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FORMATION AND EVALUATION OF HAp FILMS BY ELECTROCHEMICAL METHOD

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ABSTRACT

The calcium phosphate including Hydroxapatite ($Ca_{10}(PO_4)_6(OH)_2$: referred to as HAp) utilizes as a biomaterial, because that resembles the principal ingredient of the tooth and bone and have superior biocompatibilty. Through coating calcium phosphate on metallic biomaterial such as the commercially pure titanium, the biocompatible character can be given to the material together with its mechanical strength. Some trials have been conducted for applying these coated materials to the artificial bone and so on.

In this study, the optimum condition of the HAp films formation by electrochemical method was investigated by employing QCM(Quartz Crystal Microbalance), FE-SEM and EDX. Then, adhesive strength of coated HAp films was evaluated by the scratch test. Also, biocompatible character was examined by immersion test into guasi-human body fluid. As a result, the activation in precipitation of HAp was recognized at the electrode potential around –650mV[vs. SCE] due to the frequency change detected by QCM measurement and the cathodic current density increase. FE-SEM observation and EDX analysis on specimen surface used for QCM measurement revealed the uniform precipitation of HAp. Also, well developed crystal structure of HAp can be obtained under the condition detected by QCM measurement and the improvement in adhesion strength between HAp films and substrate metal was recognized.

KEYWORDS : HAp films, biomaterial, electrochemical method, biocompatibility, QCM, FE-SEM, EDX

INTRODUCTION

The calcium phosphate including HAp utilizes as a biomaterial, because that resembles the principal ingredient of the tooth and bone and have superior biocompatibilty. Through coating calcium phosphate on metallic biomaterial such as the commercially pure titanium, the biocompatible character can be given to the material together with its mechanical strength. Some trials have been conducted for applying these coated materials to the artificial bone and so on[1]. At present, Plasma-spray method was applied for making HAp coating. However, the temperature in the plasma-spray coating process becomes up to 5,000～20,000℃[2,3]. For this reason, the phase of calcium phosphate becomes amorphous. As a result, the problem of the biocompatible character of coated film being degraded is brought about. On the other hand, HAp coating made by electrochemical method can be obtained under relatively mild conditions compared with plasma-spray method. Also, more crystallized structure can be obtain by the electrochemical coating method. However, poor adhesion strength between coated layer and substrate metal and poor reproducibility of this coating method become problems to be solved.

Therefore, authors have been investigated reproducibility of HAp coating by electrochemical coating method. As a result, it was recognized that pitting corrosion of substrate Ti and poor adhesion strength between coated layer and substrate caused the delamination of coated HAp film. Therefore in this study, the optimum condition of the HAp films formation by electrochemical method was investigated employing QCM (Quartz Crystal Microbalance), FE-SEM and EDX. Then, adhesive strength of coated HAp films was evaluated by the scratch test. Also, biocompatible character of HAp film was examined by immersion test into guasi-human body fluid.

EXPERIMENTAL PROCEDURES

Determination of the optimum condition of the HAp films formation by QCM

Activating potential condition of HAp deposition on specimen surface can be detected by QCM, because of its ability to measure ng order precipitate through detecting the frequency change of quarts crystal vibration with the cathodic current density sweep. QCM measurements were conducted using three electrode method composed of Ti coated specimen (working electrode), Pt (counter electrode) and the saturated calomel electrode (S.C.E) (reference electrode). Then, optimum conditions of electrode potential for better HAp film formation was determined. Solution temperature was selected to be 310 K and the potential was swept from natural corrosion potential up to -1000 mV with the sweep rate of 20 mV/min. Detailed observation of specimen surface was conducted by FE-SEM. Also, the characterizasion of deposited materials were conducted by EDX.

Cathodic polarization curve measurement

It is difficult to conduct QCM measurement under the potential condition up to -1500 mV due to HAp precipitation on Ti electrode. Therefore, cathode polarization curve measurement were also conducted in the same solution using three electrode method composed of Ti (working electrode), Pt (counter electrode) and the saturated calomel electrode (S.C.E) (reference electrode). Solution temperature was selected to be 310 K

and the potential was swept from natural corrosion potential up to -2000 mV with the sweep rate of 20 mV/min. Detailed observation of specimen surface was conducted by FE-SEM. Also, the characterization of deposited materials were conducted by EDX.

