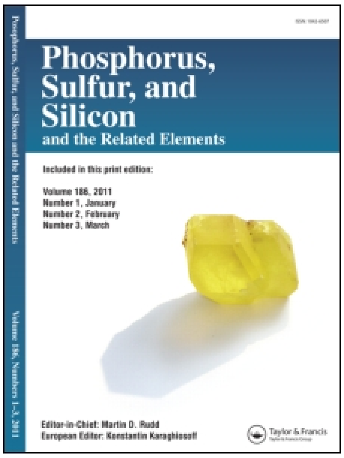

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Calcium Phosphate Coating on Titanium Plate

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CALCIUM PHOSPHATE COATING ON TITANIUM PLATE

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Abstract Calcium phosphate films, obtained by electrophoresis and sputtering were studied by ESCA, IR and X-ray diffraction.

INTRODUCTION

Coating on metals and ceramics by calcium phosphate films(CP films) has been attempted for the purpose of fabrication of reinforced biomaterials[1,2]. Hydroxyapatite(HAp) films are also expected to function as gas sensors.

HAp and CP films on Ti plate were formed by electrophoresis and sputtering. The structure and composition of those films were investigated by means of IR, X-ray diffraction, ESCA and EPMA.

EXPERIMENTAL

MATERIALS

HAp powders were prepared by the method as described previously [3]. HAp of Central Glass Co.(HAp-BN) was also used. Alcohols, N,N-dimethylacetamide(DMA) and N,N-dimethylformamide(DMF) (the reagent grade of Kanto Chemicals Co.) were used for electrophoresis.

The powder of $CaCO_3$ was dissolved into 85% phosphoric acid in a ratio of CaO/P_2O_5 = 55/45. The CP glass target was fabricated by melting the above mixture at 1200-1250℃ for 1 hr and, after molding, annealing the phosphate glass at 600-650℃ for 5 hr.

ELECTROPHORESIS OF HAp

HAp was electrophoretically deposited in alcohols, amides and the mixtures of alcohols and amides under the following conditions; the applied voltage gradient 60-100 V/cm, the distance between the two Ti electrodes 3mm, the temperature 30 ℃, the concentration suspension of HAp 5-10 g/l.

ANALYSES AND MEASUREMENTS OF CALCIUM PHOSPHATE FILMS

As-deposited films on Ti plates and the powder samples gathered from the substrates were used for analyses. The amount of the HAp films deposited by electrophoresis was determined by the weight difference between the coated Ti plate and the bare plate.

RESULTS AND DISCUSSION

ELECTROPHORETICAL DEPOSITION OF HAp

In spite of high dielectric constant and low viscosity, water and the mixture of water and alcohols were not appropriate for deposition of HAp probably because hydrogen gas formed at the surface of plate by electrolysis of water and the aggregation of HAp particles was disturbed. The weight of deposited film in ethyl alcohol increased as the electrophoresis time and the applied voltage gradient increased, as shown in Fig.1. The changes in the deposited amount in case of some other HAp's were similar

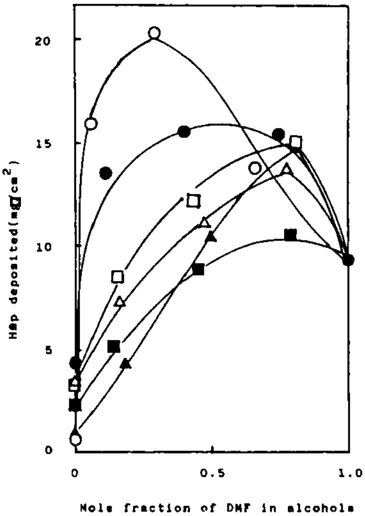

FIGURE 2 HAp film formation in the mixtures of DMF and alcohols.
○:methanol ●:ethanol
□:propanol △:iso-propanol
■:butanol ▲:iso-butanol
time:2 min, voltage:100 V/cm

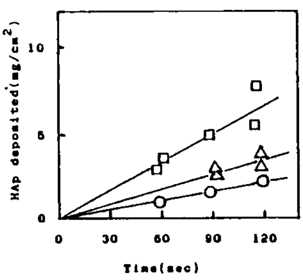

FIGURE 1 Time change in amount of HAp
□:100 △:66.7 ○:50(V/cm)

to that in Fig. 1 although the particle size distribution of those apatite samples might be different. Probably, only portions of fine particles in each sample powder of HAp might be transported along the potential gradient. From the results in Fig.2, the most appropriate media for suspension might be the mixtures of alcohols and amides, taking the amount of the HAp films into consideration. In the mixture of alcohols and amides, hydrogen gas formation might be restrained since oxygen or nitrogen atoms in amides combined with protons in OH of alcohols.

