

Synergistic Toughening of SiC Whiskers in Gel Injection Molded Oral Braces

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Abstract

ZTA ceramic materials are widely used in the field of orthodontics, however, the existing material preparation and its properties do not meet the requirements of orthodontic instruments. In this paper, SiC whiskers with high purity, high aspect ratio and stable properties were prepared by adding high hydrogen-containing silicone oil to ZTA ceramics to improve their fracture toughness and densities, and the ceramic matrix was prepared by gelation, curing and sintering with cellulose acrylic acid graft co-polymer as binder. In particular, the synergistic toughening effect with zirconia in the gel-injected film of oral bracket materials.

Keywords

ZTA Ceramics; Gel Injection Mold; SiC Whiskers; Synergistic Toughening Technology.

1. Introduction

Carberry[1] et al. summarized the development of orthodontic brackets into five stages: the 1st generation orthodontic brackets were metal brackets with metal wear rings; the 2nd generation orthodontic brackets were metal brackets directly bonded to the tooth surface without metal wear rings; the 3rd generation orthodontic brackets were lingual brackets belonging to lingual braces; the 4th generation orthodontic brackets were plastic brackets; and the 5th generation orthodontic brackets were ceramic brackets. the early 20th century was the early stage of orthodontic bracket development. The early 20th century was the early stage of orthodontic bracket development, orthodontic bracket materials are mostly precious metal materials, followed by other types of metal brackets, such as stainless steel brackets, magnetic brackets, etc.[2] In 1986, ceramic orthodontic brackets were introduced. After the introduction of ceramic brackets, it was found that the hardness, tensile strength, bio-compatibility and bond strength with enamel of ceramic brackets are much better than traditional metal oral dislocations, and ceramic brackets have a more desirable appearance, but ceramic brackets are brittle and prone to fracture.[3, 4] Subsequently, a lot of research on toughened ceramic brackets was conducted by domestic and foreign material scientists, among which the most extensive and effective research on ZTA ceramic bracket materials was conducted.

The all-ceramic bracket material studied and prepared in this paper belongs to ZTA ceramics, whose toughening and reinforcing materials include, in addition to calcium oxide, homemade low-cost, high-performance SiC whiskers, which are known as the "king of whiskers"[5, 6]. High strength, high modulus of elasticity, good chemical stability, etc.[7] Silicon carbide whiskers have been extensively studied in the toughening of polymer-based [8], metal-based [9, 10] and

ceramic-based [7]composites.[11]The phase change in zirconia is the basis for the toughening of zirconia ceramics, so the toughening effect is limited by the temperature. At medium to high temperatures, the thermodynamic state is stable and the phase change toughening effect disappears. The fracture stress and the critical stress of the phase change are mutually constrained within the ceramic, and the strength and fracture toughness values are often not maximized at the same time.[12]

The molding technology of the material also determines the micro-structure of the material to a certain extent, and the gel injection molding technology will be used in this project. Gel injection molding is a new technology for preparing complex shaped ceramic parts. Although this technology has not been developed for a long time, it is widely used because of its stable performance, short molding cycle, and wide range of mold selection.[13, 14]

2. Experimental Process

2.1. Experimental Drugs

Sodium carboxymethyl cellulose (CMC), acrylic acid (AA), zirconium oxide (ZrO_2), ammonium persulfate (APS), aluminum oxide (Al_2O_3), SiC whiskers, trimonium citrate ($C_6H_5O_7(NH_4)_3$), magnesium oxide (MgO), titanium dioxide (TiO_2), silicone grease, etc.

2.2. Experimental Method

Firstly, SiC whiskers with stable properties and uniform and controllable morphological properties were prepared, followed by the preparation of ceramic powder gels, and finally, SiC whisker-toughened ZTA ceramic bracket samples were produced by curing and sintering. In this process, the toughening effect of different forms of SiC whiskers in the bracket material was studied, as well as the factors affecting the distribution and toughening effect of SiC whiskers. The synergistic toughening effect of SiC whiskers with zirconia in the prepared oral brackets was systematically investigated.

In this experiment, ZTA ceramics were prepared by gel injection molding, toughened by SiC whiskers, and a "three-factor, three-level" orthogonal experiment was designed using CMC content, ZrO_2 solid content, and SiC whisker content as three variables [15].

