Fabrication of Porous Ceramics with Well-Controlled Open Pores by Sintering of Fibrous Hydroxyapatite Particles

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1. Introduction

Hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$; HAp) is the chief inorganic material present in a vertebrate’s hard tissues. Practically, the HAp is applicable to the fields of biomaterials, ion exchangers for harmful ions, adsorbents for chromatography, solid ionics and catalysts. The uses of porous ceramics as bioreactors when their pore sizes are above 1 mm, as supports of biopolymers or the DNA, RNA and proteins. Generally, the supports of biopolymers (enzymes, etc.) when their pore sizes are below 0.1 mm and as supports of cells and microorganisms when their pore sizes are above 1 mm. The porous ceramics can be utilized as biotechnological ceramics, such as bioreactors for fixing the enzymes, cells and microorganisms in pores or ceramic filters for separating the ions, molecules and cells.

Among these HAp shapes, the porous ceramics may be effective for use as the biomaterials, the ion exchangers and the adsorbents for chromatography. In addition, if one can control the sizes, distributions, volumes and areas of pores which channel to the outer surfaces, the resulting porous ceramics can be utilized as biotechnological ceramics, such as bioreactors for fixing the enzymes, cells and microorganisms in pores or ceramic filters for separating the biopolymers or the DNA, RNA and proteins. Generally, the uses of porous ceramics as bioreactors are classified, according to the pore size. Porous ceramics are used as supports of biopolymers (enzymes, etc.) when their pore sizes are below 0.1 mm and as supports of cells and microorganisms when their pore sizes are above 1 mm. The porous ceramics with various pore sizes at nanometer to micrometer scales are used as the adsorbents for chromatography. In addition, if one can control the sizes, distributions, volumes and areas of pores which channel to the outer surfaces, the resulting porous ceramics can be utilized as biotechnological ceramics, such as bioreactors for fixing the enzymes, cells and microorganisms in pores or ceramic filters for separating the biopolymers or the DNA, RNA and proteins. Generally, the uses of porous ceramics as bioreactors are classified, according to the pore size.

2. Experimental procedure

2.1 Preparation and characterization of the fibrous HAp particles

As reported previously, the starting solution with the Ca/P ratio of 1.67 was prepared by mixing the 0.167 mol·dm$^{-3}$ Ca(NO$_3$)$_2$, 0.100 mol·dm$^{-3}$ (NH$_4$)$_2$HPO$_4$, 0.004 mol·dm$^{-3}$ NH$_4$CO and 0.10 mol·dm$^{-3}$ HNO$_3$ aqueous solutions. The fibrous HAp particles were prepared by heating 0.75 dm$^3$ of the solution at 80°C for 24 h and then at 90°C for 72 h. The pH in the solution increased from 3 to 8, owing to the NH$_3$ formed by the hydrolysis of the urea as a precipitating agent, as shown in Eq. (1).

\[
\text{NH}_4\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2
\]

The present HAp was produced via (i) the calcium hydroxyapatite (CaHPO$_4$·3H$_2$O; OCP) and then (ii) octacalcium phosphate (Ca$_8$H$_2$(PO$_4$)$_5$·5H$_2$O; OCP), both were stable in the acidic region of pH 3.0 to 4.0, as shown in Eqs. (2) and (3).

\[
\begin{align*}
8\text{CaHPO}_4\cdot3\text{H}_2\text{O} + 5\text{H}_2\text{O} & \rightarrow 8\text{Ca}_3\text{H}_2(\text{PO}_4)\cdot5\text{H}_2\text{O} + 2\text{H}_2\text{PO}_4 \\
5\text{Ca}_3\text{H}_2(\text{PO}_4)\cdot5\text{H}_2\text{O} + 3\text{H}_2\text{O} & \rightarrow 4\text{Ca}_10(\text{PO}_4)\cdot(\text{OH})_2 + 6\text{H}_2\text{PO}_4
\end{align*}
\]

The yield of the fibrous HAp particles was about 52.4%. The characterization of the resulting powders was carried out as follows: the crystalline phases of the powders were identified using an X-ray powder diffractometer.
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2. Fabrication and evaluation of porous HAp ceramics

About 2 g of the resulting HAp powder was uniaxially compressed at 20, 30 and 40 MPa to form a compact with a diameter of 20 mm and a thickness of 3 mm. The porous HAp ceramics were fabricated by firing these compacts at 1000°C, 1100°C, 1200°C and 1300°C for 5 h; the heating rate was 10°C·min⁻¹.

