Microstructure and Mechanical Property of Hydroxyapatite/Calcium-Deficient Hydroxyapatite Composites Prepared by a Colloidal Process

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Calcium-deficient hydroxyapatite (DAP) having a rod-like or thin-blade-like shape was produced by hydrolysis of α -tricalcium phosphate (α -TCP) at different pH values. Mixed powder composed of 40 mass%DAP and 60 mass% stoichiometric hydroxyapatite (HAP) was suspended in an aqueous solution containing a small amount of dispersant by colloidal process. After dehydration, HAP-40 mass%DAP consolidated samples were sintered at 1473 K for 2 h. Rheological behaviour of the slurry, microstructure and bending strength of HAP-40 mass%DAP prepared by this process depended strongly on quantity of the dispersant. Good dispersion of HAP and DAP powders at an optimum quantity of the dispersant resulted in high relative density of HAP/DAP composites with homogeneous microstructure. DAP starting powder readily decomposed to α -TCP and HAP at 1473 K, while the formation of α -TCP phase took place less intensively in HAP-40 mass%DAP composites sintered at that temperature. In contrast to HAP/ α -TCP composites, an interdiffusion of ions between HAP and DAP during sintering may result in the increase in the thermal stability of DAP. HAP-40 mass%DAP composites prepared by a suitable colloidal process exhibited higher bending strength than HAP-40 mass% α -TCP composites and stoichiometric HAP alone.

(Received June 11, 2001; Accepted September 10, 2001)

Keywords: hydroxyapatite, calcium-deficient hydroxyapatite, biomaterial, colloidal process, bone, mechanical property, microstructure

1. Introduction

Calcium phosphate (CaP) ceramics such as hydroxyapatite (HAP) and tricalcium phosphate (TCP) have attracted much attention as bone implants because of their excellent biocompatibility and nontoxicity.¹⁻³⁾ In particular, HAP is the most biocompatible material since it is the major mineral constituent of human hard tissues. However, its mechanical properties of bending strength and fracture toughness are insufficient to sustain loads independently as bone implants. CaP ceramics differ from each other in concentration, mechanical properties and biocompatibility.⁴⁾ Therefore, CaP composites are favourable for development of superior biomaterials with high strength and excellent biocompatibility.⁵⁾ For instance, the combination of more stable HAP and more soluble α -TCP *in vivo* was found to exhibit faster bone growth than HAP alone.⁶⁻⁹⁾ In our previous paper, we reported the preparation of HAP/ α -TCP composites by colloidal process.¹⁰⁾ α -TCP could be homogeneously distributed in HAP matrix by suppressing the spontaneous agglomeration of the powder under the optimum condition of the colloidal process. However, large α -TCP contents of more than 40 mass% result in a decrease of both relative density and bending strength of the composites sintered at 1473 K, since highly dense α -TCP sintered compact is rarely obtained at the sintering temperature. Although α -TCP powder can be densely sintered above 1773 K, HAP decomposes into several phases in this temperature range resulting in the loss of biocompatibility.⁵⁾ Thus, the different combination of CaP ceramics is desirable to improve the mechanical properties and the biocompatibility.

It is well known that α -TCP is transformed to calcium-deficient hydroxyapatite (DAP) in hot water by hydrolysis.¹¹⁻¹⁴⁾ Stoichiometric hydroxyapatite has a Ca/P ratio of 1.67 and a water content of 1.79 mass%. On the other hand, the general formula of DAP is expressed as $\text{Ca}_{10-z}(\text{HPO}_4)_z(\text{PO}_4)_{6-z}(\text{OH})_{2-z}\cdot n\text{H}_2\text{O}$ (Ca/P = 1.50–1.67).

Moreover, DAP particles treated at pH = 6–9 exhibit higher crystallinity compared with HAP produced by the usual precipitation process, resulting in an increase in strength. For example, α -TCP ceramics whose surface is hydrated in water, demonstrate higher tensile strength than those without hydration.¹⁵⁾ Therefore, biphasic CaP ceramics composed of HAP and DAP are expected to show higher strength than HAP alone. In this paper, we report the preparation of HAP/DAP composites by colloidal process focusing on the thermal stability of DAP.

