Application of 3D Printing Technology in the Field of Ceramic Material Manufacturing

An Xu
Jingdezhen University School of Economics and Management, Jiangxi 333000, China.
xzhsuda@126.com

Abstract. 3D printing has been widely used in medical model manufacturing, tissue organ regeneration, clinical repair treatment and drug development testing, especially in the field of dental ceramic material manufacturing. Based on microfluidic extrusion 3D printing technology, micro ceramic components with complex shapes can be customized by a selective slurry extrusion system. In this paper, zirconia ceramic slurry is used as the molding object, and the physicochemical properties of zirconia ceramic slurry are improved by tourmaline. The zirconia all-ceramic crown is rapidly manufactured by micro-flow extrusion 3D printing technology, and the process is further tested and analyzed. The influence of the mechanical properties of zirconia ceramics.

1. Introduction
3D printing technology stands out among many technologies due to its short manufacturing time, high forming precision, low cost, and the ability to make arbitrarily complex parts. 3D printing technology can complete parts that are difficult to form by traditional techniques, such as ceramics, alloys, and complex shaped cavities, at a relatively high speed and high precision, which is especially helpful for the formation of ceramic parts. Due to the high strength and hardness of ceramic parts, it is difficult for conventional manufacturing techniques to process the formed parts, which results in the ceramic parts being manufactured with low precision and failing to meet the requirements for use [1]. With the improvement of people's living standards and the increasing awareness of the Chinese people's love of teeth, the subjective requirements of patients for dental diseases are becoming more and more strict, which makes the tasks faced by dental restoration workers in China more and more difficult. The traditional crown making process is complicated, time-consuming and has low precision. Due to the advantages of short manufacturing time, low production cost and the ability to manufacture complex parts, 3D printing technology has become more and more widely used in the field of oral prosthetics. Especially for forming all-ceramic crowns, there are advantages that other technologies can't match [2].

2. Dental ceramic zirconia crystal material structure and properties
The content of zirconium in the earth's crust is 0.025%, and the reserve amount is more than that of Cu, Zn, Sn, Ni and other metals. In nature, there are mainly two types of ore containing zirconium: oblique zircon and quartz. The high-purity zirconia is white, has a molecular weight of 123.22, a theoretical density of 5.68 g·cm⁻³, a melting point of 2715 °C, a boiling point of 4275 °C, and a Mohs hardness of
7. Zirconium oxide has good chemical stability, good stability to acid and alkali, except hydrofluoric acid and sulfuric acid, and has strong resistance to chemical attack and microbial attack. Zirconium oxide has higher mechanical properties than other ceramics because of its unique phase transformation toughening properties. The strength and fracture toughness of tetragonal zirconia can reach 1.5GPa and 15MPa·m0.5. Pure zirconia exhibits three crystal structures with changes in temperature under normal pressure. It is a symmetrical monoclinic phase at room temperature to 1170°C. It is a tetragonal phase at 1170°C to 2370°C and a cubic phase at 2370°C to the melting point. Its theoretical density is 6.27 g·cm³ and 6.10 g, respectively. Cm³, 5.68 g·cm³. The crystal structure and temperature conversion of the three crystal forms are shown in Fig. 1.

![Fig. 1 Three crystal structures of zirconia](image)

(1) Density and porosity. According to the Archimedes drainage method, the density of the sample is measured. The dry weight M1 of the ceramic sample is weighed in air, then boiled in deionized water for 2 hours [3], soaked for 4 hours, the ceramic sample is fully saturated, and then the ceramic test is measured. Take the weight M2 in the water, take out the ceramic sample, wipe the moisture on the surface of the sample with a saturated wet towel, and quickly measure the wet weight M3 of the sample. The formula (1) is:

\[ \rho = \frac{\rho_{\text{water}} M_1}{M_1 - M_2} \]  

Where M1 is the dry weight of the sample, the unit is g; M2 is the weight of the sample in water, the unit is g; M3 is the wet weight of the sample, the unit is g; \( \rho \) is the bulk density of the sample, the unit is g/cm³; \( \rho_{\text{water}} \) is the density of water in g/cm³.

(2) Relative volume. The relative bulk density calculation formula (2) is:

\[ K = \frac{\rho}{\rho_0} \times 100\% \]

Where K is the relative bulk density of the ceramic sample; \( \rho \) is the density of the ZrO2 ceramic sample measured in accordance with the Archimedes drainage method, in g/cm³; \( \rho_0 \) is the theoretical density of the ZrO2 ceramic material, here 6.08g / cm³.

