

Apatite Formation on Electrochemically Treated Titanium

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A titanium oxide gel was electrochemically prepared on Ti with a cell consisting of Ti as the working electrode, Pt as the counter one, AgCl as the reference one, and an aqueous solution of 0.1 mol/L $\text{Ca}(\text{NO}_3)_2$ as the electrolyte solution. The Ti electrode was kept at 9.5V for 1 hr for oxidation and subsequently kept at -3.0V for 10 min (Ca9.5-3.0): calcium ions were expected to be adsorbed at the latter treatment. Other Ti specimen was kept at -3.0V for 10 min (Ca-3.0). Both specimens were found so bioactive as to deposit apatite in 12 hr (Ca9.5-3.0) and in 1 day (Ca-3.0) when soaked in a simulated body fluid (Kokubo solution). Calcium carbonate detected on the surface of Ca9.5-3.0 caused no harmful effects on spontaneous deposition of apatite in the fluid.

1. INTRODUCTION

When oxidized in an aqueous solution of hydrogen peroxide doped with tantalum chloride (<5m mol/L) titanium implant surface was modified to hydrated titania gel, which could derive nucleation and growth of apatite under a body environment [1]. The titanium implant can bond directly to living tissues with the apatite layer which plays a role of glue. Such apatite deposition was also confirmed in a medium or a simulated body fluid (SBF) [2], known as Kokubo solution [3]. Kim *et al.* [4] prepared the surface gel layer by treating titanium with a concentrated sodium hydroxide aqueous solution. However, the gel layer required subsequent heating at 600°C to deposit apatite in SBF. The present study was initiated to explore an alternative method of providing such gel layer able to induce apatite deposition by treating titanium implants under ambient conditions.

In the field of household industry titanium oxide protective layers are yielded by electrochemical treatment of titanium in a sulfate solution under applying a high voltage (about 50 V). Unfortunately, the layers consist of stable oxide and would not deposit apatite when soaked in SBF. Nevertheless, electrochemical reactions under more mild conditions may lead to formation of a hydrated titania gel on the surface. We then investigated correlation between the conditions of electrochemical treatment of titanium in some aqueous solutions and ability of apatite deposition or tissue-bonding ability of thus treated titanium substrates.

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2. EXPERIMENTAL

A sheet of commercially available pure type II Ti was cut into pieces of 25x5x1 mm in size. The Ti pieces were then ultrasonically rinsed with acetone prior to the chemical polishing: soaking for 3 min in a 1 mass% HF aqueous solution and subsequently for 5 min in a mixed aqueous solution of 4.2 mass% H₂O₂ and 1 mass% HF. After ultrasonically rinsed for 5 min with distilled water and dried in an oven at 40°C, they were stored in sealed polystyrene containers until use. The apparatus for the electrochemical treatment was schematically shown in Fig. 1: it consisted of a potentiostat, the Ti piece as the working electrode, a piece of Pt plate of 25x5x1 mm in size as the counter electrode, the salt bridge, and an Ag/AgCl electrode as the reference. The electrolyte in the reference electrode cell was a 3 mol/L KCl solution, and that in the working electrode was a 0.01, 0.1 or 1 mol/L calcium nitrate solution. The salt bridge was a gel in a glass tube derived from an agarose gel dissolved in a 100 mL of 0.1 mol/L KCl aqueous solution. Cyclic voltammetry was performed to give Current-Voltage (CV) curves. The voltage of the electrodes was represented by an as-measured figure: V vs Ag/AgCl = +0.205 V vs the normal hydrogen electrode. SBF was prepared by adding inorganic salts according to a specific recipe and standard procedure [3]. It was kept at 7.4 in pH at 36.5°C. The electrochemically treated titanium specimens were soaked in SBF up to 14 days. Their surface microstructure was observed by scanning electron microscopy (SEM), thin film X-ray diffractometry (CuK α : XRD), and Fourier transform infrared spectroscopy (FT-IR).

