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Characteristics of calcium phosphate powders synthesized from cuttlefish bone and phosphoric acid

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Fine calcium phosphate powders were fabricated by using recycled cuttlefish bone. A raw cuttlefish bone easily turned to CaO by a calcining process and the calcined cuttlefish bone was mixed with phosphoric acid by a wet, ball-milling method. The crystalline phases of the heated mixtures were dependent on the mixing ratio (wt%) of the calcined cuttlefish bone to phosphoric acid. In a wide mixing ratio range of 1:1.1-1:1.7 wt%, calcium phosphates were synthesized and fully crystallized HAp and β -TCP were observed at about 900°C and above. The synthesized powders showed fine particles of below 0.5 μ m in size. In this study, the crystalline development and Ca/P molar ratios of the synthesized calcium phosphate powders were studied by X-ray diffractometry and chemical analysis using ICP AES. In addition, the microstructures of the cuttlefish bone and synthesized calcium phosphate powders were examined by scanning electron microscopy.

Key words: synthesis, powder, cuttlefish bone, calcium phosphate, crystallization.

Introduction

It is generally acknowledged 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 [1-3]. HAp and TCP have been synthesized by wet-chemical methods. However, the methods resulted in the formation of non-stoichiometric powders [4-6].

TCP has polymorphic behavior, such as: β -TCP is stable below 1180°C, and α -TCP between 1180°C and 1400°C [6-9]. In particular, bioresorbable β -TCP can be used as a transient, clean and effective scaffold for bone reconstruction [10]. HAp and dicalcium phosphate (CaHPO₄·2H₂O) are stable in the human body and in the body fluid at pH>4.2 and pH<4.2, respectively [11]. It is well known that the pH of human blood is about 7.3. Therefore, dense HAp has been recognized for applications as bioimplants such as the repair of bone defects in dental and orthopaedic implants and tooth root replacements etc. [12].

Recently, biocompatible and highly sinterable hydroxyapatite and β -tricalcium phosphate ceramics were successfully fabricated by using recycled eggshell and phosphoric acid [13, 14]. In the new method using natural material, eggshell was a very acceptable material for application to the synthesis of calcium phosphate ceramics. Calcium phosphate ceramics synthesized from eggshell were expected to be a superior biocompatible material than other chemically synthesized powders. And a mass product was also possible in this low cost and simple process. In the process, the observed phases in the powder synthesis process were dependent on the mixing ratio of the eggshell to phosphoric acid, the starting conditions of the eggshell and calcination temperature. The HAp and β -TCP were stably synthesized in the 1:1.1-1:1.2 and 1:1.3-1:1.5 wt% mixing ratios of eggshell to phosphoric acid, respectively. The syntheses were achieved at about 900°C in an air atmosphere.

In this study, calcium phosphate powders are synthesized by a new wet-chemical method using cuttlefish bone and phosphoric acid. In comparison with the eggshell process, a possibility of the use of another natural material for the preparation of calcium phosphate is examined using the same fabrication process as for the eggshell method. In particular, the effects of the mixing ratio of cuttlefish bone to phosphoric acid on the synthesis behavior are examined.

Experimental Procedure

Powder synthesis

Washed cuttlefish bone was calcined in an air atmosphere at various temperatures for 1 h. The phase change during the calcination process was examined by XRD observation. To synthesize calcium phosphate powders, phosphoric acid was mixed to the calcined cuttlefish bone, which has a pure CaO phase. The mixing ratios (wt%) of the cuttlefish bone to phosphoric acid were changed from 1:1.0 to 1:1.7. The mixtures were ball-

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milled with zirconia (Y-TZP) ball media under isopropyl alcohol for 12 h, to break up agglomerates of the calcined cuttlefish bone and achieve homogeneous mixing. After mixing, the slurries were dried at 80°C. Finally, the dried powders were heated at various temperatures in an air atmosphere for synthesis of calcium phosphate.

Characterization

The development of crystalline phases of the synthesized calcium phosphate powders was studied, as functions of the mixing ratio of calcined cuttlefish bone to phosphoric acid and synthesis temperature, using an Xray diffractometer (Rigaku D/Max 2200) with CuK_{α} radiation (40 kV, 30 mA). The morphological characteristics of the cuttlefish bone and synthesized powders 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 s. The Ca/P molar ratios at each wt% mixing ratio were examined by chemical analysis using ICP AES (Spectroflame EOF) of the synthesized powders. Five-point BET analysis from nitrogen gas absorption (Model Autosorb-1, Boynton Beach, FL) was used to obtain the BET specific surface area of the synthesized calcium phosphate powders.

Results and Discussion

Micrographs of the raw cuttlefish bone and the 800



Fig. 1. SEM micrographs of raw cuttlefish bone (a) internal structure and (b) enlargement of pillars.

°C calcined cuttlefish bone are shown in Figs. 1 and 2. The raw cuttlefish bone showed a unique microstructure with layered uniform pillars (Fig. 1(a)). The pillars were like smooth-surface sticks with an almost uniform thickness of 50 μ m (Fig. 1(b)). In the calcined cuttlefish bone, the microstructure was porous as shown in Fig. 2. The calcined bone was white-colored, quite soft and ground easily. The layered structure with uniform pillars had collapsed and turned to granular particles.

