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Microstructure Designed Porous Apatite Ceramics Prepared by Hydrothermal Method

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Microstructure designed porous ceramics of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) were prepared by hydrothermal method. The particle size, shape, and the micro-pore size of the porous hydroxyapatite ceramics could be controlled. The hydroxyapatite was non-stoichiometric apatite with calcium deficient compositions (Ca/P ratio<1.67). The composition of non-stoichiometric hydroxyapatite ceramics could be controlled from 1.50 to 1.63 in Ca/P ratio. The hydroxyapatite ceramics prepared at 105°C under the saturated vapor pressure for 20 h were composed of rod-shaped crystals with about 10 μm in length with the mean aspect ratio of 40. The porous ceramics of calcium deficient hydroxyapatite had about 45% porosity with the inter-connecting pore structure. Porous hydroxyapatite ceramics prepared hydrothermally had the compressive strength of about 10 to 30 MPa. In addition, porous ceramics of β-tricalcium phosphate (β-$Ca_3(PO_4)_2$) were prepared from the calcium deficient hydroxyapatite.

Key words : Hydroxyapatite, β-tricalcium phosphate, Hydrothermal

I. Introduction

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$: HA) is one of the most bio-compatible materials owing to similarities with inorganic constituents of bones and teeth.[1,2] The apatite in bones is calcium deficient hydroxyapatite with non-stoichiometric composition.[2] Therefore, the calcium deficient HA must be more bio-compatible than stoichiometric HA. The implant materials for human bones and teeth require not only bio-compatibility but also suitable microstructure for promoting bone formation. The inter-connecting pore structure is essential to bonding with natural bone.

Porous materials with precisely controlled microstructures and compositions are necessary for the quantitative characterization of the new bone formation on materials and of the resorption of materials *in vivo.* The authors prepared the translucent dense HA ceramics by hydrothermal hot-pressing,[3,4] and the hardened materials of calcium-alumino-silicate glass and some kinds of calcium phosphate by the hydrothermal treatment.[5,6] The present paper deals with the preparation of microstructure designed porous ceramics of calcium deficient HA with inter-connecting pore structure by the hydrothermal technique. In addition, porous ceramics of β-tricalcium phosphate (β-$Ca_3(PO_4)_2$: β-TCP) with almost same microstructure could be prepared by heating the calcium deficient HA.

II. Experimental Procedure

Commercial α-tricalcium phosphate powders (α-$Ca_3(PO_4)_2$: α-TCP, Taihei Chemical Industrial Co., Ltd., Japan) were used as the starting material. The powder was formed into cylindrical shape of 8 mmϕ × 10 mmL with about 60% porosity. The samples were set in a 105 cm^3 autoclave with 10 cm^3 of ion-exchanged water addition, then they were exposed to vapor of water under the various conditions at the temperatures from 30°C to 250°C for 20 h.

The produced phases were identified by powder X-ray diffractometry with Ni filtered CuKα radiation, operating at 40 kV and 20 mA (XRD; Mac Science, MXP3, Japan). The HA content in the prepared samples was estimated by XRD measurement. The relative intensity of XRD lines for HA was used in order to determine the HA content.[7] The samples prepared were dissolved in 0.1 M nitric acid, and then the chemical composition of them was analyzed by inductively coupled plasma spectrometer (ICP-MS; Seiko Instruments, SPQ 9000, Japan).

The microstructure of specimens was observed by scanning electron microscope for the surface and for the fractured surface (SEM; JEOL, JSM-25S, Japan). Pore volume and distribution of pore diameter were measured by marcury intrusion porosimetry (MIP; Carlo Elba, Porosimeter 2000, Italy). The compressive strength of porous materials was measured by mechanical testing machine (Tokyo Testing Machine, UTM Type RAT 30, Japan).

