Preparation and characterization of nanostructured titania for biomedical application

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Introduction

I Bioactivity and apatite-forming ability

The defects and replacements of organs and tissues of the human body are a very frequent occurrences due to the infection, disease or health problems [1]. The above problems can be overcoming through the clinically applicable treatment or reconstruction methods using various biomaterials with excellent osteoconductive, tissue procompetitive and osteoinductive properties [2, 3]. It was most desirable for implant materials to possess the bone-bonding ability with the surrounding hard tissues and perform the expected biological functions. Such superior bone-bonding ability exhibited by direct contact between the living bone and the implant can be referred as bioactivity, and is expected to improve not only the initial fixation of the implant device but also the long-term function.

Some ceramic biomaterials categorized as bioactive materials exhibit the bonebonding ability. They included bioactive glass (Bioglass[®]), glass-ceramics and composites, hydroxyapatite and other resorbable calcium phosphates [4-6]. The first discovery of bioactive glass containing sodium oxide (Na₂O), calcium oxide (CaO), phosphorous pentoxide (P₂O₅) and silica (SiO₂) was made by Hench et al. [7] in 1971. The ability to regenerate a bond with the surrounding tissues and bones constitutes an important factor of bioactive glass. In fact, Bioglass[®] can bond to the host bones or tissues via the hydroxyapatite layer induced by the dissolution of bioactive glass and subsequent formation of hydrated silica gel layer on the surface [6, 7]. Soluble silica, calcium ions and phosphate ions were dissolved from the bioactive glass and can improve the osteogenic properties with the surrounding bone matrix and tissues [8]. Several kinds of bioactive glass containing the conventional silicates (Bioglass[®] 45S5), borated-based glasses [9-13], and phosphate-based glasses [14-17] have been reported in the recent years.

On the other hand, alumina ceramic and zirconia ceramic are categorized as bioinert ceramics which have been used in the prosthetic and dental application due to their excellent performance in the mechanical properties such as hardness, resistance and wear behavior [18, 19]. Though they both exhibited excellent mechanical performance, the above bioinert ceramics showed the weak bonding ability with surrounding tissues [20] when they were inserted into the body. Hydroxyapatite is the most widely used calcium phosphate-based bioceramics. They have the similar inorganic phase with the mineralized tissues as well as show excellent biocompatibility [21, 22]. An important indicator of the bioactivity of bioactive materials is their ability to form bone-like apatite layers [23] on their surface after being soaked in Kokubo's simulated body fluid (SBF), which has ion concentrations similar to human blood plasma.

The present study is about the surface modification to provide metallic biomaterials such as titanium and its alloys with bone-bonding ability. In the next section, the recent biomedical application of metals will be introduced briefly.

II Titanium and its alloys for biomedical application

Recently, biomedical implants and devices have assumed great attention in the application of dentistry due to the rise in the aging population or the growing in the osteoporosis-related fracture among people of all age [24, 25]. Commercially pure titanium (cpTi) and its alloys are widely used in biomedical implants and reliable devices owing to their superior mechanical properties such as high fracture and corrosion resistance, together with adequate strength [25-29]. In addition, the Ti-based implants are considered to have the acceptability with bony tissues in the human environment due to their low electrical conductivity [29]. Some elements such as niobium (Nb), zirconium (Zr), and (Ta) have been developed for fabrication of the orthopedic implants with better mechanical property because the existence of important alloying component [30-33]. Unfortunately, the above-mentioned metal implants cannot attach and bond to the bony tissue without any modification because they are categorized as the bioinert materials [34-36]. The implantation failure is determined when the metal implants fail to form firm bonds with the bony tissues.

To overcome the failure of implantation, one attempt was to improve the fixation of metal implants with the bony tissue [37]. For example, the rough surface of metal implants has been pointed out according to Cochran et al. [38] to improve fixation between metal and the surrounding tissues or bones by acid-etching methods [38, 39]. It has been demonstrated that the roughened surfaces of metal implants have improved contacts with bony tissues than the smooth surfaces. However, it still needs a long period of time for the metals after the implantation to bond with the surrounding tissues, and the bonds between implants and tissues are weak.

To further develop the bone-bonding ability of metal implants, hydroxyapatite layers have been applied to cover the implants by the plasma spraying and sol-gel method [40, 41]. Unfortunately, the hydroxyapatite layers obtained by the above-mentioned way tend to peel off the implant surface after the long-term implantation and they cannot be regenerated after peeling off. Thus, a lot of surface modifications have been applied to provide the surface of titanium or other metal materials with the *in vitro* apatite-forming ability. In the following section, the current status of the *in vitro* apatite-forming ability of titanium or its alloys will be introduced.

III In vitro apatite-forming ability of titania and titanates

The characteristic property of titanium must be relied on the titanium oxide layers on its surface, which was the first time to be indicated by Tengvall et al. [42]. Except for a coating layer of hydroxyapatite, crystalline titania polymorphs (anatase and rutile) were recognized as the common bioactive ceramics layers that induced bone-like apatite formation in SBF as described below. Titania have been prepared on the surface of silica glass [43] or mixed with bioactive glass [44] which have been proved to induce apatite deposition after being soaked in SBF for more than 3 d. The surface structure of deposited layers on metallic implants is highly relied on the treatment process.

Chemical modifications on the titanium substrate with hydrogen peroxide (H_2O_2) solution can lead to the formation of amorphous titania layers on the surface [45-48]. This kind of amorphous titania layers can transfer to anatase layers after heat or aging treatment, which can induce apatite deposition within 5 d. Sol-gel methods have been reported to generate the titania gel layers on the surface of metal substrate by Peltola et al. [49, 50] and Uchida et al. [51], and their apatite deposition have been shown in their reports. As described by Uchida et al. [51], the anatase layers deposited much apatite particles due to small lattice mismatching between anatase and apatite crystal. Either heat treatment alone or combining other methods like alkali or acid treatment [51-53] have been employed to obtain titania layers on the surface of titanium and its alloys.

Kokubo's group [54] employed 10 M NaOH aqueous solution for alkali treatment on the titanium alloys. They further optimized the treatment conditions, 3-15 M NaOH aqueous solution at 60 or 80°C for 1-7 days and subsequent heat treatment at 500-700°C for 1h. They reported that the as-prepared titanium alloys with 5 M NaOH and thermal treatment at 600°C can get optimum rate of apatite deposition in SBF [55]. The alkali treatment can lead to the formation of sodium titanate hydrogel layers on the surface, and Na ions of these sodium titanate hydrogel layers can exchange with H_3O^+ ions in SBF to form Ti-OH groups. Those Ti-OH groups induced the nucleation of apatite on the surface [52-55]. Same modification with the alkaline solution also was applied on the tantalum and zirconium metals [56-59]. The induction time for apatite deposition on the surface of various substrates modified with various preparation methods was summarized in Table. 1. However, the significant issue of the alkali treatment was that the formation of Ti-OH groups was dependent on the chemical stability of sodium-involved layers on Ti, Ti6Al4V, Ta and Zr substrate. Indeed, thermal treatment was involved in most of surface modifications. This kind of heat treatment was considered to destroy the Ti-OH groups on the surface [43].

In spite of the bioactivity of titanium, its alloys and other metals subjected to surface modifications according to the above description, better surface modifications to produce bioactive layers with further enhancement *in vitro* apatite formation and bioactivity are still needed for biomedical applications.

IV Methods for improving bioactivity and antibacterial property of titania

For improving the success rate of implantation, the following strategies have been proposed to improve the bioactivity and antibacterial property of titania:

1. Surface topography related to the degree of roughness of titania layers

Chang et al. [60] pointed out previously that titania layers with porous surface morphology is related to the cell adhesion, proliferation and differentiation. Furthermore, it has been shown that cell adhesion to the material is strongly related to surface roughness [61]. On the other hand, the surface with microtopography or latterly nanotopography [62, 63], or surface with high surface to volume ratio [64] have been documented strongly affected the cell adhesion. The conclusions of the above discussion were that rough titania surface or titania with nanostructures on its surface were proved to have enhanced cell adhesion or bone growth. Therefore, when the titania layers are prepared with the mentioned surface structures, the similar *in vivo* behavior of them is expected to obtain. In this regard, the titania layers with broad kind of surface structures should be tried to prepare and discuss their bioactivity.

Considering the above conclusions, the titania nanostructures are expected to be synthesized on the surface of metal implants, and *in vitro* bone-like apatite-forming ability of titania nanostructures is also promising to investigate.

2. Titania layers with exposed high surface energy facets

Titania with a higher surface energy and highly reactive facets also attracted much research interest [65-67]. The photocatalytic activity of titania layers with exposed high surface energy have been explored in many reports. Some researchers, for example, Yang et al. [65] and Ohno et al. [66] have proposed that for the different atomic arrangements on facets with higher surface-free energy, such as anatase {001} facet (0.90 J/m²) and rutile {011} facet (1.58 J/m²), which lead to the dislocation of electrons and holes, the dislocation phenomena may modify or promote their photocatalytic property. As pointed out by Sutiono et al. [67], they strongly insisted that titania layers consisting of anatase and [101]-oriented rutile have enhanced photocatalytic activity. It can be confirmed that titania provided with exposed high surface energy was expected to improve their activity. The surface energies for various facets of rutile phase titania computed from periodic discrete Fourier transform (DFT) calculations have been reported as follows: it increases in the order of E_{surf} (110) $< E_{surf}$ (100) $< E_{surf}$ (101) $< E_{surf}$ (001). The most commonly available rutile would be one of the stable facets with a lower surface energy, such as rutile {110} (0.60 J/m²) [68]. We [69] have previously synthesized titania layers with rutile specific surface facets on titanium substrate via chemical treatment, and discussed their ability to induce apatite *in vitro*. They indicated that the excellent apatite-forming ability of the titania with exposed rutile (101) plane was due to the small lattice mismatching between rutile (101) plane and apatite. There is one important problem that has not been solved: how to prepare pure rutile with exposed (101) plane on the surface of metal implants. Therefore, it is very promising to prepare pure rutile layers with specific facets like {101} facets for getting the improved bioactivity.

3. Titania layers incorporating antibacterial agents

When metal implant was entered into the human condition, diseases were highly possible to occur due to the subsequent accumulation of bacteria on their surface [70]. Therefore, the titania layer is highly desirable to prepare for offering the antibacterial activity and stopping the occurrence of infection on the implants. Organic [71] and inorganic agents [71-77] have been used to enhance the antibacterial property of the implants. As indicated by Brayner et al. [78], inorganic agents have an enhanced safety

and stability when they were compared to organic antibacterial agents. The inorganic metal elements such as silver (Ag) [72, 73], copper (Cu) [74, 75] and zinc (Zn) [76, 77] have widely used for antibacterial application due to their excellent stability, and broad-spectrum antimicrobial property. Dizaj et al. [79] have reported the antibacterial property of metal nanoparticles, and indicated the particle size of metal nanoparticles was strongly related to the antibacterial property.

On the basis of the above knowledge, an attempt for improving the success rate of implantation of metal implants was to incorporate antibacterial inorganic metal particles on the surface of titania layer, which were proved to be bioactive. Moreover, it is highly possible that titania layers could provide higher bioactivity when they exist together with inorganic metal particle with smaller size.

V Structure of the present thesis

Chapter 1 describes a simple treatment at low temperature to prepare rutile nanorod arrays on the titanium substrates. The detailed approach involved a chemical treatment in the treating solution at 80°C for 3 days and followed aging treatment in the ultra-pure water at 80°C for 1 days. As-received commercially available pure titanium substrates were ultrasonically cleaned in ultra-pure water and acetone, respectively. After the treatment, the highly ordered rutile nanorods were formed on the surface of titanium substrates. The surface morphology and structure of formed titania layers on the substrates were modified by changing the concentration of titanyl sulfate in treating solution. The possible mechanism for the formation of rutile nanorods on the surface of titanium substrates was proposed.

Chapter 2 describes the facile chemical approach to fabricate titania layers on the Nb, Zr, Ta and Ti6Al4V alloy substrates. In the chemical approach, titania layers were formed on the Nb, Zr, Ta and Ti6Al4V alloy substrates by soaking them in treating solution. After the chemical treatment, rutile layers with exposed (101) plane were formed on the surface of Ta and Ti6Al4V alloy substrates. However, Nb substrate can deposit the anatase layers on the surface after the chemical treatment, no deposited layer can be obtained on the surface of Zr substrate. The influence of substrate on the formation of titania layers was discussed. Besides, the possible growth model for anatase layers on Nb substrate was proposed in this chapter.

