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Effect of drying conditions during synthesis on the properties of hydroxyapatite powders

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Abstract The effect of the drying conditions during the hydroxyapatite (HAp) powder synthesis on the size and microstructure was studied. The starting materials were agitated in water, dried at 60–150 °C, and heat-treated at 720 °C. The heat-treated HAp powders were crystalline, and their particle sizes decreased with an increase in the drying time, but were independent of the drying temperature. For a 3 day drying period, it was 1.61 μm, and 0.55 μm for 21 days. The surface zeta potential of the HAp powder with a long drying period was more negatively charged than that from the short drying period. The average primary particle sizes of the HAp powders seem to be almost equivalent, and so the drying period may be related to the dispersibility of the primary particles, and may lead to a small HAp particle size.

Introduction

With the growing demands of bioactive materials for orthopedic as well as maxillofacial surgery, the utilization of hydroxyapatite (HAp) as fillers, spacers, and bone graft substitutes has received great attention mainly during the past two decades, primarily because of their biocompatibility, bioactivity, and osteo-conduction characteristics with respect to the host tissue [1, 2].

The powder properties, such as crystallinity, particle size and surface area, will determine the effectiveness of the HAp ceramics in its specific application. For example, large powders (around 100 μm in size) are beneficial for producing an HAp coating by plasma-spraying [3]. For the production of HAp-polyethylene composites, small changes in the particle size and morphology were shown to have significant effects on the mechanical properties of the composite [4, 5]. The characteristics of the HAp powder, such as specific surface area, particle size, surface potential, significantly influence the rheology of its slurry [6]. The mechanical properties of the HAp ceramics are quite dependent on the particle properties and microstructure of the final sintered product [5, 7–14].

Recent it was demonstrated that products based on HAp show rather improved mechanical properties, and high strength HAp are practically used as a spacer for intervertebral spinal disc prostheses. The significant improvement in mechanical properties proved the importance and relevance of the development of sinterable HAp powders with fine structures. The colloidal approach for consolidation of fine HAp powders is useful in production of highly porous HAp ceramics as well as that with uniform and dense microstructure [15]. HAp ceramics with porous configuration has been attracting attention as bone grafts because of the evidence of tissues ingrowth and biological responses.

Numerous studies have examined the characteristics of the HAp powders that were produced by various synthetic routes in the laboratory [8]. The HAp powder synthesis is

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composed of two steps, which are chemical reaction in solution to form HAp precursor and heat-treatment to crystallize into HAp crystals [16]. Drying process is between the two steps, although little information about the relationship between the drying process and properties of the powders was found in past references. The aim of this study is to investigate the effect of the drying conditions during the powder synthesis on the properties of the HAp powders, and to reveal optimum conditions as to yield the HAp powders with fine structure suitable for production of HAp ceramics for medical applications.

Materials and methods

Materials

All chemicals used in this study were supplied by Wako Pure Chemical Industries, Ltd. and used without further purification. The mixture of calcium hydrogen phosphate di-hydrate ($CaHPO_4 \cdot 2H_2O$) and calcium carbonate ($CaCO_3$) at the molar ratio of 3:2 was added to 90 wt% pure water to make a slurry. The slurry was agitated using zirconia balls in a zirconia pot mill at 50 rpm for 24 h at room temperature. The reacted slurry was dried at 60, 80, 100, 120 and 150 °C, for 3, 7, 10, 14, 18, and 21 days, respectively, and heat-treated in air at 720 °C for 8 h to produce the HAp powder.

Characterization

The crystal phase of the synthesized powder and sintered powders were each examined by an X-ray powder diffraction method using an X-ray diffractometer at 40 KV and 20 mA with CuKα radiation (wavelength = 1.54056 Å) (MAC Science, MXP^3). Identification of the phases was achieved by comparing the diffraction patterns with ICDD (JCPDS) standards. The lattice parameters of each powder were calculated from the XRD results using high-purity Si powder (99.999%, Aldrich) as the internal standard. Data were collected over the 2θ range of 10–60° with a step size of 0.02° and a count time of 5 s. The crystallite size of the powder was evaluated from the peak broadening of the XRD patterns based on Scherrer's formula. The (002) and (310) peaks were chosen since the peaks were well developed and separated from the others.

