Microstructure-designed Hydroxyapatite Ceramics Prepared by Hydrothermal Hot-Pressing

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Abstract

Microstructure-designed hydroxyapatite ceramics, i.e. dense ceramics and porous ceramics, were prepared by hot-pressing under hydrothermal conditions. Fully dense hydroxyapatite ceramics could be obtained from ultra-fine hydroxyapatite single crystals by sintering at 1050 ℃ for 3h in air, after hydrothermal hot-pressing at 300℃ under 30MPa of mechanical pressing for 2h. This ceramics had homogeneous grain size of about 0.5μm with few pores. Porous hydroxyapatite ceramics with 42% porosity, about 300μm pores in diameter, was prepared from mixture of $Ca(OH)_2$ and $(NH_4)_2HPO_4$ by sintering at 1050℃ for 3h in air, after hydrothermal hot-pressing at 300 ℃ under 30MPa of mechanical pressing for 2h. This ceramics had comparable compressive strength of 150 ± 20MPa to that of cortical bone.

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$: (HAp), is expected as implant materials because of HAp's bio-compatibility due to similarity to natural bones and teeth mineral[2]. The implant materials for human bones and teeth require not only bio-compatibility but also mechanical strength at a certain level and porosity to promote the connection with tissues. Thus HAp ceramics as the implant materials requires various microstructure ; dense one and/or porous one[3-6]. The dense HAp ceramics is suitable for the bones substitute in high stress-bearing situations. While the porous HAp ceramics is applied to filling up defects of the bones. The pore size of this ceramics is required to be larger than the 100 μm above we may expect ingrowth of bone tissue[7].

While several ceramics can be prepared by pressing powders mechanically under hydrothermal conditions by hydrothermal hot-pressing technique[8-11], therefore this technique should be effective for preparation of the ceramics with hydroxyl group. This paper describes preparation of dense HAp ceramics and porous HAp ceramics with designed microstructure by hydrothermal hot-pressing.

2. Experimental methods

The autoclave for hydrothermal hot-pressing used in this work (Fig. 1) was a cylinder made of steel. A starting sample and cast rods were surrounded by a case consisted of three pieces, thus the sample could be taken out easily. The starting sample with distilled water in the chamber was compressed uniaxially by cast rods from above and below. The cast rods had a space for water retreat, into which water included in the starting sample was released. Gland packing made of Teflon between cast rod and piston prevented leakage.

Preparation of the HAp ceramics by hydrothermal hot-pressing is shown following process. Dense HAp ceramics was obtained from ultra-fine HAp single crystals[12]. The crystals were prepared hydrothermally in an autoclave at 200℃ for 10h from the precipitate of the solutions of $Ca(NO_3)_2$ (reagent gade, Wako Pure Chemical Industries, LTD.) and $(NH_4)_2HPO_4$ (reagent grade, Wako) in the HAp

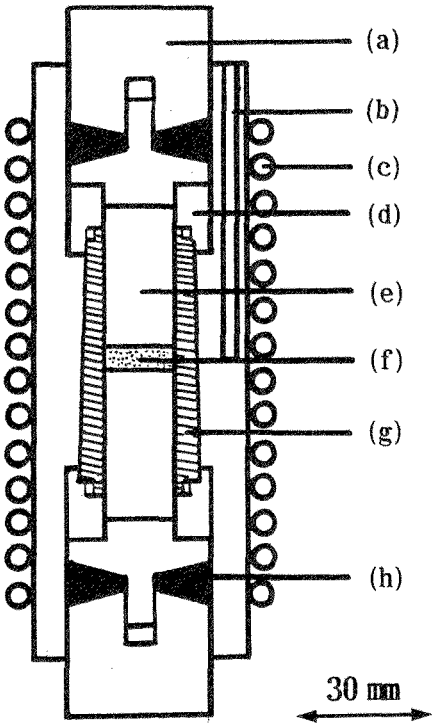

Fig. 1 Autoclave for hydrothermal hot-pressing; (a) piston for packing, (b) well for thermocouple, (c) heater, (d) space for water retreat, (e) cast rod, (f) sample, (g) sample case, and (h) gland packing.

