Preparation of bioactive Ti and its alloys via electrochemical treatment in sulfuric acid solution

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An electrochemical method was established for achieving apatite formation on the surfaces of Ti and its alloys in simulated body fluid (SBF). Crystalline titania layers are formed on pure Ti, Ti–6Al–4V, Ti–6Al–2Nb–1Ta and Ti–15Mo–5Zr–3Al alloy surfaces when these alloys are anodized in H2SO4 solutions of different concentrations and at different applied voltages. The anodically oxidized substrates form a dense and uniform bone–like apatite layer on their surfaces in SBF that contains ions in concentrations similar to those present in human body blood plasma. The apatite formation on the surfaces of Ti and its alloys in SBF is proposed to be induced and nucleated by the lattice-matching relationship of the crystal structures between the apatite and rutile phases in the titania layers. As the surface morphology of titania layers on anodically oxidized Ti and its alloys is a three-dimensional, open, porous structure, the resultant surface structure can provide strong adhesive strength between the apatite layer and the substrates. Therefore, use of the described anodic oxidation is expected to result in Ti and its alloys being suitable for use in bioactive implant materials, even under load-bearing conditions.

Key-words: Ti and its alloys, Anodic oxidation, Rutile, Anatase, Apatite

1. Introduction

Artificial materials are generally encapsulated by fibrous tissue after implantation into living bone defects, which eventually results in their being isolated from the surrounding bone. Some ceramics, such as Bioglass, have been sintered into fabric form and are effective for apatite nucleation. Glass-ceramic A–W, have been shown to bond to living bone without forming fibrous tissue. These materials are called bioactive ceramics and are currently used as important bone-repairing materials in clinical fields. However, even glass-ceramic A–W, which has the highest mechanical strength among the above bioactive ceramics, cannot be used to repair high-load-bearing bone defects, such as femoral and tibia bones. Metallic materials, such as Ti, Ti–6Al–4V alloy, etc., have been widely used for these applications because of their good mechanical properties and biocompatibility. However, none of these metallic materials can directly bond to living bone.

Over the past decade, various surface modification techniques have been used in efforts to obtain titanium metal with bioactive bone-bonding ability. The most common method currently used for actual clinical applications is plasma spraying an HA coating onto titanium metal at elevated temperatures. Hydroxyapatite in powder form is briefly melted in a flame at temperatures higher than 1000°C. The HA layer then decomposes and peels off the substrate. The resultant coating therefore becomes unstable and degrades after long periods of implantation in a living body. Hence it is most desirable that the metallic materials themselves exhibit bone-bonding ability, i.e., bioactivity.

It has been determined that an essential requirement of an artificial material, in order for it to bond to living bone, is the formation of a bone-like apatite layer on its surface in the living body. The apatite layer can be reproduced on the surface of the artificial material even in an acellular simulated body fluid (SBF) with ion concentrations similar to those found in human blood plasma. Therefore, if the metallic materials themselves form the biologically active bone-like apatite layer on their surfaces in the body, as in the case of bioactive ceramics, then the bioinert problem can be overcome. Recently, we found that the crystalline structure of the titania layers formed on the surface of titanium metal exhibits high apatite-forming ability in SBF after being anodized in sulfuric acid. The anodic oxidation can produce an oxidized layer but also a porous structure on the sample surface. The formation of the porous structure will give a favorable effect on the adhesion between apatite and substrate. Furthermore, it can be speculated that Ti–OH groups with specific structure, which are effective for apatite nucleation, are formed on the sample surface, since the anodic oxidation is performed in the aqueous solution. Such surface structural changes can not be achieved by the simple oxidation in air. Therefore, we have employed the anodic oxidation method to induce apatite-forming ability on the titanium surface.

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In this study a simple electrochemical surface treatment was used to prepare bioactive Ti and its alloys in sulfuric acid solutions. The characteristics and bioactivity of the anodic films on the resultant surfaces were investigated in vitro.

2. Materials and methods

2.1 Preparation of specimens
Anodic oxidation treatment in sulfuric acid solutions was carried out with pure Ti (Nilaco Co., Ltd., Tokyo, Japan), Ti–6Al–4V, Ti–6Al–2Nb–1Ta and Ti–15Mo–5Zr–3Al (titanium alloys were kindly supplied by Kobe Steel Co. Ltd., Kobe, Japan) to form crystalline titania films on their surfaces. The chemical compositions of the metals used in the present study are listed in Table 1. The substrates, 10 × 10 × 1 mm³ in size, were mechanically abraded with a diamond plate (No. 400), and then washed with pure acetone, ethanol and distilled water in an ultrasonic cleaner.

