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Formation of porous calcium phosphate films on partially stabilized zirconia substrates by the spray-pyrolysis technique

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Porous calcium phosphate films could be formed on partially stabilized zirconia (3YZ) substrates by a spray-pyrolysis technique. The use of calcium metaphosphate as a binder was effective to enhance the binding strengths of these films to the substrates. The crystalline phase in the resulting films was mainly β-calcium orthophosphate. This phase was thermally stabilized by solid solution with Y^{3+}. The thickness of the film (30–150 μm) was dependent upon the spraying time; the pore size was about 15 μm. The films were still present on the substrate after Scotch tape (810) was adhered to the film side and then taken off from the substrate. The films prepared in this study were found to bind strongly to the substrate.

1. Introduction

Sintering materials of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAp) and those of β-calcium orthophosphate (β-$Ca_3(PO_4)_2$; β-TCP) are typical bioactive ceramics, and are used as substitute materials for human hard tissues [1]; however, the mechanical strengths, especially the toughness, of these ceramics are inferior to those of natural bone and teeth [2]. Thus these ceramics are difficult to use as loading parts in the human body. In order to improve the mechanical strengths, much attention is being devoted to fabricating a composite of calcium phosphates either with various metals or with high-strength ceramics, such as titanium alloys, alumina or zirconia ceramics.

Many researchers have attempted to fabricate composites with excellent mechanical strength and biocompatibility. Various techniques are reported by which the 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 pyrolysis [7] and spray pyrolysis [8]. Most of these techniques are suitable for the preparation of dense films, but not porous films. The porous calcium phosphate films, where the pores are utilized as formation sites of new bone, may be formed by the spray-pyrolysis technique. In addition, this technique has two advantages in the film preparation: first, the composition of materials deposited on substrates can be controlled easily by varying the composition of the starting solutions, and second, the deposited materials are able to be coated on a wide area of the substrate.

Previously, 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 the formation of the porous calcium phosphate films. We have reported that porous films of thickness 10–30 μm could be formed on a bio-inert TiO_2 substrate by the spray-pyrolysis technique [8]. Because the partially stabilized ZrO_2 ceramics containing 3 mol % Y_2O_3 (3YZ) are bio-inert materials and have high strength, especially toughness, we investigated the preparation of the porous calcium phosphate films on this 3YZ substrate by the spray-pyrolysis technique.

2. Experimental procedure

2.1. Preparation of 3YZ substrate

The 3YZ substrates with dimensions of about 4 mm × 4 mm × 3.5 mm were prepared by firing the compressed powder at 1400 °C for 5 h; the commercial 3YZ powder (Tosoh Corp, TZ-3Y) was used as starting material. The relative density of the sintered compact or substrate was about 97% of the theoretical density.

2.2. Preparations of starting solutions

Two kinds of solution were prepared using the desired amounts of $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$ and HNO_3 (61 wt %) as starting materials. One solution with a Ca/P ratio of 1.67 corresponds to the composition of HAp; the other solution with a Ca/P ratio of 0.50 corresponds to that of calcium metaphosphate ($Ca(PO_3)_2$; CMP). These solutions are designated "HAp solution" and "CMP solution", respectively. The preparation conditions of these spraying solutions are listed in Table I.

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TABLE I Preparation conditions of the starting solutions

	$Ca(NO_3)_2^a$ (mol dm^{-3})	$(NH_4)_2HPO_4^a$ (mol dm^{-3})	HNO_3 (10^{-3} dm^3)	Ca/P
HAp solution	1.00	0.60	5	1.67
CMP solution	1.50	3.00	30	0.50

[a] 0.1 dm^3 of solution.

2.3. Formation of films on the substrate

The overall view of the spray-pyrolysis apparatus has been reported previously [8]. The calcium phosphate films were prepared on the substrate in the following manner: the substrate was first fixed by a clip in the upper part of the reaction tube; then the starting solution was sprayed into the reaction tube heated at 600 °C from the lower part (flow rate of air = 10 dm^3 min^{-1}); the substrate which was heated at about 220 °C was coated by the spray-pyrolysed materials in the upper part of the reaction tube.

Three kinds of technique were applied to form the films on the substrates. Details are shown in Table II. The "single-step process" is a technique in which the films are directly formed on the substrate by spray pyrolysing the HAp solution. The "two-step process" is a technique in which the films are formed on the substrates by spraying first the CMP solution for 5 h and then the HAp solution for 5–15 h. The "modified two-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 1 h, and then spraying HAp solution for an additional 5–15 h. Calcium phosphate films formed on the substrates by these three techniques were heated to enhance the binding strengths of the films to the substrates at a temperature from 1000–1300 °C for 1–10 h; the heating rate was 10 °C min^{-1}.

2.4. Properties of the films

The crystalline phases of the calcium phosphate films were examined using an X-ray powder diffractometer with nickel-filtered CuK_α radiation (40 kV, 25 mA; RAD-IIA, Rigaku, Tokyo). The amounts of the crystalline phases were estimated by comparing with X-ray intensities of individual compounds.

The surfaces and cross-sections of the films were observed by scanning electron microscopy (SEM; S-430, Hitachi, Tokyo). The thickness of the films was calculated from the scales shown in the scanning electron micrographs.

The binding strength of the films to the substrate was examined using a tape test [10]. Details of this test are as follows: a piece of Scotch tape (810) was first adhered to the film and then was removed from it. The binding strengths were evaluated as "strong" or "weak" from the viewpoint of whether or not the films remained on the tape surface.

3. Results and discussion

3.1. Single-step process

3.1.1. *Effects of heating temperature*

The calcium phosphate films containing mainly HAp [8] were directly coated on the substrate by spraying HAp solution; however, these films could easily be removed from the substrate because they were only in contact with it. In order to enhance the binding

TABLE II Processes for preparing calcium phosphate films

Process	Spray pyrolysis (CMP solution) (h)	→	Heat	→	Spray pyrolysis (HAp solution) (h)	→	Heat
Single-Step	–		–		5–15		1000–1200 °C for 1–10 h
Two-Step	5		–		5–15		1100–1300 °C for 1–10 h
Modified two-Step	5		1000 °C for 1 h		5–15		1100–1300 °C for 5 h

TABLE III The crystalline phases in the film prepared by the single-step process

Sample	Spraying time (h) (HAp solution)	Heating conditions		Crystalline phases
		(°C)	(h)	
1	5	1000	5	HAp, t-ZrO_2
2	5	1100	5	HAp > β-TCP, t-ZrO_2
3	5	1120	5	β-TCP, t-ZrO_2
4	5	1150	5	β-TCP > α-TCP, t-ZrO_2
5	5	1200	5	α-TCP, t-ZrO_2
6	5	1120	1	HAp ≫ β-TCP, t-ZrO_2
7	5	1120	3	HAp > β-TCP, t-ZrO_2
8	5	1120	10	β-TCP > α-TCP, t-ZrO_2
9	10	1120	10	HAp > β-TCP, t-ZrO_2
10	15	1120	10	HAp > β-TCP, t-ZrO_2

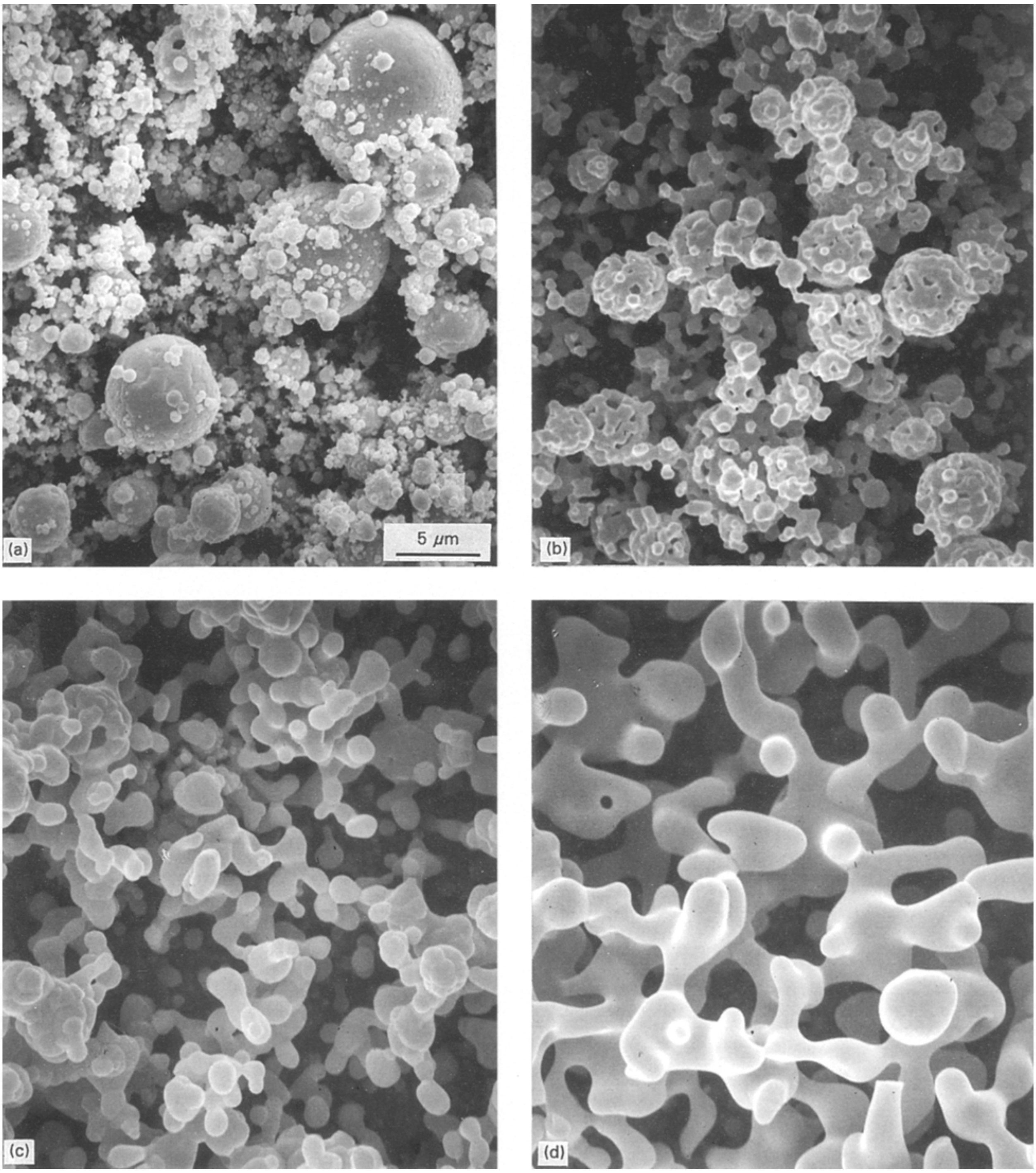

Figure 1 Scanning electron micrographs of the films on 3YZ substrates. The spray-pyrolysing time/heating conditions were: (a) 5 h/as-sprayed; (b) 5 h/1000 °C, 5 h; (c) 5 h/1120 °C, 5 h; (d) 5 h 1200 °C, 5 h.

strength of films to the substrate, the substrate coated with the materials was heated at a temperature from 1000–1200 °C for 5 h.

The crystalline phases in the resulting films are listed in Table III (samples 1–5). The crystalline phase in the films heated at 1000 °C was HAp (sample 1). When the temperature was raised to 1100°C, some β-TCP was also formed, besides HAp (sample 2); at 1120 °C (sample 3), β-TCP alone was present, instead of HAp. At 1150 °C (sample 4), β-TCP and a small amount of α-TCP were formed; at 1200 °C (sample 5), α-TCP alone was present, instead of β-TCP. The crystalline phase of the substrate, that is, tetragonal zirconia (t-ZrO_2), remained unchanged during the heating from 1000–1200 °C for 5 h.

As described in previous papers [11, 12], the stoichiometric HAp was obtained by spray pyrolysing the HAp solution; this HAp was present up to ~ 1200 °C. Therefore, the formation of β-TCP at and above 1100 °C in this work reveals that the stoichiometric HAp may react with the substrate to form β-TCP and amorphous phase in the $CaO–ZrO_2–Y_2O_3$ system. The presence of this phase is suggested from the upsurge of the background signal in the XRD patterns. Such phases might be present at the interfaces between the films and the substrates. The formation of α-TCP at and above 1150 °C is due to the transformation of β-TCP. This temperature is in accordance with the transformation temperature, 1120–1180 °C [13, 14], from β-TCP to α-TCP.

The scanning electron micrographs of the surfaces of the as-sprayed and the heated samples are shown in Fig. 1. The as-sprayed sample (Fig. 1a) showed that both spherical agglomerates with diameters of about 5 μm and small particles with sizes of < 1 μm were attached to the substrate. At 1000 °C (Fig. 1b), the spherical agglomerates have contracted owing to the sintering of the individual particles, together with the sintering of the spherical agglomerates. At 1120 °C (Fig. 1c), the sintered particles or grains were bonded to form the porous network. At 1200 °C (Fig. 1d), this network was developed with grain growth; the pore sizes were about 15–25 μm.

The above SEM observations indicated that the porous films can be formed by the following routes: as the agglomerates and the small particles are packed closely, the agglomerates present in the as-sprayed powder are contracted with an increase of temperature; these particles are sintered to form the films with a porous network structure. Because the pore sizes of the films are 15–25 μm, the new bone seems to be induced into such porous films [15]; this material is expected to be useful for biomaterials.

3.1.2. Effect of heating time

The substrate coated with the sprayed materials was heated at 1120 °C for 1–10 h (corresponding to samples 3, 6, 7 and 8 in Table III). The heating temperature was selected to be 1120 °C, to avoid the formation of α-TCP, which has higher solubility than HAp and β-TCP.

The crystalline phases in the films heated for 1 h (sample 6) were HAp and a small amount of β-TCP.

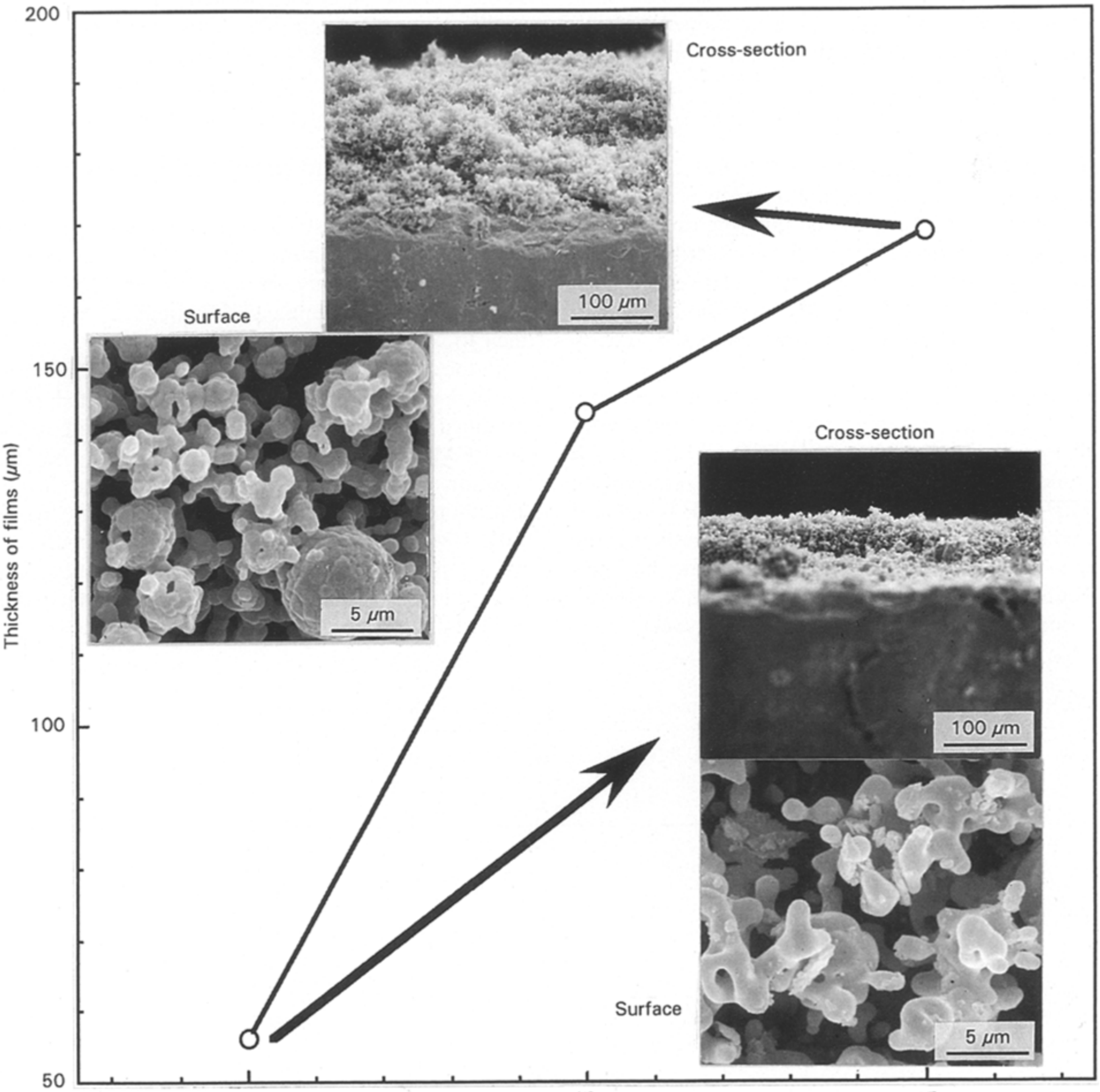

Figure 2 Changes in the film thickness with the spraying time of HAp solution; scanning electron micrographs of the surface and the cross-section of a substrate coated with the porous calcium phosphate films. Heating conditions: 1120 °C, 10 h.

When the heating time was prolonged to 3 h (sample 7), β-TCP was partly formed, besides the HAp; for 5 h (sample 3), only β-TCP was present, instead of HAp. For 10 h (sample 8), β-TCP and a small amount of α-TCP were present. The crystalline phase of the substrate was t-ZrO_2, which remained unchanged when the heating time was prolonged from 1 h to 10 h.

The results of SEM observations of the surfaces of the above samples (3, 6, 7 and 8) were as follows: for the heating time of 1 h (sample 6), the spherical agglomerates with diameters of about 5 μm were contracted by the sintering of the particles with sizes of <1 μm. For 3 h (sample 7), the sintering of the particles progressed; for 5 and 10 h (samples 3 and 8), the sintered particles or grains were bonded to form the porous network structure.

The above results show that the crystalline phases and microstructure in the films are affected by heating time; HAp reacts with the substrate to form β-TCP, and then a part of β-TCP was transformed to α-TCP with increasing the heating time. On the other hand, the porous network structure was developed by heating the substrates coated with the sprayed material at 1120 °C or higher for 5 h.

3.1.3. Effect of the spraying time

The crystalline phases and the microstructure in the films obtained by changing the spraying time of HAp solution from 5 or 10 h to 15 h are described in this section. The substrates coated with sprayed material were heated at 1120 °C for 10 h and the amount of sprayed material on the substrate increased linearly with spraying time.

As shown in Table III, for the spraying time of 5 h (sample 8), the crystalline phases in the films were β-TCP and a small amount of α-TCP; for 10 and 15 h (samples 9 and 10), HAp and a small amount of β-TCP were formed. The amount of TCP is reduced with increasing spraying time, which suggests that the reaction between HAp and the substrate becomes difficult; the reactions are proceeded by a solid-state reaction initiating at the interface between films and substrates. As the amount of sprayed material increases linearly with increasing spraying time, the amount of unreacted HAp may also increase with it.

The relationship between spraying time and thickness of calcium phosphate films is shown in Fig. 2, together with the scanning electron micrographs. The upper parts of the cross-section correspond to the film, while the lower parts represent the substrate. The thickness of the films increased with spraying time from 5–15 h. In spite of an increase in the amount of films with an increase of the spraying time, however, little change in the resulting film thickness was observed, regardless of this increase in spraying time from 10–15 h. This fact suggests that the particles in the films are arranged toward the closer packing with increasing spraying time. This assumption seems to be supported by the SEM observations.

The binding strength of the films to the substrate was enhanced by heating under various conditions. Results of the tape tests showed that the films were easily removed from the substrate; the binding strength of the films to the substrate appears to be weak.

3.2. Two-step and modified two-step processes

CMP has the lowest melting point (975 °C) among the calcium phosphates [16]. If CMP was used as a binder, the binding strength of the films to the substrates may be enhanced through changing the melt to solid phase by quenching.

In the case of the two-step process, the films consisting of mainly CMP [17] and HAp were heated. In the modified two-step process, after the substrate coated with CMP was heated at 1000 °C for 1 h, the HAp solution was spray-pyrolysed and then heated. The films obtained by heating the substrate coated with CMP at 1000 °C for 1 h consisted mainly of β-$Ca_2P_2O_7$ and t-ZrO_2. The crystalline phases in these films examined by XRD are summarized in Table IV.

TABLE IV The crystalline phases in the films prepared by the two-step and modified two-step processes

Sample	Process	Spraying time (h) (HAp Solution)	Heating conditions		Crystalline phases
			(°C)	(h)	
11	Two-step	5	1100	5	β-TCP, t-ZrO_2 > m-ZrO_2
12		5	1200	5	β-TCP, m-ZrO_2 > t-ZrO_2
13		5	1300	5	β-TCP, m-ZrO_2 ≫ t-ZrO_2
14	Two-step	5	1200	1	β-TCP, m-ZrO_2 > t-ZrO_2
15		5	1200	3	β-TCP, m-ZrO_2 > t-ZrO_2
16		5	1200	10	β-TCP, m-ZrO_2 > t-ZrO_2
17	Two-step	10	1200	5	β-TCP, m-ZrO_2 ≫ t-ZrO_2
18		15	1200	5	β-TCP > α-TCP, m-ZrO_2 ≫ t-ZrO_2
19	Modified two-step	5	1100	5	β-TCP, t-ZrO_2 > m-ZrO_2
20		5	1200	5	β-TCP, m-ZrO_2 > t-ZrO_2
21		5	1300	5	β-TCP, m-ZrO_2 ≫ t-ZrO_2
22	Modified two-step	10	1200	5	β-TCP, m-ZrO_2 > t-ZrO_2
23		15	1200	5	β-TCP > α-TCP, m-ZrO_2 ≫ t-ZrO_2

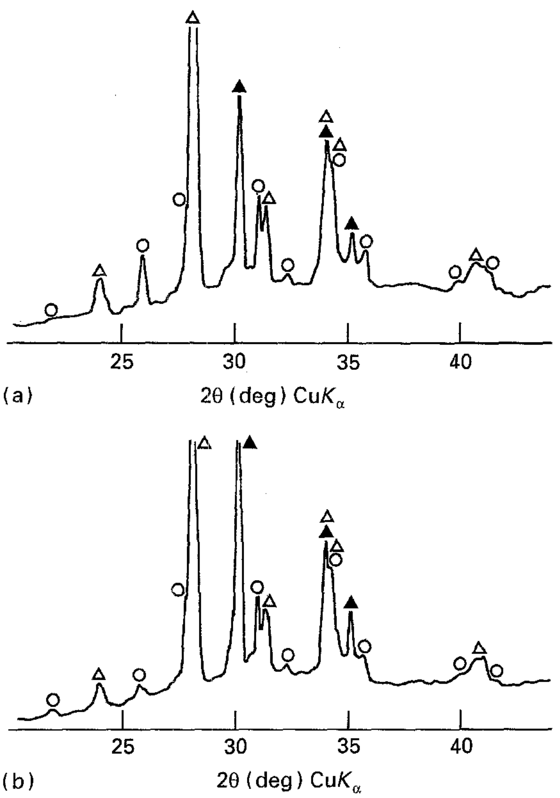

Figure 3 X-ray diffraction patterns of the calcium phosphate films prepared by the two-step and modified two-step processes (heating conditions: 1200 °C, 5 h). (a) Two-step process, sample 12; (b) modified two-step process, sample 20. (○) β-TCP, (▲) t-ZrO_2, (△) m-ZrO_2.

3.2.1. Effects of heating temperature and time

The temperature was changed from 1000–1300 °C in both processes (two-step process, samples 11, 12 and 13; modified process, samples 19, 20 and 21). β-TCP was detected in all samples; the crystalline phases of the substrate were t-ZrO_2 and monoclinic ZrO_2 (m-ZrO_2). In both processes, at 1100 °C, the amount of t-ZrO_2 was larger than that of m-ZrO_2; at 1200 and 1300 °C, however, t-ZrO_2 decreased with increasing m-ZrO_2. Comparing the amount of m-ZrO_2 with that of t-ZrO_2, the amount of m-ZrO_2 in two-step process (a) was larger than that in modified process (b), as shown in Fig. 3. Moreover, β-TCP was present even at temperatures exceeding the transformation temperatures (1120–1180 °C) of β-TCP into α-TCP.

β-TCP may be formed by the reactions of HAp with CMP in the two-step process and of HAp with $Ca_2P_2O_7$ in the modified process; β-TCP is present at temperatures exceeding the transformation temperature of pure β-TCP. β-TCP is known to be stabilized by the formation of solid solution with various cations [18–20]. In this study, β-TCP may also be stabilized by the solid solutions of cations in the substrate-side and β-TCP. Here it is possible to contain two kinds of cations, Y^{3+} or Zr^{4+}, in TCP. Because Akao *et al.* [18] reported that β-TCP is stabilized thermally by the presence of Y_2O_3 in the TCP–3YZ system, we think that the solid solution of Y^{3+} and TCP is formed in this study.

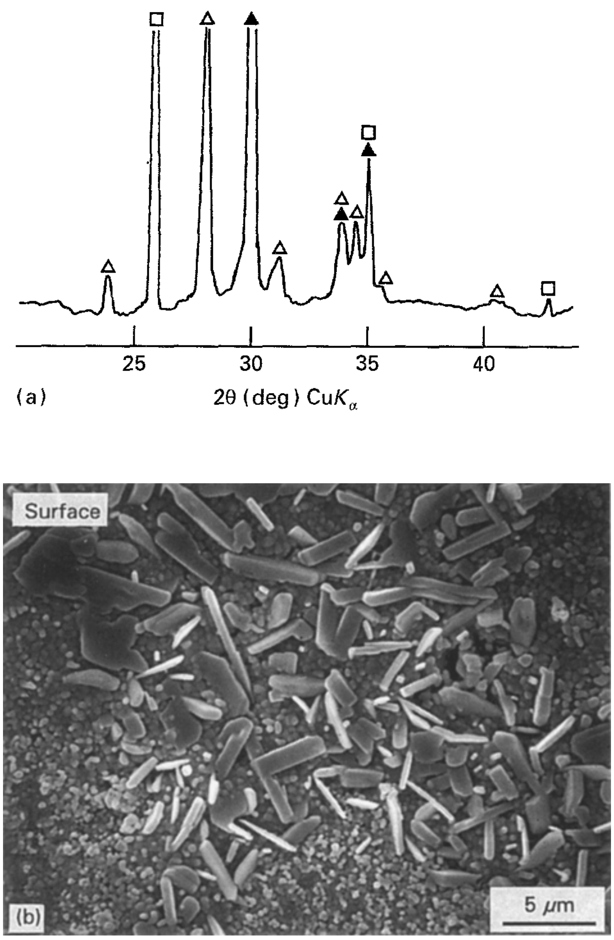

Figure 4 (a) X-ray diffraction pattern and (b) scanning electron micrograph after immersing sample 12 in HNO_3. Immersion conditions: 0.1 mol dm^{-3} HNO_3 solution for 1 h. (□) YPO_4, (▲) t-ZrO_2, (△) m-ZrO_2.

The results obtained by immersing the substrate coated with the films (sample 12) into 0.1 mol dm^{-3} HNO_3 solution for 1 h are shown in Fig. 4. In addition to t- and m-ZrO_2, YPO_4 was detected from the substrate-side (Fig. 4a); this YPO_4 seems to result from the reaction of the calcium phosphates and the Y_2O_3 removed from the substrates [21]. The scanning electron micrograph (Fig. 4b) shows that the bar-like crystals were present on the substrates; these crystals correspond to YPO_4. From the mixture of β-TCP [22] and YPO_4 [23] (10 mol %), only β-TCP was formed during heating at 1300 °C for 1 h. This fact demonstrates that β-TCP may also be stabilized by YPO_4. Thus β-TCP in the films is stabilized by Y^{3+} in the presence of YPO_4. Besides YPO_4, the amorphous phase of $CaO–P_2O_5–ZrO_2–Y_2O_3$ system might also be present at the interface between the films and the substrates.

The presence of the m-ZrO_2 is due to the release of Y_2O_3 from the substrates. As shown in Fig. 3, the reason why the amount of m-ZrO_2 in the two-step process is larger than that in the modified process is explained in terms of the fact that the reactivity of CMP with HAp is higher than that of $Ca_2P_2O_7$ with HAp. The present data are supported by Kawamoto *et al.* [24], who refer to the TCP–$Mg(PO_3)_2$–3YZ system.

The scanning electron micrographs of the surfaces of the substrates heated at 1100, 1200 and 1300 °C for 5 h are shown in Fig. 5. In the case of the two-step process, at 1100 °C (sample 11) and 1200 °C (sample 12), plate-like grains were present on the substrate; the presence of fused materials was found on the substrate; at 1300 °C (sample 13), these materials were bound to the substrates. These observations indicate that the fused materials are formed during heating; the binding strength of the films to the substrates may be enhanced through the solid materials formed from the melts.

In the case of the modified process, at 1100 °C (sample 19), 1200 °C (sample 20) and 1300 °C (sample 21), these grains were bound to one another; the grain growth was observed with the rise of temperature; in particular at 1300 °C, the grains were packed closely. These results show that the bindings of the films to the substrates and of the grains to one another are achieved through the reactions of HAp with $Ca_2P_2O_7$ produced by heating CMP coated on the substrates.

The bindings of the films to the substrate and of the grains to one another in the case of the two-step process are different from those in the case of the modified process; the fused materials are formed in a two-step process, while the solid reactions of HAp with $Ca_2P_2O_7$ occur in a modified process.

The crystalline phases in each substrate with the films prepared by the two-step process and heated at 1200 °C for 1–10 h were β-TCP, m- and t-ZrO_2 for all heating times (see Table IV; samples 14, 15, 12 and 16). The amount of m-ZrO_2 increased with prolonged heating time, while that of t-ZrO_2 decreased. The microstructures of these surfaces were almost the same as those of sample 12. The formation of m-ZrO_2 and the stabilization of β-TCP may be explained in the same way as those in Section 3.2.1. The above results are quite similar to those of the modified process.

3.2.2. *Effect of the spraying time of HAp solution*

After the spraying time of the HAp solution was varied from 5–15 h in both processes, the crystalline phases and the microstructure in the resulting films were examined (two-step process, samples 12, 17 and 18; modified process, samples 20, 22 and 23).

For both processes, after 5 and 10 h spraying time, the crystalline phases detected from the films were β-TCP, m- and t-ZrO_2; after 15 h, α-TCP was also detected, along with the above compounds. The formation of α-TCP is explained as follows: for the spraying times of 5 and 10 h, β-TCP is stabilized by the solid solution of Y^{3+} in it; however, because the solid solution of Y^{3+} in β-TCP becomes difficult as the films thicken, α-TCP may be formed after 15 h spraying time. The m-ZrO_2 increased with increasing amounts of calcium phosphates formed on the substrate. The amount of m-ZrO_2 formed by the release of Y_2O_3 from the substrate increased with increasing the amount of calcium phosphate. The amount of m-ZrO_2 in the two-step process is larger than that in the modified process. We attribute this to the difference in reactivity between CMP and $Ca_2P_2O_7$ with HAp.

The cross-sections and surfaces of these substrates were observed by SEM; the relationship between spraying time and film thickness is shown, together with typical scanning electron micrographs, (sample 18) in Fig. 6. In both cases, the film thickness increased with increasing spraying time. The films prepared by the two-step process were thinner than those prepared by the modified process. This suggests that the reactivity of CMP with HAp may be different from that of $Ca_2P_2O_7$ with HAp, as described above. A porous network structure was formed when the HAp solution was sprayed for 10 h or longer; a typical scanning electron micrograph in Fig. 6 shows that the pore sizes in the films were 15–25 μm and the thickness was about 60 μm. The porous films may be formed by contraction of the spherical agglomerates due to the sintering of the particles, as described in Section 3.1.1.

3.3. Evaluation of the binding strength of the films to the substrates

The binding strengths of the films formed by these three kinds of process were examined by a tape test. The results are given in Table V. The calcium phosphate films formed by the single-step process were easily removed from the substrate. On the other hand, in the two-step and the modified process, the materials in the films were still slightly adhered to the tape side after the test; the X-ray intensities of β- and α-TCP in the films remained unchanged before and after the test; SEM observations showed that the microstructure of the films was still porous. Thus the use of CMP as a binder was found to be effective for enhancing the binding strength of the films to the substrates.

The binding strength may be enhanced by the reaction between calcium phosphates and the substrate. In the case of the single-step process, HAp mainly reacts with substrate to form TCP. On the other hand, in the two-step process, HAp and CMP mainly react with the substrate to form TCP and YPO_4; in the modified process, CMP first decomposes to form mainly $Ca_2P_2O_7$ and then $Ca_2P_2O_7$ reacts with HAp to form TCP. β-TCP in the films obtained by the two-step and the modified process may be stabilized by the solid solution of Y^{3+} in it. In the reaction layer, the amorphous phases in the $CaO–ZrO_2–Y_2O_3$ system are present in the single-step process, whereas YPO_4 and the amorphous phase in the $CaO–P_2O_5–ZrO_2–Y_2O_3$ system are present in the two-step and the modified processes. These phases may enhance the binding strength of the films to the substrates.

As described above, the calcium phosphate films which are strongly bound to the substrate can be prepared by the two-step process and the modified process. Although the operation of the two-step process is more simple than that of the modified process, the amount of t-ZrO_2 prepared by the modified process is larger than that from the two-step process. The presence of t-ZrO_2 results in an increase in the mechanical strength, especially the toughness, of this coating material. We conclude that a modified two-step

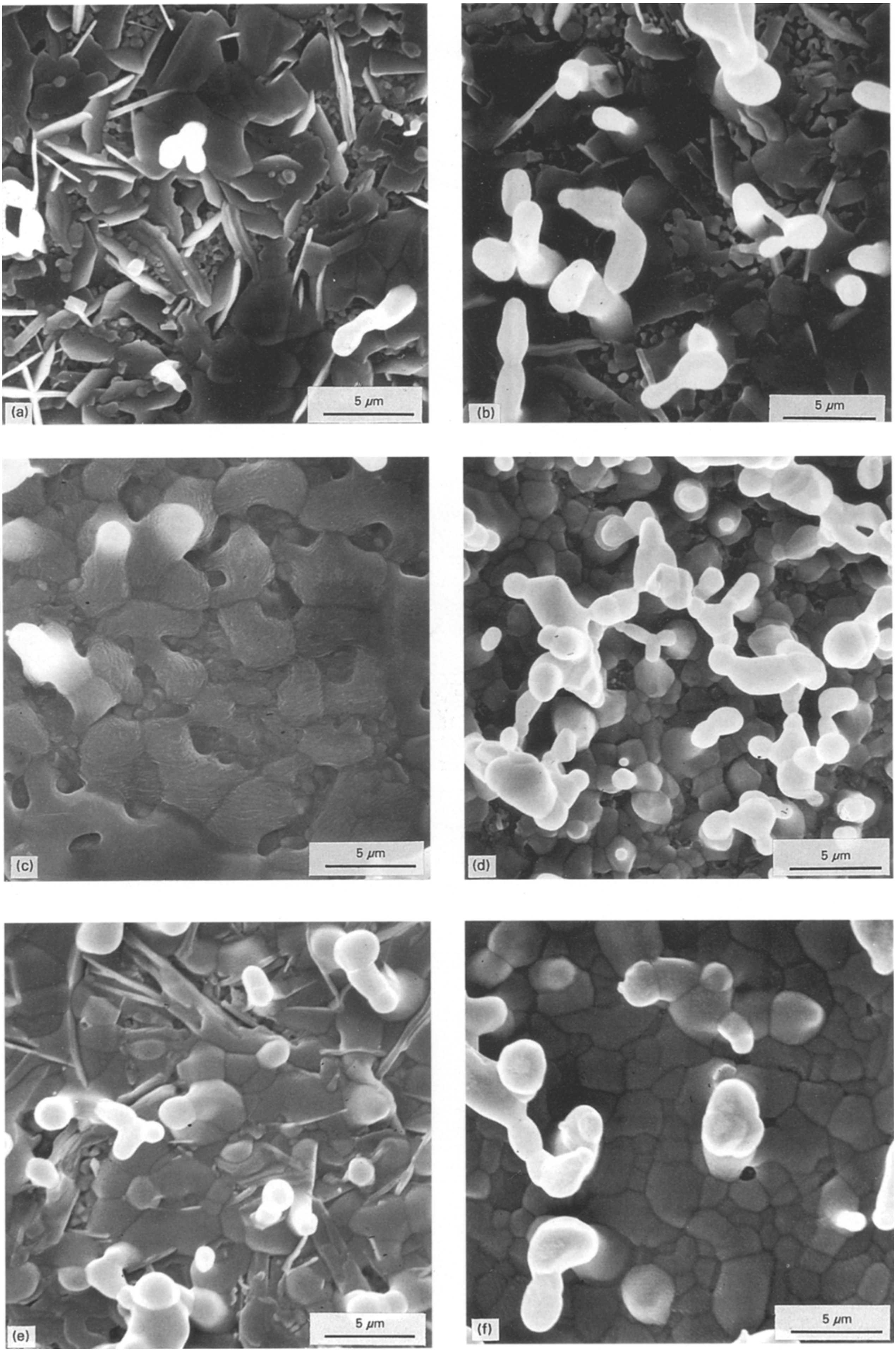

Figure 5 Scanning electron micrographs of the calcium phosphate films prepared by (a–c) the two-step and (d–f) the modified two-step processes. Heating conditions: (a, d) 1100, (b, e) 1200 and (c, f) 1300 °C for 5 h.

