O U R N A L O F

Ceramic Processing Research

# Characteristics of calcium phosphate fabricated using a natural material

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Calcium phosphate bioceramics, such as hydroxyapatite (HAp) and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP), were simply fabricated using a natural material, recycled oyster shell. The oyster shell turned to pure CaO after calcination, and phosphoric acid was mixed to the calcined CaO powders. The observed phases of the fired mixtures were dependent on the mixing ratio of the calcined oyster shell to phosphoric acid, and heating temperature. The HAp and  $\beta$ -TCP were stably synthesized at about 800-900 °C in an air atmosphere and in the 1 : 1.0~1 : 1.1 and 1 : 1.3~1 : 1.4 wt% mixing ratios, respectively. The synthesized HAp and  $\beta$ -TCP powders, which have Ca/P molar ratios of 1.70 (HAp) and 1.48 ( $\beta$ -TCP), showed fine particles of about 0.5  $\mu$ m in size and the powder compacts were fully densified, showing a sintering shrinkage of 18.0%, by sintering at 1200~1250 °C for 1 h.

Key words: Hydroxyapatite, β-tricalcium phosphate, Oyster shell, Phosphoric acid, Synthesis, Densification.

# Introduction

It is generally known that calcium phosphate ceramics such as hydroxyapatite (HAp) and tricalcium phosphate (TCP) are good candidates for bone substitutes due to their chemical similarity to bone mineral. Additionally, bone substitutes should have degradation characteristics that allow the organism to replace the foreign material by fully functional bone in a balanced time schedule [1, 2]. Synthesis of fine calcium phosphate powders may be an important step in processing parts with high sintered density for application to the body scaffold. In addition, good biocompatibility and easy processing for fabrication are also necessary.

HAp and TCP have been synthesized by wet-chemical methods, such as sol-gel techniques, hydrothermal reactions and emulsion or microemulsion syntheses [3-9]. However, the methods resulted in the formation of non-stoichiometric powders, which off the required Ca/P molar ratios of 1.66 (HAp) and 1.50 (β-TCP) [3-6, 10]. Layrolle et al. [11] have synthesized HAp powders with an average particle size of 200 nm with a strongly agglomerated morphology having an average agglomerate size of 45 µm. Lim et al. [12] have reported the synthesis of HAp powders with particle sizes between 0.5 and 1.0 µm with an agglomerated morphology. As another useful method, HAp powders were successfully synthesized by using re-cycled eggshell [13, 14]. In the process, calcined eggshell was mixed with phosphoric acid, and the powder characteristics were dependant on the mixing content of phosphoric acid and the calcination temperature. HAp was synthesized at 900 °C and it had fine particles with a submicron size with a strongly agglomerated morphology. Stoichiometric HAp powder was not synthesized, however, the mixing range for the stoichiometry was found, and the exact Ca/P ratio can be easily adjusted by the control of the mixing ratio of eggshell to phosphoric acid.

In this study, calcium phosphate powders are synthesized using oyster shell and phosphoric acid. As a natural material, oyster shell is a good source of CaO and it is mixed phosphoric acid through a wet-chemical method. The effects of the mixing amount of phosphoric acid on the synthesis behavior were examined. In addition, the sintering behavior of the synthesized calcium phosphate powders was also studied.

#### **Experimental Procedure**

## Fabrication of calcium phosphate

For the source of calcium oxide, raw oyster shells were calcined in an air atmosphere at various temperatures with holding for 1 h at each temperature. Phosphoric acid, which is the source of phosphor, was mixed with the calcined oyster shell. The mixing ratios (wt%) of the oyster shell to phosphoric acid were varied from 1 : 1.0 to 1 : 1.7. The mixtures were wet ball-milled with a zirconia (Y-TZP) ball media with isopropyl alcohol solvent for 12 h for homogeneous mixing. After drying the slurry at 90-100 °C for 24 h, the dried powders were heated at various temperatures with a 4 K·minute<sup>-1</sup> heating rate, in an air atmosphere.

The synthesized calcium phosphate powders were ballmilled to remove agglomerates and reduce the particle size. Wet milling was conducted with isopropyl alcohol solvent and zirconia ball media for 12 h. The ball-milled powders were sieved and uni-axially pressed under 30 MPa

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pressure. Cylindrical-type pellets (diameter : 12 mm) were sintered at various temperatures for 1 h in an air atmosphere.

