

Preparation of TiO₂ layers by spin coating-pyrolysis and *in-vitro* formation of calcium phosphate

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We have prepared nano-crystalline TiO₂ layers on a soda-lime-silica glass substrate using titanium naphthenate in order to test the formation of calcium phosphate in simulated body fluid. The TiO₂ layer was confirmed by X-ray diffraction analysis after annealing at 500°C. Field emission-scanning electron microscope and atomic force microscope observations revealed that the annealed layer undergone a homogeneous 2-dimensional grain growth, resulting in no observable increase of root mean square (RMS) roughness. After immersion in simulated body fluid, the surface of the TiO₂ layer was wholly covered with calcium phosphate as well as relatively small amounts of other ions such as Na and Cl.

Key words: TiO₂ layer, Calcium phosphate, Simulated body fluid.

Introduction

Chemical solution deposition to prepare thin oxide layers has several advantages; it is a room temperature process, it has a low processing cost, it uses inexpensive equipment and would be easy to convert to industrial scale [1-3]. Recently, sol-gel technology has become an effective and competitive alternative for oxide layer preparation.

TiO₂ layers have been prepared on many kinds of substrates by many researchers [4-8]. Among various bioceramics, TiO₂ has long been a candidate biomaterial. Many previous studies have shown that hydroxyapatite (HAP) can be successfully deposited on TiO₂ layers in simulated body fluid (SBF) [9-12].

Among various techniques, it is well known that the sol-gel process is an efficient method to prepare TiO₂ coatings from alkoxide solutions containing polymers. Generally, solutions prepared from metal naphthenates are very stable in air, in contrast to metal alkoxide solutions, which are commonly used in the sol-gel method. Presently, as far as we know, there has been little information on the bioactivity of titanium naphthenate-derived TiO₂ layers. Titanium naphthenate is more advantageous than titanium alkoxide as a starting material, in terms of stability in air and ease of handling. Preparation of the coating solution using titanium

naphthenate was easy by the addition of toluene, while a complicated procedure was needed for coating a metal alkoxide-derived solution. Furthermore, it should be noted that vaporization of additives, such as alcohol, H₂O and catalyst etc. during pre-firing and annealing might cause cracks and pores in the product layer, and thus disturb the preparation of high-quality oxide layers. By contrast, in our work, pre-firing is the process for pyrolytic conversion of titanium naphthenate into TiO₂, while the final annealing is a process for a solid-state reaction. In our previous studies [13, 14] using metal naphthenates, the annealed films exhibited smooth surface structures and it was difficult to identify cracks and pores, while defects were easily observed at the surface of the metal alkoxide-derived layers.

In biological applications, a partially deteriorated layer may present several disadvantages, such as delamination and fracture at the film-implant interface during long-term application.

In the present study, a bioactive nano-crystalline TiO₂ layer was prepared from titanium naphthenate on which to deposit calcium phosphate (CaP). The formation of CaP on the TiO₂ layer after immersion in SBF as well as the properties of the layer such as crystallinity, surface morphology and surface roughness were investigated.

Experimental

Metal naphthenates which consist of cyclopentanes or cyclohexanes, methylene chains, carboxylates and

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metals mainly have the following structure:



They were stable in air and were viscous liquids at room temperature.

A coating solution was prepared from titanium naphthenate (Soekawa Rika Co., Ltd., Japan) followed by diluting the solution with toluene (concentration: 0.03 g metal/ml coating solution) to achieve an appropriate viscosity for the deposition of smooth films.

Soda lime silica glass (SLSG) substrates were cleaned in neutral solution, immersed in H_2O_2 and rinsed in acetone. The starting solution was spin coated onto the cleaned SLSG substrates at 1500 rpm for 10 s in air. The as-deposited layer was pyrolyzed at 500°C for 10 minutes in air. The coating process was repeated three times to prepare a thick coating. The final annealing was performed in air at 500°C for 30 minutes in air by directly inserting the samples into a pre-heated tube-type furnace, followed by fast cooling.