A fourier transform infrared (FT-IR) analysis (Jasco, MFT-2000) using KBr was also done. The TG/DTA of the as-dried powders was conducted using a thermal analyzer (Rigaku, TMA8310) from room temperature to 800 °C at 5 °C/min under an air flux of 100 mL/min. The Ca/P molar ratio of the synthesized powder was determined by ICP (Seiko, ISM7000s). The average particle diameter of the synthesized powder was calculated by a centrifugal sedimentation method with a 0.2% solution of sodium pyrophosphate as a dispersion medium using SA-CP3 from the Shimadzu Co. The specific surface area of the powders was determined by the Brunauer–Emmett–Teller method using a surface area analyzer (Shimadzu, Flow SorbII 2300). The surface potential was measured using surface potential measurement equipment (Otsuka electron, LEZA-600) with a 10 wt% solution of NaCl. Scanning electron microscopy (SEM) and EDX analysis of the powders and sintered powders were performed using a Hitachi S-3000, and a Horiba EMAX-2200 X-ray analyzer.

Results and discussion

Powder properties

The pH value of the slurry before the reaction of the wet-milling was 7.89 at 26.5 °C, and that after wet-milling at 50 rpm for 24 h at room temperature was 6.33 at 27.6 °C. The pH value was slightly reduced, but almost remained at around the neutral value, which may be due to high amounts of carbonate and phosphate ions in slurry.

The phase changes of the products were analyzed by XRD, as shown in Fig. 1. XRD analysis showed that HAp

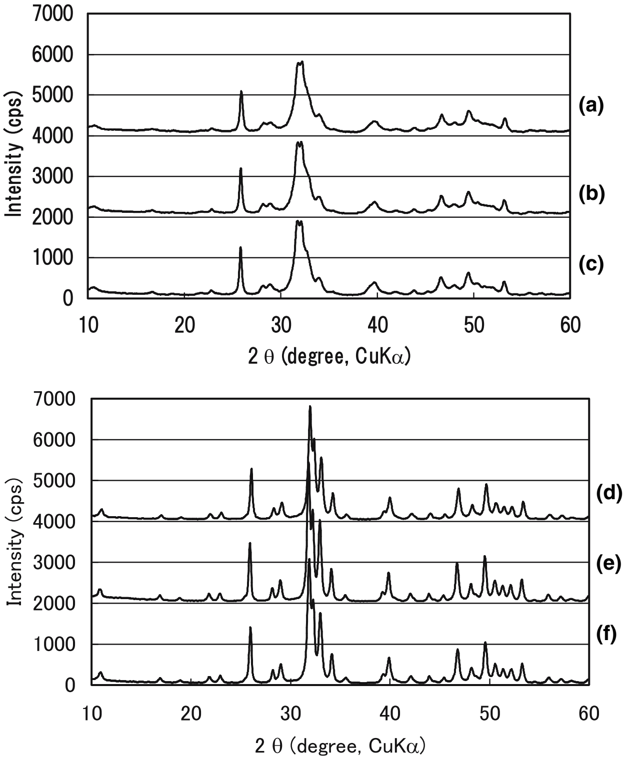
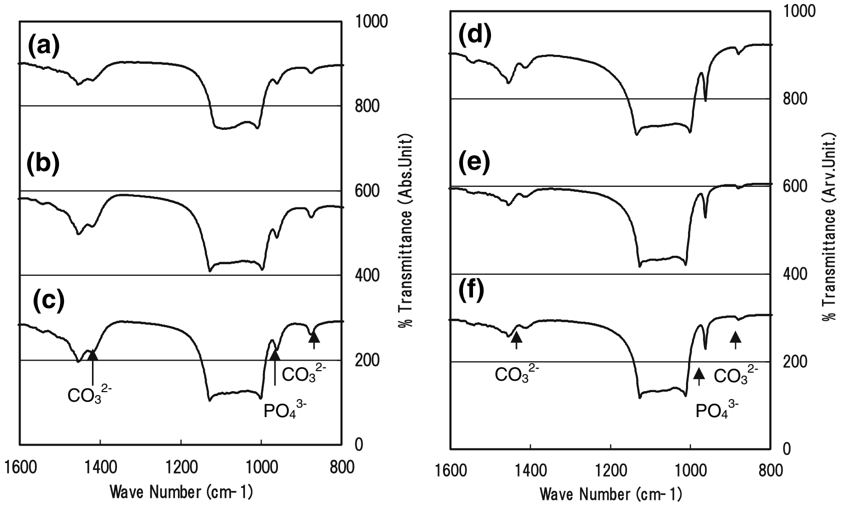


