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Complex shaped boron carbides from negative additive manufacturing

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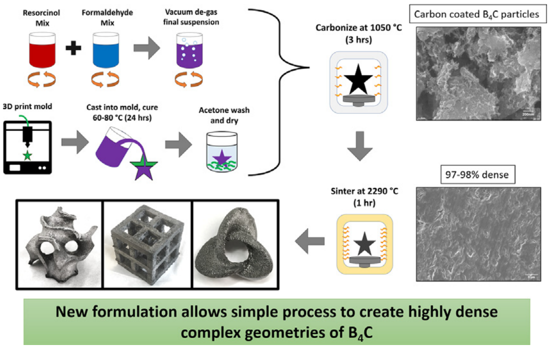
HIGHLIGHTS

- High density, complex shaped B_4C/C parts were produced by gelcasting into 3D printed molds with resorcinol-formaldehyde and then pressureless sintering.
- Two-part B_4C suspensions containing either resorcinol or formaldehyde were formulated to gel when combined and thermally initiated at 60-80 °C.
- Resorcinol-formaldehyde also served as a carbon sintering aid after pyrolysis at 1050 °C.
- Meso-scale structures of sintered B_4C/C were produced, demonstrating the ability to retain fine features down to 100 μm scale.
- The optimum density obtained for B_4C/C was $97.2 \pm 1.2\%$ with a Vickers hardness of 23.0 ± 1.8 GPa.

GRAPHICAL ABSTRACT



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ABSTRACT

Complex shaped boron carbide with carbon (B_4C/C) at near-full densities were achieved for the first time using negative additive manufacturing techniques via gelcasting. Negative additive manufacturing involves 3D printing of sacrificial molds used for casting negative copies. B_4C powder distributions and rheology of suspensions were optimized to successfully cast complex shapes. In addition to demonstrating scalability of these complex geometries, hierarchically meso-porous structures were also shown to be possible from this technique. Resorcinol-Formaldehyde (RF) polymer was selected as the gelling agent and can also pyrolyze into a carbon aerogel network to act as the sintering aid for B_4C. Due to the highly effective distribution of in situ carbon for the B_4C matrix, near-full sintered density of 97–98% of theoretical maximum density was achieved.

1. Introduction

Boron carbide (B_4C) is the third hardest known material, after only diamond and cubic boron nitride [1,2]. With a high melting point (~2430 °C), relatively low density (2.52 g/cm^3), superior wear resistance, and high neutron absorption cross section, B_4C has held leading interest in applications for lightweight armors, blasting nozzles, grinding wheels, and control rods in nuclear reactors [3–5]. In order to achieve the desired properties for such applications, B_4C must be sintered to full theoretical maximum density (TMD). Traditionally, external applied pressure along with high temperatures are required to

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Table 1
Wt% of each component in suspension.

Component	R-mix	F-mix	Combined
Acetic	6.02	6.24	6.13
Resorcinol	11.67	0.00	5.94
Formalin Soln.[a]	0.00	16.33	8.02
PEI	0.82	0.85	0.83
Water	23.15	16.14	19.71
B_4C	58.34	60.44	59.37

[a] Solution is 37% formaldehyde, 10–15% methanol, 48–53% water by weight.

achieve full densification via hot pressing or spark-plasma sintering [6]. However, these techniques are limited to simple geometries such as discs, cylinders, and moderately curved parts. Alternatively, full densification is also achievable by creating composite systems such as reaction-bonded boron carbides [7,8]. However, these systems commonly involve molten silicon or aluminum infiltration into a porous B_4C preform which also limits the geometry that can be obtained.

Colloidal forming techniques and pressureless sintering, with the help of additives, can produce near-full density parts and is often preferred to avoid expensive diamond machining or laser cutting processes required to form complex shapes from simple geometries. One of the most effective additives for pressureless sintering of B_4C is carbon [9–11]. Commonly, the carbon source comes from the pyrolysis of a Novolac-type phenolic resin which yields ~50 wt% carbon on decomposition to form B_4C/C composite systems [4,12].

Gelcasting is a colloidal forming technique that is relatively inexpensive, produces high yields with minimal defects, and has fast forming times. In gelcasting, a ceramic suspension with organic monomers is poured into a mold which polymerizes in situ to act as a binder [13–15]. Depending on the gelling agent, the green body ideally should hold the mold cavity shape and be strong enough to handle for subsequent processing steps.

