Effect of colloidal silica addition on the formation of porous spherical α-calcium orthophosphate agglomerates by spray pyrolysis technique

Kiyoshi ITATANI,[†] Ari OOE, Ian J. DAVIES,^{*} Tomohiro UMEDA, Yoshiro MUSHA^{**} and Seiichiro KODA

Department of Materials and Life Sciences, Sophia University, 7–1, Kioi-cho, Chiyoda-ku, Tokyo 102–8554 *Department of Mechanical Engineering, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia **Department of Orthopaedic Surgery, School of Medicine, Toho University, 2–17–6, Oohashi, Meguro-ku, Tokyo 153–8515

The effect of colloidal silica (SiO₂; CS) addition on the formation of porous spherical α -calcium orthophosphate (α -Ca₃(PO₄)₂; α -TCP) agglomerates has been examined. The starting powder was prepared by the spray pyrolysis of calcium phosphate (Ca/P ratio = 1.50) solution containing 0.9 mol·dm⁻³ Ca(NO₃)₂, 0.6 mol·dm⁻³ (NH₄)₂HPO₄, CS (mean particle size; 14, 24 and 39 nm) and concentrated HNO₃ at 600°C, using an air-liquid nozzle; the amounts of CS in the spray-pyrolyzed powder were adjusted to be 0.1–0.4 mass%. The heat-treatment of spray-pyrolyzed power with 0.4 mass% of CS addition at 1200°C for 10 min showed that the transformation from β - to α -TCP was restricted as the diameter of CS decreased from 24 to 14 nm. The heat-treatment of spray-pyrolyzed powder containing 0.1 mass% of CS (mean diameter: 24 nm) at 1200°C for 10 min resulted in not only the complete transformation of β - to α -TCP but also preservation of original spherical framework. The immersion of porous spherical α -TCP agglomerates in simulated body fluid (SBF) brought about the rapid formation of hydroxyapatite, due to higher specific surface area (17.0 m²·g⁻¹) compared to that of commercial powder (10.9 m²·g⁻¹). The hardened body with the porosity of 66.3% could be fabricated by mixing the calcium-phosphate paste with 50 mass% of the present porous α -TCP agglomerates, using the malaxation liquid. Immersion of this hardened body in SBF at 37.0°C resulted in the formation of hydroxyapatite within three days.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Spray pyrolysis technique, Colloidal silica, Porous spherical *a*-calcium orthophosphate agglomerates, Calcium-phosphate paste

[Received December 1, 2008; Accepted January 15, 2009]

1. Introduction

Calcium phosphates, *e.g.*, hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2;$ HAp) and calcium orthophosphate (Ca₃(PO₄)₂; TCP), are known to be suitable for use as bone and tooth implant materials.^{1),2)} Amongst these, HAp may be used in both its porous and dense forms, as a bone substitute material for biological fixation and as a space filler, respectively.^{2),3) On the other hand, the practical} uses of TCP depend on whether it is the α or β form; porous β -TCP ceramic is used as a bio-resorbable material,³⁾ whereas α -TCP powder is a major component of calcium-phosphate paste for the repair of defects in living bones.⁴⁾ In both cases, the utilization of porous α - and β -TCP particles is beneficial for the design of such applications with a higher porosity and thus surface area generally being preferred for such implant materials due to a higher reaction rate with the body's environment. The spray pyrolysis technique, *i.e.*, the simultaneous spray pyrolysis of solutions containing desired types and amounts of metal ions into the "hot zone" of an electric furnace, is a promising technique for the preparation of such porous particles.⁵⁾

