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Preparation of $CePO_4$-coated zirconia ceramics and their mechanical behavior

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Abstract

Tetragonal ZrO_2-3 mol% Y_2O_3 (3Y-TZP) coated with $CePO_4$ was synthesized by a co-precipitation method and the effects of $CePO_4$ content and sintering temperature on its mechanical properties were investigated. The microstructure and phase composition of the products were characterized using scanning and transmission electron microscopy as well as X-ray diffraction, respectively. The machinability index of $CePO_4$-coated zirconia was calculated to be 1.05 when the $CePO_4$ content is 25 wt.%. The sample hardness, bending strength and fracture toughness are 7.08 GPa, 457.85 MPa and 9.75 $MPa \cdot m^{1/2}$, respectively, when the sintering temperature is 1400°C. The results show that as-prepared $CePO_4$-coated 3Y-TZP ceramics are highly suitable biomaterials for dental applications and are expected to be used in a computer-aided design and computer-aided manufacturing (CAD/CAM) system to make dental crowns or bridge prostheses in a one-step sintering process.

Keywords: ceramic materials; zirconia; machinability; X-ray analysis; biomedical engineering

1. Introduction

Ceramic materials are widely used in many fields because of its features of excellent mechanical properties, heat resisting and corrosion prevention. However, ceramic materials are commonly hard and brittle, resulting in increased machining damages. Therefore, the conception of machinable ceramics was brought forward. Zirconia is a type of structural ceramic that was developed in the 1970s and is widely applied in electronics, the chemical industry, metallurgy, machinery, instrumentation and refractories [1]. In 1969, the first article on the application of zirconia in biomedicine was published [2]. Currently, zirconia is used for all-ceramic restoration in prosthodontics [3-4], artificial tooth roots [5-6], complex ceramic artificial bones [7] and artificial femoral joints [8] because of its good biocompatibility, excellent chemical stability and higher fracture toughness and abrasion resistance than alumina. The machining method of zirconia used as all-ceramic restoration is the computer-aided design and computer-aided manufacturing (CAD/CAM) system. It is hard to be machined as a result of the hardness and brittleness of the ceramic [9]. A common solution is to mill ceramic blanks in a porous, pre-sintered and yet easily machinable state, which are then sintered to full density [10]. However, the process requires a two-fold sintering and the shrinkage rate during sintering must be strictly controlled, which make the process quite complicated.

The machinability has been improved by adding an auxiliary phase such as glass sintering aids that are low in mechanical strength or by adding machinable rare earth phosphate to zirconia. Rong *et al.* produced machinable dental zirconia ceramics by the addition of CaO-Al_2O_3-SiO_2 sintering aids [11]. Davis *et al.* reported on the preparation and preliminary testing of metallic oxide/rare earth phosphates composite ceramics [12]. In comparison, for the second method, some different preparation processes can be used and it is easier to achieve uniform distribution of the two phases. However, the relationship between phosphate content, sintering temperature and some mechanical properties has not been investigated.

In this work, we prepared $CePO_4$-coated ZrO_2-3 mol% Y_2O_3 (3Y-TZP). The effect of $CePO_4$ content and sintering temperature on its mechanical performance was studied in detail. The material is expected to be used in a CAD/CAM system with a one step sintering process in future.

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2. Experimental

In this study, the suspension containing 3 wt.% 3Y-TZP were obtained by dispersing 3Y-TZP powders (40 nm, 99.9%, Tosoh, Japan) ultrasonically for 15 min in deionized water. The dispersant PEG and the release agent ammonium citrate were dissolved in deionized water at a specific temperature and then added to a suspension of 3Y-TZP at a weight ratio of PEG : ammonium citrate : 3Y-TZP of 0.02:0.015:1. After ultrasonic treatment for 15 min, a suitable amount of $NH_4H_2PO_4$ solution was added and the pH value was adjusted to 4.0 to 4.8 using H_3PO_4. $Ce(NO_3)_3$ was then added to the mixture and stirred for 2 h at 50°C until flocculation was complete. The molar ratio of $NH_4H_2PO_4$:$Ce(NO_3)_3$ was 1:1. The products were collected and washed by centrifugation and dried in an oven. The purified products were calcined at 1000°C for 2 h.