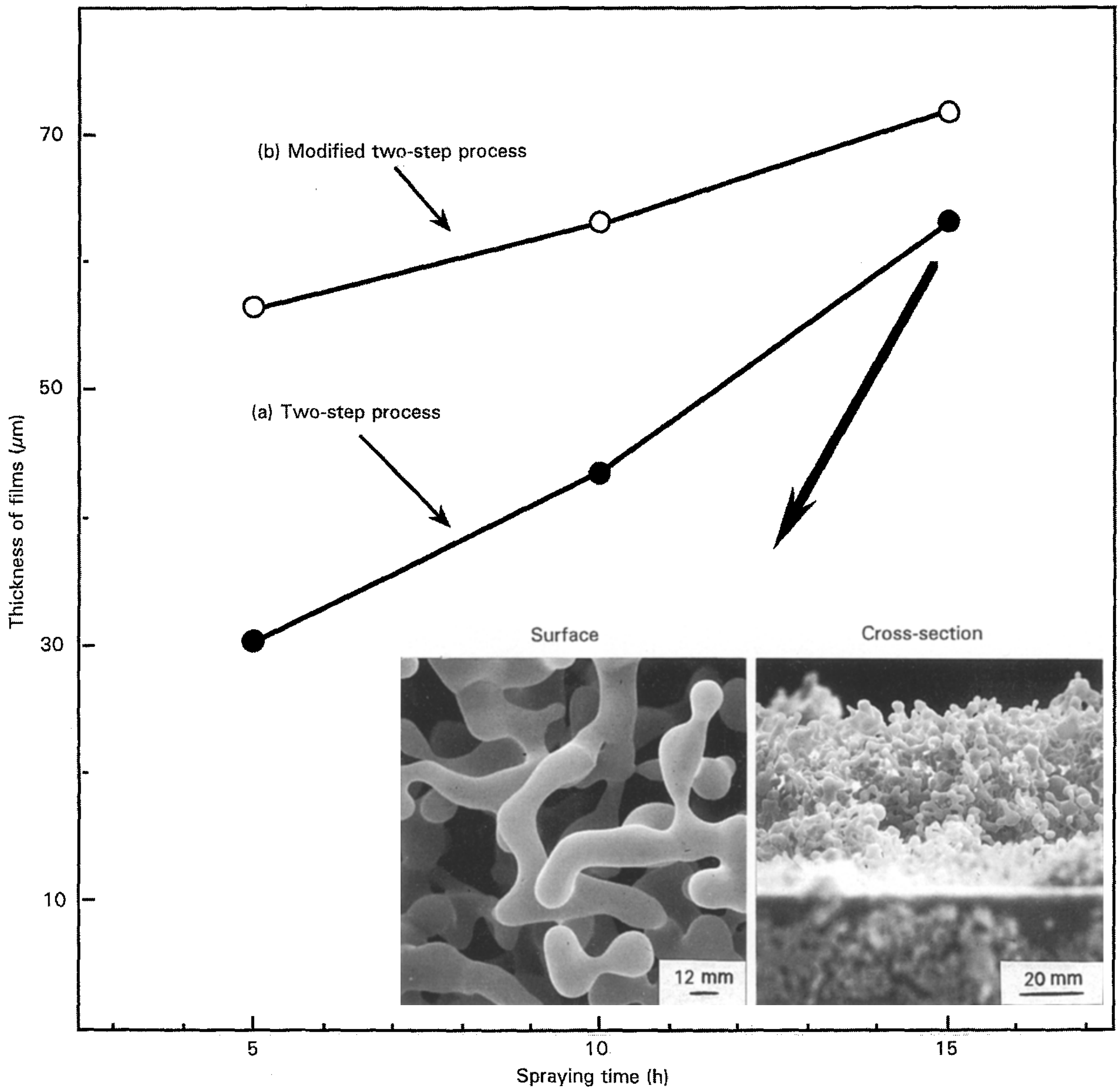

Figure 6 Changes in the film thickness with the spraying time of HAp solution; scanning electron micrographs of the surface and the cross-section in the substrate coated with the porous calcium phosphate films. (a) The two-step process, (b) the modified two-step process. Heating conditions: 1200 °C, 5 h.

process is the most suitable one for the formation of porous calcium phosphate films on 3YZ substrates.

4. Conclusions

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

1. Porous calcium phosphate films containing β-TCP as the main phase were formed by this process; in two-step process and the modified process, β-TCP was stabilized by formation of a solid solution with Y^{3+}. The average pore sizes were about 15–30 μm.
2. The films were thickened when the spraying time was prolonged from 5 h to 15 h in all three processes. The film thickness could be controlled by changing the spraying time.
3. The binding strength of the films to the substrate was enhanced by using CMP as a binder. The microstructure of the films remained unchanged before and after the tape test.
4. In the two-step process and the modified process, Y_2O_3 or the stabilizer was removed from substrate side by the reaction of calcium phosphates with the substrate and then $t\text{-}ZrO_2$ was transformed to $m\text{-}ZrO_2$; Y_2O_3 released from the substrates reacted with calcium phosphates to form YPO_4 and TCP.

TABLE V Tape-test results of films prepared by the single-step, two-step and modified two-step processes

Sample	Process	Spraying time (HAp solution)	Results of tape test
8	Single-step	5	Weak
9		10	Weak
10		15	Weak
12	Two-step	5	Strong
17		10	Strong
18		15	Strong
20	Modified two-step	5	Strong
22		10	Strong
23		15	Strong

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