The crystallinity of the layer was examined by X-ray diffraction (XRD, Philips International, Inc., XPERT-MPD, Netherlands) analysis. Thermogravimetric-differential thermal analysis (TG-DTA, SSC-5000, SEIKO, Japan) of the coating solution was performed. The surface morphology and the surface roughness of the annealed layer were observed by a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) and an atomic force microscope (AFM, Nanoscope Multimodel SPM, SPM-Digital Instruments, U.S.A.). All the AFM measurements were performed in air using the tapping mode with silicon probes having a ~ 260 kHz resonant frequency. The thickness of the layer (about $\sim 0.3 \mu\text{m}$) was confirmed by FE-SEM observation of the fractured cross section of the annealed layer.

The *in vitro* formation of CaP was evaluated by immersing the annealed samples in 15 mL SBF for 5 and 20 days. The SBF was prepared by dissolving NaCl, NaHCO_3 , KCl, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 and Na_2SO_4 in deionized water. To this solution, 50 mM tris-(hydroxymethyl) aminomethane $[(\text{CH}_2\text{OCH}_3)\text{CNH}_2]$ and 45 mM hydrochloric acid (HCl) were added as

buffering agents to maintain the pH of the SBF at 7.25 at 36.5°C [15].

The *in-vitro* test was performed in a constant temperature-circulating bath (Model 90, Poly Science, U.S.A.) at a temperature of 36.5°C . After immersion for 5 and 20 days, the samples were removed from the SBF, carefully rinsed with distilled water, dried at room temperature, and stored in a vacuum container.

The crystallinity of the TiO_2 layer after immersion was examined by XRD. The morphology and composition of the surface of the immersed samples were evaluated using FE-SEM equipped with an energy dispersive X-ray spectrometer (EDX) that had a Robinson type back-scattered electron detector.

Results and Discussion

Figure 1 shows the XRD pattern of the TiO_2 layer, which was prepared on a SLSG substrate and annealed at 500°C for 30 minutes. The layer after being pre-fired at 500°C for 10 minutes exhibits an amorphous character, not shown here. After annealing at 500°C , the XRD pattern exhibits the (110) reflection ($2\theta = 25.1\text{--}25.5^\circ$) of the anatase form of TiO_2 .

FE-SEM photographs of the free surface (a) and the fractured cross-section (b) for the 500°C -annealed layer

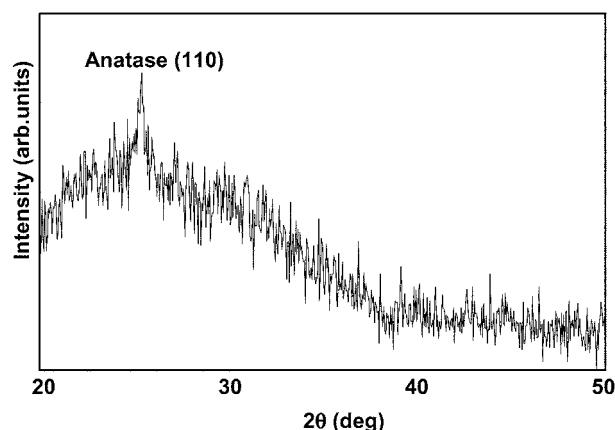


Fig. 1. XRD pattern of the TiO_2 layer, which was prepared on a SLSG substrate and annealed at 500°C for 30 minutes.

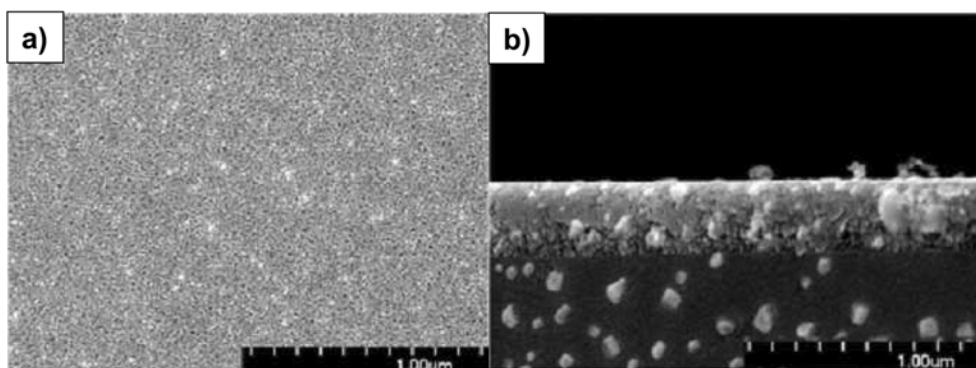


Fig. 2. FE-SEM photographs of the free surface (a) and the fractured cross-section (b) for the 500°C -annealed layer.

