Experimental Research on Light-curing Rapid Prototyping Silicon Oxide Ceramics

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Abstract. 3D printing technology is an emerging technology that is rapidly developing in the manufacturing field. It can easily and automatically manufacture complex three-dimensional shapes that are difficult to be produced by various processing methods. Printable ceramic materials are prepared by mixing photosensitive resin and different ceramic powders. By studying the effects of dispersant, slurry, PH value, silica particle size and solid phase content on slurry viscosity and fluidity, low viscosity Ceramic slurry with high solid phase content and good fluidity. The effects of different solid phase contents on the bending strength, firing shrinkage, porosity and density of ceramics were tested. The results show that the bending strength of sintered SiO₂ ceramics reaches 15.78Mpa at a solid content of 70vol %. The density was 76.21%, porosity was 40.04%, sintering shrinkage was 0.89%.

1. Introduction

Additive manufacturing technology is a new type of rapid prototyping technology developed in the 1990s[1]. It has the advantages of high manufacturing accuracy, no molds, short development cycle and low manufacturing cost[2]. Thus, The fast manufacturing of hollow and thin-walled structures such as aeroengine blades can be realized. 3D-printed SiO₂ ceramics are widely used in aviation, chemical industry, jewelry, biomedical and other fields, and some progress has been made in its research at home and abroad. Zhou et al. studied the effect of dispersant on the viscosity of water-based SiO₂ ceramic slurry, and believed that when the content of sodium polyacrylate dispersant reached 0.3%, low-viscosity silica ceramic slurry could be prepared. The density of silicon ceramic green body reached 62.45% after sintering[3].

In this paper, the effects of dispersant, slurry pH, silica particle size and solid phase content on the viscosity and fluidity of silica ceramic slurry are studied. The ceramic green body was quickly manufactured using photo-curing printing technology. After being degreased and sintered, the effects of different solid phase contents on the bending strength, density and porosity of silica ceramics were tested.

2. Preparation and performance test of photocurable ceramic paste

2.1. Raw materials
The polymerization system is acrylic resin monomer (Shenzhen Baolimo Technology Co., Ltd.), dispersant, leveling agent (BYK-333), photoinitiator (benzoin dimethyl ether), ammonia, dilute hydrochloric acid, silica ceramic powder. The particle size is: 10 μm, 8 μm, 6 μm, 2 μm.

2.2. Preparation of ceramic samples
Acrylic acid, dispersant (relative to the mass of ceramic powder), BYK-333 (0.3 wt%, relative to the mass of acrylic acid), benzoin dimethyl ether (1%) and ammonia (dilute hydrochloric acid) are mixed in a certain proportion. The ceramic powder was added to the photo-curable resin in batches, and ball milled for 6 hours to prepare a ceramic slurry.

2.3. Ceramic green body molding
Import the processed 3D model data into the control software of the light curing molding machine PLM-I (Shenzhen Baolimo Technology Co., Ltd.), inject the silicon oxide ceramic slurry into the tank of the molding machine, adjust the light curing molding machine's working parameters, printing and forming of ceramic blanks.

2.4. Degreasing and sintering
Through the thermal weight loss analysis of the photosensitive resin, the degreasing process of the ceramic green body is determined. The ceramic sample is densified at high temperature by sintering.

3. Performance characterization
A rotary viscometer (Shanghai Nirun Intelligent Technology Co., Ltd., DV-T2 type) was used to measure the viscosity of the silicon oxide ceramic slurry. A thermal weight loss analyzer (Perkinelmer Company, TGA-7 type, N2 atmosphere, heating rate 10 ℃/min, test range 25 to 600 ℃) was used to study the thermal decomposition process of the photosensitive resin. Refer to HB5353.2-2004 standard to test the firing shrinkage of ceramic samples. Refer to GB/T6569-2006 standard for three-point bending test of SiO2 ceramic samples. Refer to the QB/T1642-2012 standard to calculate the porosity of the sample. Use the density tester to measure the density of the ceramic sample.

4. Results and discussion
Figure 1 is a comparison chart of the effects of three dispersants, ammonium polyacrylate, trisodium citrate and polyvinylpyrrolidone, on slurry viscosity. When no dispersing agent is added, the slurry viscosity is 2280 mPa·s. With the increase of the dispersing agent content, the slurry viscosity tends to decrease first and then increase, indicating that there is an optimal value for the dispersing agent content. It can be seen from Fig. 1 that the viscosity of the ceramic slurry containing polyammonium acrylate dispersant has a minimum value. When the content of the ammonium polyacrylate dispersant is less than 1.0wt%, with the addition of the dispersant, the dispersant interacts with the particle surface, effectively preventing the agglomeration between the particles. In the process of ball milling, the particles are easy to disperse, which reduces the viscosity of the slurry and improves its fluidity. When the content of the dispersant added is 1.0wt%, the viscosity of the slurry is 432 mPa·s, at this time the particle surface reaches saturation adsorption, and the slurry has good fluidity. As the dispersant continues to be added, the ceramic particles are bridged by excess dispersant, causing the particles to agglomerate, thereby increasing the viscosity of the slurry and reducing the fluidity.