Chapter 3 describes the *in vitro* apatite-forming ability of rutile layers prepared on the cpTi substrate and Ti6Al4V alloy substrate. Soaking in SBF for various periods was employed to examine the *in vitro* apatite deposition behavior of rutile nanorod arrays on the cpTi and Ti6Al4V alloy substrate. Rutile layers on the cpTi and Ti6Al4V alloy can deposit apatite in SBF within 1 d. The behavior of apatite nucleation and growth on rutile nanorod arrays for the cpTi and Ti6Al4V alloy substrates was investigated.

Chapter 4 describes the photo-deposition method for fabricating the silver (Ag) particles on the rutile nanorod arrays. The silver nitrate solution (AgNO₃) was used to deposit the Ag particles on the rutile layers under ultraviolet (UV) irradiation. The photo-

deposition behavior of Ag on rutile layers and cpTi substrate was investigated depending on the photo-deposition time. The effect of various metallic substrates (cpTi, Zr, Nb and Ta substrates) on the photo-deposition behavior was discussed.

| | Table 1 Induction time for apatite form | iation in Kokubo's SBF from publ | lished articles (w: we | ek; d: day) |
|---------------|---|----------------------------------|------------------------|----------------|
| Substrate | Preparation Method | Surface Structures | Induction Time | References |
| | Heat (750 °C) | | 2 w | [48] |
| | $H_2O_2 + Aging / Heat$ | Anotoco | rc C | [07][97][97] |
| | Sol-gel | Allalase | n 7 | [ك+] [0+] [C+] |
| Titanium | Sol-gel + Heat | Titania | Within 2 w | [50] [51] |
| | Sol-gel + Aging | | 2 d | [50] |
| | NaOH + Acid | Hydrogen Titanate | 1 d | [63] |
| | NaOH + Acid +Heat | Hydrogen Titanate | 1 d | [دد] |
| Т. С АТАТ | NaOH (10 mM) + Heat (600 °C) | Sodium Titanate + Rutile | 4 w | [54] |
| 110A14 V | NaOH (5 mM) + Heat (600 $^{\circ}$ C) | Sodium Titanate | 3 d | [55] |
| Toutolism | NaOH (0.2/0.5mM) | Sodium Tantalate Hydrogel | Within 1 w | [56] |
| 1 מוונמו חווו | NaOH (0.2/0.5mM) + Heat (500 °C) | Crystalline sodium tantalates | 1 w | [57] |
| Zirconium | NaOH (5 mM) | Hydrated Zirconia | 4 d | [59] |

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Chapter 1

Chemical deposition of rutile nanorod arrays on titanium substrates from titanyl sulfate and hydrogen peroxide solution at low temperature

1.1. Introduction

The preparation of nanometer-scale titania in form of rods [1-4] and tubes [5, 6] has been studied in a number of reports. In particular, titania nanorod arrays have attracted much attention for their specific properties like excellent photochemical stability and high biocompatibility as photocatalytic devices and biomedical implants [1-4]. For example, Wu et al. [1] have fabricated TiO₂ nanorod arrays on the titanium substrate via an acid pretreatment at 60°C and a subsequent chemical oxidation method at 80°C, and they reported that those titania nanorods showed extremely high photocatalytic activity.

Anatase, rutile and brookite are three kinds of titania crystal phase. Rutile phase has been prepared by Ohno et al. [7] for the photocatalytic oxidation and reported that its oxidation was more active than anatase. The enhanced efficiency for dye-sensitized solar cells of rutile phase have been reported by Lv et al. [3]. In addition, current studies [4, 8] for in vitro apatite deposition have emphasized the importance of rutile. Wu et al. [8] proposed that the complicated surface morphology and nanosized rutile crystallites can induce the apatite in vitro effectively. For the above reason, further work is still required to develop a detailed understanding of bioactivity, focusing on pure rutile layers.

A hydrothermal method at 160°C involving titanyl sulfate (TiOSO₄) was developed to fabricate the titania polymorphic layer containing anatase and rutile on the surface of commercially available pure titanium (cpTi) plates with H₂O₂ pre-treatment, and in vitro apatite deposition of titania polymorphic layer have been demonstrated [4, 9] by soaking them in Kokubo's simulated body fluid. However, the above hydrothermal method have a limit in producing the pure rutile phase on the cpTi substrates. For overcoming this problem, a reasonable method is needed to design for fabricating the pure rutile nanorod arrays.

The chemical treatment with H_2O_2 at 80°C has been reported by Wu et al. [10] to produce an amorphous titanium oxide gel or anatase layer with low crystallinity on the surface of cpTi substrate. The titania layers with high crystallinity can be developed after the followed aging treatment in ultra-pure water at 80°C. Considering the above background, the aging treatment is reasonable to improve the crystallinity of titanium oxide.

In the present chapter, a successful chemical approach in TSs at 80°C for 3 d together with an aging treatment in ultra-pure water at 80°C for 1 d was developed to fabricate pure rutile nanorod arrays on the surface of cpTi substrate. These TSs contained titanyl sulfate (TiOSO₄), hydrogen peroxide (H₂O₂), and nitric acid (HNO₃). The possible growth mechanism of rutile nanorods was illustrated. The investigation into the possible mechanism of rutile nanorod arrays will develop a way to fabricate a series of nanorod structures.

1.2. Experimental

1.2.1. Preparation of titania layers on titanium substrate

Employed cpTi substrates were supplied by GC Corp. (Tokyo, Japan). They were polished using SiC (#1000) abrasive sandpaper to obtain a smooth surface and were then ultrasonically cleaned in ultra-pure water and acetone for 5 min, respectively. The latter cleaning cycle was repeated three times.

An appropriate amount of reagent-grade TiOSO₄ (Maikun Chemical Company, Shanghai, China) was added to a solution containing 15 mol·m⁻³ H₂O₂. After stirring for about 10 min, the solution became clear. Then, the pH value of clear solution was adjusted to 0.70 by using the HNO₃. The final molar content of TiOSO₄ (0.10, 0.14 and 0.18 mol·m⁻³) and H₂O₂ (15 mol·m⁻³) in the treating solutions (TSs) was achieved.

The cleaned cpTi substrates were soaked in polypropylene bottles, which were filled with 30 mL of TS, and then those bottles were kept in a constant-temperature oven at 80°C for 3d. After that, the treated cpTi substrates were ultrasonically cleaned in ultrapure water for 15 min. Finally, samples were soaked in ultra-pure water at 80°C for 1 d, and then were dried at room temperature.

1.2.2. Characterization for the titania layers

The surface structure of titania layers thus derived was examined with a thin-film Xray diffraction (TF-XRD, X'Pert-ProMPD, PANalytical, Almelo, the Netherlands: Cu $K\alpha$, λ =0.15418 nm, 45 kV-40 mA), where all data were collected in step-scan mode (step size: 0.02° in 20, counting time: 1 s per step) with a constant X-ray incident angle of 1.0° in 0. The chemical structure of titania layers deposited on the samples was characterized by Fourier transform infrared (FT-IR) spectrometry (Thermo Nicolet model Nexus 470, Thermo Fisher Scientific Inc., Chicago, IL, USA) with a deuterium triglycine sulfate detector, where spectral data were measured using the KBr disc method. Surface morphology of those titania layers with aging treatment was observed by a Field-emission scanning-electron microscopy (FE-SEM; JSM-6701F, JEOL, Ltd., Tokyo, Japan), where those substrates were coated with highly pure osmium for FE-SEM observation by using a Neoc-STB Osmium Coater (Meiwa Fosis Co. Ltd., Osaka, Japan).

1.3. Results

1.3.1. Surface structure on chemically treated cpTi substrates before and after aging treatment

Fig. 1.1 shows TF-XRD patterns of chemically treated cpTi substrates in various TSs at 80°C for 3 d. The samples of 0.10 mol·m⁻³ TiOSO₄ TS showed the diffraction peaks of α -titanium (ICDD-JCPDSPDF#44-1294) at 2 θ = 35°, 38°, and 40°, which were

assigned to the (100), (002), and (101) planes. No other diffraction peaks except for titanium can be detected on this samples. It is indicated that titania layers cannot be fabricated on the surface of chemically treated cpTi substrates in 0.10 mol·m⁻³ TiOSO₄ TS. Increasing the concentration of TiOSO₄ in the TS resulted in the appearance of diffraction peaks at ca. 27° and 36°, which corresponded well with the (110) and (101) planes of rutile titania (ICDD-JCPDSPDF#21-1276). 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs in Fig. 1.1 gave the similar TF-XRD patterns on the cpTi substrates. No other diffraction peaks except for rutile and titanium was detected from samples of 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs be clearly observed that the intensity of the diffraction peak corresponding to rutile (101) decreased in sample of 0.18 mol·m⁻³ TS compared with that of 0.14 mol·m⁻³ TiOSO₄ TS.

Fig. 1.2 shows the TF-XRD patterns of cpTi substrates after the chemical treatment in various TSs at 80°C for 3 d after the aging treatment in ultra-pure water at 80°C for 1 d. A strong intensity of diffraction peak at 25° and a weak peak at 36° were observed on the sample of 0.10 mol·m⁻³ TiOSO₄ TS, which were attributed to the (101) plane of anatase and (101) plane of rutile, respectively. By comparing the TF-XRD patterns of the sample of 0.10 mol·m⁻³ TiOSO₄ TS before and after the aging treatment, it can be found that aging treatment induced the formation of titania polymorphs. Aging treatment caused no significant change on the samples of 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs.

1.3.2. Chemical structure on chemically treated cpTi substrates before and after aging treatment

For showing the influence of the aging treatment on the molecular structure, FT-IR absorption spectra of deposited layers on the chemically treated cpTi substrates in 0.10 mol·m⁻³ TiOSO₄ TS before and after the aging treatment was illustrated in Fig. 1.3. This sample showed a strong absorption band at around 1630–1618 cm⁻¹ which was assignable to the H–O–H bending of physisorbed H₂O. A very strong absorption band at around 488 cm⁻¹, which was attributed to the vibration of Ti–O bonds in amorphous titania gel can be seen on the sample before the aging treatment. In addition, two weak adsorption peaks were detected at around 887 cm⁻¹ and 694 cm⁻¹, which can be assigned to the O-O stretching vibration for physisorbed H₂O₂[12] and the vibration of Ti–O–O bonds [12,13], respectively. The intensity of those peaks were decreased and even disappeared after the aging treatment. Meanwhile, a broad adsorption band in the range from 700 to 500 $\rm cm^{-1}$, and a peak at around 542 cm^{-1} , were assigned to the framework vibration of anatase lattice. On the basis of those results, it is suggested that an amorphous titanium oxide layer was formed on the chemically treated cpTi substrate in 0.10 mol·m⁻³ TiOSO₄ TS, and aging treatment yielded anatase layer on the surface.

Fig. 1.4 illustrates the FT-IR absorption spectra of titania layers deposited on the chemically treated cpTi substrates in 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs before and after the aging treatment. It showed no clear difference in the samples of 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs before the aging treatment. Both samples gave a strong absorption

band corresponding to the H–O–H bending of physisorbed H₂O. The absorption peaks were detected at around 461 and 526 cm⁻¹, in spite of the type of samples, this is which were assigned to Ti–O stretching vibration. Furthermore, three absorption bands were found at 1061, 1124 and 1198 cm⁻¹, which corresponded to the S–O stretching. An absorption band at 603 cm⁻¹ was attributed to the O–S–O bending vibrations in sulfate anion. Aging treatment led to the disappearance of the absorption bands corresponding to S–O stretching and O–S–O bending vibrations in sulfate anion on the sample of 0.18 mol·m⁻³ TiOSO₄ TS. The FT-IR spectra of chemically treated cpTi substrate in 0.14 mol·m⁻³ TiOSO₄ TS remained unchanged after the aging treatment.



Fig. 1.1 TF-XRD patterns of chemically treated cpTi substrates in 0.10, 0.14 and 0.18 $mol \cdot m^{-3}$ TiOSO₄ TSs at 80°C for 3 d.



Fig. 1.2 TF-XRD patterns of chemically treated cpTi substrates in 0.10, 0.14 and 0.18 mol \cdot m⁻³ TiOSO₄ TSs at 80°C for 3 d after the aging treatment in ultra-pure water at 80°C for 1 d .



Fig. 1.3 FT-IR absorption spectra of deposited layers on chemically treated cpTi substrates in 0.10 mol \cdot m⁻³ TiOSO₄ TS before and after aging treatment at 80°C for 1 d.



Fig. 1.4 FT-IR absorption spectra of titania layers deposited on chemically treated cpTi substrates in 0.14(a) and 0.18 (b) mol·m⁻³ TiOSO₄ TS before and after aging treatment at 80°C for 1 d.

