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Effect of grain size and density of spray-pyrolyzed hydroxyapatite particles on the sinterability of hydroxyapatite disk

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Abstract

The effect of grain size and density of hydroxyapatite particles, which were prepared by different spray-pyrolysis temperatures, on the sinterability of hydroxyapatite disk was investigated. Calcium phosphate solution (Ca/P ratio of 1.67 and 0.1 M concentration) was prepared by reacting calcium nitrate tetrahydrate and diammonium hydrogen phosphate solutions, and adding nitric acid. Spray-pyrolysis was carried out at 900 °C, 1200 °C, and 1500 °C at a carrier gas flowing rate of 10 L/min. The particles synthesized at 900 °C were large, hollow spheres with a hole at the outer surface, a broad size distribution, but had small grain sizes. Conversely, the particles synthesized at 1500 °C were small, solid spheres with a narrow size distribution, but had large grain sizes. The particles synthesized at 1200 °C had intermediate properties. A sinterability test conducted at 1100 °C for 1 h demonstrated that small and dense particles with large grain sizes showed a higher relative sintered density compared with large and hollow particles with small grain sizes. The results were explained in terms of the grain size and density of a particle, which were inversely and proportionally affected to sinterability. The practical implication of these results is that highly sinterable hydroxyapatite powders can be synthesized through spray-pyrolysis at a high temperature under a fixed initial concentration of calcium phosphate solution and flow rate of carrier gas.

Keywords: Hydroxyapatite; Spray-pyrolysis; Particle density; Temperature; Sinterability

1. Introduction

Hydroxyapatite has been considered as a representative material for bone grafts due to its similarities to the apatite in bone; consequently, there has been much research aimed at its production. Spray-pyrolysis is one method to produce hydroxyapatite because it provides a relatively easy way to control stoichiometry, purity, reproducibility, and mass production due to the homogeneity of the starting solution and a continuous process [1]. However, there have been few reports on synthesizing hydroxyapatite powders with this method due to its delicate procedures [2–11]. It is difficult to control the shape, size, and size distribution of hydroxyapatite powders, [1] which are critically dependent on processing conditions, such as reaction temperature, flow rate of the carrier gas [10], concentration of the initial solution, and generating power of the spray. Actually, gas evolved during spray-pyrolysis by decomposing reactants hinders particle densification, producing hollow hydroxyapatite particles [10]. Thus, sodium nitrate [6], citric acid [7], and polyethylene glycol [11] are used to disintegrate the hollow hydroxyapatite particles into small, dense particles that have high sinterability. However, these processes are complicated when producing powders in mass. Therefore, before using spray-pyrolysis to synthesize hydroxyapatite powder, the optimal process to achieve highly dense spherical particles with a narrow size distribution must be determined to obtain high sinterability.

In this investigation, the effect of grain size and density of hydroxyapatite particles, which were dependent on spray-pyrolysis

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temperature, on the sinterability of hydroxyapatite disk was examined. For obtaining highly sinterable powders, small and dense particles with small grain size are desirable because the densification rate is inversely and proportionally dependent on the grain-size and density of a particle, respectively [12]. However, the particles which are satisfied the requirements of the small grain size and high density can hardly be obtained together because high spray-pyrolysis temperature causes highly dense particles but inversely (contrary?) provokes large grain growth.

We adopted three different spray-pyrolysis temperatures in this experiment, which produced different grain sizes and density of a particle, and examined which factors were more critical to the densification of hydroxyapatite disk during sintering.

2. Materials and methods

2.1. Synthesis of hydroxyapatite particles

Single-phase hydroxyapatite powder was synthesized by spray-pyrolysis. A calcium phosphate solution with a Ca/P ratio of 1.67 was prepared by dissolving calcium nitrate tetrahydrate (Aldrich) and diammonium hydrogen phosphate (Aldrich) in deionized water and adding 0.19 M nitric acid (60%; Aldrich) to dissolve the precipitated hydroxyapatite powders [10]. The concentration of the calcium phosphate solution was 0.1 mol/L. The calcium phosphate solution was then made into small droplets using an ultrasonic spray generator with a generating power of 1.7 MHz by 17 vibrators (Donglim Engineering) and fed into a quartz reaction tube 120 cm long and 7 cm in diameter at 900 °C, 1200 °C, and 1500 °C with a carrier gas (air) flow rate of 10 L/min. The hydroxyapatite powders prepared at 900 °C, 1200 °C, and 1500 °C will hereafter be referred to as T900, T1200, and T1500, respectively. The droplets were collected in a Teflon® filter placed in the exhaust line of the reactor, which was kept at around 100 °C to avoid water condensation.

