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# Spherical shape hydroxyapatite powders prepared by flame spray pyrolysis

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Micrmetre-sized HA powders with dense or porous morphologies were prepared by flame spray pyrolysis from a spray solution with citric acid and ethylene glycol. The powders prepared by high temperature flame spray pyrolysis had hexagonaldipyramidal structures of HA regardless of the flow rates of the carrier gas. When the carrier gas flow rate was 20 Lminute<sup>-1</sup>, the powders prepared had a micrometre size, spherical shape and dense morphology. The mean size of the HA powders with a spherical shape and dense morphology was 1.1  $\mu$ m. However, the powders prepared at high flow rates of carrier gas above 30 Lminute<sup>-1</sup> had sizes of several micrometre and porous morphologies. The composition ratio of calcium and phosphorous components of the HA powders with a spherical shape and dense morphology was 1.69. The morphology of the micrometresized powders with a spherical shape and dense morphology was maintained after post-treatment at a temperature of 900 °C.

Key words: Hydroxyapatite, Flame spray pyrolysis, Tricalcium phosphate.

# Introduction

Hydroxyapatite  $(Ca_{10}(PO_4)_6(OH)_2, HA)$  powders are widely applied in the biomedical fields because of their biocompatibility, bioactivity, and affinity to biopolymers. The morphology and mean size of powders affect the characteristics of HAp, such as surface characteristics, bioactivity, etc. HA powders have various morphologies, such as needle-like, spherical, plate-like according to the powder preparation methods [1-5].

Liquid-solution methods, such as sol-gel, hydrothermal, microemulsion, and precipitation, have been applied to the preparation of HA powders with various morphologies [6-11]. Liquid solution-methods have advantages in controlling the morphology and mean size of the HA powders. However, a low preparation temperature causes the contamination by the preparation additives and a low crystallinity of the HA powders. Spray pyrolysis, which has the advantages of the liquid solution and gas phase reaction methods, is also being applied to the preparation of HA powders [12-14]. Itatani et al. investigated the microstructures of spherical HA powders prepared by spray pyrolysis [12]. The spray pyrolyzed and heat-treated powders had hollow or dense spherical agglomerates according to the concentrations of spray solutions. An et al. prepared nano-sized HA powders by salt-assisted ultrasonic spray pyrolysis [14]. The nano-sized powders prepared by salt-assisted spray pyrolysis were rod-type and single phase HA with high crystallinity and good stoichiometry.

Flame spray pyrolysis, which is analogous to conventional spray pyrolysis except for its energy source for drying and decomposition of droplets, is considered a potential process for the preparation of dense particles by melting the particles at a high temperature [15-19]. Although flame spray pyrolysis has a shorter residence time than conventional spray pyrolysis using an electric furnace, dense pooders can be produced by melting them at a high temperature. A flame using fuel gas such as propane and hydrogen can achieve high temperatures above 2000 °C, and the temperature can be controlled by varying the amounts of fuel gas and oxidizing gas.

In this study, HA powders were prepared by a high temperature flame spray pyrolysis process. Micrometresized HA powders with dense or porous morphologies were prepared by controlling the residence times of powders inside the high temperature flame.

#### **Experimental Procedure**

Figure 1 shows a schematic diagram of the flame spray pyrolysis apparatus. The system of flame spray pyrolysis has an ultrasonic droplet generator, flame nozzle, quartz reactor, powder collector and blower. Propane and oxygen were used each as the fuel and oxidizing gases to create the diffusion flame. The flame nozzle has five concentric pipes. Droplets generated from the precursor solution are supplied to the diffusion flame through the center pipe by oxygen which is used as a carrier gas. The flow rates of fuel and oxidizing gases were each 4.5 and 35 *l*minute<sup>-1</sup>. The flow rate of carrier gas was changed from 10 to 40 *l*minute<sup>-1</sup>. The starting materials used in the synthesis of HA powders were Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. The concentration of Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was fixed at 0.4 M. The concentrations of

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Ultrasonic nebulizer

Fig. 1. A schematic diagram of the flame spray pyrolysis process.

citric acid and ethylene glycol used as organic additives were each 0.2 M. The as-prepared powders obtained by flame spray pyrolysis were post-treated at a temperature of 900 °C for 3 h in an air atmosphere.

The crystal structures of the as-prepared and posttreated HA powders were investigated using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu-K $\alpha$ radiation ( $\lambda$ = 1.5418 Å). The thermal properties of the HA powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range from 40 to 1200 °C. The morphological characteristics of the HA powders were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060). The compositions of the HA powders were analyzed using energy dispersive X-ray (EDX) spectroscopy.