Potentiostatic measurement

Potentiostatic measurement ware conducted under various peak potentials for HAp film formation obtained by QCM and cathode polarization curve measurement. Therefore, -700, -1200, -1500, and -2100 mV were selected as the constant potential condition for potentiostatic measurement. The measurements were continued up to 100 min. under above-mentioned various constant potential conditions.

Adhesion strength evaluation

To determine the optimum condition for HAp film formation, adhesion strength between coated HAp thin film and substhate Ti was measured using scratch testing machine of REVETEST made by Nanotec Co., Ltd. with testing conditions shown in Table 1.

The critical load Lc for initiation of microdelamination of thin film obtained by scratch test was determined employing the JSME (Japan Society of Mechanical Engineers) Standard S 010-1996 "Standard Method for Evaluating the Defects in the Coatings Made by Dry Processings"[4,5]. The value of Lc was synthetically evaluated from both changes in friction load and AE count and the morphology changes in scratch trace detected by microscopic observation.

Table 1 Condition of scratch test

Indenter	Tip radius	200 μ m
	Material	Diamond
Loading rate		100N/min
Sliding rate of Tip		10mm/min
AE sensitivity		5

EXPERIMENTAL RESULTS AND DISCUSSIONS

Determination of the optimum condition of the HAp films formation by QCM

The solution used in this study was deionized water in which $Ca(NO_3)_24H_2O$ and $(NH_4)2HP$ were dissolved with the mole ratio of Ca/P=1.67. By using this solution, the optimum condition for HAp film formation by electrochemical method was investigated employing QCM measurement whose specimen was Ti deposited electrode. Correlation between the cathodic potential vs. the current density and the cathodic potential vs. the vibrating electrode frequency was obtained by QCM measurement and shown in Fig. 1. From this figure, under the cathodic electrode potential condition around -650～-850 mV (S.C.E.), abrupt increase in cathodic current density and also sudden decrease in electrode vibration frequency were detected. For these reason, accelerated precipitation and deposition of HAp on Ti coated electrode can be expected. Under the potential range over -850 mV (S.C.E.), the frequency measurement of electrode was prohibited due to excessive precipitation of HAp on itself. Therefore, mophology of HAp deposited on QCM electrode was observed by FE-SEM and shown in Fig. 2. At the same time, examination of chemical composition of deposited film was conducted by EDX measurement. As a result, precipitation of HAp was recognized.

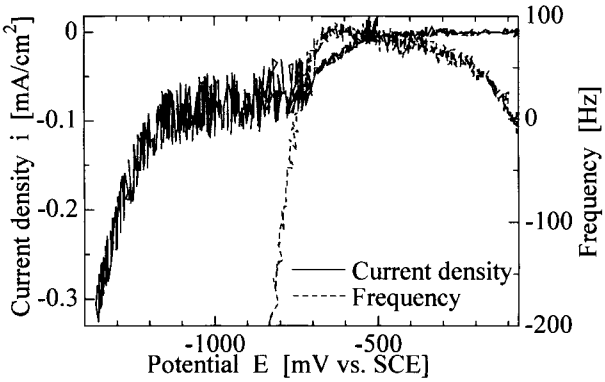
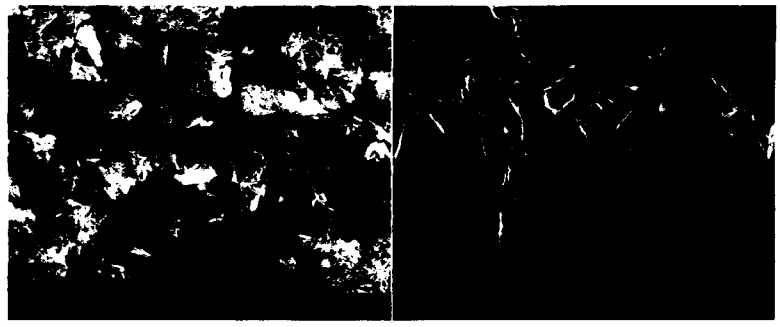


Fig. 1 Polarization Curve and QCM Data



a) 5.0kV×500 **b)5.0kV×5.00k**

Fig. 2 Surface Morphology of HAp on QCM Electrode

Cathodic polarization curve measurement

To grasp the precipitation behavior of HAp under potential condition beyond -1500 mV, the cathodic polarization measurement was conducted employing the same Ti electrode. Obtained result was shown in Fig. 3.By comparing the results shown in Fig. 3 with those obtained by QCM measurement, the same trend of increase in the current density was recognized under the potential condition from about -650 mV up to -850 mV (S.C.E). The cathodic current density gradually increased up to the potential condition of -1250 mV. Then, abrupt decrease in the current density was recognized. After showing local minimum value in current density under potential condition around -1400 mV, the current density gradually increase again up to the potential condition of -2000 mV.

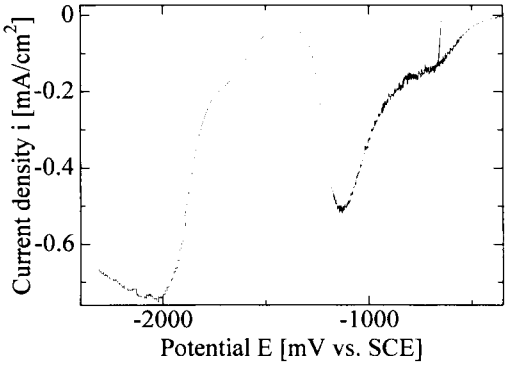


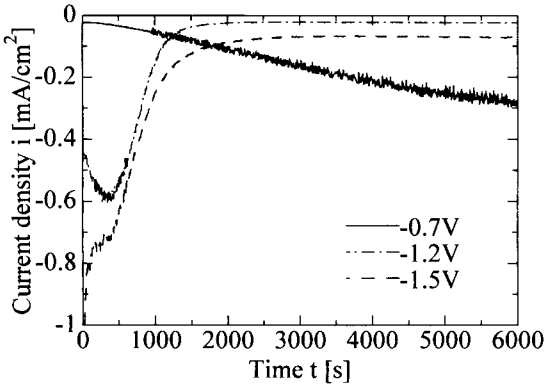
Fig. 3 Cathodic Polarization Curve

Constant potential measurement

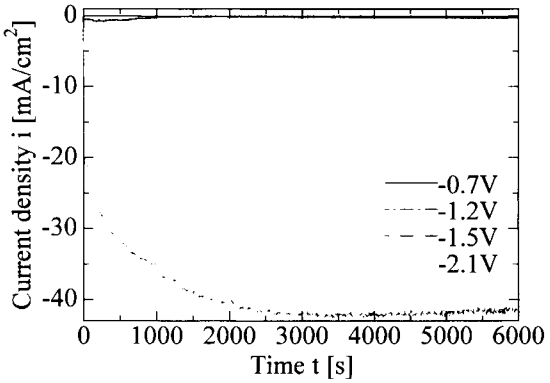
-1200 mV, -1500 mV, and -2100 mV were detected as the local peak potential values from the cathode polarization measurement shown in Fig. 3. Constant potential measurements were conducted under these three kinds of potentials and also under -700 mV at which abrupt increase in cathodic current density and sudden change in vibration frequency of electrode were recognized in the QCM measurement.

The results of current density measurement were shown in Fig. 4. From these figures, only under the potential condition of E = -2100 mV (S.C.E), gradual increase in the current density was observed. Therefore, accelerating cathodic reaction was generated on the Ti substrate surface under the potential condition of -2100 mV. Out of other three potential conditions, at -700 mV the cathodic current density was recognized to be kept under relatively stable larger value state. It may result in excessive HAp precipitation on the substrate surface. Microscopic observation on the substrate surface after constant potential electrochemical test revealed that HAp uniformly precipitated on specimen surface under the potential condition of -700 mV. Under the potential condition of -1200 mV, precipitation of HAp was also recognized. In this case, double

layered HAp precipitation was observed by the microscopic observation on specimen surface. Under the potential condition of -1500 mV, delamination and precipitation of secondary HAp layer may be balanced.



