SYNTHESIS OF CALCIUM-PHOSPHATE MICROSPHERE WITH WELL-CONTROLLED PARTICLE SIZE BY ULTRASONIC SPRAY-PYROLYSIS TECHNIQUE AND THEIR SINTERABILITY

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Abstract: We performed to synthesize the calcium-phosphate microsphere with well-controlled particle size by changing the frequency of the ultrasonic transducer. The crystalline phases of the resulting powders were composed of β-tricalcium phosphate (β-TCP) and hydroxyapatite (HAp); the Ca/P molar ratios were about 1.50. The SEM observation indicated that the resulting powders were composed of microspheres with a diameter of ~1 to ~2.5 μm. The particle sizes increased with decreasing ultrasonic frequency, and the distributions were quite narrow. The above results show that the particle size can be easily controlled by changing the frequency of ultrasonic transducer during spray-pyrolysis.

INTRODUCTION

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; HAp) and tricalcium phosphate (Ca₃(PO₄)₂; TCP) are widely used as biomaterials for substituting with human-hard tissues¹. We have synthesized the above-mentioned HAp and the apatite-family compounds by ultrasonic spray-pyrolysis technique and examined the properties the resulting powders²-⁵.

An ultrasonic spray-pyrolysis technique is one of the powder preparation techniques via the liquid phases. This technique has advantages that one can prepare the stoichiometric and homogeneous compounds instantaneously by spraying the solutions with the desired amounts of cations into the hot zone of electronic furnace.

In the case of the powder preparation based on ultrasonic spray-pyrolysis, the particle size is dependent on the size of droplet generated by ultrasonic transducer. The droplet size, \(d_p\), is defined by the following equation⁵:

\[
d_p = 0.34 \left( \frac{8\pi\sigma}{\rho g} \right)^{1/3}
\]
where, \( f \) is a frequency, \( \rho \) density of the spraying solution, \( \sigma \) a surface tension. Thus, the particle sizes of resulting powder may be well-controlled if one can control the size of droplet by changing the frequency in the ultrasonic transducer.

In the present investigation, we have focused on one of the biodegradable bioceramics, TCP, and prepared the calcium-phosphate powders via the above process using the starting solution with the Ca/P ratio of 1.50. Our aims were to synthesize the calcium-phosphate microspheres with well-controlled particle size by changing the frequency of the ultrasonic transducer, and to examine the sinterability of the resulting powders.

**EXPERIMENTAL**

Calcium-phosphate powders were synthesized by spray-pyrolysing the starting solution. The starting aqueous solution was prepared by mixing 0.60 mol·dm\(^{-3}\) Ca(NO\(_3\))\(_2\), 0.40 mol·dm\(^{-3}\) (NH\(_4\))\(_2\)HPO\(_4\) and 0.40 mol·dm\(^{-3}\) NH\(_3\). The droplets were formed by ultrasonically-vibrating the starting solution at the frequency of 0.5, 1, 1.5, 2.5 and 3 MHz. As previously reported\(^{2-5}\), the hot zone of the present apparatus was composed of two electric furnaces. In the present investigation, the lower furnace was set at 300 °C for drying of droplets and higher one at 850 °C for pyrolysis of the precipitated salts.

The resulting powders were characterized by the following techniques: X-ray diffractometry (XRD), Fourier transform infrared spectrophotometry (FT-IR), X-ray fluorometry (XRF), scanning electron microscopy (SEM), and BET method for measurement of the specific surface area.

About 0.2 g of the as-prepared powder was uniaxially pressed at 100 MPa to form disk-shaped compact with a diameter of 10 mm and a thickness of ~2 mm. The compacts were fired at 1050, 1150 and 1200°C for 5 h (the heating rate: 10 °C·min\(^{-1}\)). The relative density was calculated by dividing the bulk density of the sintered compact by the theoretical densities of β-TCP (3.07 g·cm\(^{-3}\)) and α-TCP (3.07 g·cm\(^{-3}\)). The microstructure was observed using a SEM and the crystalline phase was identified by the above XRD.

**RESULTS AND DISCUSSION**

**Effect of the ultrasonic frequency on the powder properties**

Figure 1 shows the XRD patterns of the powders prepared by changing the frequency from 0.5 to 3.0 MHz on spray-pyrolysis process. These XRD patterns indicated that the as-prepared powders were composed of β-TCP and HAp biphase in all the examined sample powders. As examining the phase changes with ultrasonic frequency based on typical XRD intensities of β-TCP (0210) and HAp (211), the fraction of β-TCP phase decreased from ~65% down to ~45% with increasing
ultrasonic frequency, while that of HAp increased from ~35% up to ~55%.