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1.3.3. Surface morphology of chemically treated cpTi substrates after aging treatment

The surface morphology of chemically treated cpTi substrates in 0.10, 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs after the aging treatment was shown in Fig. 1.5. It is found that the resulting titanium substrates yield rough surfaces. The 0.10 mol·m⁻³ TiOSO₄ TS in Fig. 1.5 (a) shows some clusters made up of "rod-like" structures. The estimated width of those rods was around 30 nm in high magnification of Fig. 1.5 (a'). Those nanorods were stacked randomly, and their degree of growth orientation was low. Based on the TF-XRD patterns in Fig. 1.2, those nanorods consisted of anatase and rutile. On the other hand, 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs in Fig. 1.5 (b, b') and (c, c') gave highly oriented rutile arrays according to Fig. 1.2. The growth direction of rutile nanorods with width of less than 20 nm was perpendicular to the surface of cpTi substrates. By comparing the Fig 1.5 (b') and (c'), the width of nanorods on the samples of 0.18 mol \cdot m⁻³ TiOSO₄ TS seemed slightly larger that of 0.14 mol·m⁻³ TiOSO₄ TS. The estimated density of the nanorod arrays, which is defined as the number of nanorods per unit area was approximately 4.5×10^2 , 1.0×10^3 , and 1.3×10^3 µm⁻² for chemically treated cpTi substrates in the 0.10, 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs, respectively. Therefore, the chemically treated cpTi substrates in the 0.18 mol·m⁻³ TiOSO₄ TS showed the densest nanorods.

1.3.4. Cross-sectional investigation of chemically treated cpTi substrates after aging treatment

The cross-sectional images of the chemically treated cpTi substrates in 0.10, 0.14, and 0.18 mol·m⁻³ TiOSO₄ TSs after aging treatment are shown in Fig. 1.6. The middle of each figure was defined as the interface between deposited layer and cpTi substrate. The deposited layers existed above the interface. Titania layers were formed on the samples of 0.10, 0.14, and 0.18 mol·m⁻³ TiOSO₄ TSs. 0.10 and 0.14 mol·m⁻³ TiOSO₄ TSs in Fig. 1.6 (a) and (b) yielded many nano-size pores on the bottom of deposited layers, whereas very dense layers were observed on the surface of cpTi substrates in 0.18 mol·m⁻³ TS. The thickness of dense and porous layers obtained in TSs was shown in Fig 1.6 (a-c). The increment in the concentration of TiOSO4 in TS caused the decrement in the thickness of porous layer and a rise in that of dense layer. In the high magnification in Fig. 1.6 (a'-c'), it can be clearly seen that the 0.10 and 0.14 mol·m⁻³ TSs gave a multilayer structure. Pores can be confirmed on the bottom of multilayer. Bilayer structure was fabricated on the samples of 0.18 mol·m⁻³ TS. The top surface of bilayer and multilayer was the thin nanorod layer. Rods on the samples of 0.18 mol·m⁻³ TS seemed to pack tightly.

1.3.5. Growth orientation of rutile nanorods

To determine the growth orientation of rutile nanorods, the XRD patterns obtained in 2 θ and 2 θ/θ scan mode of chemically treated cpTi substrates in the 0.18 mol·m⁻³ TS after the aging treatment were shown in Fig. 1.7. When the incident angle was increased from 1° to 3°, the intensity of diffraction peaks corresponding to (101) and (110) plane of rutile phase was enhanced in the TF-XRD patterns of 20 scan mode. The depth of deposited layer which can be detected by XRD measurement was increased when the incident angle was increased from 1° to 3°. In 20/0 scan mode, the diffraction peaks which can be attributed to the (110), (101), (111) and (211) planes of rutile were detected. And a strong intensity of diffraction peak which was assignable to the (002) plane of rutile was observed. The rest diffraction peaks corresponded well with α -Ti. The relative intensity ratio of diffraction peaks corresponding to the (101) and (110) plane (I (101)/ I (110)) was ca. 7.1, which was higher than the value of 2.2 in our previous report [4]. Therefore, rutile crystals on the samples of 0.18 mol·m⁻³ TS were forced to grow along *c*-axis.

On the basis of above results and analysis, an amorphous titanium oxide layer was produced on the chemically treated cpTi substrate in 0.10 mol·m⁻³ TS, and aging treatment can give the appearance of anatase layer together with the elimination of Ti-O-O-H, Ti-O-O bonds. Pure rutile nanorod arrays were fabricated on the cpTi substrates after being soaked in 0.14 and 0.18 mol·m⁻³ TSs. 0.18 mol·m⁻³ TS gave the rutile nanorods with high rod density.











Fig. 1.7 XRD pattern in $2\theta/\theta$ scan mode and TF-XRD patterns in 2θ scan mode (incident angles of 1° and 3°) of chemically treated cpTi substrate in 0.18 mol·m⁻³ TS after aging treatment.

1.4. Discussion

 H_2O_2 pre-treatment of cpTi substrates gave an amorphous layer on the titanium substrate as reported in previous studies [4.9], and it has been reported that nanocrystalline titania layers grew on the amorphous layer. In addition, aging treatment induced the formation of anatase layers on the H₂O₂-oxidized cpTi substrates [16,17]. Our results of samples obtained in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TS indicated that the amorphous titanium oxide layer existed on the surface before the aging treatment, and aging treatment gave the titania nanorods mainly consisting of anatase. Those results were similar with that of Wu et al. [16,17]. Therefore, the interaction of H_2O_2 on the cpTi substrates should be responsible for the formation of amorphous titanium oxide layer with Ti-O-O bonds on the cpTi substrate in TS. The amorphous titanium oxide layer was transformed to the anatase layer after the aging treatment. As shown in the cross-sectional SEM images in Fig. 1.6, multilayer containing rod, dense and porous layer can be found on the samples of 0.10 mol·m⁻³ TiOSO₄ TSs after the aging treatment. The porous layer can be regarded as an indicator of the formation of the amorphous titanium oxide layer in TS.

Wu et al. [18] reported that rutile phase was expected to produce in a titanium (IV) solution with a low pH value. Inada et al. [19, 20] have successfully fabricated rutile powders in TiOCl₂ starting solution with a low pH value at 50°C or 100°C. Yamabi et al. [21] have reported the formation of titania in anatase or rutile phase on the surface of glass must be dependent on the pH value of TiOSO₄ treating solution. They demonstrated

that TiOSO₄ solution whose pH value was less than 1 resulted in the preferential deposition of rutile phase from Ti complexes. In our present work, the formation of pure rutile nanorods on the chemically treated cpTi substrates in 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs can be explained by considering the pH and TiOSO₄ concentration of the TSs. Ti ions in the 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs (pH value=0.7) favor the production of Ti-complex species, which will dehydrate to form rutile. In TF-XRD patterns in Fig. 1.2 and cross-sectional images in Fig. 1.6 (b), rutile nanorods can be found on the top surface of porous layer. 0.18 mol·m⁻³ TS favored the formation of rutile nanorods with high rod density, and the thickness of the porous layer was remarkably decreased with the increase in TiOSO4 concentration. On the basis of above results and discussion, the possible growth mechanism of rutile nanorod was illustrated in Fig. 1.8. When the cpTi substrates were soaked in TS, an amorphous titanium oxide layer is produced firstly owing to the chemical interaction of H₂O₂ in TS. Ti-complex species in the TS result in the nucleation of rutile on the amorphous titanium oxide layer, the rate of rutile nucleation depends on the concentration of TiOSO₄ in TSs. The rutile grows by consuming the amorphous titanium oxide layer and its growth orientation is perpendicular to the cpTi substrate.

The amorphous titanium oxide layer remains on the chemically treated in the 0.10 mol·m⁻³ TiOSO₄ TS because only a little rutile nucleus can be produced, and then is transformed into anatase nanorods during the aging treatment. Thus, titania nanorods mainly consisting of anatase were found on the samples of 0.10 mol·m⁻³ TiOSO₄ TS after

the aging treatment. In 0.14 and 0.18 mol·m⁻³ TiOSO₄ TS, the rutile nucleation are accelerated. The nucleation and growth of rutile are accompanied by the consumption of the amorphous titania gel layers due to their transformation into rutile. As a result, a thinner titanium oxide layer were observed on the samples of 0.14, and 0.18 mol·m⁻³ TiOSO₄ TSs.

The differences in the thickness of porous layer and rutile rod density on the samples of 0.14 mol·m⁻³ TiOSO₄ TS and 0.18 mol·m⁻³ TiOSO₄ TSs can be explained by the following discussion. In 0.18 mol·m⁻³ TiOSO₄ TS, the rate of rutile nucleation and growth is increased on the amorphous titania gel layer, where the nucleation and growth of rutile nanorods exceeds the formation of the porous layer. So, 0.18 mol·m⁻³ TiOSO₄ TS yields dense rutile nanorod arrays with high rod density. In the Fig. 1.1 and 1.2, 0.14 mol·m⁻³ TS gave the stronger diffraction intensity of rutile. The above findings suggest that density of rutile rods depends on the concentration of TiOSO₄ in the TSs. The rutile rod density could be improved by optimizing the TiOSO₄ concentration in the TSs.

In Fig. 1.4, aging treatment removed sulfate bands on the samples of $0.18 \text{ mol}\cdot\text{m}^{-3}$ TS, whereas sulfate bands still remained on the sample of $0.14 \text{ mol}\cdot\text{m}^{-3}$ TS after the aging treatment. According to Fig. 1.6, it is suggested that water molecule during the aging treatment cannot enter into the porous structures on the bottom due to the hindrance of the upper dense layer. Therefore, the sulfate ions are expected to keep in the porous structure of chemically treated cpTi substrate in 0.14 mol·m⁻³ TS after the aging treatment.



Fig. 1.8 Possible growth mechanism of highly ordered rutile nanorods on the cpTi substrate in TS. H₂O₂ treatment yields the amorphous titania layer, rutile nucleation will occur on the amorphous layer. Rutile will extend along c-axis. In this case, rutile rods grow perpendicular to the surface of cpTi substrate.

1.5. Conclusion

Titania nanorod structures were obtained on the surface of commercially titanium substrates via a chemical treatment in various TSs including TiOSO₄, H₂O₂, and HNO₃ at 80°C for 3 d followed by an aging treatment in the ultra-pure water at 80°C for 1 d. The random titania nanorods with the phase composition of anatase and rutile grew on the surface of chemically treated cpTi substrate in 0.10 mol·m⁻³ TiOSO₄ TS after the aging treatment. Pure rutile nanorod arrays were deposited on the chemically treated cpTi substrates in 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs. Those highly ordered rutile nanorods were forced to grow perpendicular to the surface of cpTi substrate. Multilayer consisting of nanorod, dense and porous layer was obtained on the samples of 0.10 and 0.14 mol·m⁻ ³ TiOSO₄ TSs, whereas 0.18 mol·m⁻³ TiOSO₄ TS gave the bilayer containing nanorod and dense layer. The thickness of porous layer decreased and that of dense layer increased with the increase in the TiOSO₄ concentration. The formation of rutile nanorods was resulted from the nucleation and growth of rutile on the amorphous titania gel layer, accompanied by consumption of the amorphous titania gel.

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Chapter 2

Chemical deposition of rutile on various metallic substrates from titanyl sulfate and hydrogen peroxide solution at low temperature

2.1. Introduction

In the past decade, commercially available pure titanium and some titanium-based alloys have been widely applied in the orthopedic and dental implants [1-4]. Many researchers have developed bioactive layers on titanium substrates [5, 6] and its alloys like Ti6Al4V alloys [7, 8] via various methods and examined the *in vitro* apatite deposition on the layer.

Nb (Niobium), Zr (Zirconium), Ta (tantalum) and their alloys have attracted a lot of attention because they showed the excellent mechanical property, biocompatibility and non-toxicity as metallic implants [9-13]. Furthermore, Nb, Zr and Ta metals are well known to have the similar chemical and mechanical properties with Ti metal. However, the above metallic substrates cannot form a bond with bony tissues without any surface modification. In the chapter 1, we have successfully prepared pure rutile layers on the surface of cpTi substrates by soaking the substrates in 0.14 mol·m⁻³ TiOSO₄ TS. The chemical treatment in 0.14 mol·m⁻³ TiOSO₄ TS is expected to be suitable to give titania (rutile, anatase or titania polymorphs) layers on the surface of Nb, Zr, Ta and Ti6Al4V

alloys.