The present authors have previously reported the properties of spray-pyrolyzed calcium-phosphate powders with different Ca/P ratios, such as HAp (Ca/P = 1.67),⁶⁾ TCP (Ca/P = 1.50),⁷⁾ calcium diphosphate (Ca₂P₂O₇) (Ca/P = 1.00),⁸⁾ and calcium metaphosphate (Ca(PO₃)₂) (Ca/P = 0.50).⁸⁾ Also examined were the mor-

phological and microstructural changes of β -TCP agglomerates during heat-treatment; the porous spherical β -TCP agglomerates were noted to form under certain heating conditions. However, rapid sintering above 1100°C, which corresponds to the transformation temperature of β - to α -TCP (1120–1180°C),⁹⁾ makes preservation of the original hollow spherical framework difficult and leads to a significant decrease in porosity and surface area. The authors have also noted that the incorporation of colloidal silica (SiO₂; CS) into the spraying solution may be beneficial with respect to preparing hollow spherical α -TCP agglomerates, because sintering and/or solid-state reactions may be inhibited through the addition of CS, and also because small amounts of CS may assist in inducing apatite-formation¹⁰⁾ and the bonding of bones bioactively¹¹⁾ within the living body.

On the basis of such information, the present paper is concerned with the effect of CS addition on the preparation of porous spherical α -TCP agglomerates, with the viewpoint that these hollow spherical agglomerates will be utilized as calciumphosphate paste in biomedical applications.

Experimental procedure

2.1 Powder preparation

The starting calcium-phosphate solution (1 dm^3) , whose chemical composition corresponded to that of Ca₃(PO₄)₂ (Ca/P ratio = 1.50), was prepared using 0.90 mol·dm⁻³ Ca(NO₃)₂, 0.60 mol·dm⁻³ (NH₄)₂HPO₄, acidic CS and 60 cm³ of concentrated nitric acid. Three types of aqueous solutions containing spherical

[†] Corresponding author: K. Itatani; E-mail: itatani@sophia.ac.jp

CS particles with different mean diameters, *i.e.*, Snowtex O (specific surface area, 214.7 m²·g⁻¹; primary particle diameter, 14 nm; designated as CS(14)), Snowtex O40 (126.0 m²·g⁻¹; 24 nm; CS(24)) and Snowtex OL (76.27 m²·g⁻¹; 39 nm; CS(39)), were obtained from Nissan Chemical Ind. (Tokyo, Japan). The calcium-phosphate solutions with and without CS addition were sprayed into the "hot zone" of an electric furnace heated at 600°C, using an air-liquid nozzle.⁶⁾ The spray-pyrolyzed powder was further heat-treated in air at a temperature between 900 and 1200°C for 10 min; the heating rate from room temperature to the desired temperature was fixed to be 10°C·min⁻¹.

The resulting α -TCP powder was mixed with commercial calcium-phosphate paste (Biopex R[®], HOYA Corp., Tokyo; 74.9 mass% α -TCP, 18.0 mass% tetracalcium phosphate (Ca₄(PO₄)₂O), 5.0 mass% calcium hydrogenphosphate dihydrate (CaHPO₄·2H₂O), 2.0 mass% HAp and 0.1 mass% magnesium orthophosphate (Mg₃(PO₄)₂). The resulting powder was further mixed with malaxation liquid (12.0 mass% disodium succinate ((CH₂COONa)₂), 5.0 mass% sodium chondroitin sulfate (C₁₄H₂₂NNaO₁₅S), 0.3 mass% sodium hydrogensulfite (NaHSO₃) and 82.7 mass% water (H₂O)) in order to fabricate the hardened body with a diameter of 7 mm and a height of 14 mm; the resulting specimen was immersed in simulated body fluid (SBF)¹⁰ at 37.0 ± 0.2°C for period of up to 14 d.

