Corrosion Behavior of Pure Titanium and Titanium Alloys in Various Concentrations of Acidulated Phosphate Fluoride (APF) Solutions

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The corrosion behaviors of Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys, and an experimentally produced Ti-0.5Pt alloy in 0.05% to 2.0% concentrations of Acidulated Phosphate Fluoride (APF) solutions (corresponding to 226 to 9,050 ppm fluoride at pH 3.5 or 3.6) were examined. While the corrosion of Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys might occur easily even in a diluted 0.05% APF solution, dissolution of Ti from the Ti-0.5Pt alloy was observed only in test solutions with APF concentration exceeding 0.2%. When Ti-6Al-7Nb and Ti-6Al-4V alloys were immersed in 2.0% APF solution, their surfaces were entirely covered by compact corrosion products of NaF due to severe corrosion. As a result, Ti dissolution was prevented and the amount of Ti dissolved decreased. However, since Ti was covered by porous, large-sized corrosion products of NaF and that Ti-0.5Pt alloy was not covered with any corrosion product, the amount of Ti dissolved increased in the 2.0% APF solution.

Key words: Titanium alloy, Corrosion, Acidulated phosphate fluoride (APF) solution

INTRODUCTION

Titanium (Ti) and titanium alloys are useful for clinical applications in dental implants and denture bases because of their superior corrosion resistance and biocompatibility. Ti and Ti alloys are characterized by a high corrosion resistance and the formation of a stable passive film on their surface. In the case of an orthodontic Ni-Ti wire, its corrosion resistance is lower than that of pure Ti or other commercial dental Ti alloys since its Ti content is approximately 50 at%1,2.

It is known that the high corrosion resistance of Ti and Ti alloys is significantly reduced in an environment in which the passive film is destroyed due to the existence of and contamination by fluoride content3-13. Against this background, the high corrosion resistance behavior of Ti alloys in a fluoride-containing solution is examined16-19. Ide et al.20 reported that an albumin contained in saliva reduced the corrosion of Ti. Fluoride content can be introduced into the oral environment through various sources, such as from dentifrices, mouth rinses, and tooth surface embrocations. Dentists usually recommend brushing the teeth or using a mouth rinse at least three times a day to avoid the formation of dental plaque and caries. However, if these recommendations are followed with titanium-based restorations and orthodontic Ni-Ti wires, the latter’s contact with fluoride-containing prophylactic agents may result in titanium corrosion.

Fluoride-containing prophylactic agents, particularly the acidulated phosphate fluoride (APF) solution, have been used to prevent caries in teeth. The fluoride concentration and pH of a commercial APF solution are approximately 10,000 ppm and 3.5. Such an environment promotes the corrosion of Ti and Ti alloys5,6,9,12,26. After the APF solution is embrocated on teeth, it is thought that its concentration will be diluted by saliva or other aqueous fluids. Therefore, it would be important to investigate the corrosion behavior of pure Ti and Ti alloys in solutions with various APF concentrations that accurately simulate the oral environment.

The corrosion resistance of pure Ti and Ti alloys largely depends on the fluoride concentration and pH of the environmental solution. Probability of corrosion can be accurately predicted by the pH versus NaF concentration diagram, where this diagram shows a linear boundary between corrosive and non-corrosive regions as established by our previous results16,17. In an acidic condition, the fluoride ion forms hydrofluoric acid (HF) and the presence of a HF concentration over 30 ppm results in the destruction of the passive film on the Ti surface. In our previous study, we found that Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys — which are commercially available as dental implants — exhibited the tendency for corrosion in the presence of a small amount of fluoride (0.1% of NaF) with acidic condition16,17. However,
we found that Ti alloys with a small amount of Pt or Pd proved to be very effective in improving the corrosion resistance of Ti in NaF solutions of various concentrations. In particular, as shown in our previous study [31], Ti-0.5Pt alloy was the optimal alloying composition in improving the corrosion resistance in a fluoride-containing environment.

The purpose of this study was to examine the corrosion behavior of pure Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys, and an experimentally produced Ti-0.5Pt alloy when exposed to 0.05% APF solution that contained 20 g NaF and 15 g phosphoric acid in 1,000 ml of distilled water, which would be diluted by saliva and other aqueous fluids.

The specimens of pure titanium, Ti-6Al-7Nb and Ti-6Al-4V alloys, and an experimentally produced Ti-0.5Pt alloy were polished using the argon-arc casting machine and then cast into the mold. The alloy specimens were melted by the argon arc and kept for 60 seconds under the melting condition before they were melted twice by changing the top and bottom, and then cast into the mold. The Ti-0.5Pt specimens were melted twice by changing the top and bottom, and then cast into the mold.