In this chapter, Nb, Zr, Ta and Ti6Al4V alloy substrates were used as substrates, and then the chemical treatment in $0.14 \text{ mol}\cdot\text{m}^{-3}$ TiOSO₄ TS as described in the chapter 1 was choose to deposit layers on the surface of Nb, Zr, Ta and Ti6Al4V alloys. The effects of the substrate on the surface structure of deposited layers was examined. The possible growth mechanism of deposited layers on the Nb, Zr, Ta and Ti6Al4V alloys substrates was discussed. Ti pieces before and after the chemical modification in 0.14 mol·m⁻³ TiOSO₄ TS was selected as a control group in order to compare the surface structure of other modified metallic substrates (Nb, Zr, Ta and Ti6Al4V alloy substrates).

2.2. Experimental

2.2.1. Materials

A sheet of pure niobium (Nb, 99.9%), zirconium (Zr, 99.2%), tantalum (Ta, 99.95%) and titanium pieces (Ti, 99.5%) which were purchased from The Nilaco Co. Ltd. (Tokyo, Japan) were cut into specimens of $10 \times 10 \times 0.1$ mm³ in size, respectively. Ti6Al4V alloy discs ($12\Phi \times 1$ mm), which were purchased from Teijin-Nakashima Medical Co. Ltd. (Okayama, Japan) were ground with the sandpaper 1000 grit to get smooth-textured surface. Nb, Zr, Ta pieces and Ti6Al4V alloys were ultrasonically washed in acetone and ultra-pure water, respectively. The washing process was repeated for 3 times. The nontreated substrates were denoted as NT-samples.

2.2.2. Preparation of chemically treated samples

The chemical treatment was performed by soaking the NT-samples in the bottles filled with 30 mL treating solution (TS), heated to 80°C and held for 3d. Reagent grade TiOSO₄ (Maikun Chemical Company, Shanghai, China) was dissolved into a solution containing 15 mol·m⁻³ H₂O₂ to yield a concentration of 0.14 mol·m⁻³ TiOSO₄ solution, and then its pH value was adjusted to 0.7 by using the nitric acid (HNO₃). After the chemical treatment, samples were washed with ultra-pure water by using the ultrasonic machine for 15 min, and dried at room temperature (denoted as CT-samples).

2.2.3. Structural characterization

An optical investigation (Canon EOS x7i) was carried out to observe the surface of NT-/CT-samples. Thin film X-ray diffraction (TF-XRD) were performed to analyze the surface structure of samples before and after the chemical treatment. TF-XRD spectra (TF-XRD, X'Pert-ProMPD, PANalytical, Almelo, the Netherlands: Cu K α , λ =0.15418 nm, 45 kV-40 mA) were recorded in step-scan mode for 20 from 20°- 45° at a rate of 0.02°/1s. The change in the weight of samples before and after the chemical treatment was measured by using an electronic balance (ATX 224, Shimadzu, Kyoto, Japan) with a 0.1 mg precision.

2.3. Results

2.3.1. Surface structure of Nb and Zr substrates

Table 2.1 shows the photo-images and the weight change of Nb and Zr substrates before and after the chemical treatment in 0.14 mol·m⁻³ TiOSO₄ TS. The chemical treatment caused significant differences on the surface of the Nb substrate. Chemical treatment gave a yellow color on the surface of Nb substrate. In addition, it was evident that the weight of Nb substrates was reduced after the chemical treatment. However, no significant changes in the surface color and weight of Zr substrates can be found.

Fig. 2.1 shows the TF-XRD patterns of Nb and Zr substrates before and after the chemical treatment in 0.14 mol·m⁻³ TiOSO₄ TS at 80°C for 3d. The diffraction peak at 25.1° and a weak peak around 37.8°, which were respectively ascribed to (101) and (004) plane of anatase (ICDD-JCPDS PDF#21-1272), were clearly detected on the surface of CT-Nb substrate. It is obvious that the intensity of diffraction peak at 38.6° corresponding to Nb decreased after the chemical treatment. It is indicated that pure anatase phase was formed on the surface of CT-Nb substrate. However, the diffraction peaks at 35.0° and 38.5° which were assignable well with the Zr (ICDD-JCPDS PDF#01-072-5842) was clearly observed on the Zr substrate before and after the chemical treatment. It is suggested that no deposited layer was formed on the Zr substrate after chemical treatment.

2.3.2. Surface structure of Ta, Ti6Al4V alloy and Ti substrates

The photo-images and weight change of Ta, Ti6Al4V alloy substrates and Ti piece

before and after the chemical treatment are shown in Table 2.2. A gray film with some cracks was formed on the CT-Ta substrate. Chemical treatment gave a brown color on the surface of Ti6Al4V alloy and Ti substrate. In addition, it is clearly seen that Ta, Ti6Al4V alloy and Ti substrate gained the weight after the chemical treatment. The gained weight of substrates was increased in the order: Ta < Ti6Al4V < Ti.

TF-XRD patterns for the Ta, Ti6Al4V alloy and Ti substrates before and after the chemical treatment are shown in Fig. 2.3. The diffraction peak at 35.7° and 41.1° corresponded to the (101) and (111) plane of rutile (ICDD-JCPDS PDF#21-1276), indicating that the precipitate on the Ta substrate consisted of pure rutile phase. CT-Ti6Al4V alloys gave the diffraction peaks corresponding to (110), (101) and (111) planes of rutile. It is suggested that pure rutile phase was successfully produced on the CT-Ti6Al4V alloy substrate after chemical treatment. The diffraction peaks at 27.1°, 35.7° and 41.1° corresponded well to (110), (101) and (111) planes of rutile on the CT-Ti species. No other diffraction peaks except for titanium can be observed in Fig. 2.2 (c). This means that pure rutile can be confirmed on the CT-Ti species. The TF-XRD patterns of CT-Ti6Al4V alloy were very similar to that of CT-Ti species. The intensity for (101) plane of rutile was increased in the order: Ta < Ti6Al4V < Ti.

On the basis of the above results, pure rutile layers with the exposed {101} facets can be successfully prepared on the Ta and Ti6Al4V alloy substrates after the chemical treatment.

Table 2.1 Photo-images and weight change of Nb and Zr substrates $(10 \times 10 \times 0.1 \text{ mm}^3)$ before and after the chemical treatment





Fig. 2.1 TF-XRD patterns of Nb (a) and Zr substrates (b) before and after the chemical treatment in 0.14 mol·m⁻³ TiOSO₄ TS at 80°C for 3d. \Box : niobium, \bigcirc : zirconium.

Table 2.2 Photo-images and weight change of Ta $(10 \times 10 \times 0.1 \text{ mm}^3)$, Ti6Al4V alloy $(12\Phi \times 1 \text{ mm})$ and Ti substrates $(10 \times 10 \times 0.1 \text{ mm}^3)$ before and after the chemical treatment

| Substrate | NT | СТ | Weight change / g |
|-----------|----|----|-------------------|
| Ta | | | 0.0004 |
| Ti6Al4V | | | 0.0005 |
| Ti | | | 0.0007 |





2.4. Discussion

According to the present experimental results, pure rutile layers was prepared on the surface of Ta and Ti6Al4V alloy substrates. The results of Ta and Ti6Al4V alloy substrate after the chemical treatment in a 0.14 mol·m⁻³ TiOSO₄ TS was extremely similar to that of cpTi substrate in chapter 1. This strongly suggests that a growth mechanism of rutile layers on the Ta and Ti6Al4V alloy substrate is similar to the mechanism for cpTi to provide rutile layers. As presented schematically in the chapter 1, rutile nucleation occurred on the amorphous titania layer of cpTi substrate due to the H₂O₂ oxidation. According to the above, it is supposed that Ta and Ti6Al4V alloy substrates produce the amorphous oxide layer under the treating solution containing TiOSO₄, HNO₃ and H₂O₂, and then the Ti complexes in TS contribute to the rutile nucleation on the amorphous oxide layer. The growth of rutile proceed at the expense of amorphous oxide layer. The diffraction intensity of (101) plane for rutile was increased in the order: Ta < Ti6Al4V <Ti as shown in Fig. 2.2. One possible explanation is that not only TiOSO₄ but also the metal substrates can provide Ti complexes for rutile nucleation on the surface of Ti and Ti6Al4V alloy substrates. However, the above description does not apply to the Nb substrate.

In Fig. 2.1, note that only diffraction peaks assignable to (101) and (004) plane of anatase can be indicated on the Nb substrates. The weight of Nb substrate was decreased after the chemical treatment. This result indicates that Nb substrates are oxidized by H_2O_2 in TS and Nb ions are eluted from the substrate. It is adequate to propose that the eluted

Nb ions are supposed to form the complicated Ti-Nb complexes in the treating solution, leading to the nucleation of anatase. The possible mechanism of the anatase layer formation on the Nb substrate was illustrated in Fig. 2.3.





2.5. Conclusion

Anatase layers were prepared on the Nb substrate with the facile chemical treatment. However, pure rutile layers with the exposed $\{101\}$ facets were successfully formed on the surface of Ta and Ti6Al4V alloy substrates. It should be emphasized that the intensity of diffraction peak corresponding to (101) plane for rutile was reduced in the order Ti >Ti6Al4V >Ta. The concentration of Ti in the treating solution can be responsible for the decreased order. Nb ions released from the Nb substrates in the treating solution form Ti-Nb complexes, leading to nucleation of anatase on the surface of Nb substrate.

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Chapter 3

In vitro apatite formation on highly ordered rutile nanorod arrays on cpTi and Ti6Al4V alloy substrates

3.1. Introduction

In the recent years, hydroxyapatite (HA) coatings have been widely applied on the metallic implants for the biomedical application, which have the ability to bond with the bony tissues [1-3]. Several coating methods like sol-gel methods [5], electron-beam deposition [6], and thermal spraying treatment [7, 8] have been successfully to form the HA coating on the surface of substrates. However, among the above techniques each one has some disadvantages. For example, extremely high temperature was employed in the thermal spraying treatment, which may cause the particular weakness in the fatigue resistance of HA coatings [8]. On the other hand, recent research has shown that the in vitro deposition of bone-like apatite layers on the surface is one of the most promising way for evaluating the bioactivity of implants [9-11].

Titanium and some of its alloy (Ti6Al4V) are widely used as biomedical implants due to their excellent biocompatibility. For improving the bone bonding ability of those metallic implants, titanium oxide layer has been prepared on the surface. It has been shown that the titania layer covering titanium and its alloys induced the apatite deposition in Kokubo's simulated body fluid (SBF), which has similar inorganic ion concentrations with human blood plasma [12].

The possible factors of titania layers in inducing apatite nucleation and growth in the conventional SBF have been investigated recently. Shozui et al. [13, 14] showed that in vitro apatite-forming ability depends on the metallic substrates. In addition, for some titanium alloys (Ti6Al4V), the effects of aluminum species released into the SBF cannot be ignored in the apatite nucleation and growth [15]. For preventing the release of aluminum species from the Ti6Al4V alloy substrates, a liquid-phase-deposited titania coating was applied to cover the Ti6Al4V alloy substrates [16]. In this case, properly designed gaps (GRAPE technology [16-18]) were required to provide the apatite-forming ability of titania coating on Ti6Al4V alloy substrates. Nevertheless, if the liquid-phase deposition cannot provide very thick titania coating, the inhibiting effect of the aluminum species derived from the substrates may not be eliminated completely.

The importance of rutile layer in inducing apatite deposition has been demonstrated by Xiao et al. [19]. Xiao et al. [19] indicated that the excellent apatite-forming ability of rutile was contributed to the small lattice mismatch between oxygen atoms on specific facets of rutile and apatite. As proposed by Wu et al. [20], a complicated surface morphology and nanosized rutile crystallites were also the important keys in effectively inducing apatite formation in vitro. Rohanizadeh et al. [21] have reported that a rutile layer produced by H_2O_2 oxidation together with a subsequent heat treatment also exhibited the excellent apatite-forming ability, and this rutile layer showed the strong binding force with deposited apatite layer.

Titania micro/nanostructures on Ti or Ti-based metals also draw a lot attention in the apatite deposition [17, 19, 22-24]. The advantage of titania nanotubular arrays by the anodization method in inducing apatite formation was reported [24, 25] in recent year. For example, Tsuchiya et al. [24] indicated the titania nanotubular can provide excellent apatite-forming ability in vitro because nanotubular structures own a very large surface area. Though the apatite formation on the titania rods have been reported by some studies [18, 19], the effect of titania rods in inducing apatite nucleation and growth has been rarely discussed. On the basis of the above, a detailed understanding of the mechanism via which the nucleation and growth of apatite are induced on rutile rods is necessary.

