

Calcium Phosphate Film Coating on Titanium Substrate by Electrochemical Deposition

Dujreutai PONGKAO KASHIMA*, and Achariya RAKNGARM

*Research Unit of Advanced Ceramics, Department of Materials Science,
Faculty of Science, Chulalongkorn University, Phayathai Rd.,
Patumwan, Bangkok 10330, Thailand.*

Abstract

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Calcium phosphate film on titanium substrate was achieved by electrochemical method in four different kinds of electrolyte. The pure titanium metal (99.99%) with 0.8 cm in width and 2 cm in length was used as a substrate and it was subsequently etched by 2M HF for 1 minute before electrochemical deposition. Calcium phosphate film could form at a different current density for each kind of electrolyte as follows: 10 mA/cm² for MCPM based aqueous solution, 20 mA/cm² for MCPM based aqueous solution with ions addition, 10 mA/cm² and 20 mA/cm² for MCPM based 20% V/V ethanol and 50% V/V ethanol solution, respectively. The variation in film thickness depended on the kind of electrolyte and deposition time. The major phase that appeared in the film from MCPM based aqueous solution was brushite in coexistence with monetite. Apatite was induced in the film using MCPM based aqueous electrolyte with ions addition of NaNO₃ and NaF. On the other hand, monetite was formed as a major phase under the electrolyte condition of MCPM based ethanol solution. The highest adhesion value of film to substrate that formed in MCPM electrolyte based aqueous solution investigated by balance beam scrape adhesion and Mar tester was 150 g. After incubation in R-SBF for interval times, the amorphous bone like apatite formed.

Key words : Calcium phosphate film, Titanium, Electrochemical deposition, Brushite, Monetite

Introduction

Titanium is a useful metal which has been used in biomedical application over the past decade. Though it proves to be satisfactory in strength as it is so close to the human bone but it is classified as a bio-inert material.⁽¹⁾ The stable form of titanium at physiological pH is titanium dioxide (TiO₂), which is spontaneously formed when the metal is exposed to air. The interfacial tension⁽²⁾ between TiO₂ and water is -11.7 mJm⁻², implying that the interface formed between TiO₂ and aqueous phases is thermodynamically unstable and it would be less biocompatible when used as an implant. It is therefore desirable to coat such surfaces with a more biocompatible material as a calcium phosphate phase in order to form a satisfactory biological base for bone ingrowth and interface stability. To fulfill the purpose of strong adhesion of calcium phosphate coating on titanium metal, coating by electrochemical technique is interesting as a simple technique and can be achieved at room temperature. Based upon the solubility product constant of

Ca(OH)₂-H₃PO₄-H₂O system⁽³⁾ at 25°C, it can be estimated that brushite (CaHPO₄·2H₂O) and monetite (CaHPO₄) can be easily deposited on titanium substrate by electrochemical method. Monocalcium phosphate monohydrate (Ca(H₂PO₄)₂·H₂O, MCPM)-the most soluble calcium orthophosphate - was used as a starting material for preparation of electrolytes in every condition of deposition processes. The present work aims at studying effects of different kinds of electrolyte on the formation of calcium phosphate films on titanium substrates. The effects of MCPM based ethanol electrolytes which have not been studied by any researchers will be reported in this paper.

Materials and Methods

The working electrode used in the present study was made of pure titanium (99.99%) sheets axially embedded in Araldite holders to offer a Ti exposed surface area of 2.3 cm². Prior to each experiment, the working electrode (WE) was mechanically polished with different grades of