## **Results and Discussions**

The effects of the flow rate of the carrier gas on the morphologies of the HA powders prepared by flame spray pyrolysis are shown in Fig. 2. The increase of the flow rate of the carrier gas decreased the residence time of the powders inside the high temperature diffusion flame. The powders prepared with a low flow rate of carrier gas such as 10 *l*minute<sup>-1</sup> had bimodal size distributions with nanometre and micrometre sizes. One micrometresized powder was formed from a one micrometre-sized droplet. On the other hand, the nano-sized powders were formed by a chemical vapor deposition (CVD) process. Some of the materials evaporated inside the high temperature diffusion flame. Nano-sized powders were formed by a CVD process from the evaporated materials through nucleation and growth mechanisms. When the carrier gas flow rate was 20 *l*minute<sup>-1</sup>, the prepared powders had micron size, spherical shape and dense morphology. The mean size of the HA powders with a spherical shape and dense morphology was 1.1 µm. However, the powders prepared at high flow rates of carrier gas above 30 *l*minute<sup>-1</sup> had sizes of micrometre and porous morphologies. An

d) 4.5-35-40



Fig. 2. SEM micrographs of as-prepared hydroxyapatite powders (fuel-oxidizer-carrier gas)

c) 4.5-35-30



40

20

45

Hydroxyapatite

4.5-35-40

 $\Box \alpha - TCP$ 



Fig. 4. EDX spectrum of the hydroxyapatite powders.

appropriate residence time of the powders inside the high temperature diffusion flame produced powders with a spherical shape and dense morphology by melting. On the other hand, a fast drying and decomposition rates of droplets or precursors produced powders with large sizes and porous morphologies when the residence time of the powders inside the high temperature diffusion flame was short.

The effects of the flow rate of the carrier gas on the crystal structures of the powders prepared by flame spray pyrolysis are shown in Fig. 3. The powders had the hexagonal-dipyramidal structures of HA regardless of the flow rates of carrier gas. However, the crystallinities of the powders were affected by the flow rates of carrier gas. The powders prepared at a flow rate of carrier gas of 30 *l*minute<sup>-1</sup> had sharp XRD peaks. Small peaks of the  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) phase were observed in all the powders. The decomposition of HA partly into  $\alpha$ -TCP occurred because of the high temperature of diffusion flame above 2000 °C.

The composition of the HA powders prepared by flame spray pyrolysis was analyzed from the SEM-EDX spectrum. Figure 4 shows the SEM-EDX spectrum of the HA powders shown in Fig. 2(b). In the EDX spectrum, the composition ratio of calcium and phosphorous components was 1.69. The composition ratio of calcium and phosphorous components in stoichiometric HA powders is 1.67.



Fig. 5. TG/DSC curves of the hydroxyapatite powders.

Therefore, the HA powders prepared by flame spray pyrolysis had an appropriate stoichiometry.

The TG/DSC curves of the HA powders shown in Fig. 2(b) are shown in Fig. 5. In the TG curve, a steep slope was not detected in the measured temperature range. The total weight loss of the HA powders in the TG curve was low as 4.2 wt%. In the DSC curve, no other endothermic and exothermic peaks up to 1200 °C were detected because of the purity and stability of the HA powders prepared by flame spray pyrolysis.

Figure 6 shows the SEM images of the post-treated HA powders at a temperature of 900 °C. The HA powders obtained at a low flow rate of carrier gas of 10 lminute<sup>-1</sup> had bimodal size distributions with submicrometre and micrometre sizes. The morphology of the micrometresized powders shown in Fig. 2(a) was maintained after post-treatment at a high temperature. On the other hand, growth of the nano-sized powders occurred after posttreatment. The morphology of the powders shown in Fig. 2(b) was also maintained after post-treatment. In Fig. 6(a) and (b), the high thermal stability of the micrometre-sized HA powders obtained by melting maintained the morphology of the powders after posttreatment. On the other hand, the HA powders obtained at high flow rates of carrier gas above 30 lminute<sup>-1</sup> had aggregated morphologies after post-treatment. The porous structures of the powders obtained by flame spray pyrolysis at high flow rates of carrier gas deformed the morphologies of the HA powders at a high post-treatment temperature. Figure 7 shows the XRD spectra of the post-treated HA powders. The crystallite sizes of the HA powders increased after post-treatment. The mean crystallite sizes of the powders changed from 36.01 to 40.61 nm when the flow rates of carrier gas were changed from 40 to 10 lminute<sup>-1</sup>. Peaks of the  $\alpha$ -TCP phase were detected in all post-treated powders. However, the peak intensity of the  $\alpha$ -TCP phase was low when the flow rate of carrier gas was high as 40 *l*minute<sup>-1</sup>. When the flow rate of carrier gas was high, decomposition of HA to  $\alpha$ -TCP was minimized because of short residence time of powders inside the high temperature diffusion flame.

Intensity

20

Spherical shape hydroxyapatite powders prepared by flame spray pyrolysis



Fig. 6. SEM micrographs of post-treated hydroxyapatite powders (fuel-oxidizer-carrier gas).



Fig. 7. XRD spectra of post-treated hydroxyapatite powders.

# Conclusions

In flame spray pyrolysis, micrometre-sized HA powders with dense or porous morphologies were prepared by controlling the residence times of powders inside the high temperature diffusion flame. An increase of the flow rate of the carrier gas decreased the residence time of the powders inside the high temperature diffusion flame. The appropriate residence time of the powders inside the high temperature diffusion flame produced HA powders with a spherical shape, dense morphology, and appropriate stoichiometry by melting. On the other hand, a fast drying and decomposition rates of droplets or precursors produced powders with large sizes and porous morphologies. Post-treatment of the HA powders obtained by flame spray pyrolysis improved the mean crystallite sizes of the HA powders. However, the morphology of the HA powders with a spherical shape and dense morphology was maintained after post-treatment.

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