a) -0.7, -1.2, -1.5, -2.1 V



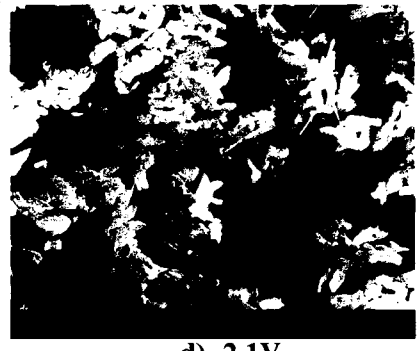
b) -0.7, -1.2, -1.5 V

Fig. 4 Current Density Change during Constant Potential Tests

a) -0.7V

b) -1.2V

c) -1.5V



d) -2.1V

Fig. 5 Surface Morphology of HAp

Adhesion strength evaluation

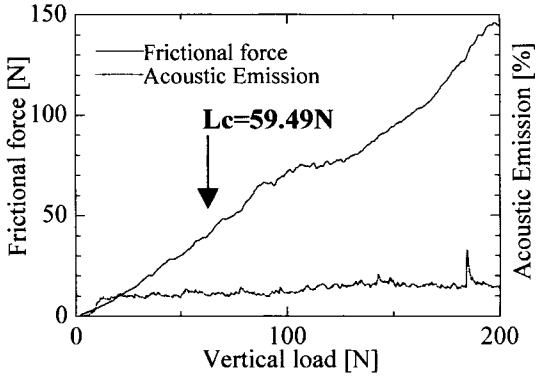
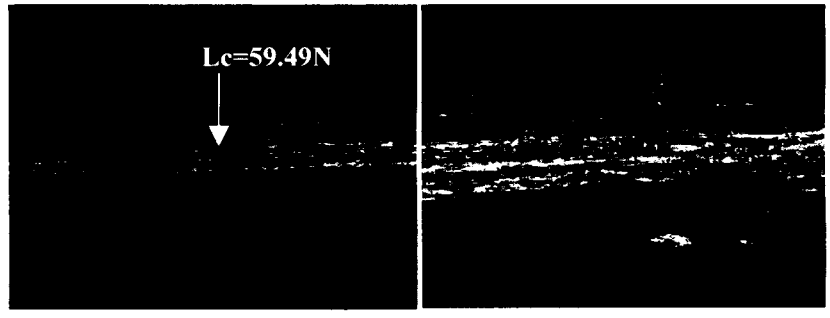


Fig.6 Result of scratch test of HAp film, Thickness of film : 280 μ m



a) 59.47 [N]

b) 89.56 [N]

Fig.7 Surface morphology of HAp film after scratch test, Thickness of film : 280 μ m

To evaluate adhesion strate of precipitated HAp film on Ti substrate, scrtch test was conducted. The result of

scratch test is shown in Fig. 6 and the surface morphology of HAp film after scratch test is shown in Fig. 7. In Fig. 6, the diagrams of frictional force and acoustic emission count changes depending upon vertical load were indicated. Fig. 7 shows the optical micrographs of scratch trace observed on 280 μ m thick HAp film that was formed under -700 mV. In this paper, the critical load of Lc for the initiation of micro delamination was mainly determined by examining the morphological changes in the scratch trace observed by optical microscope. At the same time, no aboupt change in AE count and also in frictional force were recognized as shown in Fig. 6. Therefore, critical load Lc was determined by the optical microscopic observation of the scratch trace and obtained to be 59.5 N in this case. This Lc value is almost the same revel as that of TiN/AISI304 coating obtained under the temperature condition of 900 ℃ by plasma CVD method[4].

CONCLUSIONS

The optimum condition of the HAp films formation by electrochemical method was investigated by employing QCM (Quartz Crystal Microbalance), FE-SEM and EDX. Then, a adhesive strength of coated HAp films was evaluated by the scratch test. As a result, the activation in precipitation of HAp was recognized at the electrode potential around -650 mV[vs. SCE] due to the frequency change detected by QCM measurement and the cathodic current density increase. FE-SEM observation and EDX analysis on specimen surface used for QCM measurement revealed the uniform precipitation of HAp. Also, well developed crystal structure of HAp can be obtained under the condition detected by QCM measurement and the improvement in adhesion strength between HAp films and substrate metal is recognized. Biocompatible character is expected to be examined through immersion test into guasi-human body fluid.

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