Materials and Methods

Materials

In this study, we examined commercially pure titanium (Kobe Steel Co. Ltd., Kobe, Japan), a Ti-6Al-7Nb alloy (GC Co. Ltd., Tokyo, Japan), and a Ti-6Al-4V alloy (Daido Steel Co. Ltd., Nagoya, Japan), which are presently used in clinical practice, and an experimental Ti-0.5 wt% Pt (Ti-0.5Pt) alloy.

Specimens of pure titanium, Ti-6Al-7Nb and Ti-6Al-4V alloys were made from as-received materials using an argon-arc casting machine (Cyclarc II, J. Morita Co., Kyoto, Japan). The alloy specimens were melted by the argon arc and kept for 60 seconds under the melting condition before they were cast into the mold (Titavest CB, Morita Co., Kyoto, Japan).

For Ti-0.5Pt, the specimens were made from Ti and 99.95% Pt using the argon-arc casting machine. The Ti-0.5Pt specimens were melted twice by changing the top and bottom, and then cast into the mold.

Then, for all the fabricated specimens, a Ni lead wire was spot-welded on their back surface and the alloy specimens were embedded in epoxy resin. They were then polished using #1500 waterproof grinding paper and washed in ethanol. The exposed surface area of the specimens ranged from 0.4 cm² to 0.6 cm².

Test solutions

Test solution prepared by the authors was a 2.0% APF solution that contained 20 g NaF and 15 g phosphoric acid in 1,000 ml of distilled water, which had the same components as those in the tooth surface embrocation of Fluol N (Bee Brand Medico Dental Co. Ltd., Osaka, Japan). The fluoride concentration and pH of the prepared 2.0% APF solution were 9,050 ppm and 3.5 respectively. The APF solution was diluted by distilled water to produce APF concentrations of 1.0% (4,025 ppmF), 0.4% (1,810 ppmF), 0.2% (905 ppmF), 0.1% (453 ppmF), and 0.05% (226 ppmF). The pH values of all diluted APF solutions were in the range of 3.5 to 3.6.

Corrosion test

A platinum electrode and a KCl-saturated Ag/AgCl electrode were the counter and reference electrodes respectively. Potential of the reference electrode was denoted by E (Ag/AgCl) = E (Normal Hydrogen Electrode: NHE) - 215 mV at 37°C. Anodic polarization curves were obtained from a corrosion potential of +2,000 mV (vs. KCl-saturated Ag/AgCl electrode) at a scanning rate of 1.0 mV/sec (HZ-5000, Hokuto Denko, Kyoto, Japan) in 1,000 mL of test solution at 37°C. Exposed surface area of the specimens ranged from 1.6 cm² to 1.8 cm².

Dissolution test

To measure the amount of Ti ions, specimens were polished using #1,500 waterproof grinding paper, washed in ethanol, and immersed in a test solution with 40 ml of 2.0, 1.0, 0.4, 0.2, 0.1, or 0.05% APF solution. Test samples were kept in a 37°C environment for three or 30 minutes. Amount of alloy elements dissolved was measured by an atomic absorption spectrophotometer (AAAnalyst 300, Perkin Elmer, Boston, USA). Results were then statistically analyzed by ANOVA with Scheffe’s test at a significance level of 1%.

Surface observation and X-ray diffraction

Specimens were polished to a luster using aluminum powder (particle size less than 0.3 μm). Specimens with an effective surface area of 0.9 cm² to 1.3 cm² were immersed in a 40 ml test solution for three or 30 minutes. After immersing the specimens, SEM micrographs were obtained using a JEOL JSM-5400LV (JEOL Ltd., Tokyo, Japan).

The corrosion products on the surfaces of pure Ti and Ti alloys immersed in 40 ml solutions with 0.2% and 2.0% APF for 48 hours were examined using an X-ray diffractometer (XRD). The XRD patterns were recorded with a vertically mounted diffractometer system (Rigaku Rint 2500 V, Tokyo, Japan) using counter-monochromatized CuKα radiation of wavelength λ =1.54056 Å in the 2θ range from 10° to 80° operated at 50 kV and 200 mA.

