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3D printing of open-porous cellular ceramics with high specific strength

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ABSTRACT

We present a novel processing route for manufacturing highly open porous, hierarchically structured ceramics via direct ink writing. We manufactured cellular samples with overall porosities up to 88% that exhibit fully open-porous struts with porosities between 45 and 60% and pore sizes $x_{50,3} < 6\,\mu m$ using capillary suspension based inks. An innovative processing strategy enabled manufacturing crack-free, undeformed cellular ceramic samples.

We printed hexagonal honeycomb structures that showed exceptionally high specific strength under compression load and significantly enlarged the strength-density range that was covered by sintered capillary suspensions, so far. Without loss of mechanical strength the density of ceramic parts was decreased by about a factor of 2–3. Strength of in-plane and out-of-plane loaded hexagonal honeycomb structures varies according to common scaling laws for cellular structures. The honeycombs are mechanically more efficient than bulk specimens from capillary suspensions, since they show a distinctly lower sensitivity of strength on density.

1. Introduction

Highly porous ceramic materials with low density are extensively used in various technical applications, including filtration membranes for processes with hot or chemical reactive media, catalyst supports, energy storage systems, tissue-engineering scaffolds or lightweight construction materials [1–4]. The structure of a porous material strongly determines its properties and this also defines the field of application. Generally, we can distinguish between open and closed porous structures, while open porous ceramics exhibit a high permeability with a high accessible surface area, and closed-porous structures show good thermal insulation properties [5,6]. Engineering materials with a tailored mechanical strength at low densities are often inspired by natural materials, like wood, weed or cancellous bone, that are hierarchically structured [7–9]. These materials consist of lattice-like architectures that define cells in the mm-range, while the struts may be porous as well with pores in the μm-range, or they are complex composite materials [7,10–12]. 3D printing is a common way for manufacturing ceramic structures with well-defined cell geometry in the mm-range, but controlling also the porosity in the struts is a great challenge up to now. This is especially valid for fully open-porous structures that are not only a high-strength structural ceramic, but also a functional material.

3D printing methods enable the fast and versatile manufacturing of prototypes, products at low number of units and tailor-made products. Next to ceramic parts [13,14], also polymers [15] and metals [13] and even food-products [16], are manufactured with 3D printing processes. However, 3D printing of ceramics is challenging due to complex process requirements. Typically, fabrication of dense ceramic components is addressed, but also porous ceramic materials are fabricated, especially for medical products like tailor-made implants or bone scaffolds [13,14,17,18], since these products cannot be manufactured economically via common processes like injection molding. A common 3D printing technique for porous ceramics is the so-called direct ink writing (DIW) where the desired body is assembled by specifically depositing small amounts of an ink or a paste [19]. This can be realized by a filamentary-based approach, like robocasting [13,20] and fused deposition modeling [14,20], or by a droplet-based approach, such as ink-jet printing [21,22].

Various processes are established for processing porous ceramic materials, including direct foaming, sacrificial templating, partial sintering, and using sacrificial fugitives [5,6]. Most of these techniques were originally developed for manufacturing macroporous bulk ceramics, but are partially combined with 3D printing

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techniques to achieve custom shaped, hierarchically structured ceramics. Porous calcium phosphate granules have been used in combination with a sugar solution as organic binder to fabricate scaffold structures suitable for bone tissue engineering with porous struts (microporosity 60%) via 3D printing. Quadratic grid structures with mesh sizes in the order of 150–750 μm were obtained. The overall porosity was about 75% and the mechanical compressive strength was below 1 MPa not suitable for carrying high loads [23]. Garcia et al. [24] have synthesized very complex scaffold materials with a hierarchical pore structure ranging from 4 nm to 400 μm. They combined a sol-gel process including a surfactant providing the nm-sized pores, biopolymer sacrificial templating (methylcellulose) to achieve 30-80 μm pores, and direct ink writing of a suitable paste finally creating large 400 μm pores. In this case an overall porosity of about 40% was achieved. A printed structure including a regular arrangement of large pores with aligned microporous struts was obtained via 3D co-extrusion of a frozen alumina/camphene feed stock. The overall porosity of these scaffolds was 67–77% and the compressive strength varied between 10 and 30 MPa [25].

Direct ink writing processes also enable to create lightweight construction materials with distinct mechanical properties. Lewis et al. [11] reported about cellular structures made from fiber-filled epoxy resins with mechanical properties approaching the unique specific mechanical strength of balsa wood. This was accomplished due to the orientation of added silicon carbide and carbon fibers achieved during DIW and a distinct printed cellular structure. Another bio-inspired approach to obtain highly porous and high strength materials was presented by Fu et al. [26] Glass scaffolds with 60–80% porosity and a strength of 40–130 MPa under out-of-plane compression could be fabricated via DIW using a hydrogel based glass ink. However, in these latter approaches the printed struts did not include pores. Fabricating similar cellular structures with highly porous struts are an intriguing option to clearly enlarge the available specification range and to achieve lightweight materials with higher overall porosities and high specific strength. Recently, Muth et al. [12] as well as Minas et al. [10] published a concept for 3D printing hierarchically structured, lightweight ceramic solids with inks based on ceramic foams. Both authors used foams stabilized by surface modified Al_2O_3 particles. Muth et al. [12] presented cellular lightweight parts with closed-porous struts that exhibit a high specific stiffness [$>10^7$ Pa/(kg/m^3)] tailored by the printed geometry. In contrast, Minas et al. [10] printed struts with closed *and* open porosity but did not try to improve the mechanical efficiency due to tailored cellular structure. Specimens with an open-porosity between 83 and 94% and a compressive strength between 3 and 16 MPa were achieved.