Fig. 1 XRD patterns of the hydroxyapatite (HAp) powders as-dried at 60 °C for 3 (**a**), 10 (**b**) and 18 days (**c**), and those dried at 60 °C for 3 (**d**), 10 (**e**) and 18 days (**f**), and then heat-treated at 720 °C for 8 h

Fig. 2 Infrared absorption spectra of the powder obtained by wet-milling a mixture of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ at 50 rpm for 24 h at room temperature, dried at 60 °C for (**a**) 3, (**b**) 10 and (**c**) 18 days, and then heated at 720 °C for 8 h (**d**), (**e**) and (**f**), respectively



before and after sintering produced only peaks corresponding to those of HAp, and the material created in this study was single-phase and did not decompose to secondary phases upon heating. The as-dried sample was poorly crystalline, as shown by the broad diffraction peaks, which is characteristic of HAp prepared by an aqueous precipitation route [17, 18]. The HAp powders heat-treated at 720 °C produced distinct diffraction patterns, which corresponded to a crystalline material, with narrow diffraction peaks. The heat treatment improved the crystallinity of the HAp.

Figure 2 shows the FT-IR spectra of the HAp powders before and after the heat-treatment. In the as-dried HAp powders, the peaks of the CO_3^{2-} band (870 and 1,460 cm^{-1}) indicated that the CO_3^{2-} containing precursor remained in the form of HAp [16]. In the spectrum of the heat-treated HAp powers, the peak of the P–O bands (500–600 and 900–1,000 cm^{-1}) became sharp and weak peaks of CO_3^{2-} band were observed. The peaks of the O–H stretching mode were observed at 640 cm^{-1}, which confirmed the formation of the characteristic HAp structure containing a hydroxyl group.

The results of the ICP analysis showed that the Ca/P molar ratios of HAp with the heat-treatment at 720 °C for 8 h were 1.665–1.678 whereas those with the as-dried were 1.732–1.744. The Ca/P molar ratios in these samples are listed in Table 1. The molar ratios in the sample with heat-treatment were near the value of its stoichiometry, but those of the as-dried sample have relatively higher values. From the results of the XRD and FT-IR analyses, a large amount of CO_3^{2-} and hydroxyl ions may exist in the as-dried product which leads to the high Ca/P molar ratio.

Table 1 The Ca/P molar ratio of hydroxyapatite (HAp) powers with different drying conditions

Drying period (day)	Heat-treatment at 720 °C	As-dried
3	1.678 ± 0.006	1.744 ± 0.033
7	1.675 ± 0.004	1.738 ± 0.037
10	1.668 ± 0.005	1.734 ± 0.028
14	1.665 ± 0.009	1.732 ± 0.030

Particle size and drying period

The effect of the drying period on the average particle diameters of the HAp powders either as-dried or heat-treated are shown in Fig. 3. The average particle sizes of the HAp powders decreased with an increase in the drying period. A drop was observed within 10 days of drying, and there were slight changes in the average particle sizes after 10 days of drying. Both the as-dried and heat-treated HAp powders showed the same tendency. However, the particle

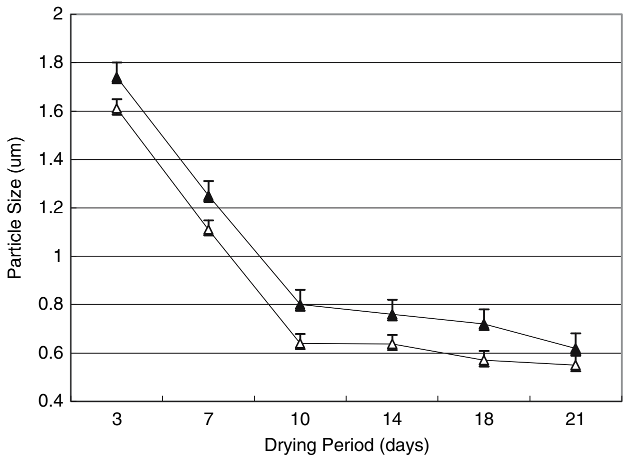


Fig. 3 Relation between drying period and the particle size of the powder obtained by wet-milling a mixture of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ at 50 rpm for 24 h at room temperature, dried at 60 °C (▲) and those dried at 60 °C and heat-treatment at 720 °C for 8 h (△)