To evaluate the sinterability of the powders, three powders were compacted into a disk 10 mm in diameter and 2 mm in high at 20 MPa and then sintered at 1100 °C for 1 h in microwave furnace at a heating rate of 20 °C/min.

2.2. Characterization

All microstructures were observed by field emission scanning electron microscopy (FE-SEM; S-4700, Hitachi). The crystal phases of the specimens before and after sintering were evaluated using X-ray diffractometer (XRD; D8 Discover, Bruker). The functional groups of the specimens before and after sintering were analyzed by Fourier transform infrared spectroscopy (FT-IR; Spectrum 100, Perkin-Elmer). For FT-IR spectroscopy measurements, pulverized specimens were diluted 250-fold with KBr powder and background noise was corrected with data from pure KBr. A total of 128 scans was averaged to yield spectra at a resolution of 4 cm^{-1}. The relative densities of the sintered specimens were measured by the Archimedean method.

3. Results

Microstructures and size distributions of specimens (a) T900, (b) T1200, and (c) T1500 with a flow rate of 10 L/min are shown in Figs. 1 and 2. The inset micrographs in Fig. 1 are detailed microstructures (30,000 ×). All particles have a nearly spherical shape (Fig. 1) and their average sizes and size

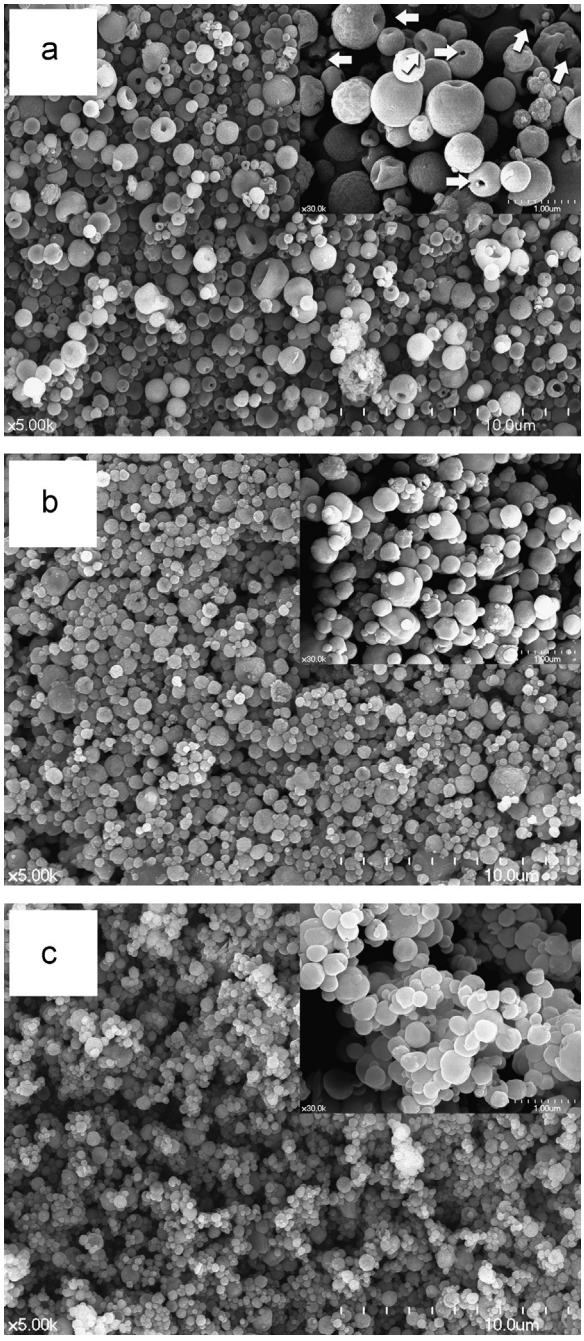

Fig. 1. FE-SEM images (5000 ×) of hydroxyapatite powders after spray-pyrolysis at (a) 900 °C, (b) 1200 °C, and (c) 1500 °C with a carrier gas flow rate of 10 L/min (inset micrographs are detailed microstructures, 30,000 ×).