Results

Anodic polarization curves

Fig. 1 shows the anodic (potentiodynamic) polarization curves of Ti, Ti-6Al-7Nb, Ti-6Al-4V, and Ti-0.5Pt alloys in 0.05, 0.1, 0.2, and 2.0% APF solutions. In the case of 0.05% APF solution, the current densities of Ti, Ti-6Al-7Nb, and Ti-6Al-4V drastically increased at the potential around −1,000 mV and attained a maximum of about 1600 μA/cm² around −500 mV. This increase in current density corresponded to the
Fig. 1 Anodic potentiodynamic polarization curves of Ti, Ti-6Al-7Nb, Ti-6Al-4V, and Ti-0.5Pt alloys in (a) 0.05% APF, (b) 0.1% APF, (c) 0.2% APF, and (d) 2.0% APF solutions.

Fig. 2 Amounts of Ti dissolved from pure Ti, Ti-6Al-7Nb, Ti-6Al-4V, and Ti-0.5Pt alloys in (a) 0.05% APF for 30 min, (b) 0.1% APF for 30 min, (c) 0.2% APF for 30 min, and (d) 2.0% APF for 3 min.
active dissolution of Ti. Following which, the passive current density of Ti-6Al-4V was maintained at about 150 $\mu$A/cm$^2$, whereas those of Ti and Ti-6Al-7Nb were maintained at 50 $\mu$A/cm$^2$. However, in the Ti-0.5Pt alloy, active dissolution did not occur and passive current density was maintained at about 30 $\mu$A/cm$^2$.

The polarization curves of 0.1% and 0.2% APF solutions were shown in Figs. 1(b) and (c) respectively. Pure Ti, Ti-6Al-4V, Ti-6Al-7Nb, and Ti-0.5Pt alloys exhibited the same tendency. Active corrosion current density and passive current density were observed to increase with fluoride concentration. As shown in Fig. 1(d) for the 2.0% APF solution, the active corrosion current density and passive current density of all specimens exhibited very high values exceeding 20,000 $\mu$A/cm$^2$. However, the passive current density of Ti-6Al-4V decreased to less than 2,000 $\mu$A/cm$^2$.

**Dissolved Ti amounts**

Fig. 2 shows the amounts of Ti dissolved from pure Ti, Ti-6Al-7Nb, Ti-6Al-4V, and Ti-0.5Pt alloys in APF solutions with various concentrations. After 30 minutes’ immersion, the amounts of Ti dissolved from pure Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys ranged from 10 to 60 $\mu$g/cm$^2$ in APF solutions with concentration less than 0.2%; on the other hand, the amount of Ti dissolved from Ti-0.5Pt alloy was below detection limit in these same solutions.

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**Fig. 3** SEM images of Ti (a) after polishing, (b) after immersion in 0.05% APF solution for 30 min, (c) 0.1% APF solution for 30 min, (d) 0.2% APF solution for 30 min, (e) 1.0% APF solution for 3 min, and (f) 2.0% APF solution for 3 min.
Fig. 2(d) shows the amounts of Ti dissolved from Ti, Ti-6Al-7Nb, Ti-6Al-4V, and Ti-0.5Pt in the 2.0% APF solution for three minutes. Although the immersion time was only three minutes, the amounts of Ti dissolved from Ti and Ti-0.5Pt alloy were approximately 95 μg/cm² and 145 μg/cm², respectively. These values were remarkably large compared with those of Ti-6Al-7Nb and Ti-6Al-4V alloys. The dissolution of Ti from Ti-0.5Pt alloy was confirmed in the APF solution with a concentration of more than 0.4%, but the results are not shown in Fig. 2. The dissolution of Al, Nb, V, and Pt was not detected in all concentrations of APF solutions.

Changes in microscopic surface morphology
Fig. 3 shows the SEM images of pure Ti after polishing (a) and after immersion in 0.05% (b), 0.1% (c), and 0.2% (d) APF solutions for 30 minutes, and 1.0% (e) and 2.0% (f) APF solutions for three minutes. A few small pits were observed on the specimens immersed in 0.05% and 0.1% APF solutions. A large number of pits and cracks on the surface, as well as remarkable corrosions, were observed on the specimens immersed in 0.2% and 1.0% APF solutions for three minutes. In the specimen immersed in 2.0% APF solution for three minutes, many corrosion products were observed on the surface.

