Formation of Hydroxyapatite on Composites in CaO-P₂O₅-SiO₂-Al₂O₃ System by Hydrothermal Treatment

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水熱処理による CaO-P₂O₅-SiO₂-Al₂O₃ 系複合体上への水酸アパタイトの生成

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Nine kinds of composite powders in CaO-P₂O₅-SiO₂-Al₂O₃ system were prepared by the sol-gel process. Although the as-prepared powders were amorphous, hydroxyapatite (HAp) and tricalcium phosphate (TCP) were formed as a calcium phosphate phase when they were heated from 800 to 1300°C. Additionally, anorthite (CaAl₂Si₂O₈) was formed in the composites containing 25 mol% of Al₂O₃ and 25 mol% of SiO₂ at 1100°C. The dense composite of 2.69 g·cm⁻³ bulk density was obtained by sintering powders with compositions of 38.48CaO·11.52P₂O₅·25SiO₂·25Al₂O₃ at 900°C for 5h. When this composite was hydrothermally treated at 160°C for 24h, β-TCP was changed into HAp to form a porous layer with the ~8 μm thickness on the surfaces of composites. The porous composite of 2.33 g·cm⁻³ bulk density was obtained when the powders with the compositions of 40CaO·10P₂O₅·10SiO₂·40Al₂O₃ were sintered at 1200°C for 5h. Ricelike HAp particles were formed on the surfaces and fracture surfaces of the porous composite treated hydrothermally at 160°C for 12h.

Key-words: Hydroxyapatite, Sol-gel process, Composite, CaO-P₂O₅-SiO₂-Al₂O₃ system, Hydrothermal treatment

1. Introduction

Much attention is being devoted to making use of the glass and glass-ceramics containing CaO, P₂O₅ and SiO₂ as main components in the fields of biomaterials,¹⁻⁴⁾ due to the advantages of (i) bonding to living bone,¹⁾ (ii) faster bone-inducing ability than hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; HAp)²⁾ and (iii) recombining ability, after the materials would break inside the body.^{3,4)} These multi-component powders may be prepared by a sol-gel process which has an advantage that the sol composition is homogeneous on the molecular level.⁵⁾ By making use of this process, we prepared the composites in the CaO-P₂O₅-SiO₂ system with and without B₂O₃,^{6,7)} the sinterability and the mechanical strength are enhanced by the incorporation of B₂O₃ into the composites in the CaO-P₂O₅-SiO₂ system.

A further improvement of the sinterability and mechanical strength of the CaO-P₂O₅-SiO₂ system

may be expected by incorporating Al₂O₃ into them instead of B₂O₃, because Al₂O₃ is known to behave as an intermediate oxide in a glass network.⁸⁾ One of the present authors reported that the structures of the phosphate glasses, such as those in the Na₂O-Al₂O₃-P₂O₅ and K₂O-Al₂O₃-P₂O₅ systems, are stabilized by the incorporation of Al₂O₃ into them.⁹⁾

In this investigation, we prepared nine composite powders in the CaO-P₂O₅-SiO₂-Al₂O₃ system by a sol-gel process and then examined some properties, such as the phase changes during the heating and the sinterability of powders. In addition, we describe the formation of HAp on the composites by the hydrothermal treatment as an attempt to develop a novel process for HAp coating.

2. Experimental

2.1 Preparation of gel powders

The compositions of the prepared sols are given in Table 1. As reported previously in detail,^{6,7)} these sols with nine kinds of compositions in the CaO-P₂O₅-SiO₂-Al₂O₃ system were prepared in the following manner: the starting materials were weighed to prepare 10 g of the composite powders. At first, Si(OC₂H₅)₄ was dissolved into ethanol and this mixture was then stirred vigorously. Next, after the nitric acid solution prepared by mixing Ca(NO₃)₂, (NH₄)₂HPO₄ and Al(NO₃)₃ was added to the above ethanol solution, the mixed solutions were stirred for

Table 1. Compositions and Ca/P Ratios of As-Prepared Sols

Sp. No.	Compositions (mol%)				Ca/P ratio
	CaO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	
1	37.50	12.50	40.00	10.00	1.50
2	38.48	11.52	40.00	10.00	1.67
3	40.00	10.00	40.00	10.00	2.00
4	37.50	12.50	25.00	25.00	1.50
5	38.48	11.52	25.00	25.00	1.67
6	40.00	10.00	25.00	25.00	2.00
7	37.50	12.50	10.00	40.00	1.50
8	38.48	11.52	10.00	40.00	1.67
9	40.00	10.00	10.00	40.00	2.00

an additional hour.

