

Chemical/Hydrothermal Modification of Titanium Surface for Improvement of Osteointegration

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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 less than bioactive ceramics. Therefore, various surface modification techniques have been developed to improve it. The purpose of the present work was to synthesis TiO₂ and CaTiO₃ films on pure Ti substrate by chemical/hydrothermal combined treatment and to investigate formability of hydroxyapatite (HAp) on the films. Pure Ti disks were chemically treated with H₂O₂/HNO₃ solutions at 353K for 20min to introduce an amorphous-like TiO₂ layer on the surface. The specimens were then hydrothermally treated in an autoclave at 453K for 12h. Anatase-type TiO₂ and perovskite-type CaTiO₃ films with high crystallinity were obtained by the treatments with distilled water and Ca(OH)₂ aqueous solution, respectively. Cracks in the amorphous-like TiO₂ films were disappeared after the hydrothermal treatments; uniform and crack-free films could be obtained by the present process. Obtained samples were immersed in SBF (Simulated Body Fluid), which was adjusted at 310K. Precipitation of HAp on Ti was dimly observed after 6days immersion. On the TiO₂ and CaTiO₃ films, in contrast, it was obviously confirmed to precipitate after 2days.

Key words: Titanium, Surface modification, Hydrothermal treatment, Hydroxyapatite

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 less than bioactive ceramics. Therefore, various surface modification techniques have been developed to improve it [1-6]. We have investigated a chemical/hydrothermal synthesis of oxide films by using precipitation of titanium dissolved from the titanium and its alloys substrates [7]. Such wet process is suitable for the surface modification of substrates with complex shape and/or large surface area. The purpose of the present work was to synthesis TiO₂ and CaTiO₃ films on pure Ti substrates by chemical/hydrothermal combined treatment and to investigate a formability of hydroxyapatite (HAp) on the surfaces.

2. MATERIALS AND METHOD

Pure Ti disks (6mm^φ×2mm^t) were mechanically polished with #400-1500 emery papers and alumina paste. The disks were then chemically treated with 5M H₂O₂/0.1M HNO₃ aqueous solutions at 353K for 5-60min. The specimens were placed into a Teflon-lined autoclave with an internal volume of 50ml, which was then filled with distilled water or 20mM Ca(OH)₂ aqueous solution up to 50% volume. The reactor was kept at 453K for 12h, and then allowed to cool down naturally. Obtained samples were immersed in SBF (Simulated Body Fluid), which was adjusted at 310K. After soaking for various periods up to 20days, the samples were washed with distilled water and dried at

323K for 3h.

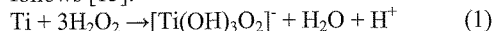
Low angle X-ray diffraction (XRD, Cu-K α radiation) analysis was performed using a Rigaku RINT2500 at an incident angle of 1degree. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6500F.

3. RESULTS AND DISCUSSION

3.1 Chemical/hydrothermal modification of Ti surfaces

There are several routes used for preparing oxide films, such as sputtering, sol-gel and anodic oxidation etc [8-12]. In this study, a preparation of TiO₂ and CaTiO₃ films with high crystallinity was attempted at low temperature on pure Ti substrates using chemical and hydrothermal treatments.

Titanium is known to dissolve in H₂O₂ solution as follows [13]:



This formula implies that a reverse reaction can be induced by pH control. The dissolved titanium is supposed to precipitate as titanium oxide under low pH conditions. Then, a chemical treatment with H₂O₂/HNO₃ solution was carried out.

Figure 1 shows the change in XRD profile of surface products on the Ti substrates prepared by the chemical treatment with H₂O₂/HNO₃ solution, as a function of the treatment time. Broad peaks corresponding to anatase-type TiO₂ are observed in addition to sharp peaks from the Ti substrates. The TiO₂ peaks become more distinct with increasing time period of the chemical treatment. This implies an increase in thickness of the films. In this paper, the TiO₂ showing such broad XRD peaks is termed "amorphous-like" TiO₂.

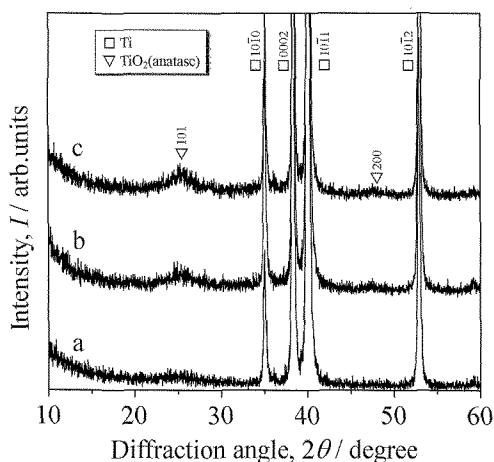


Fig.1 X-ray diffraction patterns of the product films on pure Ti substrates prepared by chemical treatment with $\text{H}_2\text{O}_2/\text{HNO}_3$ aqueous solution for (a) 10, (b) 20 and (c) 40min.

