Research Article

Preparation of CePO_4 Modified ZrO_2 Ceramics with Different Particle Sizes and Their Mechanical Behaviors

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Different particle size 3 mol% Y_2O_3 -stabilized tetragonal zirconia polycrystalline (3Y-TZP) coated with CePO_4 was prepared by a coprecipitation method and the effect of zirconia particle-size on its mechanical properties was investigated. The phase composition and microstructure of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), respectively. The machining characteristic of as-prepared samples was calculated to be 0.54 for a zirconia particle size of around 30–50 nm. In this grain size range, the hardness, fracture toughness, and bending strength of the coated sample were found to be 10.72 GPa, 5.76 $\text{MPa}\cdot\text{m}^{1/2}$, and 463 MPa. Our results show that the grain size of the zirconia before coating greatly influences the mechanical properties of the coated samples because the different particle sizes result in different fracture styles.

1. Introduction

Zirconia is widely used in the fields of oxygen sensors, catalysts, solid oxide fuel cells, and structural engineering ceramic currently [1] because of its high temperature ionic conductivity, good mechanical strength and toughness, and corrosion prevention characteristics. However, its brittleness and hardness hinder the application in dentistry to a great extent [2]. Some studies have shown that adding an auxiliary phase [3], which has a low mechanical strength, or adding some rare earth phosphate [4] to zirconia can efficiently improve its machinability. We have previously studied the mechanical property of CePO_4 coated ZrO_2 and determined the optimum CePO_4 content and the best sintering temperature [5].

A finer grain size gives ceramic materials better mechanical properties [6], and when the size ranges from microns to the nanoscale, a series of groundbreaking new features such as low-temperature superplasticity and scalability are produced. We tried to control the grain size growth of zirconia by sparking plasma sintering and have made some

progress [7]. However, a question arose about the effect of the grain size of zirconia on the coating process and the mechanical properties of the coated products. We reviewed the literature and found no research concerned with this question.

In this study, we prepared different particle size 3 mol% Y_2O_3 -stabilized tetragonal zirconia polycrystalline (3Y-TZP) coated with CePO_4 , and the effect of grain size on the microstructure and mechanical properties of the sintered samples was determined to further improve the machinability of the zirconia.

2. Materials and Methods

2.1. Materials. 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP; Hangzhou Wanjing Advanced Materials Co., Ltd., Hangzhou, China) was the main starting material used in this study. In accordance with the grain size, the zirconia powder was divided into four groups: group A (50–80 nm), group B (100–150 nm), group C (300–500 nm), and group D (500 nm–1 μm). Transmission electron microscopy (TEM) images of

FIGURE 1: TEM images of the 3Y-TZP powders.

the four groups are shown in Figure 1. The other chemicals such as polyethylene glycol 20000 (AR) and cerous nitrate (AR) were all purchased from Beijing Chemical Plant.

2.2. Coating the Zirconia Powder. In this study, 3 wt% 3Y-TZP powders with different particle sizes were dispersed ultrasonically in distilled water for 10 minutes. PEG was added as a dispersant at 2% of the weight of 3Y-TZP, and ammonium citrate was added at 1.5% of the weight of 3Y-TZP as a release agent. They were dissolved in deionized water at a temperature of 50°C and then added to a suspension of 3Y-TZP. An as-prepared $\text{NH}_4\text{H}_2\text{PO}_4$ solution was added to the suspension after 10 minutes of ultrasonic treatment and then the pH of the solution was adjusted to 4.0–5.0 via adding H_3PO_4 . $\text{Ce}(\text{NO}_3)_3$ was added drop by drop to the solution up to 1/3 of the mole ratio of 3Y-TZP and the mixture was stirred for 2 h at 50°C. Finally, the solid-phase content was separated by centrifugation and dried in an oven, milled, calcined at 800°C, and then milled again. The powder was analyzed using TEM.

