Effects of Fluoride and Dissolved Oxygen Concentrations on the Corrosion Behavior of Pure Titanium and Titanium Alloys

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The effects of dissolved-oxygen concentration and fluoride concentration on the corrosion behaviors of commercial pure titanium, Ti-6Al-4V and Ti-6Al-7Nb alloys and experimentally produced Ti-0.2Pd and Ti-0.5Pt alloys were examined using the corrosion potential measurements. The amount of dissolved Ti was analyzed by inductively coupled plasma mass spectroscopy. A decrease in the dissolved-oxygen concentration tended to reduce the corrosion resistance of Ti and Ti alloys. If there was no fluoride, however, corrosion did not occur. Under low dissolved-oxygen conditions, the corrosion of pure Ti and Ti-6Al-4V and Ti-6Al-7Nb alloys might easily take place in the presence of small amounts of fluoride. They were corroded by half or less of the fluoride concentrations in commercial dentifrices. The Ti-0.2Pd and Ti-0.5Pt alloys did not corrode more, even under the low dissolved-oxygen conditions and a fluoride-containing environment, than pure Ti and Ti-6Al-4V and Ti-6Al-7Nb alloys. These alloys are expected to be useful as new Ti alloys with high corrosion resistance in dental use.

Key words : Titanium alloy, Corrosion, Fluoride

INTRODUCTION

Recently, titanium and Ti alloys have been widely used for clinical applications such as denture bases or dental implants, because they have high corrosion resistance and biocompatibility. There is a problem that the corrosion resistance of Ti is decreased in the presence of fluoride, which is clinically used for the prevention of dental caries^{1–7)}. The corrosion of Ti may cause fracture of the dental implant. It was reported that the presence of fluoride promotes the corrosion cracking of pure titanium under stress⁸⁾. The corrosion resistance of Ti depends on the passive film formed on the alloy surface. The authors have shown that the presence of fluoride causes formation of HF under acidic conditions and that an HF concentration of greater than 30 ppm causes the destruction of the passive film⁷⁾. Since the passive film on Ti is an oxide such as TiO₂, oxygen is essential for the stability of the passive film and for regeneration of the passive film broken by some other reasons.

The oxygen concentration in the subgingival part, where the dental implant, crown or bridge are set, is much lower than the other intraoral parts exposed to the open-air. Mettraux *et al.*⁹⁾ measured the oxygen partial pressure (pO₂) in human periodontal pockets (subgingival). According to their results, moderately deep pockets (5–6 mm) had a mean pO₂ of 15.0 mmHg (O₂=0.8 ppm), whereas deep pockets (7–

10 mm) showed a significantly lower pO_2 of 11.6 mmHg ($O_2=0.6$ ppm). It was suggested that the oxygen concentration was also low in the mucosal surface of denture bases. Therefore, there is a possibility that regeneration of the broken passive film may be delayed. The synergism of such a low-oxygen condition and the presence of fluoride may cause the corrosion of Ti.

In view of the increasing demands for dental titanium implants or restorations, it is important to develop Ti alloys that can maintain high corrosion resistance in low-oxygen concentration environments and even in the presence of fluoride. The addition of elements that help stabilize passive film or promote its formation will improve the corrosion resistance of Ti. The Pt as well as Pd is known to have an effect of promoting the formation of passive film on Ti^{10,11)}.

The purpose of the present study was to examine the effects of the dissolved-oxygen concentration and fluoride concentration on the corrosion behaviors of commercial pure Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys, which are currently used in clinical dentistry. In addition, the corrosion behavior of Ti-0.2Pd alloy which has a high corrosion resistance in a fluoride-containing acidic solution¹²⁾, and Ti-0.5Pt alloy which is expected to have an effect of promoting the formation of a passive film, were also investigated.

MATERIALS AND METHODS

Materials

The commercially pure titanium (CP Ti, JIS grade 2), Ti-6Al-4V and Ti-6Al-7Nb alloys presently used in clinical practice and the experimental Ti-0.2Pd and Ti-0.5Pt alloys were examined in this study. Ti-0.2Pd and Ti-0.5Pt alloys were made from CP Ti and 99.99% Pd and 99.95% Pt using an argon arc casting machine (TICAST Super R., Kobelco Research Institute, Japan).

The alloy specimens (7 mm square $\times$ 1.5 mm thick) were embedded in epoxy resin. They were then polished to #1,500 with waterproof grinding paper and washed in ethanol. The exposed surface areas of the specimen were 0.4 to 0.6 cm².

