Calcium phosphates deposited on titanium electrode surface —Part 1: Effect of the electrode polarity and oxide film on the deposited materials

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We report experimental results about the effect of polarity of electrode and anodized titanium oxide film on the deposited materials by electrolysis of an acidic calcium phosphate solution. Mirror-polished titanium and anodized titanium were used as anode or cathode, and a Pt plate was used as a counter electrode. The load voltage was held constant at 20 VDC. No deposited materials were found on the anode surface. On the other hand, dicalcium phosphate dihydrate (DCPD) was deposited on the cathode surface at the beginning of the electrolysis. After the electrolysis time 600 s, the non-stoichiometric hydroxyapatite (HAp) with several hundred nanometers was formed on the specimen surface. Based on X-ray photoelectron spectroscopy data, the anodized oxide film contained both P^{5+} and P^{3+} ions. This characteristic of the oxide film and the electrolysis conditions were related to the behavior of the deposition of ultra fine HAp with high crystallinity.

Keywords: Calcium phosphate, Titanium, Electrolysis, Anodic oxidation

INTRODUCTION

Titanium is widely used in medical materials and dental implants because of its high biological affinity¹⁾. The titanium surface is covered with thin passive film, which plays an important role in ensuring a favorable tissue response to titanium implants. In addition, the surface modification of titanium may also improve its biocompatibility and osteoconductive properties. The range of biomaterial applications can be increased by depositing a thicker layer of titanium oxide on the titanium surface or by covering it with another biocompatible material, such as hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$)²⁻⁴⁾. HAp is one of the most attractive materials for bone implants because of its osteoconductive properties, but because of its poor mechanical properties, it is usually used to coat titanium substrates⁵⁾. HAp is also commonly employed as a coating for bioinert metallic and ceramic implants made of titanium and alumina.

There are both wet and dry methods for modifying the surface of titanium to improve the adhesion between the implant and bone to accelerate the growing in of the implant⁶⁾. Dry methods include the formation of thin films at low temperature by ion sputtering and ion implantation, and wet methods involve electrochemical synthesis. Ban *et al.*⁷⁾ reported that needle-like calcium phosphate compounds were electrochemically deposited on a titanium plate. We have previously reported that a calcium phosphate similar to HAp was electrochemically formed on valve metals in an acidic calcium phosphate solution through an alternating polarization technique⁸⁾. This is a unique electrolysis method where the polarity of the applied voltage is inverted. The phase of the deposited material depended on the pH of the electrolyte and the electrolytic current density. The critical grain

size of the deposited HAp on valve metal surface was on the order of several hundred nanometers. Moreover, the type of phosphoric ions around the electrode influenced the deposited materials during electrolysis.

In this paper, we evaluated the effect of polarity of electrode on the deposited materials during electrolysis and examine the electrochemical precipitation on anode and cathode surfaces. Furthermore, we investigated the effect of the anodized titanium oxide film on the characteristics of the deposited materials.

MATERIALS AND METHODS

Specimens

Specimens of mirror-polished CP-titanium (diameter 15 mm, thickness ~5 mm) were used. The mirror polishing was performed on an auto polishing machine (TegraPol-11, Struers, Ballerup, Denmark) with waterproof SiC abrasive paper under running water. A buffing cloth (Chemomet I, Buehler, IL, USA) was used for the final polishing with colloidal silica (Mastermet, Buehler) which contained 10% H_2O_2 (Wako Pure Chemical Industries, Osaka, Japan). The specimens were pretreated by anodic oxidation at 20 and 50 VDC for 60 s in an aqueous solution of phosphoric acid. The specimens, electrolytic pretreatments and their abbreviated name are listed in Table 1.

Preparation of electrolyte and electrolytic treatments

The acidic calcium phosphate electrolyte solution was prepared by the following procedure. HAp (HAP-200, Taihei Chemical Industrial, Osaka, Japan) was dissolved in an aqueous solution of phosphoric acid (Wako Pure Chemical Industries) at about pH 2 at room temperature. The solution was shaken vigorously and allowed to remain for a long time to collect a clear

Table 1 Pretreatment conditions for titanium specimen

Code	Pretreatment
CPT	None
A20	Anodic oxidation (20 VDC/60 s)
A50	Anodic oxidation (50 VDC/60 s)

Electrolysis was carried out at 20 VDC for 30, 60, 180, 300, and 600 s for all specimens.

liquid by decantation. The liquid of pH was adjusted to 3 by adding NaOH (Wako Pure Chemical Industries) solution.