With the recent advances and availability of inexpensive additive manufacturing (AM) tools such as fused deposition modeling (FDM) and stereolithography (SLA), complex geometries of three-dimensional (3D) printed polymeric materials are now ubiquitously used. By taking advantage of these low-cost tools, gelcasting complex ceramic geometries is now possible with negative AM techniques [16]. Other high accuracy 3D scanning tools have also become widely available to complement the field of additive manufacturing. For instance, lightweight armors can now be customized to perfectly fit any individual's body size and shape using 3D scanning tools along with negative AM. Such design approach can provide reduced material weight and improved mobility for users. Furthermore, additive manufacturing has made sophisticated new composites possible [17,18].

Although direct ceramic AM techniques already exist such as selective laser sintering (SLS), direct inkjet printing (DIP), direct ink write (DIW), and fused-deposition modeling (FDM) with ceramic filaments, which are more suitable for prototyping and the creation of fine porous structures such as scaffolds and lattices, they have shortcomings when scaling up to larger parts [19–25]. Most of these direct ceramic AM techniques are also not feasible for high volume production due to the high cost of operations and equipment involved. Therefore, negative AM combining gelcasting and the use of inexpensive plastic molds to produce complex monolithic parts is favored at the industrial level. Furthermore, negative AM has already been demonstrated to produce complex geometries that otherwise would have been difficult to achieve through direct AM methods [26–28]. Therefore, this technique opens an avenue to create complex shaped boron carbides. The design possibilities are only limited by the shape and size of molds that are used.

To gelcast near-full density complex geometries, the casting suspension needs to be low in viscosity and contains both a gelling agent and sintering aid for B_4C. By using resorcinol (R) and formaldehyde (F), the three criteria can be fulfilled. Resorcinol and formaldehyde can undergo polycondensation reactions to form an organic aerogel network, resorcinol-formaldehyde (RF), which acts as a binder to hold the B_4C particles together. Like phenolic resins, the RF can also provide a spatially uniform distribution of clean carbon after pyrolysis to aid the sintering of B_4C [29]. Although other groups have incorporated RF and similar gelling agents to cast B_4C in the past, none have created a low viscosity suspension that can be stored long term and used for negative AM casting while achieving near-full density parts [30–32].

Here we present a novel methodology that combines traditional gelcasting, inexpensive plastic 3D printing, and a unique aerogel (resorcinol-formaldehyde) to obtain complex shaped boron carbide parts that can be easily mass produced. We demonstrate parts in a wide variety of scales and shapes, while retaining fine features on the order of ~100 μm, thus allowing for the creation of meso-scale composites. The work we present unlocks the full design potential of the boron carbide system, and the novelty of this approach can potentially be expanded into other material systems.

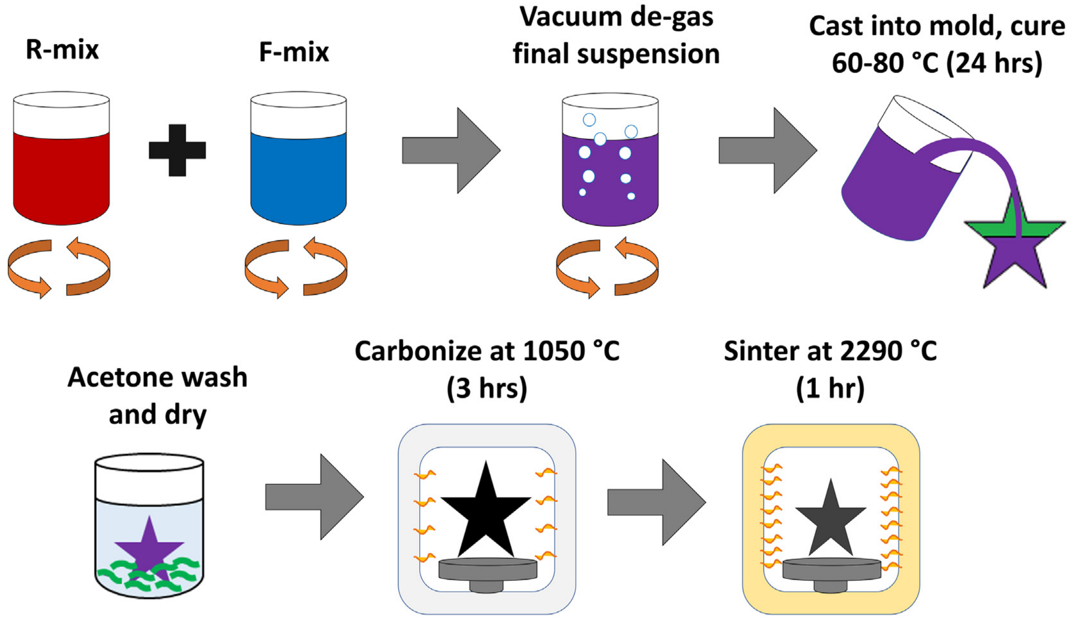

Fig. 1. Full procedure to gelcast and sinter B_4C.