2.2 Evaluation

Phase identification of the powder was carried out using an Xray diffractometer (XRD; Model RINT2100V/P, Rigaku Co., Tokyo, Japan; 40 kV, 40 mA) with monochromatic Cu K α radiation. The phase changes during heating from room temperature to 1300°C were examined using differential thermal analysis and thermogravimetry (DTA-TG; Model Thermo Plus TG8120, Rigaku Co., Tokyo, Japan), whilst the specific surface area of the powder was measured using the Brunauer-Emett-Teller (BET) technique with nitrogen as an adsorption gas. The agglomerate shapes and microstructure of the hardened body were observed using a scanning electron microscope (SEM: Model S-4500, Hitachi, Ltd., Tokyo; accelerating voltage, 10 kV), whilst the structure within agglomerates was investigated using a transmission electron microscope (TEM: Model JEM-2011, JEOL Ltd., Tokyo, Japan; accelerating voltage, 200 kV). The microstructure inside the cylindrical hardened body was further observed using micro-focus X-ray computer tomography (micro-CT; Model SkyScan 1172, Aartselaar, Belgium).

3. Results and discussion

3.1 Properties of spray-pyrolyzed powder

Typical XRD patterns and TEM micrographs of the spraypyrolyzed powder with 0.4 mass% of CS addition have been shown in **Fig. 1**, together with the case of spray-pyrolyzed powder with no CS addition. XRD patterns of the spray-pyrolyzed powders with and without CS addition all indicated the presence of relatively broad reflections identified as β -TCP¹²) and HAp.¹³ On the other hand, TEM micrographs showed the spraypyrolyzed powder with no CS addition to be composed of dense spherical agglomerates, whereas that of the powder with CS(24) addition consisted of porous hollow spherical agglomerates.

Whilst the chemical composition of the starting solutions had been adjusted to the stoichiometry of TCP (Ca/P = 1.50), XRD identification also indicated the spray-pyrolyzed powders to contain HAp (Ca/P = 1.67), in addition to the expected β -TCP. This phenomenon is related to the rapid precipitation of HAp, compared to the case of TCP, through the evaporation of water

364

from the droplets during the spray pyrolysis, because HAp is the more stable phase at the pH of 4.0 to 8.0.¹⁴⁾

In contrast to this, neither silica nor related compound was detected by XRD, following spray pyrolysis of the calciumphosphate solutions with CS addition. This result is explained in terms of the silica being present as either an amorphous form, a solid solution into TCP and/or poorly crystalline reaction products with calcium phosphate. Nevertheless, since the spray pyrolysis of calcium-phosphate solution with CS addition resulted in the formation of porous spherical agglomerates, the starting CS is conducted to have played a significant part in retarding sintering of the primary particles.



Fig. 1. XRD patterns of the spray-pyrolyzed powders with (a) no CS addition, (b) CS(14) addition, (c) CS(24) addition and (d) CS(39) addition, together with typical TEM micrographs. Note that the amount of each CS, *i.e.*, CS(14), CS(24) and CS(39), was fixed to be 0.4 mass%. •: β -TCP, \Box : HAp.



Fig. 2. Typical (a) DTA curve and (b) TG/differential TG curves of the spray-pyrolyzed powders with 0.4 mass% of CS(39) addition at the heating rate of 10° C·min⁻¹.

3.2 Phase changes during the heating of spraypyrolyzed powder

Phase changes during heating of the spray-pyrolyzed powder were examined using DTA–TG. Typical DTA, TG and differential TG curves of the spray-pyrolyzed powder with 0.4 mass% of CS(39) addition are shown in **Fig. 2**. The DTA curve (Fig. 2(a)) was noted to contain four weak endothermic events, *i.e.*, one event that occurred shortly after the commencement of heating, with the other events starting at 537, 712 and 1160°C. On the other hand, the TG curve (Fig. 2(b)) indicated step-wise mass losses in the ranges of room temperature to 200°C and 200 to 800°C, with no significant mass loss above 800°C. Furthermore, the differential mass loss curve indicated local maximum values at temperatures of 58, 587 and 745°C.

The endothermic event that occurred shortly following the commencement of heating is attributed to the elimination of residual physically-adsorbed water from the spray-pyrolyzed powder. On the other hand, the endothermic events and mass losses occurred simultaneously in the range of 200 to 900°C are ascribed to the elimination of residual nitrate and adsorbed materials.

