

# Fabrication of structure-controlled hydroxyapatite/zirconia composite

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## Abstract

The structure-controlled hydroxyapatite/zirconia (HAp/ZrO<sub>2</sub>) composites were fabricated. At first, cylindrical hydroxyapatite (HAp) samples were prepared by the extrusion process, and then the extruded HAp cylindrical samples were coated with 3 mol% of Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub> slurry, dried and aligned unidirectionally to form a composite bulk. The volume fraction of ZrO<sub>2</sub> in the HAp/ZrO<sub>2</sub> composite was estimated to be about 23 vol%. Bulk density and bending strength of the composites increased with sintering temperature. Fracture energy of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C was approximately 1.6 times higher than that of monolithic HAp. Although the bending strength of HAp/ZrO<sub>2</sub> composite prepared in this study was relatively low, it exhibited high fracture energy than HAp monolithic and a non-brittle fracture behavior was obtained without using fiber as the reinforcement.

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## 1. Introduction

Hydroxyapatite (HAp) shows excellent osteoconductivity and biocompatibility with human hard tissues such as bone and teeth, and it has been used as artificial bone and dental materials.<sup>1</sup> However, HAp shows lower mechanical strength and fracture toughness than natural bone, and hence applications of HAp to bioceramics are limited. In order to improve mechanical properties of HAp, several attempts for HAp combined with ZrO<sub>2</sub> have been made.<sup>2–11</sup> Partially stabilized zirconia (ZrO<sub>2</sub>) shows biocompatibility and high mechanical properties, and it has been applied to orthopedic uses such as hip and knee joints.<sup>1</sup> Matsuno et al.<sup>4</sup> reported the fabrication of HAp/ZrO<sub>2</sub> composites by hot-pressing at 1350 °C for 15 min in Ar atmosphere under a uniaxial pressure of 30 MPa. In this processes, the spherical HAp particles were coated with 3 mol% of yttria (Y<sub>2</sub>O<sub>3</sub>) stabilized ZrO<sub>2</sub>. Bending strength and fracture toughness of HAp/ZrO<sub>2</sub> composite increased with ZrO<sub>2</sub> content, and these values of the

composite containing 50 vol% of ZrO<sub>2</sub> were 200 MPa and 3.3 MPa m<sup>1/2</sup>, respectively. Shen et al.<sup>8</sup> used spark plasma sintering to densify HAp/ZrO<sub>2</sub> (3 mol% of Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub>) composite at 1150 °C for 5 min in vacuum using a pressure of 50 MPa, and reported that HAp composite with 50 vol% of ZrO<sub>2</sub> had high bend strength and the fracture toughness of 440 MPa and 2.5 MPa m<sup>1/2</sup>, respectively. Kim et al.<sup>10</sup> mixed HAp powders and 40 vol% of 3 mol% of Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub> in ethanol by ball-milling, and fabricated HAp/ZrO<sub>2</sub> composite by pressureless sintering at 1350 °C for 1 h in air using calcium fluoride (CaF<sub>2</sub>) as sintering additives (2.5 vol%). They achieved bending strength of 180 MPa and fracture toughness of 2.3 MPa m<sup>1/2</sup>. From the results of these studies, it is expected that mechanical properties of HAp, especially bending strength, can be improved by the reinforcement of large volume fraction of ZrO<sub>2</sub>. However, it has been well known that ZrO<sub>2</sub> is a bioinert material and it does not combine with a bone since it has no osteoconductivity. Thus, the bioactivity of HAp that is one of the advantages of bioceramics would decrease with increasing the amount of ZrO<sub>2</sub>. In consideration of bioactivity of the composite, it is desirable that the amount of ZrO<sub>2</sub> addition

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to HAp composite should be as small as possible without compromising the mechanical properties. This is possible by preparing structure-controlled composites. Fibrous ceramics with a distinct fibrous texture are one of the most effective ways to improve fracture toughness of ceramics without decrease in bending strength.<sup>12–15</sup> Hence, present authors have paid attention to the texture of fibrous ceramics, and attempted to fabricate HAp/ZrO<sub>2</sub> composite with fibrous texture.

In this study, HAp was reinforced with partially stabilized ZrO<sub>2</sub>, and the structure-controlled HAp/ZrO<sub>2</sub> composites were fabricated by a two-step processing method in order to improve mechanical properties of HAp.

