A Novel ZrO\textsubscript{2} Ceramic Suspension for Ceramic Stereolithography

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Abstract. Stereolithography have been widely applied in multiple fields. In this paper, we developed a highly filled, low viscosity stereolithography-based zirconia suspension, and successfully used to fabricate a complex shaped zirconia parts by DLP process. After debinding and sintering, the sintered bodies showed significant shrinkage, with the shrinkage between 27.28% and 29.64%.XRD, SEM and other methods were used to test the composition, microstructure and flexural strength. The XRD pattern shows that the crystalline phase of the part is the t-ZrO\textsubscript{2} phase, while SEM characterization revealed that the sintered bodies were composed of submicron-grade grains. The relative density measured by the Archimedes’ water displacement method was 96.59%.Additionally, the measured maximum flexural strength was 650MPa. These values are close to the structural properties of common zirconia ceramics prepared by conventional approaches. Hence, a novel DLP-stereolithography-based ZrO\textsubscript{2} suspension for the fabrication of complex and dense zirconia ceramic parts has been proposed in this work.

1. Introduction

Zirconia ceramics are characterized by excellent mechanical properties, good biology compatibility and stable chemical properties \[1,2\]. These properties prevent the zirconia ceramic material from being deteriorated by the action of the body fluid after being implanted into the human body as a prosthesis, and will not damage and destroy human tissue.ZrO\textsubscript{2} is mainly used for hard tissue replacement, such as dental crowns, root implants, joint heads in orthopedics, etc. There are differences in the bones, teeth and organs of the human body, hence, in order to obtain a suitable medical implant, it is necessary to personalize the implant. The introduction of additive manufacturing techniques into the fabrication of biomedical ceramics will address issues such as mold reliance and difficulties in the fabrication of complex shapes, meet individual needs.

Additive manufacturing technology (also known as rapid prototyping and 3D printing) is a new fabrication technique that combines several fields of scientific knowledge, such as digital modeling, material technology and mechanical processing, etc\[3\]. It is the process of printing by computer\[4\], first create a print model on the computer and sliced the model into several data planes, a shaping machine is then used to “print” the component layer-by-layer to form a physical model.3D printing technology has revolutionized the process and method of manufacturing, has been known as “The
most iconic production tool for the third industrial revolution”, attracted more and more attention from all over the world [5,6].

Stereolithography is one of the earliest methods of additive manufacturing, which was developed in 1986 [7]. According to different curing methods of single layer, stereolithography technology can be divided into SLA and DLP technology. Both of the two technologies use UV light (or electron beam) to initiate a chain reaction on a layer of resin or monomer solution. The monomers (mainly acrylic or epoxy-based) are UV-active and instantly convert to polymer chains after activation (radicalisation) [8]. After polymerization, a pattern inside the resin layer is solidified in order to hold the subsequent layers. The unreacted resin is removed after the completion of printing [9]. In this paper, we developed a highly filled, low viscosity stereolithography-based zirconia suspension, and successfully used to fabricate a complex shaped zirconia parts by DLP process.

2. Experimental

The materials used in this experiment include ZrO$_2$(d$_{50}$ = 500nm, Shandong Guangyin New Materials Co. Ltd., China), while the ceramic stereolithography suspension is a self-made mixture consisting of HEA (2-Hydroxyethyl acrylate, Aladdin), HDDA (1,6-Hexanediol diacrylate, Aladdin), IPA (isopropanol, Aladdin), PPTTA (ethoxylated pentaerythritol tetraacrylate, Aladdin). First, take oligomers, reactive diluents, inert diluents, photo-initiators stir in water bath for 30-60 minutes, make sure the resin fully mixed. Second, the powder and dispersant were added to the mixed resin in three times, and the mixture was ball milled for 12 hours to prepare a slurry. Then the ceramic stereolithography experiment was performed using a DLP stereolithography printer, the printing of models was performed by inputting the STL files corresponding to each model into the printer's software. Figure 1 shows the principle of the DLP printer. The main component is a Digital Micromirror Device (DMD). It dynamically generates an image, which represents the geometric information of one layer. By projecting the light through the transparent bottom of the material vat, the containing slurry is selectively cured. After each exposure the coating blade provides a new film of slurry for the building of the following layer. The designed model is finally printed out by repeating layer by layer. Finally, the green body is debinding and sintered to obtain dense sintered bodies.

![Figure 1. The working principles of DLP.](image-url)
Figure 2. The 3D models of the fabricated parts.

Figure 2 shows the lattice structure model, as mentioned above, the DLP printer complete the transformation of the model to the green bodies layer by layer. The bitmap for each layer is obtained by slicing the native CAD design, and the thickness of the slice layer can be changed by the slicing software before printing starts, the smaller the thickness of the slice layer, the higher the accuracy of printing, but the printing time increases with the thickness of the slice decreases. Therefore, it is necessary to design a reasonable layer thickness, and this experimental model uses a layer thickness of 50μm.