Table 1. Orthogonal experimental design

Serial No	CMC(g)	ZrO_2 (wt%)	SiC whiskers(wt%)
1	0.80	27	4
2	0.80	30	3
3	0.80	33	2
4	0.85	27	3
5	0.85	30	2
6	0.85	33	4
7	0.90	27	2
8	0.90	30	4
9	0.90	33	3

The specific operation steps are: Firstly, a certain amount of CMC is dissolved in 50 ml of deionized water and stirred at 30°C in water to make sol-gel, and when no agglomerates exist in the solution, it indicates that the sol-gel is completed. Weigh 1 g of MgO and 4 g of TiO₂, and then weigh 0.26 g of triammonium citrate dissolved in 5 ml of deionized water. The ZTA ceramic powder and SiC whiskers were mixed with the above raw materials and put into a ball mill with a ball mill speed of 198 r/min and a ball milling time of 1.5 h. 7.5 ml of AA monomer was added and the ball mill was continued at the same speed to obtain a concentrated suspension with a high solid phase volume fraction. The initiator APS was added and 0.8 g of APS was dissolved in 10 ml of deionized water and the ball milling was continued for 5 h. At this time, the AA monomer polymerized, resulting in a wet blank with a flexible three-dimensional mesh structure. The prepared wet blanks were injected into the molds and a layer of silicone grease was applied to the inside of the molds for easy release after drying. After that, the mold was put into a vacuum drying oven for 12 h at 35°C, and then the temperature was increased to 60°C for 24 h. Gradually increasing the temperature of drying can avoid the wet blank from shrinking too fast and leading to cracking. The dried billets were slightly trimmed and sintered at a rate of 4°C/min below 750°C and 2°C/min from 750°C to 1500°C. The samples were held at 1500°C for 1 h to obtain ZTA ceramics.

3. Results and Discussion

3.1. Relative Densitometry Analysis

The bulk density of ZTA ceramics was tested by Archimedes drainage method [16], and the relative densities of each group of specimens were calculated by using the formula, and the data were substituted into the orthogonal experimental table to calculate the extreme difference analysis table for each factor when the relative densities were indicators, and the data are shown in Table 2

Table 2. Results of orthogonal experiments with relative densities as indicators

Volume density	CMC (g)	ZrO ₂ (wt%)	SiC whiskers(wt%)
average value k ₁	3.634	3.411	3.158
average value k ₂	3.390	3.228	3.158
average value k ₃	2.538	2.922	3.245
Range R	1.096	0.489	0.087

The test factors and levels were plotted against the objective function to obtain the trend curve of the effect of each factor level on the maximum relative densities, as shown in Figure 1.

According to Figure 1 and Table 2, it can be seen that:

- (1) CMC dosage is the most important factor affecting the relative densities of ZTA ceramics. The relative densities of ZTA ceramics decrease with the increase of CMC dosage, and reach the maximum when the CMC dosage is 0.80 g.
- (2) The influence of ZrO₂ powder on the densities of ZTA ceramics is also very large, and the relative densities of ZTA ceramics also decrease as the content of ZrO₂ powder increases, and the relative densities of ZTA ceramic materials are greatest when the content of ZrO₂ powder is 27%.
- (3) The amount of SiC whisker addition has almost no effect on the relative denseness of ceramic materials. The first and second levels of SiC whisker addition have the same degree of

influence on the denseness of ceramic materials, and the difference between the third level and the first two levels is not large.

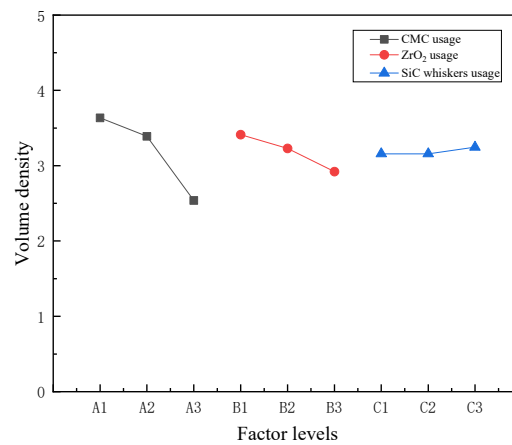


Figure 1. Effect of factors on relative densities

In summary, the best relative denseness of the ceramic material was achieved with a CMC dosage of 0.8 g, a ZrO₂ powder content of 27%, and a SiC whisker addition of 2%.

3.2. Flexural Strength Test

Flexural strength: also known as bending strength, is the ultimate breaking stress per unit area of the specimen when subjected to bending moment, is an important indicator of material strength.

Due to the epidemic, the universal testing machine was temporarily unavailable for testing, and this experiment was conducted with an electric tablet press instead. A three-point flexural strength test was performed by taking two padded sticks so that their internal spacing was 25 mm fixed under the indenter of the press, then taking a press rod and pressing it between the specimen and the indenter, and tightening the indenter to make the press rod fixed. Before the test, the fracture section width and fracture section height of each specimen are recorded, and two specimens are taken for each group of ratios, and the average value is taken as the final flexural strength value. The formula for three-point flexural strength is:

$$\delta = \frac{3PL}{2bh^2} \text{ (formula 3.2.)}$$

the formula

δ —flexural strength, MPa;

P—fracture load, N;

L—span between the two pivot points of the support, mm;

b—fracture section width, mm;

h—height of fracture section, mm.