Two electrolysis experiments were carried out in 10 mL of electrolyte at a constant voltage of 20 VDC for 30, 60, 180, 300, and 600 s. Firstly, the specimen and a Pt plate were connected to the positive and negative poles of the power source, respectively. The distance between the electrodes was 1 mm. Secondly, the electrode polarities were swapped; *i.e.*, the specimen and the Pt plate were connected to the negative and positive poles of the power source, respectively. The electrolysis was performed under the same conditions. The current on the power source digital display was read every 10 s, and the temperature of the electrolyte bath was measured every 10 s with a digital multi-meter (PC510, Sanwa Electric instrument, Tokyo, Japan). The experimental setup for the electrolysis is illustrated schematically in Fig. 1.

X-ray photoelectron spectroscopy (XPS)

The specimen was analyzed by a XPS (Quantum 2000, Ulvac-Phi, Chigasaki, Japan) under the following conditions: monochromatic Al-K α X-ray excitation of 25 W at 15 kV, an analysis area of $\sim 100\ \mu\text{m}$ in diameter and pass energy of 58.70 eV for the electron analysis. Ar⁺ ions with energy of 3.5 keV, a scan size of $2\times 2\ \text{mm}^2$ and a 1 min sputter interval were used for depth profiling. These conditions result in a typical sputter rate of 27 nm min⁻¹ for SiO₂, which corresponds to an approximate rate of 15 nm min⁻¹ for the as-prepared TiO₂ film. In order to minimize the effects of charging during the XPS analysis, a neutralizer was used. The binding energy and Ca/P atomic ratio were calculated by MultiPak software (Ulvac-Phi) provided with the instrument.

Atomic force microscopy

The specimen was set on a stage of an atomic force microscopy (AFM) in a JSPM-4210 system (JEOL, Tokyo, Japan). The particle morphology and size of the deposited powder were evaluated by AFM operating in the AC mode in the intermittent contact regime or in the non-contact regime. The lateral scan frequency of 160 kHz resulted in a total recording time of 1,200 s for each image. Their characteristics were determined through SPIP image analysis software (Image Metrology, Horsholm, Denmark).

X-ray diffraction analysis

The analysis preparation consisted of scraping the deposited materials from the specimen with a blade to obtain material for a X-ray diffraction (XRD). The phase identification of the deposited materials was performed by a XRD (Assemble, Rigaku, Tokyo, Japan) using Cu-K α radiation at 40 kV and 30 mA. Non-reflective silicon plate was used with the powder method at a scanning speed of $1^\circ\ \text{min}^{-1}$. The phases were identified using the structural data in the Powder Diffraction File 1998 (ICDD, PA, USA).

Fourier transform infrared spectroscopy

The deposited materials were scraped from the specimen with a blade to obtain material for a Fourier transform infrared spectroscopy (FTIR). FTIR studies were carried out on an FTIR spectrometer (FTIR-7300, JASCO, Hachioji, Japan) by the KBr method over the range 4,600–400 cm⁻¹, at a 4 cm⁻¹ resolution, after 500 scans. The presence of chemical bonding in the deposited materials was also confirmed.

Statistical analysis

All data for the current density and temperature are presented as mean $\pm$ SD, $n=3$. Data were analyzed with a statistical analysis program (Excel 2002, Microsoft, WA, USA). The significant differences between the electrolysis properties were determined by Student's *t*-test ($p<0.05$).

RESULTS

Polarity of electrode and precipitation

Before the electrolysis treatment, the specimens were bluish purple after they were anodized at 20 VDC and grayish yellow at 50 VDC. The CPT, A20 and A50 specimens were used as the electrodes (Fig. 1). When the

Fig. 1 Schematic illustration of electrochemical deposition process.

specimens were anode and a constant power supply (20 VDC) was applied to this circuit, no deposited materials were observed on the surface of specimens for any length of time for electrolysis. The temperature of the bath was the same before and after electrolysis.

However, when the specimens were cathode under the same electrolysis conditions, bubbles were formed at the both electrodes during the electrolysis, and the deposited materials were found on the specimen surface. The surface color of the CPT specimen did not change,

Fig. 2 Mean current density of all specimens during electrolysis.

Fig. 3 Changes in the bath temperature for all specimens.

whereas the surface color of A20 and A50 was lighter after the electrolysis. The current density and the bath temperature were plotted against the electrolysis time (Figs. 2 and 3). There was no significant difference in the current density and in the temperature over the electrolysis time ($p < 0.05$). However, the current density of A50 specimen tended to be smaller than that of the other specimens at the end of the electrolysis. The temperature rate in the bath ranged from 0.3 to 0.4°C s⁻¹ during the first 120 s of electrolysis. After 120 s, the rates ranged from 0.01–0.08°C s⁻¹. The bath temperature of all specimens approached 60–70°C at the end of the electrolysis period.