## 2. Experimental

The schematic illustration of the fabrication process of HAp/ZrO<sub>2</sub> composite in this study is shown in Fig. 1. HAp (Kishida Chemical, Japan) and 3 mol% of Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub> (TZ-3Y, Tosoh, Japan) powders were used as the starting materials. Aqueous slurry of HAp powder was prepared and used for extrusion. Agar dissolved in hot water was used as the binder. Cylindrical HAp rods with a diameter of about 1.0 mm were prepared by extrusion method. ZrO<sub>2</sub>

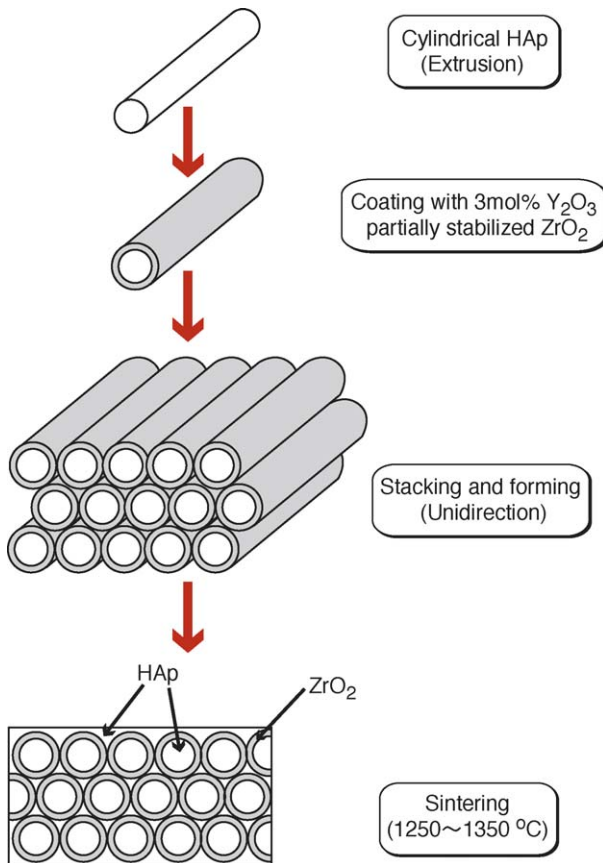


Fig. 1. Schematic illustration of fabrication process of HAp/ZrO<sub>2</sub> composite in this study.

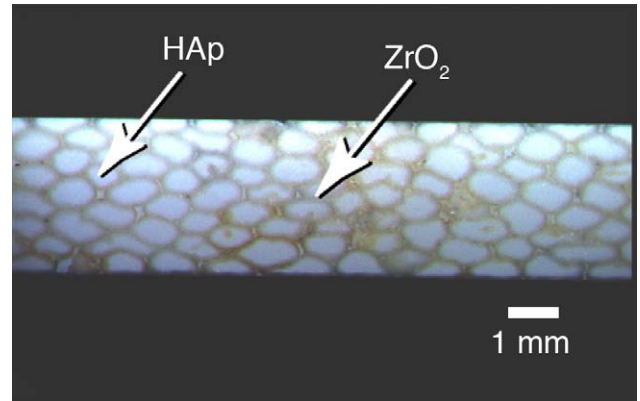


Fig. 2. Optical micrograph of HAp/ZrO<sub>2</sub> compact before sintering.

powder was mixed with 3 mass% polyvinyl alcohol aqueous solution and the extruded cylindrical HAp rods were dipped into ZrO<sub>2</sub> slurry. After drying, the cylindrical HAp rods with ZrO<sub>2</sub> coating were unidirectionally aligned to form a bulk, and HAp powder was filled in between each cylindrical HAp rod in order to increase the density of HAp/ZrO<sub>2</sub> composite. The compact was formed under a uniaxial pressure of 25 MPa, followed by cold isostatic press under a pressure of 190 MPa. The optical micrograph of the compact is shown in Fig. 2. The microstructure of the compact was very similar to the microstructure of SiC/SiC composite fabricated by Ube Industries (TyrannoHex).<sup>16</sup> The compact was pressureless sintered between 1250 °C and 1350 °C in air for 12 h.