The obtained sols were allowed to stand for 15 d at room temperature (R.T.); during this time they were gelated. The dried gel powders were obtained by heating these sols up to 200°C over a period of 140 h. After the gel powders were calcined at 600°C for 1h, they were ground fine enough to pass through 75 μm sieves.

2.2 Phase identification

The phase changes were examined using an X-ray powder diffractometer (XRD) with Ni-filtered Cu K α radiation (40 kV, 25 mA) (RAD-II A, Rigaku Corp., Tokyo); the crystalline phases were identified by reference to the JCPDS cards. The lattice constants were measured by an internal standard technique using silicon. FT-IR measurements were carried out by a powder diffusion reflection method (Shimadzu 8200D) using KBr.

2.3 Fabrication of sintered bodies

After about 0.3 g of the calcined powders were uniaxially pressed at 100 MPa to form the cylindrical compacts with a diameter of 10 mm and a height of ~ 3 mm, the compacts were pressed at 150 MPa using a cold isostatic press (CIP). These compacts were fired at 800–1200°C for 5h at the heating rate of 10°C·min⁻¹. The bulk density of the composite was calculated from the dimensions and the weight.

2.4 Mechanical properties

About 2 g of the calcined powders were pressed at 86 MPa to form rectangular-solid specimens with dimensions of 45 $\times$ 5 $\times$ 4 mm. These specimens were then pressed at 150 MPa using CIP. The three-point bending strengths of the sintered specimens were measured (Autostrain, Model 216YZ-500-1-PC, Yasuda Seiki, Tokyo). The crosshead speed was 0.5 mm·min⁻¹ and the span was 30 mm.

2.5 Hydrothermal treatment

After the specimens were soaked in a Teflon vessel with 100 cm³ of purified water, the pH of the solution was adjusted to ~ 10 , using 2.8 mass% NH₄OH solution.⁷⁾ Each composite was hydrothermally treated at 160°C for 24–72 h using an autoclave (Taiatsu Scientific Glass, TEM-V Type).

The surfaces and fracture surfaces of the specimens before and after the treatments were observed using a scanning electron microscope (SEM: S-430, Hitachi Ltd., Tokyo).

3. Results and discussion

3.1 Properties of calcined powders

The phase changes of the calcined powders during the heating from 800 to 1300°C are described in this Section. The heating was conducted from room temperature up to the desired temperature at the rate of 10°C·min⁻¹; no holding was conducted at the desired temperature. In the case of Nos. 1–3, β -tricalcium phosphate (β -TCP) was present as a calcium phosphate phase during heating; the other crystalline phases were tridymite, cristobalite and calcium

silicates such as CaSiO₃. Since the phase changes of Nos. 4–6 during the heating were similar to one another, the typical XRD patterns of No. 5 containing 25 mol% of SiO₂ and 25 mol% of Al₂O₃ are shown in Fig. 1. Poorly crystallized HAp was present in the range of 800 to 900°C (Figs. 1(a) and (b)), whereas β -TCP was present in the range of 1000 to 1300°C (Figs. 1(c)–(f)). The other crystalline phases which appeared during the heating were anorthite (CaAl₂Si₂O₈), tridymite, cristobalite, CaSiO₃, mullite and α -Al₂O₃. Anorthite and β -TCP were mainly present at and above 1200°C (Figs. 1(e) and (f)). An upsurge of X-ray intensities in the ranges of 20°–30° indicated the presence of amorphous materials. On the other hand, in the case of Nos. 7–9, HAp and TCP were formed during the heating; the formation behaviours of these calcium phosphates were almost the same as those in Nos. 4–6; the other crystalline phases were α -Al₂O₃, mullite and anorthite.