Typical XRD patterns of powders with and without CS addition heat-treated at 1200°C for 10 min have been presented in **Fig. 3.** The only crystalline phase found in the heat-treated powder with no colloidal silica was α -TCP¹⁵ (Fig. 3(a)), whereas the powder with CS(14) addition contained both α -TCP and β -TCP (Fig. 3(b)). The intensity of X-ray reflection attributed to β -TCP was reduced with increasing mean diameter of CS from 14 to 24 nm or larger (Fig. 3(c) and (d)).

As shown in Fig. 1, the spray-pyrolyzed powders with CS(14), CS(24) and CS(39) addition contain poorly-crystalline β -TCP and HAp, whilst the heat-treatment of the spray-pyrolyzed powder with no CS addition at 1200°C for 10 min results in the presence of a single phase α -TCP. In contrast to this, heattreatments of the spray-pyrolyzed powders with CS(14)–CS(39) addition results in the presence of not only α -TCP but also β -TCP. In all cases, the presence of TCP alone confirmed that the composition of the spray-pyrolyzed powder is in accordance with the stoichiometric composition of TCP, *i.e.*, Ca/P = 1.50. On the other hand, the retarded transformation of β - to α -TCP, due to the addition of CS, is believed to be associated with the solid solution of silica into TCP. This assumption is supported by the fact that the intensity of X-ray reflection of β -TCP was found to significantly increase as the CS diameter was reduced from 24 to 14 nm.

Since the transformation of β - to α -TCP was retarded by the addition of 0.4 mass% of CS, the amount of CS addition was then reduced from 0.4 down to 0.1 mass% by fixing the heat-treatment temperature and time to be 1200°C and 10 min, respectively. Typical XRD patterns of the heat-treated powders containing 0.1 to 0.4 mass% of CS(24) addition have been presented in **Fig. 4**. X-ray intensity of the β -TCP reflection was lowered with decreasing amount of CS(24) addition from 0.4 to 0.3 mass% (Fig. 4(d) and (c)), and became almost zero with a further decrease in CS(24) addition to 0.2 mass% or less (Fig. 4(b) and (a)).

As shown above, the complete phase transformation of β - to α -TCP in powder heated at 1200°C for 10 min occurred when the amount of CS(24) was reduced down to 0.1 mass%. In light of this, the morphologies of α -TCP agglomerates prepared with 0.1 mass% of CS(24) and heat-treated at 900°C and 1200°C were examined using the SEM. Typical SEM and TEM results have been presented in **Fig. 5**. SEM micrographs of the α -TCP agglomerates, following heat-treatment at 900°C for 10 min, indicated the presence of porous spherical agglomerates with diameters of 1 to 10 μ m. Also, TEM observations showed the spherical agglomerates within this powder to be hollow. Similarly, SEM and TEM micrographs of α -TCP agglomerates following heat-treatment of β -TCP at 1200°C for 10 min also indicated the presence of porous hollow spherical agglomerates with diameters of 1 to 10 μ m (mean diameter: 5.6 μ m).

As the results so far have indicated, the sintering of TCP particles appears to be inhibited by the addition of CS, thereby preserving the original spherical framework of the agglomerates. The present CS, therefore, is concluded to act as a sintering inhibitor of primary particles and/or restricted bonding amongst the spherical agglomerates. The retardation of the sintering of TCP due to the presence of silica appears to confirm previous work by the present authors,¹⁶ from the viewpoint that the rela-



Fig. 3. XRD patterns of the powders with (a) no CS addition, (b) 0.4 mass% of CS(14) addition, (c) 0.4 mass% of CS(24) addition and (d) 0.4 mass% of CS(39) addition heated at 1200°C for 10 min in air. \bigcirc : α -TCP, \bigoplus : β -TCP.



Fig. 4. XRD patterns of the powders with (a) 0.1 mass%, (b) 0.2 mass%, (c) 0.3 mass% and (d) 0.4 mass% of CS(24) addition heated at 1200°C for 10 min in air. \bigcirc : α -TCP, \bullet : β -TCP.



