Chemical-Hydrothermal Synthesis of Bioinert ZrO$_2$-TiO$_2$ Film on Ti Substrates

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The synthesis of bioinert oxide films on pure Ti surfaces by a combined chemical-hydrothermal treatment was investigated. Pure Ti substrates were chemically treated with $\text{H}_2\text{O}_2$/HNO$_3$ to form a TiO$_2$ gel layer. The specimens were then hydrothermally treated with Zr(OH)$_4$ dispersed NH$_3$/CH$_3$OH/COOH aqueous solution in an autoclave at 453 K for 12 h. As a result, Zr$_2$O$_3$-TiO$_2$ composite films were successfully produced on the surface, and the volume fraction of ZrO$_2$ in the film was found to gradually increase from the substrate to the surface. The graded Zr$_2$O$_3$-TiO$_2$ film suppressed the deposition of hydroxyapatite on the surface during soaking in simulated body fluid.

Keywords: biomaterials, bioinert, zirconia, hydrothermal treatment, titanium

1. Introduction

Titanium and its alloys have been widely used as biomaterials for orthopedic and dental implants because of their excellent mechanical properties and biocompatibility. These alloys have also been employed in bone plates/screws, which must be removed after recovery. Although Ti and its alloys are classified into bioinert materials, a conduction of living bone occurs on the surface of implanted materials that reside in the body for a long period. This can lead to fracture of cured bone in removal operations.

Recently, Zr based alloys have received much attention in the field of biomaterials comparable to Ti based alloys. The alloys do not directly bond to living bone, and they are expected to be employed as materials for easily removable implants. However, such alloys are at an early stage of development compared with Ti based alloys in biomedical application. The inhibition of bone conduction is thought to be due to the presence of a thin layer of ZrO$_2$ on the surface, which is classified as a bioinert ceramic similar to Al$_2$O$_3$. As is well known, Ti based alloys are matured materials in biomedical fields. Furthermore, various surface modifications have been developed to improve their bioactivity. If bioinert films can be synthesized on Ti alloys, their field of application will be further extended. The simplest method of achieving this is to deposit bioinert ceramic films on Ti based substrates. Ceramic films are generally deposited on substrates by methods such as plasma spraying, sputtering, and sol-gel. The coatings are generally carried out at temperatures higher than 773 K, which leads to deterioration of the mechanical properties of Ti based alloys. Recently, we have investigated the synthesis of bioactive oxide films such as TiO$_2$ and CaTiO$_3$ on Ti and its alloys using a combined chemical-hydrothermal treatment. In this process, oxide films with high crystallinity can be fabricated at low temperature through a cycle of dissolving and precipitating titanium oxides, which is activated by a hydrothermal reaction.

The purpose of the present study was to apply this method to synthesize bioinert films, including ZrO$_2$ on pure Ti surfaces. In addition, of the ability to form hydroxyapatite (HAp) on the synthesized oxide films during soaking in simulated body fluid (SBF) was also investigated.

2. Materials and Methods

Commercial pure Ti disks ($6$ mm $\times$ $2$ mm$^2$) were chemically treated with $5$ M $\text{H}_2\text{O}_2$/0.1 M HNO$_3$ aqueous solutions (2.5 ml for each specimen) at 353 K for 20 min. The disks were placed into a Teflon-lined autoclave with an internal volume of 50 ml (eight disks per batch), which was filled with Zr(OH)$_4$ gel-dispersed 5 M NH$_3$/C$_4$H$_9$OH/COOH (lactic acid, C$_4$H$_9$OH/COOH 5 M) aqueous solutions up to 50% volume. The Zr(OH)$_4$ gel was obtained by dropping a 1 M NH$_3$ aqueous solution into a 0.3 M ZrCl$_2$O aqueous solution until precipitation had completed (up to pH 9.9), followed by filtration. The concentration of the dispersed Zr(OH)$_4$ gel was adjusted to almost 0.01 M in the suspensions. The reactor was kept at 453 K for 12 h.