(3) Anisotropy. Because of the anisotropy of the ceramic sample, the lengths L0 and L1 and the widths B0 and B1 of the ZrO2 ceramic sample before and after sintering were accurately measured by Vernier calipers, and the line shrinkage of the length and width of the ceramic sample was calculated. The formula is:
(4) Microhardness. Vickers hardness is the indenter of diamond quadrangular pyramid with a face angle of 136°. Under the load of 9.8~490N, it is pressed into the ceramic surface. After a certain time, the load is removed and the surface of the material is left. Indentation. Figure 2 shows the Vickers hardness diagram. The length of the diagonal of the indentation is measured and the area of the indentation is calculated. The load per unit area, the stress, is the Vickers hardness HV (GPa). Since the ceramic is a brittle material, in many cases, the edge of the indentation is broken, and cracks are generated in the diagonal direction of the indentation. Therefore, the ceramic sample is polished and polished into a mirror surface after the sample preparation. The measurement was carried out using a Shimadzu HMV-2T microhardness tester with a load of 49 N and a loading time of 15 s. Its calculation formula is as follows:

\[
HV = \frac{P}{S} = \frac{2P \sin(\theta/2)}{d^2} = \frac{1.8544 \times 10^{-2} P}{d^2}
\]

In the formula, P is the load (N), S is the surface area mm² of the indentation, \(\theta\) is the opposite angle of the diamond indenter (136°), and d is the average length (mm) of the diagonal of the indentation.

![Fig. 2 Schematic diagram of Vickers hardness measured by indentation method](image)

(5) Bending strength. Ceramic materials are rarely tested for tensile strength due to their inherent brittleness and are typically tested for flexural strength. The bending strength of the sample was measured by a three-point bending test using a microcomputer-controlled electronic universal testing machine CMT-6104 [4]. Adjust the span of the machine to 20mm, the loading speed is 0.5mm/min, and the formula for calculating the three-point bending resistance is:

\[
\sigma = \frac{3PL}{2bd^2}
\]
In the formula, P is the loading force when the material is broken, L is the span of the three-point bending resistance of the sample, b is the width of the sample, and d is the thickness or height of the sample.

(6) Ceramic materials have strong crack sensitivity. Due to this property of ceramics, fracture mechanical properties are important factors affecting the mechanical properties of ceramic materials. Fracture toughness (KIC) is an important index for evaluating the fracture mechanics of ceramics. The SENB method was used to test the fracture toughness of the sample, and the experimental instrument was used to control the universal electronic testing machine. The SENB sample is shown in Figure 3. The calculation formula for fracture toughness is:

\[ K_I = \frac{Y \cdot 3PL}{2bh^2 \sqrt{a}} \]  

Where Y is a dimensionless coefficient, P is the loading force, L is the length of the specimen, b is the width of the specimen, h is the thickness or height of the specimen, and a is the height or thickness of the gap.

3. Preparation of ceramic slurry

(1) Prepare an aqueous solution of ammonium polyacrylate with a mass fraction of 1.0% in deionized water, and then add zirconia powder to form a solid phase content of 35%, 38%, 42%, 45%, 48%, 52%. The ceramic slurry was then adjusted to pH 3, 4, 5, 6, 7, 8, 9, 10, 11 with hydrochloric acid and ammonia water, ball milled for 20 h with a planetary ball mill, and ultrasonically dispersed for 25 min with an ultrasonic cleaner. Part of the slurry was taken, the Zeta potential of the slurry was measured by a nano-particle size and Zeta potential display, and the viscosity of the ceramic slurry was measured by a viscometer. Then, 100 ml of each set of slurry was taken to a measuring cup, and the sedimentation volume was measured for 7 days.

(2) A 48% solid phase zirconia ceramic slurry was prepared with deionized water, and the prepared ceramic slurry was divided into two groups, and 2% of ammonium polyacrylate was added to one of the groups, and the other group was unchanged. The pH of the slurry was adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10 with hydrochloric acid and ammonia water, ball-milled for 20 h with a planetary ball mill, ultrasonically dispersed for 25 min with an ultrasonic cleaner, and measured with a rotational viscometer. The viscosity of the ceramic slurry was measured by a nano-particle size and potentiometer to measure the zeta potential of the slurry. In the group without dispersing agent, seven groups were selected, the pH was adjusted to 9 with ammonia water, and then the dispersant contents were added 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 4%, respectively. The sample was placed in a 100 ml
measuring cylinder and allowed to stand for 5 days to measure the zeta potential, suspension height and viscosity of the ceramic slurry [5].

(3) Two sets of ceramic slurry with a solid content of 48% were prepared with deionized water, one group was not added with tourmaline, and one group was added with tourmaline having a mass fraction of 1.5%. The pH of the slurry was adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10 with hydrochloric acid and ammonia water, ball-milled for 20 h with a planetary ball mill, ultrasonically dispersed for 25 min with an ultrasonic cleaner, and measured with a rotational viscometer. The viscosity of the ceramic slurry was measured by a nano-particle size and potentiometer to measure the zeta potential of the slurry. In the group without dispersing agent, six groups were selected, the pH was adjusted to 9 with ammonia water, and then the tourmaline with mass fraction of 0.5%, 1%, 1.5%, 2%, 3%, 5% was added, and the measurement was performed. Ceramic paste Zeta potential and viscosity [6].

(4) Disposing ceramic slurry with solid content of 35%, 38%, 42%, 45%, 48%, 52% with deionized water, dispersant, zirconia and tourmaline powder, respectively, and observe selective slurry extrusion. Forming the precision and effect of the extrusion of the blank.