XPS

XPS depth profiles of the P 2*p* spectra obtained from the CPT and A50 pretreatment specimens are shown in Fig. 4. Significant differences in peak shape were found between the interior and the outermost surface of the specimens. The P 2*p* spectra at the non-sputtered surface, which is the outermost surface of the specimen,

were compared with all the sputtered specimen surfaces. The new peak at 129.5 eV was confirmed to be from the interior surface of the A50 pretreatment specimen, and contributes to P³⁺.

The calculated Ca/P atomic ratio using MultiPak software was about 1.1 for all specimens after an electrolysis time of 30 and 60 s. However, the ratio was about 1.4 for all specimens after 300 and 600 s. The Ca/P ratio from the XPS results for the deposited HAp was lower than that of the stoichiometry (Ca/P=1.67).

AFM

AFM images for all the specimen surfaces for an electrolysis time of 600 s are shown in Fig. 5. The

Fig. 4 Depth profiles of P2*p* for the CPT (left) and A50 (right) pretreatment specimens.

Fig. 5 AFM images of all specimens for an electrolysis time of 600 s.

Fig. 6 XRD patterns for the deposited materials obtained from the CPT, A20, and A50 specimens after different electrolysis times.

images revealed that the surface was coated with tightly arranged the deposited materials in all specimens. Plate like and rectangular particles with about 400 to 500 nm in size were observed for the CPT specimen. The A20 specimen contained fine spherical and oval particles with mean particle size of 270 nm. From AFM image of the A50 specimen, it was found that fine granular particles were about 100 nm in size. The size of deposited materials on the anodized specimens was smaller than that of on the CPT specimen.

XRD

The XRD patterns for the deposited materials in the CPT, A20 and A50 specimens after electrolysis are shown in Fig. 6. The XRD patterns were similar to standard DCPD (File 72-0713, JCPDS), DCP (CaHPO_4 , File 71-1759, JCPDS), and HAp (File 84-1998, JCPDS) crystal structures. DCPD was found on the CPT, A20 specimens after an electrolysis time of 30 and 60 s, and on the A50 specimen after 30 and 180 s. DCP was observed on the CPT specimen after 180, 600 s, and on the A20 specimen after 180 and 600 s. HAp was found on the all specimens after 180, 300, and 600 s. The crystallinity of HAp deposited on the A50 specimen improved with electrolysis time.

FTIR

Figure 7 shows the FTIR spectrum for the deposited materials obtained from the A50 specimen after an electrolysis time of 600 s. The broad bands around $3,600\text{--}3,000\text{ cm}^{-1}$ and $1,700\text{--}1,600\text{ cm}^{-1}$ were assigned to H_2O adsorbed on the surface, and the characteristic OH stretching bands appeared at 3565 cm^{-1} . The strong bands for HAp in the $1,100\text{--}1,000\text{ cm}^{-1}$ region were attributed to PO_4 and HOPO_3 stretching modes. Three stretching modes were generally observed for the HOPO_3 group between about $1,150$ and 950 cm^{-1} , and the bands for HAp in this region occurred at $1,092$ and $1,040\text{ cm}^{-1}$. In

Fig. 7 FTIR spectrum for the deposited materials obtained from the A50 specimen for an electrolysis time of 600 s.

some samples of well-crystallized HAp, the strong band in the $1,040\text{ cm}^{-1}$ region was split. The HAp bands at around 550 cm^{-1} were probably components of the triply degenerate PO_4 bending mode. The three additional transmission bands at $1,470$, $1,414$ and 872 cm^{-1} were attributed to carbonates that had been substituted into the phosphate positions in the HAp lattice. Similar results were obtained in other specimens.

DISCUSSION

Effect of the specimen polarity on the deposited material

Electrolysis at constant voltage and constant current is usually used for depositing a bioinert calcium phosphate coating on a cathode surface. Tanaka *et al.*⁹⁾ reported that when the electrolysis was performed at voltages up to 20 VDC, the coatings contained DCPD, DCP, and HAp, whereas it consisted entirely of HAp at higher voltages. However, Wang *et al.*¹⁰⁾ examined the HAp coating film at electrolysis voltages 3 VDC. In our experiments, the electrolysis was carried out at a constant voltage of 20 VDC in an acidic calcium phosphate solution. The deposited materials were observed on the cathode surface for all specimens. The XRD results showed that the deposited material was DCPD for an electrolysis time of ~ 60 s, and was mainly HAp and DCP for electrolysis times of greater than 180 s. According to the results of the Ca/P atomic ratio calculated by XPS, XRD, and FTIR, a calcium-deficient HAp was formed. The following electrolysis reaction should occur at the cathode surface under acidic condition.