The relative density of the resulting porous HAp ceramics was calculated by dividing the bulk density by the theoretical density (3.16 g·cm⁻³) of HAp. The total porosity (Ptotal; %) of the ceramics was estimated by subtracting the relative density (Drela; %) from 100 %. The open porosity (Popen; %) and closed porosity (Pclosed; %) were determined on the basis of the apparent density (DApp) of the resulting ceramics and the theoretical density (Dtheo) of HAp as follows:

\[ P_{\text{total}} = 100 \times \left(1 - \frac{D_{\text{App}}}{D_{\text{theo}}}\right) \]  
\[ P_{\text{open}} = P_{\text{total}} - P_{\text{closed}} \]  
\[ P_{\text{closed}} = 100 \times \left(1 - \frac{D_{\text{App}}}{D_{\text{theo}}}\right) \]

The DApp was measured by pycnometry. The measurement temperature was 27 ± 0.5°C; the ethanol was used as an immersion liquid. The pore size distribution of the ceramics was estimated using a mercury porosimeter (Autoscan 60, Yuasa Ionics). The samples of 0.6 to 1000 μm (1.7 nm) to 200 μm were set in the cell for measurement after the absorption of the samples was measured.

3. Results and discussion

3.1 Characterization of the fibrous HAp particles

Figure 1 shows two XRD patterns for the fibrous HAp particles. One is the as-prepared fibrous HAp particles (Fig. 1(a)) and the other is the powder obtained by crushing the fibrous particles (Fig. 1(b)). The XRD pattern of Fig. 1(a) indicated that only HAp was present in the powder; particularly, the (100), (200) and (300) reflections of this HAp were much higher than those of typical HAp pattern listed in the JCPDS card.15) As shown in Fig. 1(b), the above XRD pattern was changed to the typical HAp pattern when the fibrous HAp was crushed using a pestle and mortar. These facts indicate that the fibrous HAp particles give preferred orientation to the a- or b-plane of the hexagonal crystals.

Figure 2 shows the FT-IR spectrum of the resulting HAp powder. The absorptions assigned to the PO₄³⁻ groups at 1300-900, 600 and 570 cm⁻¹ and those assigned to the CO₃²⁻ group at 3570 and 630 cm⁻¹ were detected. In addition, the absorptions assigned to the CO₂⁻ were detected at 1600-1400 and 880 cm⁻¹ in the present investigation, as shown by the arrow mark.

In regard to the incorporation of CO₃²⁻ into HAp, Monma and Takahashi16) reported as follows: (i) when the CO₃²⁻ group substitutes for the PO₄³⁻ group in the HAp (Type B of CO₃HAp), the characteristic absorptions appear at 1455, 1430, 1415, 862 or 372 cm⁻¹; (ii) when the CO₃²⁻ group substitutes for the OH⁻ group in the HAp (Type A of the CO₃HAp), the absorptions appear at 1542 or 1546, 1465, 879 or 883 cm⁻¹. As shown in Fig. 2, the present absorptions indicate that the CO₃²⁻ group substitutes for both PO₄³⁻ and OH⁻ groups in the HAp structure. Thus the present HAp powder can be referred to as Type AB of CO₃HAp. The formation of this CO₃HAp may be due to the generation of CO₂ through the hydrolysis of the (NH₄)₂CO.

The XRF results indicated that the Ca and P contents in the fibrous CO₃HAp particles were 38.3 mass% and 17.5 mass%, respectively; the Ca/P ratio was found to be 1.69. The C content in the CO₃HAp particles was 1.04 mass%. The above fact that the Ca/P ratio in the fibrous particles exceeds 1.67 also supports the substitution of CO₃²⁻ for PO₄³⁻ in the HAp structure.

