Formation of Titania/Hydroxyapatite Composite Films by Pulse Electrolysis

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The aim of this study was to examine the formation of titania (TiO_2)/hydroxyapatite (HAp) composite films on a titanium substrate using anodic-cathodic pulse electrolysis. The TiO_2/HAp composites were coated on commercially pure titanium plates (surface area: 1.0 cm²) using pulse electrolysis in an autoclave in an aqueous solution that consisted of 0.3 mM Ca(H_2PO_4)_2 and 0.7 mM CaCl_2 and pH = 5.5 at 120°C. The pulse potentials were applied at +8.7 V vs. Ag/AgCl sat. KCl as anodic potential and −9.3 V as cathodic. The total electrolysis time was 1800 s. We examined the effects of the electrolysis cycle (60 ~ 600 s) and duty ratio on such properties of the coatings as the surface morphology, the amount of precipitated HAp, and the size of the HAp crystals. Prior to the pulse electrolysis, cathodic and anodic electrolysis experiments were also conducted. With pulse electrolysis, we could obtain TiO_2/HAp composite films with fine HAp particles dispersed uniformly on a thin TiO_2 coating. [doi:10.2320/mattrans.48.322]

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1. Introduction

Calcium phosphates, specifically hydroxyapatite (Ca_{10}(PO_4)_6(OH)_2, HAp), are of interest in bone-interfacing implant applications because of their demonstrated osteoconductive properties. Hydroxyapatite is considered to be a bioactive material and is used in the fabrication of medical and dental implants, usually in the form of a coating on a metallic substrate to compensate for its poor intrinsic mechanical properties. Many methods of forming HAp and other calcium phosphate coatings on metallic substrates have been reported (e.g., the thermal substrate method, magnetron sputtering, cathodic electrolysis precipitation, electrophoretic precipitation and sol-gel coating); however, plasma spraying remains the most commonly used method. Electrochemical coating of HAp from an aqueous solution has received considerable attention because of some advantages of the hydroprocess, such as low temperatures, and the ability to deposit on a substrate with porous surface topography, complex shape, or large surface area. Therefore, we have applied the cathodic electrolysis precipitation method in an aqueous solution containing Ca^{2+} and PO_4^{3-} to create HAp coatings on Ti substrates.

It is well known that TiO_2 ceramic has excellent biocompatibility, and many researchers have focused on its bioactivity. Furthermore, TiO_2 coatings on Ti substrates have been used to improve the adhesion between an HAp coating and a Ti substrate. From the viewpoint of bioactivity, we thought that the preparation of the TiO_2/HAp composite coating would be a more promising approach than using individual coatings of HAp or TiO_2. In previous papers on TiO_2/HAp composite films, reported methods included HAp coating on the TiO_2 substrate, composite HAp coating from a solution to which TiO_2 particles had been added and sol-gel coating using media containing HAp and TiO_2 particles.

We hoped to form TiO_2/HAp composite films on a Ti substrate using a single process, i.e., anodic-cathodic pulse electrolysis in an aqueous solution that did not contain TiO_2 particles before coating. Shirkhanzadeh used pulse electrolysis to improve the properties of HAp coatings on porous substrates. However, to our knowledge, the formation of TiO_2/HAp composite film using pulse electrolysis for the enhancement of the level of the bioactivity has not been reported. In this experiment, TiO_2/HAp composite films on Ti substrates were formed by using anodic-cathodic pulse electrolysis in an autoclave, and changing anodic and cathodic potentials, the electrolysis cycle, and the duty ratio.

2. Coating Theory of HAp and Titania by Electrolysis in Aqueous Solution

Cathodic electrolysis will induce the precipitation of HAp on the substrate with increasing pH because of the H_2 gas generation in the aqueous solution containing Ca^{2+} and PO_4^{3-}. Therefore, electrolysis at a more negative potential should initiate strong HAp precipitation. In general, H_3PO_4 dissociates into four species (H_3PO_4^0, H_2PO_4^-, HPO_4^{2-}, and PO_4^{3-}) in an aqueous solution; the proportions depend on the pH. As the concentration of PO_4^{3-}, of which HAp consists, increases drastically with increasing pH in the alkaline region, this encourages the precipitation of HAp. However, there is a possibility that strong H_2 gas generation will peel the precipitated HAp from the substrate.

It is well known, on the other hand, that anodic electrolysis coating of Ti in inorganic acid solution forms titanium oxide on the Ti substrate (anodizing). The thickness and surface morphology of the TiO_2 formed depend on the anodic potential (current density), the type of inorganic acid, and temperature, among other factors.

Accordingly, anodic-cathodic pulse electrolysis should result in a TiO_2/HAp composite coating on Ti substrates in aqueous solutions containing Ca^{2+} and PO_4^{3-}.