Fig. 5. SEM (above) and TEM (below) micrographs of the heat-treated powders with 0.1 mass% of CS(24) addition.

tive density was slightly reduced with increasing amount of silica addition. Similar results have been obtained by Toriyama et al.,¹⁷⁾ who pointed out that the bending strength, as well as the bulk density of sintered β -TCP compact, was reduced by the incorporation of 5 mass% of silica addition.

3.3 Properties of hardened body after the immersion of calcium-phosphate paste containing porous spherical α-TCP agglomerates in SBF

As mentioned earlier, α -TCP is a major component of calcium-phosphate paste for the repair of defects in living bones. Prior to checking the properties of calcium-phosphate paste containing porous spherical α -TCP agglomerates, the phase changes during the immersion of porous spherical α -TCP agglomerates with 0.1 mass% of CS(24) addition in SBF were examined with the results being shown in **Fig. 6**, together with the case of commercial dense α -TCP particles. The X-ray intensity of α -TCP in the commercial powder (Fig. 6(a)) was reduced, whereas that of HAp increased, with increasing immersion time in SBF; however, α -TCP was still detected even following immersion of the specimen for 5 d. On the other hand, α -TCP in the present powder had almost completely disappeared after the same time period (Fig. 6(b)).

The phase change from α -TCP into HAp in SBF may be expressed as follows:¹⁸⁾

$$10Ca_3(PO_4)_2 + 6H_2O \rightarrow 3Ca_{10}(PO_4)_6(OH)_2 + 2H_3PO_4$$
 (1)

Rapid hydrolysis of the present α -TCP powder, compared to that of the commercial α -TCP powder, is mainly attributed to the specific surface area of the present α -TCP powder (17.0 m²·g⁻¹) being higher than that of the commercial α -TCP powder (10.9 m²·g⁻¹). It should be noted that the resulting HAp formed by the hydration of α -TCP is regarded to be calcium-deficient HAp (general formula: Ca_{10-x}(HPO₄)_x(PO₄)_{6-x}(OH)_{2-x}),¹⁹⁾ and silicon-substituted apatite (Ca₁₀(PO₄)_{6-2x}(SiO₄)_{2x}(OH)_{2-2x}) due to the substitution of orthosilicate anion (SiO₄⁴⁻) for phosphate anion (PO₄³⁻) accompanying OH site deficiency (*V*_{OH}) with respect to charge compensation, *i.e.*, PO₄³⁻ + OH⁻ \rightarrow SiO₄⁴⁻ + *V*_{OH}.^{20,21)}

On the basis of the above-mentioned information, the present α -TCP agglomerates (0.1 mass% of CS(24) addition) were



Immersion time / d

Fig. 6. Phase changes during the immersion of α -TCP compact at 37.0 ± 0.2°C in SBF solution. (a) Commercial α -TCP, (b) Present α -TCP with 0.1 mass% of CS(24) heat-treated at 1200°C for 10 min. \bigcirc : α -TCP (2 θ = 30.9°), \Box : HAp (2 θ = 34.5°).

mixed with calcium-phosphate paste, using malaxation liquid. Although the total porosity of the hardened body with no α -TCP addition was 42.2%, that of the hardened body containing porous spherical α -TCP agglomerates varied from 48.3 to 66.3% as the amount of α -TCP addition increased from 10 to 50 mass%. Reflecting the higher total porosities of the hardened bodies, the powder (P)/liquid (L) ratio was reduced from 1.8 to 1.2, *i.e.*, the amount of liquid increased, as the quantity of α -TCP addition increased from 10 to 50 mass%. Judging from the fact that the P/L ratio for the hardening of calcium-phosphate paste with no α -TCP addition was 2.0, it was concluded that larger amounts of liquid may be introduced into the hardened body for the case of porous spherical α -TCP agglomerates. The fluidable paste formed by the addition of larger amounts of liquid has advantage of being inject into the bone defects, using a syringe.