The crystalline development of the calcined cuttlefish bone is shown in Fig. 3. The dried, raw cuttlefish bone showed a CaCO₃ phase, and CaO was observed in the calcined cuttlefish bone in the results of XRD analysis. The initial decomposition of CaCO₃ was observed at 700 °C and the CaCO₃ was completely decomposed at 800 °C and turned to pure CaO. The CaO phase continued up to 1000 °C.

Mixing ratios of the calcined cuttlefish bone to phosphoric acid had an effect on the final crystalline phase of calcium phosphate powders. The results of final phases of the calcium phosphate powders according to the mixing ratio, and the Ca/P molar ratios and final observed phases at each mixing ratio are presented in Figs. 4 and 5, and in Table 1, respectively. The



Fig. 2. SEM micrograph of 800°C calcined cuttlefish bone.



Fig. 3. XRD patterns of cuttlefish bone calcined at (a) 600° C, (b) 700° C, (c) 800° C, (d) 900° C and (e) 1000° C for 1 h.



Fig. 4. XRD patterns of synthesized calcium phosphate powders, heated at 900°C for 1h, derived from a) 1:1.0, b) 1:1.1, c) 1:1.2 and d) 1:1.3 mixing ratios (wt%).



Fig. 5. XRD patterns of synthesized calcium phosphate powders, heated at 900°CC for 1 h, derived from a) 1:1.4, b) 1:1.5, c) 1:1.6 and d) 1:1.7 mixing ratios (wt%).

HAp phase excluding un-reacted CaO phase was observed in the mixing ratio of 1:1.1 wt% at 900 °C for 1 h. And the HAp phase continued up to a mixing ratio of 1:1.3 wt%. With a smaller amount of phosphoric acid (1:1.0 wt%), un-reacted CaO was observed. In the ratio of 1:1.4 and more phosphoric acid content, β -TCP was effectively synthesized. In the 1:1.7 ratio, the intensity of β -TCP peaks was increased more. As shown in Fig. 5, the β -TCP was stably synthesized in a wide mixing range. The Ca/P molar ratio was not correspondent with the initial wt% mixing ratio because the initial amount of phosphoric acid could be decreased through the mixing and drying processes. In this study, it can be speculated that the Ca/P ratios of

 Table 1. Ca/P molar ratios and observed phases at each wt% mixing ratio

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wt% mixing ratio	Ca/P ratio	Observed phases ^a
1:1.0	1.82	HAp + (CaO)
1:1.1	1.70	HAp
1:1.2	1.64	HAp
1:1.3	1.57	$HAp + (\beta - TCP)$
1:1.4	1.48	β-ΤСΡ
1:1.5	1.44	β-ΤСΡ
1:1.6	1.41	β-ΤСΡ
1:1.7	1.38	β-ΤСΡ

^aFrom the specimens fired at 900°C for 1 h.

(): minor phase.



Fig. 6. XRD patterns of synthesized HAp powder, derived from 1:1.2 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.

stoichiometric HAp (1.66) and β -TCP (1.50) exist between the wt% mixing ratio of 1:1.1-1:1.2 and 1:1.3-1:1.4, respectively, as shown in Table 1.

Figure 6 shows XRD patterns of synthesized HAp powder, derived from 1:1.2 ratio, fired at various temperatures. In the 1:1.2 ratio, the HAp phase was detected at 800 °C, and fully crystallized HAp was observed above 900 °C. In the case of β -TCP, 1:1.4 ratio, which is closer to the stoichiometric β -TCP than the other mixing ratios, was used for the study of the temperature effect on synthesis behavior. The results of phase development are presented in Fig. 7. The result was almost similar to the synthesis behavior of HAp (Fig. 6). Finally, the HAp and β -TCP powders synthesized by using cuttlefish bone were fully crystallized at 900°C with the condition of the Ca/P ratio close to the stoichiometric composition.

The synthesized calcium phosphate powders were white-colored and soft. SEM micrographs of the calcium phosphate powders synthesized at 900 °C are presented in Fig. 8. The synthesized β -TCP powders were more agglomerated than the HAp powders and pre-sintered



Fig. 7. XRD patterns of synthesized β -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.



Fig. 8. SEM micrographs of the (a) HAp powder (1:1.2 ratio) and (b) HAp powder (1:1.4 ratio) synthesized at 900°C.

powders were partially observed. The soft and agglomerated powders were easily ground by a simple ball milling process similar to the calcium phosphate powders fabricated by the eggshell process [11]. The HAp and β -TCP powders showed an average particle size of about 0.5 μ m with specific surface areas of 18.1 m²/g and 13.2 m²/g, respectively.

Conclusions

The synthesis behavior of calcium phosphate powders was studied through a new special synthesis route using cuttlefish bone and phosphoric acid. In this process, stoichiometric HAp and β -TCP powders were not synthesized, however, the mixing ranges of cuttlefish bone and phosphoric acid for stoichiometry could be found, and the exact Ca/P ratio can be easily adjusted by a control of mixing ratio of cuttlefish bone to phosphoric acid. The synthesized calcium phosphate powders, which were derived from 1:1.2 ratio for HAp and 1:1.4 ratio for β -TCP, had an average particle size of 0.5 μ m, and were nearly fully crystallized by treatment at 900°C for 1 h. As a result, cuttlefish bone is also an acceptable material for application to the synthesis of calcium phosphate ceramics. And with the new process it may be possible to make a mass product in a low cost and simple process.

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