In the earlier report [26], dense and thick pure rutile nanorod arrays were successfully prepared on the entire surface of a cpTi substrate. If the same dense rutile layer can be fabricated on the surface of Ti6Al4V alloy substrate, the inhibiting effect of Al from the Ti6Al4V alloy substrate into the SBF may be highly avoided, which will be beneficial to deposit apatite layers on their surface in SBF. In this chapter, the chemical treatment in our previous paper [26] was employed to produce the rutile nanorod arrays on their surface of cpTi and Ti6Al4V alloy substrates. The effect of rutile nanorod arrays in apatite nucleation and growth on the cpTi and Ti6Al4V alloy discs was discussed. The nucleation and growth process of apatite on the rutile nanorod arrays for the cpTi and Ti6Al4V alloy discs was shown.

3.2. Experimental

3.2.1. Fabrication of rutile nanorod arrays on cpTi and Ti6Al4V

Titanium discs ($15\Phi \times 1 \text{ mm}$) and Ti6Al4V alloy discs ($12\Phi \times 1 \text{ mm}$), which were respectively provided by the GC Corp. (Tokyo, Japan) and Teijin-Nakashima Medical Co. Ltd. (Okayama, Japan), were polished using SiC (#1000) abrasive sandpaper to achieve a smoother substrate. The polished samples were washed ultrasonically in the ultra-pure water and acetone for 5 min, respectively. The cleaning cycle was repeated three times.

The chemical treatment in our previous study was employed to produce rutile nanorod arrays on the cleaned cpTi and Ti6Al4V alloy discs. Briefly, clear treating solution (TS, pH 0.7) was obtained by mixing 0.14 mol·m⁻³ TiOSO₄ (Maikun Chemical Company, Shanghai, China), 15 mol·m⁻³ hydrogen peroxide (H₂O₂), and nitric acid (HNO₃). The cleaned cpTi or Ti6Al4V alloy discs were loaded in the 30 mL of TS at 80°C for 3 d and then cooled at room temperature. The samples were subsequently placed in ultra-pure water and cleaned by using the ultrasonic cleaning machine for 15 min. The aging treatment in 30 mL of ultra-pure water at 80°C for 1 day was employed to improve the crystallinity of deposited layer. Finally, the treated samples were dried in air at room temperature, and denoted as CT-specimens (CT-cpTi and CT-Ti6Al4V).

3.2.2. In vitro evaluation of the ability to induce apatite deposition

Kokubo's SBF was prepared as described in the literature [12]; its ion concentration

was similar to that of human blood plasma. Reagent-grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄•3H₂O, MgCl₂•6H₂O, CaCl₂, and Na₂SO₄ were sequentially dissolved in ultra-pure water. (CH₂OH)₃CNH₂, and 1 mol·dm⁻³ HCl were used to adjust the pH to 7.4. In order to evaluate the apatite-forming ability, the CT- samples according to section 3.2.1 were soaked in 40 mL of SBF at 36.5°C for various periods. And then the samples were slightly cleaned with ultra-pure water and dried in the air at room temperature.

3.2.3. Structure characterization

The thin-film X-ray diffraction (TF-XRD, X'Pert-ProMPD, PANalytical, Almelo, the Netherlands: Cu K α , λ = 0.15418 nm, 45 kV-40 mA) was used to investigate the surface structure of the samples. TF-XRD patterns were measured in the step-scan mode with a constant X-ray incident angle θ of 1.0°. The field-emission scanning-electron microscopy (FE-SEM; JSM-6701F, JEOL, Ltd., Tokyo, Japan) and scanning electron microscopy (SEM; VE-9800, Keyence Co. Ltd., Osaka, Japan) were used to observe the surface morphology of samples before and after being soaked in SBF. A Neoc-STB Osmium Coater (Meiwafosis Co. Ltd., Tokyo, Japan) was used to coat the highly pure osmium for the FE-SEM observation. A platinum-palladium coating (thickness: 10 nm) was prepared on the samples with using a sputter coater (Ion Sputter E-1030, Hitachi High-Technologies Co. Ltd., Tokyo, Japan) for the SEM observation. The SEM images were analyzed using ImageJ software (version 1.51, Wayne Rasband, NIH, Bethesda, MD, USA) to derive the quantity, size, and surface coverage of the deposited apatite particles.

3.3. Results

3.3.1. Surface morphology of CT-cpTi and CT-Ti6Al4V samples

Chemical method was employed to construct titania layers on the cpTi and Ti6Al4V alloy substrates. Fig. 3.1 shows a set of FE-SEM images of the CT-cpTi and CT-Ti6Al4V specimens. In low-magnification images (Fig. 3.1 (a1) and (b1)), dense and rough nanorod arrays were found on both samples. Dense nanorod arrays were further confirmed on the CT-cpTi specimen in Fig. 3.1 (a2). By comparing Fig. 3.1 (a1) and (b1), some pores and gaps with 100–250 nm in size (Fig. 3.1 (b1)) were observed on the surface of CT-Ti6Al4V specimens as the white arrows shown. More careful observation in (Fig. 3.1 (a3) and (b3)), these layers were made up of rod-like structures. For the CT-cpTi specimen, the width of those rods was estimated to 21-25 nm, and rods with approximately 14–20 nm width can be seen on the surface of CT-Ti6Al4V specimen. In addition, those nanorods grew along the same orientation though the width of those nanorods on the CT-cpTi and CT-Ti6Al4V specimens was slightly different. In order to evaluate the density of the nanorod arrays (DA), the number of nanorods per unit area on the surface of a specimen was calculated. According to FE-SEM images in (Fig. 3.1 (a3) and (b3)), the DAs on the CT-cpTi and CT-Ti6Al4V specimens were approximately (1.04 ± 0.06) $\times 10^3$ and $(0.70 \pm 0.10) \times 10^3 \ \mu m^{-2}$. The above results demonstrated that nanorod arrays were successfully prepared on the surface of CT-cpTi and CT-Ti6Al4V specimens, denser nanorods with larger size were fabricated on the CT-cpTi substrates.

Fig. 3.2 shows the cross-sectional backscattered electron (BSE) SEM images of the

CT-cpTi and CT-Ti6Al4V specimens. It presented the thickness of the deposited layers. In the middle of each figure, the interface line between substrate and deposited layer was found. The part above the interface line was the deposited layer, and the part below the line was the substrate (cpTi and Ti6Al4V alloy). As seen in the Figure, the estimated thickness of layers was presented. The thickness of deposited layer on the CT-cpTi specimens was $1.8 - 2.6 \mu m$. On the other hand, a relatively thin layer with $1.4 - 1.7 \mu m$ in the thickness can be observed on the of the CT-Ti6Al4V specimen.

3.3.2. Surface structure of CT-cpTi and CT-Ti6Al4V samples

To determine the crystalline phase of CT-cpTi and CT-Ti6Al4V specimens, their TF-XRD patterns are presented in the Fig. 3.3. The similar TF-XRD patterns of CT-cpTi and CT-Ti6Al4V specimens were obtained. Both samples gave diffraction peaks at 20 angles of approximately 27°, 36°, and 38°, corresponding to diffraction from the (110), (101), and (111) planes, respectively, of rutile titania (ICDD-JCPDS PDF#21-1276). The rest diffraction peaks corresponded to the metallic substrates. Therefore, pure rutile phase was produced on both samples after the chemical treatment. By comparing, the diffraction intensity of the (101) planes of rutile was greater on the CT-cpTi specimen.


Fig. 3.1 FE-SEM images of CT- cpTi (a1: $\times 10k$, a2: $\times 30k$, a3: $\times 100k$) and CT-Ti6Al4V specimens (b1: \times 10k, b2: \times 30k, b3: \times 100k), white arrow: hole.



Fig 3. 2 SEM micrographs for cross-sectional profiles of CT- cpTi and CT-Ti6Al4V



Fig 3.3 TF-XRD patterns of CT-cpTi and CT-Ti6Al4V specimens.

3.3.3. Surface structure and morphology of CT-cpTi and CT-Ti6Al4V after being soaked in SBF

The TF-XRD patterns of the CT-cpTi and CT-Ti6Al4V specimens after being soaked in SBF for various periods from 0 to 72 h are illustrated in Fig. 3.4. The diffraction peaks at 25° and 32° in 20 were assignable to the apatite (ICDD-JCPDS PDF#09-432), which meant that CT-cpTi and CT-Ti6Al4V specimens can deposited apatite in SBF after being soaked in SBF for 12h. The diffraction intensity of apatite grew with the increase in the soaking time. In Fig. 3.4 (a), 30 h was required for the CT-cpTi specimen to detect the diffraction peaks of apatite, and the soaking time required for showing apatite diffraction peaks on the CT-Ti6Al4V alloy specimen is at least 48 h. After being soaked in SBF for 72 h, the intensity of the diffraction peak at approximately 32° on the CT-cpTi specimen was stronger than that on the CT-Ti6Al4V alloy specimen. TF-XRD measurements have the limit in detecting the diffraction peak of apatite, therefore the SEM micrographs of samples after soaking in SBF were required to confirm the induction time for apatite deposition.

Surface morphology of the samples before and after immersion in SBF for various periods are indicated in Fig. 3.5. Small hemispherical particles (1–2 µm diameter) appeared on the surface of the CT-cpTi and CT-Ti6Al4V specimens after being soaked in SBF for 12 h, implying that CT-cpTi and CT-Ti6Al4V specimens can deposit particles within 12 h of soaking in SBF. The number of the hemispherical particles was smaller on the CT-Ti6Al4V specimens. The diameter of those apatite seemed smaller on the CT-

Ti6Al4V specimens. When the soaking time was increased to 24 h, the number of hemispherical particles grew on the surface of both samples. In addition, according to Fig. 3.4, those deposited hemispherical particles can be identified as apatite. With the further increase in the soaking time, the number and diameter of apatite particles was increased. Finally, the apatite covered the entire surface of CT-cpTi and CT-Ti6Al4V specimens.

3.3.4. Analysis of quantity, size, and surface coverage of apatite

The quantity, size, and surface coverage of the deposited apatite particles was analyzed with ImageJ software as illustrate in Fig. 3.6. Fig. 3.6 (a) estimates the diffraction peak area at 32°. This peak corresponds to the apatite calculated from the TF-XRD patterns of Fig. 3.4 as a function of the soaking time. In Fig. 3.4, the peak area on the CT-Ti6Al4V specimens was corrected by considering the apparent surface area of the CT-cpTi and CT-Ti6Al4V specimens. Here, the induction time for apatite was further determined. 12-24 h for the CT-cpTi specimen and 30-36 h for the CT-Ti6Al4V specimen was required for detecting diffraction peak of apatite, respectively. Those analysis imply that CT-cpTi specimen gave a large amount of apatite on the surface. Fig. 3.6 (b) and (c) show that the number and size of the hemispherical apatite particles on the CT-cpTi and CT-Ti6Al4V specimens were plotted as a function of the soaking time in the range of 0–72 h according to the SEM micrographs in Fig. 3.5. Both samples exhibited similar monotonically increasing behavior of the particle number. More apatite particles on the CT-cpTi specimen can be confirmed throughout the soaking time in SBF. In addition, CT-cpTi specimen gave apatite particles with slightly larger in diameter. The number and size of the hemispherical apatite particles increased with the soaking time in the range from 0 h to 40 h. (Fig. 3.6 (b) and (c)) This implies that the primary and secondary nucleation and growth of apatite occurred until 40 h.

The number of apatite particles is plotted as a function of the coverage in Fig. 3.6 (d). The CT-cpTi and CT-Ti6Al4V specimens both gave a similar increasing behavior, though the number of deposited apatite particles on the samples was different. The CT-cpTi specimen reached the plateau stage around 35% of coverage, while the CT-Ti6Al4V specimen did so around 45% of coverage. The curve in Fig. 3.6 (d) shows a monotonic increase in the number of particles in the 0–40% coverage range due to the primary and secondary nucleation and growth of apatite followed by the plateau stage due to the secondary nucleation and growth of apatite.



Fig 3.4 TF-XRD patterns of CT- cpTi (a) and CT-Ti6Al4V (b) after being soaked in SBF at 36.5°C for 0, 12, 24, 30, 36, 48, 60 and 72 h.



Fig 3.5 SEM micrographs of CT-cpTi and CT-Ti6Al4V after being soaked in SBF for various period at 36.5°C.



Fig 3.6 Thin-film X-ray diffraction peak area at $2\theta=32^{\circ}$ corresponding to apatite (a), number of deposited apatite particles (b), and average diameter of deposited apatite particles (c) as a function of soaking time in SBF; (d) The number of apatite particles is plotted as a function of coverage, which is the fraction of the surface covered by the apatite particles.