2.3. Sintering Process and Microstructure Characterization. The coated and uncoated powders were produced in a steel mold, mashed, sieved to 50 meshes, and reformed. The formed body was pressed under a load of 200 MPa for

5 min in a cold isostatic press machine. Then the body was sintered as follows: the temperature was raised to 450°C at a rate of 100°C/h and maintained for 1 h, and then it was raised to 1200°C within 2.5 h to decrease the tetragonal to monoclinic phase transition. Finally, the temperature was raised to 1250°C, 1300°C, 1350°C, 1400°C, 1450°C, and 1500°C, respectively, at a rate of 200°C/h and maintained for 2.0 h. The Archimedes method was used to measure the density of the samples. An electronic vernier (accuracy: 0.01 mm) was used to determine the diameters of the samples before and after the sintering process and the values were l_0 and l , respectively. The formula $[(l_0 - l)/l_0] \times 100\%$ was used to determine the linear shrinkage.

The phase and the microstructure of the as-prepared ceramic samples were determined by using X-ray diffraction (XRD) (Rigaku D/MAX-2550V) and scanning electron microscopy (SEM). Besides, transmission electron microscopy (TEM) was used to determine the morphology of the particles.

2.4. Mechanical Testing. The sintered ceramics samples were shaped into cuboid with dimensions 3 mm × 4 mm × 36 mm and 4 mm × 6 mm × 30 mm, respectively. An EZ-100 Universal Test Instrument was used to measure the bending strength by means of the three-point bending method and

FIGURE 2: XRD patterns of the uncoated and coated 3Y-TZP powders.

the fracture toughness of the as-prepared samples and the rate of loading was set at 0.5 mm/min. The bending strength was calculated by using the equation $\sigma_f = 3P_0 \times l / (2b \times h^2)$ (P_0 is the load; l is the span of the sample; h is the height of the fracture; b is the width of the fracture), and the fracture toughness was calculated according to the formula $K_{IC} = 3Y \times P \times L \times a^{1/2} / (2b \times w^2)$ (P is the load; L is the span; w is the height of the sample; a is the depth of the fracture; b is the width of the sample; Y is a dimensionless coefficient). The hardness of samples was measured in HD-187.5 type Brinell's Hardness Tester. Load was kept on stable value as a force of 294 N (denoted as P) and the HXD type microhardness equipment was used to determine the length of the diagonal of the indentation (denoted as d). The formula $HV = (1.8544P/d^2) \times 10^{-3}$ was used for the hardness test. Finally, the machinability rating (M) was calculated using the equation $M = K_{IC}/HV$.

Seven samples in each experimental group were selected for evaluation. One-way analysis of variance (ANOVA) and Tukey's multiple comparison test were used to analyze the data. The significance was set at 0.05.

3. Results and Discussion

The TEM images show that the particle sizes of the four kinds of 3Y-TZP powders that were purchased from Hangzhou Wanjiang Advanced Materials Co., Ltd., are 30–50 nm, 50–100 nm, 100–300 nm, and 300–500 nm. The particles have a near ball-shaped morphology and the size uniformity decreases with an increase in the particle size.

XRD patterns of the uncoated and coated powders are shown in Figure 2. From these patterns, the content of the tetragonal phase of the two samples within 100 nm is similar and when the particle size exceeds 100 nm, the content of the tetragonal phase decreases rapidly and it is barely visible

FIGURE 3: Linear shrinkage of the samples at different temperatures (1: 30–50 nm, uncoated; 2: 50–100 nm, uncoated; 3: 100–300 nm, uncoated; 4: 300–500 nm, uncoated; 5: 30–50 nm, coated; 6: 50–100 nm, coated; 7: 100–300 nm, coated; 8: 300–500 nm, coated).

FIGURE 4: XRD patterns of the sintered 3Y-TZP samples.

when the particle size is 300–500 nm. The characteristic peak for $CePO_4$ is present in the XRD patterns of the coated samples, which indicates that the coating process was successful.