Test solutions

An artificial saliva (NaCl 0.04%, KCl 0.04%, CaCl₂ 0.795%, NaH₂PO₄ 0.078%, Na₂S 0.0005%, urea 0.1%) and artificial saliva containing 0.05 to 0.5% NaF were used as the test solutions. To examine the effect of dissolved oxygen concentrations, a solution exposed to air (open-air, $O_2 \geq 8.1$ ppm) and a solution deaerated by N₂ gas bubbling (non-O₂, $O_2 \leq 0.1$ ppm) were used in the immersion test. The dissolved-oxygen concentration was measured using a DO meter (TOX-90, Toko Chemical Laboratories, Japan). The temperature of the test solution was kept at $37 \pm 0.1^\circ\text{C}$ and was stirred at 200 rpm with a magnetic stirrer. To examine the effect of pH and fluoride concentration, the 0.05 to 0.5% NaF solutions were also used as the test solution. The 0.05 to 0.5% NaF concentrations correspond to 226 to 2,262 ppm fluoride. The pH levels of NaF solutions were controlled within the range of pH 5.0 to 6.5 by

adding H_3PO_4 .

Corrosion test

The counter and reference electrodes were platinum and KCl saturated Ag/AgCl electrodes, respectively. The potential of this reference electrode is denoted by E (Ag/AgCl) = E (saturated calomel electrode: SCE) + 48.4 mV. Immediately after polishing the specimen, changes in the corrosion potential with immersion time were measured in the test solution for 30 min (Potentiostat HA-301, HOKUTO DENKO, Japan).

Dissolved titanium analysis

The concentrations of Ti dissolved in the test solution after immersion for 24 hrs were analyzed by inductively coupled plasma mass (ICP-MS) spectroscopy (PMS 2000, YOKOGAWA, Japan). The immersion test was performed five times under the same conditions. Results were statistically analyzed by ANOVA with Scheff's test at a significance level of 1%.

RESULTS

Corrosion potential in artificial saliva

Fig. 1 shows the changes in the corrosion potentials of pure Ti and Ti alloys in artificial saliva under the open-air and non- O_2 conditions. The results for pure Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys are shown in Fig. 1(a). Under the open-air condition, the corrosion potentials of all alloys increased and those values were greater than -0.6 V. In contrast, when the dissolved-oxygen concentration was less than 0.1 ppm (non- O_2), the corrosion potential values were 0.2 V lower than those of the open-air conditions. Fig. 1(b) shows the results for Ti-0.2Pd and Ti-0.5Pt alloys. Changes in the corrosion potential of these alloys under the non- O_2 conditions were similar to those of the open-air condition. Those values were greater than -0.6 V. Fig. 2 shows changes in the corrosion potentials of Ti, Ti-6Al-4V, Ti-6Al-7Nb, Ti-0.2Pd and Ti-0.5Pt alloys in an artificial saliva containing 0 to 0.5% NaF (pH 4.9 to 6.5) under a dissolved-oxygen concentration of less than 0.1 ppm. When the dissolved-oxygen concentration was low and fluoride was present, the corrosion potentials of Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys markedly decreased as shown in Fig. 2(a), (b) and (c). The corrosion potential of Ti decreased to less than -1.0 V by the addition of 0.2% NaF. Those of Ti-6Al-4V and Ti-6Al-7Nb alloys decreased to less than -1.0 V by the addition of 0.1% NaF. The decreases of the corrosion potential by the addition of NaF in Ti-6Al-4V and Ti-6Al-7Nb alloys were more marked than that of pure Ti. The corrosion potentials of Ti-0.2Pd and Ti-0.5Pt alloys increased even under the low dissolved-oxygen concentration conditions as shown in Fig. 2(d). Even the addition of 0.5% NaF did not decrease the corrosion potential of Ti-0.2Pd and Ti-0.5Pt alloys. Fig. 3 shows the changes in the corrosion potentials of Ti, Ti-6Al-4V, Ti-6Al-7Nb, Ti-0.2Pd and Ti-0.5Pt alloys when they were immersed in artificial saliva containing 0.2% NaF under the dissolved-oxygen concentration of less than 0.1 ppm. The

Fig. 1 Changes in the corrosion potential of (a) Ti, Ti-6Al-4V and Ti-6Al-7Nb and (b) Ti-0.2Pd and Ti-0.5Pt with immersion time in the open-air and non-O₂ artificial saliva.

corrosion potential of Ti-0.2Pd and Ti-0.5Pt alloys increased during the early stage of immersion and the final values were between -0.7 and -0.6 V. However, the corrosion potential of Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys decreased with time immediately after immersion and the values were between -1.0 and -1.1 V.

