Calcium-Ion Incorporation into Titanium Surfaces Accompanied by Electrochemical Apatite-Deposition

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The depths of calcium-ion incorporation into a commercially pure titanium and an experimental β -type titanium alloy were determined using Auger electron spectroscopy. After the electrochemical deposition of apatite, new compositional gradients appeared in the profiles in which the Ca and P concentrations gradually decreased as a function of the depth up to 6–8 nm. The relative concentration of Ca in the outermost layer was higher than that of P. On the other hand, after the soaking in a simulated body fluid, the relative concentration of P was higher than that of Ca in the outermost layer. These results suggested that Ca ions were well incorporated into the outermost oxide layer of titanium accompanied by the electrochemical apatite-deposition on its surface.

Key words : Electrochemical deposition, Titanium, Auger electron spectroscopy

INTRODUCTION

Various coating methods of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, have been studied as a bioactive surface treatment for metal implants. We reported that the electrochemical deposition of apatite can be used to easily create a homogeneous apatite coating on substrates having complicated shapes such as dental implants, and requires simple and small devices^{1,2)}. Varying the electrochemical conditions can easily control the morphology of deposits. Both the size and the crystallinity of the needle-like apatite markedly increased with the electrolyte temperature^{3–7)}. Furthermore, we reported that the electrochemical deposition of needle-like apatites on the surface of titanium significantly increased the bonding strength between bone and titanium in the early stages of implantation^{8–10)}. Harada⁹⁾ reported that the electrochemically deposited apatite was completely converted to new bone at 9 weeks after implantation in rabbit femora. However, the bonding strength between bone and the titanium implant were maintained high. On the other hand, Hanawa *et al.*¹¹⁾ reported that calcium ions were incorporated into the titanium surface even immediately after soaking in the solutions containing calcium ions. Then, it can be assumed that calcium ions must be incorporated into the titanium surface after electrochemical deposition of apatite.

The purpose of the present study was to evaluate the calcium-ion incorporation into titanium surfaces accompanied by the electrochemical deposition of apatite using Auger electron spectroscopy (AES).

MATERIALS AND METHODS

The electrolyte was heated in a stainless steel-autoclave assembled with two electrodes, a stirring screw, a pressure gauge, a pressure valve, a thermo-couple and an electric heater. A platinum plate, $20 \times 20 \times 0.5$ mm, was used as the counter electrode. A commercially pure titanium (cpTi) plate (KS-50, Kobelco, Kobe, Japan) and an experimental Ti53.4-Nb29-Ta13-Zr4.6 (TNTZ) alloy¹²⁾ plate, $20 \times 20 \times 0.5$ mm, were employed as the working electrodes. These metal plates were ground using 600-grit to 1200-grit abrasive papers and polished with $1\mu\text{m}$ and $0.3\mu\text{m}$ Al_2O_3 powder on a metallographic polishing wheel. The electrolyte was prepared by dissolving given amounts of reagent-grade chemicals of 137.8 mM of NaCl, 1.67 mM of K_2HPO_4 , and 2.5 mM of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ into distilled water. The solution was buffered to pH 7.2 with 50 mM tris(hydroxymethyl)aminomethane [$(\text{CH}_2\text{OH})_3\text{CNH}_2$] and an adequate amount of hydrochloric acid. The electrolyte was heated at 100°C using an electric heater and agitated by a stainless steel screw. The current was maintained at 12.5 mA/cm^2 by a DC power supply for 1 hr. After loading of the constant current, the titanium plates loaded as cathodes were rinsed with distilled water and dried at 37°C in air. The deposited apatite was mechanically removed by adhesive tape and polishing cloth, and finally cleaned in acetone using an ultrasonic cleaning bath.