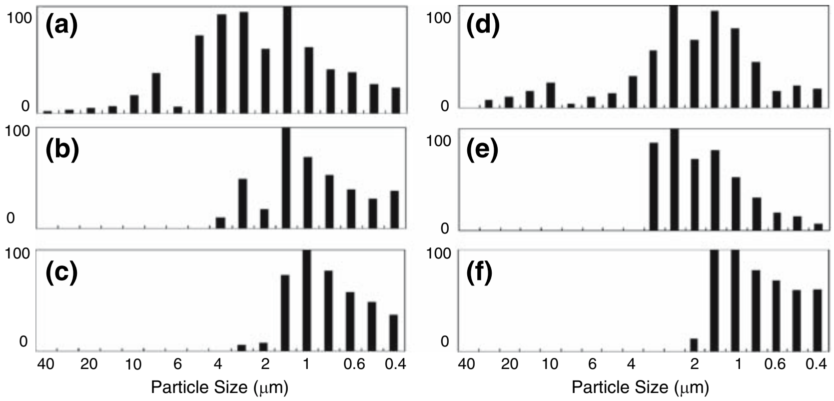


Fig. 4 The typical particle size distributions of the powders as-dried at 60 °C for (**a**) 3, (**b**) 10, (**c**) 18 days, and those dried at 60 °C for (**d**) 3, (**e**) 10, (**f**) 18 days, and then heat-treated at 720 °C for 8 h

sizes of the heat-treated HAp powders were smaller than those of the as-dried ones.

The particle size distributions of the powders are illustrated in Fig. 4. The particles of the HAp products dried for 3 days were distributed from 40 to 0.4 μm in size, and those dried for 10 days or more were from 4.0 to 0.4 μm. With an increase in the drying period, the particle size distributions of the HAp products seemed to be narrow. For the heat-treated HAp products, the particle size distribution was from 30 to 0.3 μm for the 3 day drying period, and that was from 3.0 to 0.3 μm for 10 days or more. Similar to the as-dried sample, if the drying period is longer, the particle size distributions of the heat-treated HAp products became narrower.

The relation between the specific surface area and drying period of the HAp powders are illustrated in Fig. 5. The small crystallites of the as-dried HAp result in a very high specific surface area, whereas those with the heat-treatment at 720 °C also had high, but relatively low specific surface areas. For the as-dried HAp, with the increasing drying period, the decrease in the specific surface area was observed. However, for the HAp heat-treatment at 720 °C, a decrease in the specific surface area was less and seemed to remain around 20 m^2/g.

The effect of the drying temperature on the average particle sizes of the as-dried or the heat-treated HAp powders is shown in Fig. 6. The average particle size seemed to be unchanged with a change in the drying temperature.

The TEM photos of heat-treated at 720 °C for 8 h and the as-dried HAp powders for various drying periods are shown in Fig. 7. The products dried for 3, 10 or 18 days were long spindle-shaped, and the crystal sizes of the as-dried HAp powders seem to increase somewhat with the increasing drying period but be almost within dozens nm in length. Those heated at at 720 °C were round-shaped, and the crystal sizes are almost same, 20–50 nm in size, regardless of the drying period.