The as-prepared composite powders were milled after a 3 wt.% PVA liquor (the adhesive) was added and then formed into a steel mold and mashed. The mashed powders were formed again after sieving through a 50 mesh sieve. The formed body was then placed in a sealed rubber film and put into an isostatic press machine for pressing under a load of 200 MPa to obtain higher green density and to crush the reunion. The body of the $CePO_4$-coated 3Y-TZP that was prepared using the cold isostatic pressing method was sintered in a high-temperature box-type furnace. The sintering schedule was as follows: the body was calcined at 450°C for 1 h and the temperature was raised to 1200°C in 2.5 h to decrease the phase transition of zirconia from a tetragonal to a monoclinic phase, which occurred between 850°C and 1000°C; the final temperature (1250, 1300, 1350, 1400, 1450, and 1500°C, respectively) was then reached by increasing the temperature at a rate of 200°C/h and kept there for 2.0 h. The sample density was measured using the Archimedes method. The diameter of the disk-shaped samples was determined using an electronic vernier (accuracy: 0.01 mm) before and after the cold isostatic pressing and the values were denoted l_0 and l, respectively. We got the linear shrinkage rate using the formula: $\left[(l_0 - l)/l_0\right]\times 100\%$.

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) with a Rigaku D/MAX-2550V diffractometer (Rigaku, Japan; Cu K_α radiation) were used to determine the microstructure and the phase composition of the as-synthesized ceramic samples. For the SEM analyses, the sample surfaces were milled, polished, exposed to hot corrosion and coated with a gold-palladium coating to prevent charging due to the electron beam. Particle morphology was determined using a transmission electron microscopy (TEM).

The three-point bending strength and fracture toughness were measured using an EZ-100 universal test instrument and the two tests were performed on 3 mm × 4 mm × 36 mm bars at a crosshead speed of 0.005 mm/min and on 4 mm× 6 mm× 30 mm bars at a crosshead speed of 0.05 mm/min. The formula $\sigma_f = 3p_0 l/(2bh^2)$ (p_0: load; l: span of the sample; h: height of the fracture; b: width of the fracture) was used for three-point bending strength tests and the formula $K_{IC} = 3YP_1 L a^{1/2}/(2bw^2)$ (P_1: load; L: span of the sample; w: height of the sample; a: depth of the fracture; b: width of the sample; Y: dimensionless coefficient) was used for fracture toughness tests. The samples were tested for Vickers hardness in a HD-187.5 type Brinell's hardness tester after being polished. A force of 294 N (denoted P) was used for indentation and the length of the diagonal of the indentation (denoted d) was determined with HXD type microhardness equipment. The hardness of the samples could thus be obtained using the formula $HV = (1.8544P/d^2)\times 10^{-3}$. Finally, the machinability rating (M) was evaluated using the formula $M = K_{IC}/HV$.

Seven samples were tested in each of the different experimental conditions. The data were analyzed with one-way analysis of variance (ANOVA) and Tukey's multiple comparison test. The significance was set at 0.05.

3. Results and discussion

TEM images show that granules of 3Y-TZP (Fig. 1(a)) exhibit ball-shaped morphology with diameters of about 50 to 60 nm. $CePO_4$ (Fig. 1(b)) granules, as derived from $Ce(NO_3)_3$ and $(NH_4)_2HPO_4$, had lengths of around 30 to 40 nm and diameters of about 10 nm and were finger-like. Fig. 1(c) shows a TEM image of 3Y-TZP after coating with $CePO_4$ and the $CePO_4$ was found around the 3Y-TZP matrix. These particles drew support from the matrix or nucleated and grew by themselves. We used chemical deposition to coat the 3Y-TZP granule surfaces and they formed core/shell structures. The nucleation rate of $CePO_4$ which was affected by pH values, temperature and concentration is very important during the formation of the core/shell structure according to heterogeneous nucleation theory. The isoelectric points of ZrO_2 and $CePO_4$ were 4.0 and 4.8, respectively. Therefore, we controlled the pH values between 4.0 and 4.8, where ZrO_2 granules are negatively charged and $CePO_4$ granules are positively charged so that the two kinds of granules attract each other and the coating process could occur. At a reaction temperature of 50°C and a $CePO_4$ content of 25 wt.%, we obtained a satisfactory TEM result (Fig. 1(c)).

The microstructure of the $CePO_4$-coated 3Y-TZP ceramics that were sintered at different temperatures was investigated by SEM, as shown in Fig. 2.