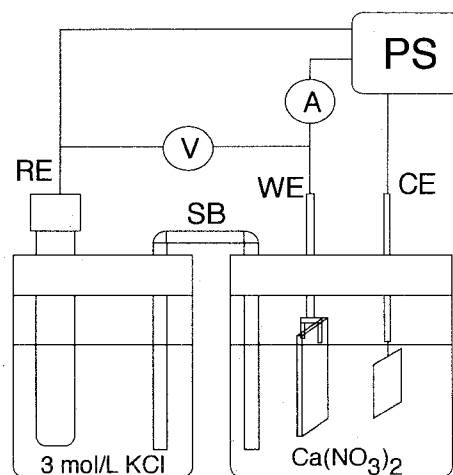


Fig. 1. A schematic representation of the electrochemical cell. RE: Ag/AgCl, WE: Ti, CE: Pt, SB: salt bridge of agarose gel/KCl. PS: potentiostat. The concentration of the calcium nitrate was varied: 0.01, 0.1, and 1 mol/L.

3. RESULTS AND DISCUSSION

3.1 CV curves in calcium nitrate solutions

A typical CV curve is illustrated in Fig. 2 showing the voltammogram obtained for the 0.01 mol/L calcium nitrate solution: the voltage was swept at the rate of 20 mV/s first from 0 to -1.5 V and up to 2.5 V, then back to 0 V, as shown by the arrows in the figure. A few peaks were observed at -1.1 V (A), -0.5V (B), 0.9 V (C), and 1.8 V (D). Each found in anodic polarization may correspond to the change in the oxidation state of titanium, yielding TiO₂•2H₂O (C), and TiO₃•2H₂O (D). In cathodic polarization, the peak may correspond to the reactions yielding Ti(OH)₃ (A) due to reduction of surface oxides, and to TiO (B).

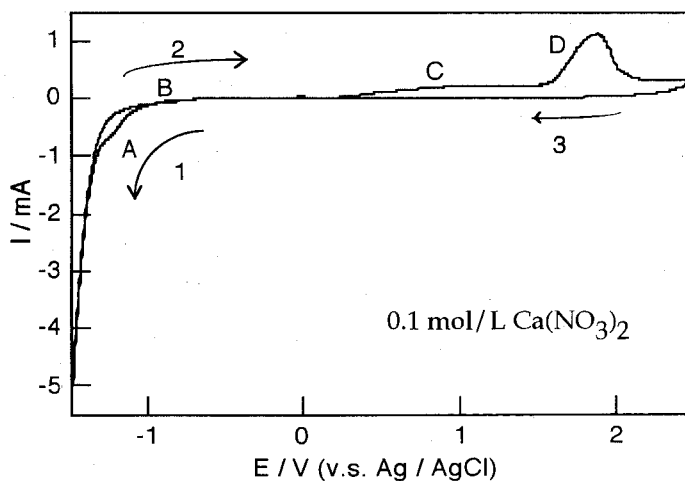


Fig. 2. CV curve for Ti: the electrolyte solution was 0.1 mol/L Ca(NO₃)₂. Sweep rate: 20 mV/s.

It is difficult, however, to identify the reactions because reactions involving oxidation-reduction of nitrogen oxide took place and their responses were superimposed to the curve [5]. Another reason was that smaller thickness of the film prevented from application of analytical techniques: X-ray photoelectron spectra for the sample polarized at constant voltages could not be deconvoluted to a component peak for Ti under each oxidation state.

CV curves for varied electrolyte concentrations were shown in Fig. 3. At 1.8 V polarization bubbling was observed on both anode and cathode, corresponding to formation of H_2 (cathode, Pt) and O_2 (anode, Ti) due to the electrolysis reaction of H_2O . The electrode current depended on three factors: one is the diffusion of the reacting species, blocking effects of bubbles, and the formation of non-conductive surface layer. The 1.8 V peak height and shoulder or the current profile, however, varied only a little with increased concentration of calcium nitrate. The results thus indicated little contributions of those factors, probably because of rigorous stirring effects due to bubbling assisting diffusion of the reactants and products to and from the electrode surface.