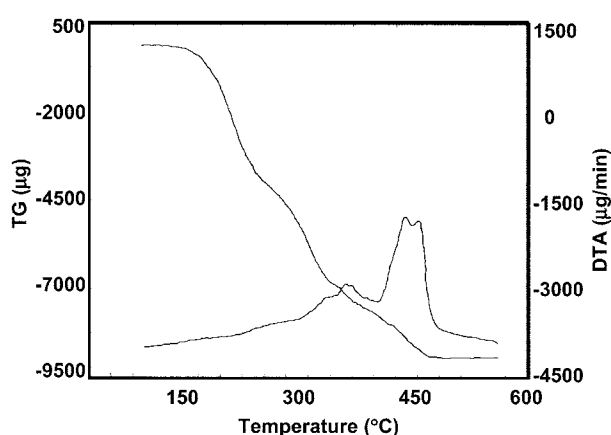


Fig. 3. TG-DTA curves of the starting solution (heating rate: 10 Kminute⁻¹) after drying at 110°C for 24 h.

are shown in Fig. 2. A densely packed grain structure became evident. Generally, using the chemical solution method of film preparation, pores and cracks due to vaporization of organics are easily recognized in the product layers. By contrast, the surface of the layer seen here was flat and smooth. Moreover, the fractured cross-section of the layer of about ~0.3 μm thickness appears dense and uniform.

According to the thermal analysis on the titanium naphthenate solution, a large weight loss corresponding to pyrolysis of titanium naphthenate began around 150°C and was completed just below 500°C, as shown in Fig. 3. TGA curves of the starting sol (heating rate: 10 K minute⁻¹) dried at 110°C for 24 h showed large exothermic peaks due to the combustion of organics which were recognized in the final stage of pyrolysis at 400–500°C. Therefore, pyrolysis of the starting titanium naphthenate solution is completed below 500°C.

To elucidate the surface roughness and micromorphology of the annealed layer, AFM analysis was performed. Figure 4 shows AFM images of the SLSG substrate (a) and the TiO₂ layer after annealing at 500°C (b). The surface of the TiO₂ layer is very smooth. It is difficult to identify the formation of the 3-dimen-

sional Na_xTiO₂ phases caused by sodium diffusion from the SLSG substrate into the TiO₂ layer [16].

Figure 5 shows an AFM top-view image and surface roughness profile of the TiO₂ layer annealed at 500°C. The layer shows a low root mean square (RMS) roughness, as shown in Fig. 5. The surface roughness of the TiO₂ layer was easily increased by three-dimensional grain growth due to sodium diffusion during annealing, which resulted in a higher RMS roughness [16]. In this case, we conclude that the increase of the surface roughness may be suppressed by a homogeneous 2-dimensional layer growth of the annealed TiO₂ layer, resulting in no observable increase of RMS roughness.

Furthermore, we studied the surface roughness characteristics of the nano-crystalline TiO₂ layer using power spectral density (PSD) curves obtained from AFM measurements. In order to investigate a larger PSD database, PSD curves obtained from combined AFM results, which were recorded over scan areas from 0.1 μm×0.1 μm and 1 μm×1 μm to 10 μm×10 μm, were investigated.

When one is evaluating surface roughness, the PSD function is used increasingly as a valuable tool for a topographical description of surfaces, such as in the case of epitaxial silicon or optical thin films. Any randomly rough surface can be considered as a Fourier series of sinusoidal waves with different amplitudes, periods, and phases. The grating equation shows that a single grating with spacing, d , causes scattering at an angle, q , according to $\sin q = \lambda/d$, where λ is the wave-

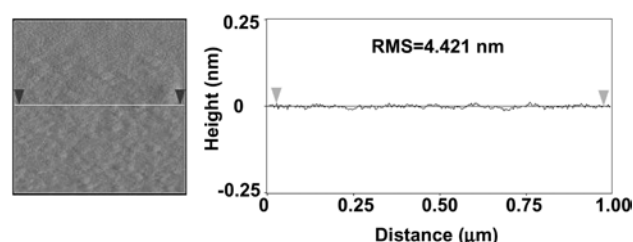


Fig. 5. AFM top-view image and surface roughness profile of the TiO₂ layer annealed at 500°C.

