Hydroxyapatite Sheet Prepared by Hydrothermal One-process Method

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$: HA) is widely used as ceramic biomaterials. In general, sintering process is indispensable to shape 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 one-process method. The HA sheet prepared at 120 ºC under the saturated vapor pressure of water for 3 h 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 and carrier for drug delivery system (DDS).

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) has excellent biocompatibility. So, it 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 of hexagonal crystal system). Adsorption properties of HA depend on the crystal face and these areas of crystal face depend on its morphology. There are two typical HA morphology. One is plate-shaped crystal grown at *a* axis direction. Another is rod-shaped crystal grown at *c* axis direction. As for rod-shaped 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 prepared by the unique hydrothermal methods [3-10]. 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 [7,8,10]. This material must be suitable as scaffold for cultured bone, for bone graft material and for carrier of drug delivery system (DDS).

2. Experimental Methods

2.1. Sample Preparation

Preparation method of HA sheet was shown in Fig. 2. Commercial powders of α-tricalcium phosphate (α-$Ca_3(PO_4)_2$: 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 square shape of about 10 mm. Then they were heated at 1200 ºC 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 ºC, for 5 h under saturated vapor pressure. Parts of samples treated hydrothermally were heated at 900 ºC for 3h in air for estimation of Ca and P compositional rate. Calcium deficient HA (Ca/P molar 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 [11,12] and then the Ca/P molar ratio was calculated.

2.3. Characterization The produced phases were identified by powder X-ray diffractometry with graphite-monochromatized CuKα 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 pore distribution were measured by mercury intrusion porosimetry (MIP; Carlo Elba, Porosimeter 2000, Italy).

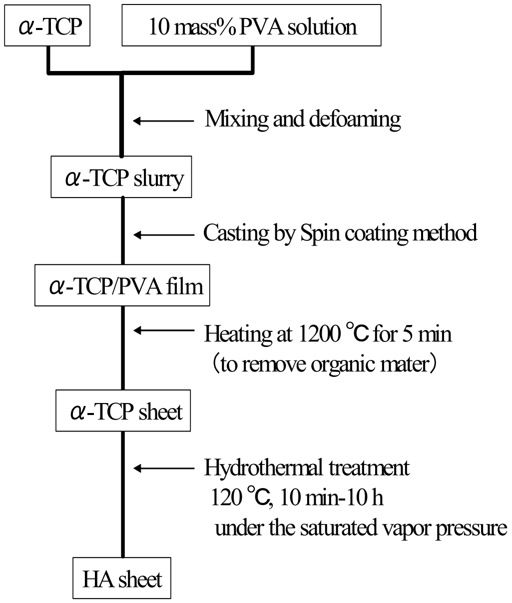

Fig. 1. Preparation method of the HA sheet.

FT-IR spectra were obtained by KBr method using Fourier transform infrared spectroscopy (FT-IR; Perkin Elmer Spectrum 2000, USA). The sample was diluted with spectroscopic grade KBr and about its concentration was 2 mass%. Measurements were taken in N_2 at room temperature. Spectral resolution was 4cm^{-1} and the number of scans was 10.

3. Results and Discussion

The thickness of α-TCP film was controlled from about 50 μm 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 ºC for 5 min in air. The shape of α-TCP sheets changed 15% in length and handling of the sample was not difficult (Fig. 2).

From XRD, there were no phases other than α-TCP after heating at 1200 ºC. Fig. 3 shows α-TCP changed into HA under hydrothermally condition at 120 ºC for indication reaction time. Hydration of α-TCP leads to make HA and harden. Under hydrothermally condition, α-TCP was completely changed HA by 3 h. The HA sheet after heating at 900 ºC 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.

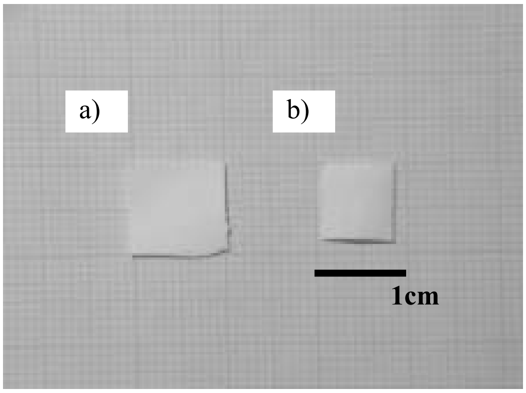

Fig. 2. Shrinkage of α-TCP sheet.
a) before heating.
b) after heating at 1200 ºC for 5 min.