The pH levels on the specimen (cathode) varied from an acid to a neutral and basic by Eq. (1), and then the following chemical reaction (Eq. (2)) should also occur.

The cathodic polarization increased the pH on the specimen surface. Okawa *et al.*¹¹⁾ reported that the pH levels of the electrolyte around the cathode varied from 3 to 7.5 within 30 s after loading under the same electrolysis condition. Lin *et al.*¹²⁾ presented that cathodic polarization of Ti alloy leads to an increase in pH at the interface between the alloy and electrolyte due to the formation of OH^- ions. On the other hand, based on the relationship between solubility of calcium phosphate salts and pH of the solution, DCPD and DCP were deposited when the pH of the solution was less than pH 4.2, and HAp was deposited when it was more than pH 5.4¹³⁾. These deposition reactions held when the liquid-solid equilibrium condition was provided. Therefore, DCPD and DCP were deposited on the cathode surface at the beginning of the electrolysis. However, no equilibrium condition appeared possible during the long time electrolysis, because the pH of the electrolyte varied greatly.

On the other hand, according to the relationship

between the concentration of phosphate ions and the pH¹⁴⁾, the ratio of the phosphoric acid in the bath was $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-=0.1/0.9$ at pH 3, and at pH 5 it was almost entirely H_2PO_4^- . The ratio for $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}=0.5/0.5$ at pH 7. Moreover, the H_2PO_4^- ion was reduced to HPO_4^{2-} ion by an electrochemical reaction (Eq. (3)), and therefore, DCP and DCPD were readily deposited on the electrode surface (Eqs. (4) and (5)).

HAp crystal deposition was observed for electrolysis times greater than 180 s. This indicated that HAp was not deposited directly by the electrochemical reaction at the initial electrolysis period. The DCPD, which was deposited initially, was converted to HAp by the electrochemical reaction (Eq. (6)). The XRD peaks that originated from the crystalline calcium phosphate were not observed in the A50 specimen for an electrolysis time of 60 s. Therefore, an amorphous deposited material was formed on the specimen, which might well be an intermediate in the conversion of DCPD to HAp. Fulmer *et al.*¹⁵⁾ reported that HAp crystals were formed through the hydrolysis of DCPD. Moreover, it is also well known that calcium phosphate is converted to another type of calcium phosphate by hydrolysis, and that DCPD hydrolyzes to HAp in neutral or basic medium^{16–19)}. Stulajterova *et al.*²⁰⁾ demonstrated the effect of calcium ions on transformation of DCPD to HAp. It usually takes a long time for the hydrolysis. However, the hydrolysis of DCPD could easily occur under the influence of much Ca^{2+} and OH^- ions. Moreover, the bath temperature for the CPT, A20, and A50 specimens at the electrolysis time of 600 s was about 70°C , 65°C , and 60°C , respectively. At electrolysis times greater than 180 s, a temperature change was little observed for all specimens. The temperature in the bath eventually stabilized at the long electrolysis time. Consequently, both Ca^{2+} and OH^- ions around electrodes, and the temperature raise in the bath must have played an important role in the conversion reaction. In addition, we believe that HAp crystals are formed by the electrochemical reactions at long electrolysis period (Eq. (7)).

When we made the specimen the anode, no deposited materials were observed on the surface of the anode. Moreover, after anodic oxidation occurred initially, almost no electrolysis current was detected (data not shown). Under these conditions, the pH around the electrode should be the same as the pH of the electrolyte, and as above mentioned, the initial concentration of H_2PO_4^- around the electrode would be high. Needless

to say, this ion was not reduced to HPO_4^{2-} and did not contribute to the formation of calcium phosphates.

Anodized titanium oxide film and deposited materials

The oxide film thickness of A50 specimen had thicker than that of the A20 and CPT specimens. The intensity of the electrolytic current was low when the specimens were anode (data not shown), whereas it was high when their specimens were cathode (Fig. 2). The electrolytic current differed depending on the polarity of the specimen. Thus the oxide film had a unique electrical resistance. The electrolyte current density of A50 was somewhat smaller than that of the other specimens, and the bath temperature for all specimens finally reached to 60–70°C. Therefore, the effect of the temperature on the crystallinity was minimal. Some characteristics of the oxide film formed by the anodization could affect the DCPD hydrolysis rate and the formation of HAp. The XPS results showed that the oxide film contained P^{5+} and P^{3+} ions. We could speculate that P^{3+} ions were formed by the reduction of P^{5+} ions. P^{5+} ions adsorbed on the outermost surface would migrate towards metallic titanium due to high electric field, and then reduction of P^{5+} ions to P^{3+} ions by metallic titanium could occur at the beginning of the anodic oxidation. Nakahira *et al.*²¹⁾ reported the synthesis of TiO_2 doped with P ions by anodic oxidation in phosphoric acid at electrolysis voltage 350 VDC. According to their results, P ions inside TiO_2 film existed as P^{3+} . On this point, our results are consistent with their results. However, the electrolysis voltage in our experiments was only 20 VDC lower than 350 VDC.

On the other hand, on the base of the XRD results, the splitting of the broadened peaks over the 2 θ region 30–35° showed that the powder from A50 specimen for an electrolysis time of 600 s had good crystallinity in comparison to the CRT specimen under the same conditions. Consequently, the anodized titanium oxide film containing P^{3+} played an important role in easy deposition of calcium phosphate and the local could increase in the concentration of Ca^{2+} , which in turn would promote the crystal growth of HAp. Anodic oxide film containing Ca and P of titanium resulted in to be bioactivity²²⁾.

The AMF images showed that the mean particle size of the deposited materials on the A50 specimen for an electrolysis time of 600 s was on the order of several hundred nanometers. Fujino *et al.*²³⁾ showed that HAp having a lower Ca/P ratio than stoichiometry was deposited in an acidic solution, and the morphology of HAp depends on both the pH values of the starting solution and temperature. Ma *et al.*²⁴⁾ reported that the morphology of HAp crystals deposited by electrochemical deposition on titanium depends on the aqueous system. Furthermore, Ban *et al.*²⁵⁾ suggested that both size and shape of HAp depend on the electrolyte temperature, current density, and current loading time. With the exception of the crystal shape, a similar conclusion was drawn from this work. Besides these conditions, the morphology of crystal could be affected by the characteristics of the anodic oxide film.

Significance of polarity inversion for electrolysis

Valve metals such as titanium were electrochemically coated with calcium phosphate through the polarity inversion method (an alternating polarization technique⁸⁾). In an attempt to study the effect of the polarity inversion on the deposited materials, a constant polarity voltage was applied to the electrodes. No deposition occurred on the anode of the specimen. In contrast, a certain kind of calcium phosphate was deposited on the cathode of the specimen. Thus the deposition and none-deposition of materials was repeated through the polarity inversion method. The deposited materials could dissolve in the electrolyte, when the specimen was anode. The deposited HAp had none-stoichiometric Ca/P ratio, and its crystal was ultra fine in size. The polarity inversion method was effective in producing coatings of ultra fine HAp particles by the electrolysis of the acidic calcium phosphate solution.

On the other hand, the specimen was cathode in the traditional electrolysis method. A great deal of research²⁶⁾ has been devoted to synthesize HAp by the electrolysis in a solution. In most cases, the solution containing for Ca^{2+} and PO_4^{3-} ions at about pH 7 was used for the electrolyte. HAp almost having the stoichiometric Ca/P ratio was electrochemically deposited on a cathode surface, and it exhibited good crystallinity. An average HAp crystal size was in the micron and submicron range. Moreover, the thickness of the deposited materials was thicker than that of by the polarity inversion method. Consequently, the ultra fine HAp particles deposited by the polarity inversion method could dissolve easily in the living body, and Ca^{2+} ions could be released around the living body tissue, suggesting that these factors should enhance bone induction.

CONCLUSIONS

We studied the effect of polarity of electrode and anodized titanium oxide film on the deposited materials by electrolysis of acidic calcium phosphate solution. Within the limits of our experiment, the peaks corresponding to P^{5+} and P^{3+} binding energy were detected by XPS in the anodized titanium oxide film. No deposited materials were observed on the anode surface during the electrolysis. On the other hand, DCPD was deposited on the cathode surface at the beginning of the electrolysis. After the electrolysis time 600 s, the non-stoichiometric HAp with Ca/P=1.4 was obtained on the surface. The HAp formed on the anodized titanium had good crystallinity, and the particle size of the HAp was on the order of several hundred nanometers. The surface property of the anodized titanium is also responsible for depositing the ultra fine HAp.

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