Phase changes taking place during the immersion of a hardened body containing 50 mass% of porous spherical α -TCP agglomerates (0.1 mass% of CS(24) addition) in the SBF at 37.0°C have been presented in **Fig. 7**, together with typical SEM micrographs. When the hardened body was immersed in SBF for 3 h, both α -TCP and HAp were detected (Fig. 7(a)). However, the X-ray intensity of α -TCP decreased and that of HAp increased with immersion time in SBF from 3 h to 1 d (Fig. 7(b)). Finally, the presence of α -TCP was not able to be detected when the hardened body was immersed in SBF for 3 d (Fig. 7(c)), whilst the X-ray intensity of HAp increased with a further increase in immersion time to 7 d (Fig. 7(d)).

SEM micrographs indicated the appearance of needle-like particles on the surface of the original α -TCP agglomerates following the immersion in SBF for 1 d. On the other hand, such



Fig. 7. XRD patterns after the immersion of hardened bodies containing 50 mass% of α -TCP (0.1 mass% of CS(24) addition) in SBF at 37.0 ± 0.2°C for (a) 3 h, (b) 1 d, (c) 3 d and (d) 7 d, together with SEM micrographs. \bigcirc : α -TCP, \square : HAp. Note that the original α -TCP with 0.1 mass% of CS(24) addition was obtained by the heat-treatment of spraypyrolyzed powder at 1200°C for 10 min.

needle-like particles completely covered the surfaces of original α -TCP agglomerates after immersion for 3 d.

As the calcium-phosphate paste chiefly includes $Ca_4(PO_4)_2O$ (18.0 mass%) and CaHPO₄·2H₂O, together with α -TCP (74.9 mass%), the chemical reaction to form HAp may be expressed as follows:²²⁾

$$2Ca_{3}(PO_{4})_{2} + Ca_{4}O(PO_{4})_{2} + H_{2}O \rightarrow Ca_{10}(PO_{4})_{6}(OH)_{2} \quad (2)$$

$$2Ca_{4}O(PO_{4})_{2} + 2CaHPO_{4} \cdot 2H_{2}O \rightarrow Ca_{10}(PO_{4})_{6}(OH)_{2} + 4H_{2}O \quad (3)$$

Additionally, the hydration of α -TCP to form HAp must also occur, as given by the reaction route in Eq. (1). The plate-like grains observed on the surfaces of original α -TCP agglomerates are regarded to be calcium-deficient HAp and silicon-substituted apatite.

Figure 8 illustrates micro-CT photograph and SEM micrograph following immersion of the hardened body containing 50 mass% of porous spherical α -TCP agglomerates (0.1 mass% of CS(24) addition) in SBF solution at 37.0°C for 7 d. Note that the total porosity of the original specimen with 50 mass% of α -TCP addition was 66.3%. The micro-CT photograph indicated the microstructure of the immersed body to be homogeneous. In addition to this, the higher magnification micrograph (SEM) suggested the original spherical agglomerates to be homogeneously coated with the small plate-like particles.

As mentioned previously, the plate-like particles are considered to be calcium-deficient HAp and silicon-substituted apatite. The larger number of plate-like HAp particles on the surfaces of original α -TCP agglomerates, compared to the case of commercially available powder, may be attributed to the increased activity of the chemical reactions shown in Eqs. (1) to (3), due to the higher porosity of the present powder.

Figure 9 shows the changes in compressive strength during the immersion of hardened body containing α -TCP agglomerates



Fig. 8. Micro-CT photograph and SEM micrograph after the immersion of a hardened body with 50 mass% of α -TCP addition (0.1 mass% of CS(24) addition) in SBF solution at 37.0 ± 0.2°C for 7 d. Note that the α -TCP with 0.1 mass% of CS(24) addition was obtained by the heat-treatment of spray-pyrolyzed powder at 1200°C for 10 min.