The line analysis for the cross section of the hot-pressed HAp film by EPMA indicated the diffusion of P atoms into the Ti plate and the lack of P atoms at the top surface of the film.

HAp and Ti plate were tightly combined and the sintering of HAp film proceeded by heating and slight pressing.

Amorphous calcium phosphate and fluoroapatite films were electrophoretically deposited on Ti plate, while neither monetite nor $\alpha-Ca_3(PO_4)_2$ coating was obtained.

SPUTTERED CALCIUM PHOSPHATE FILMS

The as-sputtered CP film was recognized to be amorphous from the halo X-ray pattern.

Figure 3 shows the multiple internal reflection IR spectrum of the CP film. In addition to the normal vibration of PO_4 tetrahedron, the weak absorption of 736 cm^{-1} corresponding to the bending of P-O-P was detected, which suggested the presence of polyphosphates. Therefore, the sputtered film might contain orthophosphates and a small amount of polyphosphates. The CP glass used as a target was known to consist of polyphosphates with straight chains. Then, the chains were partially decomposed during sputtering. The ratios of Ca/P at the CP film surface decreased as etching time increased whereas the average Ca/P for the inside of the films was about 1.6. The P-rich layers of the films were removed by 2-3 minute Ar^+ etching. The spectra of Ca 2p, P 2p, O 1s and Ti 2p

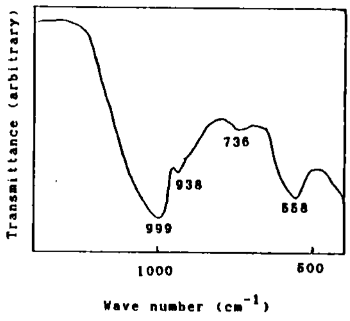

FIGURE 3 IR spectrum of sputtered CP film.

for the CP film are shown in Fig. 4. The peak shifts of O 1s and Ti 2p indicated the sputtered film consisted of phosphate compounds containing titanium of different oxidation states in the boundary layer between CP film and Ti plate. No chemical shift was found in Ca 2p and P 2p.

The thickness of the sputtered films might be very thin compared with that of the apatite films obtained by electrophoresis, although precise thickness has not been measured.

Probably, a certain thermal treatment will be needed for the sputtered films to stick the calcium phosphate to the substrate.

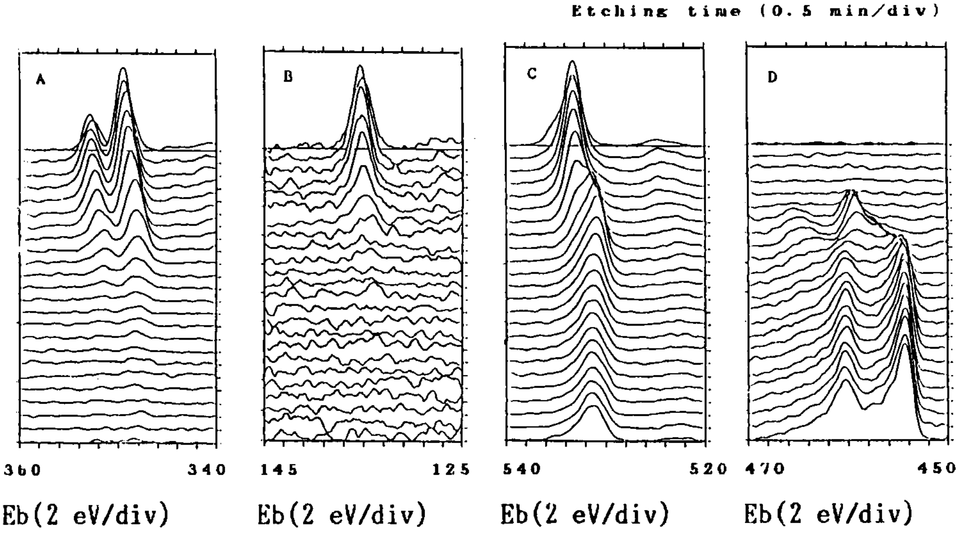

FIGURE 4 Change in ESCA of CP film with etching time: A;Ca 2p, B;P 2p, C;O 1s, D;Ti 2p.

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