The composites were cut into rectangular bars (width: 3.5 mm, thickness: 2.5 mm, length: 25 mm) and were used for further characterizations. Bulk density of the composite was measured by Archimedes' method using ethanol. Three-point bending strength measurement (span length: 20 mm) was performed at room temperature in air with a crosshead speed of 0.5 mm/min using testing machine (AG-I, Shimadzu, Japan). The volume fraction of ZrO<sub>2</sub> and the crystalline phase of the composite were determined by X-ray diffractometry (XRD; RINT-1500, Rigaku, Japan). Element analysis of the composite was performed by electron probe X-ray micro analyzer (EPMA; JXA-800, JEOL, Japan). Microstructure and fracture surface of the composite were observed by scanning electron microscope (SEM; JSM-6400, JEOL, Japan).

## 3. Results and discussion

Fig. 3 shows microstructure of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C for 12 h. From the result of EPMA analysis, it was found that cylindrical HAp phase was surrounded by ZrO<sub>2</sub>, and HAp homogeneously existed around ZrO<sub>2</sub> layer-coated cylindrical HAp rod. The volume fraction of ZrO<sub>2</sub> in the composite determined by XRD analysis was about 23 vol%. XRD analysis indicated that the composite mainly consisted of crystalline phases such as HAp and Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub>. In addition, small amount of α-

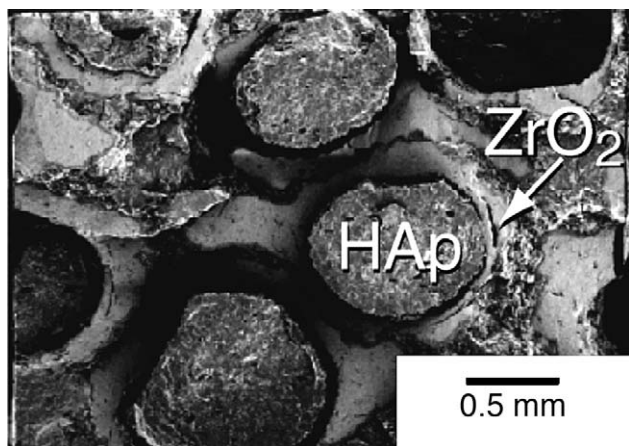


Fig. 3. Microstructure of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C.

tricalcium phosphate formed by the decomposition of HAp during sintering could be detected.

Bulk density and bending strength of HAp/ZrO<sub>2</sub> composites were shown in Fig. 4 as a function of sintering temperature. For comparison, bulk density and bending strength of monolithic HAp was also measured. Bulk density of monolithic HAp increased with sintering temperature, whereas its bending strength decreased from 120 MPa to 90 MPa with increasing sintering temperature due to grain growth at higher sintering temperatures. On the other hand, bulk density and bending strength of the composites increased with increasing sintering temperature, and the highest bending strength exhibited by composite, i.e. 100 MPa, is nearly the same as that of monolithic HAp sintered at 1300 °C and 1350 °C. This is attributed to the amount of porosity of the composite (12–20%) at higher temperature. This might be attributed to the different sintering rate of HAp and ZrO<sub>2</sub>.

Fig. 5 shows the typical load–displacement curves of HAp/ZrO<sub>2</sub> composite sintered at different temperatures and

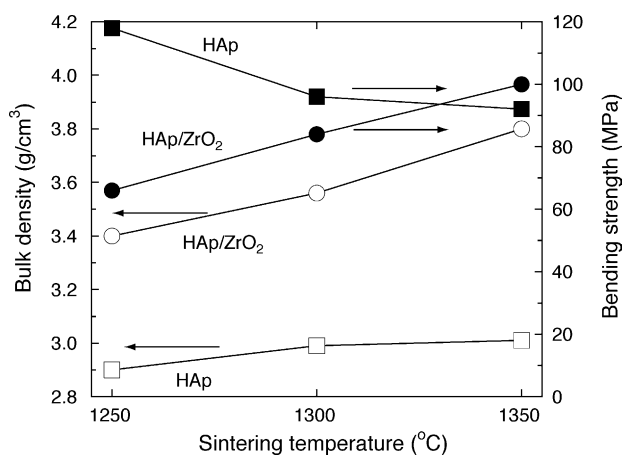


Fig. 4. Bulk density and bending strength of monolithic HAp and HAp/ZrO<sub>2</sub> composites sintered at various temperatures (square mark: monolithic HAp; circle mark: HAp/ZrO<sub>2</sub> composite; open mark: bulk density; solid mark: bending strength).

