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Effect of hot water and heat treatment on the apatite-forming ability of titania films formed on titanium metal via anodic oxidation in acetic acid solutions

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Abstract Titanium and its alloys have been widely used for orthopedic implants because of their good biocompatibility. We have previously shown that the crystalline titania layers formed on the surface of titanium metal via anodic oxidation can induce apatite formation in simulated body fluid, whereas amorphous titania layers do not possess apatite-forming ability. In this study, hot water and heat treatments were applied to transform the titania layers from an amorphous structure into a crystalline structure after titanium metal had been anodized in acetic acid solution. The apatite-forming ability of titania layers subjected to the above treatments in simulated body fluid was investigated. The XRD and SEM results indicated hot water and/or heat treatment could greatly transform the crystal structure of titania layers from an amorphous structure into anatase, or a mixture of anatase and rutile. The abundance of Ti–OH groups formed by hot water treatment could contribute to apatite formation on the surface of titanium metals, and subsequent heat treatment would enhance the bond strength between the apatite layers and the titanium substrates. Thus, bioactive titanium metals could be prepared via anodic oxidation and subsequent hot water and heat treatment that would be suitable for applications under load-bearing conditions.

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1 Introduction

It is well known that artificial materials become encapsulated by fibrous tissue after implantation into bone defects, so that the implant materials cannot integrate with surrounding bones. Recently, some bioactive ceramics, such as Bioglass® [1], sintered hydroxyapatite (HA) [2, 3], and glass–ceramic A-W [4], were found to bond with living bones without forming a fibrous tissue. They have therefore gained widespread application as artificial bone-repairing materials in clinics [5–7]. In spite of having the highest mechanical strength among the above bioactive ceramics, glass–ceramic A-W cannot be used to repair high-load bearing bone defects because its fracture resistance is lower and its elastic modulus higher than those of cortical bone. In these cases, titanium and its alloys greatly aroused scientists' interest and have been used as bone substitutes under load-bearing applications because of their good mechanical properties and biocompatibility. However, these materials cannot directly bond to living bones after being implanted into the living body [8]. Therefore, various surface modifications have been made in the past decade in attempts to provide titanium metal with bioactive bone-bonding ability [9–14]. Currently, the most common

method is plasma spray HA coating on titanium metal performed at elevated temperatures [9]. However, the apatite layers prepared by this technique differ considerably from the apatite in bone in composition and structure, and bond weakly to the substrates [15–17]. Therefore, it is most desirable for the titanium metal to form a bioactive bone-like apatite on its surfaces in the body and exhibit bone-bonding ability [18, 19].

Recently, the present author showed that titania layers with the crystal structures of rutile and anatase formed on the surface of titanium metal can exhibit high apatite-forming ability after anodic oxidation (AO) in sulfuric acid and sodium sulfate solutions, whereas the amorphous titania layers cannot induce apatite formation in simulated body fluid (SBF) after anodizing in acetic acid or phosphoric acid solutions [20, 21]. This implies that the crystal structures of the titania layers could greatly affect the apatite-formation ability. From these results, it could be seen that, if the amorphous titania layers transformed into the crystal structure, the titania layers could possess the ability to induce apatite formation.

In previous research, Uchida et al. found that the apatite-forming ability of titanium induced by alkali treatments can be greatly enhanced by combining hot water and subsequent heat treatments [22]. They thought that the enhancement of the apatite-forming ability could be ascribed to the formation of anatase from the conversion of the sodium titanate gel on the alkali-treated titanium metal after hot water and heat treatments. Moreover, it was shown that titania gels with the specific structure of anatase and rutile prepared by the sol–gel process had higher apatite-forming ability in SBF, while amorphous titania showed no apatite-forming ability in SBF [23]. In addition, a material with apatite-forming ability and mechanical properties analogous to those of human cancellous bones was obtained by hydrolysis and polycondensation of Si–PTMO and TiPT followed by hot water treatment to precipitate nanosized anatase particles [24, 25]. Therefore, it could be concluded that the hot water and/or heat treatment are effective methods to modify the crystal structure of titania layers and promote the induction of apatite deposition on the surface of treated materials in SBF.

