

PREPARATION OF HYDROXYAPATITE COATINGS USING R.F. MAGNETRON SPUTTERING

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Abstract

The well-crystalline hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp) layer having a biocompatibility was successfully coated onto titanium substrate using a radio-frequency magnetron sputtering, and effects of sputtering gas and the thickness of HAp film on a crystal growth of the HAp layers were investigated. The deposition rate of the layer sputtered with water-vapour gas was slower than that of the layer sputtered with argon gas. The results of X-ray diffraction demonstrated that the about $0.8\mu\text{m}$ thick HAp film under water-vapour gas was an amorphous phase, the about $1.2\mu\text{m}$ thick film was (100) plane-oriented HAp, and the about $1.5\mu\text{m}$ thick film was (001) plane-oriented HAp. FT-IR analysis proved that hydroxyl group of the layer sputtered with argon gas was defected, but that of the layer sputtered with water-vapour gas was not defected. From these results, it was favorable to use water-vapour gas on the HAp coatings onto metal surface.

Key words : Biomaterials, Hydroxyapatite, r.f. magnetron sputtering, Sputter gas)

1. INTRODUCTION

Metals used for biomaterials such as titanium, titanium alloys and stainless steel have excellent mechanical strength and toughness, however their metals are bioinert materials and a poor biocompatibility in living body. In order to overcome these disadvantages, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp) coating having a good-bio-

compatibility has currently been studied. For the preparations of HAp coating, sputtering^{1, 2)} plasma spray³⁾, ion-beam sputtering⁴⁾, flame spraying and sol-gel deposition^{5, 6)} have recently been developed. One of them, a radio-frequency magnetron sputtering (rf-magnetron sputtering) has been able to coat a characteristic layer: excellent adhesion, thickness uniformity and the ability to coat metals with difficult sur-

face geometries. However, there are the problems in this method, which the coated films have been defected a part of hydroxyl group from the HAp structure and left to amorphous phase.

In the present study, the HAp layer was directly coated on titanium surface using a rf-magnetron sputtering, and effects of sputtering gas and the film thickness of HAp on a crystal growth of the obtained HAp layers were investigated.

2. EXPERIMENTAL PROCEDURE

The coating layer on titanium substrate has been produced by a rf-magnetron sputtering using a radio-frequency generator operating at 13.56MHz and power level at 100W per a target. The sputtering conditions were shown in Table 1. Target was used porous HAp ceramics made of stoichiometric HAp(Ca/P molar ratio of 1.67) : discoid green body was prepared to press at 51MPa, and was sintered at 800°C for 20h(heating and cooling rates of 2.0°C/min). The dimensions of target were ϕ 63.5mm diameter and 5.0mm thickness. The number of target was one, two and three. The test substrate was mounted on the substrate holder and was rotated at 100rpm. The distance between target and substrate was about 40mm. Before sputtering, all metal substrates were cleaned ultrasonically in 99.50% acetone bath. A liquid nitrogen cold

trap was used all sputtering runs and a base pressure of $<10^{-5}$ Pa was obtained before starting a sputtering. Sputter gases were argon(Ar) or water-vapour(H₂O) at 3.9×10^{-1} Pa. For all runs the sputter time was limited to 20h.

The identification of coating layer on titanium substrate was carried out with a thin film X-ray diffractometer(MAC SCIENCE MXP3A). The X-ray diffraction pattern(XRD) of coating layer was measured from 10° to 60° in step of 4°/min with Cu-k α radiation source at 40kV and 30mA, and was compared with the Joint Committee of Powder Diffraction Standard(JCPDS) files. The molecular structures of phosphate, carbonate and OH group were examined with Fourier transform-infrared spectroscopy(FT-IR : Jasco FT-IR230). The morphology of coatings was observed with a scanning electron microscope(SEM : JEOL JSM-6300). Before observing, gold was coated on the surface of specimen. Electron spectroscopy for chemical analysis(ESCA : JEOL JPS-90SX) was used to obtain information about the chemical composition of the sputtered layer. The surface of specimen was subjected to ESCA analysis after being ion-etched with Ar gas.

3. RESULTS AND DISCUSSION

XRD patterns of the layers sputtered with Ar or H₂O gas were shown in Fig. 1. The comparison sample was used the HAp target of single-phase sintered at 800°C. The layer sputtered with Ar gas showed a broad pattern indicating an amorphous structure. On the other hand, the layer sputtered with H₂O gas showed well-crystalline peaks of HAp. From this result, it was

Table 1. Sputtering conditions

Sputter	Ar or H ₂ O
Gas pressure (Pa)	3.9×10^{-1}
Rf power (W)	100
Sputter time (h)	20
Substrate	Ti or (Si)
Target	HAp(Ca/P : 1.67)

