<table>
<thead>
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<th>Title</th>
<th>Discoloration of titanium alloy in acidic saline solutions with peroxide</th>
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<td>Takemoto, S; Hattori, M; Yoshinari, M; Kawada, E; Oda, Y</td>
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INTRODUCTION

Dental implants and prostheses made of titanium or its alloys are widely used in clinical dentistry. Although titanium is well known for its superior corrosion resistance, there have been reports of discoloration occurring with the practical application of titanium implants and denture bases. One reason for this discoloration is peroxide produced during inflammatory reaction or contained in denture cleaners and bleaching agents. Some studies using a surface reaction model have suggested that a titanium-peroxide complex is formed due to interaction with hydrogen peroxide when titanium is implanted in the human body. Furthermore, the titanium surface was oxidized and dissolved by peroxide produced by bacteria and leukocytes during inflammatory reactions. Studies in vitro have reported a decrease in resistance to corrosion and signs of pitting corrosion in titanium in the presence of hydrogen peroxide. Similarly, in vitro studies have reported a decrease in resistance to corrosion and signs of pitting corrosion in titanium in the presence of hydrogen peroxide. Therefore, although the mechanical properties and biocompatibility of titanium and its alloys are excellent, discoloration resistance in an oral environment remains a major challenge.

In an earlier study, we investigated discoloration and dissolution in several titanium alloys in a neutral solution containing hydrogen peroxide and found that color difference in Ti-6Al-4V and Ti-55Ni alloys was greater than that in other alloys, although little release of metallic elements was observed, except in Ti-55Ni alloy. However, the corrosion behavior of titanium alloys in an acidic environment in which peroxide has been produced during an inflammatory reaction remains to be clarified.

In view of the problem of discoloration, which hinders the practical application of titanium alloys, this study had two aims: (1) to compare metal release and discoloration in several titanium alloys with exposure to acidulated peroxide-containing solutions; and (2) to determine whether there was any association between discoloration and the corrosion reaction of the titanium alloy.

MATERIALS AND METHODS

Alloy specimens

Seven types of titanium alloy were prepared: commercially pure titanium (Ti), Ti-Pd (TPD), Ti-Al-V (TAV), Ti-Al-Nb (TNB), Ti-Ni (TNI), Ti-Cu (TCU) and Ti-Cr (TCR). The composition and manufacture of the alloys are listed in Table 1. These experimental TCU and TCR alloys were made in an argon-arc melting furnace (ACM-01, Diavac, Chiba, Japan). The obtained alloy was arc-melted and cast using an argon-arc melting/pressure casting machine (Cyclarc II, J. Morita, Kyoto, Japan), as described in the literature.

Specimens of 14×14×1 mm in size or 15–20 mm in diameter and 2 mm in height were cut from a sheet or rod of commercially available titanium or titanium alloy. Each specimen was embedded in epoxy resin and the surface polished with abrasive paper according to the standard metallurgical procedure. Polishing was completed with 0.02-µm colloidal silica particles and ultrasonic washing in distilled water for 10 min.

Test solutions

Twelve discoloration test solutions were prepared with different concentrations of hydrogen peroxide and pH. Hydrogen peroxide concentration in the test solutions was 0, 50, 100, or 150 mM hydrogen peroxide (H2O2, Wako Chem., Osaka, Japan) with 154 mM sodium chloride (Wako Chem.). Solutions were adjusted to a pH of 4.0 or 5.0 by addition of lactic acid at 37°C (denoted as pH 4 or pH 5 hereafter), or used as received (pH of approximately 5.5–5.8: denoted as pH 6 hereafter).
Table 1  Titanium and its alloys used in this study

