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Corrosion Resistance of Ti-29Nb-13Ta-4.6Zr Alloy in a Fluoride-Containing Solution

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Abstract. The objective of this study was to evaluate the corrosion behavior of Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) with immersion in an acidic saline solution containing fluoride by investigating change in color and the surface structure of the oxide film. With immersion in fluoride-containing solution, TNTZ showed a less marked change in color than commercially pure titanium (TI), and a smaller decrease in glossiness. The outermost surface was covered with oxides from its constituent elements at before and after immersion in solution with or without fluoride. When immersed in fluoride-containing solution, the film consisted of larger niobium and tantalum oxides than that before or after immersion in solution without fluoride. In summary, TNTZ showed superior resistance to discoloration to TI after immersion in fluoride-containing solution. The results suggest that the subsequent increase in niobium and tantalum fractions in the oxide film in TNTZ improves resistance to corrosion.

Introduction

Their superior corrosion resistance with exposure to body fluids and biocompatibility make titanium and its alloys a popular choice for implants and prosthetic devices in clinical dentistry. These qualities are believed to be related to the formation of oxide film on these alloys. On exposure to the oral environment, such alloys sometimes show discoloration, turning a medium brown color, and corrosion [1, 2], possibly due to the presence of fluoride in prophylactic agents [3-5]. Fluoride breaks down the passive film on titanium alloys. Therefore, it is necessary to improve the resistance of such alloys to fluoride-induced corrosion.

Noguchi et al suggested that the degree of discoloration of titanium alloys in fluoride-containing solution and the total amounts of released elements from titanium alloys differed among alloys [6]. Trace platinum and palladium alloying to titanium [7] or addition of 20 mass% chromium [8] were reported to improve resistance to fluoride-induced corrosion in comparison with commercially pure titanium. Therefore, the constituent elements of such alloys may influence resistance to fluoride-induced corrosion.

Recently, Ti-29Nb-13Ta-4.6Zr alloy (TNTZ), which consists of non-toxic and allergy-free elements with superior mechanical properties, has been introduced as a new alternative for dental prostheses [9]. This new alloy offers inhibition of bone atrophy and enhancement of bone remodeling, as it has a lower Young’s modulus than other biomedical alloys such as commercially pure titanium or stainless steel. However, the resistance of TNTZ to fluoride-induced corrosion remains to be determined.

The objective of this study was to evaluate the corrosion behavior of TNTZ with immersion in acidic saline solution containing fluoride by investigating change in color and the surface structure of the oxide film.
Materials and Methods

Specimens were prepared from TNTZ alloys and commercially available pure Grade 2 titanium (TI). The TNTZ specimens were composed of 29.4 mass% niobium, 13.0 mass% tantalum, 4.64 mass% zirconium, trace elements such as oxygen, carbon, and nitrogen, and titanium. Specimens $15 \times 15 \times 1.5$ mm were cut from a rod. Each specimen was polished with a series of abrasive papers according to the standard metallurgical procedure. Polishing was completed with 0.02-μm colloidal silica particles and buff. They were then ultrasonically washed 3 times for 5 min each time in acetone and distilled water.

Fluoride-containing saline solution consisted of 9.00 g sodium chloride (NaCl; Wako Chem., Osaka, Japan) and 2.00 g sodium fluoride (NaF; Wako Chem., Osaka, Japan) in 1 L distilled water, hereafter referred to as NAF. A fluoride-free saline solution was also prepared as a reference solution. The two solutions were adjusted to pH 5.0 using lactic acid (Wako Chem., Osaka, Japan) at 37°C.

The color and glossiness values of the polished TNTZ and TI specimens were determined with a color meter (MCR-A, Luck Office, Tokyo, Japan) and a gloss meter (GS-26D, Murakami Color Research Laboratory, Tokyo, Japan). The color value was evaluated according to the CIE L*a*b* color coordinator system.

After measuring color and glossiness, the specimens were immersed in each test solution in a bottle at 37°C. The volume of the solution was 1 mL per 10 mm² of specimen. They were then removed from the solution after a 3-day immersion period and gently rinsed with distilled water. The color value of each specimen was then measured again to determine change in color. Color difference, $\Delta E^{*ab}$, was calculated using the following equation:

$$
\Delta E^{*ab} = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}
$$

where $L_0^*$, $a_0^*$ and $b_0^*$ are brightness and chromaticness values at before immersion and $L^*$, $a^*$ and $b^*$ are those values at after immersion, respectively. Color difference and glossiness between TI and TNTZ were statistically analyzed using a $t$-test at a significance level of 95%.

