Formation of Porous Calcium Phosphate Films on α - Al_2O_3 Substrates by Spray-Pyrolysis Technique

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噴霧熱分解法による α - Al_2O_3 基板上への多孔質リン酸カルシウム膜の形成

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Porous calcium phosphate films could be formed on α - Al_2O_3 substrates by spray-pyrolysis technique. The use of calcium metaphosphate as a binder was effective to enhance the binding strength of calcium phosphate films to substrates. The films obtained by spray-pyrolyzing the starting solutions were heated at a temperature between 1000 and 1400°C for 5h. The crystalline phase of the heated films was mainly β -calcium orthophosphate. The thickness of this film was dependent on the spraying time and the pore sizes were about 15 μm .

Key-words: Porous calcium phosphate films, β -calcium orthophosphate, Calcium metaphosphate, α - Al_2O_3 substrates, Spray-pyrolysis technique

1. Introduction

Calcium phosphate ceramics, such as hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp) and β -calcium orthophosphate (β - $\text{Ca}_3(\text{PO}_4)_2$; β -TCP), have excellent biocompatibility and are used as substitute materials for human hard tissues;¹⁾ however, the mechanical strengths, especially the toughness values, of these ceramics are inferior to those of natural bones and teeth.²⁾ Thus use of these ceramics as load-bearing parts in the human body is difficult. In order to improve the mechanical strengths, much attention is being devoted to fabricate a composite of calcium phosphates either with metals or with high-strength ceramics.

Attempts to fabricate the composites with excellent mechanical strength and biocompatibility have resulted in many reports of various techniques by which calcium phosphate films could be formed on metal rods or on high-strength ceramics: sputtering,³⁾ electrophoresis,⁴⁾ A-W glass coating,⁵⁾ plasma spray,⁶⁾ dipping-pyrolysis⁷⁾ and spray-pyrolysis.⁸⁾ Most of the above techniques are suitable for the preparation of dense films but not for porous films spray-pyrolysis being an exception. The porous calcium phosphate films where the pores are utilized as formation sites of new bone may be formed by the spray-pyrolysis technique. Moreover, the spray-pyrolysis technique has the following advantages: (i) the desired compositions of the films

can be fabricated by controlling the compositions of the starting solutions and (ii) homogeneous films can be coated on the substrate.⁸⁾

Chae et al.⁹⁾ have prepared the porous TCP films on Co-Cr implants by the plasma-spray technique; the binding strength of implants to bone could be enhanced after the new bone was induced into the porous films. Except for this, however, there are few investigations on formation of the porous calcium phosphate films. The authors have reported that the same films with thicknesses of 10–30 μm can be formed on the bio-inert TiO_2 substrate by spray-pyrolysis technique.⁸⁾ Since an α - Al_2O_3 ceramics has high strength and is a bio-inert material, we investigated the preparation of the porous calcium phosphate films on this α - Al_2O_3 substrate by spray-pyrolysis technique.

2. Experimental

2.1 Preparation of α - Al_2O_3 substrate

The α - Al_2O_3 substrate with diameter of 8.5 mm and thickness of about 2.5 mm was prepared by firing the compressed powder at 1700°C for 5h; the commercial α - Al_2O_3 powder (Sumitomo Chem. Co., Ltd.: Akp-30) with purity of 99.99% was used as a starting material. The relative density of the sintered compact or substrate was about 95% of the theoretical density.

2.2 Preparations of starting solutions

Two types of solutions were prepared using the desired amounts of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and concentrated nitric acid (HNO_3). One solution with Ca/P ratio of 1.67, corresponding to the composition of HAp, was prepared by mixing the solutions of 0.50 $\text{mol} \cdot \text{dm}^{-3}$ $\text{Ca}(\text{NO}_3)_2$, 0.30 $\text{mol} \cdot \text{dm}^{-3}$ $(\text{NH}_4)_2\text{HPO}_4$ and 0.4 $\text{mol} \cdot \text{dm}^{-3}$ HNO_3 ; the other solution with Ca/P ratio of 0.50, corresponding to the composition of calcium metaphosphate ($\text{Ca}(\text{PO}_3)_2$; CMP), was prepared by mixing the solutions of 0.75 $\text{mol} \cdot \text{dm}^{-3}$ $\text{Ca}(\text{NO}_3)_2$, 1.50 $\text{mol} \cdot \text{dm}^{-3}$ $(\text{NH}_4)_2\text{HPO}_4$ and 2.0 $\text{mol} \cdot \text{dm}^{-3}$ HNO_3 . These solutions are designated as "HAp solution" and "CMP solution", respectively.

2.3 Formation of films on substrates

The films on substrates were prepared by spray-pyrolysis technique. The over-all view of the spray-pyrolysis apparatus has been reported previously.⁸⁾ The α - Al_2O_3 substrate was coated with calcium phosphate films in the following manner: α - Al_2O_3 substrate was first fixed by a clip in the upper part of the reactor tube; then the starting solution was sprayed into the reaction tube heated at 600°C from the lower part (the flow rate of air: $10 \text{ dm}^3 \cdot \text{min}^{-1}$); the α - Al_2O_3 substrate which was heated at about 220°C was coated by the spray-pyrolyzed materials in the upper part of the reaction tube.

Three kinds of techniques were applied to form the films on α - Al_2O_3 substrates. "Single-step process" is a technique in which the films are directly formed on α - Al_2O_3 substrates by spray-pyrolyzing the HAp solution. "Two-step process" is a technique in which the films are formed on the substrates by spraying the CMP solution for 5h and then HAp solution for 5–15h. "Three-step process" is a technique in which the films are formed on the substrates by spraying the CMP solution, then heating at 1000°C for 1h, and spraying HAp solution for an additional 5–15h. Calcium phosphate films formed on α - Al_2O_3 substrates by three kinds of techniques were heated to enhance the binding strength of films to substrates at a temperature between 1000 and 1400°C for 5h; the heating rate was $10^\circ\text{C} \cdot \text{min}^{-1}$.

2.4 Phase identification and microstructure observation of films

The crystalline phases of the calcium phosphate films were examined by an X-ray powder diffractometer (XRD) with Ni-filtered Cu K α radiation (40 kV, 25 mA), (RAD-II A, Rigaku Corp., Tokyo).

The surfaces and cross sections of the films were observed by a scanning electron microscope (SEM; S-430, Hitachi Ltd., Tokyo). Moreover, the distributions of Ca, P and Al in the film- and substrate-sides were examined by electron probe microanalysis (EPMA; EMAX 1500; Horiba Ltd., Kyoto).

2.5 Examination of binding strength of films to substrates

The binding strength of films to substrates were examined using a tape test.¹⁰⁾ Details of this test are as follows: a piece of Scotch tape (#810) was first adhered to the substrate and then was removed from it. The evaluations of the binding strength were carried out as "strong" or "weak" from the viewpoint of whether the films remained on the tape-side or not.

3. Results and discussion

3.1 Single-step process

The α - Al_2O_3 substrate was directly coated with the spray-pyrolyzed materials, mainly HAp.⁸⁾ The amount of HAp formed on the α - Al_2O_3 substrate increased with an increase in the spraying time from 5 to 15h. From SEM observations, it was found that the spherical agglomerated HAp were in contact

with the substrate and that the amount of HAp increased with the spraying time.

The above results suggest that the films of the desired thickness may be formed on the substrate by changing the spraying time; however, the films can easily be removed from the substrate, because the spherical agglomerates are only in contact with the substrate. In order to coat the films on the substrate with sufficient strength, the substrate coated with the calcium phosphate films was heated at a temperature from 1000 to 1200°C for 5h. The crystalline phases in the films are listed in Table 1. First, the temperature was changed from 1000 to 1200°C. The crystalline phases in the films heated at 1000°C were HAp and very small amounts of β -TCP. When the temperature was raised up to 1100°C, α -TCP was formed, besides the above two compounds; at 1200°C, however, α -TCP and β -TCP were formed instead of HAp. Next the spraying time of the HAp solution was changed from 5 to 15h. The amount of α -TCP increased with increasing the spraying time.