Although β -TCP was present at and above 1200°C, which exceeds the transformation temperatures (1120¹⁰–1180°C¹¹) of β -TCP to α -TCP, this may be due to the solid-solution of Al³⁺ into β -TCP.¹²⁾ In order to confirm the solid-solution of Al³⁺ into β -TCP, the lattice constants of β -TCP were measured using (220) and (217) reflections. The lattice constants of the a -axis of the β -TCP derived from the composites were ~ 1.034 nm, which is smaller than the lattice constant (1.043 nm) of the a -axis of the pure β -TCP.¹³⁾ This result is supported by Toriyama et al.,¹⁴⁾ who reported that the contraction of the a -axis is caused by the solid-solution of AlPO₄ into TCP. The XRD patterns in Fig. 1 show that the tridymite and cristobalite were formed during the heating. Since AlPO₄ is isostructural with SiO₂, it is difficult to determine by XRD whether the tridymite and

Fig. 1. XRD patterns of the calcined powder of No. 5 heated at (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C, (e) 1200°C and (f) 1300°C.

Fig. 2. Relationship between firing temperature and bulk density of sintered composites. Firing time: 5h.

cristobalite formed during the heating are AlPO₄ or SiO₂.

The sinterability of the compressed powder was examined by firing at temperatures from 800 to 1200°C for 5h. The densification behavior of these powders depended upon the contents of Al₂O₃ and SiO₂ in the samples. Figure 2 shows the typical relationship between firing temperature and bulk density of the composites of Nos. 2, 5 and 9 with the various contents of Al₂O₃ and SiO₂.

The overall trend revealed that the bulk densities of Nos. 4–6 were higher than those of Nos. 1–3 and 7–9. Particularly, the bulk densities of the composites in Nos. 5 and 6 fired at 900°C for 5h were maxima, i.e., 2.69 and 2.75 g·cm⁻³, respectively; however, they decreased with an increase of the heating temperatures.

The decrease of the bulk density corresponds to the increase of the amount of anorthite formed during the heating, as shown in Fig. 1. Since the density (2.76 g·cm⁻³) of anorthite¹⁵ is lower than the density (3.16 g·cm⁻³) of HAp and that (3.07 g·cm⁻³) of β -TCP, the increase in the amount of anorthite during the heating leads to the volume expansion of the composites, thus reducing the bulk density.

3.2 Hydrothermal treatment of sintered composites

Among the samples examined in Section 3.1, the dense composite of No. 5 fired at 900°C for 5h has the highest bulk density, whereas the porous composite of No. 9 fired at 1200°C for 5h has a low bulk density and contains α -TCP, which is hydrolyzed more easily than β -TCP. We therefore selected the sintered composites of Nos. 5 and 9 as the samples for the hydrothermal treatment.

Figure 3 shows the typical phase changes before and after the hydrothermal treatments of Nos. 5 and 9. The crystalline phases before the treatment of No. 5 were β -TCP and a small amount of HAp; however, the diffraction intensities of HAp were enhanced after the treatment at 160°C for 24h. β -TCP was detected from the composite sintered at 900°C for 5h, although HAp was only present as a calcium phosphate phase in the composite heated at 900°C (see Fig. 1(b)). This β -TCP may be formed by the long period of firing, 5h. The FT-IR spectra of the powdered composite (No. 5) after the treatment are

Fig. 3. XRD patterns of the composites (Nos. 5 and 9) in the CaO-P₂O₅-SiO₂-Al₂O₃ system before and after the hydrothermal treatments.

The hydrothermal treatment conditions: No. 5: 160°C, 24h; No. 9: 160°C, 12h.