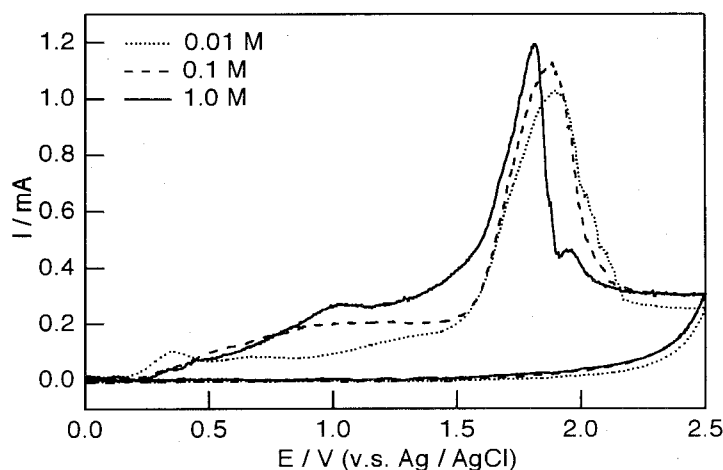


Fig. 3. CV curves for Ti dependent on the concentration of the electrolyte, 0.01, 0.1 and 1 mol/L $Ca(NO_3)_2$. Sweep rate: 25 mV.

3.2 Properties of the surface layers

The Ti specimens treated at the anodic polarizations in the range up to +2 V could not deposit apatite within 14 days when soaked in SBF. One of the possible reasons was lesser thickness of the surface oxide gel layer. Then electrochemical treatment under stronger voltage was attempted to yield a thicker surface layer. Moreover, since calcium ions released from the surface of a material to SBF were generally accepted to favor the apatite deposition, calcium incorporation was also attempted into the hydrated oxide layer by cathodic polarization after the anodic polarization. That is, with a 0.1 mol/L $Ca(NO_3)_2$ aqueous solution as the electrolyte solution several titanium specimens were first treated at 9.5 V for 1 hr and subsequently at -3.0 V for 10 min. The specimens after the first polarization were tinted purplish on the surface. This suggested the film was about 0.04 μm in thickness [6]. They were denoted as Ca9.5-3.0. Some specimens were only treated for 10 min at -3.0 V without anodic polarization. They were denoted as Ca-3.0 and also were expected to deposit calcium ions on the surface.

Rough surfaces were observable in Figs. 4 (a) and (b) for Ca9.5-3.0 and Ca-3.0, respectively, after the electrochemical treatment. Figs. 4 (c) and (d) represent the surface structures of them after soaked in SBF for 3 days where brighter and dark area were seen. Regardless to the electrochemical treatment, EDX analyses detected only calcium in the dark area besides Ti or O while both calcium and phosphorus were present in the brighter area as well as Ti and O. The images of the brighter area in a greater magnification were shown in Fig. 4 (e) and (f); both of which showed spherical agglomerates similar to those found on bioactive materials after soaking in SBF [2, 7], suggesting they were apatite. Indeed, the substance at the brighter area was apatite as indicated by the XRD patterns in Fig. 5. After soaking for 12 hr and 1 day apatite diffractions were detected for specimens Ca9.5-3.0 and Ca-3.0, respectively. According to the

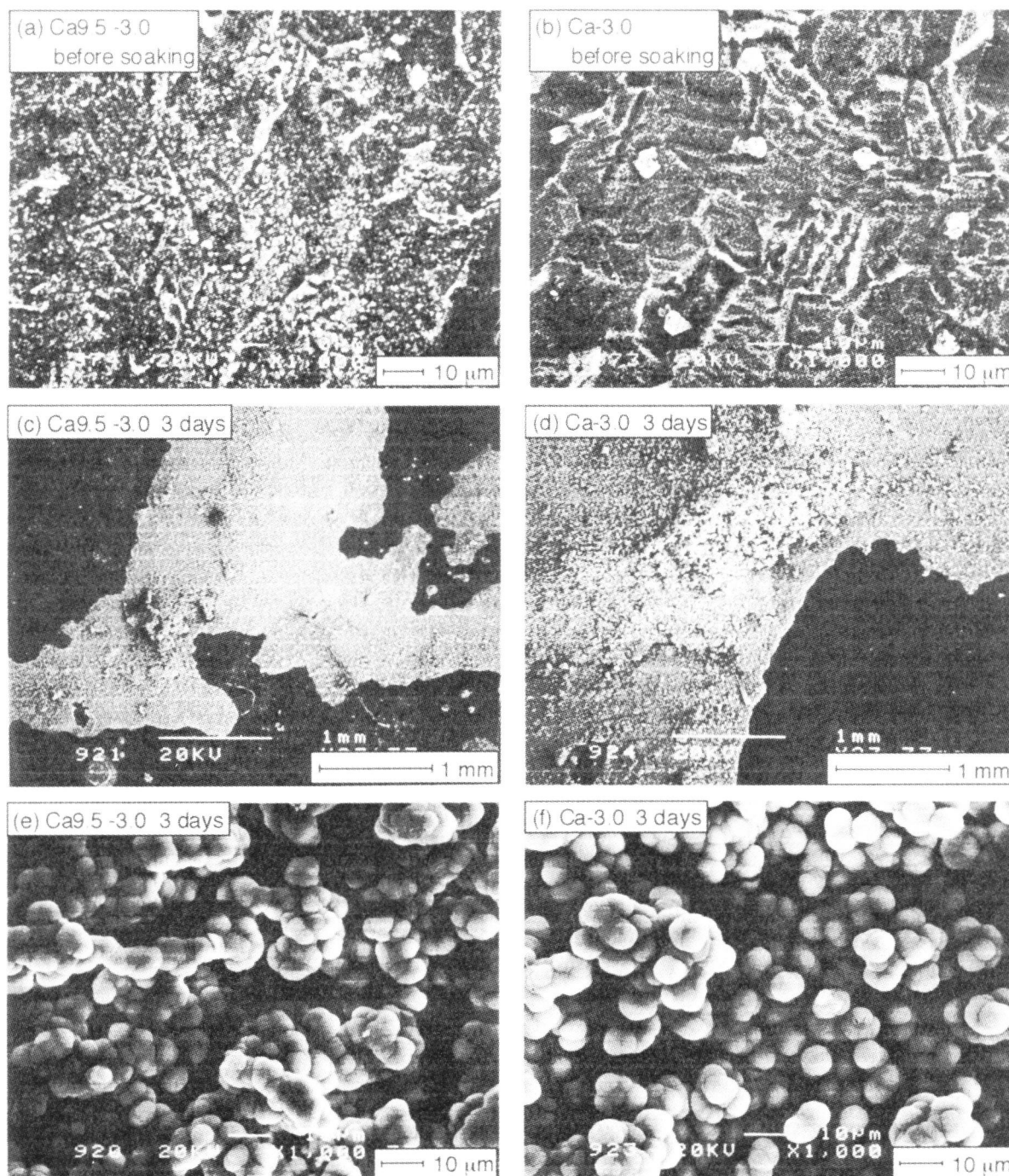


Fig. 4. SEM photographs representing surface morphology of Ca9.5-3.0 and Ca-3.0 specimens after soaking in SBF up to 3 days. The bright and dark areas in (c) and (d) resulted from bubbling at the Ti surface.

