Fracture Toughness of Sintered Hydroxyapatite and β -Tricalcium Phosphate

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[Received April 11, 1984])

水酸アパタイト及び β -リン酸三カルシウム焼結体の破壊靱性

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(1984年4月11日受付)

Key-words : Hydroxyapatite, β -tricalcium phosphate, Fracture toughness, Bending strength,
Single edge notched beam

The chemical and physical properties of hydroxyapatite (HAp), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and β -tricalcium phosphate (TCP), $\text{Ca}_3(\text{PO}_4)_2$, closely resemble those of bone and tooth minerals. Recently intense interest has been shown towards using these ceramics as bone and tooth implant materials, because of their superior compatibility with these tissues⁽¹⁻⁴⁾. The mechanical properties of dense HAp and TCP ceramics have been reported by several workers⁽⁵⁻¹¹⁾. Some fracture toughness data on HAp are reported⁽¹⁰⁾ but data on TCP are not available at all. This paper briefly describes the fracture toughness of dense, sintered HAp and TCP measured by bending fracture of single edge notched beams.

A suspension of $\text{Ca}(\text{OH})_2$ (0.5 and 0.6 M for preparing HAp and TCP, respectively) in 1000 ml distilled water was vigorously stirred at room temperature, and a solution of H_3PO_4 (0.3 and 0.4 M for HAp and TCP, respectively) in 1000 ml distilled water was added in drops to produce a gelatinous precipitate. A solution of 3% ammonia

(about 30 ml) was also added for preparing TCP. The resulting slurries were filtered and dried at 80°C. The products were calcined at 800°C for 3 h. They contained approximately 0.3 wt% MgO as impurity. The finely ground powders, mixed with 3 wt% polyvinyl alcohol, were pressed in a mould with a pressure of 60–80 MPa. The compacts were heated in air at 1100°–1300°C for 1 h. Density was measured by the fluid displacement method in distilled water. The theoretical densities of HAp and TCP were assumed to be 3.16 and 3.07 g/cm³. The average grain size was estimated by the linear intercept method using SEM micrographs of the specimens after etching in 0.1 M acetic acid solution for 1–2 min. The density and grain size results are summarized in Table 1. Phase composition of the sintered bodies was determined by X-ray powder diffraction method. In the diffraction patterns of the HAp ceramics, α - and β -TCP phases were not detected. The TCP ceramics obtained below 1200°C indicated as single β -phase, but those

Table 1. Density and grain size results for sintered hydroxyapatite and β -tricalcium phosphate.

Sample	Sintering temp. (°C)	Density* (g/cm ³)	Grain size (μm)
HAp-1	1100	2.94 (93.0)	0.4±0.2
HAp-2	1150	3.05 (96.4)	0.5±0.3
HAp-3	1200	3.07 (97.2)	0.7±0.3
HAp-4	1250	3.08 (97.5)	1.9±1.4
HAp-5	1300	3.09 (97.8)	3.0±2.1
TCP-1	1100	2.63 (85.6)	0.6±0.4
TCP-2	1150	3.03 (98.6)	1.1±0.6
TCP-3	1200	3.04 (99.4)	1.3±0.7
TCP-4	1250	3.06	2.0±1.5
TCP-5	1300	3.07	7.8±4.8

*Relative values (in %) are given in parentheses.

obtained at 1250°C and 1300°C (samples TCP-4 and 5) contained 5 wt% HAp. The maximum sensitivity for detection was 2 wt% in these systems.

Small specimens (of dimensions 2×4×20 mm³) for bending strength and large specimens (of dimensions 3.7×3.7×20 mm³) for fracture toughness were cut from discs of the sintered bodies with a low-speed diamond saw. Bending strength of the small specimens was measured in a four-point bending test using an inner span of 5 mm and an outer span of 15 mm with a cross-head speed of 0.1 mm/min. The displacement value was measured by a differential transformer.

Fracture toughness measurement of the large specimens was done in the same four-point bending setup. In each fracture toughness specimen, a notch of width 150 μm and relative depth 0.25 μm

was sawn. Pre-cracking was done by a Vickers hardness indentation with 1 N load. Fracture toughness value, K_{IC} , was calculated according to Brown and Srawley¹²⁾. For each test, the number of specimens tested was between 10 and 13.

Figure 1 shows the fracture toughness of the sintered HAp and TCP measured by the bending fracture of notched beams. For the toughest HAp (i. e. samples HAp-2, 3 and 4), the values of K_{IC} are 0.95, 0.95 and 0.96 MPa·m^{1/2}, respectively. The K_{IC} values of samples HAp-1 and 5 are approximately 20 and 30% lower than the toughest. These values agree well with the previous data (1.0 MPa·m^{1/2})¹⁰⁾ for a dense HAp ceramic containing α -TCP as second phase. K_{IC} of the sintered TCP increased steadily with an increase in sintering temperature. The toughest TCP (sample TCP-5) has an average fracture toughness value of 1.30 MPa·m^{1/2}; this sample contains 5 wt% HAp as second phase (Table 2). In general, the fracture toughness and bending strength of TCP ceramics tend to be higher than those of HAp ceramics.

Table 2. Fracture toughness results for sintered hydroxyapatite and β -tricalcium phosphate.

Sample	Fracture toughness (MPa·m ^{1/2})	Bending strength (MPa)	Young's modulus (GPa)
HAp-1	0.77±0.12	84±8	87±4
HAp-2	0.95±0.07	113±8	89±4
HAp-3	0.95±0.06	102±9	92±4
HAp-4	0.96±0.08	103±12	94±4
HAp-5	0.69±0.04	105±9	94±2
TCP-2	1.14±0.05	126±10	95±5
TCP-3	1.24±0.07	133±7	87±4
TCP-4	1.28±0.10	122±14	94±3
TCP-5	1.30±0.08	118±9	91±4

Fig. 1. Fracture toughness of sintered hydroxyapatite (HAp) and β -tricalcium phosphate (TCP).

The fracture toughness values of the sintered HAp and TCP are somewhat higher than those of SiO₂ glass¹³⁾, but are about 1/3-1/5 th of sintered Al₂O₃¹⁴⁾, 1/40-1/70 th of Ti alloy¹⁵⁾, and 1/50-1/100 th of maraging steel¹⁵⁾. From the mechanical point of view, the dense HAp and TCP ceramics in their present form have some difficulties in utilizing as bone replacement in loaded places of the skeleton. However, the results demonstrated that the sintered products have sufficiently good mechanical properties to be utilized as the artificial tooth roots which are designed to be free from tensile stress.

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