Scripta Materialia 145 (2018) 14–18

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

Fabricating geometrically-complex B_4C ceramic components by robocasting and pressureless spark plasma sintering

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ARTICLE INFO

Article history:
Received 31 July 2017
Received in revised form 15 September 2017
Accepted 2 October 2017
Available online xxxx

Keywords:
B_4C
Robocasting
Pressureless spark plasma sintering
Complex-shaped parts

ABSTRACT

Robocasting and pressureless spark plasma sintering are combined for the first time to fabricate geometrically-complex B_4C components. It is shown that robocasting allows B_4C green pieces to be printed with near-net shape from inks with suitable rheological properties, and that subsequent pressureless spark plasma sintering permits an ultrafast, energy-efficient, solid-state densification that yields B_4C parts with adequate mechanical properties. Furthermore, the usefulness of cold-isostatic pressing to improve the densification of the pieces is evaluated, and the benefits of robocasting over conventional dry powder compaction are identified. Finally, the scalability for the production of large B_4C pieces is discussed.

Fabricating geometrically-complex ceramic articles with near-net shape is a long-sought objective of the ceramic industry with a view to reducing, and ideally to eliminating, the production costs associated with the post-sintering machining and finishing operations required to extract complex shapes from pieces with simple geometries. The motivation soars for ultra-hard ceramics because these operations can become prohibitively expensive and time-consuming, even inviable in some cases. B_4C, also known as black diamond, is one of these super-hard and ultralight engineering ceramics demanded at the industrial scale in parts with complex geometries. For example, one B_4C application receiving great attention today is that of personnel and vehicle armour components [1–4]. The former must have ergonomic designs to protect body zones with different curvatures without penalizing mobility, and the latter custom designs to offer maximal coverage of the chassis or fuselage without jeopardizing maneuverability. Another major application of B_4C is in tribocomponents [1,2,5] such as nozzles for blasting and water-jet cutting, cutting tools and dies, and other wear-resistant parts.

The near-net shape fabrication of a geometrically-complex ceramic article entails the shaping of the corresponding green compact (normally by any wet or plastic forming method), followed by its pressureless sintering. Unfortunately however, B_4C is hardly densifiable in the pure state by conventional pressureless solid-state sintering [2]. Thus, hot-pressing is the reference sintering technique for the consolidation of pure B_4C powders into dense pieces [2]. The undesirable consequence is then that the external uniaxial pressure and the confinement in the die limit the production to simple geometries. Spark plasma sintering with pressure has the same limitations, and hot-isostatic pressing is intrinsically problematic (glass encapsulation problems) and therefore is used rather as a post-sintering complement [2]. Thus, there is a real need to develop routes enabling the production of near-net shaped B_4C parts by the combination of innovative forming and sintering techniques.

In this context, additive manufacturing techniques have opened new doors for preparing ceramic green articles with complex shapes that are hardly or not-at-all manufacturable by traditional ceramic processes. Robocasting (RC) is a unique additive manufacturing method particularly well-suited to 3D-printing ceramic pieces. Green parts are built by extruding highly-concentrated aqueous suspensions (inks) of the desired ceramic powders through a fine nozzle. A robotic system moves the nozzle following a computer-aided design (CAD) model in order to build the part layer by layer [6,7]. Meanwhile, electric current activated or assisted sintering (ECAS) techniques have revolutionized the science of ceramic processing in general, especially for these hard-to-sinter ceramics. Pressureless spark plasma sintering (PSPS) is one of these novel ECAS techniques, consisting of the repeated application of high energy, low voltage, pulsed direct electrical current [8,9], without the help of external pressure. This combination of features enables the ultra-fast and energy-efficient densification of geometrically-complex ceramic green parts.