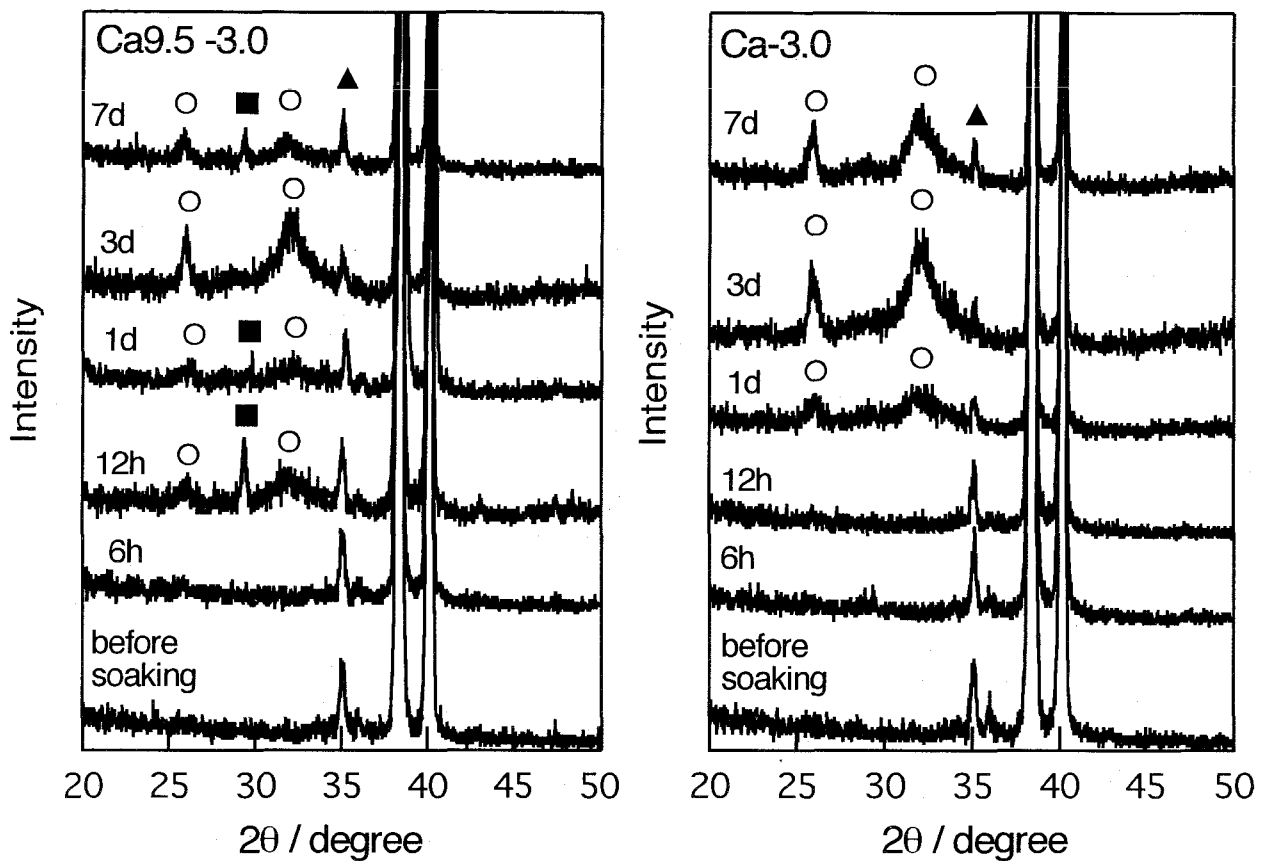


Fig. 5. X-ray diffractions for specimens Ca9.5-3.0 (left) and Ca-3.0 (right) after soaked in SBF up to 7 days. Note CaCO_3 (■) and unknown phase (▲) that did not retard apatite (O) formation.

growth of those peaks the apatite deposited continuously to the surface despite that the patterns at $\sim 29^\circ$ and $\sim 36^\circ$ in 2θ indicated the presence of calcium carbonate (calcite) and an unknown phase, respectively. The electrochemical treatment provided a surface rich in hydrated calcium ions. They might yield calcium carbonate when dried in the air or soaked in SBF due to reactions with carbon dioxide or HCO_3^- ions. Calcite form of calcium carbonate was bioactive to spontaneously yield an apatite layer *in vivo* and to strongly bond to rabbit cortical bone though it did not deposit apatite under *in vitro* conditions [8]. Strangely, however, it was also reported that sea-ear shell, containing aragonite, was active to yield an apatite layer both *in vitro* and *in vivo* whereas no bonding to the rabbit cortical bone was observed [8]. In the present case, therefore, the presence of calcite will not obstruct the deposition of apatite, but it even favors *in vivo* bioactivity.

4. SUMMARY

Cyclic voltammetry was performed at a sweep rate of 20mV/min with a system consisting of Ti as the working electrode, Pt as the counter one, and Ag/AgCl as the reference one. The electrolyte solutions were 0.01, 0.1 and 1 mol/L Ca(NO₃)₂ aqueous solutions. A few peaks appeared at -1.1 V, -0.5V, 0.9 V, and 1.8V: they were difficult to definitely assigned to specific reactions though assumption due to Pourbaix diagram was made. The electrolyte concentration affected little the profile of the CV curves. The titanium specimens electrochemically oxidized at 1.8V could not deposit apatite in a simulated body fluid (SBF; Kokubo solution). Then the specimens, denoted Ca9.5-3.0, were kept at 9.5V for 1 hr for oxidation and subsequently kept at -3.0V for 10 min: calcium ions were expected to be adsorbed at the latter treatment. The specimens were also prepared that were kept at -3.0V for 10 min, denoted as Ca-3.0. Both specimens were found so bioactive as to deposit apatite in 12 hr (Ca9.5-2.0) and in 1 day (Ca-3.0) when soaked in SBF. Calcium carbonate detected on the surface of Ca9.5-3.0 by an X-ray diffraction analysis seemed to cause no harmful effects on but even favor the bioactivity.

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