The effect of the drying period on the ζ-potential of the as-dried and heat-treated HAp powders is illustrated in

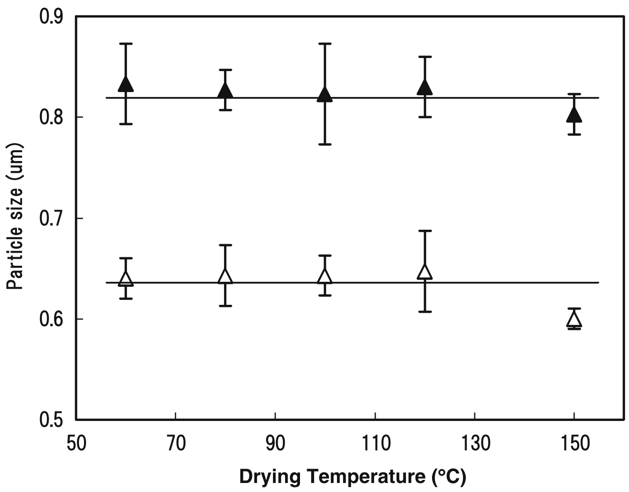


Fig. 5 Relation between drying temperature and the particle size of the powders dried at 60 °C for 10 days (▲) and those dried for 10 days and heat-treated at 720 °C for 8 h (△)

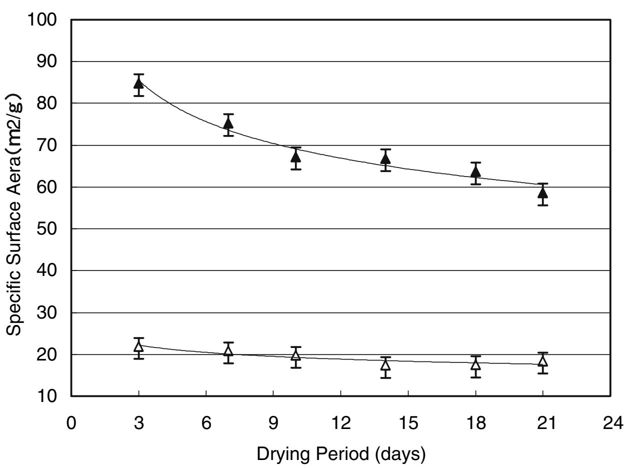


Fig. 6 The relation between the drying period and the specific surface area of the hydroxyapatite (HAp) powders as-dried at 60 °C (▲) or those dried at 60 °C and then heat-treated at 720 °C for 8 h (△)