3.4. Discussion

Rutile nanorod arrays on the both CT-cpTi and CT-Ti6Al4V specimens can induce apatite formation on their surface, in spite of rod density and thickness of rutile layers. Takadama et al. [27] reported that alkali treatment in NaOH solution was employed to produce a layer on a Ti6Al4V alloy substrate, the layer induced apatite deposition in vitro after immersion in SBF for 120 h. They demonstrated that the exchange between Na ions on the Al and V-free sodium titanate layer and H_3O^+ in the SBF was contributed to the formation of Ti-OH groups, which were beneficial for apatite deposition. A similar process of apatite deposition on the Ti substrate with NaOH treatment also has been reported recently [28]. On the other hand, Yamaguchi et al. [29] have shown that a mixed acid treatment and subsequent heat treatment were employed to produce a bioactive surface on the Ti6Al4V alloys. The ability of Ti6Al4V alloys with acid and heat treatment in depositing apatite was discussed, treated Ti6Al4V alloys did not form apatite in SBF within three days. In the present chapter, the fact that rutile nanorod arrays fabricated on both cpTi and Ti6Al4V alloys are effective to deposit apatite within 1d. Besides, the different behavior of apatite deposition on the CT-cpTi and CT-Ti6Al4V specimens is noteworthy.

Uchida et al. [30] reported that apatite was formed on titania layers because the atomic oxygen arrangements in titania crystal structures were suitable for the epitaxy of the hydroxyl groups of apatite crystals in SBF. As shown by Xiao et al. [19] the crystal

lattice matching between rutile and apatite should be responsible for the apatite deposition in SBF. On the other hand, Li et al. [31] have proposed that the presence of Ti–OH groups on the titania layers was attributed to the apatite deposition in vitro. They reported that the number of Ti-OH groups together with the surface charge of titania layers took the associated responsibility for the apatite-forming ability. Uetsuki et al. [32] revealed that Ti-OH groups would exist on titania layers in two kinds of states, acidic and basic. That means, when titania was exposed to the SBF, the positively charged $Ti-OH_2^+$ and negatively charged Ti-O⁻ coexisted on the surface of titania. The surface charge of titania must be dependent on the arrangement of $Ti-OH_2^+$ and $Ti-O^-$ sites on the surface. Besides, the surface energy and primary apatite nucleation also were influenced by the arrangement of Ti-OH₂⁺ and Ti-O⁻ sites. Both Ti-OH₂⁺ sites and Ti-O⁻ sites on the titania surface welcome the positive (calcium ions) and negative (phosphate ions) ions of SBF to simultaneously form an apatite nucleus. The secondary apatite nucleation and growth depended on the rate of primary apatite nucleation. As shown in our results, the rod density of rutile nanorod arrays should be discussed to affect the primary nucleation and growth of apatite. On the basis of the above results and discussion, the following points about apatite nucleation and growth on the rutile nanorod arrays can be concluded as follows.

a) The top surface of rutile nanorod arrays can provide the active sites for apatite primary nucleation. Those active sites contain the Ti–OH₂⁺ sites and Ti–O⁻ sites of rutile rods. The number of sites corresponds to the number of deposited

hemispherical apatite particles on the surface.

- b) The density of active sites on the rutile rod arrays determine the rate of primary apatite nucleation and growth and the frequency of the nucleation.
- c) The density of rutile rods and active sites determine the rate of secondary apatite nucleation and the growth and frequency of the nucleation. The diameter of hemispherical apatite particles must depend on the secondary apatite nucleation and the growth.

The possible behavior of apatite formation on the rutile nanorod arrays of CT-cpTi (a) and CT-Ti6Al4V specimens (b) is illustrated in Fig. 3.7. The induction time for apatite on CT-cpTi was longer that on CT-Ti6Al4V in Fig. 3.6 (a). In addition, a greater amount of apatite can be produced on the CT-cpTi substrate. The number of apatite particles (Fig. 3.6 (b)) indicated that the number of active sites for apatite nucleation on the CT-cpTi specimen was larger than that on the CT-Ti6Al4V specimen. In Fig. 3.6 (d), the maximum number of apatite particles was greater on the surface of the CT-cpTi specimen. According to the results, it is indicated that rutile nanorod arrays on the CT-Ti6Al4V specimen cannot provide many active sites for apatite nucleation and growth. In Fig. 3.1, the density of rutile nanorods is lower on the CT-Ti6Al4V specimen. The densities of the rod-like structures are approximately $(1.04 \pm 0.06) \times 10^3$ and $(0.70 \pm 0.10) \times 10^3 \mu m^{-2}$ on the CT-cpTi and CT-Ti6Al4V specimens, respectively. The diameter of rutile nanorods on both samples was quite close (approximately 20 nm). Therefore, the effective surface area of each rutile rod for producing the active site was ca. $3.14 \times 10^{-4} \,\mu\text{m}^2$. According to Fig. 3.6 (b), the number of active sites for apatite nucleation could be estimated when apatite particles covered the entire surface at 48 h of soaking in SBF. The densities of the active sites were ca. 0.16 and ca. 0.13 μ m⁻² on the CT-cpTi and CT-Ti6Al4V specimens respectively. Table. 3.1 indicated the possible relation between the rutile rod density (per square micron) and active-site density (per square micron). Here it is indicated that the rutile rod density varies as approximately 4.6 × 10⁴–6.9 × 10⁴ (effective surface area: 14.44–21.66 μ m²) on the surface. The active-site density must correspond to the density of rutile nanorods, and increases as the density of rutile nanorods grows.

Rutile nanorod arrays on the Ti6Al4V specimen provide smaller number of active sites for primary apatite nucleation. It means that, superior apatite nucleation occurs on the rutile nanorod arrays for the cpTi substrate in supersaturated SBF because of high rod density. This implies that a relatively large number of apatite nuclei are provided on the rutile rod array of the CT-cpTi specimen. The number and diameter of apatite particles increased with the soaking time in the range from 0 h to 40 h due to the primary and secondary nucleation and growth of apatite. The secondary nucleation and growth of apatite. The secondary nucleation and growth of apatite on CT-cpTi specimen contributes to the large size of apatite secondary particles. The CT-cpTi specimen exhibited a stronger intensity of diffraction peaks corresponding to apatite after being soaked in SBF for 72 h in Fig. 3.4. This intensity could be attributed to the thick apatite layer on its surface. In addition, thick rutile layers were obtained on the surface of the CT-cpTi specimen as shown in Fig. 3.2 (a). One possible explanation for the strong diffraction intensity of apatite is that thick rutile layers with high rod density

provide more active sites for apatite formation.

In conclusion, cpTi and Ti6Al4V alloys produced the highly ordered rutile nanorod arrays on the surface after the chemical and aging treatment. The chemically-treated cpTi and Ti6Al4V alloys deposited apatite within 1 d of soaking in SBF. The dense and thick rutile nanorod arrays with high rod density on cpTi substrate showed the superior ability in inducing apatite deposition in vitro. High rod density and thickness of rutile nanorod arrays should be responsible for the high ability in depositing apatite.





Table 3.1 Relation between rutile rod density and active-site density for CT-cpTi and CT-Ti6Al4V specimens.

| Samples | CT-cpTi | CT-Ti6Al4V |
|--------------------------------------|-------------------------------|-------------------------------|
| Rod density (μm^{-2}) | $(1.04 \pm 0.06) \times 10^3$ | $(0.70 \pm 0.10) \times 10^3$ |
| Active-site density (μm^{-2}) | 0.16 | 0.13 |
| Rods (per active site) | 6.1-6.9×10 ⁴ | 4.6-6.1×10 ⁴ |

3.5. Conclusion

A chemical treatment and subsequent aging treatment were employed to produce the highly ordered rutile nanorod arrays on the surface of cpTi and Ti6Al4V alloys. The substrate affect the thickness and rod density of rutile nanorod arrays. The cpTi specimen favored the formation of rutile rods with high density. Rutile nanorod arrays on the CT-cpTi and CT-Ti6Al4V alloy specimens induced apatite formation after soaking in SBF for 1d. However, the behavior of apatite deposition was different between the two specimens. More deposited apatite particles with larger diameter after three days of soaking in SBF can be found on the CT-cpTi specimens. The low density of rutile rods on the surface of the CT-Ti6Al4V alloy specimen is responsible for the inferior ability to induce apatite nucleation on the CT-Ti6Al4V alloys at an early stage, indicating that the amount of deposited apatite corresponded to the density of rutile rods. CT-cpTi specimen showed apatite-forming ability superior to that of the CT-Ti6Al4V alloy specimens because they own the dense and thick rutile layer with high rod density.

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Chapter 4

Photo-deposition behaviors of Ag on highly ordered rutile nanorod arrays

4.1. Introduction

In recent years, titania layers, especially anatase and rutile, have attracted a lot of attention as coating layers of implant device due to their in vitro apatite-forming ability, cell responses, long-term stability and low cost [1-7]. It is commonly known that titania has three kinds of crystal phase, namely anatase, rutile, and brookite. Recent studies [5-7] have shown the importance of rutile in inducing apatite formation in vitro. It is widely accepted that rutile with {110} facets is more stable compared to other facets of rutile. However, the special facets of rutile, such as rutile {101} facet have been reported to show the excellent ability in inducing apatite in vitro [6]. In the special field of biomedical implants, when implants were introduced into the body, their surface is generally sensitive to infection due to the accumulation of various proteins. This kind of protein accumulation on their surface may make it appropriate for bacteria production under physiological conditions [8]. The subsequent accumulation of bacteria on the implant is still one of the causes of inflammatory diseases [9]. Recent investigation in the property of noble metals such as Ag or Au incorporated into titania layer have been attracted a lot of attention due to their good anti-bacterial ability, and satisfactory stability [8,10-12].

Rai et al. [10] have reviewed that the antibacterial properties of Ag ions, and reported Ag nanoparticles can also inhibit bacterial attachment onto the implant surface. Bosetti et al. [11] indicated that in vitro silver-coated material exhibited excellent cells spreading, and silver is neither genotoxic nor cytotoxic. In vivo studies, implants coated with silver have no any local or systemic side-effects. Among the above-mentioned noble metal, silver is a good choice to introduce into titanium or other metal implants for improving their antibacterial ability or catalytic activity.

We have successfully synthesized pure rutile layers with the exposed (101) on the cpTi disc by the chemical treatment and the following aging treatment [13]. Since many studies have reported Ag particles was deposited on pure anatase [14, 15] or anatase nanosheets with exposed high surface energy [16], there is no clear evidence that pure rutile nanorod arrays with exposed (101) plane decorated Ag particles. In this chapter, we prepared pure rutile nanorod arrays with exposed (101) plane according to our previous report [13] and decorated Ag particles onto the surface of rutile layers by a photodeposition method. We demonstrated a series of Ag-decorated rutile layers with various photo-deposition time on the cpTi substrates. The aim of this study was to discuss the photo-deposition behaviors of Ag on the rutile layers with exposed (101) plane. In addition, the effect of various substrates such as niobium (Nb), zirconium (Zr), tantalum (Ta) and commercially available pure titanium (cpTi) substrates on the photo-deposition behavior.

4.2. Experimental

4.2.1. Materials

A sheet of pure niobium (Nb, 99.9%), zirconium (Zr, 99.2%), and tantalum (Ta, 99.95%) which were purchased from The Nilaco Co. Ltd. (Tokyo, Japan), and cpTi discs (GC Corp, Tokyo, Japan) were polished by using the sandpaper #1000, then washed in acetone and ultra-pure water at room temperature. The cleaning process was repeated up to 3 times. The as-cleaned substrates were denoted as NT-samples (NT-cpTi, NT-Nb, NT-Zr and NT-Ta).

4.2.2. Preparation of rutile nanorod arrays on cpTi

In brief, rutile layers were prepared on the NT-cpTi discs of size of 15 $\Phi \times 1$ mm by soaking them in the treating solution at 80°C for 3 days and then aged in ultra-pure water at 80°C for 1 day. Treating solutions (TSs) contained titanyl sulfate (TiOSO₄; 0.14 mol·m⁻³), 15 mol·m⁻³ hydrogen peroxide (H₂O₂), and its pH value was adjusted to 0.7 by using nitric acid (HNO₃). The NT-cpTi samples after the chemical and aging treatment were denoted as CT-sample (CT-cpTi).

4.2.3. Deposition of Ag under the UV-irradiation

A 30 mL of 0.2 mol·m⁻³ AgNO₃ aqueous solution was placed in a glass petri dish and then each sample prepared according to section 4.2.2 or each as-cleaned substrate (NT-cpTi, NT-Nb, NT-Zr and NT-Ta) was held in a glass petri dish, respectively. Ultraviolet light irradiation was carried out for 0, 30, 60 and 90 min at the room temperature using a UV curing apparatus equipped with high pressure Hg lamp (HLR100T-2, SEN LIGHTS Corp., Osaka, Japan, primary wavelength 365 nm, 170 mW/cm²). After UV irradiation, the substrate was taken out of the glass petri dish, and slightly washed three times with ultra-pure water. Finally, the substrates were dried in a constant temperature incubator at 60°C. The NT-cpTi and CT-cpTi substrates in the 30 mL of 0.2 mol·m⁻³ AgNO₃ aqueous solution for 90 min without UV irradiation was choose as the control group, which were denoted as NT-cpTi_WoUV and CT-cpTi_WoUV.