Figure2 shows the morphologies of amorphous-like TiO_2 prepared by the chemical treatment with $\text{H}_2\text{O}_2/\text{HNO}_3$ solution for 20min. Uniform film can be formed under the condition, though a small amount of discontinuous micro-cracks are observed, as shown in Fig.2(a). In the treatment shorter than 10min, the surface of Ti substrate is partly exposed. On the other hand, the treatment longer than 40min resulted in the formation of continuous cracks in the amorphous-like TiO_2 films. The cracks became more prominent when the treatment time was extended. The surface of the films shows a sponge-like morphology with large surface area irrespective of treatment time, as shown in Fig.2(b). It is

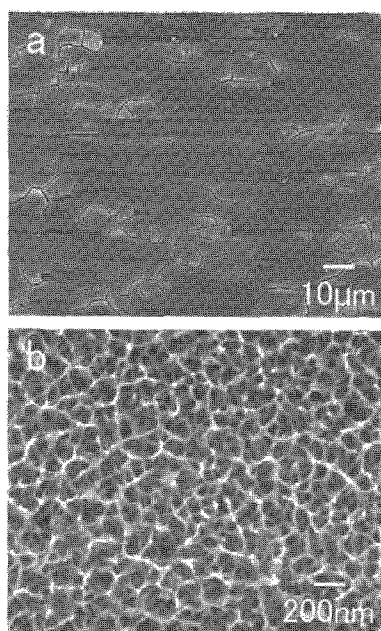


Fig.2 SEM images of amorphous-like TiO_2 on pure Ti substrate prepared by the chemical treatment with $\text{H}_2\text{O}_2/\text{HNO}_3$ aqueous solution for 20 min. (b) Magnified image of (a).

quite similar to that obtained by the NaOH treatment [1,2], though the present morphology is finer than it.

Following the chemical treatment, hydrothermal treatments with distilled water and $\text{Ca}(\text{OH})_2$ aqueous solution were carried out. In $\text{Ca}(\text{OH})_2$ solution, a saturated concentration of 20mM for distilled water was selected. The amorphous-like TiO_2 films prepared by 20min treatment were employed as precursors because the films contained only a few cracks.

Figure3 shows the XRD profiles of the oxide films obtained by the chemical/hydrothermal combined treatment. Anatase-type TiO_2 and perovskite-type CaTiO_3 are obtained by the treatments with distilled water and $\text{Ca}(\text{OH})_2$ aqueous solution, respectively. Normally, synthesis of such oxides with high crystallinity needs to high temperature heating. By the present route, the crystallized oxide films could be easily obtained at low temperature.

In the surface modification of Ti with NaOH solution, heat treatment at 873K is generally carried out following the chemical treatment. Following the most popular surface modification process, the heat treatment was carried out at 673K after the hydrothermal treatments. Mechanical properties of Ti and its alloys are strongly influenced by a heat treatment above 773K. In order to avoid deterioration of the properties, relatively lower annealing temperature of 673K was employed. Although the XRD profiles of the films after the heat treatments are not shown here, additional phases could not be confirmed to appear. All peaks except for Ti substrate become slightly sharp, however. It implies that the heat treatments improve the crystallinity of TiO_2 and CaTiO_3 . In order to estimate changes in the crystallinity of films, FWHMs (Full Width Half Maximum) in 200 peak of TiO_2 and 040 peak of CaTiO_3 were measured. And then, the average crystallite size (d) was estimated from the FWHMs with use of the Debye-Scherrer equation after peak separation and curve fitting [14]:

$$d = k\lambda / \beta \cos\theta \quad (2)$$

where λ is radiation wavelength (0.154051nm), β is the peak halfwidth, θ is a diffraction angle and $k = 0.9$. In this paper, the calculated result was shown by adding "apparent-", since the XRD profiles were taken by thin film method (2θ scan). The apparent crystallite size of TiO_2 and CaTiO_3 in each treatment state such as

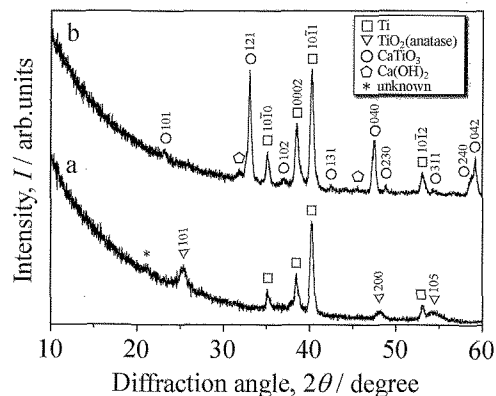


Fig.3 X-ray diffraction patterns of the product films on pure Ti substrates prepared by hydrothermal treatment with (a) distilled water and (b) $\text{Ca}(\text{OH})_2$ aqueous solution.