3. Materials and Methods

Figure 1 shows the experimental apparatus (autoclave) used to produce the TiO_2/HAp composite coatings on a titanium substrate. The aqueous solution for the electrolysis consisted of 0.3 mM Ca(H_2PO_4)_2 and 0.7 mM CaCl_2. The
pH of the solution was adjusted to 5.5 at room temperature by the addition of aqueous NaOH solution. Commercially pure titanium plates (surface area: 1.0 cm²) were used as substrates. They were wet polished with SiC emery paper (#400 grit) in advance, and dry polished with #400 SiC emery paper again, just before the coating experiment. The working electrode (Ti plate), counter (Pt coil), quasi-reference (Pt), and a thermocouple were immersed in 0.2 dm³ of aqueous solution. The electrode potential was calibrated by using the potential corresponding to H₂ gas generation at 20 and 80°C and the rest potential of Ti at 20 ~ 120°C, and is expressed as Ag/AgCl sat. KCl in this paper. A magnetic stirrer agitated the electrolyte solution during the experiments.

Before heating, the pressure in the autoclave was increased to 0.7 MPa by the introduction of Ar gas to prevent changes in the solute content caused by loss of the solution by volatilization, thus allowing higher experimental temperatures. The temperature was maintained at 120°C by an external heater. Prior to the pulse electrolysis, cathodic potential, anodic, and simple rectangular waves (anode-cathode and cathode-anode) were applied to the Ti substrates as an anodic potential of +8.7 V and changing the cathodic potential (−1.3, −5.3, −9.3 V). The pulse electrolysis experiments were carried out for 1800 s at +8.7 V anodic potential and −9.3 V cathodic. The effects of the electrolysis cycle (60 ~ 600 s) and duty ratio on the properties of the coatings were examined. The coatings were identified by using X-ray diffraction (XRD), and the surfaces and the cross-sections of the samples were observed by scanning electron microscopy (SEM).

4. Results and Discussion

4.1 Cathodic electrolysis

Typical SEM photographs, and XRD patterns for the surface of the specimens are shown in Figs. 2 and 3(d). They were electrolyzed at +8.7 V for 900 s at 120°C in the same solution as for the cathodic electrolysis. There were no differences in the surface morphology between anodized and as-polished (nonanodized) samples (e), and polishing traces remained on the surface. From the XRD analysis, we detected small peaks of TiO₂ (anatase type) on the substrate after anodizing at 120°C (Fig. 3(d)); trace peaks were detected in the anodized sample at 20°C. The anodized TiO₂ even at 120°C was so thin that we could not measure the thickness of the TiO₂ films using SEM-EDX analysis of the cross-section of the coated substrate, and the sample surface displayed the interference color (yellow-gold) uniformly by visual observation. It is thought that it is easier to form more TiO₂ on the Ti substrate by applying more positive potentials, even in neutral aqueous solutions. However, electrolysis at more positive potentials results in the dissolution or peeling of HAp precipitated by cathodic electrolysis, because of decreasing pH or O₂ gas generation, from the viewpoint of the anodic-cathodic pulse electrolysis. Therefore, we selected +8.7 V as the anodic potential for pulse electrolysis at 120°C.

4.2 Anodic electrolysis

Typical SEM photographs, and XRD patterns for the surface of the specimens are shown in Figs. 2 and 3(d). They were electrolyzed at +8.7 V for 900 s at 120°C in the same solution as for the cathodic electrolysis. There were no differences in the surface morphology between anodized and as-polished (nonanodized) samples (e), and polishing traces remained on the surface. From the XRD analysis, we detected small peaks of TiO₂ (anatase type) on the substrate after anodizing at 120°C (Fig. 3(d)); trace peaks were detected in the anodized sample at 20°C. The anodized TiO₂ even at 120°C was so thin that we could not measure the thickness of the TiO₂ films using SEM-EDX analysis of the cross-section of the coated substrate, and the sample surface displayed the interference color (yellow-gold) uniformly by visual observation. It is thought that it is easier to form more TiO₂ on the Ti substrate by applying more positive potentials, even in neutral aqueous solutions. However, electrolysis at more positive potentials results in the dissolution or peeling of HAp precipitated by cathodic electrolysis, because of decreasing pH or O₂ gas generation, from the viewpoint of the anodic-cathodic pulse electrolysis. Therefore, we selected +8.7 V as the anodic potential for pulse electrolysis at 120°C.

4.3 Anodic-cathodic and cathodic-anodic electrolysis (simple rectangular wave)

Based on the above cathodic and anodic results of electrolysis, the application of simple rectangular waves (anodic-cathodic and cathodic-anodic) was investigated to obtain TiO₂/HAp composite coatings. In the anodic-cathodic electrolysis, an anodic potential of +8.7 V and cathodic potentials of −1.3, −5.3, and −9.3 V were applied for 900 s. In the cathodic-anodic experiments, −9.3 V as cathodic potential and +8.7 V as anodic were used. Figure 4 shows changes with time of current densities corresponding to the applied potentials. Typical SEM photographs and XRD patterns for the surface of the specimens are shown in Figs. 2 and 3(f)–(i). In the anodic-cathodic waves, both TiO₂ and
HAp were obtained with all cathodic potentials. The intensity of the XRD peaks indicated that there was no difference in the amount of TiO$_2$, independent of cathodic potentials; moreover, the amount was almost the same as in simple anodic electrolysis (d). This indicates that Ti substrates were anodized to TiO$_2$ rapidly and that the TiO$_2$ could not be reduced by the cathodic potentials used in this experiment. On the other hand, the amount of HAp decreased in comparison with simple cathodic electrolysis (c). This is because it took a longer time for the cathodic electrolysis to increase pH near substrates because of the decrease in pH caused by the anodic electrolysis. That is HAp precipitation,
which is an indirect reaction, requires more time than the formation of TiO$_2$ by direct reaction.

