Hydrothermal Crystallization of TiO₂ Gel Films on Ti Substrates and Formability of Hydroxyapatite

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The crystallization of chemically-synthesized TiO₂ gel films by hydrothermal treatment was investigated. Pure Ti substrates were chemically treated with H₂O₂/HNO₃ to form a TiO₂ gel layer. The specimens were then hydrothermally treated with distilled water or an aqueous NH₃ solution in an autoclave at 453 K. By using NH₃, an adhesive and sufficiently crystallized TiO₂ could be synthesized on the Ti surface. TiO₂ greatly enhanced the deposition of hydroxyapatite on the surface during immersion in simulated body fluid.

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1. Introduction

Titanium and its alloys have been widely used as biomaterials for hard tissue substitutes because of their good mechanical properties and biocompatibility. However, their osteointegration is lower than those of bioactive ceramics. Therefore, various surface modification techniques have been developed to improve their osteointegration.¹–⁶ The simplest way is to synthesize bioactive ceramic films on titanium-based substrates. In general, ceramic films are deposited on substrates by such methods as plasma spraying, sputtering, and sol-gel.⁷–⁹ Although these conventional methods are well-established, they each have their shortcomings. Thus, we have sought new fabrication methods for oxide films.⁹

Surface modifications using chemical reactions have attracted great attention in the design of biomaterials.¹,² Indeed, the NaOH treatment has been clinically employed. Such wet processes are suitable for substrates with a complex shape and/or large surface area. However, a post-heat treatment at high temperature is required after the chemical treatments to induce the deposition of hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂).¹,² As is well known, mechanical properties of titanium-based alloys are strongly influenced by heat treatment above 773 K.¹⁰ In order to avoid deterioration of these properties, the post-heat treatment must be performed below this temperature.

The hydrothermal technique is a wet chemical process that is widely used to fabricate nanocrystalline oxide materials, such as BaTiO₃, ZrO₂ and TiO₂.¹¹,¹² The treatment is carried out at a temperature between the boiling point and the critical point of water. Even though it is a low-temperature process, the synthesized materials show extremely high crystallinity. Thus, the conventional post-heat treatment is expected to be replaced by a hydrothermal treatment at a maximum temperature of 473 K. The present study examines the effect of the hydrothermal treatment on the crystallization of chemically-synthesized TiO₂ gel films on Ti substrates and to investigate the formability of HAp on the surfaces by an SBF (Simulated Body Fluid) immersion.

2. Materials and Methods

Pure Ti disks (φ6 mm × 2 mm³) were chemically treated with 5 kmol/m³ H₂O₂/0.1 kmol/m³ HNO₃ aqueous solutions (2.5 mL for each specimen) at 353 K for 20 min. The specimens were placed into a Teflon-lined autoclave with an internal volume of 50 mL (8 disks per batch), which was then filled with distilled water or 1 kmol/m³ NH₃ aqueous solution up to 50% volume. The reactor was kept at 453 K for 12 or 24 h, and then allowed to cool naturally. Some of the specimens were heat-treated at 673 K for 1 h in air.

In this paper, the abbreviations “Chem-”, “Hyd (solution, period)-” and “HT-” will be used to denote chemical, hydrothermal (H₂O or NH₃, 12 or 24 h) and heat treatments, respectively. But “Chem-” will be appropriately omitted because the hydrothermal and heat treatments are always preceded by the chemical treatment.

A Hanks’ solution with an ion concentrations (Na⁺ 142.0, K⁺ 5.8, Mg⁡⁺ 0.9, Ca⁺ 1.3, Cl⁻ 145.6, HCO₃⁻ 4.2, HPO₄²⁻ 0.8, SO₄²⁻ 0.4 mol/L) nearly equal to those of human blood plasma was employed as SBF. The samples obtained were immersed in the SBF (5 mL per disk), which was maintained at 310 K. After being soaked for different periods of time up to 20 days, the samples were washed with distilled water and then dried at 323 K for 3 h. The SBF was renewed every 2 days.

Low angle X-ray diffraction (XRD, Cu Kα radiation) analysis was performed using a Rigaku RINT2500 at an incident angle of 1°. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6500F.

