Hydrothermal Preparation of Apatite Composite with Magnetite or Anatase

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Abstract. Microstructure designed porous hydroxyapatite (Ca_{10}(PO_{4})_{6}(OH)_{2}) composites with magnetite (Fe_{3}O_{4}) particles or anatase (TiO_{2}) dispersion were prepared by hydrothermal treatment. These composites had micro-pores of about 0.1-0.5 µm in size. Magnetite / Hydroxyapatite composites should be suitable for medical treatment of cancer, especially in bones, because HA can bond to bones directly and magnetite can generate heat. They must be used for hyperthermia therapies of cancer in bones. Meanwhile, anatase / Hydroxyapatite composite should be suitable for environmental purification, because HA rod-shape particles expose the specific crystal face, which adsorbs organic contaminants and so on.

Keywords: Hydrothermal, Hydroxyapatite, Composite, Magnetite, anatase

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INTRODUCTION

Hydroxyapatite (HA) with the chemical formula corresponding to Ca_{10}(PO_{4})_{6}(OH)_{2}, was well known for the excellent adsorption ability. HA can adsorb DNA, protein and so on, therefore HA is used as a packing media of column chromatography [1, 2]. But conventional HA ceramics have not been controlled crystal faces on their surface, because they are prepared by sintering at high temperature. Therefore the function of HA has not been made the optimum use. On the other hand hydrothermal method using relatively low temperature could make HA rod-shaped crystals. HA rod-shaped crystals expose the specific crystal face (a face) [3], which adsorb selectively effective proteins for bone formation and organic contaminants. Thus, the surface of HA materials should be tailored by composing rod-shaped crystals [4]. HA has been extensively used for implant material due to its biocompatibility [5, 6]. HA with controlled crystal face must have rippler bone formation [7], therefore the authors have reported some kinds of unique HA ceramics with controlled crystal face on its surface [8, 9, 10].

If additional function would be given to HA by addition of functional other materials, the obtained composites should be applied in diverse ways.

In this study, we prepared functional HA composites by dispersion of high functional material particles as follows.

1. Magnetite / Hydroxyapatite composite
   Porous HA composite with magnetite particles dispersion should be suitable for medical treatment of cancer, especially in bones. Because HA can bond to bones directly and magnetite can generate heat by hysteresis loss under the high frequency magnetic field, which must be used for hyperthermia therapies of cancer in bones.

2. Anatase / Hydroxyapatite composite
   Porous HA composite with anatase particles dispersion should be applied favorably for antibacterial applications and environmental purification with less damage on environment. Because HA is the adsorbent of organic contaminants and anatase is the photocatalyst with the ability of decomposition of organic contaminants under irradiation.

EXPERIMENTAL METHOD

1. Magnetite / Hydroxyapatite composite
   Commercial powders of α-tricalcium phosphate (α-Ca_{3}(PO_{4})_{2}: α-TCP, Taihei Chemical Ind., Japan) and magnetite (Fe_{3}O_{4}: Wako Chemical Co., Japan) were used as the starting material. After the addition of 30...
vol% Fe₃O₄ particles of about 1 µm in size to α-TCP, the mixed powder was molded with water addition into cylindrical shape of about 8 mmφ×1 mmL with PLLA fiber of 400 µmφ. After molding, PLLA fiber was pulled out to make interconnecting macro-pores. The composite materials of Fe₃O₄ / α-TCP were set in a 105 cm³ autoclave (Figure 1) with 10 cm³ of water, and then they were exposed to vapor of water at 120 ºC under saturated vapor pressure for 10 h. Then the samples were retreated hydrothermally in the liquid phase at 200 ºC for 10 h in NH₃ aq. of pH 11. The molar ratio of Ca/P was determined by heating of samples at 900 ºC for 3 h in air, because Ca deficient HA decompose stoichiometric HA and stoichiometric β-tricalcium phosphate (β-Ca₃(PO₄)₂; β-TCP).

2. Anatase / Hydroxyapatite composite
Commercial powders of α-TCP and anatase (TiO₂: Titan Industrial Co., Japan) were used as the starting material. After the addition of 40 vol% TiO₂ particles to α-TCP, the mixed powder was formed into cylindrical shape of about 8 mmφ×1 mmL. The composite materials of TiO₂ / α-TCP were set in a 105 cm³ autoclave (Figure 1) with 10 cm³ of water, then they were exposed to vapor of water at 120 ºC under saturated vapor pressure for 20 h. The samples were heated at 900 ºC for 3 h in air, because of determination of Ca/P molar ratio of HA.

