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Target-Composition Effect on Hydroxyapatite Thin Films Coated on Titanium by r.f. Sputtering

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Using calcium-phosphate-powder targets with the Ca/P ratios of 1.0-1.67, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) thin films with 4-7 μm thickness were prepared on titanium metal plates by r.f. magnetron sputtering, followed an annealing at 200°C for 24 hr under a high water vapor pressure using an autoclave. All the specimens were systematically characterized by XRD, FT-IR, SEM and EDS analyses. The post-annealed films were confirmed to be a nonstoichiometric oxyhydroxyapatite by XRD and FT-IR measurements.

Key words : Hydroxyapatite, Coating, Sputtering, Powder-Target Composition, Titanium

I. Introduction

Since mechanical properties of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, denoted as HAp) monolithic ceramics are still inferior to human born and teeth, HAp coatings onto the various metal, alloy, and ceramic substrates with high mechanical strength and corrosion-resistibility have currently been developed for clinical implant use. In particular, HAp coated titanium metal is the most suitable implant materials in dental and orthopedic fields. A number of coating methods has been investigated for implant applications.

Radio-frequency (r.f.) magnetron sputtering combined with post-annealing is one of the practical coating method of HAp.[1-11] The biocompatibility of the sputtered coating was confirmed by the *in vivo* test using rabbits.[11] The advantages of sputtering method are thickness uniformity of coatings, and high adhesion strength between coating and substrate. In general, however, the composition of coating is different from that of target because of vacuum process in sputtering.

The use of the HAp ceramic target prepared by plasma spraying was reported by K. van Dijk et al.[10] The composition of the coatings was higher Ca/P ratio than that of HAp. On the other hand, we have recently succeeded in coating the HAp by sputtering from the calcium phosphate glass targets with low CaO/P_2O_5 ratio than the stoichiometric value of HAp.[1-9]

This paper first demonstrates the structure, morphology, and composition of films prepared by r.f. magnetron sputtering from various calcium phosphate targets with Ca/P ratios of 1.0-1.67.

II. Experimental Procedure

1. Preparation of powder target for sputtering

The starting powders used as sputtering targets were three kinds of the calcium phosphate powders listed in Table 1; dicalcium phosphate (DCP), α-tricalcium phosphate (α-TCP), and hydroxyapatite (HAp). All powders were produced by Taihei Chemical Industrial Company. In this work, the mole ratios of Ca/P employed for the composition of the targets were 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, and 1.67. Their Ca/P mole ratios were 1.0 for DCP, 1.5 for TCP, and 1.67 for HAp. Powder targets with Ca/P ratio of 1.1, 1.2, 1.3, and 1.4 were obtained by mixing DCP and HAp powders (Table 2). Targets for sputtering were prepared by compression of their powders. The diameter of the powder target is 85 mm, and its thickness is 3 mm.

2. Sputtering

Precursory films were prepared by radio-frequency (r.f.) magnetron sputtering (Tokki Co., SPK-301 type) from powder targets with different compositions. The substrate was 99.5% pure titanium metal plate (30×10×0.5 mm, Niraco Co.), which was mounted in a holder with cooling

Table 1. Abbreviations and Ca/P Mole Ratios of Calcium Phosphate Compound Used in this Work

Composition	Compound	Abbreviation	Ca/P ratio
$CaHPO_4$	Dicalcium phosphate	DCP	1.0
α-$Ca_3(PO_4)_2$	α-Tricalcium phosphate	α-TCP	1.5
$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite	HAp	1.67

Table 2. Compositions of Raw Powders for Sputtering Targets

Ca/P of target	DCP (wt.%)	α-TCP (wt.%)	HAp (wt.%)
1.0	100	0	0
1.1	82	0	18
1.2	65	0	35
1.3	50	0	50
1.4	36	0	64
1.5	0	100	0
1.67	0	0	100

by water flow. The substrates were not heated intentionally, however, the substrate temperature increased up to about 150°C during sputtering. The distance between the target and the substrate is 40 mm. The r.f. power was kept at 150 W (2.6 W/cm^2) operating at 13.56 MHz. The sputtering was carried out in an argon atmosphere of 0.67 Pa. In order to eliminate contamination of impurities adsorbed on the surface, all the targets were presputtered for 30 min by closing the shutter between the target and the substrate. After that, main sputtering was performed by opening the shutter. The thicknesses of the as-sputtered films were in the range of 4 to 8 μm.