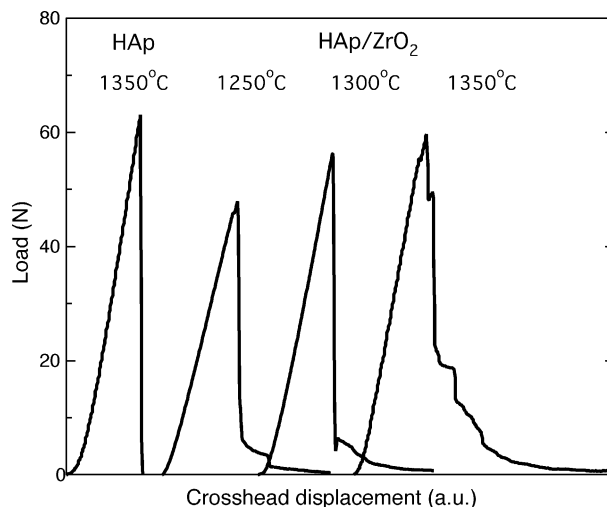


Fig. 5. Typical load–displacement curves of HAp/ZrO<sub>2</sub> composite sintered at various temperatures. Load–displacement curve of monolithic HAp sintered at 1350 °C is also shown in this figure.

monolithic HAp sintered at 1350 °C. It is observed that monolithic HAp fractured in brittle behavior, whereas the composite prepared in this study showed a non-brittle fracture behavior as can be seen in fiber-reinforced ceramic matrix composite. This might be due to crack deflection and bridging between cylindrical HAp phase and ZrO<sub>2</sub> coated layer, which resulted in a non-brittle fracture behavior as shown in Fig. 5. In the case of HAp/ZrO<sub>2</sub> composite sintered at 1250 °C and 1300 °C, the load–displacement curves showed small tails after first matrix cracking and large drop of load. In the case of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C, the load gradually decreased with increasing crosshead displacement after reaching maximum load. The difference in load–displacement curves might be attributed to the difference in bulk density, i.e. pores and gaps in HAp/ZrO<sub>2</sub> composite.

The fracture energy of HAp/ZrO<sub>2</sub> composite and monolithic HAp sintered at 1350 °C was calculated from the area of load–displacement curve. The fracture energy of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C was calculated as 140 J/m<sup>2</sup>, which is approximately 1.6 times higher than that of monolithic HAp.

The fracture toughness of HAp/ZrO<sub>2</sub> composite and monolithic HAp sintered at 1350 °C was approximately estimated from their elastic modulus and fracture energy, and fracture toughness of HAp/ZrO<sub>2</sub> composite was slightly improved in comparison with that of monolithic HAp (about 1.1 times). It could be found that the fracture energy must be increased significantly in order to increase fracture toughness of HAp/ZrO<sub>2</sub> composite.

#### 4. Conclusions

In this study, HAp was reinforced with 3 mol% of Y<sub>2</sub>O<sub>3</sub> partially stabilized ZrO<sub>2</sub> and structure-controlled HAp/ZrO<sub>2</sub>

composites were fabricated in order to improve mechanical properties of HAp.

The volume fraction of ZrO<sub>2</sub> in the composite determined by XRD analysis was about 23 vol%. Bulk density and bending strength of the composites increased with increasing sintering temperature, and the values ranged from 3.4 g/cm<sup>3</sup> to 3.8 g/cm<sup>3</sup> and 70 MPa to 100 MPa, respectively. Bending strength of the composite sintered at 1300 °C and 1350 °C was nearly the same as that of monolithic HAp sintered at 1300 °C and 1350 °C.

Monolithic HAp fractured in brittle behavior, whereas the composite obtained in this study showed non-brittle fracture behavior as seen in fiber-reinforced ceramic matrix composite. It was considered that crack deflection and bridging between cylindrical HAp and ZrO<sub>2</sub> layer would occur in fracture, resulting in non-brittle fracture behavior. Fracture energy of HAp/ZrO<sub>2</sub> composite sintered at 1350 °C was approximately 1.6 times higher than that of monolithic HAp, and the value of HAp/ZrO<sub>2</sub> composite was about 140 J/m<sup>2</sup>.

In this study, HAp/ZrO<sub>2</sub> composite with non-brittle fracture behavior and an increase in fracture energy could be obtained without using fiber as the reinforcement. In order to achieve a marked increase in bending strength and fracture energy without increasing the amount of ZrO<sub>2</sub>, optimum fabrication process and sintering conditions must be considered.

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