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The effect of Pt and Pd alloying additions on the corrosion behavior of titanium in fluoride-containing environments

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Abstract

In this study, we examined the corrosion behaviors of pure titanium, the alloys Ti–6Al–4V and Ti–6Al–7Nb, and the new experimental alloys Ti–Pt and Ti–Pd using anodic polarization and corrosion potential measurements in an environment containing fluoride. Before and after immersion in the test solutions, we made observations using a scanning electron microscope. The test solutions included an artificial saliva containing 0.2% NaF (corresponding to 905 ppm F) and an artificial saliva with a low concentration of oxygen. Although the surfaces of the Ti–Pt and Ti–Pd alloys were not affected by an acidic environment containing fluoride, the surfaces of the pure titanium, the Ti–6Al–4V alloy, and the Ti–6Al–7Nb alloy were markedly roughened by corrosion. The surfaces of the pure titanium, the Ti–6Al–4V alloy, and the Ti–6Al–7Nb alloy were microscopically damaged by corrosion when they were immersed in the solution containing a low concentration of dissolved oxygen, even with a fluoride concentration included in the commercial dentifrices. In this situation, however, the surfaces of the new Ti–Pt and Ti–Pd alloys were not affected. These alloys are expected to be of use in dental work as new titanium alloys with high corrosion resistances.
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1. Introduction

Because of their superior corrosion resistance and biocompatibility, titanium and its alloys are clinically used for dental implants and denture bases. Ti and its alloys have a high corrosion resistance because they form a passive film on their surfaces. It was reported, however, that this resistance is significantly reduced in the presence of fluoride, which is also often clinically used in the prevention of dental caries [1–12]. Therefore, it would be essential to investigate the corrosion behavior of Ti and the Ti alloys in a fluoride-containing solution that accurately simulates the above oral environment.

The corrosion resistance of Ti and its alloys largely depends on the fluoride concentration and the pH of the environmental solution that they are placed in. The possibility of corrosion is accurately predicted by the pH versus the NaF concentration diagram, in which there is a linear boundary between corrosive and non-corrosive regions, as established by our previous results [13,14]. In an acidic condition, the fluoride ion formed hydrofluoric acid (HF), and the presence of an HF concentration over 30 ppm resulted in the destruction of the passive film on the Ti surface [13]. The corrosion resistance of Ti and its alloys was also affected by dissolved oxygen in a media, which we expected would stabilize the passive oxide layer and/or promote the regeneration of the passive film.

In our previous study [15], we found that Ti, the Ti–6Al–4V alloy, and the Ti–6Al–7Nb alloy, which were commercially available as dental implants, were prone

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to corrosion in the presence of even a small amount of fluoride (0.05% of NaF) with a low oxygen level below 0.1 ppm. In the oral environment, the low-level oxygen situation seems fairly common. For instance, Mettraux et al. reported that the oxygen partial pressure in a human subgingival pocket near a dental restoration such as an implant, crown, or bridge reached about 15 mm Hg [16]. This corresponded to a concentration of 0.8 ppm dissolved oxygen that could reach as low as 0.6 ppm in a deeper periodontal pocket. In the other intraoral parts exposed to open air, those oxygen levels are much lower (about 8 ppm). It was also reported that the existence of the fluoride ion in the environment promoted the stress corrosion cracking of titanium [17–19]. This could result in the sudden destruction of the titanium restoration. Consequently, it would be significant to develop Ti alloys with a higher corrosion resistance in an oral environment that contains fluoride ions. We found that the addition of a small amount of Pt or Pd to Ti to create an alloy proved to be very effective in improving the corrosion resistance of titanium in NaF solutions of various concentrations up to 2%. In the present study, we measured the anodic polarization and the corrosion potential of Ti mixed with 0.1–2 wt% Pt or Pd to create an alloy and placed in artificial saliva containing 0.2% NaF (corresponding to 905 ppm F) fluoride concentrations with or without dissolved oxygen. To assess the morphological changes on the surface by corrosion, we examined the alloy surface after the corrosion test with a scanning electron microscope. The purpose of this study is to investigate the effect of fluoride concentrations and dissolved oxygen on the corrosion behavior of the Ti–Pt or Ti–Pd alloys and to clarify the mechanism of improvement in the corrosion resistance of titanium by alloying it with Pt or Pd.

2. Materials and methods

2.1. Materials

In this study, we examined commercially pure titanium (Kobe Steel Co. Ltd., Kobe, Japan), the Ti–6Al–4V (Daido Steel Co. Ltd., Nagoya, Japan) and Ti–6Al–7Nb (GC CO. Ltd., Tokyo, Japan) alloys, which are presently used in clinical practice, and the experimental Ti- (0.1–2.0) wt% Pd and Ti- (0.1–2.0) wt% Pt alloys. Pure titanium and the Ti–6Al–4V and Ti–6Al–7Nb alloys were used in the condition as-received. The Ti–Pd and Ti–Pt alloys were made from CP Ti and 99.99% Pd, and CP Ti and 99.95% Pt 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 s in the melting condition. They were twice melted

by changing the top and bottom and were cast into the mold. After Ni lead wire was spot-welled onto their back surface, the alloy specimens were embedded in epoxy resin. They were then polished to #1500 with waterproof grinding paper and washed in ethanol. The exposed surface areas of the specimen ranged from 0.4 to 0.6 cm^2.

2.2. Test solutions

The test solution was an artificial saliva (NaCl 0.04%, KCl 0.04%, $CaCl_2$ 0.795%, NaH_2PO_4 0.078%, Na_2S 0.0005%, urea 0.1%) that contained 0.2% NaF (corresponding to 905 ppm F). The test solution's pH level was adjusted to 4.0 by adding H_3PO_4. To examine the effect of dissolved oxygen concentrations, we used a solution exposed to air (open air, $O_2 > 8.1$ ppm) and a solution deprived of air by bubbling N_2 gas in the immersion test. After being deprived of air, the pH value of the artificial saliva rose to 5.0. The dissolved-oxygen concentration was measured using a DO meter (TOX-90, Toko Chemical Laboratories, Tokyo, Japan). We maintained the temperature of the test solution at a constant $37 \pm 0.1\,^\circ\mathrm{C}$ and it was stirred at 200 rpm with a magnetic stirrer.

2.3. Corrosion test

The counter and reference electrodes were a platinum electrode and a KCl saturated Ag/AgCl electrode, respectively. The potential of the reference electrode is denoted by E (Ag/AgCl)= E (Normal Hydrogen Electrode: NHE) -0.22 V at 25 °C. We immersed the specimens in the test solution and measured the changes in the corrosion potential with an immersion time of 30 min using a potentiostat (Potentiostat HA-301, HOKUTO DENKO, Kyoto, Japan). The anodic polarization curves were obtained from a corrosion potential to $+2000$ mV (vs. KCl saturated Ag/AgCl electrode) at a scanning rate of 1 mV/s (Function generator HB-104, HOKUTO DENKO, Kyoto, Japan). Four specimens were used for the corrosion potential and the anodic polarization measurements for each test solution. Results were statistically analyzed by a non-parametric method (Kruskal–Wallis test and Mann–Whitney test) at a significance level of 5%.

2.4. Surface observation

We polished the specimens that we were to examine under the scanning electron microscope (SEM) to a luster using an aluminum powder (particle size less than 0.3 μm). The specimens with an effective surface area of 0.9–1.3 cm^2 were immersed in the test solution of 1000 mL for 30 or 60 min. After immersing the speci-