* Corresponding author Tel: +662-218-5552, Fax: +662-218-5561
E-mail address : Dujreutai.P@Chula.ac.th, dujreutai@gmail.com

emery papers, i.e. 600, 800, 1000 and finally 1200, and then the polished electrode was rinsed with ethanol and distilled water, and finally activated in 2M HF for 1 min, followed by generous washing with distilled water, and then dipped in a conventional three-electrode cell. A small piece of platinum (2.0 cm²) was used as a counter electrode (CE). All potentials were measured against Ag/AgCl reference electrode (RE). The electrochemical deposition was performed using Potentiostat-Galvanostat Model PG-30, Metrohm connected with personal computer. The electrochemical reaction was performed in four different kinds of electrolyte containing saturated solution of monocalcium phosphate monohydrate [(MCPM, Ca(H₂PO₄)₂·H₂O), Fluka, 85% purity] by galvanostatic technique with varying current density from 5-20 mA/cm² for 3-5 minutes at room temperature. Saturated solution of MCPM was prepared by adding MCPM reagent in double distilled water and stirring over more than 3 hours until the precipitate of MCPM was observed. After that the saturated solution was kept overnight without stirring before filtering to separate the precipitate. Then MCPM based aqueous solution was obtained. The second kind of electrolyte was prepared by addition of sodium fluoride (NaF, AJAX chemical, 98% purity) and sodium nitrate (NaNO₃, AJAX chemical, 99% purity) in a saturated solution of MCPM. The chemicals of NaNO₃ 21.0 g and NaF 0.15 g were added to 50 ml H₂O, then poured into 1L of MCPM based aqueous solution because it could promote the high amount of apatite formed on the film. For the third and fourth electrolyte, ethanol was applied instead of water for preparation of MCPM based ethanol solution. At last, MCPM saturated in 20% and 50% V/V of ethanol solutions was obtained, respectively. The electrolyte used in all experiments was summarized as shown in Table 1. Phase analysis of film was carried out by XRD (Bruker, D8-Advance), using CuK_α radiation with Ni filtered at 40 kV and 40 mA. Surface morphology was investigated by SEM (JEOL JSM-5410LV). The specimen was stuck on stub by carbon tape and the surface was sputtered by gold. Film thickness was measured by mounting the specimen in clear resin, polishing it by diamond paste until the clear cross section surface was exposed and was then subjected to observation by optical microscope (Olympus BX60M Microscope). Scrape adhesion test according to ASTM D-2197-98 (Reapproved 2002) was conducted by balanced beam scrape and Mar tester (SG-8101) to evaluate the adhesion of

the coating film to titanium substrate. Finally the in vitro study of selected specimens was done in revised simulated body fluid (R-SBF)⁽⁴⁾ under human physiological condition at pH 7.4, 36.5°C.

Table 1. Summarized conditions of electrolyte used for calcium phosphate film deposition on titanium substrate

Electrolyte name	Preparation technique
MCPM based aqueous	MCPM was dissolved in distilled water until saturation point, then kept overnight, filtered; finally saturated solution of MCPM was obtained.
MCPM based aqueous with ion additions	NaNO ₃ 21.0g + NaF 0.15 g were added to 50 ml H ₂ O, then poured into 1L of MCPM based aqueous solution.
MCPM based 20% V/V ethanol	MCPM was dissolved in 20% V/V ethanol (20% V ethanol-80%V distilled water) until saturation point, then kept overnight, filtered; finally saturated solution of MCPM was obtained.
MCPM based 50% V/V ethanol	MCPM was dissolved in 50% V/V ethanol (50% V ethanol - 50%V distilled water) until saturation point, then kept overnight, filtered; finally saturated solution of MCPM was obtained.

Results and Discussion

Calcium phosphate film formed by MCPM based aqueous solution showed the obvious characteristics in phase present, film morphology and scratch test result. XRD pattern in Figure 1. showed that calcium phosphate film which formed at a current density of 10 mA/cm² was brushite incoexistence with small amount of monetite which implied that it could be a good candidate for biocompatible materials since it has been known that brushite was a precursor of biological apatite⁽⁵⁾ and monetite also occurred in the bone before the formation of apatite.⁽⁶⁾ The film thickness was 15-20 μm as clearly shown in Figure 2a and 2b. The morphology of film obtained was investigated by SEM and showed that the microstructure was a porous film with a plate-like crystal of brushite phase. Moreover there were some pores which were easily observed by SEM micrograph Figure 3. Increased deposition time resulted in a higher density of the film. Selected specimens of film formed on Ti substrate at a current density of 10 mA/cm² for 5 minutes which were subjected to the scrape adhesion test as shown in Figure 4. The

result showed that traces of the film still remained on the substrate, up to 150 g of applied load. The shear stress of which was 8.83 MPa.

