ZTA Ceramic Materials for DLP 3D Printing

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Abstract. As a new additive manufacturing method, DLP has the advantages of high precision, fast speed and low cost. ZTA ceramic is anticipated to be used in more applications due to its superior bending strength, fracture toughness and thermal conductivity. But the detailed study with ZTA printing material for DLP is still rarely reported. In this experiment, ZTA ceramic UV resin with various ZrO₂ concentration (5-15wt.%) were investigated and tested for their 3D printing performance. ZTA ceramic UV resin with low viscosity (<3 Pa·s at shear rate of 10 s⁻¹) and high solid load (55vol.%) were successfully developed. After sintering at a temperature of ≥1600°C, a relative density of >96% can be always promised. For the optimized doping level of ZrO₂ at 11wt%, a density of 99% can be achieved.

1. Introduction

It has been demonstrated that by the incorporation of zirconia could significantly improve the mechanical properties of alumina[1–5]. The t-ZrO₂ stabilized by the doped oxides could enhance the toughness of Al₂O₃ through t-m phase transformation[6–8]. More importantly, the addition of ZrO₂ phase inhibited grain growth and refined microstructure, thus increasing the path of crack growth in the fracture process, thereby improving toughness. In the past few decades, several technologies, such as dry pressing, isostatic pressing, slip-casting, tape-casting, injection molding [9-13] and so on, have been successfully implemented for preparing ZrO₂ toughened Al₂O₃ (ZTA) composite ceramics. However, these traditional methods have great limitations and are difficult to be applied to ceramic parts with complex shapes and structures (inner holes, sharp corners, etc.) and parts requiring high precision. In addition, these processes often require the use of molds and post-treatment, which not only greatly increases the manufacturing cost, reduces the production efficiency, but also limits the wide applicability of Al₂O₃-ZrO₂ ceramics. Therefore, it is necessary to explore a more economical and efficient method to prepare Al₂O₃-ZrO₂ ceramic material parts with high requirements and high precision.

In recent years, rapid prototyping (RP) technology has become an important research field for manufacturing ceramic parts directly, because of its flexible shape and easy integration with industrial machining based on digital design processing. Light curing technology is one of the earliest rapid prototyping technology. With high precision (10 to 50 micron level) and maturity, it can print high value-added ceramic devices with high requirements for dimensional accuracy and material properties. According to the different single-layer curing modes, the photoluminescence molding process is
mainly divided into two categories: Stereolithography Apparatus (SLA) and Digital Light Processing (DLP). This paper mainly discusses the technology of DLP 3D printing.

With the development of 3D printing technology and the improvement of production accuracy, speed and other performance requirements, as well as the advancement of micro-optical components technology, rapid prototyping technology based on mask forming technology has been developed rapidly. Its forming principle is that the model is sliced by slicing software to generate slicing data that can reflect the sectional figure of the part. The document drives the dynamic view generator. The dynamic view generator is illuminated by the area light source with characteristic wavelength. After the light path system, a specified section view of the part is formed on the surface of the sensitive resin, which can solidify the whole part layer at one time. When the cross section of the part in this layer is generated, the worktable moves down one layer to solidify the next layer of the part, so that the cycle lasts until the end of printing.[14]

In order to further improve the surface exposure accuracy, the Digital Light Processing (DLP), developed by Texas Instruments, plays a decisive role. It mainly solidifies photosensitive polymer liquid layer by layer through projector, thus creating 3D printing object.

In order to achieve reasonable densification and final device performance, the ceramic suspension used in DLP must meet certain standards. Ceramic suspensions should contain at least 40vol.% solid ceramic particles to ensure reasonable debinding and sintering performance. In addition, the ceramic suspensions should be stable and have the ability of self-leveling, which requires a viscosity lower than 3Pa·s at 30s⁻¹ shear rate.[15, 16] Furthermore, under operating conditions, appropriate curing depth and width of ceramic suspension are crucial to ensure the accuracy of 3D printing and good interlayer combination.

In order to prepare a stable and highly concentrated ceramic suspension with a suitable rheological behavior, an appropriate suspension composition is essential. However, the detailed study with ZTA printing material for DLP is still rarely reported. In this study, ZTA ceramic UV resin with various ZrO₂ concentration (5-15wt.%) were investigated and tested for their 3D printing performance.