The surface of the specimen was characterized by AES (JAMP-10SX, JEOL, Tokyo, Japan). AES spectra in the range between 0 to 1,000 eV were measured for 1×1 mm areas. The concentrations of calcium, phosphorus, oxygen, titanium, and niobium were determined in depth by argon ion etching for 30 s at an acceleration voltage of 3 kV and an emission current of 30 mA. The etching rate was calibrated as 12.5 nm/min using Si/ SiO_2 in which the 100 nm thick layer was removed by 16 etchings. According to a previous study¹³⁾, this sputtering rate was converted to the rate for titanium oxide, 6.25 nm/min. The metal plates as polished and after soaking in a simulated body fluid (SBF)¹⁴⁾ for 24 hr at 37°C were also characterized to compare with the results of the specimen with electrochemical apatite coating.

RESULTS

Figs. 1, 2, and 3 show the AES depth profiles of cpTi without any treatment, after soaking in SBF for 24 hr, and after the electrochemical deposition of apatite at 100°C . Judging from the changes in the relative concentration of Ti and O in the depth profiles of cpTi without any treatments (Fig. 1), the surface of untreated cpTi appears to be covered with a passive layer of titanium oxide about 15 nm thick, and this thickness was similar to those of cpTi after soaking in SBF (Fig. 2) and after the electrochemical deposition of apatite (Fig. 3). There were no marked changes in

Fig. 1 AES depth profiles of the cpTi surface without any treatment.

Fig. 2 AES depth profiles of the cpTi surface after soaking in SBF for 24 hr.

Fig. 3 AES depth profiles of the cpTi surface after the electrochemical deposition of apatite at 100°C and cleaning.

Fig. 4 AES depth profiles of the TNTZ alloy surface without any treatments.

the relative concentrations of Ca and P for the untreated cpTi as a function of depth. After the electrochemical deposition of apatite (Fig. 3), new compositional gradients appeared in the profiles in which Ca and P concentrations gradually decreased as a function of the depth up to 6-8 nm and the relative concentration of Ca in the outermost layer was higher than that of P. On the other hand, after soaking in SBF (Fig. 2), the relative concentration of P was higher than that of Ca in the outermost layer. Although K and Na ions were also contained in these solutions, neither of these cations were detected in the surface layer.

Fig. 5 AES depth profiles of the TNTZ alloy surface after soaking in SBF for 24 hr.

Fig. 6 AES depth profiles of the TNTZ alloy surface after the electrochemical deposition of apatite at 100 °C and cleaning.

Fig. 7 Critical depth of the relative concentration of Ca, P, Ti, Nb, and O in the AES profiles shown Figs. 1-6.

Figs. 4, 5, and 6 show the AES depth profiles of the TNTZ alloy without any treatment, after soaking in SBF for 24 hr, and after the electrochemical deposition of apatite at 100°C, respectively. TNTZ alloy showed similar results with those of cpTi, except for the thickness of the passive layer of TNTZ after soaking in SBF (Fig. 5). After the electrochemical deposition of apatite (Fig. 6), the Ca and P concentrations

gradually decreased as a function of the depth up to 6-8 nm and the relative concentration of Ca in the outermost layer was higher than that of P. After soaking in SBF (Fig. 5), the relative concentration of P was higher than that of Ca in the outermost layer. Although alloying species of Ta and Zr were not detected, the Nb concentration increased to a depth similar to the gradation of Ti.

Fig. 7 shows the depth of the critical change in the relative concentration profiles of elements. The critical depths were determined with extrapolation in each AES depth profile shown in Figs. 1 to 6. It is suggested that the depths of the critical concentration change of Ti and O are the thickness of the passive layer and the critical depth of Ca is the penetration depth of Ca in the passive layer. Nevertheless, with and without treatment, the thickness of the passive layer of cpTi and TNTZ were about 15 nm, except TNTZ after soaking in SBF had a thicker layer about 25 nm.