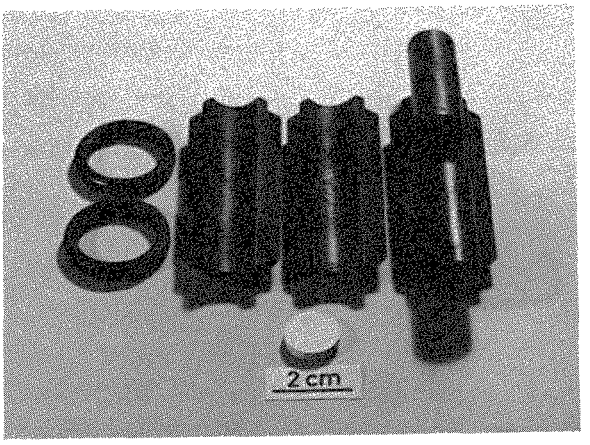

Fig. 2 Sample case for hydrothermal hot-pressing and the solidified disk of HAp hot-pressed hydrothemally at 300 ℃ under 30MPa for 2h from ultra-fine HAp single crystals (15mm ϕ × 3mm).

stoichiometry (Ca/P=1.67). The crystals were kneaded with 10wt% distilled water for 30min by mortar. Porous HAp ceramics were obtained from the mixture of $Ca(OH)_2$ (reagent grade, Wako) and $(NH_4)_2HPO_4$ in the HAp stoichiometry (Ca/P=1.67). The mixture were kneaded with 10wt% distilled water for 30min by mortar. These samples kneaded with distilled water were transferred into the sample case of the autoclave of hydrothermal hot-pressing, and pressed mechanically under 30MPa. The samples were heated to 300℃, and kept the temperature for 2h. The heating rates was kept constant for all runs at 15℃/min. Then the samples were cooled to room temperature in air. The solidified disk of HAp obtained was sintered at 900 ~ 1100℃ for 3h in air to bring about densification.

The solidified disk of HAp (15mm $\phi \times 3$mm, Fig. 2) was used for following measurement and observation. Bulk density of the samples was evaluated from the weight and the size of them. Relative density of the ceramics was calculated as ratio against theoretical density (3.16g/cm^3) of HAp[13]. Porosity of the porous ceramics was measured by the Archimedean method with water[14]. Crystalline phases of the samples were identified by powder X-ray diffractometry (XRD ; RAD-RC, Rigaku Denki Co.) with carbon monochromated Cu-Kα, operating at 40KV and 100mA. The microstructure of the sintered ceramics was observed by a scanning electron microscope (SEM ; S530, Hitachi), after the polished surface was etched thermally at the temperature below 10 ℃ of the sintering temperature. Densification of the solidified disk of HAp prepared by hydrothermal hot-pressing was investigated by dilatometry (high-temperature type TMA ; Rigaku) in air at a heating rate of 10℃/min. Compressive strength of the porous ceramics (15mm $\phi \times 7$mm) was measured by mechanical machine (RH-100, Shimazu).

3. Results and discussion

3-1. Preperation of dense HAp ceramics

No phases other than HAp were revealed by XRD in starting samples. TEM observation of the HAp powders demonstrated that the particles were fine single crystals with hexagonal prismatic shape (25nm $\times$ 90nm) (Fig. 3). Hydrothermal

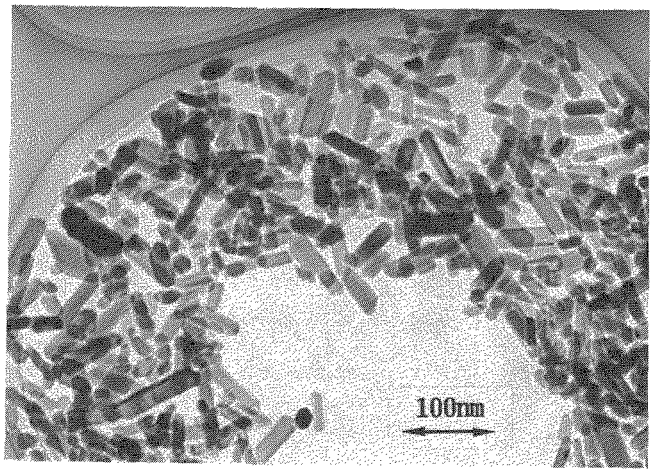

Fig. 3 TEM photograph of the HAp fine crystals synthesized hydrothermally at 200℃ under 2MPa for 10h.