Successful implementation of DIW processes for rapidly patterning complex 3D architectures crucially depends on the design of appropriate inks. According to the literature well printable inks should show a yield stress $\tau_y > 100$ Pa and storage modulus G' > 10^4 Pa [10,27]. Higher values of τ_y and G' are even better to achieve a high shape accuracy of the printed structures [11]. Paste like *capillary suspensions* with their high τ_y (>200 Pa) [28,29], high G' (>10^5 Pa) [30] and strong shear thinning behavior [29] are a promising platform for designing DIW inks [10,11]. Recently Dittmann et al. [29,31] developed a versatile new processing route based on capillary suspensions as precursors for manufacturing highly porous and mechanically stable ceramics. Capillary suspensions are ternary fluid/fluid/solid systems with a strong particle network structure controlled by capillary forces. When a small amount of a second, immiscible fluid is added to the continuous phase of a suspension, texture and flow of the admixture are dramatically altered due to the formation of a strong particle network within the suspension. Particles stick together due to capillary forces induced by liquid bridges formed by the secondary fluid. This phenomenon not only alters the rheology of the system, it also stabilizes the suspension. Settling is prevented since particles are trapped in the network [32]. Such capillary suspensions were successfully used as a precursor for manufacturing porous sintered materials [28,29,31,33]. The bulk fluid can be removed from the suspension without collapse of the particle network that forms the backbone of the subsequently sintered part, since the remaining liquid bridges between particles formed by the secondary fluid largely provide the integrity of the structure if the pair of fluids is chosen appropriately. Following thermal debinding and sintering steps transfer the highly open-porous precursor into sintered a part with a high porosity and a uniform pore structure. This new processing route gives access to a broad range of pore structures including previously hardly accessible porosity and pore size ranges (porosity $\varepsilon > 50\%$, median pore diameter by volume $x_{50,3} < 10$ μm) with a very high repeatability regarding pore structure.

In this article we report about development of ceramic capillary suspension based inks for filament based DIW. We discuss sample preparation and composition providing stability, homogeneity and rheological properties enabling a stable DIW process. Then a method to transfer the printed specimen into sintered parts. Especially the latter step is the most crucial one since crack-formation and deformation during drying has to be prohibited for mechanical stable and functional sintered parts. We manufactured cellular structures in the shape of log-piles as well as hexagonal honeycombs. The first were primary for evaluating printing behavior while the latter were for mechanical testing. The nature inspired hierarchical, honeycomb structure promises excellent mechanical strength at low density.

2. Experimental procedure

2.1. Raw materials

Commercial grade aluminum oxide (α-Al_2O_3) particles were obtained from Almatis GmbH (CT3000SG) and Sumitomo Chemical (AKP-50). The average particle size according to the manufacturer is $x_{50,3} = 0.5$ μm for CT3000SG and $x_{50,3} = 0.2$ μm for AKP-50. Both particle types have a density of $\rho = \sim 3.9$ g/cm^3 and exhibit an arbitrary, isometric shape.

As bulk phase we used a mixture of highly liquid paraffin ($\eta = 0.035$ Pa s, $\rho = 0.85$ g/cm^3; Merck KGaA), odorless mineral spirits ($\rho = 0.752$ g/cm^3; Sigma-Aldrich) and palm wax ($\rho = 1.0$ g/cm^3; Candle Wiz; received from A.C. Moore, Somerville, USA). The composition of the bulk phase was: 48.6 vol% paraffin, 50.3 vol% mineral spirits and 1.1 vol% palm wax. The wax was dissolved in the two liquid phases by mixing the components in a planetary mixer (Speedmixer DAC 600.2; FlackTek Inc.) for 10 min at 2350 rpm. The melting temperature of the palm wax is $T_m = 80$–87 °C. The bulk phase mixture has a surface tension of $\Gamma_s = 25.4 \pm 0.2$ mN/m.

The secondary phase was a mixture of 50 vol% D(+)-sucrose (Carl Roth) in pure water. The aqueous sucrose solution has a surface tension of $\Gamma_s = 77.3 \pm 0.1$ mN/m.

We determined the three-phase contact angle θ_{SB} of the secondary fluid towards the α-Al_2O_3 particle surface using the Young-Duprée equation [34] with the surface tensions of the surrounding bulk phase $\Gamma_{Ba} = 25.4 \pm 0.2$ mN/m and the secondary phase $\Gamma_{Sa} = 77.3 \pm 0.1$ mN/m, the interfacial tension of the two fluids $\Gamma_{SB} = 28.3 \pm 0.3$ mN/m, and the contact angles of the fluids on Al_2O_3 against air $\theta_{Sa} = 55 \pm 3°$ and $\theta_{Ba} = 0°$. The calculations result in a three-phase contact angle of $\theta_{SB} = 47 \pm 9°$. Thus, the secondary phase preferentially wets the alumina particles and the capillary suspensions within this work are in the pendular state [32].

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