X-ray photoelectron spectroscopy (XPS) measurement was performed using an photoelectron spectrometer (Axis-Ultra, Kratos-Shimadzu, Japan) with monochromatized Al Kα radiation (1486.6 eV). The binding energy was normalized to the C1s peak (285.0 eV) of hydrocarbon on each specimen. At least 2 specimens of each alloy were prepared. The surface of the specimen was observed under a field emission scanning electron microscope (FE-SEM: ERA-8900FE, Elionix, Tokyo, Japan) at a voltage of 15 kV.

Results and Discussion

Figure 1 shows change in color in the TI and TNTZ specimens after immersion in an acidic saline solution with or without fluoride, referred to as SAL and NAF, respectively. A slight change in color was observed in both TI and TNTZ with immersion in SAL, although the difference was not significant. After immersion in NAF, the $\Delta E^{*ab}$ in TI and TNTZ was 5.0 and 12.0, respectively. Based on literature [10], the TNTZ was classified to an appreciable change in color, although it was less than that in the TI with immersion in NAF.

Figure 2 shows the Gs(20°) values of TI and TNTZ at before and after immersion in SAL or NAF. The Gs(20°) values for both TI and TNTZ at before and after immersion in SAL were approximately 1,000%, which were similar to those without immersion. After immersion in NAF, the Gs(20°) values for TI and TNTZ showed a reduction, and the decrease in glossiness in TNTZ was smaller than that in TI. This shows that TNTZ has superior resistance to discoloration and glossiness in a fluoride-containing solution.

Figure 3 shows SEM images of TI and TNTZ after immersion in NAF. Although no adhesive or deposited substances were observed on TI or TNTZ with immersion in SAL, localized corrosion was observed in TI with immersion in NAF. The surface of TNTZ after immersion in NAF was smooth and similar to that with immersion in SAL.
According to the XPS analysis, the composition of the oxide film on TNTZ at before and after immersion in SAL was similar. The oxide film on TNTZ after immersion in NAF consisted of larger niobium and tantalum oxides than that at before immersion, and sodium and fluoride were slightly detected. Figure 4 shows the Ti2p, Nb3d, Ta4f, and Zr3d XPS spectra of TNTZ at before and after immersion in SAL or NAF. The spectrum of each constituent element in TNTZ at before immersion was decomposed to its metal (Ti⁰, Nb⁰, Ta⁰ and Zr⁰) and oxide state, and Ti⁴⁺, Nb⁵⁺, Ta⁵⁺, and Zr⁴⁺ were mainly detected in each spectrum. These results suggest that the oxide (passive) film was thin, which agrees with the results of an earlier study by Tanaka et al [11]. The fraction of the metal state in each spectrum after immersion in SAL or NAF showed a decrease, indicating that the surface of the TNTZ was oxidized. In detail, a metal state was slightly detected in the Ti2p and Nb3d spectra of TNTZ with immersion in NAF, indicating that the oxide film on TNTZ immersed in NAF was thin. Although fluoride in saline solution promotes oxidation of TNTZ, the oxide film on TNTZ here was thin.

Discoloration of alloys is caused by the deposition of corrosion products and by an increase in the thickness of the oxide film. Tanaka et al suggested that the composition of the oxide film on titanium alloy was governed by various factors such as initial oxidation potential and the oxidation energy of its elements [11]. An oxide film rich in chromium was observed to form with immersion of Ti-20 mass% chromium alloys in fluoride-containing solution [8, 12]. In the present study, the composition of the oxide film and degree of oxidation differed between specimens at before and after immersion in SAL or NAF. The fractions of niobium and tantalum oxides increased with immersion in fluoride-containing solution, suggesting them as key to improving resistance to fluoride-induced corrosion.

In summary, immersion of Ti-29Nb-13Ta-4.6Zr alloy in an acidulated saline solution containing fluoride resulted in formation of a thin oxide film, suggesting that this alloy has good resistance to fluoride-induced discoloration.
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