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Discoloration of Ti-20Cr alloy in oral environment and its surface characterization

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The objective of this study was to evaluate change in color in experimental titanium-20mass% chromium (Ti-20Cr) alloy in an oral environment. Pure Ti and Ti-6Al-7Nb and Co-29Cr-5Mo alloys, as references to compare change in color, were prepared by casting. The cast specimen was mirror-polished. Each specimen was affixed to a palatal plate and the plate then worn by a volunteer for up to 300 h. A few specimens showed a change in color. These changes and the median values among the tested alloys were not significant. Larger amounts of carbon, nitrogen, and oxygen were observed in the discolored alloys than in the slightly-discolored alloys. The spectra of the constituent elements of the alloys revealed no corrosion. In conclusion, the experimental Ti-20Cr alloys showed a level of resistance to change in color and corrosion similar to that in commercially available Ti and Co-29Cr-5Mo alloys.

Keywords: Titanium alloy, Surface characterization, Corrosion, Surface oxide film, Oral environment

INTRODUCTION

Dental alloys are exposed to an extremely corrosive environment in which humidity is high, pH varies widely due to consumption of food and drink and there are frequent changes in temperature. In some cases, corrosion causes not only allergic reaction due to release of metal ions into the saliva, but also a decrease in mechanical strength and esthetic quality1-4). Surface analysis has shown evidence of corrosion products on discolored prosthetic devices5-10). Gold and silver-palladium-copper-gold alloys have been reported to show evidence of corrosion due to production of sulfide and hydrogen sulfide by bacteria and the formation of an oxide layer has been observed on silver-based alloys6,8,9,10). It is possible that the composition of alloys and surface characteristics of restorations, configuration of the attached prosthetic device, and particular oral environment play a role in such corrosion. However, the relationship between discoloration and corrosion of dental alloys remains to be clarified.

Titanium (Ti) and its alloys are widely used in the orthopedic and dental fields due to their superior biocompatibility. A number of studies, however, have reported problems associated with discoloration5,7,8,11-19). Titanium implants showed fracture due to corrosive products, and crowns and denture bases made of Ti alloys showed discoloration7,8,17). Discoloration and corrosion of Ti alloys occurs with exposure to fluoride in prophylactic agents11-13,18-20) or peroxides generated by macrophages or peroxide-containing denture cleansers8,14-16). On the other hand, some Ti alloys have shown good resistance to corrosion by fluoride or peroxide21-24). In earlier studies by our group, binary Ti-20mass% chromium (Ti-20Cr) alloys showed superior resistance to corrosion by fluoride or peroxide in vitro22,24). However, the corrosion behavior of Ti-20Cr alloys in an oral environment remains to be clarified.

The objective of this study was to investigate resistance to discoloration by Ti-20Cr alloys in an oral environment by determining degree of change in color in Ti or cobalt-chromium alloys in situ. Resistance to corrosion was also compared among discolored Ti alloys in terms of chemical change. The influence of the oral environment is also discussed.

MATERIALS AND METHODS

Alloy specimens

Four types of alloy were prepared (Table 1): Commercially pure Ti (TI: T-alloy M, GC, Tokyo, Japan), Ti-6Al-7Nb (TNB: T-alloy tough, GC, Japan), Co-29.5Cr-5Mo alloys (COCR: Wironium, BEGO, Germany), and experimental Ti-20Cr made of sponge Ti (99.8% or above, OSAKA Titanium technologies, