Effects of Alloying Elements on the HAp Formability on Ti Alloys after Alkali Treatment

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This work presents a study on the relationship between the alloying elements such as niobium (Nb), tantalum (Ta) or zirconium (Zr) and the hydroxyapatite (HAp) formability on the surfaces of titanium (Ti) alloys subjected to alkali treatment process that is developed to form a HAp layer. The HAp formability on the surfaces of pure Ti, Ti-Nb alloys, Ti-Ta alloys, Ti-Zr alloys, pure Nb, pure Ta and pure Zr subjected to alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks was investigated.

The pure Ti, Ti-10Nb alloy and Ti-10Zr alloy have a good HAp formability because sodium titanate is formed on the surface after the alkali treatment. However, the HAp formability is decreased with increasing Nb and Zr contents. A layer including sodium titanate and sodium tantalate is formed on the surfaces of Ti-Ta alloys after the alkali treatment. Therefore, the Ti-10Ta, Ti-20Ta, Ti-30Ta and Ti-40Ta alloys have a good HAp formability. On the other hand, a sodium niobate layer and a thick crystalline sodium tantalate layer are formed on the surfaces of pure Nb and pure Ta, respectively, after the alkali treatment. Moreover, there is no component change on the surface of pure Zr after the alkali treatment. Therefore, the HAp formability on the surfaces of pure Nb, pure Ta and pure Zr is significantly low after they are soaked in a simulated body fluid for 1 week.

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1. Introduction

Pure titanium (Ti) and Ti alloys have been widely used for dental and orthopedic implants under load-bearing conditions.1,2) In biomedical applications, bone absorption and degradation of bone quality are induced by stress shielding resulting from mismatch between Young’s moduli of living bone and implant devices.3,4) Therefore, β-type Ti alloys, including Ti–29Nb–13Ta–4.6Zr alloy (mass%, TNTZ)5) and Ti–35Nb–7Zr–5Ta alloy (mass%, TNZT),6) have been developed as Ti alloys with low Young’s moduli to overcome this significant problem. Young’s modulus of TNTZ under solutionized conditions is, for example, approximately 60 GPa,7) which is much closer than those of existing Ti alloys to the value for living bones (10–30 GPa).8) Therefore, these β-type Ti alloys are expected to be key materials for next-generation implant devices.

However, it is difficult for pure Ti and Ti alloys to directly bond to living bone after implantation.9) An essential requirement is the formation of a bone-like carbonate-apatite layer on their surface in a body.9) Therefore, various surface modification processes such as alkali treatment10) have been attempted to improve the bone-like carbonate-apatite formability for pure Ti and Ti alloys. It is known that after immersion in NaOH solution, an alkali treatment process, bone-like hydroxyapatite layer (Ca10(PO4)6(OH)2; HAp) is formed on the surface of pure Ti and Ti alloys in a simulated body fluid (SBF) with ion concentrations nearly equal to those in humans.10,11) The HAp formation on these materials is attributed to a sodium titanate hydrogel layer that forms on their surfaces as a result of the alkali treatment. The mechanism for HAp formation induced by the sodium titanate can be described as follows:12) The sodium titanate releases its Na+ ions into the surrounding fluid via an exchange with the H2O+ ions in the fluid to form Ti-OH groups on its surface. These Ti-OH groups induce apatite nucleation. Once the apatite nuclei are formed, they grow spontaneously by consuming the calcium and phosphate ions contained in the body fluid.

However, the HAp formability of different types of Ti alloys with various kinds and amounts of alloying elements varies after alkali treatment. The HAp formability of TNTZ is lower than that of pure Ti,13) for example. Therefore, to improve the HAp formability on the TNTZ surface, it is important to understand the relationship between alloying elements (Nb, Ta and Zr) and the HAp formability. In this study, the structural changes occurring on the surface of the pure Ti, Ti–Nb alloys, Ti–Ta alloys, Ti–Zr alloys, pure Nb, pure Ta and pure Zr, subjected to alkali treatment were investigated. The formability of HAp on their surfaces soaked in the SBF after alkali treatment was then discussed.