#### Characterization

Development of crystalline phases of the calcined powders was examined, as functions of the mixng ratio and temperature, using an X-ray diffractometer (Rigaku D/Max 2200) with CuK $_{\alpha}$  radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 8° minute<sup>-1</sup> and a sampling interval of 0.02°, over a range of 20-70° at room temperature. The morphological characteristics of the raw and calcined oyster shell, synthesized powders and sintered samples were examined by scanning electron microscopy (SEM, Hitachi, S-3500N). The specimens were mounted on an aluminum stub and Au-Pd sputtered at 15 mA for 40 sec. The particle size of the ball-milled calcium phosphate powders were measured by an electrophoretic light scattering spectrophotometer (Photal, ELS-8000). The sample cell was ultrasonicated for several minutes. The Ca/P molar ratio of the synthesized powders at each wt% mixing ratio was examined by chemical analysis using ICP AES (Spectroflame EOF).

## **Results and Discussion**

The XRD patterns of the calcined oyster shell at various temperatures are shown in Fig. 1. The raw oyster shell showed the CaCO<sub>3</sub> phase at room temperature and the CaO phase was detected after decomposition of CaCO<sub>3</sub> as the temperature was increased to 700 °C. The CaCO<sub>3</sub> was completely decomposed and turned to CaO at about 800 °C. The CaO phase was stable at higher temperatures above 800 °C. In this study, the oyster shell calcined at



**Fig. 1.** XRD patterns of calcined oyster shell at different temperatures: (a) room temperature, (b) 700 °C, (c) 800 °C, (d) 900 °C and (e) 1000 °C.

800 °C was used for the synthesis process. The morphologies of the raw and calcined oyster shell as well as the synthesized calcium phosphate powder are shown in Fig. 2. The raw oyster shell was rough and hard showing needle-like particles in the microstructure. The hard shell was gradually turned to soft powder as the CaCO<sub>3</sub> decomposed to CaO. The calcined oyster shell was white-colored, soft and porous without showing its original needle-shape structure. The calcined oyster shell, which is the CaO phase, was like pebble-shaped granules with particles irregular in size. The synthesized powder from oyster shell showed ultra-fine particles. The calcium phosphate powder, which was fired at 900 °C, was widely agglomerated having fine and uniform particles about 0.5  $\mu$ m in size. In comparison with the



Fig. 2. SEM micrographs of (a) raw oyster shell, (b) as-calcined oyster shell at 800 °C and (c) synthesized calcium phosphate powder.

microstructure of the calcined oyster shell, the synthesized powder was significantly decreased in size. This means the starting CaO powder, calcined oyster shell, was so soft that it could be ground to a fine powder and mixed homogeneously with phosphoric acid by a simple ballmilling process.

Mixing ratios of the calcined oyster shell and phosphoric acid affected the crystallization of calcium phosphate powders. The results of XRD patterns of the mixtures according to the mixing ratios are presented in Figs. 3 and 4. HAp was synthesized from the mixing ratio of 1 : 1.0 at 900 °C for 1 h and the fully crystallized HAp was observed at a mixing ratio of 1 : 1.1. At 1 : 1.2 ratio,



**Fig. 3.** XRD patterns of calcium phosphate powders, fired at 900 °C for 1 h, synthesized from the mixing ratios of (a) 1 : 1.0, (b) 1 : 1.1, (c) 1 : 1.2 and (d) 1 : 1.3.



**Fig. 4.** XRD patterns of calcium phosphate powders, fired at 900  $^{\circ}$ C for 1 h, synthesized from the mixing ratios of (a) 1 : 1.4, (b) 1 : 1.5, (c) 1 : 1.6 and (d) 1 : 1.7.

HAp and b-TCP co-existed and HAp disappeared gradually as the temperature was increased. With the ratio of 1 : 1.4,  $\beta$ -TCP was effectively synthesized. With the 1 : 1.5 ratio, the intensity of  $\beta$ -TCP peaks was decreased and unknown peaks were observed. Fig. 5 shows XRD patterns of synthesized  $\beta$ -TCP powders, derived from 1 : 1.4 ratio, fired at various temperatures. The crystalline peak of  $\beta$ -TCP began to be observed at 700 °C, and fully crystallized  $\beta$ -TCP was observed at 900 °C or above. In the crystalline development of HAp (mixing ratio of 1 : 1.1) according to the firing temperature, the fully crystalline HAp phase was also observed at 900 °C or above.

