

ZTA-SiC_w Ceramic Modified by Pseudo Bohemite for Dental Brackets

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Abstract

In this study, zirconia (ZrO₂) toughened alumina (Al₂O₃) ceramics(ZTA) with synergistic toughening effect of Silicon Carbide Whisker (SiC_w) were prepared, which could be used as dental brackets materials. Firstly, a gel electric double layer was formed though the gelation function of pseudo-boehmite, using ammonium citrate as dispersant, concentrated nitric acid as initiator. Powder of ZrO₂, Al₂O₃ and SiC_w were distributed homogeneously in the electric double layer. Followed by drying and sintering, ZTA-SiC_w ceramics dental brackets materials were obtained. The optimal preparation technology was selected through orthogonal design by testing the bending performance and the water absorption of samples prepared under different condition. The microstructure and phase composition of ZTA-SiC_w ceramics materials were analyzed by Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) to explore the synergistic toughen mechanism of ZrO₂ and SiC_w. Results showed that, the sample which can meet the best requirement was prepared under the following condition: ZrO₂ content of 35%, SiC_w of 2.5%, and sintering at 1560°C for 6h. This sample was better suitable for making dental bracket.

Keywords: Pseudo-boehmite; Synergistic Toughening effect; Bending performance; Preparation technology

Introduction

With the development of society and the change of aesthetics, people's requirements for material standards of life are increasing. Orthodontics disciplines are becoming more and more popular in China. Materials used for orthodontic treatment are developing as the progress of aesthetics. Among all orthodontic materials, ceramic material has been the ideal one due to its beautiful color, stable physicochemical performance, anti-adhesion of plaque, and good biocompatibility [1,2]. However, ceramic orthodontic materials are brittle, and the preparation depends on special raw materials and complex production process. These shortages of ceramic orthodontic materials limit the application of all-ceramic restoration [3]. Thus, how to improve the mechanical properties and simplify preparation process of the ceramic orthodontic materials, those become the problem urgent need to be solved.

Compared with the pure Al₂O₃ ceramics, ZTA (ZrO₂ toughenedAl₂O₃) ceramic has better mechanical strength, fracture toughness and thermo-stability. However, properties of ZTA ceramic vary a lot due to different ratio of raw materials, complex preparation process, and poor mechanical properties of single phase strengthening and toughening ZTA ceramics, mismatch of phase and matrix and so on [4-7]. Especially, the uneven dewaxing process in traditional method may cause ceramic body deformation and easy to break [8]. In order to improve the mechanical properties of ZTA ceramics, the research about multiple toughening synergistic mechanisms and simple preparation process has become important research direction. Synergistic toughening technology of the study of ZTA ceramic has been reported and has obtained certain achievement [9,10]. However, the products rarely used in dental materials due to the biological compatibility, security, or unaesthetic problem. In addition, simple preparation technology could not give consideration to oral material performance.

Based on what has been discussed above, ZTA ceramics bracket with synergistic toughening effect of SiC_w was prepared, and its synergistic toughening mechanism was discussed in this study. In addition, a new ceramic preparation method using pseudo-boehmite gel without dewaxing process was proposed in this paper. In this method, firstly, ceramic raw materials and strengthening agent were evenly distributed in the electric double layer through gelation function of pseudo-boehmite [11]. Then, slurry with good mobility was formed. Under the effect of temperature, the ceramic body was formed through in situ gelation of ceramic powder. Finally, the desired material was obtained after sintering. Without the dewaxing step, this method was nontoxic and simple. Equipments used in this method were simple. Ceramic body with complex structure could be molded and showed better mechanical strength. Thus, this ceramic body could be mechanical processed into different shape before sintering to satisfy customer demand [12]. In this study, SiC_w toughened ZTA (ZTA-SiC_w) complex phases ceramic materials were prepared based on synergistic toughening effect between ZrO₂ and SiC_w with a simple and nontoxic method.