(5) Prepare a 48% solid phase zirconia ceramic slurry with deionized water and set different ball milling times to determine the viscosity of the ceramic slurry.

3.1. Effect of pH on ceramic slurry

The pH value of the ceramic slurry has a significant effect on its stability. Different pH influences the number of ions on the surface of the powder and the state of charge, which causes the electrostatic repulsion of the particles to change. The zirconia powder was slurred to adjust the pH of the slurry with hydrochloric acid and ammonia water, and the pH was measured with a 25-type acidity meter manufactured by Beijing Analytical Instruments, and then the zeta potential of the slurry was measured by a nano-particle size and potential analyzer. Figure 3.6 shows the variation of Zeta potential with pH for different solid content zirconia pastes.

![Fig. 4](image.png)

**Fig. 4** Different solid content ceramic slurry Zeta potential changes with slurry pH

It can be seen from the figure that when the slurry is acidic, the zeta potential is positive, and when the slurry is alkaline, it is negative, and as the solid content increases, the zeta potential curve of the ceramic slurry moves down overall. When the solid content exceeds 48%, the curve shows an upward trend. The particles in the slurry have the same kind of electric charge, and the particles cannot be close to each other under the action of repulsive force. Therefore, the larger the absolute value of the zeta potential, the more obvious the repulsive force is, so that the dispersion stability of the slurry is better; meanwhile, the solid content is higher. When low, the particle spacing is larger and the
repulsion is weaker. As the solid content increases, the interparticle spacing decreases and the repulsion becomes larger. When the solid content exceeds 48%, the zeta potential curve shows an upward trend. Excessive content leads to the formation of agglomerates. It can be seen from the figure that when the pH of the slurry is between 9-10 and the solid content is 48%, the absolute value of the zeta potential of the ceramic slurry is the largest, thereby determining that the slurry stability is relatively good, and the sample after forming The mechanical properties are also higher.

3.2. Effect of dispersant on ceramic slurry
The addition of an appropriate amount of dispersant can greatly reduce the amount of water in the ceramic slurry, which is an important factor in the preparation of high solids ceramic slurry. The dispersant can also change the Zeta potential of the particle surface, which affects the stability of the slurry. The effect of the dispersant on the Zeta potential is shown in Figure 5. It can be seen from the figure that after the addition of the dispersant, the Zeta potential at the same pH moves downward, which increases the absolute value of the Zeta potential, thereby increasing the repulsive force between the particles. As shown in the figure, when the slurry is acidic, its Zeta potential does not change much. As the pH increases, the Zeta potential changes more and more. When the pH is 9-10, the absolute value of the Zeta potential of the slurry has been More than 30mv. This is very important for the preparation of stable ceramic pastes.

![Fig. 5 Zeta potential change of slurry before and after the addition of dispersant](image)

4. Ceramic slurry 3D printing zirconia all-ceramic crown forming process

4.1. Process
Micro-flow extrusion 3D printing forming system is mainly a rapid prototyping technology for the formation of ceramic materials. It provides theoretical basis and experimental support for the formation of ceramic materials, and is an indispensable part of rapid prototyping technology. The forming principle is: firstly, a three-dimensional model of the target object is made on the computer and converted into an STL. file format, and then the pressure provided by the external power source is controlled by the computer to control the ceramic slurry supplied by the feeding mechanism in the nozzle. The form is uniformly extruded, and the ceramic slurry is formed on the table, and finally the process of printing out the target object by layer-by-layer accumulation. Due to the high precision of the selective slurry extrusion system, the ceramic material can be directly formed into a paste form without the need for rework, which has great application potential in the field of oral repair, which not
only allows the patient to Customizing your own aesthetic requirements and oral environment can also shorten your time and increase your success rate.

4.2. Parameter Settings

![Fig. 6 Selective slurry extrusion system to form a full crown of zirconia](image)

When the extrusion head has a diameter of 0.44 mm, a barrel diameter of 13 mm, and a pressing speed of 0.5 mm/s, the speed of the extrusion port of the selective slurry extrusion system is 8-9 mm/s. Based on the experimental values of this group, the layer thickness was 0.35 mm, and a large number of forming experiments were carried out. The results showed that when the outlet diameter of the extrusion head was 0.44 mm, the diameter of the barrel was 13 mm, the layer thickness was 0.35 mm, and the extrusion speed was 0.5 mm. At /s, the green body is formed better [7].

5. Conclusion

In this paper, a selective slurry extrusion system is used to 3D print zirconia all-ceramics, and the mechanical properties are improved by adding tourmaline to the zirconia material. Firstly, through the research on the rheology theory of ceramic slurry, the ceramic slurry suitable for the selective slurry extrusion system is prepared. Then the key parameters of the selective slurry extrusion system are determined. Finally, after the sample is sintered. The mechanical properties were tested and characterized, pointing out the effect of solids content, tourmaline content and sintering temperature on mechanical properties.

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