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Composition (mass%)</th>
<th>Manufacture</th>
<th>Code</th>
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<tbody>
<tr>
<td>Grade 2-Ti</td>
<td>Ti&gt;99.5 (KS50)</td>
<td>Kobe Steel</td>
<td>TI</td>
</tr>
<tr>
<td>Ti-Pd</td>
<td>Ti-0.15Pd</td>
<td>Kobe Steel</td>
<td>TPD</td>
</tr>
<tr>
<td>Ti-Al-V</td>
<td>Ti-6Al-4V</td>
<td>Kobe Steel</td>
<td>TAV</td>
</tr>
<tr>
<td>Ti-Al-Nb</td>
<td>86.5Ti-7Nb-6Al-0.5Bal</td>
<td>GC</td>
<td>TNB</td>
</tr>
<tr>
<td>Ti-Ni</td>
<td>Ti-55Ni</td>
<td>Daido Steel</td>
<td>TNI</td>
</tr>
<tr>
<td>Ti-Cu</td>
<td>Ti-10Cu</td>
<td>Experimental</td>
<td>TCU</td>
</tr>
<tr>
<td>Ti-Cr</td>
<td>Ti-20Cr</td>
<td>Experimental</td>
<td>TCR</td>
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Discoloration measurement
The color value of the polished titanium alloy specimens was determined with a color meter according to the CIE L*a*b* color coordinator system (MCR-A, Luck Office, Tokyo, Japan) with D65 illuminant and a 10° observer. An area 6 mm in diameter was used for these measurements. After color measurement, the specimens were immersed in 25 mL of each test solution in a polystyrene bottle at 37°C. They were then removed from the solutions after a 7-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, ΔE*ab, was calculated using the following equation:

\[
ΔE*ab=\left[\left(L^*-L^*_0\right)^2+\left(a^*-a^*_0\right)^2+\left(b^*-b^*_0\right)^2\right]^{1/2}
\]

where \(L^*_0\), \(a^*_0\) and \(b^*_0\) are values at before immersion and \(L^*, a^*\) and \(b^*\) are values at after immersion.

Dissolution measurement
Amount of released metals in the solution after the discoloration test was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES; Vista-MPX, SII, Chiba, Japan). The detection limit was below 0.01 ppm. Amount of released elements was calculated per unit metal area in contact with the solution. This area was determined with an image analysis system (HC-2500/OL, Olympus, Tokyo, Japan) and the Image-Pro PLUS software (Media Cybernetics Inc., Rockville, MD, USA).

Auger electron spectroscopy
Depth profiles of some of the specimens were obtained by Auger electron spectroscopy (AES; JAMP-7100, JEOL, Tokyo, Japan) in combination with argon-ion sputter etching. The accelerating voltage of the Auger electron was 10 kV and the vacuum in the chamber was in the order of 10^-7 to 10^-8 Pa. The differential spectra obtained by AES were determined and their peak-to-peak intensities used for quantification. Argon-ion-sputter etching was applied under 3 kV and 3 µA/cm² in 7×10^-2 Pa, and the etching rate for the SiO₂ on silicon substrate was 0.15 nm/s. Thickness of the oxide layer was determined as the oxygen signal in the oxide at the point halfway between its initial intensity and background noise[^20]. Two specimens of each alloy were prepared.

Statistical analysis
Color difference in, and the quantity of each metal released from, each alloy were statistically analyzed with a two-way analysis of variance (α=0.05) to determine the effects of concentration of hydrogen peroxide and level of pH in the solutions.

RESULTS

Discoloration of titanium and titanium alloys
Figure 1 shows color difference, ΔE*ab, in the titanium alloys immersed in acidulated saline solutions containing hydrogen peroxide at different pHs. At pH 4, 5, or 6, the ΔE*ab for all tested alloys in the solution without hydrogen peroxide (0 mM) was less than 2. At pH 4, when the solution contained 50 mM hydrogen peroxide, the ΔE*ab for all titanium alloys, except TCR, was more than 6, indicating appreciable or greater discoloration. The ΔE*ab for titanium alloys in solution containing 100 or 150 mM hydrogen peroxide was more than 12, indicating marked discoloration (very much discoloration).

At pH 5, after immersion in solutions containing hydrogen peroxide, the ΔE*ab for all titanium alloys, except TPD in 50 mM hydrogen peroxide, TAV in 150 mM hydrogen peroxide, and TNI and TCU in 50, 100, or 150 mM hydrogen peroxide, was less than 6, indicating noticeable or appreciable discoloration. When TNI was immersed in solutions containing 100 or 150 mM hydrogen peroxide, the ΔE*ab was more than 12, indicating marked discoloration.

