_4C powders (Grade HS, H.C. Starck, Newton, MA) with an average particle size of 2–4 μm and 0.8 μm, respectively. Tungsten carbide powders (product no. 12482, Alfa Aesar, Ward Hill, MA) with as-received particle size <1 μm were used for zeta potential analysis. 4 wt% B_4C powder was combined with the as-received ZrB_2 powders, and the powder mixture was then attrition milled at 600 RPM in 200-proof ethanol using 1/8″-diameter Co-bonded WC media satellites (Union Process, Akron, OH) for 2 h. The mass of the milling media was weighed before and after attrition milling to estimate the amount of WC introduced into the system. The powders were then dried at 70 °C on a hot stir plate. To break up any agglomerates formed during the drying process, the dried powders were dry ball milled for 24 h using 1/2″-diameter WC satellite media. A final drying step in a box furnace for 12 h at 100 °C in air was performed to remove any moisture from the powders. The average particle size was estimated by measuring 100 random particles in five different