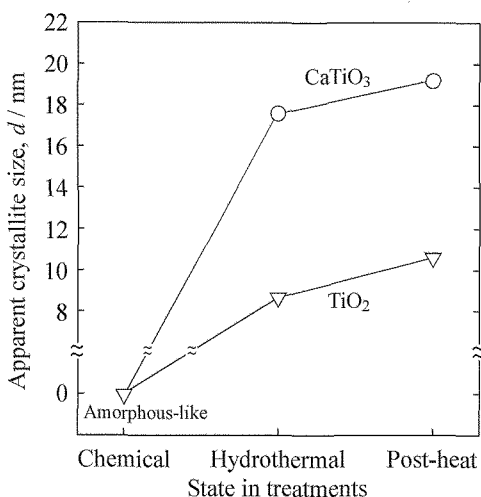


Fig.4 Apparent crystallite size of TiO₂ and CaTiO₃ in each state of chemical, hydrothermal and post-heat treatments.

chemical, hydrothermal and post-heat treatments are shown in Fig.4. The crystallite size can be utilized as an indicator of crystallinity; larger size indicates higher crystallinity of the crystals. The crystallinity is drastically increased after the hydrothermal treatment in both oxides. However, the progress of crystallization is different between them. The crystallization is drastically promoted in CaTiO₃ compared with TiO₂. Furthermore, the apparent crystallite size is coarsened after the post-heat treatment in TiO₂. In contrast, the size is not changed so much before/after heat treatments in CaTiO₃. It indicates that the crystallinity of CaTiO₃ has been sufficiently increased by the hydrothermal treatment. The TiO₂ is known to dissolve in an alkaline solution. The employed solvent in the hydrothermal treatment shows high pH, the dissolution of TiO₂ and precipitation

of CaTiO₃ seems to be taken place actively compared to the synthesis of TiO₂ with distilled water.

Figure 5 shows the morphology of TiO₂ and CaTiO₃ films synthesized by the chemical/hydrothermal combined treatments. In TiO₂ films, the sponge-like morphology is maintained as a whole, which is composed of very fine cube crystals. On the other hand, fine rectangular prism-shaped crystals are formed in the CaTiO₃ films. Cracks in the amorphous-like TiO₂ films are disappeared after the hydrothermal treatments; uniform and crack-free films can be obtained by the present process. After the heat treatment at 673K, the oxide films showed no remarkable changes in the morphologies.

3.2 In vitro bioactivity of surface modified Ti

In this study, Hanks' solution with ion concentration (Na⁺ 142.0, K⁺ 5.8, Mg⁺ 0.9, Ca⁺ 1.3, Cl⁻ 145.6, HCO₃⁻ 4.2, HPO₄²⁻ 0.8, SO₄²⁻ 0.4 [mM]) nearly equal to those of human blood plasma was employed. Obtained samples and non-surface modified Ti were immersed in the SBF, which was adjusted at 310K.

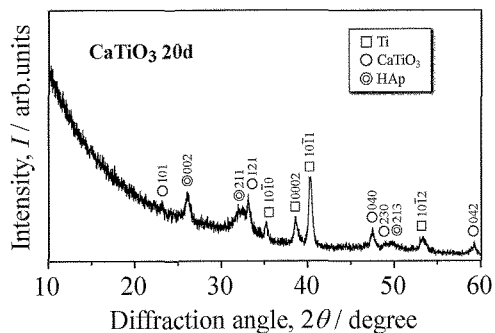


Fig.6 X-ray diffraction patterns of the product on CaTiO₃ after immersion in SBF for 20days.

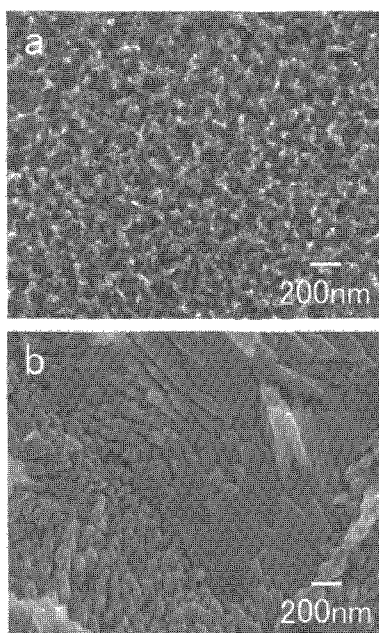


Fig.5 Surface morphologies of films synthesized by hydrothermal treatments with (a) distilled water and (b) Ca(OH)₂ aqueous solution.