The nine groups of samples were tested for their flexural strength in turn using an electric tablet press, and the following data were obtained after calculation and unit conversion. As shown in Table 3

Table 3. Flexural strength results

Serial No	1	2	3	4	5	6	7	8	9
Flexural strength	107.73	95.32	88.60	84.84	98.87	75.48	100.64	110.29	108.33

The calculated results were substituted into the orthogonal experiment table to calculate the mean and extreme deviation of each factor, as shown in Table 4

Table 4. Results of the orthogonal test with flexural strength as the index

Flexural strength	CMC (g)	ZrO ₂ (wt%)	SiC (wt%)
average value k_1	97.217	97.737	97.833
average value k_2	86.397	101.493	96.163
average value k_3	106.420	90.803	96.037
rangeR	20.023	10.690	1.796

The experimental factors and levels were plotted against the objective function to obtain the trend curve of the effect of each factor level on the maximum flexural strength, as shown in Figure 2

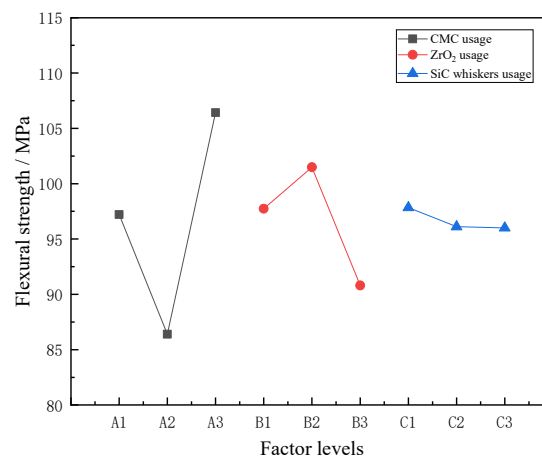


Figure 2. Trend curve of the influence of the level of each factor on the maximum flexural strength

According to Figure 2, Table 4 it can be seen that:

(1) In this group of experiments, the CMC content was the main influencing factor of ceramic properties. The flexural strength of ZTA ceramics decreased with the increase of CMC dosage and then increased, and the flexural strength of ZTA ceramics reached the minimum when the CMC dosage was 0.85 g. It is assumed that the amount of CMC is too small and not stable enough to connect the whole ceramic matrix structure, but after the amount of CMC is high, the three-dimensional mesh structure of AA monomer polymerization is more complete and the flexural strength of the specimen is improved. The high dosage of CMC led to the increase of viscosity of the system, resulting in uneven particle distribution, which was not conducive to ceramic densification.

(2) ZrO₂ solid content is the second influencing factor, the flexural strength of ZTA ceramics first reaches the maximum value with the increase of ZrO₂ dosage, then increase the dosage of ZrO₂ powder, the flexural strength of ceramics decreases sharply, when the dosage of ZrO₂ powder is 30%, the flexural strength of ceramics reaches the maximum value. This is because stress-induced phase change toughening is the toughening principle of ZrO₂, adding the right amount of ZrO₂ powder can make ZrO₂ phase change from tetragonal phase (t) to monoclinic

phase (m), the volume expansion generated by the phase change absorbs the elastic stress of ceramic samples and reduces the crack expansion force, the microcrack caused by volume expansion also absorbs energy, thus hindering crack expansion. too much ZrO_2 powder added, its generated The volume expansion will cause too many cracks in the ceramic material, resulting in a decrease in the density of the ceramic material, and too many micro-cracks will meet to form large cracks, which will eventually lead to a decrease in the flexural strength of the ceramic material.

(3) The amount of SiC whisker addition has the least effect on the fracture strength of ZTA ceramics, which is increasing with the amount of SiC whisker. Theoretically, SiC whiskers can absorb fracture energy, and when cracks encounter whiskers, the whiskers enhance the composite by crack deflection, crack diaspora, and whisker pull-out.

In summary, when the flexural strength of the material is used as the index, the optimal combination for this experiment is: A3B2C1. i.e., CMC addition of 0.90 g, ZrO_2 content of 30%, and SiC whisker addition of 4%.

4. Conclusion

In this paper, a "three-factor, three-level" orthogonal experiment was designed with CMC content, ZrO_2 solid content and SiC whisker content as three variables, and nine sets of specimens were prepared to investigate the relative densities and flexural strength of the prepared ZTA ceramic specimens. SiC whiskers and ZrO_2 nanoparticles toughening, the conclusions are as follows.

(1) the amount of CMC is the main factor affecting the performance of ZTA ceramic material, it will affect the stability of the whole ceramic material structure, adding too much or too little will make the ZTA ceramic performance lower, only adding the right amount of CMC will make the best performance of ZTA ceramic.

(2) ZTA ceramics, Al_2O_3 powder and ZrO_2 powder ratio between the best ratio, too much or too little ZrO_2 content will make the ceramic matrix porosity, thereby reducing the ZTA ceramic material flexural strength and relative denseness, the best ratio of ZrO_2 in this group of experiments is 30% of Al_2O_3 powder.

(3) SiC whisker is a good toughening ZTA ceramic material, but it does not participate in the toughening of the ceramic matrix structure, because its properties and size are too small, it is easy to agglomerate and form clumps when mixed with ceramic slurry, and it is not easy to be uniformly dispersed in the ceramic slurry.

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