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Fracture Toughness of Porous Sintered Bodies of Hydroxyapatite

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Hydroxyapatite powders having various average particle diameters were prepared by a wet process and by the calcination under various conditions. Porous sintered bodies of hydroxyapatite having relative densities of 49.4-85.8% were obtained by heating green compact bodies. The fracture toughness of these sintered bodies was measured by a Single -Edge V-Notched Beam(SEVNB) method. The fracture toughness increased linearly with an increase in relative density.

Because of the bioactive properties, many studies on hydroxyapatite (HAP) have been made aiming at the artificial bone and dental root for the last twenty years. Some papers on the physical properties of the sintered body of HAP have been published. Rao et al. reported the relationship between the relative density and the compressive strength of the sintered body.1) The result indicates that the compressive strength decreases exponentially with the decrease of the relative density. Aoki et al. and Peelen et al. concluded that the compressive strength of the sintered body of HAP was proportional to the relative density.2,3) Bending and tensile strength and Vickers hardness of the sintered body of HAP were also reported.4-7) Although there are a few papers on the fracture toughness of dense sintered bodies of HAP,7,8) there are few papers on that of porous sintered bodies.

In this study, the sintered bodies with different relative densities, average particle diameters, and particle size distributions were prepared, and the fracture toughness of those sintered bodies was determined.

0.20 mol dm^{-3} calcium nitrate aqueous solution (400 cm^3) and 0.12 mol dm^{-3} diammonium hydrogenphosphate aqueous solution (400 cm^3) were prepared from extra-pure grade reagents of Wako Pure Chemical Industries, LTD. The pH of those solutions was adjusted to 10.4 with a sodium hydroxide solution. These solutions were put at a time into a 1000 cm^3 cylindrical glass reactor equipped with a turbine impeller stirrer rotating at 1000 rpm and baffle plates and then sodium citrate was added to it so that the concentration of it was 1.0×10^{-3} mol dm^{-3}. Adjusting pH of the solution to 10.4 with the sodium hydroxide solution, the solution was heated up to 96 to 97 °C and kept at the temperature for 10 hours. The pH was always kept at 10.4 and carbon dioxide in the air was prevented from participating to the reaction by continuously blowing nitrogen gas into the reaction system. The reaction product(HAP) was washed and dried at 300 °C under vacuum(T-1). The particles of HAP with larger diameters (T-2 to T-7) were prepared by putting the powder of T-1 into a covered rectangular alumina vessel and heating them under various conditions (950-1150 °C, 30-240 min) in an electric furnace.

A disc like green compact body of HAP prepared by uniaxially compressing the dried particles of HAP for 5 min under 20 MPa in a mold 45 mm in diameter and isotropically compressing it for 15 min under 98 MPa in a hydraulic oil power unit. The green compact bodies were sintered at 1150 °C for 2 hours in an electric furnace. The fracture toughness of the sintered bodies of HAP was determined by the SEVNB(Single-Edge V-Notched Beam) method.[9,10] The 16 mm span, three-point bending test was made using 5 to 6 test pieces with the dimensions of $3 \times 4 \times 20$ mm^3 at a crosshead speed of 0.5 mm min^{-1} in an Autograph(Shimadzu) at room temperature in air.

The conditions for calcining the HAP particles and particle sizes are shown in Table 1. The average particle diameter was measured from SEM photographs of 200 particles. Comparing the standard deviations of the powders with almost the same average particle diameter(T-2 and T-3, T-4 and T-5, T-6 and T-7) with each other, the particle size distribution is broadened with the raising of the calcination temperature, and vice versa. The chemi-

Table 1. Average particle diameters and their standard deviations of prepared HAP powders

	Calcination conditions		Particle size/μm	
	Temp/°C	Time/min	Average diameter	SD
T-1			0.06	0.01
T-2	1150	30	0.32	0.17
T-3	950	60	0.31	0.06
T-4	1150	90	0.65	0.36
T-5	950	240	0.62	0.13
T-6	1150	180	0.98	0.48
T-7	1050	240	1.03	0.20

cal analysis results of CaO and P_2O_5 contents by the back titration using EDTA and the phosphomolybdate method, respectively, indicated that the molar ratio of Ca/P of the powders were 1.66 which were nearly equal to the theoretical value(1.67) of HAP. The density of green compact body of HAP is 1.21 to 1.70 g cm^{-3} which are 38.3 to 53.8% of the theoretical density of HAP of 3.16 g cm^{-3}. The relative density of the sintered body of HAP is 49.4 to 85.8%. This suggests that the sintered body contains a lot of pores. SEM photograph of the cross section of the sintered body of T-3 is shown in Fig.1. The cross section was lapped and etched with a 0.04% citric acid solution before SEM observation. The surface and cross sections of the sintered bodies were examined by X-ray diffractometry. Any of the diffraction patterns includes only peaks corresponding to HAP.