2. Experimental Procedure

DAP powder was prepared by hydrolysis of α -TCP powders (Taihei Chemical Industrial Co. α -TCP-B). α -TCP powder was stirred in distilled water at 353 K for 3 h. The pH value of the suspension was kept constant at 8.5 or 6.5 by adding ammonium solution. Thereafter, DAP powder in the suspension was separated by filtration and dried at 373 K. The obtained DAP powder was partly annealed at 1273 K, 1373 K and 1473 K for 2 h to check the thermal stability.

DAP and stoichiometric HAP (Taihei Chemical Industrial Co. HAP-200) powders were mixed in a ratio of 40 to 60 by weight. Slurries were prepared with 30 vol.% mixed powder and 70 vol.% aqueous solution containing a small amount of polycarboxylic acid ammonium (PCAA) as an anion dispersant. These slurries were ultrasonically dispersed for 20 min, and then stirred by a magnetic agitator for 5 h. The pH value of the slurries was adjusted to 8 by adding nitric or ammonium solution. The rheological behaviour was investigated using a rotation automatic viscometer at room temperature. The viscosity of the slurries was measured at a shear rate of 383 s^{-1} and they were then poured into plaster moulds and remained intact for 24 h to absorb water. After the dehydration process, the samples were sufficiently dried at 323 K for 24 h. The consolidated samples were sintered at 1473 K for 2 h at a

Fig. 1 SEM micrographs of α -TCP particles (a) and DAp powder obtained by hydrolysis of α -TCP at pH = 8.5 (b) or pH = 6.5 (c).

heating rate of 200 K h^{-1} . HAp-40 mass% α -TCP composites were also prepared by the colloidal process for comparison with HAp/DAp composites.

The phase identification was done by an X-ray diffractometry (XRD) and a Fourier transform infrared spectroscopy (FTIR). The volume fraction of each phase was estimated from the diffraction peaks. Relative density of the sintered samples was measured by the Archimedes method. The microstructure of the powders and the sintered bodies was observed by a scanning electron microscope (SEM). Three-point bending test was performed on the basis of JIS R1601 using specimens with dimensions of 3 mm in thickness, 4 mm in width and 36 mm in length at a cross-head speed of 0.5 mm min^{-1} at room temperature in air. The specimen surface was mechanically polished using diamond paste before the bending test.

3. Results and Discussion

3.1 Morphology and thermal stability of DAp powder

Figure 1 shows SEM micrographs of the starting powders of α -TCP and DAp. α -TCP primary particles are as large as a few micrometers as shown in Fig. 1(a), while the shape of DAp particle produced by hydrolysis of α -TCP depends strongly on pH value. At pH = 8.5 (Fig. 1(b)), DAp powder looks like cylindrical rod with $0.1 \mu\text{m}$ in diameter and $3 \mu\text{m}$ in length, while DAp exhibits a thin-blade-like shape at pH = 6.5 (Fig. 1(c)). The rod-like and blade-like DAPs are called r-DAP and b-DAP, respectively. An IR spectrum of HPO_4^{2-} at 860 cm^{-1} was confirmed to exist in both r-DAP and b-DAP, as discussed later in Fig. 8. From the viewpoint of crystallography, the long axis of r-DAP and the flat surface of b-DAP are parallel to the c axis and {1010} plane of apatites, respectively.¹³⁾ The morphological and crystallographic features of DAP suggest that the crystallinity of DAP produced by hydrolysis of α -TCP is relatively high. Ca/P ratios of r-DAP and b-DAP were determined to be 1.58 and 1.53 from a wet chemical analysis, respectively. The morphology and Ca/P ratio of DAP obtained in this study are in good agreement with those reported by Monma *et al.*^{13,14)} Since both powders are observed to form aggregates, a colloidal process should be applied to produce uniform HAp/DAp composites.