Materials and Methods

Materials

Alumina (Al₂O₃) (industrial pure grade), zirconia (ZrO₂) ($\geq 95\%$ purity), and pseudo-boehmite (AlOOH) (industrial pure grade), were purchased from Nuoda chemical Co., Ltd (Zibo, China). Ammonium citrate ((NH₄)₃C₆H₅O₇) ($\geq 95\%$ purity) was purchased from Bodi chemical Co., Ltd (Tianjin, China). Concentrated nitric acid (HNO₃) (analytical pure grade) was purchased from Shijiazhuang reagent factory (Shijiazhuang, China). Silicon Carbide Whisker (SiC_w) (industrial pure grade) was purchased from Jie Chuang materials technology Co., Ltd. (Xuzhou, China). All materials were used as received. Distilled water was generated from Key Laboratory of Inorganic Nonmetallic Materials of Hebei Province.

Methods

This experiment was designed by orthogonal method. The solid content was set at 37% based on former experimental results [13]. Density of each raw material was calibrated by pycnometer method before the mixture calculation [14]. The orthogonal design was shown in Table 1.

A mixture of distilled water, pseudo-boehmite, and ammonium citrate, with the mass ratio of 100: 9: 0.3 was added into a planetary ball mill and milled for 80 min at a speed of 190r/min. Then certain amount of Al₂O₃, ZrO₂ (0.02 Y) and SiC_w were added, followed by 80 min to get slurry. The pH of this slurry was adjusted to 3-4 by diluted nitric acid. Another 60-min mill was performed, followed by screening out mill beads, removing

bubbles, and gel formation. Gel was injected into molds coated with silicone grease and dried in air dry oven. During the drying process, temperature was increased from 35°C (hold on 12 h) to 60°C. hold on 24 h). Sintering process was carried out as orthogonal test method. The sintered product was cut into ceramic sample with size 30mm \times 5mm \times 3.5mm.

Characterization

Bending strength of sample was measured by three-point bending test method with span of 25 mm, pressure head loading speed of 1 mm/min (GB/T 1445-1993). Water absorption was measured by Archimedes Drainage method [15]. X-ray diffraction pattern of samples was recorded from 20° to 80° at a scanning rate of 10°/min by D/MAX2500PC diffract meter. Microstructure of sample was investigated by ZEISS LEO Supra35 field emission Scanning Electron Microscope (SEM) (Carl Zeiss NTS Ltd., UK).

Results and Discussion

The Orthogonal Test Analysis

NO.	ZrO ₂ (mass content %)	Temperature (T/°C)	Experimental		Bending Strength (MP)
			Time (t/h)	SiC _w (mass content %)	
1	25	1550	4	3	191.06
2	25	1560	5	5	195.65
3	25	1570	6	7	141.59
4	30	1550	5	7	145.41
5	30	1560	6	3	250.61
6	30	1570	4	5	196.03
7	35	1550	6	5	219.51
8	35	1560	4	7	153.48
9	35	1570	5	3	237.48
\bar{K}_1	176.1	185.33	180.19	226.38	
\bar{K}_2	197.35	199.91	192.85	203.73	
\bar{K}_3	203.49	191.7	203.9	146.83	
R	27.39	14.58	23.71	79.56	

Table 1: The orthogonal test analysis.

Orthogonal test results were listed in Table 1. The experiment was designed according to four factors and three levels orthogonal table. Four factors included ZrO₂ content, temperature, time and SiC_w content. Each factor set up three levels. The parameters involved in the calculation based on following equations

$$\bar{K}_i = \frac{K_i}{3} \quad (1)$$

Ki was defined as sum of bending strength at the level "i" corresponding to a factor

$$R = \bar{K}_{\max} - \bar{K}_{\min} \quad (2)$$

Based on the value of bending strength was plotted against ZrO₂ content, temperature, holding time, and SiC_w content respectively as shown in Figure 1. The results showed that bending strength increased as ZrO₂ content, it reached to the maximum value with ZrO₂ content of 35%. Among the three-temperature tested in this study, sample sintered at 1560°C showed the best bending strength. Bending strength also increased along with holding time, it reached to maximum with holding time of 6h. While, the bending strength decreased with increase of SiC_w content. Sample showed maximal bending strength, when SiC_w content was 3%. Among the above four factors, SiC_w content has the largest R, so it was the main factor that affected the bending strength of samples.