3. Results and Discussion

3.1 Hydrothermal crystallization of TiO₂ films

Preparation of bioactive TiO₂ films with high crystallinity was attempted at low temperature on pure Ti substrates using chemical-hydrothermal combined treatments.

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Titanium is known to dissolve in $\text{H}_2\text{O}_2$ solution as follows:\(^{13}\)

$$\text{Ti} + 3\text{H}_2\text{O}_2 \rightarrow [\text{Ti(OH)}_3\text{O}_2^-] + \text{H}_2\text{O} + \text{H}^+ \quad (1)$$

The dissolved titanium is supposed to precipitate as titanium oxide under low pH conditions. The titanium oxide film on the Ti surface was actually formed by a chemical treatment with $\text{H}_2\text{O}_2$. However, the film was not homogeneous. Wang et al. have reported that a TiO$_2$ gel layer could be obtained by a chemical treatment with a $\text{H}_2\text{O}_2$/HCl solution.\(^{2}\) They have mentioned that the addition of HCl could speed up the reaction and produce a uniform gel morphology. In our previous paper,\(^ {14}\) we confirmed the formation of similar TiO$_2$ gel films by a chemical treatment using a 9 kmol/m$^3$ $\text{H}_2\text{O}_2$/0.1 kmol/m$^3$ HNO$_3$ solution. HNO$_3$ is superior to HCl in terms of breaking passive films on the Ti surface. In the present study, a 5 kmol/m$^3$ $\text{H}_2\text{O}_2$/0.1 kmol/m$^3$ HNO$_3$ solution was used; the $\text{H}_2\text{O}_2$ concentration was diluted in order to slightly reduce the TiO$_2$ gel layer thickness.

Figure 1 shows XRD patterns of a pure Ti substrate and surface products obtained by chemical and hydrothermal treatments. It was confirmed that no reflections appeared except for those from Ti after the chemical treatment (Fig. 1(b)). However, these Ti peaks were small compared with those of non-surface-modified Ti (Fig. 1(a)). Although the XRD profiles are not shown here, broad peaks corresponding to anatase-type TiO$_2$ showed up for large samples after being subjected to the same chemical treatment for longer than 60 min. We call such TiO$_2$ with low crystallinity “TiO$_2$ gel” in this paper. Distinct reflections from anatase-type TiO$_2$ appeared after the hydrothermal treatments with distilled water and NH$_3$ solution (Figs. 1(c) and 1(d)). Normally, synthesis of oxides with high crystallinity requires high-temperature heating. By the present process, the crystallization of TiO$_2$ could be easily induced at very low temperature.

Figure 2 shows the surface morphologies of TiO$_2$ films prepared by the present process: (a) Chem-TiO$_2$, (b) HT-TiO$_2$, (c) Hyd (H$_2$O, 12 h)-TiO$_2$, (d) Hyd (H$_2$O, 24 h)-TiO$_2$, (e) Hyd (NH$_3$, 12 h)-TiO$_2$, and (f) Hyd (NH$_3$, 24 h)-TiO$_2$. The Ti surface is uniformly covered by the film showing a sponge-like morphology after chemical treatment (Fig. 2(a)). The morphology is quite similar to that obtained by the NaOH treatment,\(^ {11}\) though the present morphology is finer. The morphology is maintained during the heat treatment at 673 K (Fig. 2(b)). However, isolated micro-cracks are introduced in the films. This is caused by the contraction of the film due to dehydration. Following the chemical treatment, hydrothermal treatments using distilled water or a NH$_3$ solution were carried out to induce TiO$_2$ crystallization. An NH$_3$ solution was employed because titanium oxides are known to dissolve in alkaline solutions. In the Hyd (H$_2$O, 12 h)-TiO$_2$, the sponge-like morphology, which is composed of very fine cube crystals, is maintained. The average crystal size is measured to be approximately 10 nm (Fig. 2(c)). Extending the treatment time to 24 h decreases the film porosity (Fig. 2(d)), while the TiO$_2$ crystal size is unaffected. By contrast, the morphology changes dramatically as a result of the hydrothermal treatment with NH$_3$ solution. Cube crystals are formed in the Hyd (NH$_3$)-TiO$_2$ films (Figs. 2(e) and (f)). The average crystal size is measured to be
approximately 40 nm and 30 nm in the Hyd(NH₃, 12 h)- and Hyd(NH₃, 24 h)-TiO₂ films, respectively. Longer treatment times lead to finer crystals and decrease the size distribution. The crystals are coarser than those prepared with distilled water. It appears that the dissolution and precipitation of titanium oxides is greatly facilitated by the alkaline NH₃ solution. There are two points worth noting about the present process: i) the crystal size distribution was very narrow and ii) the micro-cracks in the TiO₂ gel disappeared after the hydrothermal treatments. Thus, uniform and crack-free crystallized films could be obtained by the present process.