III. Results and Discussion

Cylindrical samples exposed to vapor of ion-exchanged water were hardened because of formation of HA from α-

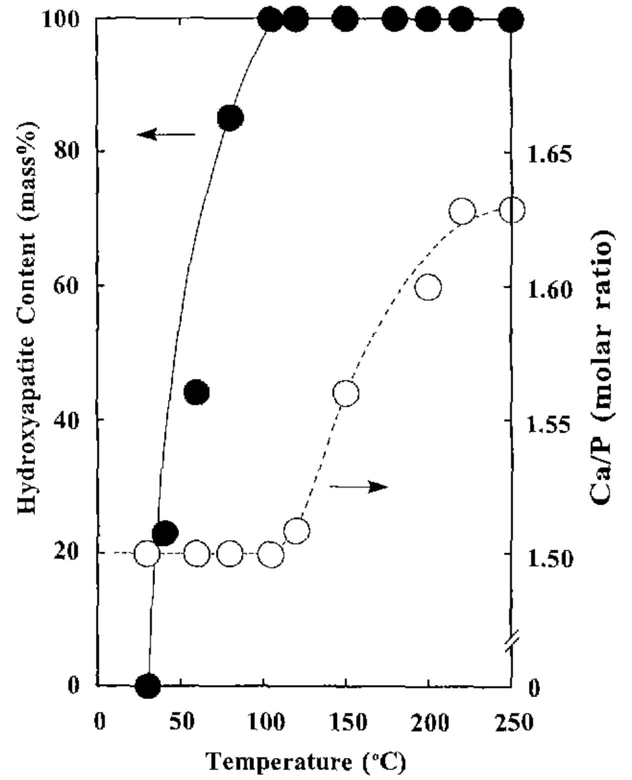

Fig. 1. Amount of formed hydroxyapatite in the porous materials and Ca/P molar ratio of the materials prepared by vapor exposure treatment at the temperatures indicated for 20 h.

TCP[8] as the bonding material. In the present experiment, HA was formed at the temperatures above 40°C and then no phases other than HA were revealed by XRD for the samples treated at the temperatures above 105°C. Relationship between the treatment temperature and the amount of formed HA was shown in Fig. 1. The reaction between α-TCP and water was considered as follows, if the obtained HA was the stoichiometric HA.

$$10Ca_3(PO_4)_2+6H_2O \rightarrow 3Ca_{10}(PO_4)_6(OH)_2+2H_3PO_4 \quad (1)$$

Indeed, the treating water after hydrothermal treatment was dilute aqueous solution of phosphoric acid according to ICP-MS analysis. The value of pH of the treating water was about 5. However, the produced HA was not stoichiometric HA, that was calcium deficient HA. In general, chemical formula of calcium deficient HA is described as follows.[8,9]

$$Ca_{10-x}H_x(PO_4)_6(OH)_{2-x} \cdot nH_2O \quad (2)$$

The composition of the apatite could be controlled. The Ca/P ratio of the samples increased with increasing treatment temperature from 1.50 to 1.63 (Fig. 1), but the Ca/P ratio of the samples was lower than that of stoichiometric HA (Ca/P ratio of stoichiometric HA=1.67).

