Study on forming accuracy of ZrO$_2$ ceramic materials prepared by DLP technology

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Abstract. DLP technology is one of the 3D printing methods for ceramic materials, and its forming accuracy is affected by the preparation of ceramic slurry, debinding and sintering process. In view of three different slurry preparation methods and solid content, the flow characteristics of slurry were studied. The reasonable debinding and sintering process was formulated, and the debinding and sintering treatment were carried out. The influence of slurry preparation methods on the forming accuracy of green parts and sintered parts was found out. The results show that with the increase of solid content, the viscosity of slurry also increases and the fluidity becomes worse. Increasing milling time and rotating speed can improve the flow characteristics of the slurry with 70% zirconia solid content. The C method can not only increase the solid content of the slurry, but also reduce the shrinkage of the sintered parts and improve the dimensional accuracy of the sintered parts.

Keywords: ZrO$_2$ ceramics, DLP technology, Forming precision, Solid content, Slurry

1. Introduction

ZrO$_2$ ceramics have excellent chemical and physical properties and are widely used in industrial production as structural and functional ceramics. Most of the traditional manufacturing methods need to make molds in advance, which makes the overall production cycle longer, and can not form ceramic parts with highly complex structure, especially hollow and porous. The application of 3D printing technology to the manufacturing of ceramic parts provides a new possibility to solve the above problems and challenges. The commonly used additive manufacturing methods for forming ceramics are selective laser singeing/melting (SLS/SLM) [3, 4], three dimensional printing (3DP) [5], fused deposition modeling of ceramics (FDM) [6, 7], lithography-based ceramics manufacturing (LCM)/digital light processing (DLP) [8, 9] and stereolithography (SLA)[10] and so on. Among them, the surface quality of ceramics formed by lithography-based additive manufacturing technology is better, including DLP.

Due to the indirect forming of ceramic green part based on DLP technology with the help of photosensitive resin, the green part preparation is affected by the scattering of ultraviolet light by ceramic slurry, and the defects such as cracking or shrinkage due to improper treatment process in the process of green part drying, degreasing and sintering affect the forming accuracy. The properties of ZrO$_2$ ceramics are closely related to slurry preparation and sintering process. Therefore, it is of great
significance to study the preparation process, flow characteristics and solid content of ZrO\textsubscript{2} ceramic slurry.

2. Experimental materials and equipment

Experimental materials
Yttria-stabilized zirconia (YSZ) produced by Shenyang Institute of rare metals is selected in this experiment. Its particle size range is 15-45 \( \mu m \), with low oxygen content, good fluidity and good sintering performance. The powder parameters are shown in Tab.1. The photosensitive resin material selected in this experiment is SP-RC70 ceramic special resin of Zhejiang Xunshi Technology Co., Ltd., which is mainly composed of oligomer, diluent, photoinitiator and binder. It has low viscosity, small curing shrinkage, fast curing rate, small swelling, high curing degree and high strength.

| Table 1. Parameters of ZrO\textsubscript{2} powder |
|-----------------------------------------------|
| Chemical composition (mass,\%)                |
| \( ZrO_2 + HfO \)                            |
| \( Bal \)                                     |
| \( SiO_2 \)                                   |
| \( <0.1 \)                                    |
| \( TiO_2 \)                                   |
| \( <0.1 \)                                    |
| \( MgO \)                                     |
| \( <0.1 \)                                    |
| \( Fe_2O_3 \)                                 |
| \( <0.1 \)                                    |
| \( GaO \)                                     |
| \( <0.1 \)                                    |
| \( Y_2O_3 \)                                  |
| \( 7.5 \)                                     |

Experimental equipment
In the experiment, QM-QX4 planetary ball mill of Nanjing Laibu science and Technology Industry Co., Ltd. was used to ball mill ZrO\textsubscript{2} ceramic slurry to obtain slurry with good fluidity. The viscosity of slurry was measured by HAAKE Viscotester E of Thermo Fisher Scientific.

3. Preparation of ceramic slurry
Slurry preparation is the basis of ceramic forming, and the viscosity and fluidity of slurry will directly affect the feasibility and quality of printing. The suitable ZrO\textsubscript{2} ceramic slurry should have the following conditions: high content of ceramic powder, low viscosity and good fluidity, stable distribution of ceramic particles in the slurry. The CeraRAY ceramic 3D printer of Zhejiang Xunshi Technology Co., Ltd. is used to prepare green part. The equipment has a scraper device, which can print high solid ceramics.