4.2.3. Characterization

The change in weight of the samples before and after the UV irradiation was examined with a precision balance (XSR205DUV, Mettler-Toledo, Switzerland). The technique of thin film X-ray diffraction (TF-XRD, X'Pert-ProMPD, PANalytical, Almelo, the Netherlands: Cu K α , λ =0.15418 nm, 45 kV–40 mA) was used to examine the crystal structure of the samples, where all data were collected in the 20 scan mode with a step-scan interval of 0.02°, a counting time of 1 s per step, and a constant X-ray incident angle θ of 1.0°. The surface morphology of samples after the photo-deposition process for 90 min was observed by using scanning-electron microscopy (SEM, VE-9800, Keyence Co. Ltd., Osaka, Japan). The samples were coated with Pt-Pd coating (thickness: 10 nm) for the SEM observation via using a sputter-coater (E-1030, Hitachi High-Technologies Co. Ltd., Tokyo, Japan).

4.3. Results

4.3.1. Surface structure of cpTi and rutile after photo-deposition for 0, 30, 60 and 90 min

Fig. 4.1 shows TF-XRD patterns of NT-cpTi (a) and CT-cpTi substrates (b) after the photo-deposition process for 0, 30, 60 and 90 min. In Fig. 4.1 (a), the intensity of the diffraction peak at 38° obviously grew with the deposition time. The diffraction peaks at 44° and 64° corresponding to (200) and (220) plane of Ag was detected after the photodeposition for 30 min. The diffraction peaks at 35.0°, 38.4°, 40.1° and 52.9° corresponded well to the titanium (ICDD-JCPDS PDF#44-1294). For the CT-cpTi substrates in Fig. 4.1 (b), the diffraction peaks at 27.2° , 36.2° and 41.3° which are assignable to (110), (101), and (111) plane of rutile (ICDD-JCPDS PDF#21-1276) were observed clearly. The rest diffraction peaks were ascribed to the titanium. The intensity of the diffraction peaks at 38°, 44° and 64° corresponding to (111), (200), and (220) plane of Ag clearly increased with the deposition time, while the intensity of diffraction peak at 36.2° for rutile (101) reduced. It is noted the diffraction peak for (101) plane of rutile disappeared after the deposition time of 90 min. In addition, no diffraction peak corresponding to Ag can be detected on the NT-cpTi and CT-cpTi substrates without UV irradiation.

Fig. 4.2 (a) shows the change in the weight of NT-cpTi and CT-cpTi substrates was plotted as a function of the photo-deposition time. Both NT-cpTi and CT-cpTi substrates gained the weight after the photo-deposition process. It is clearly observed that NT-cpTi substrates gained the more than that of CT-cpTi substrates after the photo-deposition. The weight of NT-cpTi and CT-cpTi substrates without UV irradiation remained unchanged. The peak area of diffraction peak at 38° was calculated in Fig. 4.2 (b). The peak area at 38° for NT-cpTi substrates and CT-cpTi substrates increased with the deposition time. It is suggested that amount of deposited Ag grew with the deposition time. In addition, the increased rate of Ag on NT-cpTi substrates was greater than that on CT-cpTi substrates.

XRD patterns obtained in 20/0 scan mode of NT-cpTi and CT-cpTi substrates after the photo-deposition for 90 min were shown in Fig. 4.3 and Fig. 4.4. NT-cpTi substrate gave the strong intensity of diffraction peaks corresponding to (002) and (220) plane of Ag after the photo-deposition process. In the XRD patterns with the range from 37.5° to 39.0° (Fig. 4.4 (b)), a diffraction peak at around 38.2° can be assigned to (111) plane of Ag on the NT-cpTi substrates. In addition, the intensity of diffraction peaks corresponding to titanium decreased on the NT-cpTi substrates after the irradiation. In Fig. 4.4(a), it is obvious that the diffraction peak corresponding to (220) plane of Ag was detected on the CT-cpTi substrates after the photo-deposition. In addition, a weak diffraction peak at 44° was ascribed to the (002) plane of Ag. There is no significant difference in the intensity of other diffraction peaks before and after the photo-deposition process. Furthermore, a faint diffraction peak around 38.2° attributed to the (111) plane of Ag can be confirmed in Fig.4.4(b).

4.3.2. Surface morphology of cpTi and rutile after the photo-deposition for 90 min

Fig. 4.5 shows the surface SEM images of NT-cpTi after the photo-deposition process for 30 and 90 min, respectively. Particle having polyhedral shapes can be clearly

observed on the surface of NT-cpTi substrate in Fig. 4.5 (a) and (a'). The size of this particle was around 10 μ m. After 90 min of the photo-deposition, many particles scattered on the surface of NT-cpTi substrates in Fig. 4.5 (b). In the higher magnification, those particles have polyhedral shapes. According to Fig. 4.1 (a), the deposited particles can be confirmed as Ag particles. Fig. 4.6 shows surface SEM images of CT-cpTi substrates after the photo-deposition process for 30 and 90 min, respectively. The particles with around 1 μ m in size were randomly deposited on the surface. The shape and size of deposited particles on the CT-cpTi substrate was significantly different from that on the NT-cpTi substrate in Fig. 4.5.

4.3.3. Surface structure and morphology of Zr, Nb, and Ta substrates after the photo-deposition for 90 min

Fig. 4.7 shows the TF-XRD patterns of NT-Zr, NT-Nb, and NT-Ta substrates before and after the photo-disposition process. After the photo-deposition, it can be seen that the intensity of all diffraction peaks corresponding to substrates (Zr, Nb, and Ta) was reduced. A weak intensity of diffraction peak at 44° corresponding to (200) plane of Ag can be found on the NT-Zr substrates. NT-Nb and NT-Ta substrates gave a very weak intensity of diffraction peak at 64° corresponding well with (220) planes of Ag. In the TF-XRD patterns in range of 37.5° and 40°, a weak diffraction peak at 38° was further confirmed on the NT-Zr, NT-Nb, and NT-Ta substrates, which was ascribed to (111) plane of Ag. It is indicated that Ag can be formed on the NT-Zr, NT-Nb, and NT-Ta substrates by the UV-irradiation. For further investigating the effect of various substrates on the photo-deposition behavior of Ag, the XRD patterns obtained in $2\theta/\theta$ scan mode of various metallic substrates were shown in Fig. 4.8. NT-cpTi substrates obviously yielded the strong intensity of diffraction peaks corresponding to (200) and (220) plane of Ag after the deposition for 90 min. Only diffraction peaks corresponding to substrate were detected on the NT-Zr, NT-Nb, and NT-Ta substrates. In the Fig. 4.8(b), a weak diffraction peak at around 38° corresponding to Ag was detected on all samples. Table 4.1 shows the change in the weight (W/mg) of various metallic substrates subjected to the UVirradiation for 90 min. The gained weight (GW) of those substrates was increased in the order: NT-Zr < NT-Ta < NT-Nb < NT-cpTi.

Fig. 4.9 shows the SEM images of NT-Zr, NT-Ta and NT-Nb substrates after the photo-deposition process for 90 min. In Fig. 4.9 (a), the particles on the surface of NT-Zr substrate are in the shape of diamond and polyhedron. In Fig. 4.9 (b) and (c), the particles have irregular polyhedron crystal morphology on the surface of NT-Nb and NT-Ta substrates. The size of particles on the NT-Nb substrates was larger than that of Zr and Ta substrates. Those particles were recognized as Ag according to Fig. 4.7.

From the above results, it was found that Ag particles with small size were deposited on the rutile layer under the UV irradiation. In addition, the ability to deposit Ag particles on the various metallic substrates under the irradiation was increased in the order: NT-Zr < NT-Ta < NT-Nb < NT-cpTi.



Fig. 4.1 TF-XRD patterns of NT-cpTi (a) and CT-cpTi (b) substrates after the photodeposition for 0, 30, 60 and 90 min. \blacksquare : titanium, \blacktriangle : rutile. For comparison, the TF-XRD patterns of NT-cpTi and CT-cpTi substrates obtained in AgNO₃ solution without UV irradiation for 90 min was shown.



Fig 4.2 Change in the weight (a) and the peak area at 38 degree (b) of NT-cpTi and CTcpTi substrates after 0, 30, 60, 90 min of photo-deposition. The weight change (red line) of NT-cpTi and CT-cpTi substrates in AgNO₃ solution without UV irradiation (NTcpTi_WoUV and NT-cpTi_WoUV) for 0 and 90 min was shown for comparison.



Fig 4.3 XRD patterns obtained in $2\theta/\theta$ scan mode of NT-cpTi substrates before and after the photo-deposition time of 90 min. (a): 20-70 degree, (b): 37.5-39 degree. \blacksquare : titanium. For comparison, the XRD patterns obtained in $2\theta/\theta$ scan mode of NT-cpTi in AgNO₃ solution without UV irradiation for 90 min was shown (red line).



Fig 4.4 XRD patterns obtained in $2\theta/\theta$ scan mode of CT-cpTi substrates in 0.14 mol·m⁻³ TS before and after the photo-deposition time of 90 min. (a): 20-70 degree, (b): 37.5-39 degree. \blacksquare : titanium; \blacktriangle : rutile. For comparison, the XRD patterns obtained in $2\theta/\theta$ scan mode of CT-cpTi in AgNO₃ solution without UV irradiation for 90 min was shown (red line).



Fig. 4.5 SEM images of NT-cpTi substrate after the photo-deposition for 30 (a: \times 1000, a': \times 5000) and 90 min (b: \times 1000, b': \times 5000).



Fig. 4.6 SEM images of CT-cpTi substrate after the photo-deposition for 30 (a: \times

5000) and 90 min (a': ×5000).


Fig 4.7 TF-XRD patterns of NT-Zr (a), NT-Nb (b) and NT-Ta substrates (c) before and after the photo-deposition for 90 min. \bigcirc : zirconium, \square : niobium, and \triangle : tantalum.



Fig 4.8 XRD patterns obtained in $2\theta/\theta$ scan mode of NT-Zr, NT-Nb, NT-Ta substrates and NT-cpTi substrates after the photo-deposition for 90 min. \blacksquare : titanium. (a): 20-70 degree, (b): 37.5-40 degree

4.4. Discussion

Many reports have been studied the possible factors such as irradiation time [17] and chemical agents in solution [18, 19] that affect the photo-deposition behavior of Ag. In our present work, the changes in the types of substrates (NT-cpTi, CT-cpTi, NT-Zr, NT-Nb, and NT-Ta substrates) resulted in the different photo-deposition behavior including the amount or size of deposited Ag particles. Rutile layers on the CT-cpTi substrate can deposit less amount of Ag particles than NT-cpTi substrate as shown in Fig. 4.2 (a). Besides, Ag particles with high crystallinity and large size were formed on the NT-cpTi substrates in Fig. 4.5. As shown in Fig. 4.1(a), the diffraction peak corresponding to Ag appeared after the photo-deposition for about 30 min. This result indicates that Ag particles formed on the surface of NT-cpTi substrates. Fig. 4.1(b) and Fig. 4.2 (b) indicated that Ag was produced on the CT-cpTi substrates after around 60 min of photo-deposition. According to the above results, it is supposed that the formation of Ag particles is prioritized on the surface of NT-cpTi substrates.