Given the above, it seemed that it could be worth exploring the combination of RC with PSPS as a solution to the problem of fabricating geometrically-complex B_4C components with near-net shape. This

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https://doi.org/10.1016/j.scriptamat.2017.10.001

study was aimed in this direction, to address two of the eight challenges [10] with societal import recently identified by the ceramic community: (i) ceramic processing through programmable design and assembly (*i.e.*, additive manufacturing, and RC in particular), and (ii) ceramics for extreme environments (including specifically tribological, super-abrasive, and armour materials).

With this idea in mind, we prepared an ink with 40 vol% B_4C loading and minimal organic content as follows. First, 1 wt% (relative to B_4C content) of a synthetic polyelectrolyte dispersant (Produkt KV5088, Zschimmer-Schwarz) was dissolved in deionized water at room temperature and natural pH, and the solution was agitated (ARE-250, Thinky) for 10 min at 700 rpm. Second, the B_4C powder (Grade HD 20, H.C. Starck; d_{10} ~ 0.1–0.36 μm, d_{50} ~ 0.3–0.6 μm, and d_{90} ~ 0.9–1.5 μm) was added in batches to this aqueous solution, each time agitating the resulting suspension for 10 min at 800 rpm. Third, 7 mg/mL (in the final suspension) of methylcellulose (Methocel F4 M, M_w = 3500 g/mol, 5 wt%; Dow Chemical Company) was introduced to viscosify the suspension, which was agitated for 10 min at 1000 rpm. Fourth, 4 vol% (relative to liquid content) of polyethylenimine (PEI) flocculant (10%w/v in water, Sigma-Aldrich) was added to gellify the suspension. And fifth, the resulting colloidal ink was homogenized by agitation for 2 min at 1200 rpm followed by 7 min at 700 rpm.

Fig. 1 shows representative rheological properties of the B_4C ink developed, measured using a rheometer (Discovery HR-2, TA Instruments Ltd.) configured in the parallel plate geometry (40 mm, and gap of 800 μm), demonstrating its suitability for RC. Specifically, it is seen in Fig. 1A that the ink has the shear-thinning flow behavior desirable for its extrusion as a smooth filament without die swell. Moreover, it is seen in Fig. 1B that the ink also exhibits a linear viscoelastic response at low stress with high values of stiffness (~2.5 MPa) and yield strength (~50–60 Pa, corresponding to the onset of the sudden fall), as required for the extruded filament to retain its form and support the weight of the layers above. B_4C inks were formulated before using only PEI as both dispersant and binder, and evaluated in terms of their rheological behavior and printability [11]. Compared to that work, the ink prepared here exhibits a storage modulus two orders of magnitude higher, which in principle makes it more suitable for producing parts with overhanging features or internal holes/gaps.

Fig. 2 shows optical images confirming the feasibility of obtaining geometrically-complex B_4C green articles by RC from this ink. We have printed different bulk and porous parts covering some typical B_4C applications (Fig. 2A–B). They include square and hexagonal plates to build multi-segmented armour panels, gears of different sizes and morphologies for tribological applications, conical nozzles with various dimensions and tip sizes for blasting and water-jet cutting, and square