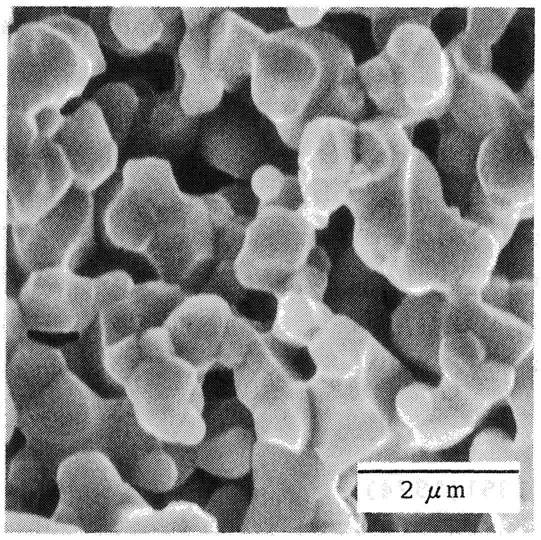

Fig. 1. SEM photograph of the cross section of the sintered body of T-3.

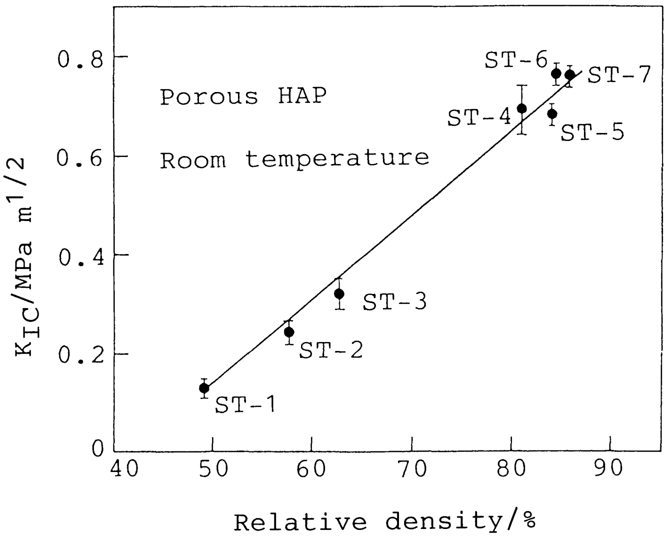

Fig. 2. Fracture toughness of sintered HAP measured by the SEVNB method as a function of the relative density.

The relative density dependence of the fracture toughness is graphically illustrated in Fig.2. ST-1 and ST-2 in the figure stand for the sintered bodies from T-1 and T-2 powders, respectively, and so forth. The figure reveals that the fracture toughness increases linearly with the increase of the relative density. Although the SENB(Single-Edge Notched Beam) method used for the fracture toughness is generally used for the test of ceramics because the result was hardly affected by the type of materials and the test piece is relatively easily processed, the results are known to largely depend upon the curvature radius of the tip of notch as the characteristics of ceramics. In this study, therefore, the SEVNB method using a V-shaped notch was adopted to minimize the curvature radius of the tip of notch.

While the average particle diameter of T-2 were nearly equal to T-3, and the molar ratio of Ca/P was the same as each other, the fracture toughness of ST-2 was different from ST-3, and 0.24 and 0.32 MPa $m^{1/2}$ for the former and for the latter, respectively. The pores in ST-3 sintered from T-3 with narrower particle diameter distribution were relatively uniformly distributed, while those in ST-2 sintered from T-2 with broader diameter distribution were relatively unevenly distributed. This may cause the difference in the fracture toughness between these two sintered bodies. Although the differences in the particle size distributions between T-4 and -5, and T-6 and -7 were similar to that between T-2 and -3, the fracture toughness were not so different between ST-4 and -5, and ST-6 and -7 as those between ST-2 and -3.

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