2. Experimental Procedures

2.1 Material preparation

The Ti–xM (nominal content x = 10, 20, 30, or 40 mass%; M = Nb, Ta, or Zr) alloys were produced by melting from pure Ti, pure Nb, pure Ta and pure Zr as raw materials (Ti: sponge, 99.7% purity; Nb: plate, 99.5% purity; Ta: wire, 99.5% purity; Zr: sponge, 99.6% purity) using a tri-arc melting furnace in an argon atmosphere, followed by a homogenization treatment at 1273 K for 21.6 ks with subsequent water quenching. The analyzed chemical compositions of these alloys are shown in Table 1.

2.2 Alkali treatment process and soaking in SBF

Specimens of pure Ti (grade 2), pure Nb (99.5% purity), pure Ta (99.2% purity), pure Zr (99.95% purity) and Ti–xM (x = 10, 20, 30, or 40 mass%; M = Nb, Ta, or Zr) alloys measuring 10 mm in diameter and 1 mm in thickness were wet-polished using SiC waterproof emery papers of up to #600 grit. After polishing, these specimens were immersed in...
1 mol/L NaOH solution at 363 K for 259.2 ks as an alkali treatment. The specimens subjected to the alkali treatments were then soaked in 20 mL of an acellular SBF, with ion concentrations (Na⁺: 142.0 mM; K⁺: 5.0 mM; Mg²⁺: 1.5 mM; Ca²⁺: 2.5 mM; Cl⁻: 147.8 mM; HCO₃⁻: 4.2 mM; HPO₄²⁻: 1.0 mM; SO₄²⁻: 0.5 mM) nearly equal to those of human blood plasma at 309.5 K for 1 week to evaluate their HA-forming ability. The SBF was prepared by dissolving reagent-grade NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl₂·6H₂O, HCl, CaCl₂ and Na₂SO₄ in distilled water and buffered at a pH value of 7.40 with tris-hydroxymethyl aminomethane ((CH₂OH)₃CNH₃) and hydrochloric acid at 309.5 K.¹⁴ After the specimens had been soaked for 1 week, they were removed from the SBF, washed with distilled water, and dried in air.

### 2.3 Surface analysis

The structural changes occurring on the surface of the specimens after the alkali treatment and subsequent SBF soaking were investigated using a scanning electron microscopy (SEM) and a thin-film X-ray diffractometry (TF-XRD). The TF-XRD analysis was carried out using a Cu target with an accelerating voltage of 40 kV and a tube current of 150 mA. The peak assignment were performed using the international centre for diffraction data (ICDD) database.¹⁵

### 3. Results

#### 3.1 Surface morphology and phase constitutions after alkali treatment

Figure 1 shows the SEM image of the surface of pure Ti subjected to alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks. Traces of grinding were still visible on the sample surface. Figure 2 shows the TF-XRD profile of the surface of pure Ti subjected to alkali treatment under the same conditions. Diffraction peaks of Ti and Na₂Ti₅O₁₁ are detected from the pure Ti surface.