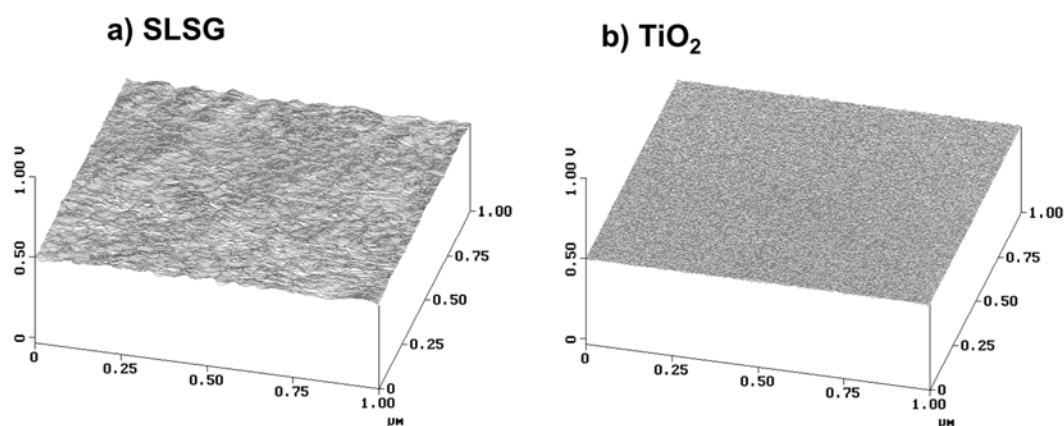


Fig. 4. AFM images of the SLSG substrate (a) and the TiO₂ layer after annealing at 500°C (b).

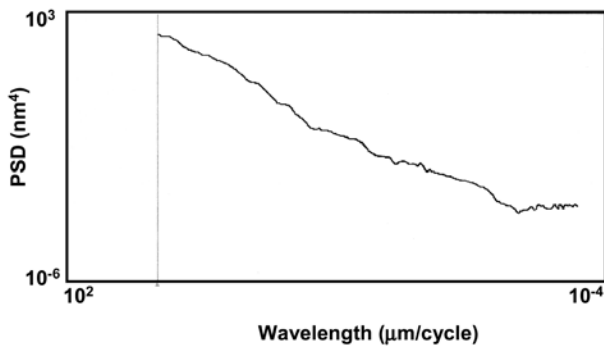


Fig. 6. PSD curve for the TiO₂ layer.

length of light. Hence, d can be considered as one spatial wavelength present on the surface, or accordingly, $f = \lambda/d$ as one spatial frequency.

For a randomly rough surface such as in the case of chemical solution-derived films, many different spatial frequencies are present. This is quantitatively expressed by the PSD curve, giving the relative strength of each roughness component of a surface microstructure as a function of the spatial frequency [17], whereas the RMS roughness as a single parameter of surface description reflects the standard deviation of all height values within the considered surface and does not provide any information on the topographical details of the surface.

Figure 6 shows the PSD function for the TiO₂ layer. The PSD of the layer displays no specific shape which one could associate with an increase in grain size. In addition, the PSD curve has a gentle gradient indicating that the layer structure has grown uniformly both in height and width.

Figure 7 shows the XRD pattern of the TiO₂ layer after immersion in SBF for 20 days. The sample shows peaks corresponding to anatase as well as HAP reflections (2θ at 25.2°–26.3° and 31°–32°).

FE-SEM and EDX analyses were performed on the samples after immersion for 5 days [Fig. 8(a)] and 20 days [Figs. 8(b) and (c)]. As shown in Fig. 8(a), partially

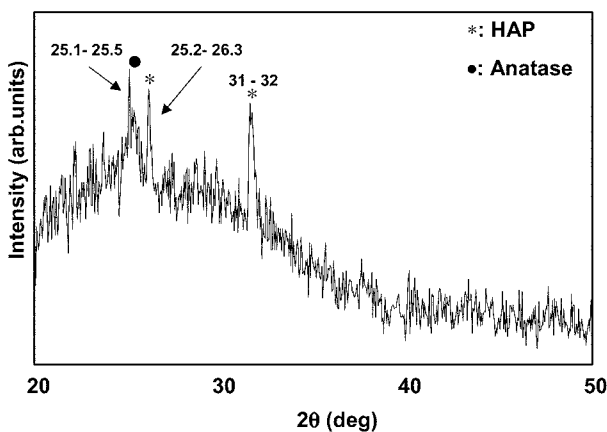


Fig. 7. XRD pattern of TiO₂ layer after immersion in SBF for 20 days.