It can be seen from the SEM observation in Fig. 3 that the resulting powder is composed of the fibrous particles with long-axis sizes of ~60 to ~100 μm. Judging from this observations and XRD results, we consider that these HAp particles may elongate along the direction of the c-axis to give preferred orientation to the a- or b-plane of the hexagonal crystals.

3.2 Properties of the porous ceramics fabricated from the fibrous particles

We have fabricated the porous ceramics with various porosities from the above fibrous CO₃HAp particles. Figure 4 shows the relationship between total porosity of the resulting ceramics and starting compaction pressure. The total porosities of the ceramics decreased with increasing compaction pressure and firing temperature; the
total porosities of the resulting ceramics were in the ranges of 16.7 to 55.0%. These results show that the porous ceramics with the porosities of 16.7 to 55.0% can be easily fabricated by changing the starting compaction pressure and firing temperature. In addition, the bending and compressive strengths of the porous ceramics are expected to be in a ranges of ~5 to ~25 MPa and ~5 to ~100 MPa, respectively, based on the relationship between porosities of the ceramics and mechanical strengths in the previous report. These strengths are sufficient for the handing operations.

Previously, the porous HAp ceramics have been fabricated by the following processes: (i) the sintering of the HAp particles in the presence of the naphthalene particles or hydrogen peroxide, (ii) the use of HAp cement prepared by the water-setting reaction of the tetracalcium phosphate (Ca4(PO4)2O) and calcium hydrogen phosphate (CaHPO4) in an aqueous solution and (iii) HAp conversion by the hydrothermal reaction of calcium carbonate (CaCO3) or marine invertebrates with diammonium hydrogen phosphate ((NH4)2HPO4). The results in the present investigation indicate that the porous HAp ceramics containing continuous open pores can be easily fabricated by the novel technique except for the above processes, in other words, the simple-sintering process of the compacts derived from the fibrous HAp particles with long-sizes of 60–100 μm.

According to the XRD results, only HAp phase was present from the resulting ceramics in all fabrication conditions. The presence of tricalcium phosphate (Ca3(PO4)2) phase, which is known to be a by-product formed by the decomposition of HAp or calcium-deficient HAp, was not found. The FT-IR measurement of the powdered ceramics indicated that the CO32- group was released from the CO3HAp to form the HAp after firing. The characteristic absorption of the HAp or OH- group was also found in the powdered ceramics.

Figure 5 shows the cumulative pore volume and the pore volume fraction of typical porous ceramics which were fabricated by compacting at 30 MPa and firing at 1000°C (Fig. 6(a)), 1200°C (Fig. 6(b)) and 1300°C (Fig. 6(c)) for 5 h. In Fig. 6(a), the cumulative pore volume increased rapidly as the pore size decreased down to ~0.3 μm; the volume became almost constant when the pore sizes became ~0.1 μm or below. The differential curves also showed a narrow pore size distribution, ranging from 0.1 to 0.5 μm. As shown in Figs. 6(b) and (c), the pore size distribution of porous ceramics fired at 1200°C and 1300°C were also similar to the case of the porous ceramics shown
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Fig. 6. Typical cumulative pore volume and the pore volume fraction of the porous ceramics fabricated by compacting at 30 MPa and firing at (a) 1000°C, (b) 1200°C and (c) 1300°C for 5 h.

in Fig. 6(a); however, the peak of pore size distribution was shifted to the larger pore size with an increase of firing temperature. These results indicate that (i) the present ceramics have submicrometer-scaled pores and that (ii) their pore size distributions are very narrow.

Similarly, the pore sizes were in the submicrometer scale and the pore-size distributions were narrow, in the cases of the porous ceramics fabricated by the other experimental conditions along with the above conditions. Judging from the above findings and the results in Figs. 4 and 5, we concluded that the present ceramics are composed of the continuous open pores with submicrometer scales.