DAp powder is known to exhibit partial reverse transfor-

mation above 1073 K .^{12,14)}

DAp powders were annealed at 1273 K , 1373 K and 1473 K for 2 h to check the thermal stability by XRD, as shown in Fig. 2. The XRD profiles of both r-DAP and b-DAP in as received state are quite similar to that of HAp and no other phase is detected, as shown in Figs. 2(a) and (b). The thermal decomposition of DAP to HAp and β -TCP (equilibrium phase of TCP at lower temperature) is found to occur in both r-DAP and b-DAP by annealing even at 1273 K . The amount of the thermal decomposition increases with increasing temperature in both HAp/r-DAP and HAp/b-DAP composites and α -TCP phase appears at 1473 K . From the quantitative analysis of XRD profiles, 41.6 mass% and 66.4 mass% of r-DAP and b-DAP, respectively, transform to α -TCP at 1473 K . SEM micrographs of r-DAP and b-DAP annealed at 1273 K , 1373 K and 1473 K for 2 h are shown in Fig. 3. The edge of both r-DAP and b-DAP particles begins to be rounded by annealing at 1273 K , as shown in Figs. 3(a) and (d). The spheroidization of DAP proceeds remarkably at 1373 K (Figs. 3(b) and (e)) and finally, the original shape of DAP powders is hardly recognized at 1473 K (Figs. 3(c) and (f)). Therefore, the thermal decomposition of DAP is implied to occur intensively at the sintering temperature of HAp/DAp composites. The shape change of DAP particles also suggests that the reverse transformation to α -TCP preferentially occurs at the corner of the particles.

3.2 Optimization of colloidal process

HAp and DAP powders were suspended in an aqueous solution containing a small amount of PCAA by colloidal process. The shear stress of HAp/r-DAP and HAp/b-DAP slurries is plotted against quantity of dispersant in Fig. 4; this stress decreases with increasing quantity of dispersant up to about 1.5 mass%. After reaching minimum in the range of 1.5–3.0 mass% dispersant, further addition of dispersant results in an increase in the shear stress. The dispersant may cover the surface of the powder in which case the powder would behave as a monodispersed particle due to the electrosteric stabilization,^{16–18)} resulting in a decrease in viscosity of the slurries.

Fig. 2 XRD profiles of r-DAP (a) and b-DAP powders (b) annealed at 1273 K, 1373 K and 1473 K for 2 h.

Fig. 3 SEM micrographs of r-DAP and b-DAP annealed at various temperatures for 2 h; (a) r-DAP at 1273 K, (b) r-DAP at 1373 K, (c) r-DAP at 1473 K, (d) b-DAP at 1273 K, (e) b-DAP at 1373 K, (f) b-DAP at 1473 K.

Therefore, variation in the shear stress with the quantity of dispersant suggests that HAp and DAP powder were well dis-

persed in the slurry containing 1.5–3.0 mass% dispersant.

Figure 5 shows change in the relative density of HAp/DAP

Fig. 4 Variation in shear stress of HAp-40mass%r-DAP and HAp-40mass%b-DAP slurries with quantity of dispersant.

Fig. 5 Change in relative density of sintered HAp-40mass%r-DAP and HAp-40mass%b-DAP composites with quantity of dispersant.

composites sintered at 1473 K for 2 h with quantity of dispersant. HAp-40mass%DAP composites show maximum relative density of more than 90% at dispersant concentrations from 1.5 to 3.0 mass%, although the relative density of HAp-40mass% α -TCP was approximately 80% at the sintering temperature. Deviation of the optimum quantity of dispersant of 1.5–3.0 mass% leads to the decrease in the relative density. Variation in the relative density corresponds to the rheological behaviour of the slurries. The good dispersion of powder under adequate colloidal process results in both lower shear stress and higher relative density. Thus, the optimization of colloidal process is necessary to realize dense HAp/DAP composites.