Immersion test in NaF solution

To examine the effects of the fluoride concentration and pH under the low dissolved-oxygen concentration conditions, the changes in the corrosion potential were measured in NaF solution with various pHs. Fig. 4(a) shows the changes in the corrosion potential of Ti with immersion time in a 0.1% NaF solution under the open-air

Fig. 2 Changes in the corrosion potential of (a) Ti, (b) Ti-6Al-4V, (c) Ti-6Al-7Nb and (d) Ti-0.2Pd and Ti-0.5Pt with immersion time in the non-O₂ artificial saliva including various NaF concentrations. pH values: 0%NaF (pH 4.90), 0.05%NaF (pH 4.92), 0.1%NaF (pH 5.16), 0.2%NaF (pH 5.50), 0.5%NaF (pH 6.20)

Fig. 3 Changes in the corrosion potential of Ti and Ti alloys with immersion time in the non-O₂ artificial saliva including 0.2%NaF.

Fig. 4 Changes in the corrosion potential of Ti and Ti alloys with immersion time in the non- O_2 artificial saliva including 0.1% NaF.

conditions. There was a marked difference in the corrosion potential on both sides of the boundary between pH 4.4 and 4.3. Similar boundaries also existed in the Ti-6Al-4V and Ti-6Al-7Nb alloys under the open-air conditions¹²⁾. Fig. 4(b) shows the changes in the corrosion potential of Ti in 0.1% NaF solution with the dissolved-oxygen concentration of less than 0.1 ppm. In the non- O_2 conditions, the boundary pH value shifted from between pH 4.4 and pH 4.3 to between pH 5.2 and 5.1. Fig. 4(c) and (d) show that similar boundaries were clearly seen in Ti-6Al-4V (between pH 5.6 and 5.7) and Ti-6Al-7Nb (between pH 5.7 and 5.8) alloys in the non- O_2 conditions. Fig. 5 shows the plots of boundary pH values in each alloy, at which the corrosion behavior changes as mentioned above. It also shows the results of the open-air conditions obtained in our previous study¹²⁾ for comparison. The boundary pH of the non- O_2 environment shifted to the higher pH side compared with the open-air environment. The results of the Ti-0.5Pt and Ti-0.2Pd (non- O_2) alloys are not included in Fig. 5 because they did not show obvious boundary pHs as seen in the pure Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys.

The amount of dissolved Ti

To compare their corrosion resistances the amount of dissolved Ti was measured. Fig. 6 shows the amount of dissolved Ti measured by ICP analysis after immersion

Fig. 5 Border between the non-corrosive and corrosive regions for each alloy after immersion in the non-O₂ and open-air solutions for 30 min.

Non-O₂ ● : Ti, ▲ : Ti-6Al-4V, ▼ : Ti-6Al-7Nb

Open-air ○ : Ti, △ : Ti-6Al-4V, ▽ : Ti-6Al-7Nb, □ : Ti-0.2Pd

Fig. 6 The amount of Ti dissolved after 24 hr immersion in the open-air 0.1% NaF solutions.

for 24 hrs in a 0.1% NaF solution at pH 4.0 under the open-air environment. At pH 4.0, the amount of Ti dissolved in the Ti-0.2Pd and Ti-0.5Pt alloys were 22.0 and 6.1 $\mu\text{g}/\text{cm}^2$, respectively, and were significantly ($p < 0.01$) smaller than that of Ti (802.1 $\mu\text{g}/\text{cm}^2$). At pH 3.4, the amount of Ti dissolved in the Ti-0.2Pd and Ti-0.5Pt alloys were 278.2 and 88.9 $\mu\text{g}/\text{cm}^2$, respectively.

DISCUSSION

In this study, corrosion resistance was evaluated from corrosion potential values. A higher corrosion potential corresponded to a higher corrosion resistance and a corrosion potential below -1.0 V meant corrosive in our previous studies^{7,12}. In the open-air artificial saliva, the corrosion potentials of Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys increased and the final values were about -0.4 V as shown in Fig. 1(a). This suggests that they maintain a good corrosion resistance. In contrast, when the dissolved-oxygen concentration was less than 0.1 ppm (non- O_2), the corrosion potential values were above 0.2 V, which was lower than those of the open-air conditions. However, the corrosion potential values were not less than -0.8 V and increased with immersion time. This suggests that the corrosion did not occur. This result suggests that a decrease in the dissolved-oxygen concentration does not cause the corrosion of Ti but can decrease the corrosion resistance. In the non- O_2 artificial saliva, the corrosion potentials of the Ti-0.2Pd and Ti-0.5Pt alloys increased and the values were similar to those of the open-air condition (Fig. 1(b)). This means that these alloys maintained their high corrosion resistances even under the low dissolved-oxygen concentration conditions.

