HYDROXYAPATITE COATING ON ALUMINA SUBSTRATE BY SOL-GEL TECHNIQUE

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ABSTRACT The purpose of the present work was to investigate synthetic condition of viscous coating sol by sol-gel technique in reaction of Ca(NO₃)₂-(C₂H₅O)₃PO-C₂H₅OH system, burning temperature after dip-coating the viscous sol onto alumina substrate and thick control of porous hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) coating on the substrate as bone substitute. The products on the substrate were characterized by using X-ray diffraction, scanning electron microscopy, infrared spectroscopy and chemical analysis. The formation of viscous sol as precursor of amorphous calcium phosphate (ACP) was remarkably affected by synthetic conditions such as aging time, Ca/P atomic ratio and pH in an initial mixed solution. In order to stabilize porous HAp coating onto alumina substrate, it was more effective to burn at 1000 °C after dip-coating onto the substrate with viscous sol which formed by aging for 8 days under conditions of Ca/P atomic ratio 1.5 and pH 8 in an initial mixed solution. Also the thickness of HAp layer on the substrate was continuously increased by repeating dip-coating processes 2 to 3 times and developed to about 20 μm after repeating 3 times. Consequently, the production of the new artificial biomaterials which joined strongly to the thin layer of HAp on surface of alumina substrate was expected.

INTRODUCTION

HAp as a main constituent of bone and teeth attracted for using to artificial biomaterials with special interest recently. Although the preparation of the artificial biomaterials using HAp has been studied by many researchers until now[1] ~[5], HAp ceramics as bone and teeth substitute has not sufficiently high mechanical strength as compared with alumina and zirconia ceramics with high impact stress. In order to obtain bioactive HAp composite materials with high mechanical strength, it will be effective that bioactive HAp coats onto bioinert alumina substrate for compensating the weak point of both HAp and
alumina.

As techniques for HAp coating onto the substrate, spray-pyrolysis\(^6\), \(^7\), plasma-spray\(^8\),\(^9\) and dip-coating\(^3\),\(^10\) were well known. The weak point of spray techniques were pointed out generally considering deposition of inhomogeneous layer and decomposition of HAp for spraying at elevated temperatures. While the dip-coating technique comparable to the spray techniques had the advantage of HAp coating with homogeneous layer and most simple to use.

Studies are made to investigate the influence of synthetic conditions such as aging time, Ca/P atomic ratio, pH in an initial mixed solution on formation of viscous coating sol by sol-gel technique, burning temperature after dip-coating the viscous sol onto alumina substrate, and further thick control of porous HAp coating onto the substrate.

EXPERIMENTAL

MATERIALS

Calcium nitrate tetrahydrate (Ca(NO\(_3\))\(_2\) • 4H\(_2\)O), triethyl phosphate ([C\(_2\)H\(_5\)O]\(_3\)PO), aqueous ammonia (29%, NH\(_3\)) and ethanol (99.5%, C\(_2\)H\(_5\)OH) as the starting materials were special-grade reagent supplied by Kanto Chemical Co., Ltd.

EXPERIMENTAL PROCEDURE

The viscous sol as precursor of ACP was prepared by sol-gel technique in reaction of Ca(NO\(_3\))\(_2\) - (C\(_2\)H\(_5\)O)\(_3\)PO - C\(_2\)H\(_5\)OH system. Thus an initial mixed solution was made to specified Ca/P atomic ratios 1.5 ~ 2.0 by adding triethyl phosphate into calcium nitrate tetrahydrate which was dissolved in ethanol (0.15 ~ 0.20 mol/50 cm\(^3\)), and then 15N aqueous ammonia was added into an mixed solution to keep them at pH 8 ~ 10 as formation range of stable HAp. Further, the resulting sol was aged for 1 ~ 30 days at 20 °C. The alumina substrate immersed in the viscous sol and then pulled up velocity of 1.5 cm/s. The alumina substrate after coating sol was heated at 100 ~ 200 °C to remove ethanol from the liquid phase and the sol changed to ACP gel, which was finally burned at 500 to 1000 °C for 3 hours under vapour steam through nitrogen gas to the formation of thin layer of HAp.

The thick control of HAp layer was also investigated by repeating 1 to 3 times for dip-coating and drying processes. The products
on the substrate were characterized by using X-ray diffraction, scanning electron microscopy, infrared spectroscopy and chemical analysis.

RESULTS AND DISCUSSION

PREPARATION OF VISCIOUS COATING SOL

The formation of viscous coating sol is remarkably affected by synthetic conditions such as Ca/P atomic ratio, pH and aging time in an initial mixed solution. The formation velocity can be confirmed by measuring transmittance corresponding to turbidity of resulting sol in the mixed solution.

