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Manufacturing porous multi-channel ceramics by laser gelling

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Abstract

This article describes a novel layer manufacturing process for forming a ceramic part with porous multi-channel architecture by laser gelling under low laser energy. The process involves bonding silica powder by gelled silica sol after exposure by a CO_2 laser. Lower laser energy density of 0.8 J/mm^2 is required to produce ceramic parts by ‘‘gelling effect’’. Therefore, the geometrical deflection and thermal distortion can be reduced after laser scanning. The inner porous structures were supported by ceramic slurries to prevent sagged deflection and to enhance dimensional accuracy due to optimal slurry suspension. The flexural strength of the green specimen was 4.7 MPa, while that of the gelled specimen was 12.5 MPa after heat-treatment at 1200 °C for 1.5 h. The proposed process has potential for fabricating complex interconnected porous ceramics for tissue engineering applications.

Keywords: A. Sol–gel processes; A. Suspensions; B. Porosity; D. SiO_2

1. Introduction

A number of rapid prototyping (RP) techniques have been employed to produce ceramic parts by sintering, melting, or bonding. During the sintering or melting process, a high-power laser is employed for laser exposure. In bonding processes, the bonding agent binds ceramic powder together to form ceramic samples using a polymer binder [1–4]. In addition, many sol–gel methods have been utilized to prepare ceramic materials. For example, SiO_2–CaO bioactive glasses were produced by a sol–gel procedure [5], hydroxyapatite (HA) powder was synthesized by a sol–gel combustion method [6], a freeze-gelation technique was employed to embed microorganisms within molded ceramic parts [7], a gel-casting technology was developed to prepare mullite-based ceramics green body using silica sol as a binder [8], an aluminum titanate–mullite ceramic composite was fabricated via silica sol gelating [9], and a sol–gel route was adopted to prepare the ZnO nanocomposites [10].

Most of the current methods can fabricate ceramic parts of outer complex shapes. However, it is difficult to manufacture complicated inner parts because it is hard to remove the support materials from the inner ceramic structure. Generally speaking, any complex-shaped sample can be fabricated by RP technologies using the three-dimensional mold created from Computer Aided Design (CAD) data. The degree of difficulty in constructing ceramic bodies by RP technologies may be categorized into undercut, overhang, and inner channel architecture [11]. Ceramic components of simple shape with undercut architecture can be easily fabricated by traditional mold forming or machining processes, but the complex-shaped ceramic components with overhang and/or inner channel can be produced only by RP technologies.

In particular, general ceramic parts produced by gelcasting or traditional machining processes are not complex enough for industrial applications because it is hard to de-mold or cut the brittle ceramic material [7], but RP technologies can fabricate ceramic parts of any shape for industrial applications. In this paper, a novel laser gelling process is proposed for fabricating a ceramic part with porous multi-channel features under low laser energy and at a faster building speed. The proposed process has potential for constructing sophisticated shape or interconnected porous ceramic parts.

2. Materials and methods

Various kinds of material, such as polymer, metal, composite, and ceramic, may be used in RP processes. These

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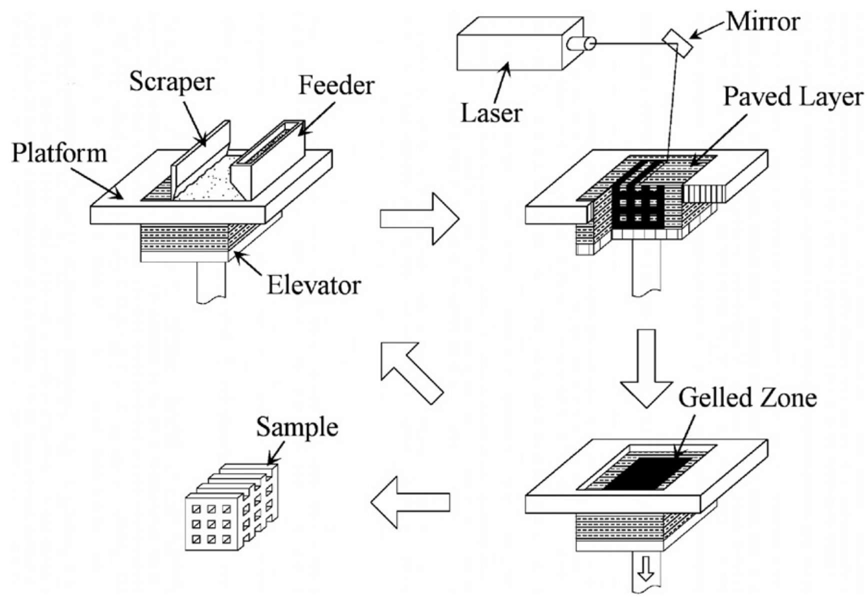