Fig. 9. Changes in compressive strength during the immersion of hardened bodies with (a) 0 mass%, (b) 10 mass%, (c) 30 mass% and (d) 50 mass% α -TCP addition (0.1 mass% of CS(24) addition) in the SBF heated at 37.0 ± 0.2°C. Note that the α -TCP with 0.1 mass% of CS(24) addition was obtained by the heat-treatment of spray-pyrolyzed powder at 1200°C for 10 min.

(0.1 mass% of CS(24) addition) in SBF. The overall trends revealed that the compressive strength increased with increasing immersion time in SBF. The compressive strengths following immersion of the hardened body with different amounts of α -TCP addition (0.1 mass% of CS(24) addition) in SBF at 37.0°C for 14 d were classified as follows: 82.0 MPa (0 mass%) > 65.2 MPa (10 mass%) > 36.7 MPa (30 mass%) > 31.0 MPa (50 mass%). The rapid increase in compressive strength at the initial stages of hydration in SBF may be attributed to the chemical reaction to form HAp (see Eqs. (1) to (3)). The plate-like parti-



Fig. 10. Relationship between porosity and $\ln \sigma$ of hardened bodies with and without α -TCP addition (0.1 mass% of CS(24) addition) after the immersion in SBF at $37.0 \pm 0.2^{\circ}$ C for various times. $\textcircled{O}: \alpha$ -TCP with no CS addition, $\bigcirc: \alpha$ -TCP with various amounts of CS(24) addition. Note that the original α -TCP with 0.1 mass% of CS(24) addition was obtained by the heat-treatment of spray-pyrolyzed powder at 1200°C for 10 min.

cles formed by the chemical reaction in SBF are noted to be densely packed and it is tentatively suggested that these platelike grains were more resistant to crushing, compared to the more loosely bound spherical agglomerates shown in Fig. 5. In contrast to this, a likely explanation for the general decreasing trend in compressive strength with increasing α -TCP content may be related to the overall change in porosity, due to the addition of porous spherical α -TCP agglomerates.

In general, the relationship between porosity (*P*) and compressive strength (σ) may be expressed as follows:²³⁾

$$\sigma = \sigma_0 e^{-bP} \tag{4}$$

where σ_0 is the compressive strength at a porosity (*P*) of zero and *b* is an empirical constant. On the basis of the logarithmic plots of the data shown in Fig. 9, the relationship between σ and *P* has been presented in **Fig. 10**. The linear relationship between *P* and ln σ was expressed as follows:

$$\ln \sigma = -7.58 \times 10^{-2} P + 7.53 \tag{5}$$

As confirmed in Eq. (5), the compressive strength (σ) is found to be dependent upon the porosity of the hardened body. In addition, the existence of a linear relationship in Eq. (5) indicates that the compressive strength of the hardened body may be controlled by changing the amount of α -TCP agglomerates incorporated into the calcium-phosphate paste.

Conclusion

The effect of colloidal silica (SiO₂) addition (0.1–0.4 mass%) on the formation of porous spherical α -calcium orthophosphate (α -Ca₃(PO₄)₂; α -TCP) agglomerates was examined, using powders obtained from the spray pyrolysis (air-liquid nozzle) of calcium-phosphate (Ca/P ratio = 1.50) solution at 600°C. The results obtained were summarized as follows:

(1) The spray-pyrolyzed powders with and without CS addition were heat-treated at 1200°C for 10 min. The heat-treated powder with no CS addition contained only α -TCP, whereas the powders with 0.4 mass% of CS addition included not only α -TCP but also β -TCP; the amount of β -TCP decreased with increasing diameter of CS from 14 to 24 nm or larger, showing the retarded transformation of β - to α -TCP due to the presence of CS. The complete transformation of β - to α -TCP and preservation of the hollow spherical framework were achieved by the addition of 0.1 mass% of CS with mean size of 24 nm.