The effect of aging time on transmittance in sol is shown in figure 1. In the case of Ca/P atomic ratio 1.5, the sol is formed rapidly at initial pH 20 higher than pH 8 in mother liquor so that the transmittance decreases at pH 10. The gelation of resulting sol in the mother liquor is promoted very much at the high level of pH. Thus the use of viscous sol in homogeneous dispersing system is more effective for HAp coating onto alumina substrate since the contact between HAp and the substrate is decreased by using gel. The transmittance of coating sol with increasing viscosity finally reaches any one the equilibrium to 70~80% after aging for 14 days under Ca/P atomic ratios 1.5~2.0 at pH 8 in the initial mixed solution. Also the formation velocity of sol has a tendency to promote with decreasing Ca/P atomic ratios 2.0 to 1.5 under initial pH 8. It is found that the suitable synthetic conditions for resulting high viscous sol in the shortest aging time are more effective to prepare Ca/P atomic ratio 1.5 and pH 8 in the initial mixed solution. Moreover the interface HAp and substrate is joined weakly by using viscous sol which obtained at pH 10, higher than pH 8.

FIGURE 1 Effect of aging time on transmittance of sol.
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It was tried to burn the products after coating the surface on substrate with viscous sol by dip-coating technique. The effect of aging time on the X-ray diffraction patterns of the production on the burned substrate is shown in figure 2.

![Figure 2](image)

![Figure 3](image)

**FIGURE 2** Effect of aging time on formation of HAp layer (500°C).

**FIGURE 3** Effect of aging time on formation of HAp layer (1000°C).

The burned product on the substrate after aging for 2 days is confirmed only X-ray diffraction peaks of Al$_2$O$_3$ due to constituent of alumina substrate so that the coating layer is suggested to be thin ACP. Although the products after aging for days from 6 to 8 are confirmed peaks of low crystalline HAp but the peaks of calcium carbonate are discovered newly besides HAp after 14 days.

The infrared spectroscopy is also used to investigate the effect of different Ca/P atomic ratios on presence of carbonate ion. In the case of aging time for 8 days, the burned substrates under Ca/P atomic ratios 1.7 or 2.0 have the absorption spectra at around 1400 and 800 cm$^{-1}$, which are relevant to the stretching and bending vibrations of CO$_3^{2-}$, even though the existence of the spectra are not confirmed in the case of Ca/P atomic ratio 1.5. Namely this finding is considered to increase amount of calcium carbonate in
order to react excess CaO in coating sol more than 1.67 as theoretical Ca/P atomic ratio of HAp and resulting CO₂ for decomposition of coating sol with burning. The results under the same conditions in figure 2 besides burning at 1000°C are shown in figure 3. The burned substrate is confirmed X-ray diffraction patterns of HAp and CaO due to thermal decomposition of calcium carbonate after aging for 14 days.

The resulting HAp at 1000°C is allowed to form higher crystalline than that of 500°C and the composition of HAp layer is approximate value of 1.70 comparable to theoretical Ca/P atomic ratio of HAp.

From the above results, it is proved that the preparation of HAp coating onto the substrate is a very useful technique to burn at 1000°C after aging for 8 days in the resulting sol under initial pH 8 and Ca/P atomic ratio 1.5.

THICK CONTROL OF HYDROXYAPATITE COATING ON ALUMINA SUBSTRATE

The thickness of HAp layer was controlled by repeating dip-coating technique. The X-ray diffraction patterns of the product which obtained by repeating 1 to 3 times are shown in figure 4.

FIGURE 4 X-ray diffraction patterns of HAp layer obtained by repeating dip-coating.

FIGURE 5 Scanning electron micrograph of interface HAp layer and alumina substrate.
The X-ray intensity of Al₂O₃ constituting substrate is decreased continuously by increasing the number of times for dip-coating technique. Thus the patterns of Al₂O₃ are not observed after repeating 3 times and the coating layer is only higher crystalline HAp. The scanning electron microscopic observation is used to determine the thickness of HAp layer, which have about 7μm by repeating at once and about 20μm at 3 times. Scanning electron micrograph of the interface HAp and alumina substrate after repeating 3 times is shown in figure 5. The porous HAp having homogeneous layer can be coated onto alumina substrate and the interface of the both is strongly joined together. As the above results, it is possible to produce the new artificial biomaterials which is joined strongly together porous HAp and the surface on alumina substrate by repeating 3 times for dip-coating.

REFERENCES