Fig. 1. Schematic of laser gelling process for fabrication of ceramics.

materials can be categorized into liquid, solid, and powder form. In this work, we mixed ceramic powder with a ceramic binder to form the ceramic slurry which is different from other RP material types. The silica powder and silica sol were mixed in a proportion of 65:35 to 55:45 wt.% and used as raw materials in the following experiments.

When a CO_2 laser beam irradiates on the mixed ceramic slurry, the ceramic powder is bonded by a ceramic inorganic binder and the ceramic slurry will then be solidified to form a thin ceramic layer. This phenomenon is called ‘‘laser gelling reaction’’. According to the experimental results, if the ceramic powder is gelled on a solid substrate through a chemical reaction, the gelled ceramic layer will bind completely on the substrate. When the laser beam scans over a ceramic layer, the surface of the ceramic layer will adhere to the underlying portion of the previous gelled ceramic layer. A cross-section of a ceramic part can be fabricated in this way [12].

According to the above mentioned principle of ‘‘laser gelling’’, a process for fabrication of ceramic parts was developed. This process, as illustrated in Fig. 1, involves the following five steps: (1) The silica powder and silica sol are mixed in a suitable proportion as raw materials. After continuous blending, the homogeneous slurry is formed. (2) The slurry is paved on a platform by a scraper to form a slurry layer. (3) The thin slurry layer is gelled along the scanning path by a focused laser beam. By controlling the laser scanning path, a thin 2D cross-section of the ceramic layer can be produced. A second layer can be built on and bonded to the first layer. (4) By repeating this procedure, a 3D ceramic part is produced layer by layer after the un-gelled slurries are removed.

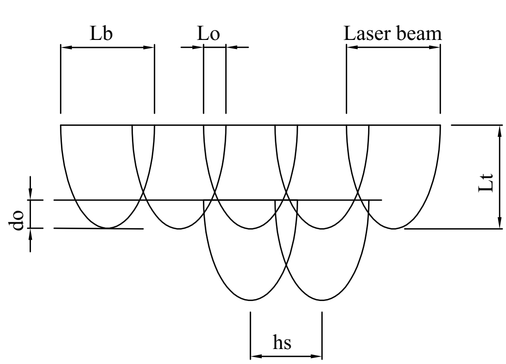

Fig. 2. Schematic of laser gelling process parameters: do—layer over-gel, hs—laser hatch spacing, Lt—line gelled depth, Lo—line overlap, and Lb—line gelled width.

Fig. 2 shows the relationships between important process parameters for forming the ceramic layers [13]. As can be seen, these parameters include layer over-gel (do), laser hatch spacing (hs), line gelled depth (Lt), line overlap (Lo), and line gelled width (Lb). In this work, the effects of these parameters on formability of gelled ceramic bodies were examined.

3. Experimental results

3.1. Optimal forming parameters

In laser gelling, the ceramic slurry could be solidified to form a desired thin ceramic layer under optimal viscosity and laser energy. The viscosity of the ceramic slurry was measured by a viscometer (LVDV-I, Brookfield). Fig. 3 shows the relationship between viscosity and rotating time. As can be seen, the viscosity of the mixed ceramic slurry is a function of rotating time at a spindle rotating speed of 10 rpm. The viscosity was 2800 cP at 5 min and decreased with increasing rotating time. According to our experimental results, the ceramic slurry can easily gel to form a solid ceramic layer when the slurry viscosity ranges between 2800 and 1800 cP. When the slurry viscosity is less than 1800 cP, the slurry can hardly be solidified by laser gelling. Thus, the slurry needs to be continuously stirred to maintain a suitable viscosity.