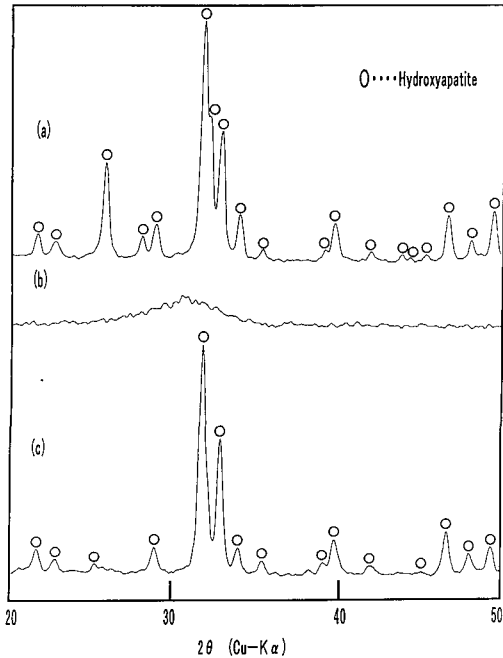


Fig. 1 XRD patterns of the sputtered layer with Ar or H₂O gas

(a) target (b) sputtered layer (Ar gas)
(c) sputtered layer (H₂O gas)

found that the crystallization of coating layer is influenced by the sputter gas.

The chemical composition of the sputtered layers is shown in Table 2. The layers with Ar or H₂O gas indicated a Ca/P molar ratio of 2.25 and 1.76, respectively. The Ca/P molar ratio of the layer was found to be close the composition value of target by using H₂O gas. The SEM observation of cross section of the sputtered layer was carried out, in order to examine the thick-

Table 2. Chemical Composition

	Composition ratio (Ca : P)	Ca/P ratio
HAp powder	10 : 5.98	1.67
Target (sintered at 800°C)	10 : 5.81	1.72
Sputter layer (Ar gas)	10 : 4.44	2.25
Sputter layer (H ₂ O gas)	10 : 5.68	1.76

ness of the layers sputtered with Ar or H₂O gas. The coating layer was sputtered on Si substrate. The thickness of the layer sputtered with Ar or H₂O gas was 2.25 and 1.20 μm and the deposition rate calculated from each thickness become 0.11 and 0.06 μm/h, respectively. The deposition rate of the layer sputtered with Ar gas was faster than that of the layer sputtered with H₂O gas.

FT-IR absorption spectra of hydroxyl (OH) and phosphate (PO₄) groups of the sputtered layers were shown in Fig. 2. The HAp target was used as a comparison sample. The absorption of OH group of the layer sputtered with Ar gas was not observed, while that of the layer sputtered with H₂O gas was observed at 3570 and 630 cm⁻¹. The absorption of PO₄ group of the layers sputtered with Ar or H₂O gas was ob-

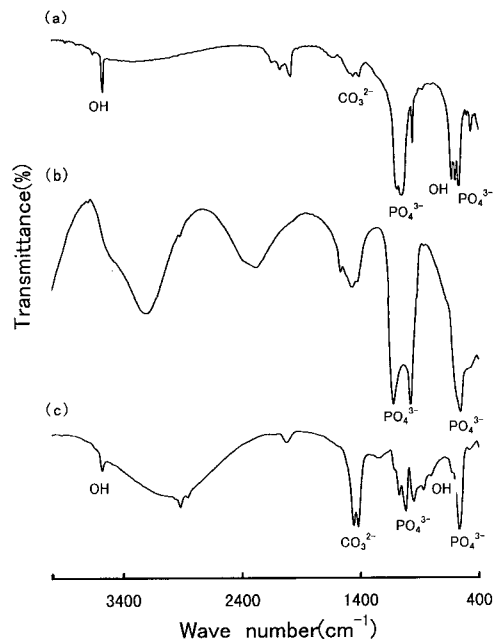


Fig. 2 FT-IR spectra of the sputtered layer with Ar and H₂O gas

(a) target (b) sputtered layer (Ar gas)
(c) sputtered layer (H₂O gas)

served at $1090\sim 960\text{cm}^{-1}$ and $600\sim 570\text{cm}^{-1}$. Furthermore, the absorption of carbonate ion substituted for phosphate in the layer sputtered with H_2O gas was observed at 1461 , 1421 and 873cm^{-1} . In general, there are A-type (OH site) and B-type (PO_4 site) with regard to carbonate substituted for phosphate of HAp. The following showed the carbonate bands at characteristic positions of substitution:

- (i) A-type : 1535cm^{-1} (ν 3b), 1458cm^{-1} (ν 3a), 878cm^{-1} (ν 2)
- (ii) B-type : 1462cm^{-1} (ν b), 1419cm^{-1} (ν b), 872cm^{-1} (ν 2)

The carbonate ion in the layer sputtered with H_2O gas was B-type substitution, and influenced the crystallization of the HAp coating.

FT-IR spectra of the sputtered layers with different thickness were shown in Fig. 3. The $0.8\mu\text{m}$ thick film was observed only a broad band of phosphate in the regions at 1100 and 600cm^{-1} . The absorption of OH group on the 1.2 or $1.5\mu\text{m}$ thick film was observed at 3570 and 630cm^{-1} . The absorption of carbonate group on the $1.2\mu\text{m}$ thick film was observed, while that of the $1.5\mu\text{m}$ thick film was not observed.