As described in the previous papers,^{11),12)} the materials obtained by spraying the HAp solution consisted of HAp, small amounts of β -TCP and some CaO-rich amorphous phase; the single phase of HAp was obtained by heating the sprayed materials above 1000°C. In this study, however, the TCP is still present above 1000°C. The presence of TCP at this temperature may be attributed to lowering of Ca/P ratio by the reaction of some CaO-rich amorphous phase with Al_2O_3 .

The thickness of the porous films formed on the substrate increased with an increase of the spraying time. The binding strength of the films to the substrates appears to be weak, because the films are easily removed from the substrates. In order to enhance the binding strength, we used the CMP as a binder between the films and the substrates. These techniques are referred to as "two-step process" and "three-step process".

3.2 Two- and three-step processes

Since CMP has the lowest melting point (975°C) among the calcium phosphates, the binding strength of the films to the substrates may be enhanced by the solid material produced from quenching of melt.

Table 1. The Crystalline Phases in the Films Formed by Single-Process and by Three-Step Process

Process	Spraying time (HAp Solution)	Heat-Treatment Conditions	The Crystalline Phases
Single-Step	5 h	1000°C for 5 h	HAp >> β -TCP, α - Al_2O_3
	5 h	1100°C for 5 h	HAp > β -TCP >> α -TCP, α - Al_2O_3
	5 h	1200°C for 5 h	α -TCP > β -TCP, α - Al_2O_3
	10 h	1200°C for 5 h	α -TCP > β -TCP, α - Al_2O_3
	15 h	1200°C for 5 h	α -TCP >> β -TCP, α - Al_2O_3
Three-Step	5 h	1100°C for 5 h	β -TCP, AlPO_4 , α - Al_2O_3
	5 h	1200°C for 5 h	β -TCP, AlPO_4 , α - Al_2O_3
	5 h	1300°C for 5 h	β -TCP, AlPO_4 , α - Al_2O_3
	5 h	1400°C for 5 h	β -TCP, AlPO_4 , α - Al_2O_3
	10 h	1200°C for 5 h	β -TCP, AlPO_4 , α - Al_2O_3
	15 h	1200°C for 5 h	β -TCP > α -TCP, AlPO_4 , α - Al_2O_3

After the substrate coated with the films consisting of CMP¹³) and HAp was heated (two-step process), the crystalline phases in the films were examined by XRD; typical results are shown in Fig. 1. First the temperature was changed from 1000 to 1200°C. The β - $\text{Ca}_2\text{P}_2\text{O}_7$ and small amounts of β -TCP and AlPO_4 were detected at 1000°C (Fig. 1(a)), while β -TCP and AlPO_4 were found at 1200°C (Fig. 1(b)). Next, the spraying time of HAp solution was varied from 5 to 15h at 1200°C. The crystalline phases in the films were β -TCP and AlPO_4 at the spraying time of 10h (Fig. 1(c)); for 15h, α -TCP was formed along with these compounds (Fig. 1(d)). These results show that TCP and AlPO_4 were produced by the reaction of HAp and CMP with Al_2O_3 .

Generally, β -TCP transforms into α -TCP at 1120¹⁴⁾–1180°C,¹⁵⁾ however, the presence of β -TCP at 1200°C suggests that β -TCP is stabilized by the solid-solution of Al^{3+} into it, because the XRD diffraction lines of β -TCP shift slightly toward the higher Bragg angles. Monma and Kanazawa¹⁶⁾ also reported that the structure of β -TCP is stabilized by Al^{3+} in the presence of AlPO_4 . The presence of α -TCP after 15h of spraying suggests that the solid-solution of Al^{3+} into TCP becomes more difficult as the films thicken.