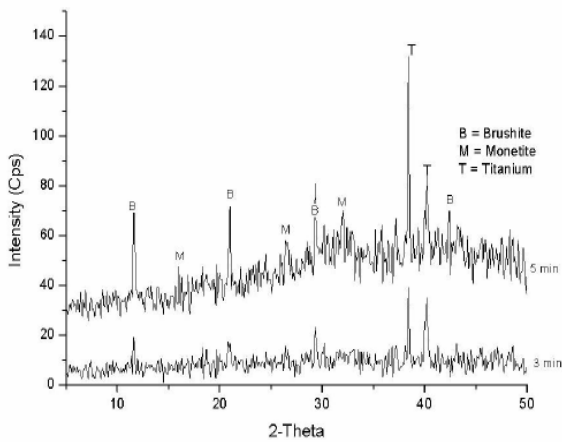


Figure 1. XRD pattern of calcium phosphate film on titanium substrate obtained from MCPM based aqueous electrolyte at 10 mA/cm^2 for 3 and 5 minutes

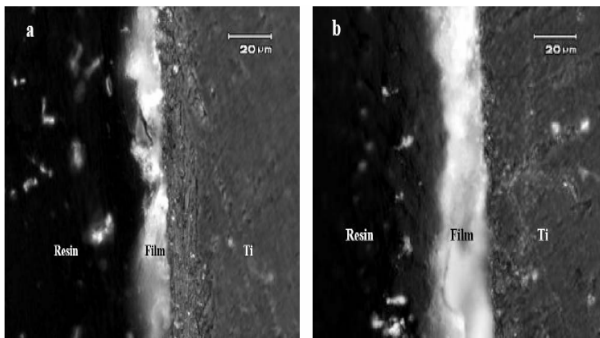


Figure 2. Optical micrographs showing the thickness of film obtained from MCPM based aqueous electrolyte at 10 mA/cm^2 for deposition time of (a) 3 minutes and (b) 5 minutes

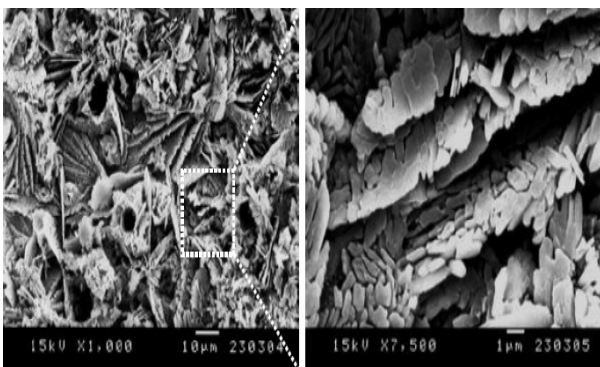


Figure 3. SEM micrographs showing the morphology of calcium phosphate film obtained from MCPM based aqueous electrolyte at 10 mA/cm^2 for 3 minutes at the magnification of (a).1,000X and (b).7,500X, respectively

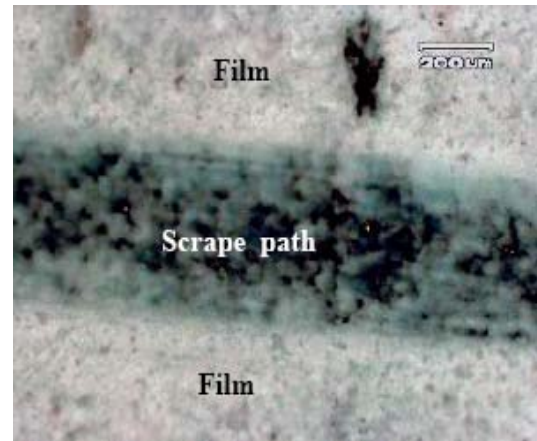


Figure 4. Optical micrograph showing the trace after scrape adhesion test of as-deposited brushite in coexistence with monetite film obtained from MCPM based aqueous electrolyte at 10 mA/cm^2 for 5 minutes