The thermogravimetric curve of the green body was obtained using a Simultaneous Thermal Analyzer (STA449C), and a debinding and sintering system was established according to the curve. The phase identification of the samples was identified by X-ray diffractometry (XRD) using X-ray diffractometer with CuKα radiation in the 2θ range from 20° to 70°. The densities of the samples were measured by using the Archimedes’ principle and given as percent of the relative densities. Scanning electron microscopy (SEM) was carried out on an electron microscope (QUANTA FEG 250). The flexural strength was measured by the three-point bending test using electronic universal testing machine (WDW-100A, China) with span of 32 mm and fixed cross-head speed of 0.5 mm/min.

Figure 3. The curve of photosensitive parameter.
3. Results and Discussion

The broadening behavior of individual cured lines of ceramic suspension can be quantified in terms of a quasi-Beer-Lambert behavior of the excess width and the cure depth [10]. The cure depth, \( C_d \), is given by

\[
C_d = S_d \ln \left( \frac{E_0}{E_d} \right)
\]

Where \( E_0 \) is the incident energy dose, \( S_d \) is the sensitivity in the depth direction (with units of length), and \( E_d \) is the critical energy dose in the depth direction. The polymerized thickness is linearly varying with \( \ln(E_0) \), the intersection of the line and the axis of abscissa is \( E_d \), the slope of the line is \( S_d \). We can obtain from Figure 3, that the \( S_d = 150.85 \, \mu m, E_d = 206.02 \, mJ/cm^2 \), which indicates the critical exposure and projection depth of the zirconia ceramic slurry are 206.02\,mJ/cm\(^2\) and 150.85\,\mu m. According to the obtained data, the printing thickness must be smaller than the projection depth while the model is sliced.

In order to minimize the fission and deformation of ceramic during debinding, the debinding procedure was optimized according to thermogravimetric analysis. Figure 4. shows the thermogravimetric curve of the ceramic green body. It can be seen from the thermogravimetric plot that the decomposition temperature of organic matter is between 100\(^\circ\)C and 600\(^\circ\)C. The DTG curve depicted in the figure has four exothermic peaks appearing at 131.4\(^\circ\)C, 258.0\(^\circ\)C, 380.4\(^\circ\)C, and 456.9\(^\circ\)C, with the 380.4\(^\circ\)C peak being the most prominent. The corresponding TG curve shows that the weight loss of the heating process is 26.03\%, and the highest mass loss is 15.81\% at 380.4\(^\circ\)C. The curve then became gentle and there was almost no mass loss after 600\(^\circ\)C, which means that the decomposition of the organics was completed before the temperature reached 600\(^\circ\)C. According to the decomposition details on the thermogravimetric curve, we have established the debinding temperature procedure. The exact temperatures scheme used in the debinding processes is shown in Figure 5., the rate of degreasing in the early stage is very slow to ensure that the fabricated components meet our requirements for precision and the density, if the heating rate too fast, the photocurable resin will decompose into a gas volatilization rapidly, and the thermal stress is generated inside the green body, which is easily to cause cracking of the sample [11]. On the basis of the completion of the decomposition of small molecular organic matter in the early stage, a slightly faster heating system can be adopted in the later section, which make the residual organic matter rapidly decomposed, leaving only the ceramic skeleton, and finally the ceramic green body tends to be densified during the sintering process. Figure 6. shows the 3D-printed parts.

![Figure 4. The TG curves of the as-prepared green body.](image-url)
Figure 5. The sintering profile of the samples.

Figure 6. The sintered bodies.

Figure 7. Scanning electron micrographs of green bodies

Figure 7. and Figure 8. shows the SEM of green bodies and sintered bodies respectively, it obviously that the fracture surface presents a layered topography unique to 3D printing, the layer thickness is about 50μm, which is consistent with the print parameters we set. The SEM image of the sintered bodies demonstrates that there are neither discernible pores nor abnormal grain growths in the
selected area, which indicates a high level of densification. This is consistent with the measured sample density of 96.59%. Besides, the XRD pattern shows that the crystalline phase of the sample is tetragonal zirconia (t-ZrO₂), as is shown in Figure 9.

![Figure 8. Scanning electron micrographs of sintered bodies](image)

![Figure 9. XRD patterns of YSZ sintered at 1400°C.](image)

![Figure 10. The shrinkage of the samples.](image)
After two-step thermal process (debinding and sintering), the samples showed significant shrinkage, and the shrinkage was most pronounced in the Z direction. And from the Figure 10, we can conclude that as the temperature increasing, the shrinkage rate of the sample shows a decreasing trend. In addition, in this experiment, the shrinkage is significantly higher than other 3D printing methods [12,13]. Of course, this is also related to the fact that the photocurable shaped slurry contains more complex organic matter, and can also be explained from a relatively low solid phase content. Besides, the three-point bending strength of the test strip is shown as 650MP.

4. Conclusions
In this study, a complex shaped zirconia parts by DLP process was successfully fabricated used the stereolithography-based zirconia suspension. The main results indicated that the shrinkage of sintered bodies was between 27.66% and 28.72%, and the relative density was 96.59%. The XRD pattern shows that the crystalline phase of the part is the t-ZrO₂ phase, while SEM characterization revealed that the sintered bodies were composed of submicron-grade grains. Additionally, the measured maximum flexural strength was 650MPa. This study shows that zirconia ceramics are a potential 3D printing material.

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