The surfaces of the films heated at various temperatures for 5h were observed by SEM; results are shown in Fig. 2. At 1000°C (Fig. 2(a)) the spherical

agglomerates with diameters of about 5 μm were bound to the small particles with sizes of <1 μm . At 1100°C (Fig. 2(b)) and at 1200°C (Fig. 2(c)) the polyhedral grains with 1–5 μm in sizes were coated on the substrate; moreover, the substrate was coated with the melt. At 1300°C (Fig. 2(d)) the polyhedral grains were packed closely.

The above results indicate that the melts were formed during heating at about 1100°C; the binding strength of the films to the substrate may be enhanced through the solid materials obtained by quenching the melts, that is, the melts act as a binder. According to the phase diagram in the CaO – Al_2O_3 – P_2O_5 system,¹⁷⁾ the liquid phase in the $\text{Ca}(\text{PO}_3)_2$ – $\text{Al}(\text{PO}_3)_3$ system may form at and above 900°C. The change of spherical agglomerates into this melt and the formation of solid materials may produce dense films on the substrate (see Fig. 1(d)).

The films prepared by changing the spraying time were heated at 1200°C for 5h. The films became more porous with as the spraying time increased; moreover, the film thickness increased from 10 to 35 μm when the spraying time lengthened from 5 to 15h.

Next, the results of the three-step process will be described below. After being coated on the substrate with CMP and being heated at 1000°C for 1h, the HAp solution was spray-pyrolyzed to this substrate. The crystalline phases in the resulting films were β - $\text{Ca}_2\text{P}_2\text{O}_7$ and AlPO_4 . The films consisted of plate-like grains with sizes of about 10 μm .

Each substrate coated with a film consisting of β - $\text{Ca}_2\text{P}_2\text{O}_7$ and HAp was heated at a temperature between 1100 and 1400°C for 5h. The crystalline

Fig. 1. X-ray diffraction patterns of the spray-pyrolyzed material on α - Al_2O_3 substrates.

The spray-pyrolyzed time/heating conditions :

(a) 5h/1000°C, 5h, (b) 5h/1200°C, 5h, (c) 10h/1200°C, 5h, (d) 15h/1200°C, 5h.

● β -TCP, ○ α -TCP, ■ β - $\text{Ca}_2\text{P}_2\text{O}_7$, ▲ α - Al_2O_3 , △ AlPO_4 .

Fig. 2. SEM micrographs of the films on α - Al_2O_3 substrates.

The spray-pyrolyzed time/heating conditions :

(a) 5h/1000°C, 5h, (b) 5h/1100°C, 5h, (c) 5h/1200°C, 5h, (d) 5h/1300°C, 5h.

phases in the films heated at various conditions are listed in Table 1. β -TCP and AlPO_4 were formed by heating at 1100, 1200, 1300 and 1400°C. When the spraying time of HAp solution was varied from 5 to 10h at 1200°C, the crystalline phases in the films were β -TCP and AlPO_4 ; in addition, in the case of 15h, a small amount of α -TCP was produced. The amount of AlPO_4 was less than that formed by the two-step process.

When the substrate coated with CMP was heated

at 1000°C, CMP reacts with Al_2O_3 to form $\text{Ca}_2\text{P}_2\text{O}_7$ and AlPO_4 . Furthermore, $\text{Ca}_2\text{P}_2\text{O}_7$ reacts with HAp to form TCP at 1100°C or higher. Since, in the above reaction, β -TCP was present at 1400°C, it seems that β -TCP was stabilized by the solid-solution of Al^{3+} into it in a manner similar to that as with the two-step process.

The surfaces and cross sections of calcium phosphate films formed by the three-step process were observed using SEM. The films formed by spraying the HAp solution for 5h were heated at various temperatures; the microstructure of these films was almost the same as those formed by the two-step process.