Preparation method of slurry
The mixed slurry of ZrO\textsubscript{2} and photosensitive resin was prepared according to the mass ratio. 200g mixed slurry was prepared by analytical balance. The ball mill was used to ball mill 360 ° rotation. The ball mill and ball mill were made of zirconia. The ratio of mixed slurry and ball milling process are shown in Tab.2.

| Table 2. Preparation method of slurry |
|-------------------------------------|
| Preparation method | Solid content (%) | Ball milling process |
|                     |                    | Rotation speed (r/min) | Time (h) |
| A                    | 50                 | 300                     | 2h   |
| B                    | 60                 | 500                     | 2h   |
| C                    | 70                 | 500                     | 5h   |

Performance test of slurry
(a) Viscosity test: use HAAKE Viscotester E viscometer to test the viscosity of the slurry prepared by the above three preparation methods, and take the average value after testing the viscosity of each ratio for three times.
(b) Fluidity test: in this experiment, a self-made fluidity testing tool was used to characterize the fluidity difference among the three preparation methods. Fix the white plastic open cylinder with a
diameter of 20mm and smooth inner wall on the ground 45# steel cylindrical platform. The cylindrical platform shows a horizontal state, as shown in Fig. 1 (a). Using a syringe to suck 3ml of slurry into the cylinder. After standing for several seconds, quickly lift the cylinder and start counting. The timer counts 10s. Then measure and record the diameter of slurry with vernier caliper. This is to characterize the liquidity, as shown in Fig. 1 (b).

Fill in the measured viscosity and flow diameter in Table 3.

![Testing tools for flow performance](image1)
![Measurement of slurry flow diameter](image2)

**Figure 1.** Flow performance test.

**Table 3.** Test results of slurry properties.

| Preparation method | Viscosity (mPa·s) | Flow diameter (mm) |
|--------------------|-------------------|--------------------|
| A                  | 1262              | 50.98              |
| B                  | 1478              | 30.02              |
| C                  | 1608              | 44.82              |

According to Tab.3, it can be seen that with the increase of solid content, the viscosity of slurry is also increasing, but with the increase of rotating speed, the increasing trend of viscosity slows down. In addition, the solid content has a great influence on the fluidity. With the increase of solid content, the flow diameter decreases. The fluidity of 60% and 70% solid content is less than that of slurry with 50% solid content. However, with the increase of milling time, the fluidity of slurry will be improved significantly, so the fluidity of C method is better than that of B method.

4. Preparation of ceramic part by DLP

**Creation of 3D model**

The test piece is designed, and the cube 20 * 20 * 8mm mesh model is created by SolidWorks 2014 software, as shown in Figure 2, and saved in STL format.
Preparation of green part
In order to further study the influence of different solid content and slurry preparation methods on the forming accuracy of green part, uniform process parameters are adopted in DLP forming process, as shown in Tab.4.

Table 4. DLP molding process.

| Printing accuracy (μm) | Layer thickness (μm) | Exposure time for printing (s) | Number of base layers | Single layer exposure time of base layers (s) |
|------------------------|----------------------|-------------------------------|----------------------|---------------------------------------------|
| 0.05                   | 20                   | 5                             | 5                    | 30                                          |

Performance analysis of sintered parts
Set the printing parameters and print with the slurry prepared by A method, B method and C method respectively. The printing process and green part are shown in Fig. 3.

Measurement of green part size
Different from the UV curing of pure resin, there are a large number of suspended ceramic particles in ceramic slurry, and their curing characteristics are affected by the light scattering effect of ceramic particles. The propagation direction of UV light is affected by ceramic particles, which leads to the decrease of penetration depth of incident light, which reduces the curing thickness and increases the curing width. Therefore, the size of the green part will deviate from the model size.

After the printed green part is removed, the excess slurry on the green part is cleaned up, and then the vernier caliper is used for measurement. Tab.5 shows the size and deviation of ceramic green part with different solid content and preparation method. The experiment shows that the forming accuracy of green part decreases with the increase of solid content. With the increase of rotation speed and time, the forming accuracy of green part increases. It can be seen from Tab.5 that the solid content of slurry prepared by method C is significantly improved, and the forming accuracy of green part is not poor.
Table 5. Measurement results of green part dimensions.

| Measurement results | Method A | Method B | Method C |
|---------------------|----------|----------|----------|
| z (mm)              | 8.32     | 9.18     | 8.90     |
| Δz (%)              | 3.88     | 14.75    | 11.25    |
| a (mm)              | 20.30    | 20.83    | 20.72    |
| Δa (%)              | 1.50     | 4.15     | 3.60     |

In the table: z is the dimension in the thickness direction; a is the dimension in the plane direction.

5. Degreasing, sintering and forming accuracy analysis

Formulation and implementation of degreasing and sintering process
For the ZrO$_2$ ceramic green part formed by DLP, the post-treatment is divided into debinding process and sintering process. The comprehensive thermal analysis of SP-RC700 ceramic resin is shown in Fig. 4. TG curve showed that the weight loss was obvious at 134 °C-705 °C, and DSC curve showed that there was a large endothermic peak at 514 °C. When the temperature is higher than 600 °C, the thermogravimetric curve has little change, so the degreasing temperature can be controlled at about 600 °C. In the places with heavy loss, the heating rate should be reduced and the holding time should be appropriately prolonged to prevent the defects such as delamination and cracking of the green part caused by too fast heating rate. The process curve of debinding and sintering of mixed powder was formulated (as shown in Fig. 5), and the degreasing sintering experiment was carried out in SA2-4-17TP-DZ muffle furnace.