In this study, the titanium metal was treated with hot water and/or heat treatment after AO in acetic acid solution, and the changes in crystal structure of the titania layers and the apatite-forming ability in SBF solutions were investigated.

2 Experimental procedures

Substrates of commercially pure titanium metal (purity: 99.9%, Nilaco Co., Tokyo, Japan), 10 × 10 × 1 mm^3 in size, were polished with No. 400 diamond plate, and then washed with pure acetone, ethanol and ultrapure water in an ultrasonic cleaner.

AO was performed in the potentiostatic mode and an extended range direct current (DC) power supply system (EX1500H, Takasago Co., Kawasaki, Kanagawa, Japan) was used. Samples of titanium metal were fixed on a titanium anode 200 × 4 × 1 mm^3 in size with titanium wires, and the cathode was made of titanium plate 200 × 15 × 1 mm^3 in size. Measurements were conducted in 2.0 *M* CH_3COOH solutions in a glass chamber at 150 V at room temperature for 1 min. In the process of anodizing, a magnetic stirrer at a given agitation speed kept the electrolyte homogeneous and accelerated the escape of gas produced in the electrochemical reaction from the surfaces of titanium substrates using a magnetic mixer (MD500, Yamato, Japan).

After AO, the titanium substrates were gently washed with ultrapure water, immersed in 10 ml of ultrapure water at 80 °C for 48 h and then dried in an oven at 40 °C for 24 h, or directly heated to 600 °C at a rate of 5 °C/min in an electric furnace, kept at that temperature for 1 h and then cooled in the furnace, or treated with a combination of the above hot water (HW) and heat treatment (HT).

After AO, HW treatment and/or HT, the specimens were immersed in 30 ml of an acellular SBF with pH 7.40, whose ionic concentrations (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM) nearly equaled those of human blood plasma at 36.5 °C [26]. The SBF was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in distilled water and buffering at pH 7.40 with tris(hydroxymethyl) aminomethane and 1 M HCl at 36.5 °C. After soaking for 1, 3 or 7 days, the substrates were removed from the SBF, washed with ultrapure water and then dried on a clean bench.

Before and after various treatments and soaking in SBF, the surfaces of the titanium substrates were analyzed by thin film X-ray diffraction (TF–XRD RINT2500, Rigaku, Japan) and field-emission scanning electron microscopy (FE–SEM S-4700, Hitachi, Japan).

3 Results

3.1 Crystal structure and surface morphology of titania layers formed on the surface of titanium metals after AO, HW treatment and/or HT

After AO in 2.0 M CH_3COOH solutions at 150 V for 1 min, a mass of pores formed on the surface of the titanium metal, the pore diameters being about 1–3 μm (Fig. 1a). When the substrates were treated with hot water at 40 °C for 24 h after AO, it can be seen from Fig. 1b that numerous small spheres appeared on the surface of the