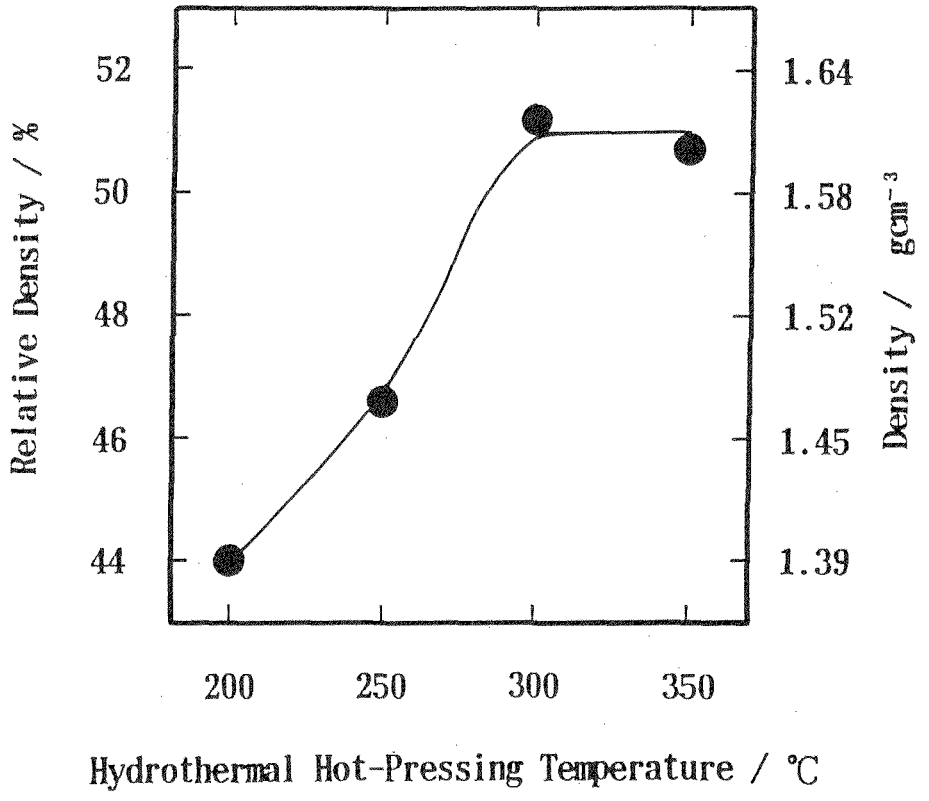

Fig. 4 Relative density of the solidified disk of HAp hot-pressed hydrothermally at 200 ° ～350 ℃ under 30MPa for 2h from ultra -fine HAp single crystals.

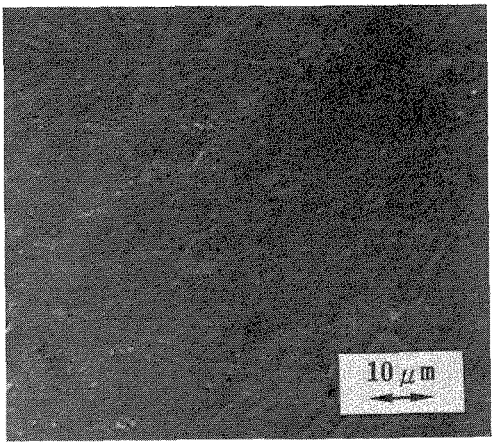

Fig.5 SEM photograph of the solidified disk of HAp hot-pressed hydrothermally at 300℃ under 30MPa for 2h from ultra-fine HAp single crystals.