The result from the *in vitro* study in R-SBF of brushite film in coexistence with minority of monetite formed at 10 mA/cm^2 , 5 min from MCPM based aqueous electrolyte showed that this film was completely converted to apatite after incubation in R-SBF for 8 hours as shown in XRD patterns in Figure 5. The microstructure of partly converted apatite from as-deposited brushite film (with minority of monetite) after 4 hours incubation in R-SBF is shown in Figure 6. SEM micrograph of partly converted apatite film in Figure 6. is in agreement with XRD pattern in Figure 5, which is composed of both brushite and apatite phase. Brushite plates were converted to apatite as can be seen that there were many agglomerate particles of apatite (round shape) deposited on plate-like crystals of brushite in Figure 6. After incubation in R-SBF for 8 hours, only apatite phase was investigated on Ti substrate as shown in XRD patterns in Figure 5. It is worth noting that the characteristic of completely converted apatite film after incubation in R-SBF for 8 hours is similar to bone-like apatite of which is previously reported that it is not-well crystallized apatite with 100-200 nm in length and 30-40 nm in width.⁽⁷⁻⁸⁾ The bone-like apatite film was scraped out and ultrasonically dispersed in ethanol, then investigated by TEM as shown in Figure 7. The needle shape of bone-like apatite was formed by the hydrolysis of brushite and monetite under the simulated human physiological condition in R-SBF, pH 7.4, 36.5°C . This evidence confirmed that brushite film in coexistence with small amounts of monetite acts as a good biocompatible material.

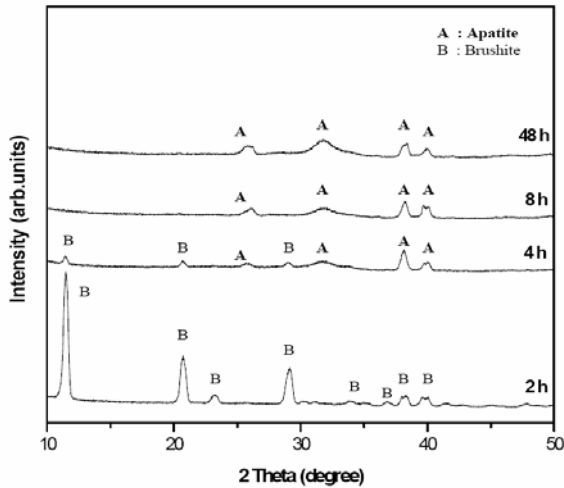


Figure 5. XRD pattern showing phase present of brushite film in coexistence with minority of monetite on Ti substrate after incubation in R-SBF, pH 7.4, 36.5 °C for 2, 4, 8, and 48 hours.

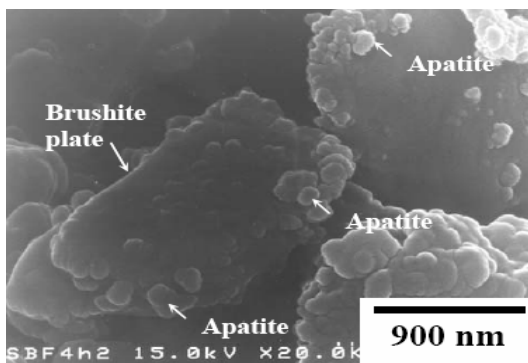


Figure 6. SEM micrograph of partly converted apatite from brushite film (with minority of monetite) after 4 hours of incubation in R-SBF.

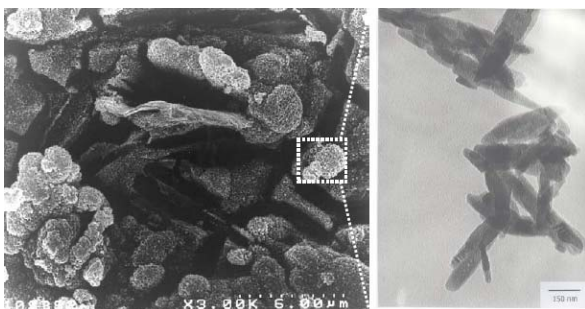
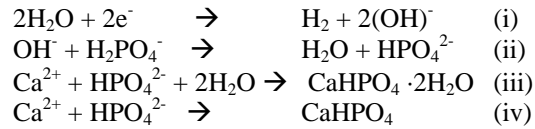
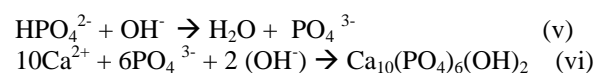