At pH 6, after immersion in solutions containing hydrogen peroxide, the ΔE*ab for all titanium alloys, except TPD in 50 mM hydrogen peroxide, TAV in 150 mM hydrogen peroxide, and TNI and TCU in 50, 100, or 150 mM hydrogen peroxide, was less than 6. At pH 6, the ΔE*ab for all tested alloys, except TNI in solutions with hydrogen peroxide, was less than 5, indicating noticeable or appreciable discoloration. When TNI was immersed in solutions containing 100 or 150 mM hydrogen peroxide, the ΔE*ab was more than 12, indicating marked discoloration.

According to the statistical analysis, the color difference in each alloy in solutions at pH 4, pH 5 or pH 6 was significant (p<0.05). Furthermore, color difference in each alloy was significant between with and without hydrogen peroxide.
Total amounts of released metals in solutions

Figure 2 shows the total amounts of released metals in saline solutions containing various concentrations of hydrogen peroxide and adjusted to different pHs after immersion for 7 days. Concentration of hydrogen peroxide was 50, 100, or 150 mM, and solution without hydrogen peroxide (0 mM) was prepared as reference. pH of solution was 4, 5, or 6. (a) TI, (b) TPD, (c) TAV, (d) TNB, (e) TNI, (f) TCU, (g) TCR.

Total amounts of released metals in solutions

Figure 2 shows the total amounts of released metals in saline solutions containing various concentrations of hydrogen peroxide after immersion for 7 days. Table 2 lists the amounts of detected elements in solutions containing 150 mM hydrogen peroxide at pH at 4, 5, and 6. Total amount of released elements was less than 15 µg/cm², except for in TNI, regardless of the presence or absence of hydrogen peroxide or the pH of the solution. Titanium was detected in all solutions for every alloy. In addition, constituent elements were released from each alloy. After immersion in solution without hydrogen peroxide, these amounts were less than 2 µg/cm². On the other hand, TNI showed dissolution in the range of 100–200
Table 2  Amount of detected elements in solutions containing 150 mM hydrogen peroxide at pH at 4, 5, and 6 after 7-day immersion of each alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
</tr>
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<tbody>
<tr>
<td>TI</td>
<td>Ti: 1.1</td>
<td>Ti: 0.5</td>
<td>Ti: 3.4</td>
</tr>
<tr>
<td>TPD</td>
<td>Ti: 1.3</td>
<td>Pd: 0.1</td>
<td>Ti: 2.4</td>
</tr>
<tr>
<td>TAV</td>
<td>Ti: 4.1</td>
<td>Al: 1.1</td>
<td>V: 1.0</td>
</tr>
<tr>
<td>TNB</td>
<td>Ti: 3.1</td>
<td>Al: 0.7</td>
<td>Nb: 1.4</td>
</tr>
<tr>
<td>TNI</td>
<td>Ti: 8.7</td>
<td>Ni: 154.9</td>
<td>Ti: 4.5</td>
</tr>
<tr>
<td>TCU</td>
<td>Ti: 2.8</td>
<td>Cu: 0.4</td>
<td>Ti: 0.3</td>
</tr>
<tr>
<td>TCR</td>
<td>Ti: 1.7</td>
<td>Cr: 0.9</td>
<td>Ti: 0.6</td>
</tr>
</tbody>
</table>

(unit: µg/cm²)

Fig. 3  AES depth profiles of relative concentrations of elements at surface oxide film of commercially pure titanium (TI). (a) Before immersion, (b) After immersion in saline solution without hydrogen peroxide (0-mM H₂O₂, pH 4), (c) After immersion in saline solution with 150 mM hydrogen peroxide (150-mM H₂O₂, pH 4)

This study measured discoloration and dissolution in titanium alloys immersed in acidulated saline solutions containing hydrogen peroxide to investigate their corrosion behavior. In order to understand the corrosion behavior of such alloys, it is important to ascertain the correlation between discoloration and dissolution. Figure 4 summarizes the correlation between color difference and amount of released elements based on Figs. 1 and 2. The TNI alloy showed a marked change in color and level of dissolution in solutions containing hydrogen peroxide, regardless of hydrogen peroxide concentration or level of pH. As shown in Fig. 4(a), at pH 4, color difference, \( \Delta E^{*ab} \), in the other alloys after immersion in solutions containing 100 or 150 mM hydrogen peroxide was more than 12, and the total amount of released elements was less than 15 µg/cm² after 7 days. At pH 5 or 6, the titanium alloys showed a value of less than 11 in color difference and less than 15 µg/cm² dissolution after 7 days. Color difference was classified into six levels²²: \( \Delta E^{*ab}=0–0.5 \), trace; 0.5–1.5, slight; 1.5–3.0, noticeable;