The SEM images of surfaces of the (a) Ti–xNb (nominal content x = 10, 20, 30, or 40 mass%) alloys and pure Nb, (b) Ti–xTa alloys and pure Ta and (c) Ti–xZr alloys and pure Zr subjected to alkali treatment under the above conditions are shown in Fig. 3. As shown in Fig. 3, for Ti–10Nb, Ti–20Nb, Ti–30Nb alloys, Ti–10Ta, Ti–20Ta and Ti–30Ta alloys, the surface still preserve the grinding trace (Figs. 3 (a, 1), (a, 2), (a, 3), (b, 1), (b, 2) and (b, 3)), which is similar with the surface of pure Ti subjected to the alkali treatment. Moreover, many microcracks are observed on the surface of the Ti–10Zr and Ti–20Zr alloys (Figs. 3 (c, 1) and (c, 2)). For the surface of Ti–30Zr alloy, the microcracks became smaller or disappear (Fig. 3 (c, 3)). On the other hand, many clear microcracks are formed on the surfaces of the Ti–40Nb alloy and pure Nb, (Figs. 3 (a, 4) and (a, 5)). The Ti–40Ta alloy surface retains traces of grading (Fig. 3 (b, 4)) while there are clear microcracks in the surface of pure Ta (Fig. 3 (b, 5)). The surfaces of the Ti–40Zr alloy and pure Zr are smoother than those of the Ti–10Zr, Ti–20Zr and Ti–30Zr alloys (Figs. 3 (c, 4) and (c, 5)).

The TF-XRD profiles of the (a) Ti–10M (M = Nb, Ta, or Zr), (b) Ti–20M, (c) Ti–30M and (d) Ti–40M alloys are shown in Fig. 4. The component of the surfaces of the Ti–10Nb, Ti–20Nb, Ti–10Zr and Ti–20Zr alloys subjected to the alkali treatment is Na₂Ti₅O₁₁ as shown in Figs. 4(a) and 4(b). Likewise, Na₅TaO₁₄ is formed on the surfaces of the Ti–10Ta and Ti–20Ta alloys. The components of the surfaces of the Ti–30Nb and Ti–40Nb alloys subjected to the alkali treatment are Na₂Ti₅O₁₁ and Ti–Nb as shown in Figs. 4(c) and 4(d). The surfaces of the Ti–30Ta and Ti–40Ta alloys...
subjected to the alkali treatment are mainly composed of Na$_5$TaO$_5$ and Na$_2$Ti$_5$O$_{11}$. The surfaces of the Ti$_{30}$Zr and Ti$_{40}$Zr alloys subjected to the alkali treatment are mainly composed of Na$_2$Ti$_5$O$_{11}$. The components of the surfaces of pure Nb and pure Ta subjected to the alkali treatment are Na$_8$Nb$_6$O$_{19}$ and Na$_5$TaO$_5$, respectively, while there is no component change on the smooth surface of pure Zr subjected to the alkali treatment as shown in Fig. 4(e). These SEM images and TF-XRD profiles suggest that the clear microcracks observed on the surfaces of Ti$_{40}$Nb, pure Nb and pure Ta correspond to a thick layer of sodium titanate, sodium niobate and sodium tantalate, respectively.

3.2 HAp precipitation in SBF

Figure 5 shows an SEM image of the surface of pure Ti soaked in the SBF for 1 week after the alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks. The pure Ti surface is completely covered by HAp, suggesting that soaking the specimen in the SBF for 1 week after the alkali treatment is sufficient to initiate formation of HAp on the surface of pure Ti. This is evidence of good HAp formability.

The SEM images of surface of the (a) Ti$_{x}$Nb (nominal content $x = 10, 20, 30, 40$ mass%), (b) Ti$_{x}$Ta alloys and pure Ta and (c) Ti$_{x}$Zr alloys soaked in the SBF for 1 week after the alkali treatment under the above conditions are shown in Fig. 6. The TF-XRD profiles of surfaces of the (a) Ti$_{x}$Nb (nominal content $x = 10, 20, 30, 40$ mass%), (b) Ti$_{x}$Ta alloys and pure Ta and (c) Ti$_{x}$Zr alloys soaked in the SBF for 1 week after the alkali treatment at above condition are shown in Fig. 7.