Figure 2 shows the change of viscosity of silica ceramic slurry (containing 1.0wt% ammonium polyacrylate) with different pH values. It can be seen from Figure 2 that the viscosity of the ceramic slurry decreases first and then increases as the pH value increases. When the pH value of the slurry reaches 9, the minimum viscosity of the slurry is 277.2 mPa·s, at which time the slurry has good fluidity. This is because at different pH values, the electrolysis degree of ammonium polyacrylate is different, and it is difficult to ionize under acidic conditions. At pH=9, ammonium polyacrylate can be completely ionized. At this time, the slurry depends on the electrostatic steric stabilization mechanism to achieve stable dispersion. When the pH>9, the ion concentration in the slurry is too high, and the
ionized ammonium polyacrylate produces a repulsive effect on the surface of the negatively charged ceramic particles, but it is not easy to adsorb, resulting in agglomeration of SiO₂ ceramic particles, which increases the viscosity of the slurry and the fluidity Decrease⁴. Therefore, when containing 1.0wt% ammonium polyacrylate dispersant and the slurry pH is 9, SiO₂ ceramic slurry with low viscosity and good fluidity can be prepared.

Figure 3 shows the viscosity of ceramic slurry with different SiO₂ powder particle size and different solid phase content. It can be seen that under the condition of the same solid phase content, as the particle size of the SiO₂ powder increases from 2 μm to 10 μm, the viscosity of the ceramic slurry gradually decreases. This is because, for a slurry with a large particle size, the number of ceramic particles per unit volume is smaller than in a slurry with a small particle size, and the interaction between the particles is weak, resulting in a small slurry viscosity and good fluidity⁵. Under the same powder particle size, as the solid content of silica increases from 40vol% to 55vol%, the viscosity of the ceramic slurry gradually increases. This is because, when the solid phase content is increased, the tendency of agglomeration between particles increases, so that the viscosity of the slurry increases and the fluidity decreases.

Figure 4 shows the viscosity of ceramic slurry with 10μm particle size SiO₂ at different solid phase content. It can be seen that with the increase of the solid content of silicon oxide, the slurry viscosity gradually increases. Ceramic 3D printing technology requires high viscosity and fluidity of the paste. When the solid phase content is 70 vol%, the viscosity of the paste is large and the fluidity is poor. It is not easy to form a ceramic green body using 3D printing technology. By analyzing the performance of ceramic slurry, this experiment selected 60vol%, 65vol% and 70vol% solid phase content to study the performance of SiO₂ ceramic green body and sintered samples.
Figure 3. Influence of particle size and solid content on viscosity of slurry

Figure 4. Influence of solid content on viscosity of slurry

Figure 5 is a TG-DTG analysis of photosensitive resin. It can be seen that the resin quality hardly changes at 25 to 300 °C. At 300 to 349 °C, the photosensitive resin begins to decompose slowly, and the quality changes little. When the temperature was raised to 455.39 °C, the weight loss rate of the resin was 85.11%. Continue to increase the temperature, the quality no longer changes after 455.39 °C, indicating that the thermal decomposition process of the resin is completed. The degreasing process of the SiO₂ ceramic green body thus formulated is: from 560 °C to 1250 °C at a heating rate of 5 °C/min, heat preservation for 2h.

Table 1 shows the performance of SiO₂ ceramics at different solid phase contents. It can be seen from Table 1 that as the SiO₂ solid content increases, the flexural strength of green body increases, flexural strength of sintered increases, from 20.39% to 28.98%, the density increases from 70.56% to 76.21%, the porosity and sintered shrinkage decrease. The porosity of the sample after sintering was reduced from 45.44% to 40.04%, and the sintered shrinkage decreased from 2.98% to 0.89%.

| Solid content /vol% | Flexural strength of Green body /MPa | Porosity /% | Density /% | Flexural strength of sintered /MPa | Sintered shrinkage rate/% |
|---------------------|-------------------------------------|-------------|------------|-----------------------------------|--------------------------|
| 60                  | 20.39                               | 45.44       | 70.56      | 12.34                             | 2.98                     |
| 65                  | 27.23                               | 42.56       | 75.82      | 14.55                             | 2.04                     |
| 70                  | 28.98                               | 40.04       | 76.21      | 15.78                             | 0.89                     |
5. Conclusion

This paper studies the effects of dispersant, slurry pH, powder particle size and solid phase content on the performance of silica ceramic slurry. Experimental results show that, under the condition that the content of ammonium polyacrylate dispersant is 1wt% and the slurry pH value is 9, a ceramic slurry with low viscosity and good fluidity can be prepared. At the same SiO₂ particle size, the viscosity of ceramic slurry increases with the increase of solid content. At the same SiO₂ content, the viscosity of the slurry decreases with the increase of particle size. With the increase of solid content, the bending strength and density of ceramic samples increase. Porosity and firing shrinkage are reduced. Under the condition of solid content of 70vol%, the flexural strength of SiO₂ ceramic after sintering reached 15.78 Mpa, the density is 76.21%, the porosity is 40.04% and sintered shrinkage rate is 0.89%.

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