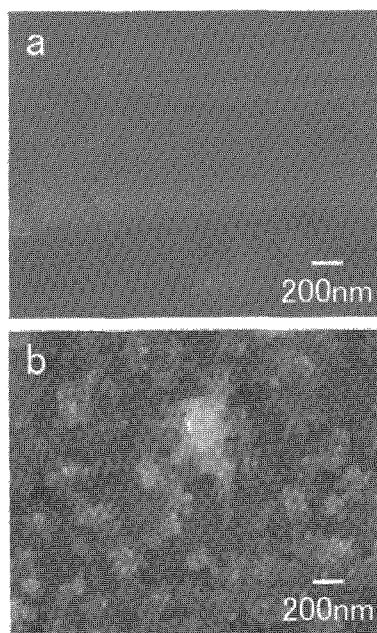


Fig.7 Surface morphologies of (a) non-surface modified Ti and (b) CaTiO₃ film immersed in SBF for 4days.

Figure6 shows the XRD profile of CaTiO_3 film after immersion in SBF for 20days, as an example. Distinct peaks corresponding to HAp are confirmed to appear in addition to the reflections from the CaTiO_3 film and Ti substrate. Precipitation of HAp could be recognized in XRD profiles after about 14days soaking in all surface modified specimens.

Figure7 shows the SEM images of (a) non-surface modified Ti and (b) CaTiO_3 films immersed in SBF for 4days. By means of SEM observation, the precipitation of HAp could be detected in early stages. Precipitation of HAp on Ti was dimly observed after 6days immersion. On the CaTiO_3 film, in contrast, it was obviously confirmed to precipitate after 2days. The precipitation was also confirmed on the hydrothermally synthesized TiO_2 films after 2days immersion in SBF, though the images are not shown here. As mentioned above, post heat treatment is generally carried out in order to introduce a precipitation of HAp. Interestingly, this result implies that the heat treatment is not necessary for the precipitation of HAp in the present surface modification of Ti. Anyway, the synthesized oxide films were confirmed to drastically promote the deposition of HAp.

Figure8 shows appearances of TiO_2 and CaTiO_3 surfaces after immersion in SBF. The oxide films are as hydrothermally synthesized. In TiO_2 film, HAp layer and oxide film are fully exfoliated from the substrate. The TiO_2 films seem to show a duplex structure composed of crystallized and non-crystallized (i.e. residual amorphous-like layers) regions. The result of

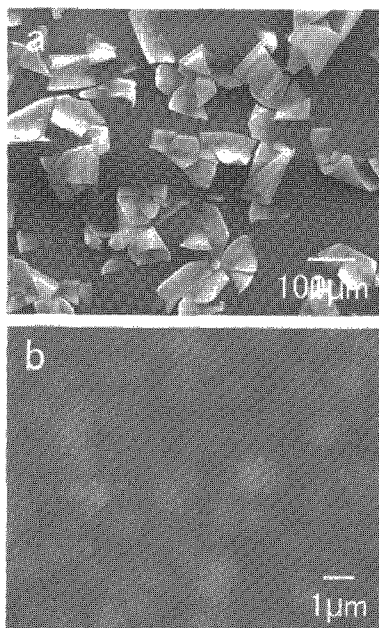


Fig.8 Appearance of (a) TiO_2 , (b) CaTiO_3 surfaces after immersion in SBF. The films are synthesized by the hydrothermal treatments.

apparent crystallite size (Fig.4) supports this conjecture. The structure must increase an internal stress between the HAp and the Ti substrate. Therefore, the HAp seems to be fully exfoliated together with the TiO_2 films. In CaTiO_3 films, on the other hand, no exfoliation of films can be confirmed in the tested soaking period. The CaTiO_3 was synthesized by the hydrothermal treatment with high pH solution. As a result, the crystallization is expected to complete perfectly. Therefore, more uniform and adhesive films seems to be obtained compared with the TiO_2 , which is prepared with distilled water. These results indicated that the CaTiO_3 prepared by the chemical/hydrothermal combined treatment is the most favorable candidate for the osteointegration from the viewpoint of the present in vitro test.

4. CONCLUSIONS

The chemical/hydrothermal modification of titanium surface and the formability of HAp on the surfaces were investigated. The following conclusions were reached:

1. Anatase-type TiO_2 films with low crystallinity (amorphous-like) was prepared on Ti substrates by chemical treatment with $\text{H}_2\text{O}_2/\text{HNO}_3$ solution.
2. Anatase-type TiO_2 and perovskite-type CaTiO_3 films with high crystallinity could be synthesized by hydrothermal treatments from amorphous-like TiO_2 precursor films.
3. Precipitation of HAp was extremely promoted by the present surface-modification of Ti.

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