The porosity rate was found to be lower when samples

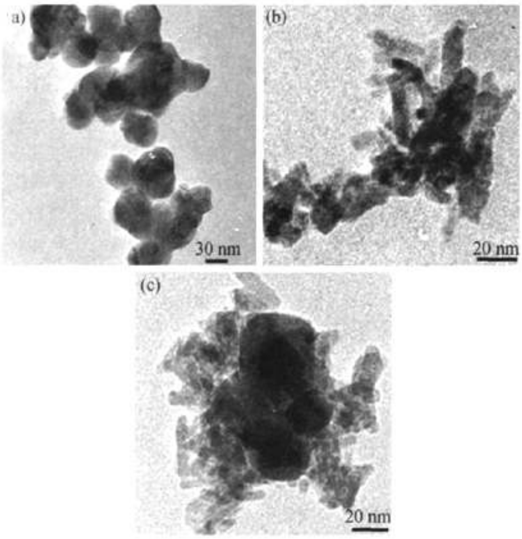

Fig. 1. TEM images of 3Y-TZP (a), $CePO_4$ (b) and 3Y-TZP powders coated by 25 wt.% $CePO_4$ (c).

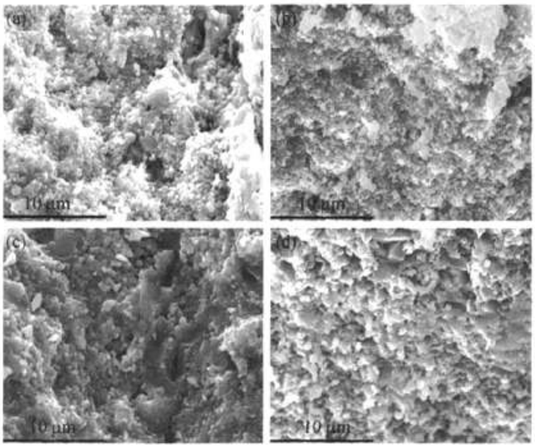

Fig. 2. SEM images of fracture surfaces of as-synthesized ceramics at different sintering temperatures: (a) sintering temperature of 1300°C, $CePO_4$ content of 20 wt.%; (b) sintering temperature of 1300°C, $CePO_4$ content of 25 wt.%; (c) sintering temperature of 1400°C, $CePO_4$ content of 20 wt.%; (d) sintering temperature of 1400°C, $CePO_4$ content of 25 wt.%.

were sintered at 1400°C compared with sintering at 1300°C. The main reason for this is that the grains of the powder were not fully developed and grew as granules when sintered at 1300°C instead of undergoing columnar growth and forming a clear layered structure as at 1400°C. At the higher temperature, the grains combine with one another more closely and the samples have a higher density.

The phase composition and structure of the products with a different $CePO_4$ content produced at 1000°C for 2 h were examined by powder XRD. As shown in Fig. 3, pure zirconia can be indexed to its tetragonal phase and the coated zirconia to its tetragonal and monoclinic phase, which worsen the mechanical properties of the ceramics. Therefore, obtaining a pure tetragonal phase 3Y-TZP coated with $CePO_4$ is worth further research to improve its mechanical properties.

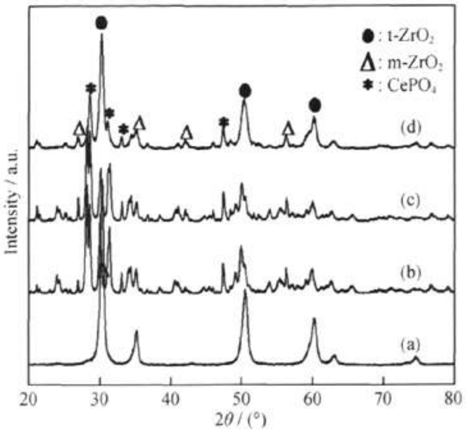

Fig. 3. XRD patterns of $CePO_4$/3Y-TZP powders precipitated by various concentrations of $CePO_4$: (a) 0 wt.%; (b) 10 wt.%; (c) 15 wt.%; (d) 20 wt.%.

The machinability rating reflects the machinability and the mechanical properties of materials as an integrative index. The specimens show significantly different machinability ratings ($p < 0.05$) due to different amounts of $CePO_4$ addition and the maximum is obtained at 25 wt.% at 1400°C (Fig. 4). The reason is that $CePO_4$ decreases the hardness of the composites with weak combinations, which results in easier rupturing during milling, with granules of 3Y-TZP. However, when the $CePO_4$ content is more than 25 wt.%, the mechanical properties decrease and this reduces the machinability rating. Therefore, we can conclude that 25 wt.%

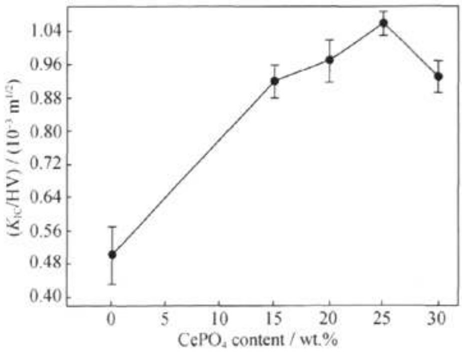

Fig. 4. Effect of $CePO_4$ content on the machinability rating of $CePO_4$/3Y-TZP powders.

is the optimum $CePO_4$ content for these samples.