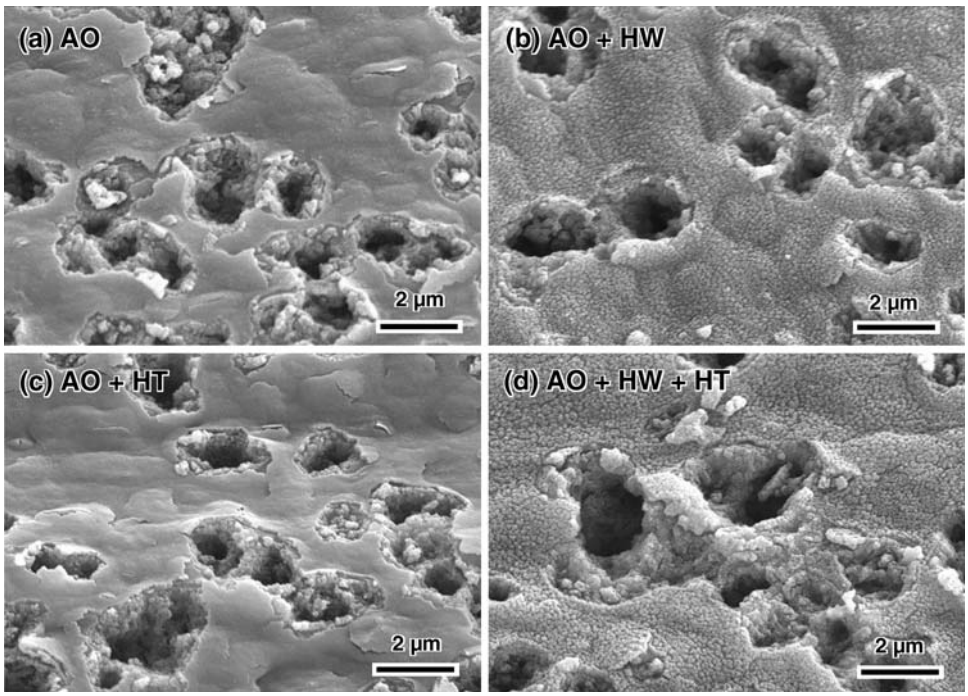

Fig. 1 SEM photographs of the surfaces of titanium metal after (**a**) AO in 2.0 *M* CH_3COOH at 150 V for 1 min at room temperature (AO), and then subject to (**b**) HW treatment (AO + HW) (**c**) HT (AO + HT) and (**d**) HW + HT treatment (AO + HW + HT), respectively

oxide films. However, there were no apparent changes to the surface of the oxide films after AO and subsequent HT at 600 °C for 1 h, compared with the surface of the oxide films after AO (Fig. 1c). When the samples were treated with HW and HT after AO, numerous small spheres also appeared on the surface of the oxide films, similar to the situation after AO and HW treatment, as shown in Fig. 1d.

Figure 2 shows the TF–XRD patterns of the surfaces of titanium metal after AO in 2.0 M CH_3COOH solution at 150 V, and then subject to HW treatment and/or HT, respectively. It can be seen from Fig. 2b that no rutile or anatase phases appeared on the surface of the oxide films after AO, while a broad peak appeared at 24–26.2° at 2θ, which was ascribed to the anatase phase after AO and HW treatment, as shown in Fig. 2c. The crystallite sizes were estimated according to the Scherrer formula:

$$d_{hkl} = \frac{k\lambda}{B\cos(2\theta)} \quad (1)$$

where λ, θ, B and k are the wavelength of the Cu$K\alpha$ radiation ($\lambda = 1.5405 \times 10^{-10}$ m), Bragg's diffraction angle, the full width at half-maximum (FWHM) intensity of the peak, and a constant (usually about 0.94), respectively [27]. The crystallite size of the anatase was calculated to be about 100 nm after AO and HW treatment.

After AO and HT, anatase and rutile phases appeared on the surface of the oxide films. This meant that the HT could induce the amorphous titania layers to transform into the anatase and rutile phases.

After AO and subsequent HW treatment and HT, the titania layers mainly consisted of a major rutile phase and a small amount of anatase. This meant that the HT could promote the anatase phase of titania layers converting into the rutile structure.

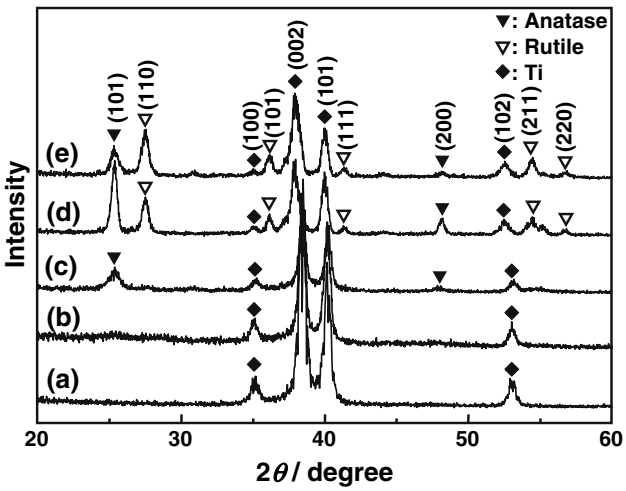

Fig. 2 TF–XRD patterns of the surfaces of (a) untreated titanium after (b) AO in 2.0 *M* CH_3COOH solution at 150 V, and then subject to (c) HW treatment (d) HT and (E) HW + HT treatment, respectively