3. Post-annealing

Since the films were deposited on titanium substrates without intentional heating during sputtering, all as-sputtered films were confirmed to be almost completely in amorphous state. Amorphous calcium phosphate films were crystallized by low temperature hydrothermal annealing, according to the previous report.[6,9] As-sputtered films, which were placed in an autoclave with a test tube containing distilled water, were annealed at 200°C for 24 hr under a high water vapor pressure. The specimens did not directly contact with liquid phase of water during annealing.

4. Characterization of deposited films

The crystal structure and its crystalline phases of the post-annealed films were determined by X-ray diffraction (XRD) measurements with Cu-K_α radiation (Rigaku Geiger-flex RAD-1C). The characteristic ion groups of PO_4^{3-} and OH^- of the post-annealed specimens was analyzed by using an FT-infrared (IR) spectroscopy (Japan Spectroscopic Company Ltd., FT/IR-230 type) with the attenuated total reflection apparatus (Japan Spectroscopic Company Ltd., ATR-500M type). The surface morphologies and the film thicknesses of the specimens were observed by scanning electron microscopy (SEM) (JEOL, JSM-5310). The composition (Ca/P ratio) and its homogeneity of the films were investigated using energy-dispersive spectroscopy (EDS) (JEOL, JED-2140). In EDS analysis, the final Ca/P ratio data of the specimens were averaged the five measurement results at different areas of each film.

III. Results and Discussion

1. XRD patterns of post-annealed films

The structural phases of the coatings were systematically characterized by XRD measurement. Fig. 1 shows the XRD patterns of the post-annealed films onto titanium substrates sputtered from different target composi-

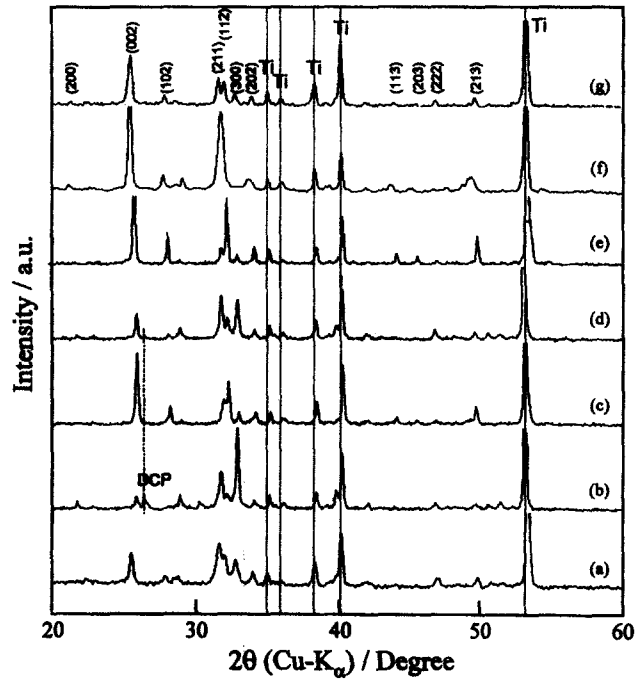

Fig. 1. XRD patterns of the post-annealed films onto titanium sputtered from the calcium phosphate powder targets with Ca/P of (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.4, (f) 1.5 and (g) 1.67. Annealing was carried out at 200°C for 24h under a high water vapor pressure. The dashed lines represent the peaks of Ti substrate.

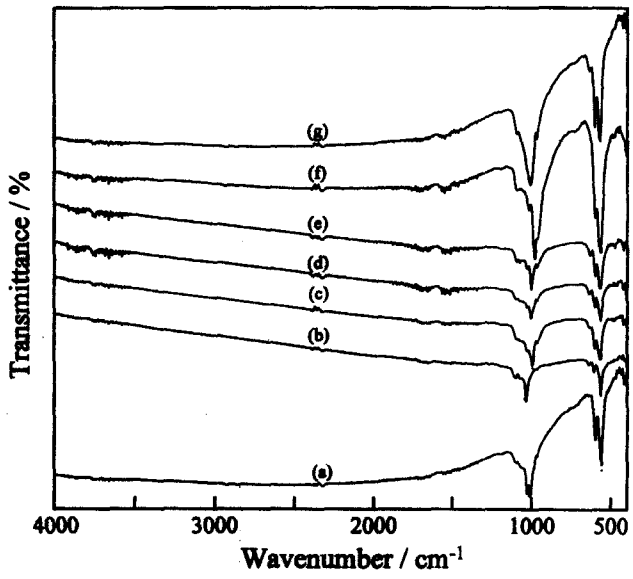

Fig. 2. FT-IR spectra of the post-annealed films onto titanium sputtered from the calcium phosphate powder targets with Ca/P of (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.4, (f) 1.5 and (g) 1.67. Annealing was carried out at 200°C for 24 h under a high water vapor pressure.

tion with Ca/P ratio of (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.4, (f) 1.5, and (g) 1.67. All the films were crystallized by the post-annealing at 200°C for 24 hr under a high water vapor pressure. The majority of diffraction peaks observed for all specimens were assigned to those of hexagonal $Ca_5(PO_4)_3OH$, HAp (Joint Committee on Powder Diffraction Standards: JCPDS #9-432) and titanium substrate. The small peak at $2\theta=26.5°$ in XRD pattern, which corresponds to DCP, was detected when the targets with Ca/P=1.1 and 1.3 were used. Other related calcium phosphates such as tricalcium phosphate and tetracalcium phosphate were not detected in the post-annealed films.

2. FT-IR spectra of post-annealed films

In order to study the local structure concerning the characteristic ion groups of PO_4^{3-} and OH^-, FT-IR analysis was carried out. Fig. 2 shows the FT-IR spectra of the specimens which were sputtered from the powder targets with Ca/P=1.0 to 1.67 and then post-annealed at 200°C under a high water vapor pressure. The IR absorption peaks at 962, 1035, and 568 cm^{-1} were assigned to the ion groups of tetragonal PO_4^{3-} in HAp structure. On the

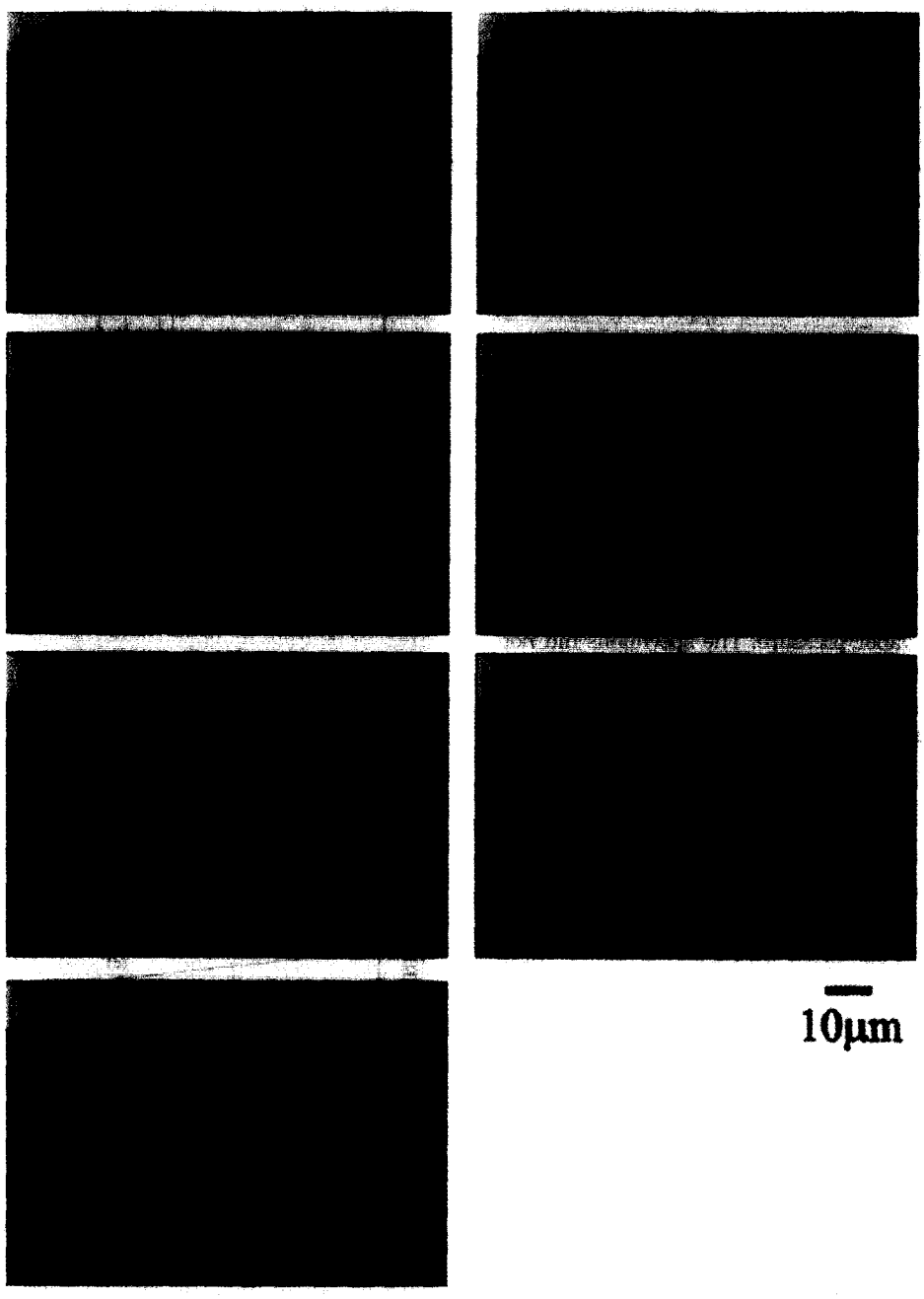

Fig. 3. SEM photographs of the surfaces of the post-annealed films onto titanium sputtered from the calcium phosphate powder targets with Ca/P of (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.4, (f) 1.5 and (g) 1.67. The film thickness was 5 to 8 μm. Annealing was carried out at 200°C for 24 h under a high water vapor pressure.

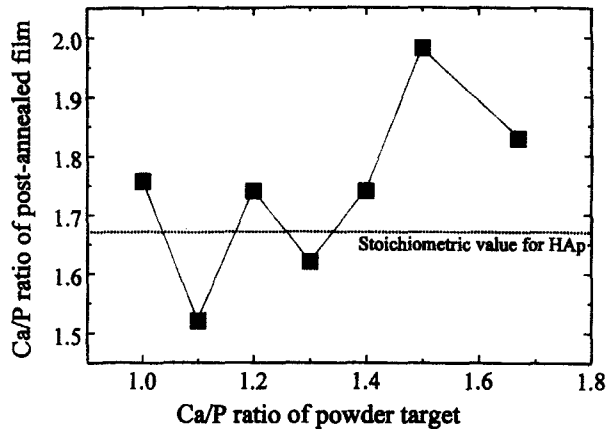

Fig. 4. Ca/P ratio of the post-annealed films sputtered from different powder targets with Ca/P ratio of 1.0 to 1.67. Annealing was carried out at 200°C for 24 h under a high water vapor pressure. The dashed line represents the value of Ca/P ratio of 1.67 for a stoichiometric HAp.

other hand, the peaks at 3571 and 628 cm^{-1} due to the OH^- ions in HAp were too weak to be confirmed. The structure of the present HAp films was assumed to be nonstoichiometric oxyhyxroxyapatite, possibly expressed as $Ca_{10}(PO_4)_6((OH)_{2-2x}O_x\square_x)$, where □ represents the vacancy at the OH lattice site.

