APATITE CERAMICS AND RELATED PHOSPHATES

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Abstract Calcium phosphate coatings on alumina by sputtering and electrophoretic deposition on alumina were studied in order to improve mechanical strength of calcium phosphate materials, taking application to materials into account.

INTRODUCTION

Biocompatibility of apatite ceramics and related calcium phosphates has been highly valued. However, sputtering, electrophoretic deposition and some other coating on tough ceramics and metals were needed to improve the mechanical strength of the phosphate materials. Moreover, hydraulic hardened bodies of calcium phosphates were prepared from the polymer-added cements for the purpose of obtaining the macro-defect free phosphate materials.

SPUTTERING

The film fabrication by sputtering was previously reported^{1,2)}. In the present paper, calcium phosphate glass targets of various Ca/P ratios were used.

As the starting materials of glass targets, calcium metaphosphates were prepared by heating the precipitates of various Ca/P ratios obtained from CaCO_3 powder and H_3PO_4 solution. The glass targets were formed by melting the metaphosphates at

1200°C, quenching and annealing at 500°C.

The radio-frequency magnetron sputtering was carried out under the conditions: Ar or CO₂-Ar mixture pressure 0.67Pa, rf-power density 7.6 w/cm², target-substrate spacing 50mm, substrate alumina.

Table 1 shows the results of analysis by EDX. It was found that the ratios of Ca/P of the films obtained were larger than those in targets.

Table 1 Compositions of targets and sputtered films

Ca /P in targets	0.75	0.62	0.42
Ca/P in films	1.63	1.59	1.53

Figure 1 shows the relationship between Ca/P ratio of target and the main constituents of the sputtered film.

Fig. 1 Main constituents of sputtered films after annealing in water vapor.

●; hydroxyapatite(HAp) , ▲; tricalcium phosphate(TCP), ■; mixture of HAp and TCP.

The film obtained from the most calcium-rich target might consist of hydroxyapatite

of stoichiometric composition since the apatite structure was maintained up to 1100°C. On the other hand, the films of lower calcium content were decomposed into TCP below 1000°C.

It may be concluded that the calcium-rich targets may be preferred for preparation of stoichiometric apatite films. However, it is difficult to obtain the glass targets of above 0.75 in Ca/P since the starting calcium metaphosphate glasses degrade and shorter chain phosphates such as calcium pyrophosphates and orthophosphates crystallize on target preparation. Moreover, vitreous calcium phosphates are not obtained if Ca/P of the starting mixtures is close to 1.5.

ELECTROPHORETICAL DEPOSITION

Ceramic coatings on metals by electrophoresis have been well known for the purpose of preventing corrosion and abrasion. Electrophoretical deposition of HAp was reported by P. Ducheyne et al.^{3,4)}. Various mixtures of organic solvents were examined for suspensions of HAp in order to increase amount of deposition^{2,5)}.

Alfa-alumina, which was coated with graphite was used for a substrate in stead of titanium metal⁶⁾. Calcium metaphosphate(CaP₂O₆) powder, synthesized from CaCO₃ and phosphoric acid, was added to HAp powder in order to improve adhesive strength between a deposited layer and a alumina substrate on heating after electrophoretic deposition. As a dispersion media, mixture of ethyl alcohol and acetylacetone was used. Experimental set up for electrophoresis was described in our previous paper⁵⁾.

Below 60wt% addition of the metaphosphate to HAp, the amount of deposition did not change with increase of the additive. However, over 80wt% of the metaphosphate in HAp prevented the film formation because deposition of the metaphosphate by itself was not found.

The calcium phosphate phases of the films obtained after heating at 1300°C are summarized in Table 2.

Table 2 Main constituents of films after heating.

Content of the metaphosphate(wt. %)	0	5	10	15	20
Phase of TCP	α	α	β	β	β

After the heat treatment, apatites in deposited films decomposed into tricalcium

phosphates. Below 1180°C, the transition of metastable alpha phase of TCP to beta proceeded easily in case of films containing large amount of the metaphosphates of low melting point.

Adhesive strength between the TCP layer and alumina substrate increased almost linearly as the content of the metaphosphate increased. Addition of the calcium metaphosphate was found to be effective for improvement of adhesive strength of electrophoretically deposited films.

CHEMICALLY BONDED CALCIUM PHOSPHATE

Water-soluble organic polymers or their monomers were added on preparation of hydraulic calcium phosphate bodies in order to reduce pores in hydraulic bodies and form chemical bonding in hardened bodies. The polymers used in the present study were as follows: Polyvinyl alcohol, poly(methyl methacrylate), polyacrylamide and polyethylene glycol.

Bending strength of hydraulic hardened calcium phosphate was about 23 MPa on addition of acryamide polymer, which was polymerized from acrylic amide monomer in the calcium phosphate cement slurry at 40°C before hydration of the phosphate.

ACKNOWLEDGMENT

The authors wish to express their thanks for financial support by Grant-in Aid for Co-operative Research (No.037305063) and Grant-in Aid for Developmental Scientific Research(No.07555275) from the Ministry of Education, Science, Sports and Culture, Japan.

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