Figure 7 shows (a) the total pore volumes, (b) the median pore sizes and (c) the specific surface areas of twelve kinds of ceramics fabricated under various experimental conditions. As shown in Figs. 7(a) and (c), the total pore volume and the specific surface area decreased with increasing compaction pressure and firing temperature; the pore volumes and the specific surface area of the ceramics were in the ranges of 0.04 to 0.36 cm³·g⁻¹ and 0.29 to 2.90 m²·g⁻¹, respectively. In Fig. 7(b), the median pore size increased with a decrease of compaction pressure and with an increase of firing temperature. The median pore sizes of ceramics were in the ranges of 0.28 to 0.78 μm. An increase of the median pore sizes with increasing firing temperature suggests that the pores have coalesced during sintering. These results show that the ceramics with total pore volumes of 0.04 to 0.36 cm³·g⁻¹, median pore sizes of 0.28 to 0.78 μm and specific surface areas of 0.29 to 2.90 m²·g⁻¹ can be fabricated by changing the compaction pressures and firing temperatures.

Typical microstructures of the porous ceramics fabricated under various experimental conditions were observed using a SEM; the results are shown in Fig. 8. In the case of porous ceramics fabricated by compacting at 30 MPa (Figs. 8(a) to (d)), the fibrous particles were sintered to one another to develop the homogeneous microstructures with continuous open pores as the firing temperature increases. The SEM micrographs of the ceramics fired at 1000°C and 1100°C indicated that the sintering was not still completed, because the morphologies of starting fibrous particles remained unchanged after firing. Although the microstructure of ceramics fired at 1300°C appears to be sufficiently developed for the practical uses, their pore volumes and specific surface areas showed the lowest values among the examined ceramics. We therefore concluded that the sintering at 1200°C was optimum for experimental conditions to fabricate the porous ceramics. The
microstructure of ceramics changed from porous to dense with an increase of the compaction pressure from 20 to 40 MPa, as shown in Figs. 8(c), (e) and (f).

An increase of the pore size with increasing firing temperature may be due to the coalescence of individual pores in the ceramics during the sintering. These SEM observations support the results on the median pore sizes of the porous ceramics, as described in Fig. 7(b). In addition, the porous ceramics fabricated by the simple-sintering process are composed of the grains whose fibrous morphologies were preserved. Such microstructure which possesses a framework structure is favorable to add the novel functions of the HAp ceramics, such as the specific adsorption of the proteins and amino acids, because the HAp crystals are known to possess positive charges in their α-planes and negative charges in their β-planes.

In this investigation, we found that the porous ceramics with controlled open pore sizes may be easily fabricated from the fibrous CO3HAp particles by changing the compaction pressure and firing temperature. Such porous ceramics are expected to be useful in many fields. For example, since the present ceramics contain open pores with sizes at the submicrometer-scale and narrow distribution, as described in the introduction, it will be hard to use them as supports for a bioreactor which fix the microorganisms (pore size; above ~10 μm) and enzymes (below ~0.1 μm). However, the present porous ceramics are effective as supports for the biofilms for water-treatments and cell culture and ceramics filters for bioseparation which utilizes the unbalanced charges of the HAp crystal planes. We also consider that the above porous ceramics can be used as the matrix for HAp–polymer hybrid materials to enhance the mechanical strength, especially the fracture toughness, of the HAp ceramics.

4. Conclusion

We fabricated twelve kinds of porous HAp ceramics using the fibrous HAp particles prepared from the aqueous solutions in the Ca(NO3)2-(NH4)2HPO4-(NH2)2CHNO3 system by the homogeneous precipitation method using urea. The results obtained can be summarized as follows:

1. The total porosities of the resulting ceramics were easily controlled in the range of 16.7 to 55.0% by changing the compaction pressures (20, 30 and 40 MPa) and firing temperatures (1000°C, 1100°C, 1200°C and 1300°C).

2. Almost all of the pores in the porous ceramics were open to outer surfaces.

3. The total pore volumes, the median pore sizes and specific surface area of the resulting ceramics could be controlled in the range of 0.04 to 0.36 cm3 g−1 and 0.28 to 0.78 μm and 0.29 to 2.90 m2 g−1, respectively, by changing the compaction pressures and firing temperatures.

The present investigation suggests that the porous ceramics with the controlled pore size and the continuous pores open to outer surfaces can be easily fabricated by the simple ceramics processing using the fibrous HAp particles. Such porous ceramics are effective as the biotechnological ceramics, such as supports for bioreactors and the ceramics filters for bioseparation.

References