Figure 6 shows SEM micrographs of HAp/ α -TCP, HAp/r-DAP and HAp/b-DAP composites sintered at 1473 K for 2 h. In HAp/ α -TCP composites, inhomogeneous grain structure with numerous large pores is observed (Fig. 6(a)), since 1473 K is not high enough for the sintering process to take place.¹⁰ In contrast, a homogeneous microstructure composed of the equiaxed grains with 1 μ m in average diameter are formed without big pores in both HAp/r-DAP and HAp/b-DAP (Figs. 6(b) and (c)), although the morphological characteristics of rod and blade are lost in both the sintered composites. Thus, the combination of HAp and DAP is more suitable for the development of dense CaP ceramics composites than that of HAp and α -TCP. The thermal decomposition of DAP to α -TCP phase was confirmed to occur by an-

alyzing XRD profiles of sintered HAp/DAP composites, as shown in Fig. 7. However, it should be noted that the α -TCP phase is slightly visible as a result of the reverse transformation in sintered HAp/DAP composites. The mass fractions of α -TCP in sintered HAp/r-DAP (Fig. 7(a)) and HAp/b-DAP (Fig. 7(b)) composites are 7.6 mass% and 13.5 mass%, respectively. However, the amount of transformed α -TCP in both composites is much smaller than that expected from the thermal decomposition of DAP starting powder; 16.6 mass% and 26.6 mass% of HAp/r-DAP and HAp/b-DAP composites, respectively, should be transformed to α -TCP phase.

The IR spectra of both DAP starting powder and HAp/r-DAP composite sintered at 1473 K are shown in Fig. 8. The characteristic band of HPO_4^{2-} at 860 cm^{-1} is observed in the r-DAP starting powder. In contrast, the spectrum cannot be clearly seen in the sintered HAp/r-DAP composite, although the PO_4^{3-} band at 957 cm^{-1} is observed in both IR profiles in the figure. Thus, HPO_4^{2-} is converted to PO_4^{3-} as follows:

Disappearance of the HPO_4^{2-} band indicates the thermal decomposition of DAP. However, the formation of α -TCP in the reverse transformation of DAP is suppressed in HAp/DAP composites, resulting in the increase in the relative density of the composites. The thermal stability of DAP depends strongly on Ca/P ratio, higher Ca/P ratio leads to lower activity of the thermal decomposition. An interdiffusion of constituent ions between HAp and DAP is believed to occur easily since the crystal structure and chemical properties of these phases are similar to each other. In fact, averaged Ca/P ratio of HAp-40 mass%DAP composites is consistent with the amount of α -TCP phase in the sintered composites. Therefore, Ca/P ratio of DAP is augmented by the interdiffusion resulting in the suppression of the formation of α -TCP phase.

3.3 Mechanical property of HAp/DAP composites

Figure 9 shows change in the bending strength of sintered HAp/r-DAP and HAp/b-DAP composites as a function of dispersant. The average of three tested samples was plotted for each condition. Addition of an optimum quantity of dispersant (1.5–3.0 mass%) leads to the maximum bending strengths of 93 MPa and 72 MPa for sintered HAp/r-DAP and HAp/b-DAP composites, respectively. In contrast, the dispersant of more than 4.0 mass% and less than 1.5 mass% results in a decrease in the bending strength of both the composites. Thus, optimization of the colloidal process results in the high bending strength of HAp/DAP composites.

Figure 10 shows the relationship between relative density and bending strength of HAp single phase, HAp-40 mass% α -TCP, HAp-40 mass%r-DAP and HAp-40 mass%b-DAP composites sintered at 1473 K for 2 h. In HAp/r-DAP composites these characteristics are higher than those of HAp/b-DAP composites because of their higher Ca/P ratio and the resultant lower activity of α -TCP formation. In contrast, the maximum bending strengths of HAp single phase and HAp-40 mass% α -TCP composites prepared by colloidal process are 88.5 MPa and 40 MPa, respectively^{10,19,20} HAp/r-DAP composites are found to exhibit higher bending strength than the other materials. Table 1 represents several param-

Fig. 6 SEM micrographs of HAp-40 mass% α -TCP (a), HAp-40 mass%r-Dap (b) and HAp-40 mass%b-Dap composites (c) mixed under optimum condition of colloidal process and sintered at 1473 K for 2 h.