Ca/P molar ratios at each mixing ratio are listed in Table 1. The Ca/P ratio can be varied from the initial wt% mixing ratio because the amount of phosphoric acid is changed during the mixing and drying process. The exact Ca/P ratios were determined with the powders fired at 900 °C. In the 1 : 1.1 and 1 : 1.4 mixing ratios, which are



**Fig. 5.** XRD patterns of synthesized b-TCP powder, derived from 1 : 1.4 ratio, fired at (a) 700 °C for 1 h, (b) 800 °C for 1 h, (c) 900 °C for 1 h and (d) 1000 °C for 1 h.

Table 1. Ca/P molar ratios and observed phases at each wt% mixing ratio  $% \left( {{{\rm{Tab}}} \right) = 0} \right)$ 

0				
wt% mixing ratio	Ca/P ratio	Observed phases <sup>¥</sup>		
1:1.0	1.79	HAp + (CaO)		
1:1.1	1.70	НАр		
1:1.2	1.62	$HAp + \beta$ -TCP		
1:1.3	1.55	$(HAp) + \beta$ -TCP		
1:1.4	1.48	β-ΤСΡ		
1:1.5	1.41	$\beta$ -TCP + unknown		
1:1.6	1.30	$\beta$ -TCP + unknown		
1:1.7	1.22	unknown		

<sup>4</sup>From the specimens fired at 900 °C for 1 h.

(): minor phase

the optimum mixing ratios for fully crystallized HAp and  $\beta$ -TCP in the XRD results, the measured Ca/P ratio was 1.70 and 1.48, respectively. In this study, the Ca/P ratio of stoichiometric HAp (1.66) and  $\beta$ -TCP (1.50) exists between the mixing ratio of 1 : 1.1~1 : 1.2 and 1 : 1.3~1 : 1.4, respectively. Therefore, a stoichiometric HAp and  $\beta$ -TCP can be synthesized in this process by exact control of the wt% mixing ratio.

The powder compacts of synthesized calcium phosphate were sintered at 1000 °C to 1250 °C for 1 h and the shrinkage during the sintering was examined. The synthesized HAp and  $\beta$ -TCP powders derived from 1 : 1.1 and 1 : 1.4 mixing ratios were used for the examination of the densification behavior. The shrinkage change at various temperatures is presented in Table 2. Most of shrinkage was observed between 1100 °C and 1200 °C. The final sintering shrinkage of HAp and  $\beta$ -TCP were 18.2% at 1250 °C and 17.8% at 1200 °C, respectively. The powder compacts showing such shrinkage were fully desified at each temperature and SEM micrographs of the densified HAp and  $\beta$ -TCP are shown in Figs. 6 and 7. The grain size of

**Table 2.** Linear shrinkage of powder compacts of synthesized calcium phosphate at each sintering temperature.

Temp (°C)	1000	1050	1100	1150	1200	1250	1300
HAp (shrinkage %)	1.8	3.9	8.0	12.4	16.2	18.2	18.2
β-TCP (shrinkage %)	1.3	3.8	7.8	12.8	17.8	18.0	18.0



Fig. 6. SEM micrographs of densified HAp sintered at (a) 1100 °C and (b) 1250 °C for 1 h.



Fig. 7. SEM micrographs of densified  $\beta$ -TCP sintered at (a) 1100 °C and (b)1200 °C for 1 h.

sintered HAp at 1250 °C was relatively uniform with an average grain size of 2.0  $\mu$ m. In the case of  $\beta$ -TCP, grain growth occurred more than with HAp and the grain size of the fully-densified sample was about 3.0  $\mu$ m.

## Conclusions

Calcium phosphate powders, which have a uniform, submicron particle size, were successfully synthesized using oyster shell. In the process, the mixing content of phosphoric acid and calcination temperature affected the crystallization behavior. The calcined oyster shell was ground to fine CaO powder through a wet ball milling process and it resulted in a homogeneous mixture with phosphoric acid and fully crystallized calcium phosphate powders at low temperature. The synthesized HAp and  $\beta$ -TCP, which are close to stoichiometric compositions, were fully densified by sintering at about 1200 °C for 1 h. The highly sinterable and fully crystallized calcium phosphates are expected as to be good bioceramics in the application field of bone substitutes.

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