2. Experimental procedure

2.1. Preparation of powder mixture

Alumina and zirconia powders were chosen to be dried at 100°C for 2h in an oven. The dried powders were sieved through a 100-mesh screen to obtain a uniformly dispersed composite powder. In the following experiments, zirconia and alumina powders need to be mixed into two groups: the first group would test the best ratio between two kinds of dispersants, in which zirconia content was kept as 10wt.% for seven groups of control experiments; the second group would test the best zirconia content, adding zirconia content of 5wt.%, 7wt.%, 9wt.%, 11wt.%, 13wt.% and 15wt.%, respectively. After weighing the above powders in proportion, the mixed powders were roll-milled for 24h at speed of 100rpm, and the mass ratio of ball to powder was 2:1.

| Proportion between dispersant A and dispersant B | Dispersant concentration/wt.% | Solid loading/vol.% |
|-----------------------------------------------|-------------------------------|---------------------|
| 2:8                                           | 3                             | 55                  |
| 3:7                                           | 3                             | 55                  |
| 4:6                                           | 3                             | 55                  |
| 5:5                                           | 3                             | 55                  |
| 6:4                                           | 3                             | 55                  |
| 7:3                                           | 3                             | 55                  |
| 8:2                                           | 3                             | 55                  |
Table 2. Composition of the ZTA ceramic suspensions elaborated with different composition of powders and solid loading.

| Proportion between alumina and zirconia powders | Proportion between dispersant A and dispersant B | Dispersant concentration/wt.% | Solid loading/vol.% |
|-----------------------------------------------|-------------------------------------------------|------------------------------|---------------------|
| 95:5                                         | 1:1                                             | 3                            | 55                  |
| 93:7                                         | 1:1                                             | 3                            | 55                  |
| 91:9                                         | 1:1                                             | 3                            | 55                  |
| 89:11                                        | 1:1                                             | 3                            | 55                  |
| 87:13                                        | 1:1                                             | 3                            | 55                  |
| 85:15                                        | 1:1                                             | 3                            | 55                  |

2.2. Preparation of ZTA ceramic suspensions
Mixed alumina and zirconia powders, UV curable resin, polymerization initiator and dispersant were weighed and ball-milled for 3h with zirconia ball media in a planetary mill at 300rpm. Finally, ZTA ceramic suspensions were obtained. To show the influence of suspension compositions, two different sets of suspensions were characterized in terms of their shear rate depending on the dynamic viscosity. Table 1 shows the composition of the ZTA ceramic suspensions elaborated with different dispersant concentrations and solid loading. Table 2 shows the composition of the ZTA ceramic suspensions elaborated with different composition of powders and solid loading.

2.3. Fabrication of the ZTA ceramic parts by DLP 3D Printing
The software is used to create a 3D model and slice it. Then the data is imported into the DLP3D printer, and the required parts are printed by DLP (Digital Optical Processing) technology. The process of manufacturing ZTA ceramics is shown in Fig. 1. The DLP projector projects the photosensitive resin on the worktable, solidifies it layer by layer, and finally obtains the ZTA green body.

Figure 1. Process of manufacturing ZTA ceramics by DLP 3D printing.

3. Results and discussion

3.1. Rheological behaviour of the suspensions.
When investigating the dispersion of high solid load powders in UV resins, it is difficult to obtain a higher Zeta potential by adjusting the pH and ion intensity owing to the Zeta potential of UV resin is generally low. Therefore, the usual method for evaluating the dispersion effect is to test the viscosity of the ceramic slurry instead of Zeta potential.

3.1.1 Effects of proportion between different dispersants. The type and content of dispersant will affect the rheological behaviour of slurry. In this experiment, two type of the polymer dispersant were
chosen to form an adsorption layer on the surface of solid particles, thus increased the charge on the surface of solid particles and formed a bimolecular layer structure, so that the electrosteric repulsion between ceramic particles is established, and eventually a uniform ZTA printing slurry can be obtained.

It is obvious from Figure 2 (a) that with the increase of shear rate, the slurries containing different proportions between two kinds of dispersant exhibit shear thinning behaviour, and when the ratio between dispersant A and dispersant B is 5:5, the ZTA slurry has the lowest viscosity of 2.4 Pa.s at the shear rate of 10 s⁻¹. The shear stress of ZTA suspensions with different dispersant ratios are shown in Figure 2 (b). There is a good linear relationship between shear stress and shear rate curve of slurry prepared by seven dispersants with different proportions.