In order to estimate the crystallinity of TiO₂, FWHM (Full Width Half Maximum) of the 200 peak of TiO₂ is measured with a respect to hydrothermal treatment time (see Fig. 3). The FWHM can serve as an indicator of crystallinity: sharper peaks indicate higher crystallinity. The crystallinity is seen to increase dramatically upon hydrothermal treatment, irrespective of the synthesis conditions. The FWHMs become narrower with treatment time, and the crystallinities of Hyd(NH₃)-TiO₂ are, on the whole, higher than those of Hyd(H₂O)-TiO₂. Through a 24 h hydrothermal treatment with NH₃, the crystallinity could be sufficiently increased, to the level of the fired TiO₂.

### 3.2 HAp precipitation on surface-modified Ti

A simulated body fluid (SBF) was employed in bioactivity *in vitro* testing. After soaking in SBF, precipitates were confirmed on the surfaces of all samples. The precipitates were identified to hydroxyapatite by XRD analysis. Figure 4 shows SEM images of Hyd(H₂O, 24 h)-TiO₂ (a),(c), Hyd(NH₃, 24 h)-TiO₂ (b),(d) after 2 day (a),(b) and 20 day (c),(d) immersions. Although the SEM image is not shown here, there was a vague indication of HAp precipitation on the non-surface modified Ti after 6 days of immersion. In contrast, on the surface of Hyd(H₂O, 24 h)-TiO₂ films, HAp precipitation could be confirmed after as few as 2 days (Fig. 4(a)). In the case of Hyd(NH₃, 24 h)-TiO₂, the morphology was the same as before SBF soaking (Figs. 2(f) and 4(b)). HAp precipitation could be confirmed after 4 days of immersion. A trend was also observed in the case of samples crystallized for 12 h. The dehydration from HAp induces an internal stress at the interface between the HAp and the oxide films or pure Ti substrates. Therefore, the stability and adherence of the films can be deduced from the appearance of the samples. The Hyd(H₂O)-TiO₂ film was observed to lift partially after 20 days of soaking (Fig. 4(c)). In contrast, the Hyd(NH₃, 24 h)-TiO₂ was stable in spite of much HAp deposition (Fig. 4(d)). In all samples, the surfaces were uniformly covered with HAp, and then spherical or sponge-like HAp began to precipitate. There was no marked difference in the amount deposited between samples.

Table 1 tabulates the beginning of HAp precipitation and the appearance of a surface with the immersion time in SBF for each specimen. In Table 1, “P” denotes the beginning of
HAp precipitation, “NC” no cracks, “MC” discontinuous micro cracks, “CC” continuous cracks, “Lift (p)” partial lifting, and “Lift (f)” full lifting of the films. Basically, the generation cracks in the HAp layer, such as “MC” and “CC”, which are induced by dehydration, is not a problem because the materials are used in a wet environment. In the case of Chem-TiO$_2$ and HT-TiO$_2$, the deposition of HAp is confirmed at an early stage (2 days). Then, partial lifting of the HAp and TiO$_2$ films is observed from 6 days onward. In the Hyd(H$_2$O)-TiO$_2$ films, HAp deposition can be observed from 2 days onward, irrespective of the treatment time. Hyd(H$_2$O, 12 h)-TiO$_2$ and Hyd(H$_2$O, 24 h)-TiO$_2$ are fully lifted from the substrates after 4 and 20 days, respectively. HAp deposition is confirmed for Hyd(NH$_3$)-TiO$_2$ after 4 days. The use of NH$_3$ dramatically suppresses the lifting of surface products.