3. Characterization of materials
The produced phases were identified by powder X-ray diffractometry with graphite-monochromatized CuKα radiation, operating at 40 kV and 20 mA (XRD; Mac Science, MXP³, Japan). The microstructure of specimens was observed by scanning electron microscope (SEM; JEOL, JSM-T300, Japan).

RESULTS AND DISSOCIATION
1. Magnetite / Hydroxyapatite composite
Porous composites of HA / Fe₃O₄ was prepared under hydrothermal conditions, because hydrothermal method using relatively low temperature could make HA easily without reaction between HA and Fe₃O₄.
Cylindrical samples prepared by hydrothermal treatment were hardened because of formation of HA from α-TCP as the bonding material [11]. The
reaction between $\alpha$-TCP and water was considered as follows, if the obtained HA was the stoichiometric HA.

$$10\alpha\text{-Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2\text{H}_3\text{PO}_4$$

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 [11].

$$\text{Ca}_{10-x}\text{H}_x(\text{PO}_4)_6(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$$

The XRD pattern of the composite sample after hydrothermal treatment is showing hydroxyapatite and magnetite (Fig.2). Magnetite did not affect the hydration of $\alpha$-TCP. Calcium deficient HA tends to decompose into tricalcium phosphates by heating in comparison with stoichiometric HA. Thus, porous ceramics of $\beta$-TCP were obtained from the porous ceramics of calcium deficient HA with Ca/P ratio under 1.67 by heating at 900 $^\circ$C for 3 h in air. Homogeneous porous structure was observed by SEM for the samples prepared by hydrothermal treatment. Porous composite materials of $\text{Fe}_3\text{O}_4$ / HA were composed of rod-shaped particles of HA with $\text{Fe}_3\text{O}_4$ particles dispersion by SEM observation (Fig.3). The HA crystals were about 10 $\mu$m in length with the mean aspect ratio of 25. This porous composite materials of $\text{Fe}_3\text{O}_4$ / HA had the porosity of about 70%. In addition, pores of about 400 $\mu$m in size could be formed as the mark of PLLA fibers which were made by pull-out fibers after molding. The size of macro-pores depended on the diameter of fiber, and pores had the interconnecting tunnel form (Fig.4).

**FIGURE 3.** SEM photograph of the surface of magnetite / hydroxyapatite composite prepared by hydrothermal method.

**FIGURE 4.** SEM photograph of the polished face of magnetite / hydroxyapatite composite prepared by hydrothermal method. Macro-pore was observed.

**FIGURE 5.** XRD patterns of (a) starting mixture of $\alpha$-TCP and TiO$_2$, (b) the composite prepared by hydrothermal method.
2. Anatase / Hydroxyapatite composite

After hydrothermal treatment, the reaction between α-TCP and anatase was not recognized according to XRD (Fig. 5), therefore it was considered that almost same reaction was occurred as shown in the case of preparation of magnetite / hydroxyapatite composite. The samples were hardened by the formation of hydroxyapatite as bonding material from α-TCP. The crystal phase of anatase did not change measurement. The obtained hydroxyapatite in this composite was non-stoichiometric hydroxyapatite with calcium deficient composition.

Figure 6 shows the surface of the composites with anatase particles prepared by hydrothermal treatment. Porous HA ceramics prepared by hydrothermal treatment were composed of rod-shaped crystals elongated along the c-axis [12]. The length crystals were about 2 μm with the mean aspect ratio over 25. Rod-shaped crystals were locked together to make micro-pores [13].

CONCLUSIONS

In this research, microstructure designed magnetite / HA and anatase / HA composites were prepared. These composites had micro-pores of about 0.1-0.5 μm in size. Porous composites of magnetite / HA and anatase / HA were prepared by hydrothermal method at 120 °C under the saturated vapor pressure for 10 h. Magnetite particles of about 1 μm in size with polyhedral shape or anatase particles of about 0.1μm in size were dispersed into HA porous matrix. This composite must have the advantage of adsorptive activity, because the HA has many specific crystal surface and micro-pores.

REFERENCES