A Hanks’ solution with ion concentrations ($\text{Na}^+$ 142.0, $\text{K}^+$ 5.8, $\text{Mg}^{2+}$ 0.9, $\text{Ca}^{2+}$ 1.3, $\text{Cl}^-$ 145.6, $\text{HCO}_3^-$ 4.2, $\text{HPO}_4^{2-}$ 1.8, $\text{SO}_4^{2-}$ 0.4 M) nearly equal to those of human blood plasma was employed as a SBF. The specimens 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 specimens 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 K$_\alpha$ radiation) analysis was performed using a Rigaku RINT2500 at an incident angle of 1°. Scanning electron microscopy (SEM) images and line profiles of chemical composition were recorded using a JEOL JSM-6500F equipped with an EDS system.

3. Results and Discussion

3.1 Synthesis of ZrO$_2$-TiO$_2$ films by combined chemical-hydrothermal treatment

First, an anatase-type TiO$_2$ film with very low crystallinity
(TiO$_2$ gel) was produced by a chemical treatment on the Ti surfaces. Details of this treatment were reported in a previous paper. Following the chemical treatment, a hydrothermal treatment was carried out on the TiO$_2$ gel films on the Ti substrates. This technique is a wet chemical process that has been widely utilized for the preparation of nanocrystalline oxide materials such as BaTiO$_3$, ZrO$_2$ and TiO$_2$. The treatment is carried out at a temperature between the boiling point and the critical point of water (647 K, 22.1 MPa). Even though it is a low-temperature process, the synthesized materials exhibit extremely high crystallinity. In the present study, an attempt was made to cause bioinert ZrO$_2$ to form on or disperse in TiO$_2$ using this hydrothermal treatment. TiO$_2$ is known to be slightly soluble in alkaline solutions. In a previous study, highly crystallized TiO$_2$ could be obtained from the TiO$_2$ gel by the hydrothermal treatment using an alkaline NH$_3$ solution. Therefore, if an alkaline solution containing Zr ion is used, it is likely that ZrO$_2$-TiO$_2$ composite films could be produced by a similar process. Neither Zr nor ZrO$_2$ are soluble in either acidic or alkaline solutions due to their high chemical stability, whereas Zr(OH)$_4$ is known to dissolve in alkaline solutions containing hydroxyl fatty acid. Lactic acid CH$_3$(CH$_2$COOH) is one such hydroxyl fatty acid, which exists in the living body, and is often employed as an ingredient in degradable plastics. Therefore, the specimens covered with TiO$_2$ gel films were hydrothermally treated with Zr(OH)$_4$ dispersed NH$_3$/CH$_3$(CH$_2$OH)COOH aqueous solutions.

Figure 1 shows the morphologies of surface-modified specimens. Following the chemical treatment, the surface of the Ti substrate is uniformly covered by a thin film with a sponge-like morphology (Fig. 1(a)). Following the hydrothermal treatment with aqueous NH$_3$, cubic crystals are homogeneously formed on the surface (Fig. 1(b)). It appears that dissolution and precipitation of titanium oxides is greatly enhanced by this treatment. On the other hand, a non-uniform distribution of rectangular prism shaped crystals is found on the surface of the specimen synthesized without lactic acid (Fig. 1(c)). In contrast, a uniform layer of very fine crystals is formed on the surface of the specimen subjected to the hydrothermal treatment with lactic acid (Fig. 1(d)). Thus, the morphology was drastically changed by the addition of lactic acid to the Zr(OH)$_4$ dispersed NH$_3$ solution.

Figure 2 shows XRD patterns from the surface products obtained by the above treatments. In addition to peaks due to Ti, sharp peaks attributed to TiO$_2$ and ZrO$_2$ appear following the hydrothermal treatments. Normally, the synthesis of highly crystalline oxides only takes place at high temperatures. However, using the present process, such oxides are easily produced at a very low temperature. Without lactic acid (C$_{LA}$ = 0 M), the surface product is mainly anatase-type TiO$_2$, although a small amount of ZrO$_2$ is present in the form of fine particles which are presumably formed by dehydration from Zr(OH)$_4$, and which lie thinly scattered on the surface of the TiO$_2$ gel. Consequently, it seems likely that the rectangular prism shaped TiO$_2$ crystals form in regions not covered by this ZrO$_2$ powder, which leads to the non-uniform distribution shown in Fig. 1(c).