3.2 Apatite-forming ability of titanium metal after AO, HW treatment and/or HT in SBF

Figure 3 shows the TF–XRD patterns of the surfaces of titanium metal after immersion in SBF for seven days after AO in 2.0 M CH_3COOH solution at 150 V and then

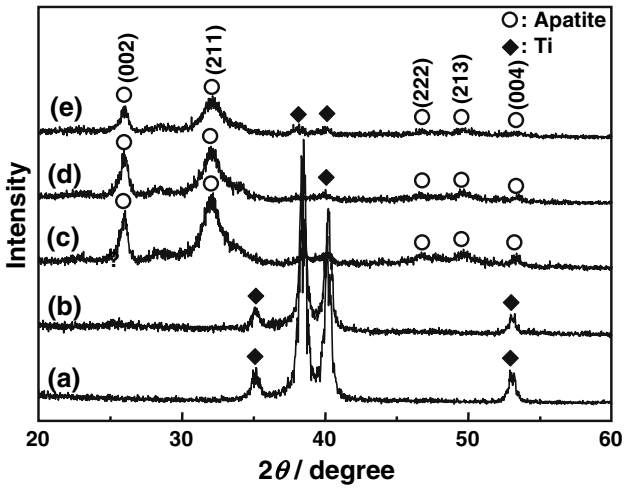

Fig. 3 TF–XRD patterns of the surface of titanium metals (a) that were immersed in SBF for 7 days after (b) AO in 2.0 M CH_3COOH solution at 150 V and then subsequent (c) HW treatment (d) HT and (e) HW + HT treatment

subject to subsequent HW, HT and HW + HT treatments. It could be seen that there was no apatite formation on the surface of titanium substrate after AO, while broad halo patterns appeared at 25–27° and 30–34° at 2θ, ascribed to the apatite on the surfaces of the titanium substrates after AO and subsequent HW treatment and/or HT. This indicates that a dense apatite layer can be formed on the surface of titanium substrates after the above treatments, except for the simple AO treatment.

Figure 4 shows the SEM photographs of the surfaces of titanium metal that had been immersed in SBF for one, three or 7 days after AO in 2.0 M CH_3COOH solution at 150 V and then underwent HW, HT and HW + HT treatments. It can be seen that there was no apatite formation on the surface of titanium metal after AO treatment and subsequent soaking in SBF solution for 7 days. However, there were numerous apatite nucleation spheres and deposition on the surfaces of titanium metal after AO + HW and AO + HW + HT treatments and subsequent soaking in SBF solution for one day, except for the AO + HT treatment. After immersion in SBF solutions for seven days, a dense apatite layer covered all the surfaces of the titanium substrates, which consumed the Ca^{2+} and PO_4^{3-} from the surrounding solutions, after AO + HW, AO + HT and AO + HW + HT treatments. In contrast, the apatite layer