2.2 Anodic oxidation
The anodic oxidation was performed in the potentiostatic mode. Electrolytes were prepared in 1.0M or 2.0M H₂SO₄ solutions in a glass vessel. A direct current power supply system (EX1500H, Takasago Co., Japan) was used. The applied voltages used were in the range of 100–180 V, for 1 min, at room temperature. Titanium plates were used as the cathode, and samples were fixed with titanium wires to the titanium anode. A magnetic stirrer (MD500, Yamato, Japan), used at a fixed agitation speed, was used to ensure homogeneity of the electrolyte and accelerate the escape of gas. On completion of the anodic oxidations the samples were rinsed with distilled water and dried in an oven at 40°C for 24 h.

2.3 Soaking in the simulated body fluid
The bioactivity of an electrochemically treated specimen was evaluated by examining apatite formation on the surface in an SBF solution. SBF was prepared by dissolving the following salts in distilled water: NaCl, NaHCO₃, KCl, K₂PO₄·3H₂O, MgCl₂·6H₂O, CaCl₂ and Na₂SO₄ (all reagent grade), buffered at pH 7.4 with tris-hydroxymethylaminomethane [(CH₂OH)₃CNH₂] and HCl at 36.5°C. Each specimen was soaked in 30 ml SBF for 1–7 d. The substrates were then rinsed with distilled water and carefully dried at room temperature.

2.4 Analysis of samples
Surface structural changes of the specimens were examined by thin-film X-ray diffraction (TF-XRD, RINT2500, Rigaku, Japan) and field-emission scanning electron microscopy with Energy Dispersive X-ray (EDX) analysis (FE-SEM, S–4700, Hitachi, Japan) both before and after anodic oxidation treatment and the subsequent soaking in SBF.

3. Results
Figure 1 shows variations in the TF-XRD patterns of the surfaces of Ti substrates subjected to anodic oxidation in 2.0M H₂SO₄ solution at 100, 150 or 180 V. There was a decrease in the intensity of the peak ascribed to the Ti metal, while peaks for the anatase and rutile appeared on the surface of the Ti substrates. The intensity of the rutile peak increased with an increase in voltage from 100 to 180 V. The titania films fully comprised the rutile phase; the anatase phase disappeared at 180 V.

Figure 2 shows the SEM photographs of the surfaces of Ti, Ti–6Al–4V, Ti–6Al–2Nb–1Ta and Ti–15Mo–5Zr–3Al substrates subjected to anodic oxidation under different
Fig. 3. TF-XRD patterns of the surfaces of Ti untreated (a) and subjected to anodic oxidation in 2.0M H$_2$SO$_4$ solution at 100 (b), 150 (c) and 180 V (d), and subsequently soaked in SBF for seven days.

Fig. 4. TF-XRD patterns of the surfaces of Ti–6Al–4V alloy untreated (a) and subjected to anodic oxidation in 1.0M H$_2$SO$_4$ solution at 150 V (b), and subsequently soaked in SBF for seven days (c).

Fig. 5. TF-XRD patterns of the surfaces of Ti–6Al–2Nb–1Ta alloy untreated (a) and subjected to anodic oxidation in 1.0M H$_2$SO$_4$ solution at 150 V (b), and subsequently soaked in SBF for seven days (c).


conditions. Titania layers with a three-dimensional, open, porous structure are formed on the surfaces of Ti and its alloys after being anodized in H$_2$SO$_4$ solutions. The resultant surface structures can improve the bonding strength of the apatite layer to a substrate. It is therefore envisaged that they will provide a high bonding strength between Ti-based implants and living bone for long periods, after implantation.

Figure 3 shows the TF-XRD patterns of the surface of Ti substrates soaked in SBF for seven days after being anodized in a 2.0M H$_2$SO$_4$ solution at 100, 150 or 180 V, compared to that of the Ti substrate without treatment. All the Ti substrates subjected to anodic oxidation formed apatite layers on their surfaces, whereas the original substrate without anodic oxidation treatment did not form apatite on its surface. The intensity of the TF-XRD peaks ascribed to apatite increased with increasing anodic voltage from 100 to 150 V, while no apparent changes occurred from 150 to 180 V. These findings indicate that the crystal structure of anodic films on the surfaces of Ti substrates can induce apatite formation on their surfaces, but the apatite formation ability differs with variations in the crystal structure.

Figures 4–6 show the TF-XRD patterns of the surfaces of Ti–6Al–4V, Ti–6Al–2Nb–1Ta and Ti–15Mo–5Zr–3Al alloys subjected to anodic oxidation in 1.0M H$_2$SO$_4$ solution at 150 or 110 V and then soaked in SBF for seven days, compared to before treatment. All the Ti alloys formed anatase and rutile phases on their surfaces after anodic oxidation treatment in H$_2$SO$_4$ solutions, as in the case of pure Ti. After treatment, all the Ti alloys also induced apatite formation on their surfaces in SBF within seven days. These results further demonstrate that the crystalline-structured titania layers process the ability to induce apatite formation.