Fig. 4 shows the SEM images of Ti-6Al-4V alloy after polishing (a) and after immersion in 0.05%
(b), 0.1% (c), and 0.2% (d) APF solutions for 30 minutes, and 0.4% (e) and 2.0% (f) APF solutions for three minutes. The metallographic structure due to corrosion was observed on the Ti-6Al-4V alloy immersed in 0.05% APF solution; it became more distinct with immersion in 0.1% APF solution. Corrosion products of the size of approximately 4 μm were observed on the surface of the metallographic structure due to corrosion of the specimen immersed in 0.2% APF solution. After immersion in 0.4% APF solution for three minutes, these corrosion products became smaller in size but increased in number. For the specimen immersed in 2.0% APF solution for three minutes, the entire surface was covered with innumerable corrosion products without any space in

between. Similar results were observed in the Ti-6Al-7Nb alloy.

Fig. 5 shows the SEM images of Ti-0.5Pt alloy after polishing (a) and after immersion in 0.05% (b), 0.1% (c), and 0.2% (d) APF solutions for 30 minutes, and 1.0% (e) and 2.0% (f) APF solutions for three minutes. In the case of the specimens immersed in 0.05% and 0.1% APF solutions, their surface smoothness was retained. A few instances of small pits due to corrosion were observed on the surfaces of the specimens immersed in 0.4% and 1.0% APF solutions. Many corrosion pits were observed on the surface of the specimen immersed in 2.0% APF solution for three minutes.

![SEM images of Ti-0.5Pt](image-url)

**Fig. 5** SEM images of Ti-0.5Pt (a) after polishing, (b) after immersion in 0.05% APF solution for 30 min, (c) 0.1% APF solution for 30 min, (d) 0.4% APF solution for 30 min, (e) 1.0% APF solution for 3 min, and (f) 2.0% APF solution for 3 min.
XRD measurement

Fig. 6 shows the XRD measurement results of Ti (a), Ti-6AI-7Nb (b) and Ti-6AI-4V (c) alloys under three conditions: after immersing in 0.2% and 2.0% APF solutions for 48 hours and without immersing in the APF solution. The X-ray profile indicated Na$_3$TiF$_6$ precipitation on the surface of pure Ti immersed in 2.0% APF for 48 hours, whereas peaks from Ti hardly appeared. As for X-ray profile of pure Ti immersed in 0.2% APF solution for 48 hours, it was almost identical to that without immersion.

In the case of Ti-6AI-7Nb alloy immersed in 0.2% APF solution for 48 hours, Na$_3$AlF$_6$ and Ti-6Al-7Nb peaks were observed. However, the main peaks of Ti-6AI-7Nb alloy immersed in 2.0% APF solution for 48 hours transformed into those of Na$_3$TiF$_6$ and Ti-6AI-7Nb. Similar XRD measurement results were obtained for the Ti-6AI-4V alloy.

DISCUSSION

In the field of dentistry where fluoride is used for the prevention of caries, the corrosion behavior of Ti and Ti alloys in an acidic fluoride-containing environment is a concern of particular importance. Many commercial toothpastes contain approximately 1,000 ppm of fluoride. Brushing teeth with a fluoride-containing toothpaste then leads to the concentration of fluoride being diluted to below 1,000 ppm in the mouth. However, an acidic tooth surface embrocation that contains approximately 10,000 ppm of fluoride (corresponding to 2.0% APF solution) for caries prevention poses a problem with regard to the corrosion of Ti and Ti alloys.

Nakagawa et al. reported on the border lines between the non-corrosive and corrosive regions of Ti, Ti-6AI-7Nb and Ti-6AI-4V alloys immersed in fluoride solutions with various concentrations. According to the results, when the concentration of fluoride was about 200 ppm, the corrosion of Ti and Ti-6Al-7Nb alloy occurred below pH 3.6, while that of Ti-6Al-4V alloy occurred below pH 4.2. Therefore, even when 2.0% APF solution was diluted to 0.05% APF solution (corresponding to 226 ppm fluoride), it was thought that the corrosion of Ti and Ti alloys would still occur.