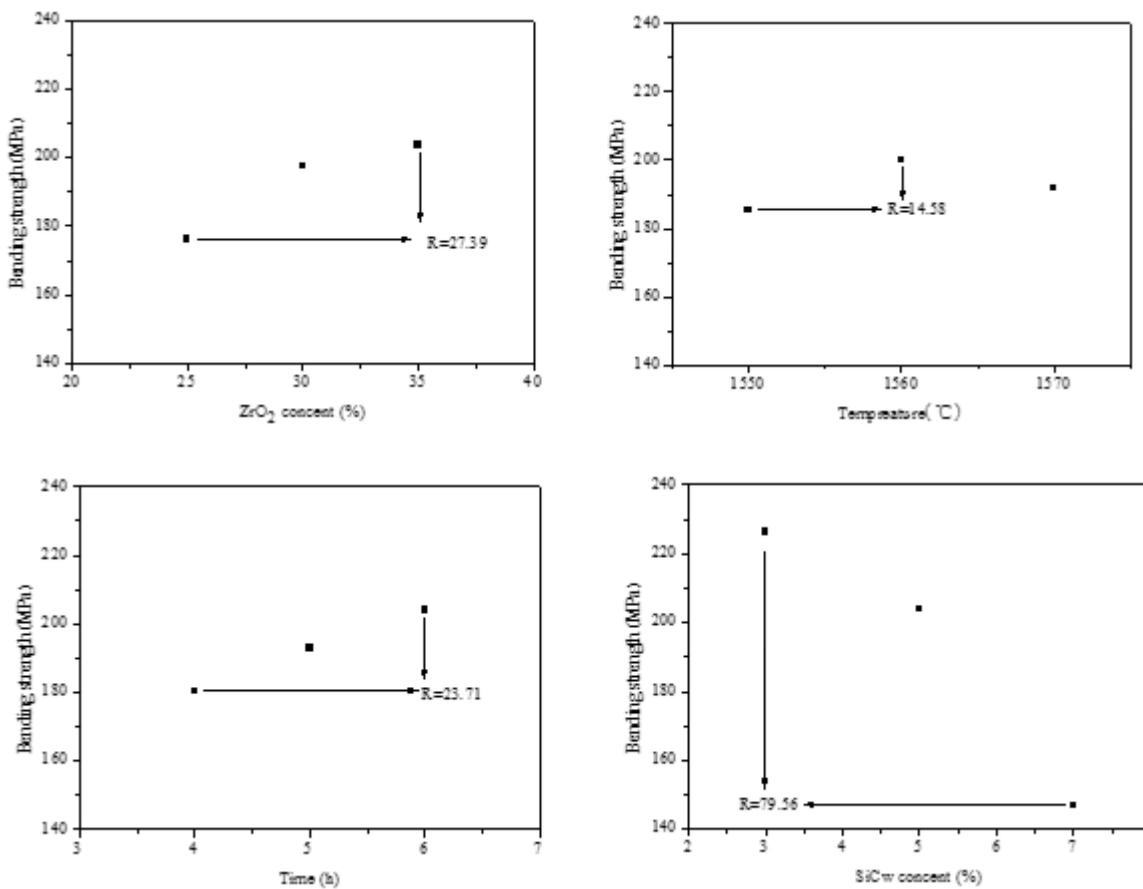


Figure 1: The trend diagram of bending strength and factors.

Based on above analysis, the best preparation process was summarized as following: ZrO₂ content of 35%, sintering temperature of 1560°C, holding time for 6 h, and SiC_w content of 3%. Among the four factors which could affect bending strength, SiC_w content took the main role, followed by ZrO₂ content, holding time and sintering temperature. And the R value of SiC_w content was great higher than that of the other three factors. Because the optimum process was beyond the scope of the nine orthogonal tests, we need to do confirmatory test.

Confirmatory Test

SEM photo of samples from NO.5 orthogonal test and confirmatory test were shown in Figure 2. In orthogonal test, sample made by the No.5 test performed best in all characterization. Compared with NO.5 orthogonal test, sample of confirmatory test had better density on both surface and structure. And the particle size of confirmatory sample was more uniform. The bending strength of confirmatory sample was 267.80MPa, which was bigger than that of the NO.5 orthogonal test (250.61MPa). The result of confirmatory test demonstrated that the optimal process proposed in this study was correct.