Figure 7 shows the SEM photographs and EDX spectra of the surfaces of Ti, Ti–6Al–4V and Ti–15Mo–5Zr–3Al substrates subjected to anodic oxidation in H$_2$SO$_4$ solutions and subsequently soaked in SBF for seven days. The SEM photographs show that a dense apatite layer formed on the surfaces of the substrates of Ti and its alloys. EDX analysis of the Ti–6Al–4V and Ti–15Mo–5Zr–3Al substrates revealed that the content of alloy elements decreased after anodic oxidation treatment.

Figure 8 shows the SEM photographs of a cross section of apatite formed on a Ti–6Al–2Nb–1Ta substrate after being anodized in a 1.0M H$_2$SO$_4$ solution at 150 V and then soaked in SBF for seven days. The dense apatite layer, with a thickness of more than 7 μm, covered the surfaces of the titania layers.

4. Discussion

The results indicate that Ti and its alloys can form apatite layers on their surfaces, in SBF, after being anodized in sulfuric acid solutions under various conditions. In an earlier paper, however, we reported that titania layers with different crystalline structures have different abilities to induce apatite
Fig. 6. TF-XRD patterns of the surfaces of Ti–15Mo–5Zr–3Al alloy untreated (a) and subjected to anodic oxidation in 1.0 M H₂SO₄ solution at 110 V (b), and subsequently soaked in SBF for seven days (c).

Fig. 7. SEM photographs and EDX spectra of the surfaces of Ti (a), Ti–6Al–4V (b) and Ti–15Mo–5Zr–3Al (c) alloys subjected to anodic oxidation in: (a) 2.0 M H₂SO₄, 180 V; (b) 1.0 M H₂SO₄, 150 V; (c) 1.0 M H₂SO₄, 110 V, and subsequently soaked in SBF for seven days.

is interesting to note the following. The ratio of the relative intensity of the rutile crystal plane (101) to (110) is greater than 0.85 for Ti and its alloys anodized in H₂SO₄; a ratio of 2.9 was achieved for anodized Ti–6Al–2Nb–1Ta, while that of the standard rutile powder XRD pattern is 0.5. This means that the rutile phase of the titania layers formed on the surface of Ti and its alloys in the process of anodic oxidation is oriented to the (101) crystal plane. This can be seen in Figs. 3–6, after the anodized substrates were soaked in SBF solution for seven days the ratio of the relative intensity of the apatite (002) crystal plane to the apatite (211) crystal plane was over 0.8, while that of the standard apatite powder XRD pattern was 0.38. This implies that the apatite formed on titanium metals is oriented to the (002) crystal plane. Yang et al. recently reported that there is a fair match between the crystal orientations of the rutile (101) and apatite (002) crystal planes, and it is therefore easy to induce apatite formation on the surface of titania layers with a rutile structure due to the lattice-matching structure, which can easily provide the nuclei for epitaxial growth, and promote crystal growth. It is considered that anatase as well as rutile has some role in inducing apatite nucleation, but the apatite-forming ability of anatase might be lower than that of rutile in this study. This can be confirmed by the experimental results that TF-XRD peak of apatite in the substrate prepared at 100 V, in which anatase was mainly precipitated, was much lower than that in the substrates prepared at 150 and 180 V, in which rutile was mainly precipitated, as shown in Figs. 1 and 3.

Moreover, after analyzing the O–O distance in the (110) plane of rutile and the Ca–Ca distance in the (100) plane of apatite, Wu et al. reported a lattice-matching relationship between rutile and apatite. This is because the calcium ions in the body fluid were absorbed firstly to the surface of the implants and then they attracted the phosphate ions to form crystalline bone-like apatite. The apatite layers formed in SBF are considered to be similar to the apatite in natural bone in terms of composition and structure, because they contain minor components such as sodium, magnesium and carbonate ions and show low crystallinity and take a calcium-deficient structure. When using the lattice parameters of this aqueous synthesized carbonate-incorporated apatite, the arrangement of the O atoms of the rutile (110) plane matches fairly well with the arrangement of Ca atoms.
of the apatite (100) plane. Thus, the difference between the O–O distance in rutile and the Ca–Ca distance in apatite became small.25 This means that the carbonate-incorporated apatite has a better lattice match with the rutile phase than with hydroxyapatite. Therefore, from the viewpoint of lattice match, the apatite can easily nucleate on the surface of titanias. In conclusion, the rutile structure of titania formed on anodized Ti and its alloys will exhibit good bone-bonding ability, i.e., bioactivity.

5. Conclusions

Anodic oxidation treatment of Ti and its alloys can yield bioactive metals that can form bone-like apatite layers in SBF via the formation of titania layers with crystalline structures on their surfaces. The fair lattice-matching relationship between the rutile and apatite crystal structures can promote apatite formation on the surface of Ti and its alloys after anodic oxidation in sulfuric acid solutions. The simple electrochemical treatment is an effective method by which to prepare bioactive Ti and its alloys with bone-bonding ability, as required in load-bearing applications.

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