In this work, gelling the silica ceramic slurry required only low laser power of less than 15 W. The laser power was adjusted

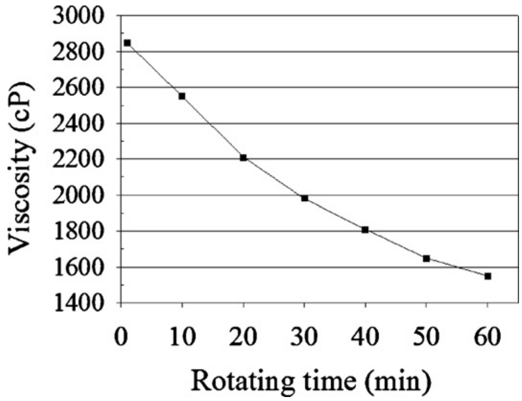

Fig. 3. Change in viscosity of mixed ceramic slurry as a function of rotating time at a spindle rotating speed of 10 rpm.

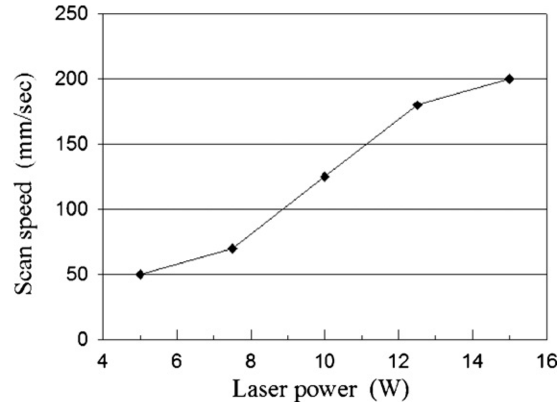

Fig. 4. Relation between laser power and laser scan speed for forming ceramic specimens.

from 5 to 15 W to generate a specimen with a size of 25 mm × 25 mm × 3 mm in a layer of 0.1 mm thick. Fig. 4 depicts the relationship between the laser power and scan speed. As can be seen, laser power increased with scan speed. When the laser power was less than 5 W, it was difficult to form gelled ceramic layer in the paved slurries due to insufficient laser power density. When the laser power was increased from 5 to 15 W, the laser scan speed also increased from 50 to 200 mm/s. With laser power exceeding 15 W, the gelled layer could not be formed because the laser power density became too large for layer forming.

3.2. Overhanging structure

The degree of difficulty in generating ceramic RP parts may be classified into undercut, overhang, and inner channel architecture [11]. Before generating the inner channel feature, a skill for generating overhanging structure must be established. Without any support material under the overhanging, the first layer of the overhang will yield a downward deflection. In order to examine the amount of deflection under the overhang, a "T-shaped" specimen was designed. Fig. 5(a) presents a T-shaped ceramic specimen fabricated using ceramic slurry with a viscosity of 1800 cP as support, and Fig. 5(b) is a schematic of the overhang feature and downward deflection.

As seen in Fig. 5(a), a sagged deflection occurs under the overhang due to insufficient suspension. Table 1 lists the variations in sagged deflection with length of the overhang in T-shaped specimen. The deflection of the overhangs was measured by a optical measuring machine (VERTEX-220) after each T-shaped specimen was separated from a base of ceramic. As can be seen, the deflection increases with the length of the overhang when the silica powder and ceramic binder are mixed in a proportion of 60:40 wt.%. It is quite obvious that the sagged deflection is too large for fabricating more accurate ceramic components because the suspension of the slurry is insufficient when the viscosity equals 1800 cP.

To improve the sagged deflection of the overhang, we increased the viscosity of the ceramic slurry. The viscosity of the ceramic slurry increases when the silica powder is increased. The slurry component in relation to slurry viscosity was listed in Table 2. Slurry of a suitable viscosity can provide enough suspension support to resist the deflection. The sagged deflection in relation to the length of overhang under a viscosity