XRD patterns of the sputtered layers with the different thickness were shown in Fig. 4. The $0.80\mu\text{m}$ thick film was an amorphous phase (amorphous calcium phosphate : ACP). However, the $1.2\mu\text{m}$ thick film was the (100) plane-oriented HAp which the reflections of (001) plane and (112) plane were low, and further the $1.5\mu\text{m}$ thick film was well-crystalline HAp oriented (001) plane.

The SEM photographs of cross section of the layers sputtered with the different thickness were shown in Fig. 5. The $0.8\mu\text{m}$ thick film was

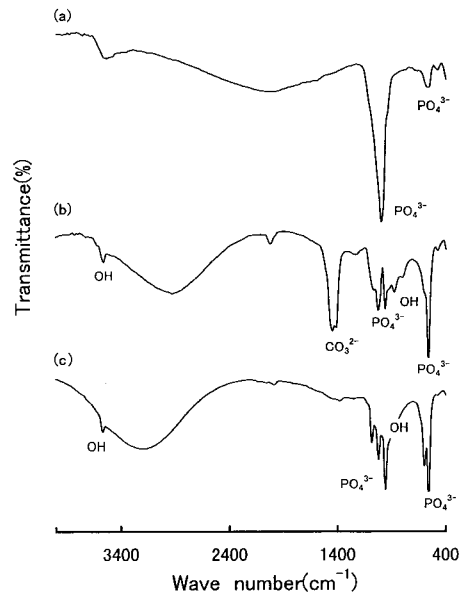


Fig. 3 FT-IR spectra of the sputtered layer with the different film thickness
(a) $0.8\mu\text{m}$ target film (b) $1.20\mu\text{m}$ target film
(c) $1.50\mu\text{m}$ target film

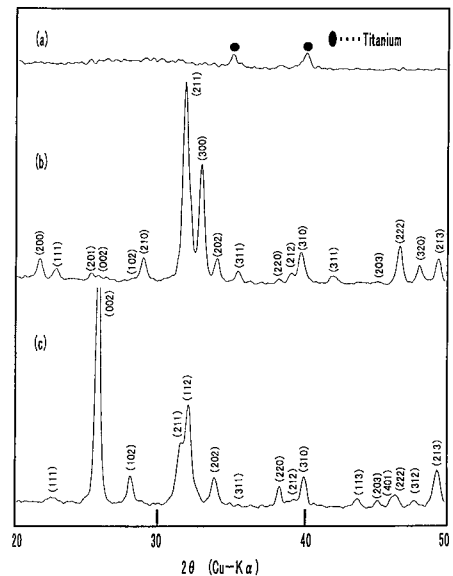


Fig. 4 XRD patterns of the sputtered layer with the different film thickness
(a) $0.8\mu\text{m}$ target film (b) $1.20\mu\text{m}$ target film
(c) $1.50\mu\text{m}$ target film

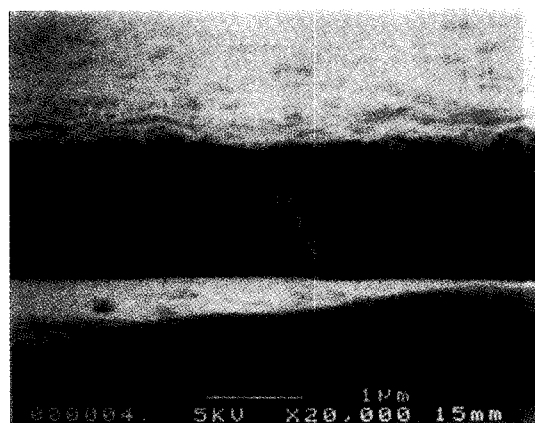
deposited fine particles, however a growth of pillar-shaped crystals was observed at the 1.2 and 1.5 μm thick films.

4. CONCLUSION

The preparation of hydroxyapatite (HAp) layer having a biocompatibility onto titanium substrate using a radio-frequency magnetron sputtering has been investigated and the obtained results were summarized as follows :



(a)



(b)

Fig. 5 SEC photomicrographs of cross section of the sputtered layers

(a) 0.80 μm target film (b) 1.50 μm target film

1) The deposition rate of the layer sputtered with water-vapour gas was slower than that of the layer sputtered with argon gas.

2) Hydroxyl group of the HAp layer sputtered with argon gas was defected, but in case of with water-vapour gas was not defected.

3) The chemical composition of the layer sputtered with H_2O gas changed with increase of the film thickness, namely, 0.8 μm thick film was amorphous calcium phosphate : 1.2 μm thick film was carbonate-containing HAp oriented to a-or b-axis directions : 1.5 μm thick film was stoichiometric HAp oriented to c-axis direction.

From the above-mentioned results, it was favorable to use water-vapour gas on the HAp coatings onto metal surface.

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