Fig. 4. FT-IR spectra of the powdered composites (No. 5) after hydrothermal treatment at 160°C for 24h.

shown in Fig. 4. The absorption peaks assigned to OH groups of HAp¹⁶⁾ were detected at ~ 3570 cm⁻¹. As the obtained spectra were broad, some amorphous materials (CaO-P₂O₅-SiO₂-Al₂O₃ system) may be contained in the composites.

On the basis of our previous data on the composites in the CaO-P₂O₅-SiO₂-B₂O₃ system,⁷⁾ this HAp appears to be formed by the hydrolysis of the crystalline β -TCP; it may also be formed as a result of the dissolution-precipitation reaction of the amorphous materials in the composites. Kokubo et al. reported that an SiO₂ gel layer induces the formation of HAp;^{17,18)} the present HAp may also be induced by the participation of SiO₄⁴⁻ ions which dissolved out of the composites.

The SEM micrographs of the surfaces and cross sections of No. 5 are shown in Fig. 5. The composite before the treatment had smooth surfaces; however, some whiskerlike particles with the sizes of ~ 3 μ m were homogeneously coated on the surfaces of the composite treated at 160°C for 24h. Such whiskerlike particles may be HAp, judging from the results of XRD and IR (see Figs. 3 and 4). The observation of the cross sections showed that the porous HAp layer had a thickness of about 8 μ m. Although the data are omitted in this paper, these whiskerlike particles were gradually changed into the prismatic or fibrous particles on increasing the treatment time. From the above results, we conclude that the porous HAp layer may form on the surface of composite by the hydrothermal treatment; these results are expected to be helpful for a novel process of HAp coatings.

Fig. 5. SEM micrographs of the surfaces and the cross sections of the composite in the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ system (No. 5) after the hydrothermal treatment.

After the treatments at 160°C for 24h, the bending strength of No. 5 was reduced from ~ 120 to ~ 85 MPa. The decrease of the bending strength in No. 5 corresponds to the increase of pore volume due to the hydrolysis from β -TCP to HAp.

As shown in Fig. 3, α -TCP, anorthite and $\alpha\text{-Al}_2\text{O}_3$ were present in the sample No. 9 before the treatment; however, α -TCP was changed into HAp after the treatment. When the powdered composites of No. 9 after the treatment were examined by FT-IR measurement, the characteristic absorption peak of HAp¹⁶⁾ was detected at $\sim 3570\text{ cm}^{-1}$, similar to the case of No. 5.

The SEM micrographs of the surfaces and fracture surfaces in No. 9 are shown in Fig. 6. Some pores were present on the surfaces and fracture surfaces before the treatments; however, ricelike particles with the sizes of below $1\text{ }\mu\text{m}$ were observed on the surfaces treated at 160°C for 12h.

These particles appear to be HAp on the basis of the XRD results. Since such ricelike particles were also present on the fracture surface, the hydrother-

Fig. 6. SEM micrographs of the surfaces and the fracture surfaces of the composite in the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ system (No. 9) after the hydrothermal treatment.

mal treatments may effectively be operating inside the composite to form the HAp. Since no change in the bending strength of the composite (~ 25 MPa) is found after the treatments, we conclude that this hydrothermal treatment process is effective for the precipitation of HAp inside the porous sintered body.

4. Conclusions

We investigated the phase changes and microstructures of the composites in the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ system before and after hydrothermal treatments.

(1) When the dense composite (No. 5) with the bulk density of $2.69\text{ g}\cdot\text{cm}^{-3}$ was hydrothermally treated at 160°C for 24h, the crystalline β -TCP was changed into HAp. A porous HAp layer with the thickness of $\sim 8\text{ }\mu\text{m}$ was formed on the composites; the whiskerlike HAp particles with the sizes of $\sim 3\text{ }\mu\text{m}$ were formed after the treatment.

(2) When the porous composite (No. 9) with the bulk density of $2.33\text{ g}\cdot\text{cm}^{-3}$ was hydrothermally treated at 160°C for 12h, the crystalline α -TCP was changed into HAp. Ricelike particles were present on the surfaces and the fracture surfaces. Such treatments may effectively be applied inside the composite to form the HAp.

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