In the 0.05% APF solution, the corrosion potentials of Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys were below −1,000 mV; further, the current density showed a remarkable increase with the potential. These increases in current density corresponded to an active corrosion (see Fig. 2(a)). The surface conditions of Ti and Ti-6AI-4V alloy immersed in 0.05% APF solution for 30 minutes did not change remarkably based on SEM observation, as shown in Fig. 3(b) and Fig. 4(b); however, approximately 20 μg/cm$^2$ of Ti dissolved with the immersion test (see Fig. 2(a)). Active corrosion was also observed in 0.1% to 2.0% APF solutions, and Ti dissolution amount increased with increase in APF concentration and active current density, as shown in Figs. 2(a), (b), and (c). Dissolution of Al, V, Nb, and Pt was
not detected in all test solutions because it was thought that: (i) the concentrations of Al, V, Nb, and especially Pt were considerably smaller than that of Ti; (ii) Al formed the corrosion compound of Na₃AlF₆ on the specimen surface rather than dissolving in the solution; and (iii) V, Nb, and Pt were electrochemically nobler than Ti. In the case of Ti-0.5Pt alloy immersed in 0.05% APF solutions for 30 minutes, active corrosion was not observed in the anodic polarization curves (see Figs. 1(a), (b), and (c)) and the surface of the specimens remained smooth after immersion (see Figs. 5(b) and (c)). Hence, amount of Ti dissolved from Ti-0.5Pt alloy was below detection limitation in this APF concentration range. In the light of this finding, it was suggested that the Ti-0.5Pt alloy had a high corrosion resistance against the APF solution when the fluoride concentration was below 0.2% and the pH value about 3.5 or 3.6.

However, in the 2.0% APF solution, the amounts of Ti dissolved from Ti and Ti-0.5Pt alloy increased remarkably, whereas those of Ti-6Al-7Nb and Ti-6Al-4V alloys decreased considerably. With regard to anodic polarization in 2.0% APF solution (see Fig. 1(d)), the passive current densities of all specimens were maintained at a high value of 20,000 μA/cm², but that of Ti-6Al-4V decreased below 2,000 μA/cm². As shown in the SEM images of Figs. 4(d) and (e) and the XRD profiles of Figs. 6(b) and (c), Ti and Al dissolved into the APF solution when the concentration of APF was low (in this study, it was below 0.4% APF). As the solubility of Na₃AlF₆ was lower than that of Na₃TiF₆, the corrosion compounds of Na₃AlF₆ were partially precipitated on the specimen surface; as a result, it was considered that the amount of Ti dissolved increased. It was thought that if the formation of titanium fluoride, titanium oxide fluoride, or sodium titanium fluoride occurred on the surface of an alloy, the corrosion of Ti would be suppressed in the fluoride solution[26,27]. In Ti-6Al-7Nb and Ti-6Al-4V alloys, drastic corrosion occurred immediately after immersion in the 2.0% APF solution (see Fig. 1(d)) and the entire surface was covered by innumerable corrosion products of Na₃TiF₆ (see the SEM image of Ti-6Al-4V alloy in Fig. 4(f) and the XRD profiles in Figs. 6(b) and (c)). As a result, the specimen surface was intercepted from the APF solution and Ti dissolution was prevented. For pure Ti immersed in 2.0% APF solution, large corrosion products of Na₃TiF₆ precipitated on the surface; however, these products were considered to be porous, as shown in Fig. 3(f). Based on these findings, it could be said that the 2.0% APF solution was a very severe environment for any Ti alloy, even the Ti-0.5Pt alloy. Moreover, since the surface of Ti-0.5Pt alloy immersed in the 2.0% APF solution had many pits due to corrosion and no corrosion products were formed, it was thus suggested that the dissolution of Ti increased (see Fig. 5(f)).

CONCLUSIONS
This study examined the corrosion behaviors of commercially pure Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys, and an experimentally produced Ti-0.5Pt alloy in acidulated phosphate fluoride (APF) solutions with various concentrations. The following main conclusions were obtained:

1. Corrosion of pure Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys might occur easily even in a diluted 0.05% (corresponding to 226 ppmF⁻) APF solution — where Ti dissolved with the formation of corrosion pits on the surface. On the other hand, the Ti-0.5Pt alloy exhibited excellent corrosion resistance. Dissolution of Ti from the Ti-0.5Pt alloy did not occur in test solutions with APF concentration less than 0.2% (corresponding to 905 ppmF⁻).

2. Corrosion products that were produced when Ti-6Al-7Nb and Ti-6Al-4V alloys were immersed in 0.2% and 2.0% (corresponding to 9,050 ppmF⁻) APF solutions were Na₃AlF₆ and Na₃TiF₆, respectively. In pure Ti, the corrosion product was produced after immersion in 2.0% APF solution. No corrosion products were formed for the Ti-0.5Pt alloy.

3. Since the entire surface of Ti-6Al-7Nb and Ti-6Al-4V alloys immersed in 2.0% APF solution was covered by compact corrosion products due to severe corrosion, the dissolution of Ti was prevented and the amount of Ti dissolved decreased. However, since pure Ti was covered by porous, large-sized corrosion products of Na₃TiF₆ and that Ti-0.5Pt alloy was not covered with any corrosion product, the amount of Ti dissolved increased remarkably in 2.0% APF solution.

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