In the FT-IR spectra of the above calcium-phosphate powders, the absorptions assigned to the PO_4 group were detected at 1300-900, 600 and 570 cm^{-1}, and the absorption of OH group was slightly detected at 3570 cm^{-1}. In addition, the absorption of 1600-1300 cm^{-1} was assigned to the NO_3 group derived from starting materials, Ca(NO_3)_2 and HNO_3. These absorptions, except NO_3 group, are assigned to the PO_4 group of the TCP and HAp.

The above results show that the ultrasonic frequency influences the crystalline phase of the resulting calcium-phosphate powders.

The Ca/P molar ratios of the resulting powders were in the range of 1.50 ± 0.03. These values are in harmony with the stoichiometric composition of TCP phase, that is, Ca/P=1.50. Thus, the apatite phase present in the resulting powder may be calcium-deficient apatite.

Figure 2 shows the particle morphologies of the resulting powders ((a)
ultrasonic frequency: 0.5, (b) 1.5, and (c) 3 MHz). These SEM micrographs indicated
that the as-prepared powders were composed of microspheres with a diameter of ~1 to
~2.5 μm. The particle sizes increased with decreasing ultrasonic frequency, and the
distributions were quite narrow.

On the bases of the SEM observations, we determined mean particle size by
measuring the diameters of the resulting particles (n=253-376 in each sample). The
result is illustrated in Fig. 3, together with the diameter of droplet generated according
to various ultrasonic frequencies. The diameter of the spray-pyrolysized particle was
smaller than that of the droplet. This may be due to the shrinkage based on the
evaporation of solvent from the surface of the droplet during spray-pyrolysis process.
In addition, the mean particle size increased from 1.0 to 2.5 μm with a decrease of the
ultrasonic frequency from 3 down to 0.5 MHz.

The above results indicate that the particle size can be easily controlled by
changing the frequency of ultrasonic transducer during spray-pyrolysis.

![Figure 3 Relationship between mean particle size and ultrasonic frequency, together with the size of the droplet.](image)

The sinterability of the calcium-phosphate microspheres was examined by
firing the green compacts at 800, 1050 and 1200 °C for 5 h. Figure 4 shows the
relationship between firing temperature and relative density of the sintered compact.
In the case of the firing temperature at 800 °C, the relative density was about 50% in
all the examined specimens. This value was almost the same as the relative density of
green compact. This result suggests that the firing temperature of 800 °C is
insufficient to promote the sintering of the resulting powders.
On the other hand, the relative densities were in the range of 90% to 96% in the case of the firing temperature at 1050 °C and these values were the highest relative density in all the examined specimens. In the case of 1200 °C, the relative density slightly decreased and the values were in the ranges of 84% to 92%. This decrease may be due to the phase transformation of β-TCP into α-TCP.

Actually, the crystalline phase of the sintered compact at 800 and 1050 °C was a single phase of β-TCP, while that of the compact at 1200 °C was a single phase of α-TCP. The FT-IR spectra of the sintered compacts also indicated that the absorptions were assigned to the PO₄ group of the

![Figure 4 Relationship between relative density of the sintered compact and ultrasonic frequency.](image)

![Figure 5 Microstructure of typical β-TCP ceramics.](image)
TCP phase. The NO₃⁻ group present in the as-prepared powder disappeared after firing.

Among the examined specimens, the most dense ceramics with 96% of relative density were obtained from the following sample powder; ultrasonic frequency: 0.5 MHz, firing conditions: 1050 °C, 5 h. The microstructure is shown in Fig. 5. It was seen from the SEM observation that the dense β-TCP ceramics were composed of uniform grain with the sizes of 2-3 µm. Thus, easily-sinterable powder may be obtained by setting the ultrasonic frequency at 0.5 MHz.

In conclusion, we make clear that the calcium-phosphate microspheres with well-controlled particle sizes can be easily synthesized by changing the frequency during spray-pyrolysis technique.

CONCLUSION

We performed to synthesize the calcium-phosphate microsphere with well-controlled particle size by changing the frequency of the ultrasonic transducer. The crystalline phases of the resulting powders were composed of β-TCP/HAp biphase. The Ca/P molar ratios were about 1.50. The SEM observation indicated that the resulting powders were composed of microspheres with a diameter of ~1 to ~2.5 µm. The particle sizes increased with the ultrasonic frequency, and the distributions were quite narrow. The above results show that the particle size can be easily controlled by changing the frequency of ultrasonic transducer during spray-pyrolysis. In addition, the calcium-phosphate microsphere had a good sinterability and the relative density attained maximum 96% in the case of the powder prepared by spray-pyrolysing at 0.5 MHz of ultrasonic frequency.

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