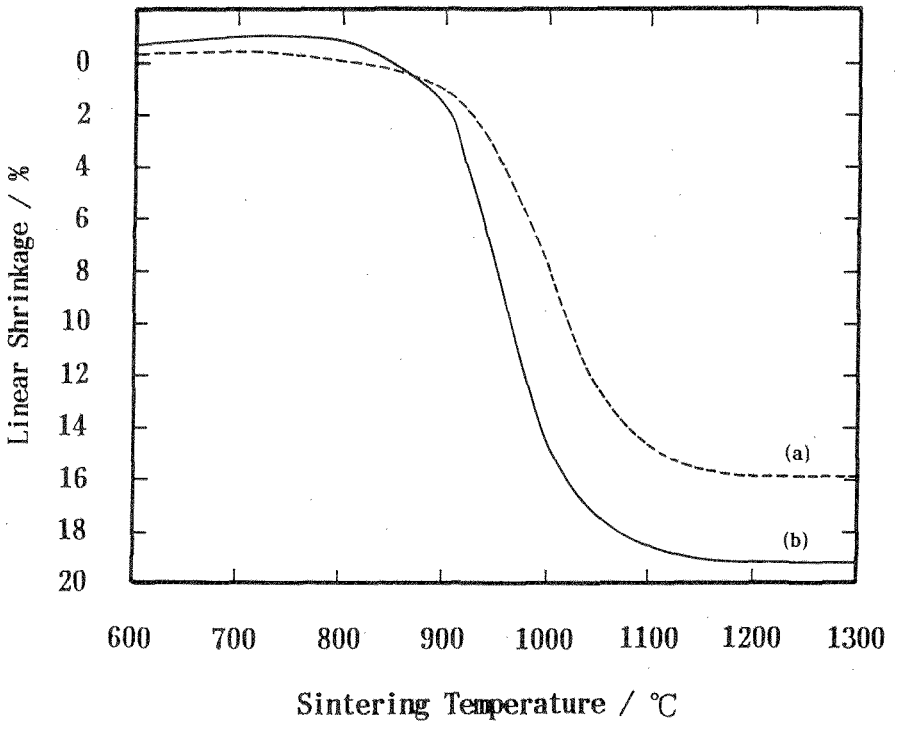

Fig.6 Densification of solidified disk of HAp prepared from ultra-fine HAp single crystals (heating rate : 10℃/min.) ;
(a) cold isostatic pressed sample (CIP'ed under 200MPa for 5min.), and
(b) hydrothermal hot-pressed sample (at 300℃ under 30MPa for 2h).

hot-pressing at the temperature from 200° to 350 ℃ under 30MPa of mechanical pressing for 2h brought about densification with increasing temperature to result in a maximum relative density (Fig. 4) of about 51% (1.61g/cm^3) at 300 ℃. Therefore hydrothermal hot-pressing temperature was decided to be at 300℃. SEM observation of the solidified disk of HAp hot-pressed hydrothermally at 300 ℃ under 30MPa of mechanical pressing for 2h demonstrated that the microstructure was homogeneous. The micro pores with pore size of about 0.1 μm were dispersed homogeneously (Fig. 5).

According to the dilatometry, densification of the solidified disk of HAp started at about 800℃ and proceeded gradually with increasing temperature to result in linear shlinkage of about 19% at 1150 ℃ (Fig. 6). The densification progressed at lower temperature than that of HAp compacts pressed isostatically (CIP) at room temperature. The solidified disk of HAp shows more homogeneous microstructure with micro-pores dispersion than that of the CIP'ed pellet (Fig. 7), because HAp particles are packed efficiently by water between particles. The CIP'ed compact of HAp, however, has pores in various sizes dispersed inhomogeneously because there are no lubricant media between particles. Therefore in the case of hydrothermal hot-pressing, efficient packing by water between particles caused the progress of the densification at lower temperature. HAp compacts with relative density of about 73% were preparedby hot isostatic pressing (HIP) at 550℃ under 140MPa for 3h from HAp powders added distilled water by Hirota et al. [15]. This indicated that hot-pressing under hydrothermal conditions was effective for densification of HAp. Accordingly hydrothermal hot-pressing should improve not only the packing of HAp particles but also the bonding between particles.

Sintering brought about densification of the solidified disk of HAp by hydrothermal hot-pressing at 300℃ to result in a relative density of about 99% (3.13g/cm^3) at 1050 ℃ for 3h (Fig. 8). SEM observation demonstrated that HAp ceramics sintered at 1050 ℃ had the dense microstructure with few pores and the grain size of about 0.5 μm (Fig. 9). Dehydrated HAp ($Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x$,