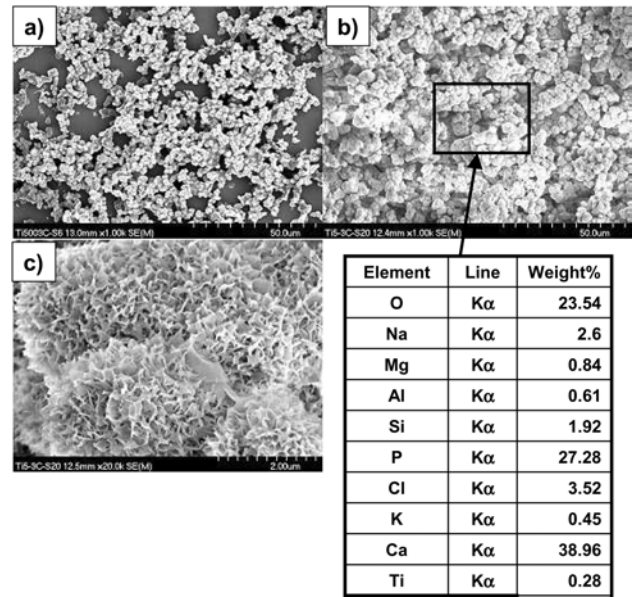


Fig. 8. FE-SEM and EDX analysis for the samples after immersion for 5 days (a) and 20 days (b) and (c).

adsorbed crystals on the TiO₂ layer were identified after immersion for 5 day. As the immersing time increased to 20 days, the TiO₂ layer surface was wholly covered with CaP as well as relatively small amounts of other ions such as Na and Cl. In order to obtain information on the micro-morphology of particles attached to the TiO₂ layer after 20-days immersion, we performed FE-SEM observation using a higher magnification. It can be seen from Fig. 8(c) that “leaf-like” particles are deposited on the surface of the TiO₂ layer. The morphology of the leaf-like particles is very similar to that of the apatite formed on the surface of bioactive glasses and glass-ceramics [15].

The calcium and phosphate ions required for hydroxy apatite (HAP) generation on the layer surface were derived from the SBF, as indicated by an increase of the formation of CaP on TiO₂. As clearly shown in Figs. 8(a) and (b), the TiO₂ layer with nano-sized crystals with a higher surface area showed a high CaP forming ability.

The first step in the nucleation of hydroxy apatite in the presence of an osteo-conductive oxide is thought to be an electrostatical-driven adsorption of Ca ions at the ionized surface hydroxyl groups onto which phosphate is subsequently adsorbed [18]. Certain hydroxyl groups, such as SiOH and TiOH, remaining in sol-gel-derived materials or absorbed during storage and immersion appear to promote HAP generation by providing the sites for CaP nucleation [15]. Peltora *et al.* [19] suggested that an increase in the sintering temperature from 400°C to 600°C decreases the amount of TiOH groups. Ti-gels annealed at 500°C formed hydroxy apatite on their surface the fastest of all coatings in their study.

Furthermore, compared to a micro- or macro-crystalline oxide layer in solution, a nano-crystalline surface

is more open for ions to be incorporated. Moreover, from an electrostatic interaction point-of-view, the surface hydroxyl groups present on or inside the oxide layer tend to attract calcium ions from the solution [20].

In our work, a nano-crystalline TiO₂ layer has been formed with titanium naphthenate. The high surface area of the titanium naphthenate-derived TiO₂ layer may be responsible for its CaP forming ability.

Conclusions

A nano-crystalline TiO₂ layer showing a high CaP forming ability was prepared from titanium naphthenate. The anatase structure was confirmed by XRD for the TiO₂ layer after annealing at 500°C. FE-SEM and AFM results showed that the annealed layer undergone a homogeneous 2-dimensional layer growth, resulting in no observable increase of RMS roughness. After immersion in SBF for 5 and 20 days, increasing with the immersing time to 20 days, the TiO₂ layer was wholly covered with CaP as well as relatively small amounts of other ions such as Na and Cl.

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