The weak reflection due to ZrO$_2$ is believed to originate entirely from the residual particles on the surface. For this reason, the film is regarded as TiO$_2$ and expressed as TiO$_2$|0 M for the sake of simplicity. On the other hand, in the film produced by the hydrothermal treatment with a lactic acid concentration of 0.37–0.87 M, distinct reflections due to ZrO$_2$ appear in addition to those from TiO$_2$ and Ti. These films are abbreviated as “ZrO$_2$-TiO$_2$|C$_{LA}$”. Some of the Zr(OH)$_4$ is thought to have dissolved into the solution by coordinate bonding with lactic acid carboxyl groups, leading to precipitation of ZrO$_2$ in the TiO$_2$ or on its surface. At a lactic acid concentration of 0.87 M, the XRD peaks of ZrO$_2$ and TiO$_2$ become very weak.

In order to determine the relative volume fractions of ZrO$_2$ and TiO$_2$, the intensity of the XRD peaks for ZrO$_2$ relative to that for all oxides was measured, as shown in eq. (1). The degree of crystallinity of each oxide was also estimated using the full width at half maximum (FWHM) of the 101 reflections. The combined results are shown in Fig. 3 as a...
function of the concentration of lactic acid. The pH values of the solutions are also indicated.

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\text{Intensity ratio of } ZrO_2 = \frac{\sum I_{ZrO_2}}{\sum I_{ZrO_2} + \sum I_{TiO_2}} \tag{1}
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The ZrO\textsubscript{2} fraction abruptly increases from \(C^{\text{LA}} = 0.19\) M and reaches a maximum at \(C^{\text{LA}} = 0.37\) M, after which it decreases slightly. The FWHM serves as an indicator for crystallinity in that sharper peaks indicate higher crystallinity. The crystallinities of both oxides are seen to decrease with increasing lactic acid concentration. Below \(C^{\text{LA}} = 0.19\) M, the FWHM cannot be measured for ZrO\textsubscript{2}. Lactic acid causes the Zr(OH)\textsubscript{4} to dissolve in the solution, but it also suppresses the dissolution/precipitation of the TiO\textsubscript{2} films due to the decrease in pH of the solution. The effect of lactic acid on the ZrO\textsubscript{2} fraction cannot be obviously confirmed at \(C^{\text{LA}} = 0.19\) M. It implies that the addition is not enough. The ZrO\textsubscript{2} fraction shows a maximum at \(C^{\text{LA}} = 0.37\) M. If the precipitated ZrO\textsubscript{2} was simply involved in the TiO\textsubscript{2} layer, its volume fraction would show a maximum for the condition \(C^{\text{LA}} = 0\) M which is most active for dissolution/precipitation of oxides. Therefore, it appears that the presence of lactic acid helps to drive the ZrO\textsubscript{2} into the synthesized film. It can be concluded that the condition \(C^{\text{LA}} = 0.37\) M is the most favorable for obtaining the largest volume fraction of ZrO\textsubscript{2} with the highest crystallinity of both oxides in the synthesized films.

Figure 4 shows a cross sectional SEM image and composition profiles for Ti and Zr along the indicated line for the ZrO\textsubscript{2}-TiO\textsubscript{2}|0.37M specimen. The vertical bright band near the center of the image is the synthesized film. The Ti content decreases gradually from the substrate towards the surface in the synthesized ZrO\textsubscript{2}-TiO\textsubscript{2} composite film, while the Zr content gradually increases, indicating a graded oxide film. The adhesive strength of such a film to the substrate is expected to be superior to that of layered ZrO\textsubscript{2}/Ti, ZrO\textsubscript{2}/TiO\textsubscript{2}/Ti or homogeneous mixed films of ZrO\textsubscript{2} and TiO\textsubscript{2}.