Depth profiles by Auger electron spectroscopy

The depth profiles in Fig. 3 show the relative concentrations of each element in the TI specimens at before and after immersion in solutions without (0 mM) or with 150 mM hydrogen peroxide. The depth profiles in Figs. 3(a) and (b) revealed that the relative concentration of oxygen and carbon sharply decreased, whereas that of titanium sharply increased. Relative concentrations reached a plateau in both TI specimens at after 100 s sputtering time. On the other hand, the depth profiles of the TI specimens immersed in solution with 150 mM hydrogen peroxide revealed that the concentration of oxygen gradually decreased with increase in titanium concentration. The specimens immersed in solution with hydrogen peroxide had a thicker oxide film than those immersed in solution without hydrogen peroxide, and the thickness of the oxide film in specimens immersed in solution with hydrogen peroxide was 10 times greater than that at before immersion.

DISCUSSION

\( \Delta E^{*ab} \) with the most released element being nickel.
3.0–6.0, appreciable; 6.0–12.0, much; 12.0–, very much. Furthermore, according to the ISO, the total amount of released elements from an alloy should be less than 200 µg/cm² per 7 days. In this study, while all titanium alloys except Ti-55Ni showed a high level of discoloration at a low pH and high concentration of hydrogen peroxide, this discoloration was particularly marked at a low pH. Level of dissolution, however, was within the acceptable range for clinical use at either a low or high pH. Although Ti-55Ni alloy showed a clinically tolerable level of dissolution in acidulated solution with hydrogen peroxide, both level of discoloration and dissolution were greater than in the other alloys.

As shown in Fig. 3, according to AES analysis, Ti immersed in solution with hydrogen peroxide had a ten-fold thicker oxide film than that immersed in solution without hydrogen peroxide. Discoloration in the titanium alloys showed a correlation with increase in thickness of oxide film. The corrosion resistance of titanium and its alloys is maintained by a passive film. Although the composition and structure of the passive film differs depending on type of alloy, it consists of a thin titanium oxide layer on the surface of the alloy. Titanium alloys with passive films were oxidized by hydrogen peroxide produced by bacteria, leukocytes and macrophages. This indicates that hydrogen peroxide works as an oxidant agent to titanium, increasing the thickness of the surface oxide film, and leading to discoloration.

In an earlier study, discoloration of several titanium alloys was investigated after immersion in a neutral solution containing hydrogen peroxide. It was found that Ti-6Al-4V and Ti-55Ni alloys showed a greater change in color than other alloys, and that nickel and titanium were released from Ti-55Ni. The results for discoloration and dissolution in a neutral solution containing hydrogen peroxide in this study agree with those of an earlier report on immersion in a solution containing hydrogen peroxide. The Ti-6Al-4V and Ti-6Al-7Nb alloys showed a greater degree of dissolution than all the other alloys, except TNI. The passive film on these alloys consisted of not only titanium oxide, but also oxides of aluminum, vanadium, and niobium. The oxidative activity of these oxides may be greater on the surface of Ti-6Al-4V and Ti-6Al-7Nb than on the surface of other alloys, which would explain why the amount of released elements was larger here. Further study is required to elucidate the corrosive effect of peroxide on Ti-6Al-4V and Ti-6Al-4V alloys.

In summary, in this study, Ti-55Ni showed a high level of change in color and dissolution in hydrogen peroxide-containing saline solutions, suggesting that discoloration in this alloy was caused by corrosion. Other alloys immersed in solution containing hydrogen peroxide at pH 4 showed a high level of dissolution, and the amount of released elements from each alloy depended on its constituent elements. Discoloration in these titanium alloys is believed to have been caused by formation of a thick oxide film. On immersion in hydrogen peroxide-containing solutions at pH 5–6, the degree of discoloration in all titanium alloys except Ti-55Ni was markedly lower than that with immersion in solution at pH 4. These discoloration behaviors suggest that oxidation of titanium alloys by hydrogen peroxide is reduced in solutions where the pH is between 5 and 6.

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REFERENCES