3. Surface morphologies of post-annealed films

Surface morphologies of the films sputtered from seven kinds of powder targets with Ca/P of 1.0 to 1.67 are shown in Fig. 3. All the post-annealed films did not have any cracks on the surface with SEM observation. The morphologies of the film surface are divided into two groups. One group shows that the film surface presents the needle-like crystals when sputtering targets were employed Ca/P ratio of 1.0 and 1.1. Another one shows that the surface morphologies were homogeneous using targets with more than 1.2 of Ca/P ratio.

4. Compositions of post-annealed films

Fig. 4 shows the Ca/P ratios of the post-annealed films sputtered from different powder targets with Ca/P ratio of 1.0-1.67. The dashed line in this figure represents a value of 1.67 for a stoichiometric HAp. Since all the films contain an excess of Ca, the sputtering yield of Ca was much higher than that of P. This result is in good agreement with K. van Dijk's experimental data.[10] The Ca/P ratio of specimens depends on composition of powder target for sputtering. Using Ca/P=1.1 and 1.3 of target, Ca/P ratio of the film was lower than that of HAp. This result can be explained by the presence of DCP from XRD pattern shown in Fig. 1 (b) and (d). Using another targets with Ca/P ratio of 1.0, 1.2, 1.4, 1.5, and 1.67, the films were higher than that of HAp. The presence of other phase (were not detected) in films with higher Ca/P ratio by x-ray analytical level. The high Ca/P ratio can be explained in terms of the presence of amorphous phase with Ca-rich.

IV. Conclusion

The polycrystalline apatite thin films onto titanium were prepared by r.f. magnetron sputtering from calcium phosphate powder targets with Ca/P molar ratios of 1.0-1.67, followed by low temploature hydrothermal annealing at 200°C for 24 hr. All the post-annealed films were confirmed to be almost completely HAp single phase from their XRD patterns. The present films were assumed to be nonstoichiometric oxyhydroxyapatite by XRD and FT-IR analyses.

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