As shown in Figs. 6 (a, 1), (b, 1) and (c, 1) the HAp completely covers the surfaces of the Ti$_{10}$Nb, Ti$_{10}$Ta and Ti$_{10}$Zr alloys after soaking in the SBF. Two typical diffraction peaks, which are corresponded to HAp, are observed in the TF-XRD profiles of the surfaces of the Ti$_{10}$Nb, Ti$_{10}$Ta and Ti$_{10}$Zr alloys (Figs. 7 (a, 1), (b, 1) and (c, 1)). The HAp formability of the Ti$_{10}$Nb and Ti$_{10}$Zr alloys is decreased as the Nb and Zr content is increased from 10 to...
100 mass% (pure metals). As shown in Figs. 6 (a, 3), (c, 3) and (c, 4), isolated HAp is formed on the surfaces of the Ti–30Nb, Ti–30Zr and Ti–40Zr alloys after soaking in the SBF. Although the two typical diffraction peaks of HAp can still be observed in the TF-XRD profiles (Figs. 7 (c, 3) and (c, 4)) of the surfaces of the Ti–30Zr and Ti–40Zr alloys, they are not detected on the surface of the Ti–30Nb alloy. These results indicate that the particle size of isolated HAp formed on the Ti–30Nb alloy surface is smaller than that on the surfaces of Ti–30Zr and Ti–40Zr alloys. In addition, there is no HAp on the surfaces of the Ti–40Nb alloy, pure Nb and pure Zr (Figs. 6 (a, 4), (a, 5) and (c, 5)). On the other hand, the HAp formability of Ti–Ta alloys is almost constant with increasing Ta content from 10 to 40 mass% (Figs. 6 (b, 2), (b, 3) and (b, 4)) and the two typical HAp diffraction peaks are observable on the surfaces of the Ti–20Ta, Ti–30Ta and Ti–40Ta alloys. However, there is no HAp on the surface of pure Ta (Fig. 6 (c, 5)). These results suggest that the Ti–Ta alloys have better HAp formability as compared with the cases in the Ti–Nb and Ti–Zr alloys.

4. Discussion

Figure 8 shows the variation in HAp coverage on the surfaces of the Ti–xM (nominal content x = 10, 20, 30, or 40 mass%; M = Nb, Ta, or Zr) alloys and each pure metal as
a function of the alloying elements content after soaking in the SBF for 1 week through the alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks as a function of the alloying elements content. The HAp coverage on the surfaces of the Ti–10Ta, Ti–20Ta, Ti–30Ta and Ti–40Ta alloys is almost constant at around 95% while it is decreased from 90–95% to 0% on the surfaces of the Ti–xNb and Ti–xZr alloys as the Nb and Zr content increase from 10 to 100 mass% (pure metals).

Pure Ti and Ti alloys have been known to form sodium titanate layers on their surfaces after an alkali treatment. The sodium titanate releases Na+ ions from the surface gel layer into the SBF via an ion exchange with H3O+ ions present in the SBF. As a result, the HAp produced from the ionic activity in the surrounding SBF is increased by an increase in OH⁻ ion concentration. The increased ionic activity products accelerate apatite nucleation on the Ti–OH groups, which could explain the good HAp formability of pure Ti after alkali treatment.

![Fig. 5 SEM image of pure Ti soaked in SBF for 1 week after subjecting to alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks.](image)

![Fig. 6 SEM images of Ti–xM (nominal content x = 10, 20, 30, or 40 mass%; M = Nb, Ta, or Zr) alloy or each pure metal soaked in SBF for 1 week through alkali treatment in 1 M NaOH solution at 363 K for 259.2 ks: (a) Ti–xNb, (b) Ti–xTa, and (c) Ti–xZr, (a, 1) Ti–10Nb, (a, 2) Ti–20Nb, (a, 3) Ti–30Nb, (a, 4) Ti–40Nb, (a, 5) pure Nb, (b, 1) Ti–10Ta, (b, 2) Ti–20Ta, (b, 3) Ti–30Ta, (b, 4) Ti–40Ta, (b, 5) pure Ta, (c, 1) Ti–10Zr, (c, 2) Ti–20Zr, (c, 3) Ti–30Zr, (c, 4) Ti–40Zr and (c, 5) pure Zr.](image)
On the basis of a similar mechanism for Ti–Ta alloys after alkali treatment, the surface sodium tantalate layers would be responsible for their HAp formability as a result of the many Ta–OH groups formed on the surface. When sodium tantalate is in a crystalline phase on the surface, it barely releases the Na\(^+\) ions, leading to the formation of only a small number of Ta–OH groups on the surface and low production of HAp from ionic activity in the SBF. However, the sodium tantalate layers should be in the amorphous state,\(^{13}\) suggesting that the Ti–xTa (x = 10, 20, 30, or 40 mass%) alloys should have good HAp formability. For pure Ta, the clear and sharp peaks of Na\(_5\)TaO\(_5\) in the TF-XRD profile (Fig. 4 (e, 2)) indicate that the thick crystalline sodium tantalate layer is formed on the surface after the alkali treatment, leading to significantly decreasing of HAp formability.

