HYDROXYAPATITE SHEET PREPARED FROM ALPHA-TRICALCIUM PHOSPHATE BY HYDROTHERMAL METHOD

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Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: HA) is widely used as bioceramics. In general, sintering process is indispensable to give shape to the ceramics. However, it is impossible to control the crystal face of materials surface. Using hydrothermal reactions for HA preparation, it is possible to control the crystal face and the chemical composition. The authors reported various kinds of HA materials prepared by the unique hydrothermal methods.

In the present investigation, porous HA sheet with tailored crystal surface were prepared by the hydrothermal method. The HA sheet prepared at 120 °C under the saturated vapor pressure of water for 3h was composed of rod-shaped HA crystals. These crystals were about 30 μm in length with aspect ratio of about 10 and they had non-stoichiometric HA composition of Ca/P molar ratio less than 1.67. This material must be suitable as scaffold for cultured bone, for bone graft material and for drug delivery system (DDS).

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INTRODUCTION

Because of excellent biocompatibility, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: HA) is widely used as implant materials [1,2]. Polycrystalline HA with random crystal surface prepared by sintering has already been used as a bone-repairing material which can directly bond to natural bones in bony defect. In addition, HA is used as a material for chromatography column.

In general, sintering process is indispensable to give shape to the ceramics. However, it is impossible to control the crystal face of materials surface. HA has typical two crystal face (*a*-surface and *c*-surface). Adsorption properties of HA depend on the crystal face. These areas of crystal face depend on morphology. Fig.1 shows typical HA morphology (Plate-shape and Rod-shape). In rod-shape HA, area of *a*-surface is larger than that of *c*-surface. If HA materials could have the tailored specific crystal surface, the HA materials should have the advantage of adsorptive activity.

Thus, crystal face control by controlling of crystal morphology leads to quick bone repairing and give good materials for regenerative medicine. The authors reported various kinds of HA materials, for example, fine single crystals, whiskers, dense or porous ceramics, sheets, spherical particles, etc., prepared by the unique hydrothermal methods [3-12]. Using hydrothermal reactions for HA preparation, it is

possible to control the crystal face, pore structures and its chemical composition.

In the present investigation, porous HA sheet with tailored crystal surface were prepared by the hydrothermal method [8,9,11]. This material must be suitable as scaffold for cultured bone, for bone graft material and for drug delivery system (DDS).

Fig. 1 Crystal morphology of HA

MATERIALS AND METHODS

Preparation method of HA sheet was shown in Fig. 2. Commercial powders of α -tricalcium phosphate (α -Ca₃(PO₄)₂: α -TCP, Taihei Chemical Industrial Co., Ltd., Japan) and polyvinyl alcohol (PVA, Wako Pure Chemical Industries Ltd., Japan) were used as the starting materials. The slurry of α -TCP with PVA was prepared by using 10 mass% PVA solution at room temperature.

To remove bubbles, the slurry was kept under vacuum condition. Films of α -TCP with PVA were prepared from this slurry by spin coating technique. This method is very popular technique to preparing polymer film. The glass dish was set on the turntable, and then the slurry was cast in the glass dish and twiddled. Films of α -TCP with PVA were dried at room temperature for about 12 h. In order to control the thickness of films, rotation speed was controlled.

The dried films were cut into circular shape of about 12 mm ϕ . Then they were heated at 1200 °C for 5 min in air to remove organic matter. The sample was set in autoclave and treated hydrothermally at the temperatures at 120 to 200 °C, for 5 h under the saturated vapor pressure. The part of samples were heated at 900 °C for 3h in air for estimation of Ca and P composition of the HA prepared by hydrothermal treatment. Calcium deficient HA (Ca/P mole ratio < 1.67) was decomposed into stoichiometric HA (Ca/P=1.67) and stoichiometric β -TCP (Ca/P=1.50). This phenomenon was used in order to determine the HA and β -TCP contents [5].

Fig. 2 Preparation method of HA sheets.

The produced phases were identified by powder X-ray diffraction with graphite-monochromatized CuK α radiation, operating at 40 kV and 20 mA (XRD; Rigaku, Geiger flex 2027, Japan). The microstructure of specimens was observed by scanning electron microscope (SEM; JEOL, JSM-T300, Japan). Pore volume and distribution of pore diameter were measured by mercury intrusion porosimetry (MIP; Carlo Elba, Porosimeter 2000, Italy). Thermal analysis and measurement (TG-DTA; Seiko Instruments Inc. TG/DTA32, Japan) were conducted up to 1200 °C with heating rate 10 °C /min, and the standard material being α -Al₂O₃ (Wako Pure Chemical Industries Ltd., Japan).

RESULTS AND DISCUSSION

The thickness of α -TCP film was controlled from about 50 μ m to about 1 mm by controlling of rotation speed. The mixture film of α -TCP and PVA could be made into a convenient form. To remove PVA, the mixture of α -TCP and PVA film was heated at 1200 °C for 5 min in air. The shape of sheets did not change and handling of the sample was not difficult. From XRD, there were no phases other than α -TCP after heating at 1200 °C.

By using hydrothermal method [8,9,11], α -TCP was changed into HA and the sample was hardened because of hydration of α -TCP. From X-ray diffraction, all peaks were assigned to HA [13]. So, all sheets treated hydrothermally between 120 and 200 °C was HA (Fig. 3). Relative Intensity of (300) diffraction were higher than (112) diffraction. This results shows HA sheets consisted rod shaped HA. The area of *a*-surface was larger than that of *c*-surface in rod shape.

The HA sheet after heating at 900 °C for 3 h in air contained HA and β -TCP. The relative intensity of XRD lines for HA and for β -TCP was used in order to determine the HA and β -TCP contents and then the Ca/P molar ratio of samples was estimated. The value of Ca/P of the HA sheet prepared by hydrothermal treatment at 120 °C for 3 h was 1.56, that was lower than Ca/P of stoichiometric HA (Ca/P=1.67). This results shows HA sheets consisted calcium deficient hydroxyapatite. The Ca/P molar ratio of HA sheets were increased treating temperatures. The highest value was 1.60 (Table1).

Fig. 3 shows the sheet prepared by hydrothermal treatment at 120 °C for 5 h under the saturated vapor pressure. The porosity of HA sheet was about 75 % and specific surface area was about 30 m²/g.

α -TCP sheet prepared by hydrothermal treatment at 120 °C for 5 h was composed of rod-shaped crystals elongated along the *c*-axis by SEM observation (Fig. 5). The rod-shaped crystals were about 10 μ m in length and locked together to make micro-pores of about 10nm and about few μ m in size. The size of micro-pores increased gradually with the hydrothermal treatment period (Fig. 6).

Fig. 3 XRD patterns of HA sheets treated hydrothermally at indicating temperatures.

Table1 Relationship of hydrothermal temperatures and Ca/P molar ratio of HA sheets

temperature / °C	Ca/P molar ratio
120	1.56
140	1.57
160	1.59
180	1.60
200	1.59

Fig. 4 HA sheet prepared by hydrothermal treatment at 120 °C for 5h under saturated vapor pressure.

Fig. 5 SEM image of the sample prepared hydrothermally at 120 °C for 5h.

Fig. 6 Pore distribution of the sample before and after hydrothermal treatment (120 °C, 5h).

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