The corrosion of Ti did not take place only in the low dissolved-oxygen condition. However, it is expected that the corrosion will be accelerated in the presence of fluoride. The corrosion potentials of Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys decreased in the non- O_2 artificial saliva containing NaF by greater than 0.05% (Fig. 2(a), (b) and (c)). This suggests that a small amount of fluoride can cause corrosion of the Ti-6Al-4V and Ti-6Al-7Nb alloys, if they are under low dissolved-oxygen conditions. Even by the addition of 0.1% NaF, the corrosion potential values were lower than -1.0 V, that is, the corrosion of Ti occurred. The corrosion potentials of the Ti-0.2Pd and Ti-0.5Pt alloys, however, increased in the non- O_2 artificial saliva containing 0.5% NaF. This shows that these alloys do not corrode and they maintain high corrosion resistances, even under conditions at which the corrosion of pure Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys occurs. Since 0.1% NaF contains 453 ppm fluoride, this result suggests that Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys can be corroded by half the fluoride concentrations that are contained in commercial dentifrices. Fig. 3 shows the changes in the corrosion potential of Ti and Ti alloys in the non- O_2 artificial saliva containing 0.2% NaF (905 ppm F). The fluoride concentration of widely used fluoride-containing dentifrices is about 1,000 ppm. The environment of the non- O_2 artificial saliva containing 0.2% NaF corresponds to the situation where the fluoride-containing dentifrice is used at an oral location with a

low dissolved-oxygen concentration. It was shown that the Ti-0.2Pd and Ti-0.5Pt alloys maintained high corrosion resistances even in conditions at which the corrosion resistance of pure Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys was lost.

Under the low dissolved-oxygen concentration conditions, the boundary pH values at which the corrosion behavior changed, shifted to higher pH values. For example, the corrosion resistance of pure Ti was maintained at a pH above 4.4 in the open-air 0.1% NaF solution conditions (Fig. 4(a)). However, the boundary pH value shifted to pH 5.2 in the non-O₂ conditions (Fig. 4(b)). Fig. 5 shows the diagram indicating the non-corrosive and corrosive regions of the fluoride concentrations and pH values in Ti and Ti alloys. This shows that corrosion resistance decreases under the non-O₂ environment. When the NaF concentration was 0.2%, for example, the corrosion occurred at a pH below 5.0 in the Ti-6Al-4V under the open-air conditions. However, under the non-O₂ conditions, the corrosion occurred at a pH below 5.7. Therefore, the Ti-6Al-4V and Ti-6Al-7Nb alloys were susceptible to fluoride in the low dissolved-oxygen concentration conditions and the corrosion occurred even at a pH value around neutrality. Even if the oxide film is broken by the presence of a little fluoride, it is suggested that the film immediately regenerates under the open-air environment at which the dissolved-oxygen is sufficient, and that the corrosion resistance is maintained. In contrast, under the low dissolved-oxygen concentration conditions, it will take more time or will not be able to regenerate the broken oxide film. At pH 4.0, the amount of dissolved Ti in the Ti-0.2Pd and Ti-0.5Pt alloys was significantly ($p < 0.01$) smaller than the pure Ti as shown in Fig. 6 and, therefore, they had a high corrosion resistance compared with pure Ti. Comparing the results under more corrosive conditions (pH 3.4), it can be seen that the Ti-0.5Pt alloy had a higher corrosion resistance than the Ti-0.2Pd alloy.

The corrosion resistance of titanium depends on the balance of a dissolution and a formation of a passive film. In the presence of fluoride, when the dissolved oxygen concentration is low, the reproduction of a passive film is delayed. It is suggested that the corrosion of titanium occurs because the balance shifts to the dissolution reaction of the passive film. The presence of Pt as well as Pd accelerated the cathodic reaction, and consequently, it was suggested that the corrosion potential of the alloy shifted into the passive region of Ti^{10,11}). The corrosion potential of the alloy was more noble than the critical potential for passivation of Ti. In these alloys, it was suggested that a reproduction of the passive film was promoted by the addition of Pd or Pt, and the high corrosion resistance was maintained under the low dissolved-oxygen concentration environment. The Ti-0.2Pd and Ti-0.5Pt alloys are expected to be useful as new Ti alloys with high corrosion resistance in dental use.

CONCLUSIONS

This study examined the effects of various dissolved-oxygen concentrations and fluoride concentrations on the corrosion behaviors of commercial pure Ti, and the Ti-6Al-4V and Ti-6Al-7Nb alloys used presently in clinical dentistry and the experimentally

produced Ti-0.2Pd and Ti-0.5Pt alloys.

1. A decrease in the dissolved-oxygen concentration tended to reduce the corrosion resistance of Ti and Ti alloys, but did not cause a severe corrosion of Ti.

2. Under low dissolved-oxygen conditions, the corrosion of pure Ti and Ti-6Al-4V and Ti-6Al-7Nb alloys might easily take place in the presence of a small amount of fluoride. Pure Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys were corroded by half or less the fluoride concentrations currently found in commercial dentifrices (less than 453 ppm F).

3. The experimentally produced Ti-0.2Pd and Ti-0.5Pt alloys did not corrode even under low dissolved-oxygen concentrations and fluoride-containing conditions. These alloys are expected to be useful as new Ti alloys with high corrosion resistance in dental use.

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