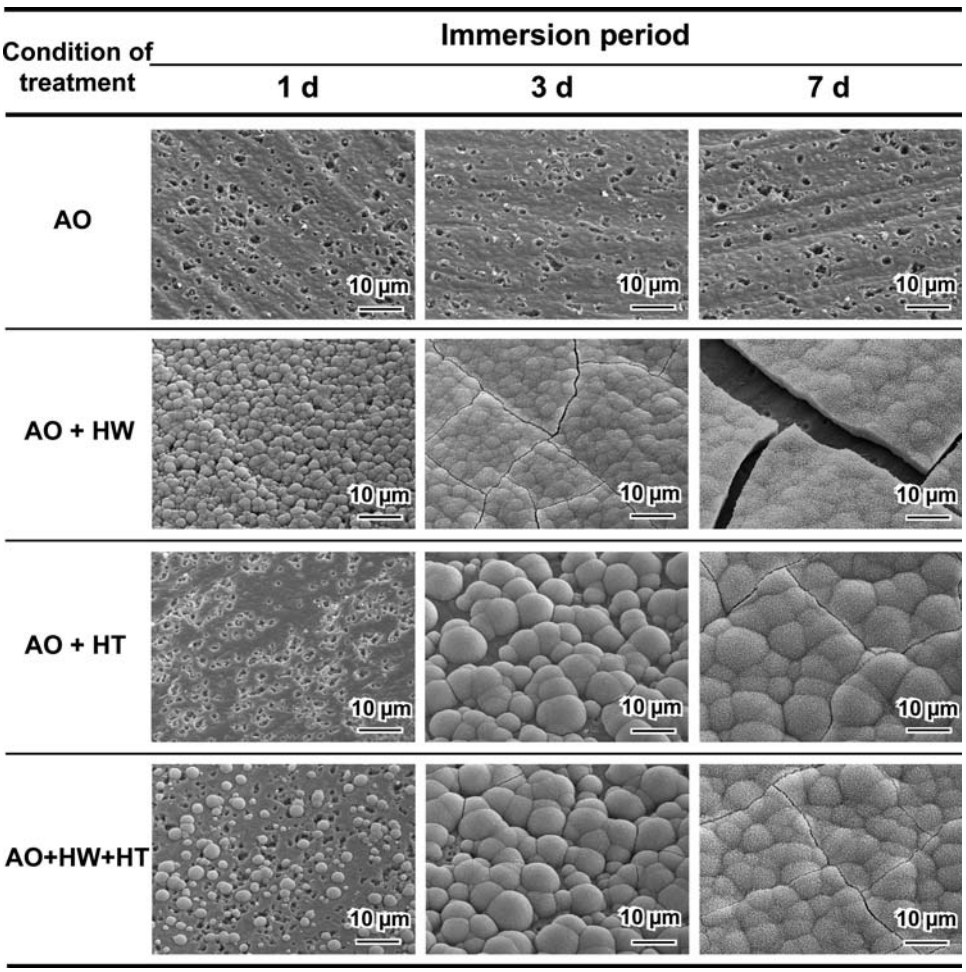

Fig. 4 SEM photographs of the surfaces of titanium metals that were immersed in SBF for 1, 3 or 7 days after AO in 2.0 *M* CH_3COOH solution at 150 V and then subsequent HW, HT and HW + HT treatment, respectively

tended to peel off from the surface of substrates after only AO + HW treatment and subsequent soaking in SBF solutions for 7 days.

4 Discussion

4.1 Crystallization mechanism of amorphous titania layers

After AO in CH_3COOH solution, the titania layer formed on the surface of the titanium metal presented an amorphous structure. However, subsequent HW treatment and/or HT could induce the amorphous structure to convert into the pure anatase structure, or a mixture of anatase and rutile phases.

Recently, several groups reported that crystalline titania films or powders could be prepared at lower temperature (<100 °C) and proposed some mechanisms concerning the low-temperature crystallization process, one of which was the dissolution–precipitation mechanism [28–32]. In the process of dissolution–precipitation, the amorphous titania layers on substrates first started to dissolve, resulting in an increase in the concentration of Ti(IV) in the solutions close to the samples, and then the Ti(IV) started to precipitate on the surface of the substrates, because the lower binding energy of the Ti–O bond favors arrangements that form in situ crystalline phases. In the present experiments, it can be seen from Figs. 1 and 2 that numerous nanosize anatase spheres precipitated on the surface of the previously amorphous titania layers after subsequent HW treatment. This result agrees well with the above dissolution–precipitation process.

After AO, the previously amorphous titania layers on titanium could be directly transformed into a mixture of anatase and rutile phases, subject to subsequent HT. This means the HT can promote transformation of titania layers from an amorphous to a crystalline structure. This result agrees with the research of Shirkhanzadeh [10], Uchida [23] and Wang [33].

4.2 Apatite-forming ability of titania layers after various treatments in SBF

It has been proposed that the formation of apatite on titania gels is induced by the abundant Ti–OH groups on its surface, implying that a large number of Ti–OH groups are essential for induction of apatite nucleation [34, 35]. Moreover, it was shown by zeta potential measurements that the process of apatite formation on the alkali- and heat-treated titanium metal was an electrostatic interaction process [18, 19]. The Ti–OH groups formed on the surface of titanium metal were negatively charged in the SBF, and then the positively charged Ca^{2+} ions first adsorbed on the surface of titanium and produced amorphous calcium titanate. With the accumulation of Ca^{2+} ions, the calcium titanate became positively charged, and hence it combined with the negatively charged phosphate ions in the SBF to form amorphous calcium phosphate. Finally, the metastable amorphous calcium phosphate transformed into crystalline apatite [36, 37].