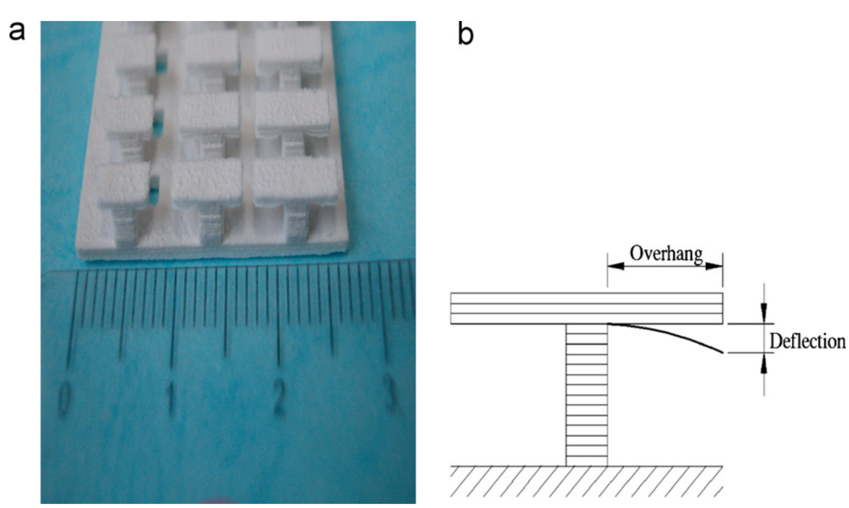

Fig. 5. T-shaped ceramic specimen generated by ceramic slurry support under a viscosity of 1800 cP: (a) a fabricated part and (b) schematic of overhang and deflection.

Table 1
Variations in sagged deflection with length of overhang with different viscosities.

Test no.	1	2	3	4	5
Overhang length (mm)	1	1.5	2	2.5	3
Deflection (μm) when cP = 1800	41	67	106	173	264
Deflection (μm) when cP = 2800	19.7	21.2	25.3	31.3	42.6

Table 2
Slurry component in relation to slurry viscosity.

Sample no.	Silica powder (wt.%)	Silica sol (wt.%)	Viscosity (cP)
1	60	40	1800
2	65	35	2800

of 2800 cP was also listed in Table 1. As can been seen, the deflection decreases sharply due to sufficient slurry suspension when the silica powder and ceramic binder are mixed in a proportion of 65:35 wt.%.

According to our experimental results, the ceramic slurry can act as the support material when fabricating ceramic green body with overhanging features. Therefore, a 30-layer ceramic part with porous inner channel features, as shown in Fig. 6, could be easily produced under a viscosity of 2800 cP. As can be seen, when the span of overhanging is 2 mm, the sagged deflection is 25.3 μm, which approximates the surface finish of 25 μm. The bottom of the inner channel has less sagged deflection due to the suspension of ceramic slurry.

3.3. Porous multi-channel ceramics

To confirm the support effect of the ceramic slurry in constructing inner channel architecture, a porous mold is designed by Pro/E CAD software as displayed in Fig. 7(a). The layers of this wood-pile-like layered are parallel to one another, and adjacent layers are twisted around by an angle of 90°. After the sliced cross-section patterns of this mold were handled by the laser gelling process shown in Fig. 1, a ceramic part with

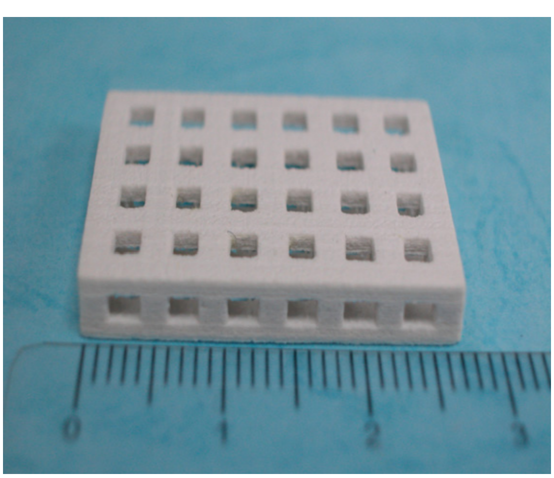

Fig. 6. Photo-micrograph of a 30-layer silica ceramic part with porous inner channels and overhanging features constructed under a viscosity of 2800 cP.

inner multi-channels was made, as shown in Fig. 7(b) and (c). It is hard to fabricate these features in ceramic samples using machining processes or traditional fabrication technologies. However, this wood-pile-like sample was successfully fabricated to confirm the formability of laser gelling process for generating the multi-channels. The suitable process parameters are as follows: laser power of 12 W, laser scan speed of 150 mm/s, scan hatch of 0.1 mm, overlapping of 25%, overgelling of 25%, layer thickness of 0.1 mm, and laser energy density of 0.8 J/mm^2.