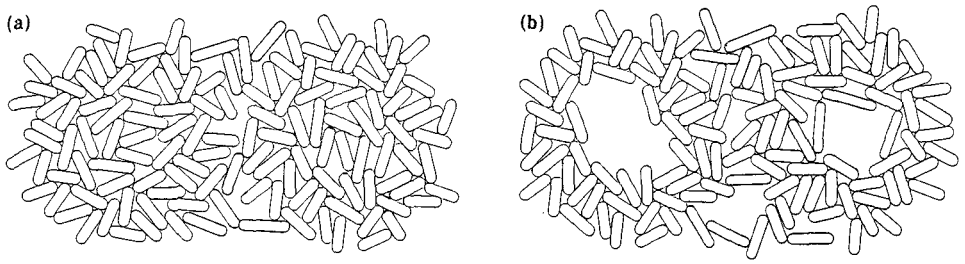

Fig.7 Packing models of the HAp particles

(a) packed by hydrothermal hot-pressing at 300 ℃ under 30MPa for 2h.

(b) packed by cold isostatic pressing under 200MPa for 5min.

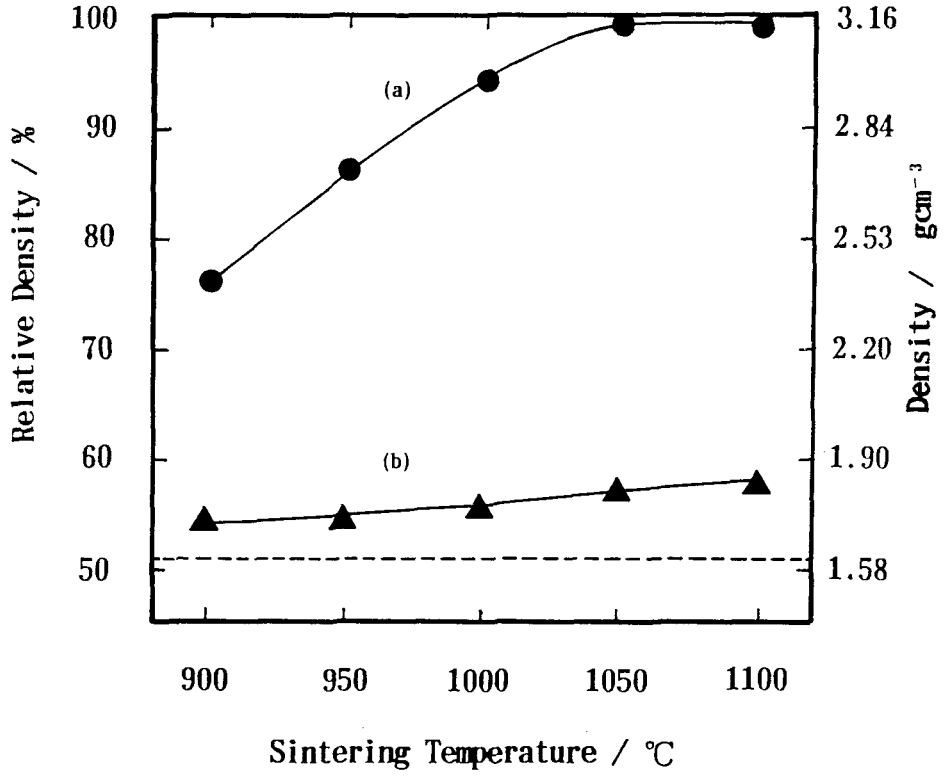

Fig.8 Densification by sintering of the solidified disk of HAp prepared from (a) ultra-fine HAp single crystals and (b) mixture of $Ca(OH)_2$ and $(NH_4)_2HPO_4$ by hydrothermal hot-pressing (heated at the indicated temp. for 3h in air).

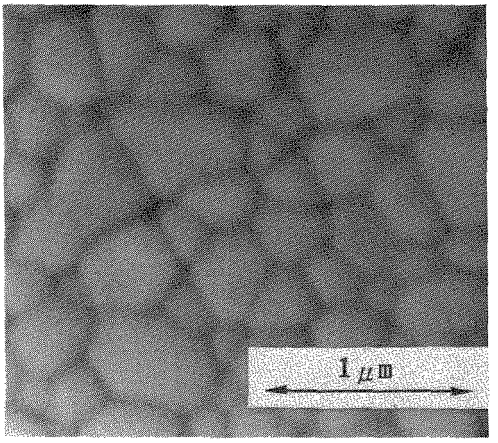

Fig. 9 SEM photograph of the dense HAp ceramics sintered at 1050℃ for 3h in air.