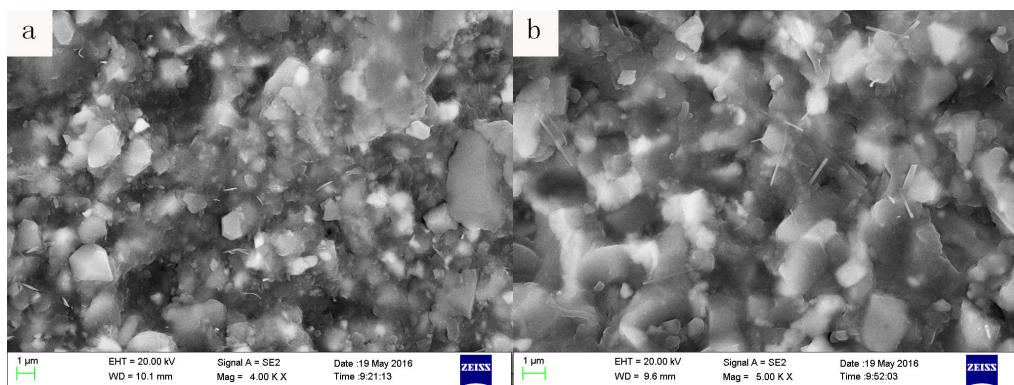


Figure 2: Surface morphology images of ceramic samples. (a): NO.5 orthogonal test; (b): confirmatory test.

Effect of SiC_w Content on Samples

Orthogonal test results showed that among the four factors which affected bending strength, SiC_w content took the main role. And bending strength was proportional to SiC_w content within the content range measured in former orthogonal test. The effect of SiC_w content on bending strength should be further researched. A larger SiC_w content range with smaller gradient (set as 1.5%, 2%, 2.5%, 3%) was adopted in following experiment.

The bending strength of samples prepared with different SiC_w content according to modified formula was shown in Figure 3. This figure showed that the ceramic samples had excellent bending strength, which increased as SiC_w content first and then decreased. The maximum of bending strength was 274.14 MPa with 2.5% SiC_w content.

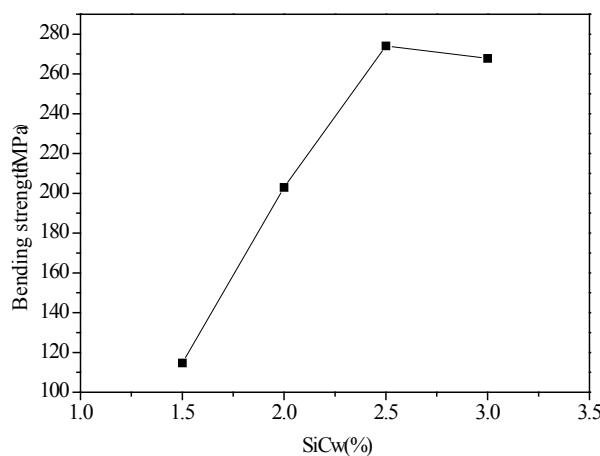


Figure 3: The bending strength of the sample with different SiC_w contents in further research.

For ceramic dental bracket materials, water absorption should within the range of 0~2% to satisfy the application requirement [16]. Generally, there was certain amount of porosity in green body. Particles in ceramic body were supported by pseudo-boehmite network structure. After sintering, the touch surface between particles was increased, which leaded to particles accumulation. The center distance between particles decreased continuously as the result of particle volume shrinkage. Grain boundary was formed consequently. During sintering, pores in ceramic body were deformed, shrank, separated and removed. Finally, dense ceramic body was obtained. Water absorption testing results were shown in Table 2. Results showed that water absorption increased as the content of SiC_w. When content of SiC_w was higher than 2.5%, the water absorption was beyond the desired range of 0~2%. The small water absorption is corresponding small porosity to a certain extent in Archimedes method. Thus, among all SiC_w contents tested in this study, sample with 2.0% SiC_w content had the lowest porosity and highest density.

contents of SiC _w (%)	1.5	2	2.5	3	5	7
water absorption (%)	1.74	1.47	1.64	4.61	6.75	7.61

Table 2: Water absorption of samples with different contents of SiC_w.