Fig. 7 XRD profiles of HAp-40 mass%r-Dap (a) and HAp-40 mass%b-Dap (b) composites sintered at 1473 K for 2 h.

Fig. 8 IR spectra of as received DAp powder and HAp-40 mass%r-Dap composites sintered at 1473 K for 2 h.

ters characterizing HAp/DAp composites. Both HAp/r-Dap and HAp/b-Dap composites contain α -TCP phase because of there lower Ca/P ratio than 1.67. Larger amount of α -TCP results in lower relative density of the composites, as

Fig. 9 Change in bending strength of HAp-40 mass%r-Dap and HAp-40 mass%b-Dap composites as a function of quantity of dispersant.

Fig. 10 Relationship between relative density and bending strength of HAp, HAp-40 mass% α -TCP, HAp-40 mass%r-Dap and HAp-40 mass%b-Dap composites sintered at 1473 K for 2 h.

listed in Table 1. However, the bending strength of HAp/r-Dap composites is higher than that of HAp single phase, although the composites show lower relative density than HAp alone. A half-value width of X-ray peaks generally reflects a crystallinity of solid; higher crystallinity results in narrower width. From the half-value width of {211} peak of apatite, the crystallinity of r-Dap is much higher than that of HAp, resulting in the increase in the bending strength of HAp/r-Dap composites. Unfortunately, the geometric effect of fiber-reinforcement cannot be obtained in either HAp/r-Dap or HAp/b-Dap composites, since the shape of Dap

Table 1 Several factors characterizing HAp/DAP composites.

	Weight fraction of α -TCP phase (mass%)	Relative density (%)	Half-value width of {211} peak of apatite
HAp	0	96.0	0.287°
HAp/r-DAP	7.6	91.9	0.258°
HAP/b-DAP	13.5	88.9	0.288°

starting powder cannot be maintained at the sintering temperature. A stress-assisted densification process at around 1273 K may result in further increase in the bending strength, since DAP powder retains original shape at this temperature. Thus, the combination of HAp and DAP is suitable for producing superior biomaterials showing high strength.

4. Conclusions

Biphasic CaP ceramics composed of HAp and DAP was prepared by the colloidal process. The following conclusions were reached.

(1) Two types of DAP powder having rod-like and blade-like shape are obtained by hydrolysis of α -TCP at selected pH values. These as-received powders easily decompose to HAp and α -TCP by annealing above 1273 K. The thermal stability of DAP powder is closely related to its Ca/P ratio.

(2) The rheological behaviour of HAp/DAP mixed slurries depends on the quantity of dispersant. Addition of an optimum quantity of dispersant leads to a decrease in shear stress of the slurries due to the electrosteric stabilization, resulting in uniform microstructure and high relative density of HAp/DAP composites.

(3) The formation of α -TCP by thermal decomposition of DAP occurs less vigorously in HAp/DAP composites than that in DAP starting powder. An interdiffusion between HAp and DAP during sintering may result in the increase in the thermal stability of DAP. Suppression of the reverse transformation from DAP to α -TCP leads to an increase in the relative density of HAp/DAP composites.

(4) The bending strength of HAp is slightly increased by addition of rod-like DAP because of its high crystallinity, although the relative density is reduced by DAP doping.

Acknowledgments

This work was supported by the Research for the Future Programme of The Japan Society for the Promotion of Science (JSPS) (Project: Biological Tissue Engineering) (JSPS-RFTF 98I00201). The authors would like to thank Dr. T. Suzuki of the National Institute for Materials Science for his helpful suggestions.

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