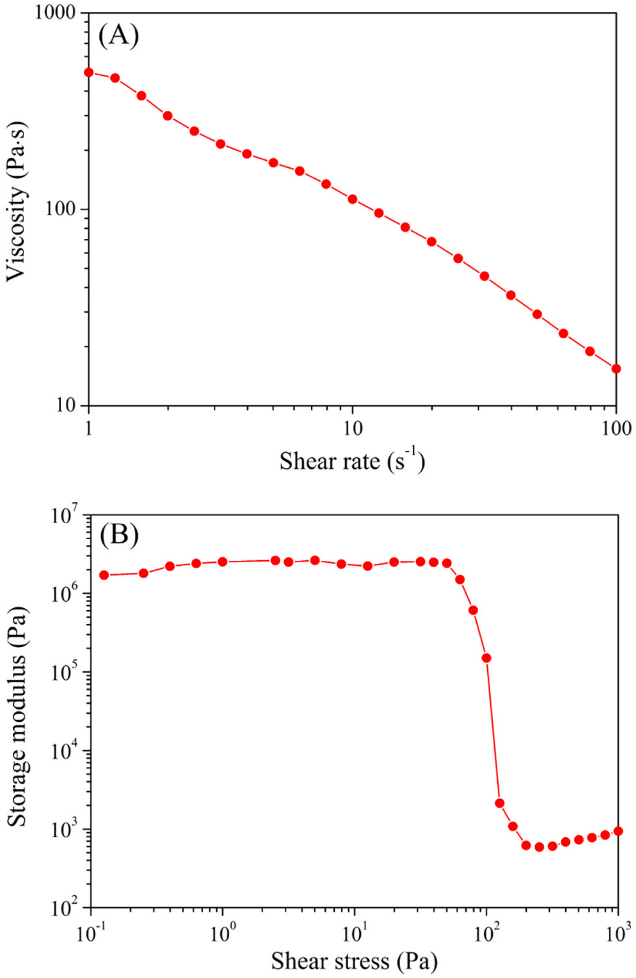

Fig. 1. Rheological characterization of the B_4C ink used in the shaping by RC showing specifically the logarithmic plots of (A) viscosity *vs* shear rate and (B) storage modulus *vs* shear stress. Points are the experimental data, and the solid lines are just to guide the eye.

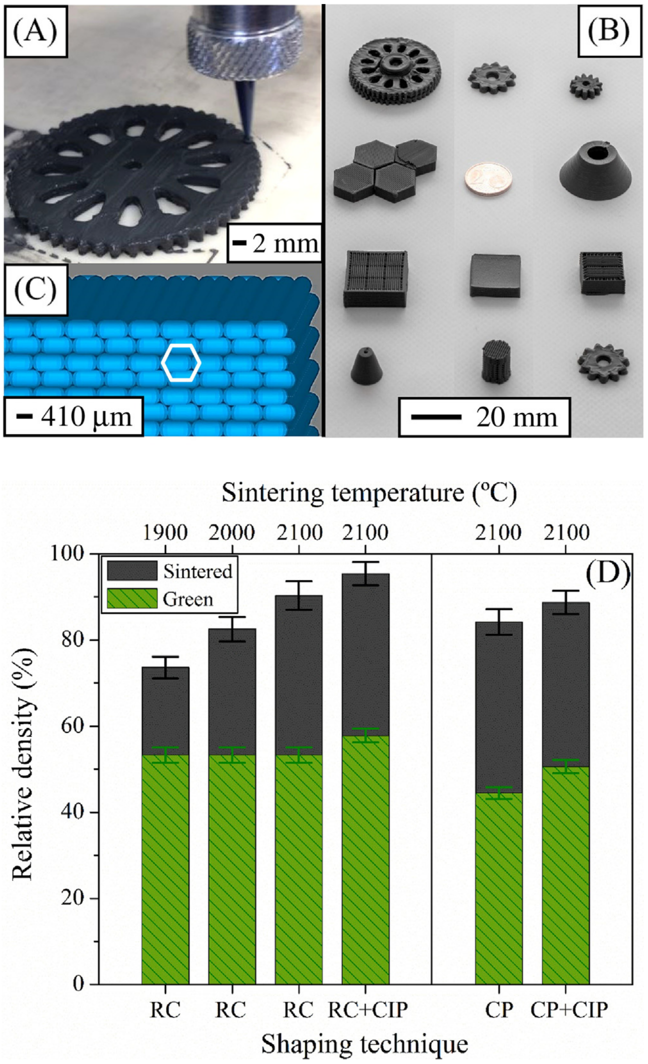

Fig. 2. (A) Optical image captured *in situ* during the 3D printing of a geometrically-complex circular gear. (B) Optical images of several B_4C green parts shaped by RC, and then dried. (C) View of a simple CAD model showing the parallel raster pattern used. (D) Relative density (average of at least 3 measurements) of both the B_4C green and the sintered parts for the different shaping procedures and sintering temperatures used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)