In the previous discussions, as SiC_w content increased, sample has a better particle distribution and better bending strength, as shown in Figure 3. However, as SiC_w content increased, water absorption of sample increased. Considering bending strength and water absorption, the maximum bending strength of 274.14MPa and qualified water absorption were obtained at 2.5% SiC_w content. So, the best content of SiC_w was 2.5%.

Toughening Mechanism

Toughening Mechanism of ZrO₂

XRD pattern of the ceramic sample was shown in Figure 4. We can find that amount of non-room temperature phase tetragonal zirconia (t-ZrO₂) was remained [17-19]. In this study, ZrO₂ and Al₂O₃ were distributed evenly in electric double layers through the gelation function of pseudo-boehmite. An independent network structure was formed which could prevent the precipitation and stratification of ZrO₂ and Al₂O₃ with different diameters. Thus, fine ZrO₂ particles stacked homogenously in the matrix of Al₂O₃. ZrO₂ and Al₂O₃ had different thermal expansion coefficient. So, during sintering and cooling, the expansion of Al₂O₃ particle had a compressive stress on ZrO₂, which limited transformation of ZrO₂ from t-ZrO₂ to monoclinic zirconia (m-ZrO₂). It leaded to the residues of t-ZrO₂, as shown in Figure 4. When ceramic

was under external shock and cracked, t-ZrO₂ could change the conduction direction of crack, shield crack tip, and prevent the expansion of crack [20,21]. Thus, the brittleness of ceramic sample was decreased and bending strength was increased. In sum, ZTA ceramic prepared by pseudo-boehmite gel could not only increase ceramic density but also take full advantage of toughening effect of ZrO₂.

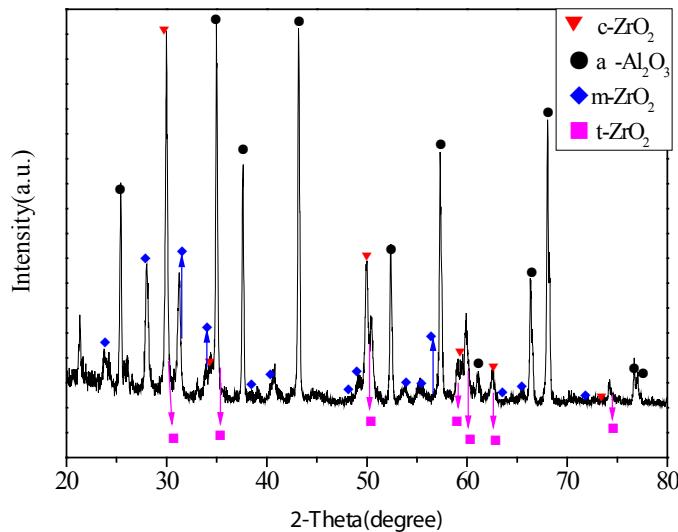


Figure 4: X-ray pattern of the ceramic sample.