DISCUSSION

The ion concentrations of the surface of titanium with various bioactive treatments have been characterized using X-ray photo-electron spectroscopy (XPS)^{11,13,15-19)} and AES^{12,20-23)}. XPS is suitable to analyze the chemical state of elements in thin layers on the surface and AES can obtain depth profiles in ultra-thin layers on the surface using argon sputtering, because XPS uses photoelectrons excited by X-rays and AES is based on Auger electrons excited by electron beams. In the present study, AES was employed to obtain depth information of calcium ion incorporation on the titanium surface accompanied with the electrochemical apatite deposition.

The thicknesses of the passive layer of titanium varied with the methods of the surface finish and their conditions. Hanawa *et al.*¹¹⁾ reported that final polishing with No.1200 SiC paper had a surface film of 4 nm. Kim *et al.*²²⁾ reported that cpTi abraded with No.400 diamond plates was covered with a titanium oxide layer about 20 nm thick. Larsson *et al.*²⁴⁾ reported that machined or electropolished titanium had thin oxides, less than 5 nm, and anodized titanium had thick oxides of 180-200 nm. It appears that the large thickness of the passive layer of TNTZ after soaking in SBF depended on the formation of Nb₂O₅. Although Nb₂O₅ was not detected by the X-ray diffraction study, it is possible that the passive oxide layer of TNTZ was a solid solution of TiO₂-Nb₂O₅, considering previous results^{25,26)}. In our previous study²⁵⁾, the oxides on the surface of TNTZ at high temperatures (1,150°C and 1,400°C) were identified as Nb₂O₅, Zr_{0.25}Ti_{0.75}Nb₂O₇, and TiO₂. It is suggested that the constituents of the alloys reacted with the oxide investments and atmospheric oxygen to form the external oxides due to the free energy of oxide formation and the concentration of each element on the metal surface. In the present study, the alloy was kept at relatively low temperatures (room temperature, 37°C, and 100°C). If the oxide that formed at these temperatures also depends on similar factors, it can be well explained that Nb was detected in relatively high concentrations in the surface oxide passive layer, because Nb existed in the solid solution of TiO₂ and Nb₂O₅. Furthermore, it is known

that Nb_2O_5 tends to be a flaky shape with apparently large volumes²⁷⁾. During the electrochemical deposition of apatite, TNTZ was kept at the same cathodic potential as the electropolishing procedure. In the cathodic reaction, the oxide of the cathode is partially deoxidized due to the production of hydrogen gas, namely the reducing process. Therefore, the growth of the oxide layer of the electrode was inhibited during the electrochemical deposition of apatite.

The penetration depths of Ca also varied with the treatment methods and conditions. Krupa *et al.*²⁸⁾ reported that the maximum concentration of Ca with Ca-ion implantation ($10^{17}\text{Ca}^{2+}/\text{cm}^2$) using ion beams occurred at a depth of about 4 nm and Ca partially penetrated into metallic titanium at about 40-50 nm deep. Ong and Lucas²¹⁾ reported that the oxides on autoclaved titanium surfaces increased from 4.5 nm to 6.9 nm after 1 week immersion in a phosphate-buffered solution. Hanawa *et al.* reported that, after immersion in Ca-containing solution, the surface was modified to form calcium-hydroxide and/or calcium titanate¹⁶⁾ and the thickness of this modified layer was only 2-3 nm¹¹⁾. As mentioned above, it is rare that an oxide layer is newly formed on the cathode during the electrochemical deposition of apatite. However, cations such as Ca^{2+} can diffuse into the oxide layer due to the coulomb potential and form calcium-titanate. As described above, K and Na ions were not detected in the surface layer of titanium and its alloy. Although K^+ and Na^+ in the electrolyte also diffused into the oxide layer, it is possible that these cations are released from the oxide layer during soaking in a solution. Since the bonding energies of K and Na to oxygen are smaller than that of calcium, these oxides are more soluble than calcium oxide.

These results suggested that Ca ions were well incorporated into the outermost oxide layer of titanium accompanied by the electrochemical deposition of apatite on its surface. Therefore, it can be expected that the oxide layer containing calcium acts as the bonding layer bonding between titanium and bone after the loss of electrochemically deposited apatite due to biological resorption.

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