The linear shrinkage of all the samples was evaluated, and from Figure 3, the optimum sintering temperature of the uncoated and coated samples was determined to be 1550°C and 1650°C, respectively. The particle size is not related to the sintering temperature and the coating process is responsible

FIGURE 5: SEM images of the fractured surfaces of the uncoated samples. (a) 30–50 nm, (b) 50–100 nm, (c) 100–300 nm, and (d) 300–500 nm.

FIGURE 6: SEM images of the fractured surfaces of the coated samples. (a) 30–50 nm, (b) 50–100 nm, (c) 100–300 nm, and (d) 300–500 nm.

TABLE 1: Relative density, hardness, and mechanical properties of the samples.

Samples (nm)	30–50 uncoated	50–100 uncoated	100–300 uncoated	300–500 uncoated	30–50 coated	50–100 coated	100–300 coated	300–500 coated
Relative density (%)	99.3	98.2	97.9	94.6	96.4	98.3	96.5	94.5
Hardness (GPa)	13.14 ± 0.1	12.53 ± 0.1	11.70 ± 0.1		10.72 ± 0.1	10.49 ± 0.1	9.27 ± 0.1	
Flexural strength (MPa)	750 ± 51	721 ± 43	643 ± 36		463 ± 63	447 ± 55	377 ± 39	
Fracture toughness (MPa ⁻²)	4.57 ± 0.1	4.79 ± 0.1	5.14 ± 0.1		5.76 ± 0.1	5.56 ± 0.1	4.17 ± 0.1	
Machinability (m ^{1/2} 10 ³)	0.35	0.38	0.44		0.54	0.53	0.45	

for an increase in the particle size. The doping with CePO₄ reduces the sintering activity of these samples.

The samples were sintered at the optimum sintering temperature. The XRD patterns of the sintered samples show that the uncoated samples are basically tetragonal phase except for the 300–500 nm sample, and the same is true for the coated samples except for the 100–300 nm and 300–500 nm samples (Figure 4). This indicates that the coated samples are more easily affected by the grain size than the uncoated samples.

Figures 5 and 6 show SEMs of the fracture surfaces of the samples. The porosity rate was low. The grain size of the coated samples was obviously larger and more even than that of the uncoated samples. CePO₄ inhibited the abnormal grain growth of ZrO₂ during the sintering process. The uncoated ZrO₂ shows both intergranular and transgranular fractures, especially the 100–300 nm samples, but the coated composite showed higher tendency toward intergranular fracturing. This phenomenon indicates that weak bonding interfaces exist between the CePO₄ and ZrO₂ granules. There are some holes on the surface of the crystalline grains of the 300–500 nm samples, which is the main reason for its porous nature. The strength of the 300–500 nm samples was so low that they could be easily broken. Therefore, their mechanical properties were not determined (Table 1).

As indicated in Table 1, The relative density of the 300–500 nm coated and uncoated samples is relatively lower than that of the other samples, which is consistent with the results shown in Figures 5 and 6. For both the coated and uncoated samples, their hardness was found to decrease with an increase in grain size. The flexural strength differences between the 30–50 nm and 50–100 nm samples are not statistically significant ($P > 0.05$). For the coated samples, when the grain size is within 100 nm, the machinability ratings are close, but when the grain size exceeds 100 nm, the value decreases sharply. The relative density, hardness, and flexural strength decrease with the increasing grain size for the uncoated samples while the fracture toughness and machinability increase which shows that the grain size has an important effect on the mechanical properties. Because the weak bonding interfaces exist between the CePO₄ and ZrO₂ granules, the hardness of the coated samples is smaller than that of the uncoated samples.

4. Conclusions

In summary, the grain size of zirconia before coating greatly influences the mechanical properties of the coated samples

because different particle sizes result in different fracture styles. When the grain size is less than 100 nm, the differences are small, and when it is larger than 100 nm, the differences are very noticeable. At the experimental limits, the 30–40 nm samples have the best flexural strength and machinability rating.

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