The amount of HAp formed in the cathodic-anodic electrolysis was much smaller than in the simple cathodic electrolysis ($/C_0$ 9:3V). It was thought that this occurred because the anodic electrolysis followed the cathodic. After the cathodic electrolysis ($/C_0$ 9:3V, 900 s), the current was turned off in the middle of the anodic electrolysis ((j) 60 s anodic and (k) 300 s anodic in Fig. 4(i)), and the surface of the specimen was observed (Fig. 2(j)(k)). These photographs show that HAp decreased when the period for anodic electrolysis was increased after cathodic electrolysis. We could not establish whether peeling by O$_2$ gas generation on the Ti substrate or dissolution of HAp by decreasing pH was the main cause of the decreased HAp. We decided that the potential of $-9.3$ V should be selected as the cathodic potential for the pulse electrolysis because of the small amount of HAp precipitated at $-5.3$ V, and we selected $+8.7$ V as the anodic potential. The effect of the electrolysis cycle and duty ratio on the properties of the TiO$_2$/HAp composites was then investigated in pulse electrolysis at 120 $^\circ$C.

### 4.4 Pulse electrolysis

#### 4.4.1 Electrolysis cycle

Anodic-cathodic pulse electrolysis ($+8.7$ V and $-9.3$ V) was applied at 120 $^\circ$C for 1800 s with cycles of 60 s (anodic: 30 s and cathodic: 30 s), 120 s (60 s and 60 s), and 600 s (300 s and 300 s), keeping the duty ratio constant at 1 : 1. Figure 5...
shows the change with time of current density. SEM photographs of the surfaces of the specimens are shown in Fig. 6(a)–(c). The anodized TiO$_2$ was so thin that we could not measure its thickness accurately by SEM-EDX analysis of the cross-section, and it was estimated to be less than 50 nm. It was thought that the TiO$_2$/HAp composite film’s structure of HAp deposited on the thin TiO$_2$ films occurred because anodized TiO$_2$ films formed more rapidly than HAp in the electrolysis, and the positive potential was applied initially for TiO$_2$ formation ahead of HAp precipitation. Pulse electrolysis with shorter cycles (a) gave finer HAp particles, uniformly dispersed on the TiO$_2$ film, although the amount of HAp was very small. On the other hand, with longer cycles (c), much HAp was precipitated and the surface morphology was almost similar to that after application of a simple rectangular wave (Fig. 2(g)(h)), and the surface of the substrate could not be seen. As much TiO$_2$ was formed with cycling as by the simple anodic electrolysis, judging from XRD charts (Fig. 7). This result confirms the estimation that it took a long time to precipitate HAp and a short time to form TiO$_2$. Therefore, to create more HAp particles that are more uniformly dispersed, it is reasonable that the duty ratio should be selected as the extension of the simple cathodic time, keeping the anodic time at 30 s, rather than the 1 : 1 duty ratio used here (a).

**4.4.2 duty ratio**

From the above results, the cathodic time was increased, keeping the anodic time at 30 s, and the total electrolysis period was 1800 s. The duty ratios selected were (d) anodic: 30 s and cathodic: 60 s, (e) anodic: 30 s and cathodic: 90 s (in
Figs. 5–7). When the cathodic time was 60 s, many fine HAp particles were uniformly dispersed on the substrate, and it was found that the amount of HAp increased according to XRD chart, compared with the sample electrolyzed for anodic: 30 s and cathodic: 30 s. However, when the cathodic period was prolonged to 90 s, too much HAp was precipitated and the surface morphology was almost similar to that after the application of pulse electrolysis (anodic: 300 s and cathodic: 300 s; Fig. 5(c)), and the surface of the substrate could not be seen. However, too much HAp ((c) and (e)) might be preferable for bioactivity, because it would disturb the effect of the bioactivity of TiO$_2$. We will give detailed results of in vivo evaluations of these composite films in our next report. It should be mentioned that selecting appropriate pulse electrolysis conditions, potentials, cycles and duty ratios, gives TiO$_2$/HAp composite films, that have fine HAp particles dispersed uniformly on a TiO$_2$ film on the Ti substrate.

5. Conclusion

(1) The TiO$_2$/HAp composite films on a Ti substrate were formed by using anodic-cathodic pulse electrolysis in aqueous solutions containing Ca(H$_2$PO$_4$)$_2$ and CaCl$_2$ at pH 5.5 in an autoclave at 120°C for 1800 s.

(2) Pulse electrolysis (anodic potential: +8.7 V and cathodic potential: −9.3 V) for an anodic period of 30 s and a cathodic period of 30 or 60 s gave fine HAp particles uniformly dispersed on the TiO$_2$ film on the Ti substrate.

REFERENCES