The strength of ceramic samples is essential for measurement in industrial applications. Test samples of size 45 mm × 4 mm × 3 mm were measured by the three-point bending method in a universal material testing machine. The flexural strength of the tested samples ranges between 1.7 and 12.5 MPa at laser energy density of 0.7–1.1 J/mm^2, as shown in Fig. 8. The dotted curve in the figure represents the gelled green specimen. As can be seen, when the laser energy density equals 1.0 J/mm^2, the flexural strength has a maximum value of 4.7 MPa. As energy density increases to 1.1 J/mm^2, the flexural strength reduces to 4.3 MPa because greater energy density leads to more thermal micro-cracks in the gelled layer. The solid curve represents the sintered specimen after post-processing at 1200 °C for 1.5 h. As can be seen, the flexural strength ranges between 7 and 12.5 MPa. The flexural strength increases with laser energy density. The maximum flexural strength of the sintered specimen was 12.5 MPa at energy density of 1.1 J/mm^2.

4. Discussion

Two features of this process are particularly worth being mentioned. First, different from other RP processes, ceramic slurries are employed to be a "support material" for maintaining an overhanging structure of the fabricated samples. Second, a porous ceramic part with inner multi-channel can be fabricated under optimal over-gelling, which is hard for conventional machining processes.

4.1. Slurry support

In several RP technologies such as stereolithography apparatus (SLA), fused deposition modeling (FDM), and laminated object manufacturing (LOM), it is necessary to create special support structures to maintain overhanging features of the fabricated part. On the other hand, in selective laser sintering (SLS) and 3D printing (3DP), it is not necessary to create support structure when creating complex-shaped components. The powder materials in selective area are locally

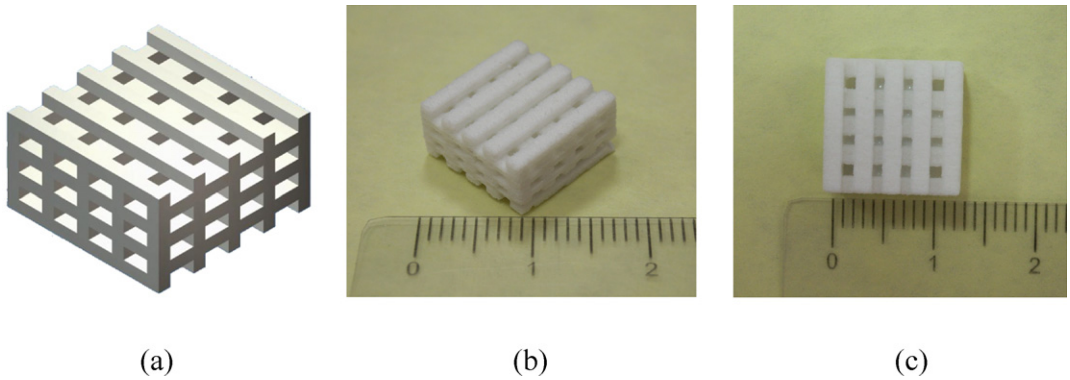

Fig. 7. A wood-pile-like ceramic part with porous multi-channels obtained by laser gelling under laser power of 12 W, scan speed of 150 mm/s, scan hatch of 0.1 mm, overlapping of 25%, over-gelling of 25%, layer thickness of 0.1 mm: (a) CAD image of mold designed from Pro/E, (b) an actual part, and (c) top view of the part.

consolidated and the remaining powders serve as support for the hanging structure [14,15].

To address this challenge, we propose using a slurry-based material employed in ceramic laser gelling process to fabricate ceramic parts with inner multi-channel. Experimental results show that the slurry support reduces the amount of sagged deflection beneath the overhang. In addition, the fluid ceramic slurry can be easily spread less than 50 μm thick when the particle size of the silica is less than 20 μm. Therefore, the slurry-based material can enhance the dimensional accuracy of samples.