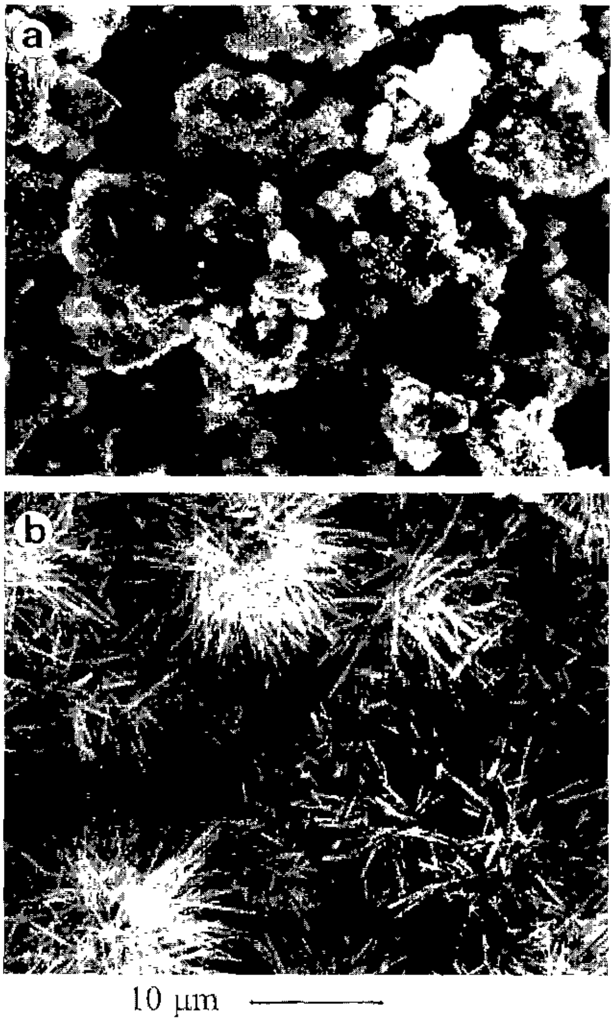

Fig. 2. SEM photographs of fractured surface of samples prepared at 80°C (a) and at 105°C (b) under the saturated vapor pressure for 20 h. Rod-shaped particles of (b) were calcium deficient hydroxyapatite.

Porous HA ceramics prepared at the temperatures below 80°C were composed of irregular formed particles (Fig. 2(a)). In the contrast, homogeneous porous structure was observed by SEM for the samples treated at the temperatures above 105°C. Porous HA ceramics prepared hydrothermally at 105°C was composed of rod-shaped crystals elongated along the c-axis by SEM observation (Fig. 2(b)). The HA crystals were about 10 μm in length with the mean aspect ratio of 40. This porous HA ceramics had the porosity of about 45%. The distribution of micro-pore size measured by MIP is shown in Fig. 3. The mean diameter of micro-pore was 82.3 nm in size. The porosity and the size of micro-pore increased slightly with increasing temperature of the hydrothermal treatment. The compressive strength of the porous HA prepared at 105 °C was about 10 MPa, and prepared at 250°C was about 30 MPa. Calcium deficient HA tends to decompose into tricalcium phosphates by heating in comparison with stoichiometric HA.[7,10] Thus, porous ceramics of β-tricalcium phosphate (β-$Ca_3(PO_4)_2$: β-TCP) were obtained from the porous ceramics of calcium deficient HA with Ca/P ratio of 1.50 by heating at 900°C for 3 h in air. This

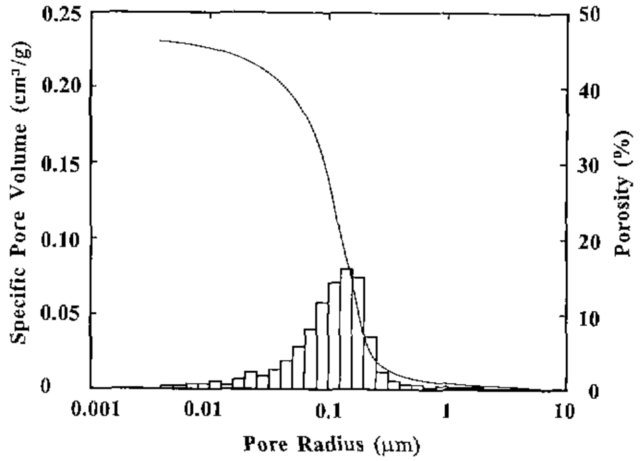

Fig. 3. Pore size distribution of porous hydroxyapatite ceramics prepared hydrothermally at 105°C under the saturated vapor pressure for 20 h.

porous β-TCP had almost same micro-structure in comparison with the porous HA before heating. The porous β-TCP was composed of rod-shaped particles with about 10 μm in length, and it had almost same porosity and micro-pore size. The compressive strength of the porous material increased by heating at 900°C in air. The compressive strength of the porous β-TCP was about 40 MPa.

New bone formation on stoichiometric HA, calcium deficient HA and β-TCP, and resorption of these materials *in vivo* have not been characterized quantitatively in the previous investigation, since the micro-structure and compositions of materials were not controlled precisely. The bone formation on materilas and resorption of materials were under the influence of the microstructure and compositions of materials.[11,12] Therefore porous ceramics of HA and β-TCP prepared in this study should be good materials for quantitative analysis of bone formation and resorption in vivo.

IV. Conclusions

The results described in this paper allow to draw the following conclusions.