(2) The porous cylindrical specimen was fabricated by mixing 50 mass% of α -TCP agglomerates (0.1 mass% of CS addition (mean diameter: 24 nm)) with commercial calcium phosphate paste. The hardened body was immersed in simulated body fluid at 37.0°C and the α -TCP was found to be changed into hydroxy-apatite (Ca₁₀(PO₄)₆(OH)₂) within three days.

Acknowledgements The authors wish to express their thanks to Mr. M. Hirano of HOYA Corp. for taking micro-CT photographs of the hardened body.

References

- M. Jarcho, R. L. Salsbury, M. B. Thomas and R. H. Doremus, J. Mater. Sci., 14, 142–150 (1979).
- 2) L. L. Hench, J. Am. Ceram. Soc., 81, 1705-1728 (1998).
- 3) D. S. Metger, M. R. Rieger and D. W. Foreman, J. Mater. Sci.: Mater. Med., 10, 9–17 (1999).
- E. M. Ooms, E. A. Egglezos, J. G. C. Wolke and J. A. Jansen, Biomater., 24, 749–757 (2003).
- 5) K. Itatani and M. Aizawa, J. Soc. Inorg. Mater. Japan, 10, 285–292 (2003).
- K. Itatani, O. Takahashi, A. Kishioka and M. Kinoshita, Gypsum & Lime, 213, 19–27 (1988).
- K. Itatani, T. Nishioka, S. Seike, F. S. Howell, A. Kishioka and M. Kinoshita, J. Am. Ceram. Soc., 77, 801–805 (1994).
- M. Aizawa, K. Itatani, Y. Miyamoto, A. Kishioka and M. Kinoshita, *Gypsum & Lime*, 237, 22–30 (1992).
- H. Monma and M. Goto, J. Ceram. Soc. Japan (Yogyo-Kyokai-Shi), 91, 473–475 (1983).
- 10) P. Li, C. Ohtsuki, T. Kokubo, K. Nakanishi, N. Soga, T. Nakamura and T. Yamamuro, J. Am. Ceram. Soc., 75, 2094–2097 (1992).
- T. Peltola, M. Jokinen, H. Rahiala, E. Levänen, J. B. Rosenholm, I. Kangasniemi and A. Yli-Urpo, *J. Biomed. Mater. Res., Part A*, 44, 12–21 (1999).
- Joint Committee on Powder Diffraction Standards, No. 9–169, International Centre for Diffraction Data, Swathmore, PA, USA (1959).
- Joint Committee on Powder Diffraction Standards, No. 9–432, International Centre for Diffraction Data, Swathmore, PA, USA (1959).
- 14) M. S.-A. Johnson and G. H. Nancollas, Oral Biol. Med., 3, 61–82 (1992).
- Joint Committee on Powder Diffraction Standards, No. 29–359, International Centre for Diffraction Data, Swathmore, PA, USA (1979).
- 16) K. Itatani, M. Takahashi, F. S. Howell and M. Aizawa, J. Mater. Sci.: Mater. Med., 13, 707–713 (2002).
- M. Toriyama, S. Kawamura, Y. Ito, H. Nagae and I. Toyama, J. Ceram. Soc. Japan, 96, 837–840 (1988).
- 18) J. D. Rimstidt, *Geochim. Cosmochim., Acta*, 61, 2553–2558 (1997).
- 19) X. Wei, Q. Ugurlu and M. Akinc, J. Am. Ceram. Soc., 90, 2315–2321 (2007).
- 20) I. R. Gibson, S. M. Best and W. Bonfield, J. Biomed. Mater. Res., 44, 422–428 (1999).
- 21) Q. H. M. S. Zaman, A. Takeuchi, G. T. Zaman, S. Matsuya and K. Ishikawa, J. Ceram. Soc. Japan, 116, 88–91(2008).
- 22) Y. Musha, M. Abe, T. Umeda and K. Itatani, *Phosphorus Res. Bull.*, 20, 149–154 (2006).
- 23) W. Duckworth, J. Am. Ceram. Soc., 36, 68 (1953).