![Figure 4. TG-DSC curve.](image)

![Figure 5. Degreasing and sintering process curve.](image)

![Figure 6. Sintered parts.](image)

In Fig.5, the temperature below 600 °C is the degreasing stage, and above 600 °C is the sintering stage. Three sintering temperatures were selected for sintering experiment: 1550 °C, 1600 °C and 1650 °C. Three green parts were sintered at different temperatures. The sintered parts were as shown in Fig. 6.

Analysis of forming accuracy of sintered parts
The sintered parts were taken out from the muffle furnace and measured with vernier caliper. The measurement results are shown in Tab.6.

Table 6. Dimension measurement of sintered parts.

| Measurement results | Method A | Method B | Method C |
|---------------------|----------|----------|----------|
| z (mm)              | 5.11     | 4.95     | 4.99     |
| Δz (%)              | 38.51    | 40.43    | 39.95    |
| a (mm)              | 13.80    | 13.62    | 13.59    |
| Δa (%)              | 32.00    | 32.89    | 33.04    |
In the table: $z$ is the dimension in the thickness direction; $a$ is the size in the plane direction; the dimensional deviation of sintered parts is the deviation between the size of sintered parts and that of green parts.

According to the measurement results in Tab.6, the histogram of shrinkage in $z$ and $a$ directions is made, as shown in Fig. 7.

![Histogram of shrinkage of sintered parts.](image)

Figure 7. Histogram of shrinkage of sintered parts.

According to Tab. 6 and Fig.7, it can be concluded that the shrinkage rate of the parts corresponding to each slurry preparation method varies at different sintering temperatures, but the change value is not large. In $z$ direction, the shrinkage rate of the parts corresponding to C method is small. At 1600 °C and 1650 °C, the change of shrinkage rate is not obvious, which indicates that the resin is close to no residual state, and the internal structure of the product tends to be stable. In addition, due to the influence of gravity in $z$ direction, the internal structure collapses during sintering, while the size in $a$ direction is relatively stable, which is also one of the factors that need to be considered when sintering ZrO$_2$ prepared by DLP method.

6. Conclusion
In this paper, the effects of different solid content and preparation methods on the flow characteristics and green part size accuracy of the mixed slurry were studied, and the influence of three sintering temperatures on the forming accuracy of ZrO$_2$ parts was studied:

(1) With the increase of solid content, the viscosity of slurry increases and the fluidity becomes worse. With the increase of rotation speed and time, the increasing trend of viscosity is slowed down and the fluidity is also improved significantly.

(2) In the preparation of ZrO$_2$ green part, the forming equipment with scraper is helpful to the formation of high solid ceramic slurry. However, due to the scattering effect of ceramic particles suspended in the slurry, the accuracy of DLP forming ceramic materials is lower than that of photosensitive resin materials only.

(3) The higher the solid content is, the smaller the shrinkage rate is, and the shrinkage rate corresponding to C method is the smallest. When the temperature is over 1600 °C, the shrinkage rate has no change. Compared with the shrinkage change in $z$ direction, the shrinkage in a direction is less affected by the solid content, while the effect in $z$ direction is greater.

(4) Under the condition of high solid phase as the primary condition, the preparation of ZrO$_2$ slurry by C method is helpful to improve the overall forming accuracy, which provides experience for further research on DLP forming of ceramic materials with higher solid phase.
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References
[1] BENGISU M. Engineering Ceramics, Berlin: Springer Science & Business Media, 2013, pp. 85-207.
[2] BLACKBURN S. New processes or old: complex shape processing of advanced ceramics, Advances in Applied Ceramics, 2005, pp. 97-102.
[3] LIU Kai, SUN Huajun, SHI Yusheng, et al. Research on selective laser sintering of Kaolin-epoxy resin ceramic powders combined with cold isostatic pressing and sintering, Ceramic International, 2016, pp. 10711-10718.
[4] Lithoz GmbH. Process Parameters for LithaCon 3Y610 Purple, Lithoz GmbH: Vienna, Austria, 2017.
[5] Tubio, Carmen R, Guitián, Francisco, Gil A. Fabrication of ZnO periodic structures by 3D printing, Journal of the European Ceramic Society, 2016, pp. 3409-3415.
[6] Tanwilaisiri A, Zhang R, Xu Y, et al. A manufacturing process for an energy storage device using 3D printing [C]// IEEE International Conference on Industrial Technology. IEEE, 2016.
[7] Penner, D., Fassbind, A., Henke, R., Mauchle, S., de Hazan, Y. Process engineering Additive Manufacturing of Ceramics by Composite Microextrusion. Ceram. forum Int. 2017, pp. E1-E3.
[8] Conti L, Bienenstein D, Borlaf M, et al. Effects of the Layer Height and Exposure Energy on the Lateral Resolution of Zirconia Parts Printed by Lithography-Based Additive Manufacturing, Materials, 2020, pp. 1317.
[9] Schventenwein M, Schneider P, Homa J. Lithography-Based Ceramic Manufacturing: A Novel Technique for Additive Manufacturing of High-Performance Ceramics, Advances in Science & Technology, 2014, pp. 60-64.
[10] Eckel Z C, Zhou C, Martin J H, et al. Additive manufacturing of polymer-derived ceramics, Science, 2016, pp. 58-62.