For the Ti–Nb and Ti–Zr alloys, the alloys showed good HAp formability when the Nb and Zr contents are lower than 10 mass% because there are enough sodium titanate molecules on the surfaces. However, when the Nb or Zr content is increased to 20 mass%, these alloys show low HAp formability. The number of Ti atoms on the surfaces should be decreased with increasing Nb or Zr content. Therefore, the sodium titanate on the surfaces is decreased accordingly and accounts for the low HAp formability of the Ti–20Nb, Ti–30Nb, Ti–40Nb, Ti–20Zr, Ti–30Zr and Ti–10Zr alloys.

Fig. 8 Variation of HAp coverage as a function of nominal alloying element content on the surfaces of Ti–xM (nominal content x = 10, 20, 30, or 40 mass%; M = Nb, Ta, or Zr) alloys soaked in SBF for 1 week through alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks.

![TF-XRD profiles of Ti-xM alloys](image)

![Graph showing HAp coverage](image)
study. Therefore, the HAp formability of pure Nb is significantly low. Uchida _et al_.\(^{16}\) have reported that pure Zr could form an apatite on its surface in SBF when it had been previously treated by NaOH solution with a concentration above 5 mol/L at 368 K for 86.4 ks, although it did not completely cover the surface. In this study, the low HAp formability of the pure Zr subjected to alkali treatment in 1 mol/L NaOH solution at 363 K for 259.2 ks is attributed to the lack of Na\(^+\) ions on the surface. Since pure Zr has higher corrosion durability in NaOH solution as compared with the cases in pure Ti, pure Nb and pure Ta, a thin Na-free zirconia hydrogel layer is formed merely on its surface, where formation of the OH\(^-\) anion species is assumed to rarely occur.

**5. Conclusions**

(1) Sodium titanate is formed on the surface of pure Ti after alkali treatment in 1 M NaOH solution at 363 K for 259.2 ks. The HAp coverage on the surface of the pure Ti is around 95% after it is soaked in the SBF for 1 week.

(2) A sodium titanate layer is formed on Ti–Nb and Ti–Zr alloys after alkali treatment in 1 M NaOH solution at 363 K for 259.2 ks. The HAp formability is decreased with increasing Nb and Zr content.

(3) A layer including sodium titanate and sodium tantalate is formed on the surfaces of Ti–Ta alloys after alkali treatment in 1 M NaOH solution at 363 K for 259.2 ks. The HAp coverage on the surfaces of the Ti–10Nb, Ti–20Ta, Ti–30Ta and Ti–40Ta alloys is almost constant at around 95% after they are soaked in the SBF for 1 week.

(4) A sodium niobate layer is formed on the surface of pure Nb after alkali treatment in 1 M NaOH solution at 363 K for 259.2 ks. A thick crystalline sodium tantalate layer is formed on the surface of pure Ta and there is no component change on the surface of pure Zr after both metals underwent the same alkali treatment. The HAp coverage on the surface of pure Nb, pure Ta and pure Zr is almost 0% after they are soaked in the SBF for 1 week.

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