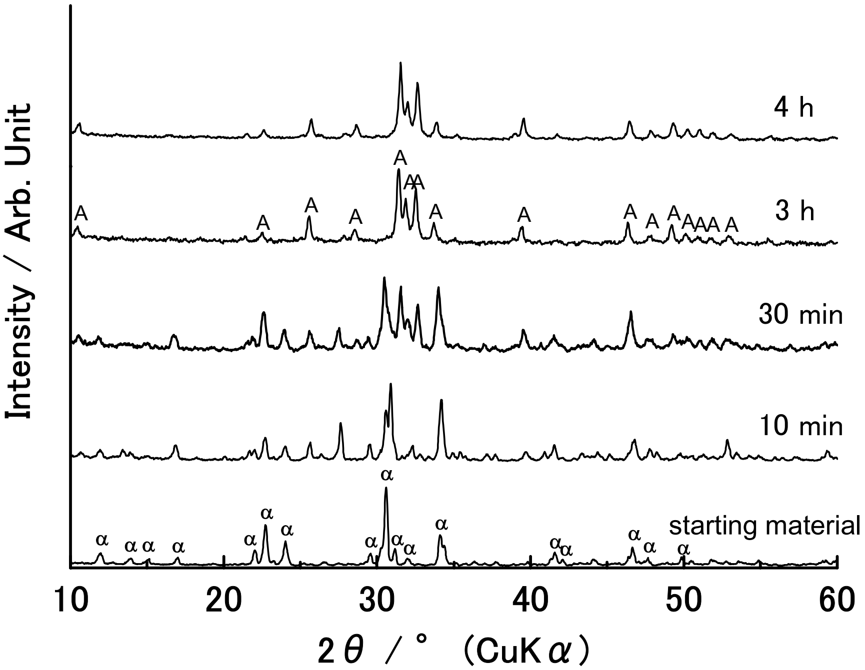

Fig. 3. Patterns of XRD of samples after hydrothermal treatment at 120 ºC for indication reaction period. α; α - tricalcium phosphate, A; Hydroxyapatite

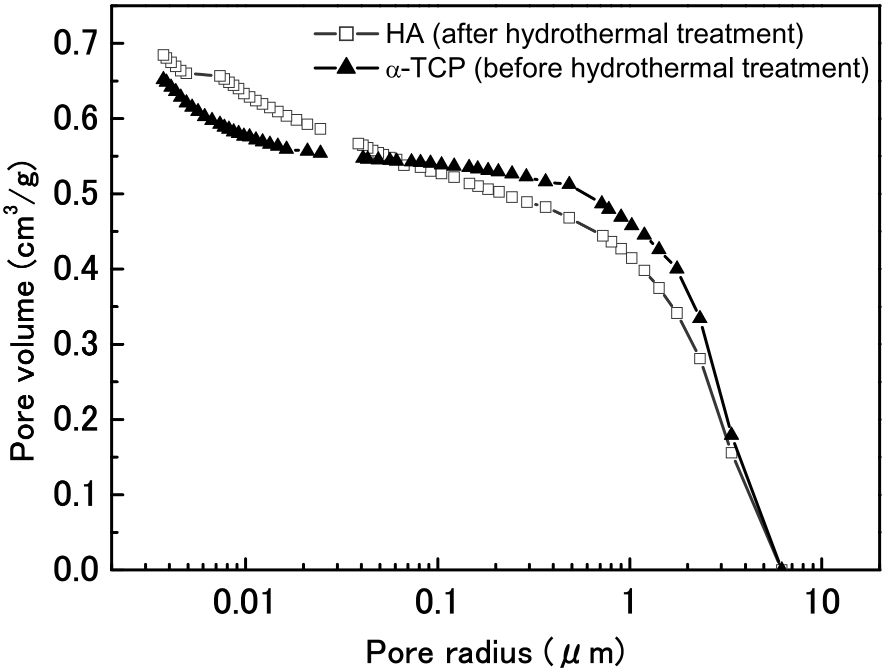

Fig. 4. Pore size distribution of samples before and after hydrothermal treatment at 120 ºC for 3 h.

The value of Ca/P of the HA sheet prepared by hydrothermal treatment at 120 ºC for 3 h was 1.56, that was lower than Ca/P value of stoichiometric HA (Ca/P=1.67). This results shows that HA sheets was calcium deficient hydroxyapatite.

α-TCP sheet prepared by hydrothermal treatment at 120 ºC for 3 h was composed of rod-shaped crystals elongated along the *c* axis by SEM observation. The rod-shaped crystals were about 10 μm in length and locked together to make micro-pores. The size of micro-pores increased gradually with the hydrothermal treatment period. The sheet prepared by hydrothermal treatment at 120 ºC for 3 h under saturated vapor pressure. The porosity of HA sheet was about 75 % and specific surface area was about 30 m^2/g. Fig.4 shows pore size distribution of before and after hydrothermal treatment at 120 ºC for 3 h. Porous sheet of α-TCP, that was the sheet before hydrothermal treatment, had a lot of pores of about 2-5 μm. After the hydrothermal treatment, these pores volume decreased. It was suggested that pores should be filled by formation of HA crystals. Then micro-pores (about 0.01 μm in size) increased. These pores were made from HA crystals locked together.

4. Conclusions

Porous HA sheet with rod-shaped crystal was prepared by the hydrothermal one-process method. This HA was calcium deficient hydroxyapatite.

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