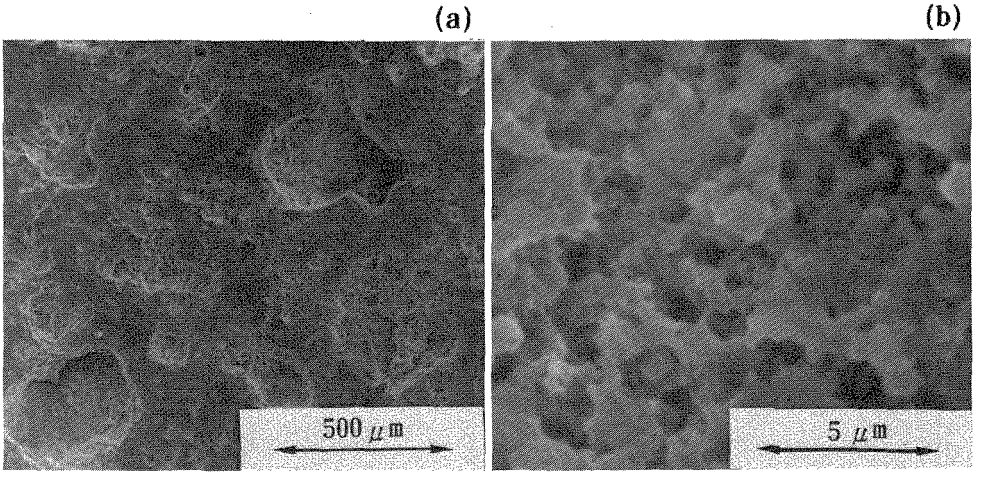

Fig. 10 SEM photograph of the solidified disk of HAp hot-pressed hydrothermally at 300 ℃ under 30MPa for 2h from mixture of $Ca(OH)_2$ and $(NH_4)_2HPO_4$.
(a) low magnification (×50) and (b) high magnification (×5000).

□ :vacancy, X < 1) ceramics can be regarded as being composed of oxyhydroxyapatite with vacancies located on OH sites and was believed to have a slightly lower bioactivity[16]. The previous paper reported that HAp synthesized under hydrothermal conditions did not dehydrate at lower temperature below 1050 ℃ [7]. Therefore sintering temperature should be lower than 1050℃ to prepare the pure HAp ceramics without dehydration. On this study, the dense HAp ceramics without dehydration could be prepared by sintering at 1050℃. The hydrothermal hot-pressing technique should be suitable for preperation of the dense HAp ceramics with stoichiometric composition.

3.2 Preparation of porous HAp ceramics

The reaction process into HAp from $Ca(OH)_2$ and $(NH_4)_2HPO_4$ expressed as follows was characterized by production of NH_3 gas to make large pores in the HAp and to keep the reaction atmosphere basic. HAp is the stable orthophosphate of calcium in neutral and alkaline media[17].

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O + 12NH_3\uparrow$$

The solidified disk of HAp prepared by hydrothermal hot-pressing at 300 ℃ under 30MPa for 2h showed about 51% relative density (1.61g/cm^3) of a porous structure with 40% open porosity (Fig.10(a)). The pore size was 100-500 μm from scanning electron micrographs (SEM), which was larger than the 100 μm above we may expect ingrowth of bone tissue[3]. Figure 10(b) showed micro-pores with the sizes in the order of 1-5μm, which were seemed closed pores. The HAp ceramics sintered at 1050℃ for 3h in air had about 58% relative density(1.83g/cm^3), therefore the open porosity scarcely decreased by sintering. In fact, the macro-pore size was almost same as that of the solidified disk of HAp before sintering(Fig.11). While the micro-pore in the solidified disk of HAp decreased extremely by sintering with increasing temperature.