As mentioned above, the post-heat treatments are always performed after the chemical treatments in order to induce HAp precipitation.\textsuperscript{2,12} Interestingly, HAp precipitation is observed on the surfaces even without high-temperature treatments. This implies that heat treatment is unnecessary for HAp precipitation in the present surface modification.

The induction ability of HAp on the surface is not that sensitive to the TiO$_2$ crystallinity because Hyd(H$_2$O, 24 h)- and Hyd(NH$_3$, 12 h)-TiO$_2$ show almost the same crystallinity (Fig. 3). The sponge-like, complex morphology composed of very fine crystals is more favorable for HAp precipitation than one composed of coarse grains. The adherence and stability of films, on the other hand, seem to be influenced by the synthesis process and the crystallinity. The weak adherence of Chem- and HT-TiO$_2$ seems to be caused by the rapid deposition of the TiO$_2$ gel (a thickness of 400 nm within 20 min). In the case of Hyd(H$_2$O, 12 h)-TiO$_2$, crystallization must be occurred close to the surface region. As a result, the TiO$_2$ film seemed to show a duplex structure composed of crystallized and non-crystallized TiO$_2$ (i.e., residual gel) layers. This duplex structure presumably increased the internal stress between the TiO$_2$ film and Ti substrate, leading to full lifting of the precipitated HAp and the TiO$_2$ films after SBF immersion. The volume fraction of residual TiO$_2$ gel could be decreased by extending the treatment time to 24 h, in which case the film lifting was delayed to 20 days. In the hydrothermal treatment with NH$_3$, the surface products were stably maintained during the SBF immersion. Using an alkaline solution increases the crystallized region from the surface and inhibits film lifting. Furthermore, no lifting or cracks were detected in Hyd(NH$_3$, 24 h)-TiO$_2$ during the tested soaking period. Although HAp precipitation was late compared to the others, Hyd(NH$_3$, 24 h)-TiO$_2$ remained stable without cracks up to 20 days. This is at least comparable to 18 days in the other samples. During the corresponding period, continuous cracks are introduced, even in Hyd(H$_2$O, 24 h)-TiO$_2$. In Hyd(NH$_3$, 24 h)-TiO$_2$, the residual TiO$_2$ gel layer seems to disappear as a result of the treatment with high-pH solution, and the crystallization is expected to proceed to completion. XRD analysis confirms that the FWHM of TiO$_2$ is nearly equal to that obtained by annealing at 673 K (Fig. 3). Thus, uniform and adhesive films can be synthesized by the present process. The hydrothermal treatment effectively improves the adherence of the TiO$_2$ films on the substrates. The above results indicate that the TiO$_2$ crystallized upon hydrothermal treatment with NH$_3$ solution over a period of 24 h is a promising coating film for osteointegration from the viewpoint of structural stability and formability of HAp.

4. Conclusions

The hydrothermal crystallization of TiO$_2$ and the formability of HAp on the surfaces were investigated. The following conclusions were reached:

1. Anatase-type TiO$_2$ was crystallized by hydrothermal treatment with distilled water or an aqueous solution of NH$_3$. The use of an alkaline NH$_3$ solution promotes the crystallization of TiO$_2$ from a TiO$_2$ gel. Hydrothermal treatment with NH$_3$ at 453 K for 24 h sufficiently increased the crystallinity to a level equivalent to that of TiO$_2$ fired at 673 K.

2. Precipitation of HAp is strongly influenced by the surface morphology: a sponge-like or complex structure is more favorable. The present surface modification of titanium promotes the deposition of HAp on the surface. A post-heat treatment at high temperature is unnecessary in the present synthesis route. Hydrothermal crystallization with NH$_3$ at 453 K for 24 h after chemical treatment is a more promising candidate for the surface modification of titanium from the viewpoint of structural stability and ability to induce HAp deposition in SBF soaking.

3. Although the crystallinity of the TiO$_2$ film is a dominant factor for film stability, the synthesis route for TiO$_2$ films is more important; the hydrothermal treatment effectively improved the adherence of the TiO$_2$ films to the Ti substrates.

REFERENCES