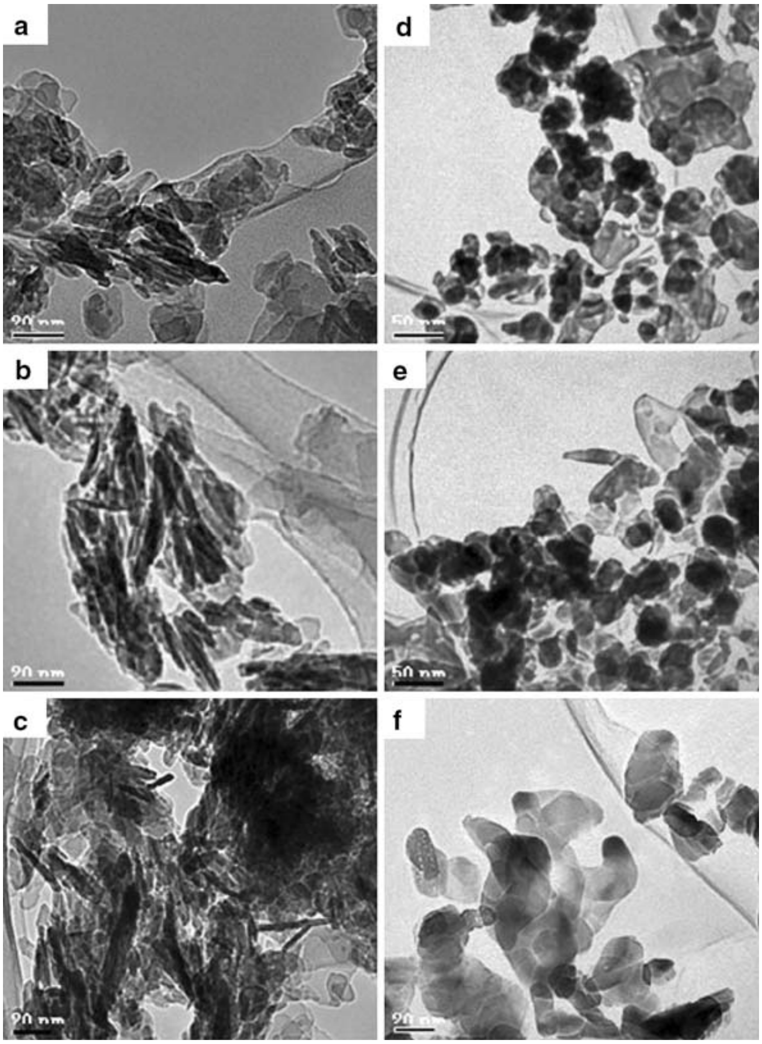


Fig. 7 TEM photos of powder obtained by wet-milling a mixture of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ at 50 rpm for 24 h at room temperature and then as-dried at 60 °C for (**a**) 3, (**b**) 10 and (**c**) 18 days, and then heated at 720 °C for 8 h (**d**), (**e**) and (**f**)

Fig. 8a and b, respectively. The HAp powders dried for short periods had low negative charged while those dried for long periods were significantly negatively charged. As shown in Fig. 2, the peak intensities of the C–O bands at 870 and 1,460 cm^{-1} observed in the as-dried powders decreased with an increase in the drying period. The heat-treated HAp powders sowed the same tendency. As shown in Table 1, the Ca/P molar ratios in the HAp powders were in the order according to the ζ-potential. The ζ-potential may have a correlation to the carbonic acid ions. During drying process, the evaporation of adsorbed water in the as-dried products may occur as well as the decomposition of the hydrocarbons [18, 19]. On the basis of these results regarding the slight change in the size of primary particle, the change in the average particle sizes can be considered to be due to its dispersiveness. For this reason, the surface potential of the as-dried and heat-treated at 720 °C HAp negatively increased with the longer drying period.

Conclusions

The effect of the drying conditions on the properties of the HAp powders during the powder synthesis was investigated. The drying conditions for producing a high purity, single-phase HAp powder by the wet milling method were examined. The properties of the HAp powders created by these conditions were significantly improved regarding the average particle diameter and specific surface area. With the increasing drying period, the average particle diameter became smaller. However, for the samples heat-treated at 720 °C, after 10 days or more of drying, the average particle diameter had almost no change. The particle diameter of the HAp powders with heat-treatment at 720 °C was smaller than that of the as-dried HAp. Moreover, within the 10 days drying period, the particle size increased versus time and was the same as the as-dried sample. This change in the particle size corresponds to the change in the crystallite size. The drying temperature had only a slight effect

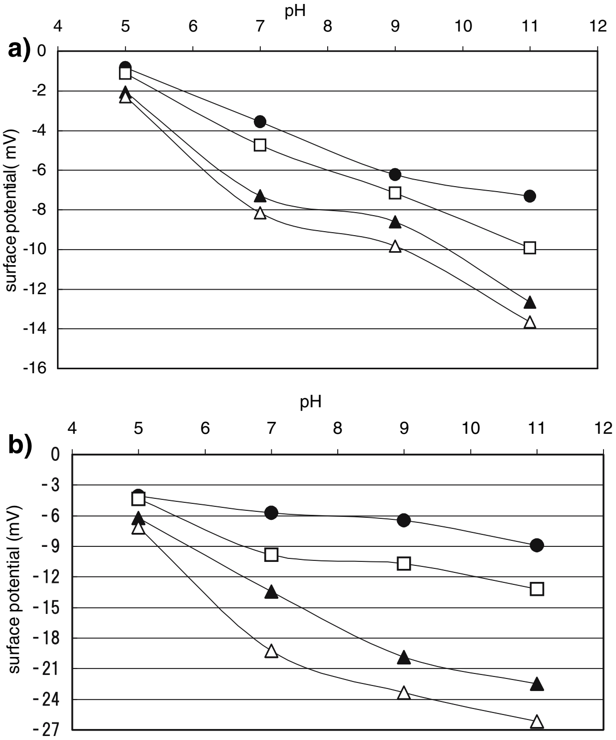


Fig. 8 ζ-Potential of the hydroxyapatite (HAp) powders (**a**) as-dried at 60 °C for 3 (●), 7 (□), 10 (▲) and 21 (△) days, and (**b**) dried at 60 °C and then heat-treated at 720 °C for 8 h

on the change in the particle size. The effect of the drying period on the average particle diameter of the HAp powder will be reflected in the porous body.

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