Figure 2. (a) Viscosity-shear rate curves of photosensitive ZTA suspensions with different ratio of dispersants. (b) Shear stress-shear rate curves of photosensitive ZTA suspensions with different ratio of dispersants(solid loading: 55vol.%; dispersant concentration: 3wt.%).
3.1.2 Effect of zirconia doping amount on ZTA rheological properties. Compared with Al₂O₃, the commercial ZrO₂ powders always possessed finer particle size and also larger specific surface area, thus the introduction of different amount of zirconia might influence the rheological properties when we only added the same amount of dispersant based on the ceramic powder weight. In general, larger surface area need to have more surfactant to reach the adsorption equilibrium. In addition, the amount of water adsorbed on the surface of fine powder or high specific surface area zirconia particles decreases accordingly the free flowing water in the suspension, resulting in the low solid content of Zirconia Suspension at the same viscosity.

![Figure 3](image.jpg)

**Figure 3.** (a) Viscosity-shear rate curves of photosensitive ZTA suspensions with different ratio between zirconia and alumina. (b) Shear stress-shear rate curves of photosensitive ZTA suspensions with different ratio between zirconia and alumina (solid loading: 55 vol.%, dispersant concentration:3wt.%).

It is obvious from Figure 3(a) that with the increase of shear rate, the slurries with various ZrO₂ concentration(5-15wt.%) exhibit shear thinning behaviour with no clear yield stress. When the content of ZrO₂ came to 11wt.%, the ZTA slurry has the lowest viscosity of 2.146Pa·s at the shear rate of 10s⁻¹.
The shear stress of ZTA suspensions with different ZrO₂ concentration(5-15wt.%) are shown in Figure3(b). There is a good linear relationship between shear stress and shear rate curve of slurry prepared by six suspension compositions.

It is interesting that the viscosity of the ZTA UV resin reaches minimum at 11wt%, the increase of the large surface area ZrO2 powder didn’t necessarily increase the viscosity. This elucidate that the dispersant dose of 3wt% should be already above the saturation level and also the interparticle force between Al2O3 and ZrO2 powders was not simple, the distribution of the ZrO2 among Al2O3 is also one critical factor for the rheology behaviour.

3.2. Density.
The density and relative density of samples with different content of ZrO₂ sintered at 1600°C are shown in Figure4. It can be observed from the figure that the sample density increased with the addition of ZrO₂ until reaching a maximum density of 4.13g/cm³at the ZrO₂ content of 15wt.%. However, there is an abnormal point at the ZrO₂ content of 13wt% that have a relatively low density and relative density. This may be because both alumina and zirconia have undergone solid phase sintering without forming solid solution. With the increase of sintering temperature, the energy provided increases, which leads to powder densification. When sintering temperature is too high, the migration rate of grain boundary is much higher than that of pore. Therefore, grain boundaries are free to move away from the holes, so that more holes will remain in the grains. In the above-mentioned pressureless solid-state sintering, the isolated pore in the sample is difficult to shrink and eliminate at the end of sintering, thus reducing the density of the sample. [17,18].

3.3. Microstructure analysis
The cross-sectional microstructures of ZTA ceramics with different zirconia content sintered at 1600°C are shown in Figure5. It can be observed that there are a few pores in the samples, and most of them are distributed at grain boundaries. Zirconia particles distribute well along the grain boundary of alumina particles, partly at the triple point. With the increase of zirconia content from 5wt% to 13wt%, the average particle size of alumina decreases from 1.09 μm to 0.69 μm, and a small amount of zirconia particles are “engulfed” into alumina particles. This is due to the uneven distribution of zirconia, the growth of alumina particles in the zirconia defect area is not inhibited, resulting in the movement of alumina grain boundary and "swallowing" of zirconia particles. The particle size of
Zirconia is small enough to initiate the Toughening Behavior of zirconia in ZTA matrix [19]. In terms of toughening mechanism, fine ZrO₂ particles are located on the grain boundary of Al₂O₃, which inhibits the movement of Al₂O₃ grain boundary and the growth of Al₂O₃ grain. Therefore, the improvement of grain boundary structure leads to the improvement of mechanical properties[20].

Figure 5. Microstructure of the fracture surface of the ZTA ceramic body with different contents of ZrO₂ (5wt.%~13wt.%) after sintering at 1600°C.

4. Conclusions
In summary, we report materials for a new method of fabricating composite ZTA ceramic parts with excellent performance by three-dimensional printing process based on DLP. A low viscosity (<3Pa·s at shear rate of 10s⁻¹) and high solid-load (55vol.%) ZTA printing material can be achieved. After sintering at 1600°C, the printed ZTA ceramic can reach a relative density of >96%. From microstructure analysis with SEM, the zirconia particles distribute well along the grain boundary of alumina. The microstructure of ZTA samples is compact, and there are only a few pores on the grain boundary. The grain size of zirconia is enough to initiate the toughening behavior of zirconia in ZTA matrix.

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