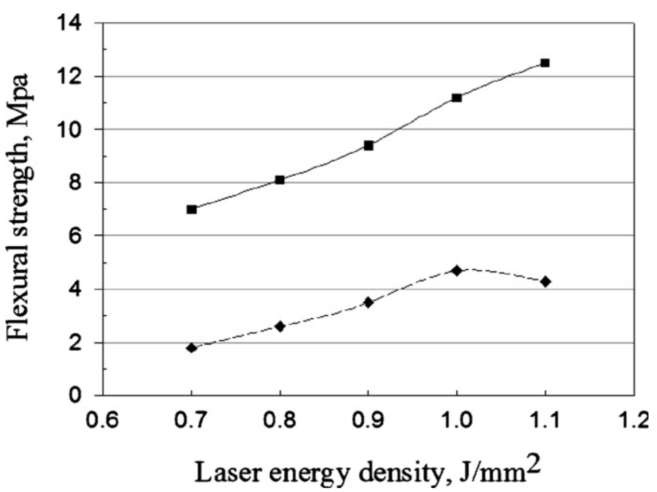

Fig. 8. Relationship between flexural strength and laser energy density. The dotted line represents the gelled green specimen. The solid line represents the sintered specimen after post-processing at 1200 °C for 1.5 h.

The formability of layer manufacturing in laser gelling is proportional to the concentration of silica sol. Adding more silica sol increases significantly the gelling reaction and the ceramic layers can be more easily fabricated. However, the sagged deflection under the overhang increases because the support of the slurry suspension is reduced. To decrease the deflection of ceramic layers, the proportion of sol in the slurries ought to reduce. Therefore, a suitable proportion of silica powder and silica sol is 65:35 wt.%, which forms ceramic slurries with a viscosity of 2800 cP to avoid precipitation and to provide suspension support. In addition, the pure silica ceramic samples can be easily produced because both silica powder and silica sol are used as raw materials.

4.2. Over-gelling

During the laser gelling process, the bonding quality between the layer over-gel (do, see Fig. 2) is very important for ceramic layer forming. The thickness of the layer in Z-direction is of importance to guarantee the over-gel rate between bonded layers. When the gelled depth (Lt, see Fig. 2)

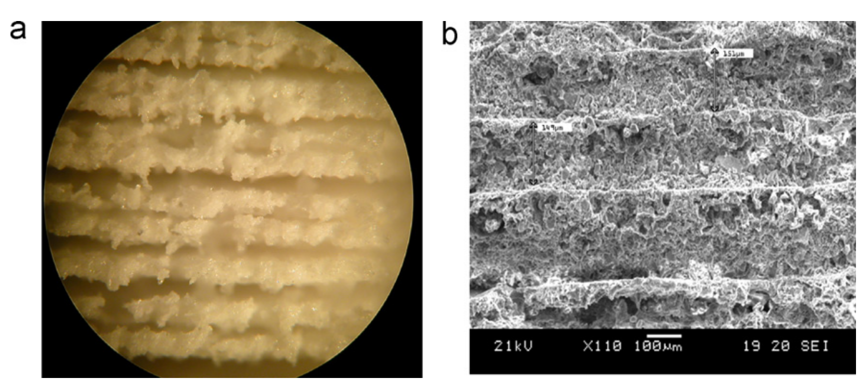

Fig. 9. Effect of over-gel on laser gelling process: (a) photo-micrograph of side view under insufficient over-gel and (b) SEM image of cross-section under adequate over-gel of 25% between bonded ceramic layers.

was less than 110% of the layer thickness, the gelled layers would separate, thus forming many crevices between ceramic layers, as shown in Fig. 9(a). It is because the bonding was inadequate due to insufficient over-gel between layers although the gelled ceramic layers could be solidified. The gelled depth of a monolayer should be 125% of the layer thickness so that 25% of the over-gel was sufficient to bond the layers together without crevice, as shown in Fig. 9(b). Therefore, the over-gelling equal 25% of the layer thickness, a porous multi-channel ceramic can be built.

5. Conclusion

The laser gelling process adopts slurry-based materials to fabricate a silica ceramic sample with porous inner multi-channel. Unlike traditional SLS processes to fabricate ceramic prototypes requires high laser power to sinter or melt the ceramic powder [12,16], which will easily yield distortion due to thermal stress. However, this process needs only low laser power to construct ceramic samples. The deflection and shrinkage of each ceramic layer will be sharply reduced. Moreover, the distortion due to the high laser energy sintering process can also be avoided. Obviously, compared with other conventional ceramic processes, the proposed approach can fabricate more precise ceramic prototypes, particularly for inner multi-channel parts constructed by a thin layer of inorganic slurry. In addition, the proposed approach has potential for fabricating complex interconnected porous ceramics for tissue engineering applications.

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