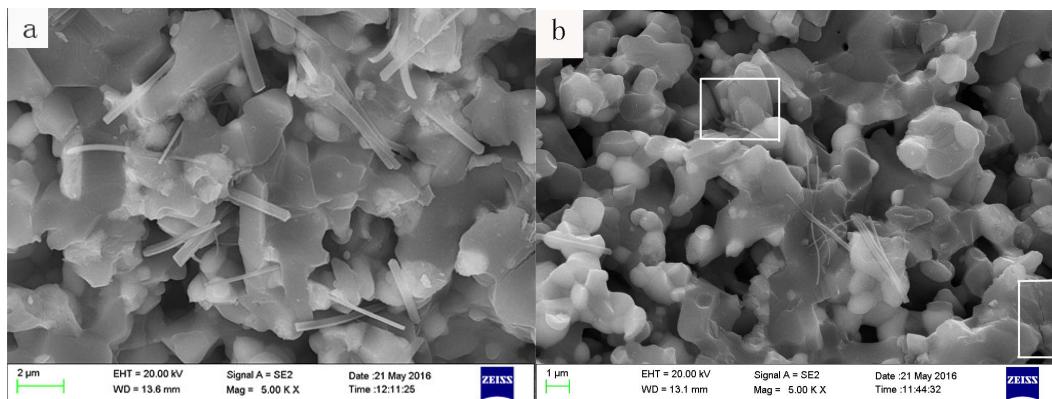
Toughening Mechanism of SiC_w

SEM images of fracture surface were shown in Figure 5. Whisker pull-out phenomenon could be observed in Figure 5 (a). When crack propagation encountered high strength whisker, near the crack tip, the interfacial shear stress between whisker and matrix reached to shear yield strength of matrix. The whisker would not break due to high tensile strength. Instead, it would be pulled out from the matrix to consume external load energy and generate fine crack to absorb more energy. In this way, ceramic was toughened by whisker [22].

The parts of Figure 5 (b) marked with white box showed the crack deflection mechanism. Crack deflection happened when the binding force between whisker and matrix interface was weak. When the cracks extended from matrix to whisker, crack would grow along grain due to the dissociation of whisker and matrix. Crack deflection could not only increase new surface area, but also prevent the crack grow beyond critical size, thus the strength has been increased [22].

In sum, toughening effect of SiC_w was shown as whisker pull-out phenomenon and crack deflection in this experiment. Besides, the addition of SiC_w had inhibition effect on particles growth in Al₂O₃ matrix. Thus, pores and cracks could be avoided

due to coarse grain and quick grain boundary migration. All of these will benefit strength of ceramic materials.



Figures 5(a-b): SEM images of fracture surface of ceramic samples.

Synergistic Toughening Mechanism

The toughness of ZTA-SiC_w composite ceramics should be determined by the combination of whisker pull-out phenomenon, crack deflection, and t \rightarrow m-ZrO₂ (tetragonal zirconia-to-monoclinic zirconia) phase transformation toughening mechanisms.

Although SiC_w had inhibition effect on particles growth in Al₂O₃ matrix, the residual content of t-ZrO₂ was reduced as the addition of SiC_w. As a consequence, the t \rightarrow m-ZrO₂ phase transformation toughening effect will decreased as the increase of SiC_w content. While the toughening effect from crack deflection and whisker pull-out phenomenon were increase. The experiment results showed that, the synergistic toughening effect of the three-mechanism obtained maximum value when SiC_w content was 2.5%. As the SiC_w content continue to increase, the synergistic toughening effect decreased. In addition, quick furnace cooling rate in the experiment would lead to thermal expansion coefficient mismatch. And this mismatch could generate tensile stress to induce t \rightarrow m-ZrO₂ phase transformation. Consequently, t-ZrO₂ content will be decreased, as well as its toughening effect.

In sum, the premise of synergistic toughening mechanism for ZTA-SiC_w composite ceramic was that: (a) volume expansion generated from t \rightarrow m-ZrO₂ phase transition should not impede whisker pulling-out and separation from matrix interface [23]. (b) The addition of SiC_w should not reduce residues of t-ZrO₂. (c) A proper furnace cooling rate was necessary to minimize the phase transition of t \rightarrow m-ZrO₂ in advance.

Conclusions

- In this study, a structure stable ceramic green body was prepared with ZrO₂, Al₂O₃, and SiC_w evenly distributed in electric double layer network through gelation function of pseudo-boehmite.

- The addition of SiC_w had obviously toughening and reinforcement effect on ZTA composite ceramic. As the content of SiC_w increased, the strength of samples increased first then decreased. The maximum strength of 274.14MPa was obtained at 2.5% SiC_w content. There was a synergistic toughening effect between phase transformation and whisker toughening.
- The best preparation technology of ZTA-SiC_w dental brackets ceramics by pseudo-boehmite was summarized as following: ZrO₂ content of 35%; SiC_w content of 2.5%; holding time for 6h; and sintering temperature of 1560°C.

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