The HW treatment can form abundant Ti–OH groups on the surface of titanium substrates after AO because the proton (H^+) in the solution can attack and break the Ti–O bond in the titania layers and eventually form the Ti–OH groups [38], which is similar to the process in the sol–gel method [22, 23, 34, 35]. This study indicates that apatite can be quickly nucleated and deposited on the surface of titanium substrates after AO + HW treatment. It shows that higher apatite-forming ability can be acquired by subsequent HW treatment at low temperature, as shown in Fig. 5. However, it can be seen from Fig. 4 that the apatite-forming ability can be decreased by subsequent HT after AO + HW treatment. This is because the number of hydroxyl groups on the surface of the titania layers is greatly decreased by subsequent HT through the processes

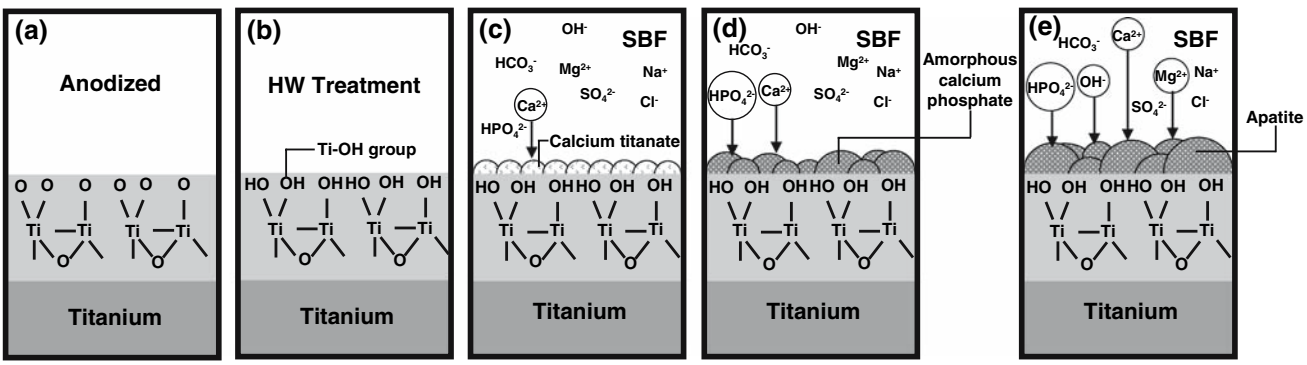

Fig. 5 Schematic representation of the process of apatite formation on the surfaces of anodized titanium subject to HW treatment and then soaking in SBF solution

of dehydration and polycondensation [23, 33]. It has been mentioned that the apatite layer can be easily peeled off from the surface of titanium substrates after AO + HW treatment, but subsequent HT could improve the apatite layer bonding to titanium substrates. This result agrees well with the improvement of bone-bonding ability of titanium and its alloys by subsequent HT after alkali treatment, as shown by Nishiguchi [39, 40]. Based on the above analysis, HT could apparently decrease the number of Ti–OH groups on the surface of the substrates, but the bond strength between the apatite layer and the titanium substrates could be greatly enhanced.

After AO and HT, the titania layers composed of the rutile and anatase phases could induce apatite formation on its surface in SBF solutions. This indicates that the amorphous titania layers could possess apatite-formation ability after HT without HW treatment. Recently, it was reported that the lattice matching between the rutile and apatite crystal structures could result in inducing apatite nucleation on the surface of titanium metal [32, 34, 41]. Therefore, we can suggest that the crystal titania layers without HW treatment in this study also induced apatite formation in SBF solutions.

5 Conclusion

The amorphous titania layers formed on the surface of titanium metal did not show apatite-forming ability after AO in acetic acid. However, subsequent HW treatment and/or HT could greatly induce the amorphous titania layer to transform into anatase, or a mixture of anatase and rutile phases. Moreover, the HW treatment could produce large numbers of Ti–OH groups on the surface of the titania layers, which would provide titanium metal with higher apatite-forming ability in SBF solution. Subsequent HT will enhance the bond strength between the apatite layer and the titanium substrates. Therefore, bioactive titanium metals can be prepared via AO and subsequent hot water and heat treatment, which will be suitable for applications under loading-bearing conditions.

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