The spraying time of HAp solution was next varied from 5 to 15h; the surfaces and cross sections of these films, observed by SEM, are shown in Fig. 3. The overall trend revealed that the amount of the films increased with an increase of the spraying time and that a porous network structure was formed by the binding of the grains and the pore sizes of about 15 μm . The microstructure of the cross section showed that the thickness of the films increased from 10 to 25 μm with an increase of the spraying time from 5 to 10h; however, almost no changes in thickness of the films were observed with a further increase in the spraying time from 10 to 15h. And so these films may be formed by packing grains closely.

The distributions of Ca, P and Al in the films prepared by the three-step process were analyzed using EPMA. The results are shown in Fig. 4. The Ca and P were chiefly distributed on the films-side, whereas the Al was present on both the substrate-side and the film-side.

The results of EPMA demonstrate that β -TCP may be stabilized by the solid-solution of Al^{3+} into it at 1200°C or higher, because Al was detected from the film-side.

Fig. 3. SEM micrographs of the films coated on α - Al_2O_3 substrates heated at 1200°C for 5h.

Fig. 4. EPMA results of α - Al_2O_3 substrates coated with the films heated at 1200°C for 5h.

3.3 Evaluation of binding strength of the films to the substrates

The binding strengths to the substrates of the films formed by the three kinds of techniques were examined by a tape test. These results are listed in Table 2. The calcium phosphate films formed by the single-step process were easily taken off from the substrate, whereas the calcium phosphate films formed by two- and three-step processes were strongly bound to the substrate.

The results from XRD to the surfaces of substrates after the tape test showed that the X-ray intensities of β -TCP were the same before and after the tests; SEM micrographs revealed that the films were bound to the substrate after the tape test.

The binding strength can be enhanced by the reaction between calcium phosphate and Al₂O₃. The differences in binding of calcium phosphate films with Al₂O₃ substrates among the three techniques will be described below. In the case of single-step process, HAp mainly reacts with Al₂O₃ to form TCP and the amorphous material in the CaO-Al₂O₃ system. In the two-step process, HAp and CMP mainly react with Al₂O₃ to form TCP and AlPO₄. In the case of the three-step process, however, CMP first reacts with Al₂O₃ to form Ca₂P₂O₇ and AlPO₄ and then Ca₂P₂O₇ reacts with HAp to form TCP. The β -TCP may be stabilized by the solid-solution of Al³⁺ into it. In the reaction layer, the amorphous materials in the CaO-Al₂O₃ system are present in the single-step process, whereas AlPO₄ is present in the two- and three-step processes. These reaction products and the amorphous materials in the CaO-P₂O₅-Al₂O₃ system enhance the binding strength of the films to the substrate.

As described above, the calcium phosphate films which are strongly bound to the substrate can be prepared by two- and three-step processes. Since the operation of the two-step process is simpler than that of the three-step process for preparations of the

films, the results of this work indicated that the two-step process was the most suitable for the formation of porous calcium phosphate films on α -Al₂O₃ substrates.

4. Conclusions

Porous calcium phosphate films could be formed on the substrates by using spray-pyrolysis technique. The following results were obtained:

- (1) Porous calcium phosphate films containing mainly β -TCP were formed by using the spray-pyrolysis technique; in the cases of two- and three-step processes, β -TCP was stabilized by the solid-solution of Al³⁺ into it. The average pore sizes were about 15 μ m.
- (2) The films were thickened with an increase of the spraying time from 5 to 15h in all three processes.
- (3) The binding strength of the films to the substrate was enhanced by using calcium metaphosphate as a binder. Almost no changes in microstructure of the films were observed from before to after the tape test.

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Table 2. Tape-Test Results of Films Formed by Single-, Two- and Three-Step Processes

Process	Spraying time (HAp Solution)	Results of Tape Test
Single- Step	5 h	Weak
	10 h	Weak
	15 h	Weak
Two- Three- Step	5 h	Strong
	10 h	Strong
	15 h	Strong