Figure 7. SEM and TEM micrographs showing the morphology of needle shape bone-like apatite converted from brushite film coexisted with minority of monetite (formed at 10mA/cm², 5 minutes from MCPM based aqueous electrolyte) after incubation in R-SBF for 8 hours.

We mentioned above that the as-deposited brushite film coexisted with monetite obtained from MCPM based aqueous solution at a current density of 10 mA/cm². Thus, the possible reaction might be as follows:



Firstly, (i) water is reduced at the cathode surface, Ti surface, to produce hydrogen gas and hydroxide ions. Thus, by controlling the current density that passed, the pH was controlled at the surface of the cathode (Ti). The hydroxide ions generated at the surface then might react with dihydrogen phosphate according to the equilibrium shown in (ii). The following equilibrium for precipitation of brushite (CaHPO₄·2H₂O) and monetite (CaHPO₄) is relevant in the presence of calcium ions as shown in (iii) and (iv) respectively. Brushite formed as a major phase because the hydrated ions in solution would be more readily incorporated into a hydrated crystal, and a hydrated structure has also a lower surface energy at the nucleation stage. It would therefore be favoured thermodynamically over anhydrous crystal nuclei.⁽⁹⁾ On the other hand monetite formed as a major phase coexisted with minority of brushite when MCPM based ethanol solution (20% V/V and 50% V/V) was used as an electrolyte. Ethanol might reduce the number of hydrated ions in solution, and as a result, anhydrous form as CaHPO₄, monetite, was driven to form. Though the film surface of as-deposited film formed by MCPM based 50% V/V ethanol electrolyte was very smooth, it was easily peeled off. The as-deposited film from MCPM based 50% V/V ethanol electrolyte would not be selected to do the scratch test. As-deposited film formed when adding NO³⁻ and F⁻ into MCPM based aqueous electrolyte which was mainly composed of monetite and some apatite. The possible reaction (v-vi) might be as follows:



Calcium phosphate films with different phase compositions were obtained from different electrolyte conditions. The result could be summarized as shown in Table 2.

From all the above conditions in Table 2, MCPM based aqueous electrolyte resulted in the highest adhesion between the film and titanium substrate. The maximum applied load was 150 g, 100 g and 70 g for electrolyte condition 1, 2 and 3, respectively. The as-deposited film of brushite and monetite on titanium formed by MCPM based aqueous electrolyte at 10 mA/cm², 5 minutes was incubated in R-SBF, pH 7.4, 36.5°C. After incubation in R-SBF at interval, bone-like apatite appeared clearly with a needle-like shape. The morphology of apatite as needle-like has been believed to be apatite crystals found in a calcified tissue.^(7, 8)

Table 2. Summarized conditions of calcium phosphate film formed on titanium substrate by galvanostatic technique

Electrolyte condition	Current density (mA/cm ²)	Phase obtained
1. MCPM based aqueous	10	Brushite* and monetite
2. MCPM based aqueous with ion additions	20	Monetite* and apatite
3. MCPM based 20% V/V ethanol	10	Monetite* and brushite

NB. * represents the major phase formed in the film.

Conclusion

The different kinds of calcium phosphate could induce to form on titanium substrate by different kinds of electrolyte. Brushite with minority of monetite film could form from MCPM based aqueous electrolyte. Monetite with minority of brushite could form from MCPM based ethanol electrolyte. Apatite could form in coexistence with monetite when NO³⁻ and F⁻ ions were added into MCPM based aqueous electrolyte. The best adhesion of film to substrate appeared on the as-deposited film from MCPM based aqueous electrolyte. The as-deposited film from this condition was transformed to bone-like apatite after incubation in R-SBF, pH 7.4, 36.5 °C.

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