The compressive strength (Fig.12) of the solidified disk of HAp was about

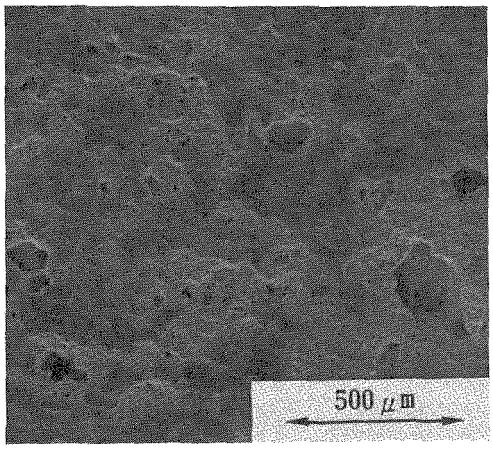

Fig. 11 SEM photograph of the porous HAp ceramics sintered at 1050℃ for 3h in air.

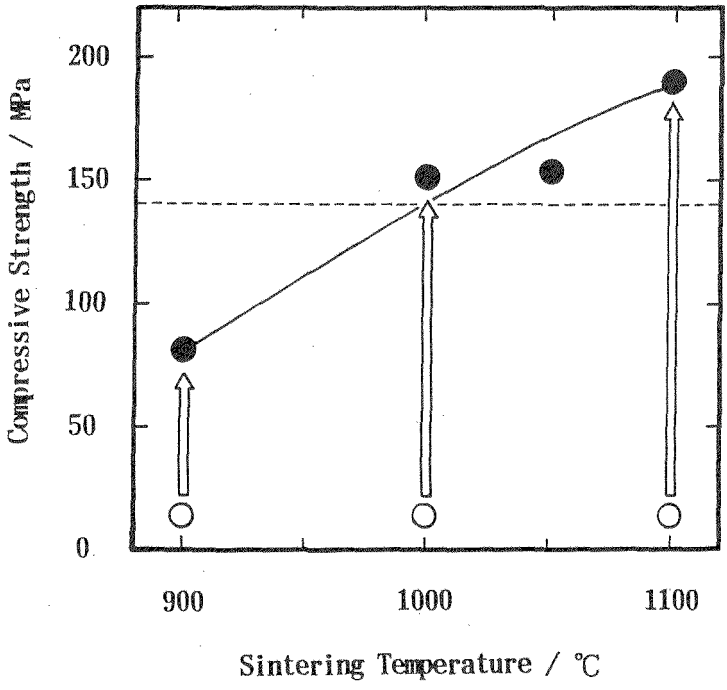

Fig. 12 Compressive strength of the porous HAp ceramics.

○: before sintering (hot-pressed hydrothermally at 300 ℃ under 30MPa for 2h).

●: after sintering at 900～1100℃ for 3h in air.

--- : compact bone.

15MPa. It was quite low compared with bone tissues (88.3～163.8MPa for cortical bone[1], 40 ～60MPa for cancellous bone[18]). The HAp ceramics sintered at 1050 ℃ for 3h showed comparable strength (150 ±20MPa) to that of cortical bone. Peelen et al.[18] have reported that the compressive strengths of porous apatite ceramics made by sintering ; ranged from 30 to 170MPa. The maximum strength is almost same as that of the ceramics prepared by sintering at 1050 ℃ after hydrothermal hot-pressing, but the sintering temperature performed by Peelen et al. was quite higher to obtain pure HAp ceramics without dehydration, that was 1250 ℃.

The compressive strength of porous HAp ceramics from the solidified disk prepared by hydrothermal hot-pressing could be varied within wide limits (15 ～ 150±20MPa) by changing the sintering temperature below 1050 ℃. These porous ceramics without dehydration had over 40% porosity with large pore size, therefore the ceramics can be expected to have good bonding-osteogenesis.

4. Summary

The solidified disk of HAp hot-pressed hydrothermally at 300 ℃ under 30MPa for 2h from ultra-fine HAp single crystals had about 51 % relative density. The solidified disk showed homogeneous microstructure, thus sintering at 1050 ℃ for 3h in air brought about densification of the HAp ceramics up to 99% density with few pores and the grain size of about 0.5 μm.

The solidified disk of HAp hot-pressed hydrothermally at 300 ℃ under 30MPa for 2h from the mixture of $Ca(OH)_2$ and $(NH_4)_2HPO_4$ showed porous microstructure with about 49% porosity (open pore 40 %). The open pore with the sizes in the order of above 100μm scarcely decreased by sintering at 1050℃ for 3h in air. This ceramics had comparable compressive strength of 150±20MPa to that of cortical bone.

The microstructure-designed HAp ceramics could be prepared by hydrothermal hot-pressing without dehydration.

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