Values for the relative density and the linear shrinkage rate at a $CePO_4$ content of 25 wt.% and at different sintering temperatures are shown in Figs. 5(a) and (b). At 1400°C, the value for the relative density is 95.4%, which is quite close to the theoretical density. Meantime the linear shrinkage rate is 2.5%, which reaches the maximum.

Figs. 6 and 7 show hardness and bending strength values, fracture toughness and machinability rating values at different temperatures and at a $CePO_4$ content of 25 wt.%. At 1400°C, all the performance indexes are the best compared with other groups ($p < 0.05$).

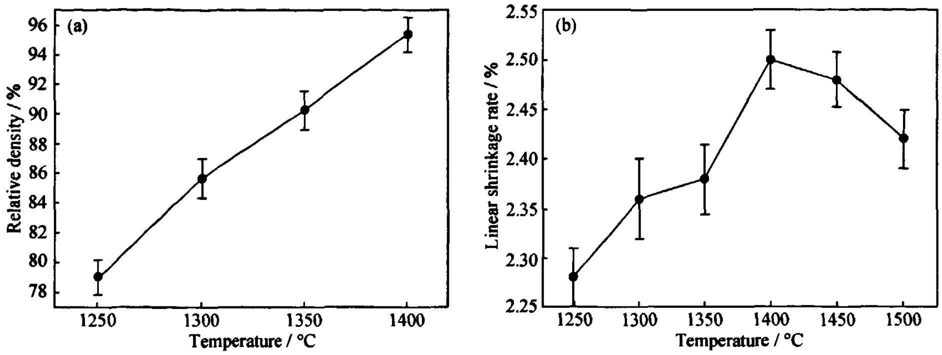

Fig. 5. Relative density (a) and linear shrinkage (b) of $CePO_4$/3Y-TZP powders obtained at different temperatures.

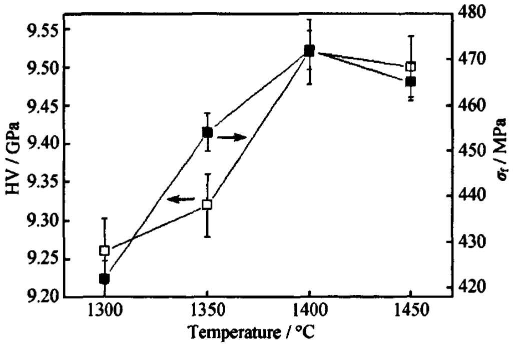

Fig. 6. Hardness and bending strength at different temperatures.

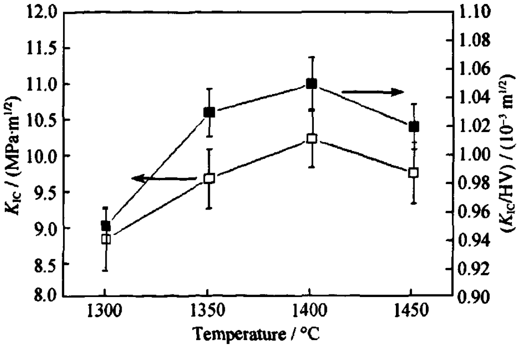

Fig. 7. Fracture toughness and machinability rating at different temperatures.

Therefore, we can conclude that 1400°C is the optimum sintering temperature for these samples.

4. Conclusions

In summary, using $Ce(NO_3)_3$ and $(NH_4)_2HPO_4$ as raw materials and controlling the reaction conditions, 3Y-TZP ceramics coated with $CePO_4$ were synthesized by a co-precipitation method and combined with solid-state sintering processing. The machinability rating of $CePO_4$-coated 3Y-TZP is higher than pure 3Y-TZP ceramics. The optimum machinability rating of about 1.05 is obtained when the $CePO_4$ content is 25 wt.%. At a sintering temperature of 1400°C, the hardness, bending strength and fracture toughness of the samples reaches 7.08 GPa, 457.85 MPa and 9.75 MPa·m$^{1/2}$, respectively. Therefore, the one-step sintering dense ceramic block is expected to be machined directly using a CAD/CAM system.

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