3.2 HAp formation on ZrO\textsubscript{2}-TiO\textsubscript{2} films during SBF soaking

A simulated body fluid (SBF) was used for bioactivity in vitro testing. After soaking in the SBF, precipitates were observed on the surfaces of all specimens. After 14–20 days soaking, broad peaks from the precipitates began to appear in the XRD spectrum, and they could be assigned to HAp. SEM observations were used to monitor the growth of these HAp precipitates from the incipient stages up to 14 days soaking. Figure 5 shows SEM images of specimens after soaking in SBF. Cotton-like spherical precipitates are observed on the non-modified Ti surface and the TiO\textsubscript{2} at the horizontal line for the specimen treated with Zr(OH)\textsubscript{4} dispersed-5 M NH\textsubscript{3}/0.37 M CH\textsubscript{3}CH(OH)COOH solution.

Fig. 3 Intensity ratio of ZrO\textsubscript{2} XRD peaks and FWHMs of 101 reflections for ZrO\textsubscript{2} and TiO\textsubscript{2} as a function of the concentration of lactic acid in the hydrothermal treatment. pH values of the solution are also indicated.

Fig. 4 Cross sectional SEM image and composition profiles for Ti and Zr at the horizontal line for the specimen treated with Zr(OH)\textsubscript{4} dispersed-5 M NH\textsubscript{3}/0.37 M CH\textsubscript{3}CH(OH)COOH solution.

Fig. 5 Surface morphologies of TiO\textsubscript{2}|0M (a), (c), and ZrO\textsubscript{2}-TiO\textsubscript{2}|0.37M (b), (d) after immersion in SBF for 4 days (a), (b) and 6 days (c), (d), respectively.
immersion, respectively,\textsuperscript{19,20} and the surfaces of oxide film appeared coarser than the present ones. Fine complex surface structures have been reported to promote the deposition of HAp during SBF soaking.\textsuperscript{24} Since HAp formation occurs face structures have been reported to promote the deposition formation of HAp on these surfaces during SBF soaking were by a combined chemical-hydrothermal treatment and the modification has considerable potential for suppressing direct bonding to living bone, and it is expected to be applicable to easily removable implants made from existing Ti alloys.

4. Conclusions

The synthesis of bioinert ZrO\textsubscript{2}-TiO\textsubscript{2} films on Ti surfaces by a combined chemical-hydrothermal treatment and the formation of HAp on these surfaces during SBF soaking were investigated. The following conclusions were reached:

1. ZrO\textsubscript{2}-TiO\textsubscript{2} composite films could be synthesized on Ti surfaces by hydrothermal treatment with Zr(OH)\textsubscript{4} gel-dispersed NH\textsubscript{3}/CH\textsubscript{3}CH(OH)COOH aqueous solution after chemical treatment with H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3} aqueous solution. Some of the Zr(OH)\textsubscript{4} was found to dissolve in the solution by coordinate bonding with lactic acid carboxyl groups, leading to the precipitation of ZrO\textsubscript{2} in the TiO\textsubscript{2} or on its surface. Both the ZrO\textsubscript{2} volume fraction and the crystallinity of the oxides were highest for C\textsubscript{LAC} = 0.37 M in the hydrothermal solution.

2. Very fine crystals of ZrO\textsubscript{2}-TiO\textsubscript{2} were homogeneously formed on the surface by the hydrothermal treatment with lactic acid. The synthesized film had a graded structure of ZrO\textsubscript{2} and TiO\textsubscript{2}, with TiO\textsubscript{2} content gradually decreasing from the substrate to the surface, while the ZrO\textsubscript{2} content increased.

3. The present ZrO\textsubscript{2}-TiO\textsubscript{2} films suppressed the precipitation of HAp on the surfaces regardless of the fine morphology. Therefore, this method has a large potential for inhibiting direct bonding to living bone, and can be applied to easily removable implants made from existing Ti alloys.

REFERENCES