The photo-deposition of Ag on the surface of substrates was conducted by two processes: (1) activation of electrons (e^-) by the UV light and (2) photoreduction of Ag⁺ to Ag⁰. When the energy of the photon is greater than the work function of materials, the e^- will be excited from the atom. If the photon cannot reach the energy of the work function, it is hard to enable e^- ejection from the atom. Therefore, the photoelectric effect plays an important role in the generation of e^- . As reported by Michaelson et al. [20], the electron work function of various substrates decreases in the order Ti (4.33 eV) > Nb (4.30 eV) >Ta (4.25 eV)> Zr (4.05 eV). The high-pressure Hg lamp of UV curing instrument provide the lines at 365 nm, 315 nm and 254 nm. According to equation (Eq (1)), energy of the incident photon is 3.40, 3.90 and 4.89 eV at the wavelength of 365 nm, 315 nm and 254 nm for Hg lamp.

$$E = hv = h \times (c \div \lambda) \tag{1}$$

Where E is the energy of the incident photon, h represents the Planck constant (h =6.63×10⁻³⁴ Js), c is the speed of light in a vacuum, $c = 3 \times 10^8$ m/s. λ is the light wavelength. The work function of rutile has been reported to depend on its crystal faces and treatment for preparing rutile [21,22]. The work function for rutile was indicated in the previous paper [21,22] is 4.31–6.33 eV. In our case, all NT-samples and CT-cpTi substrates (rutile) can deposit Ag particles after the UV-irradiation. In case of the 365 and 315 nm wavelength, no electrons can be ejected due to the low frequency of light. The gained weight of CT-cpTi was less than that of NT-cpTi substrates after the photo-deposition in Fig. 4.2 (a). Considering the above discussion, the work function of rutile layers on the CT-cpTi substrates is 4.33(function work of Ti) – 4.89 eV. The electrons will be activated preferentially on the surface of NT-cpTi substrates and then can be captured by Ag ions in the aqueous solution. In this case, the aggregated rate of Ag into the large particles will be accelerated on the NT-cpTi substrates. Owing to high work function of rutile, the activated rate of electrons is so slow that photoreduction of Ag ions is inhibited on the rutile. Therefore, the Ag particles with small size would be deposited on the rutile. In

addition, the basic Ti-OH groups can be generated on the surface of titania by the UV irradiation as indicated by some researchers [23,24]. Wang et al. [25] have reported that the addition of PEG resulted in the formation of Ag with smaller size, they indicated that PEG acquired OH radicals on the surface of ZnO. Therefore, one other possible explanation for deposited Ag particles with small size is that Ag ions in the AgNO₃ solution capture the H of Ti-OH groups and the pH value of solution is increased, which may be adverse for the photoreduction from Ag ions to Ag.

However, the work function of metal materials (Ti (4.33 eV) > Nb (4.30 eV) > Ta (4.25 eV) > Zr (4.05 eV)) cannot be accounted for the results that the weight of metal substrates decreases in the order: NT-cpTi > NT-Nb > NT-Ta > NT-Zr. In this regard, the work function of Ag (4.26 eV [26]) should be took into consideration. Therefore, it is supposed that deposited Ag on the NT-Ta and NT-Zr substrates are unstable, the e⁻ from the Ag can be activated, leading to the adverseness changes from Ag ions to Ag. In other word, the deposited Ag particles are transferred to the Ag ions, which would cause that NT-Ta and NT-Zr substrates gain less weight than that of NT-cpTi and NT-Nb substrates.

Table 4.1 Weight change of various substrates by the photo-deposition of Ag for 90 min

| Substrates | NT-cpTi | CT-cpTi | NT-Zr | NT-Nb | NT-Ta |
|-------------|-----------------|-------------|-------------|-------------|-------------|
| Weight | 1 65 + 0 02 | 0 037+ 0 04 | 0 019+ 0 01 | 0 060+ 0 04 | 0 025+ 0 02 |
| change / mg | 1.05 ± 0.02 | 0.037± 0.01 | 0.017± 0.01 | 0.000± 0.01 | 0.025± 0.02 |



Fig.4.9 SEM images of NT-Zr (a: ×1000), NT-Nb (b: ×1000) and NT-Ta substrate (c: ×1000) after the photo-

deposition for 90 min.

4.5. Conclusion

The NT-cpTi and CT-cpTi substrates deposited Ag under the UV- irradiation for about 30 min. The Ag particles with size in the range of 5-10 μ m having polyhedral shapes were deposited on the surface of NT-cpTi substrates, and some particles with about 1 μ m in size were formed on the rutile layers of CT-cpTi substrates after the 30 min of UV-irradiation. The size and number of deposited Ag particles were increased with the photo-deposition time. The difference in the size and amoint of Ag particles was owing to the different electric photoelectric effect of Ti and rutile. NT-Zr, NT-Ta and NT-Nb substrates provided them with ability to deposit Ag under the UVirradiation for 90 min. However, the weight gain of various substrates after the photodeposition for 90 min increased in the order of NT-Zr < NT-Ta < NT-Nb < NT-cpTi. It is supposed that the Ag ions are released from the deposited Ag on the surface of NT-Ta and NT-Zr substrates due to the relatively higher work function of Ag under the UV light.

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Summary

The present thesis has developed a facile chemical treatment combining an aging treatment to fabricate nanometer-scale rutile rod arrays on titanium substrate or other metallic substrates, like niobium, zirconium, tantalum and Ti6Al4V alloys. In addition, their bioactivity has been investigated in terms of *in vitro* apatite-forming ability. Preparation and characterization of Ag photo-deposited on the rutile nanorod arrays and other metallic substrates, like titanium, niobium, zirconium, and tantalum have been demonstrated and their photo-deposition behavior under the UV-irradiation have been examined and discussed.

Chapter 1 has described the treatment to fabricate the nanometer-scale titania rods on the surface of titanium substrates. The fabrication process is a combination of a chemical treatment with a titanyl sulfate concentration-controlled treating solution (0.10, 0.14 and 0.18 mol·m⁻³) including hydrogen peroxide and nitric acid, and subsequent aging treatment in the ultra-pure water at 80°C for 1 day. The chemical treatment was proceeded up to 3 day at 80°C. After the aging treatment, random or highly ordered, nanorod arrays of rutile or titania are prepared on the surface of titanium substrates. The surface morphology and thickness of rutile/titania layers are dependent on the titanyl sulfate concentration in the treating solution. 0.10 mol·m⁻³ TiOSO4 TS provided randomly packed aggregates of oriented anatase and rutile rods, while 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs yielded highly ordered rutile rods. In order to explain the effect of titanyl sulfate concentration in the treating solution, the fabrication of rutile nanorods arrays have been proposed though the following steps:

- 1. The chemical interaction of titanium substrates with hydrogen peroxide yields an amorphous titanium oxide layer.
- 2. The nucleation of rutile must be dependent on the titanium complexes in the treating solution.
- The growth of rutile proceeds at the expense of the amorphous titanium oxide layer.

It was concluded that proper control in the concentration of titanyl sulfate will be critical to generate the highly ordered rutile nanorod arrays.

Chapter 2 demonstrated the chemical approach to fabricate rutile layers on the various metallic substrates including niobium (Nb), zirconium (Zr), tantalum (Ta) and Ti6Al4V alloys. The fabrication process is similar to that employed in Chapter 1, it employs chemical treatment in 0.14 mol·m⁻³ titanyl sulfate of treating solution to deposit titania layers on the surface of various metallic substrates. Nb substrate can produce the pure anatase layer, no deposited layer can be fabricated on the Zr substrate, whereas the pure rutile layers with exposed {101} facet were formed on the surface of Ta substrate and Ti6Al4V alloys. The X-ray diffraction intensity of {101} facets of rutile increased in the order of Ta < Ti6Al4V alloy< Ti substrate, which were due to the concentration of titanium complexes in treating solution. Chemical treatment gave a decrease in the weight

of Nb substrate and a rise in the weight of Ta and Ti6Al4V alloy substrates due to the formation of rutile layer. Rutile layers fabricated on Ta and Ti6Al4V alloy substrates was in a similar way with that on Ti. Chemical reaction of substrate with treating solution gives an amorphous tantalum/titanium oxide layer on the Ta and Ti6Al4V alloys, and then the rutile nucleation which was derived from treating solution, is expected to occur at the surface of the amorphous layer. Finally, the rutile layers are formed by consuming the amorphous layer. The possible process for anatase formation on Nb substrate is that the complicated Ti-Nb complexes are formed due to the releasing of Nb ions, which favor the nucleation of anatase.

Chapter 3 showed the highly ordered rutile nanorod arrays were fabricated on the surface of cpTi and Ti6Al4V alloy substrates via the chemical treatment and following aging treatment as described in the chapter 1: 0.14 mol·m⁻³ titanyl sulfate of treating solution was choose to proceed the chemical treatment. The structure and the in vitro apatite-forming ability of the chemically treated cpTi specimens and Ti6Al4V alloy specimen were compared. Both rutile nanorod arrays on cpTi and Ti6Al4V alloy specimens can be confirmed to deposit apatite particle after being soaked in SBF within 1 day. The cpTi specimens showed superior rate of apatite nucleation and favored the formation of a large number of apatite particles with lager diameter. Such excellent apatite-forming ability of cpTi substrate can be attributed to the dense and thick titania layers with higher rutile nanorod density on the surface. Highly ordered rutile nanorod arrays will be promising for bone and vascular implants due to their excellent

biocompatibility, controllable dimensions, and large surface-to-volume ratio. Generally, the requirements for biomedical implants are good biocompatibility. By changing the diameter, rod density or thickness of rutile nanorods on the metallic implants, rutile nanorod arrays on implants can be tailored to achieve extremely stable and excellent biocompatibility.

Chapter 4 concentrated on the photo-deposition behaviors of Ag on the rutile nanorod arrays of titanium substrates. Besides, the effect of Nb, Zr, Ta, and cpTi substrates on the photo-deposition of Ag was discussed. The rutile layer on the cpTi substrate inhibited the formation of Ag particles, and cpTi substrates favored the formation of polyhedral Ag particles with larger size. Ag was also successfully fabricated on the surface of Zr, Ta and Nb substrates after the photo-deposition for 90 min. However, the intensity of Ag on the Zr, Ta and Nb substrates was weaker than that of cpTi substrates. The weight gain of various substrates after the photo-deposition for 90 min increased in the order of Zr < Ta < Nb < cpTi. It was considered that the photo-deposition behavior of Ag on the various substrates can be attributed to the photoelectric effect. In the future prospects, along with bioactivity if antibacterial property is provided by the titania incorporating antibacterial agent on the metallic implants, the risk of those implants can be minimized. The incorporation of the amount or size of Ag particles on the metallic substrates should be optimized by evaluating their antibacterial activity, compatibility together with bioactivity.

In summary, those above conclusions were described. Those results indicate that the

present surface modification on the titanium and its alloy (Ti6Al4V) was effective to produce the rutile nanorod arrays that can provide excellent in vitro apatite-forming ability.

List of publication

- I Publications
- The fabrication of nanostructured titania polymorphs layer with high crystallinity and its apatite-forming ability <u>Xingzhu Liu</u>, Fan Xiao, Satoshi Hayakawa, Akiyoshi Osaka Surface and Coatings Technology, Vol. 363, pp.338-343 (2019).
- Effect of titanyl sulfate concentration on growth of nanometer-scale rutile rod arrays on the surface of titanium substrate <u>Xingzhu Liu</u>, Tomohiko Yoshioka, Satoshi Hayakawa Journal of the Ceramic Society of Japan Vol. 127, No. 8, pp.545-550 (2019)
- II Presentation in academic conference
- A. International conferences
- <u>Xingzhu Liu</u>, Toshiisa Konishi, Tomohiko Yoshioka, Satoshi Hayakawa, "Chemical growth and apatite-forming ability of titania layer with tailored facets on titanium substrate," The 17th Asian Bioceramics Symposium (ABC 2017), Okayama, Japan, November 30th-December 1st, 2017.

- Xingzhu Liu, Tomohiko Yoshioka, Satoshi Hayakawa, "Chemical growth and apatite-forming ability of rod-like rutile titania layers with tailored facets on titanium substrate," The 30th Symposium and Annual Meeting of International Society for Ceramics in Medicine, Nagoya, Japan, October 26th-29th, 2018.
- B. Domestic conference
- Xingzhu Liu, Toshiisa Konishi, Tomohiko Yoshioka, Satoshi Hayakawa, "In vitro enhanced apatite-forming ability on titania film with tailored facets via facile synthetic route at low temperature," The 30th Fall Meeting of the Ceramic Society of Japan, Kobe, Japan, September 19th-21st, 2017.
- III Other publications
- A. Papers
- 1. Apatite-forming ability of hydrothermally deposited rutile nano-structural arrays with exposed {101} facets on Ti foil

Fan Xiao, Guaang-Qiang Jiang, Jin-Yu Chen, Zhen-Lan Jiang, <u>Xing-Zhu Liu</u>, Akiyoshi Osaka, Xiao-Chun Ma

Journal of Materials Science, Vol. 53, No. 1, pp. 285-294 (2018).

 Low-temperature fabrication of titania layer on 3D-printed 316L stainless steel for enhancing biocompatibility

Fan Xiao, Chen Zong, Wei Wang, <u>Xing-zhu Liu</u>, Akiyoshi Osaka, Xiao-chun Ma Surface and Coatings Technology, Vol. 367, pp.91-99 (2019).

IV Award

1. ABC student award. (ABC 2017)

"Chemical growth and apatite-forming ability of titania layer with tailored facets on titanium substrate,"

Xingzhu Liu, Tomohiko Yoshioka, Satoshi Hayakawa,

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