

Preparation of Porous Ceramics of β -Tricalcium Phosphate Composed of Rod-shaped Particles

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Porous ceramics of β -tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$: β -TCP) with much amount of micro-pores of about 0.2 μm in size were prepared from porous ceramics of the non-stoichiometric hydroxyapatite with calcium deficient composition in Ca/P ratio of 1.50. The porous ceramics of calcium deficient hydroxyapatite prepared hydrothermally at 105 $^\circ\text{C}$ 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. This apatite ceramics had about 50 % porosity with the inter-connecting pore structure. The porous β -TCP ceramics prepared by heating of the hydroxyapatite at 900 $^\circ\text{C}$ for 3 h in air had the almost same microstructure as the porous hydroxyapatite. The compressive strength of the porous β -TCP was about 40 MPa.

Key words: β -tricalcium phosphate, hydroxyapatite, microstructure, porous material

1. INTRODUCTION

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: HA) and β -tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$: β -TCP) are currently used as bone graft substitutes [1-5]. They have been known to be biocompatible and osteoconductive [6]. Several previous studies have also confirmed that β -TCP is a more biodegradable implant material than HA [7-9]. The authors reported that micro-pores of β -TCP with about 0.1-0.5 μm in size were important for bio-resorption in bones, therefore micro-pores should be controlled for ceramics of β -TCP.

The present paper deals with the preparation of microstructure designed porous ceramics of β -TCP.

2. EXPERIMENTAL PROCEDURE

Commercial powders of α -tricalcium phosphate (α - $\text{Ca}_3(\text{PO}_4)_2$: α -TCP, Taihei Chemical Industrial Co., Ltd., Japan) were used as the starting material. The powder was formed into cylindrical shape of 8 mm ϕ $\times$ 10 mmL with about 60 % porosity. The samples were set in a 105 cm³ autoclave with 10 cm³ of dilute aqueous ammonia addition, then they were exposed to vapor of the solution at 105 $^\circ\text{C}$ under the saturated vapor pressure for 20 h. The samples were heated at 900 $^\circ\text{C}$ for 3 h in air for preparation of β -TCP.

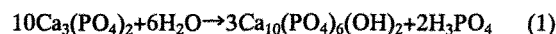
The produced phases were identified by powder X-ray diffractometry with Ni filtered $\text{CuK}\alpha$ radiation, operating at 40kV and 20mA (XRD; Mac Science, MXP³, Japan). The HA content in the prepared samples was estimated by XRD measurement. The relative intensity of XRD lines for HA was used in order to determine the HA content [10]. The samples prepared were dissolved in 0.1 mol $\cdot$ dm⁻³ nitric acid, and then the chemical composition of them was analyzed by inductively coupled plasma spectrometer (ICP-MS; Seiko Instruments, SPQ 9000S, 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 mercury 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).

3. RESULTS AND DISCUSSION

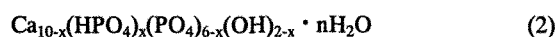
3.1 Porous ceramics of hydroxyapatite

Cylindrical samples exposed to vapor of aqueous ammonia were hardened because of formation of HA from α -TCP [11] 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. The reaction between α -TCP and water was considered as follows, if the obtained HA was the stoichiometric HA.



Indeed, the treating solution after hydrothermal treatment was dilute aqueous solution of phosphoric acid according to ICP-MS analysis. The value of pH of the treating solution 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.



The authors reported that composition of this apatite could be controlled [12]. The Ca/P ratio of the samples increased with increasing treatment temperature from 1.50 to 1.63 [12], but the Ca/P ratio of the samples was lower than that of stoichiometric HA (Ca/P ratio of stoichiometric HA=1.67).

Porous HA ceramics prepared at the temperatures below 80 °C were composed of irregular formed particles. 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. The HA crystals were about 10 nm in length with the mean aspect ratio of 40. This porous HA ceramics had the porosity of about 50 %. The distribution of micro-pore size measured by MIP is shown in Fig. 1. The mean diameter of micro-pore was 0.08 μm 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.

3.2 Porous ceramics of β -tricalcium phosphate

Calcium deficient HA tends to decompose into tricalcium phosphates by heating in comparison with stoichiometric HA [10, 13]. Thus, porous ceramics of β -tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$; β -TCP) were obtained from the porous ceramics of calcium deficient HA with Ca/P ratio of 1.50 by heating it at 900 °C for 3 h in air. This porous β -TCP had almost the 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. The mean diameter of

micro-pore of β -TCP ceramics was slight larger than that of HA ceramics, the value was about 0.2 μm in size (Fig. 1). The compressive strength of the porous material increased by heating at 900 °C for 3 h in air. The compressive strength of the porous β -TCP was about 40 MPa.

New bone formation on HA and β -TCP, and resorption of these materials *in vivo* have not been characterized quantitatively in the previous investigation, since the microstructure and compositions of materials were not controlled precisely. The bone formation on materials and resorption of materials were under the influence of the microstructure and compositions of materials [14, 15]. Porous β -TCP with much amount of micro-pores prepared in this study should be more bio-degradable than the conventional materials.

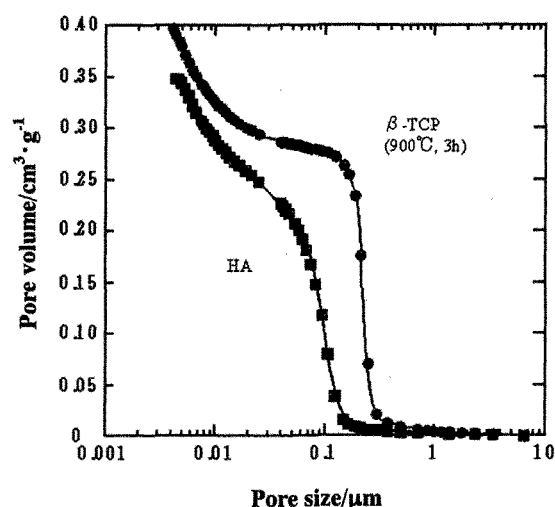


Fig. 1 Pore size distribution of porous ceramics of hydroxyapatite (■) and β -tricalcium phosphate (●).

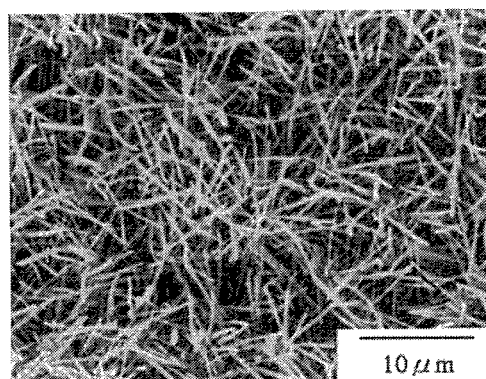


Fig. 2 Porous ceramics of β -tricalcium phosphate composed of rod-shaped particles.

4. CONCLUSIONS

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

(1) Porous ceramics of calcium deficient hydroxyapatite were prepared hydrothermally at 105 °C for 20 h. This ceramics were composed of rod-shaped crystals of about 10 µm in length.

(2) Porous ceramics of β-tricalcium phosphate were prepared from the calcium deficient hydroxyapatite by heating it at 900 °C for 3 h in air. This ceramics were composed of rod-shaped particles of about 10 µm in length, and had much amount of micro-pores. The mean diameter of micro-pores of β-TCP ceramics was slight larger than that of HA ceramics, the value was about 0.2 µm in size

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