(1) Porous HA ceramics were prepared hydrothermally. The porous HA ceramics prepared at 105°C were composed of rod-shaped crystals of about 10 μm in length with homogeneous microstructures.

(2) The HA was calcium deficient hydroxyapatite. The Ca/P molar ratio of the HA could be controlled from 1.50 to 1.63.

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References

1. S. F. Hulbert. "History of the Use of Hydroxyapatite as a Biomaterial", pp. 509-512 in Apatite Vol. 1 (Proc. 1st Int. Sympo. Apatite, Mishima, Japan), Ed. by H. Aoki, M. Akao, N. Nagai, T. Tsuji, Japan Assoc. Apatite Sci., Tokyo, 1992.
2. H. Aoki, "Medical Applications of Hydroxyapatite," Ishiyaku EuroAmerica, Tokyo and St.Louis, 1994.
3. K. Ioku, K. Yamamoto, K. Yanagisawa and N. Yamasaki, "Low Temperature Sintering of Hydroxyapatite by Hydrothermal Hot-Pressing," *Phosphorus Research Bulletin*, **4**, 65-70 (1994)
4. K. Ioku, K. Yanagisawa, T. Kai, K. Yamamoto and N. Yamasaki, "Apatite Ceramics Prepared by Hydrothermal Hot-Pressing," pp. 118-121 in Solvo-Thermal Reactions Vol. 1 (Proc. 1st Int. Conf. Solvo-Thernal Reactions, Takamatsu, Japan), Ed. by Organizing Comittee of Solvo-Thermal Reactions, 1994.
5. S. Goto, M. Hirata, T. Obana and K. Ioku, "Hardened Material of Calcium-Alumino-Silicate Glass and Calcium Phosphate by Hydrothermal Treatment," *Phosphorus Research Bulletin*, **4**, 95-98 (1994).
6. S. Goto, M. Hirata, T. Obana and K. Ioku, "Hydrothermal Hardening of Calcium-Alumino-Silicate Glass with Calcium Phosphate," pp. 61-64 in Solvo-Thermal Reactions Vol. 1 (Proc. 1st Int. Conf. Solvo-Thermal Reactions, Takamatsu, Japan), Ed. by Organizing Comittee of Solvo-Thermal Reactions, 1994.
7. K. Ioku, T. Murakami, Y. Ikuma and M. Yoshimura, "Preparation of Microstructure-Controlled Porous Hydroxyapatite-β-Tricalcium Phosphate Composites by Reaction Sintering," *J. Ceram. Soc. Japan, Int. Edition*, **100**, 1001-1005 (1992).
8. H. Monma and T. Kanazawa, "The Hydration of a-Tricalcium Phosphate," *J. Ceram. Soc. Japan* (Yogyo-Kyoka-i-Shi), ***84***(4), 209-213 (1976).
9. S. R. Kim, K. Hirota, F. P. Okamura, Y. Hasegawa and S. J. Park, "Densification of Calcium-Deficient Hydroxyapatite by Hot Isostatic Pressing," *J. Ceram. Soc. Japan* (Seramikkusu Ronbunshi), **98**(3), 257-263 (1990).
10. K. Ishikawa, P. Ducheyne and S. Radin, "Determination of the Ca/P Ratio in Calcium-deficient Hydroxyapatite using X-ray Diffraction Analysis", *J. Mater. Sci.: Materials in Medicine*, **4**, 165-168 (1993).
11. K. Ioku, S. Goto, H. Kurosawa, K. Shibuya, H. Yokozeki, T. Hayashi and T. Nakagawa, "Reaction of Porous β-TCP with Different Microstructure *in Vivo*," pp. 201-204 in Bioceramics Vol.9, Ed. by T. Kokubo, T. Nakamura and F. Miyaji, Elsevier Science, Japan, 1996.
12. H. Yokozeki, T. Hayashi, T. Nakagawa, H. Kurosawa, K. Shibuya and K. Ioku, "Influence of Surface Microstructure on the Reaction of the Active Ceramics *in Vivo*," *J. Mater. Sci.: Materials in Medicine*, **9**(7), 381-384 (1998).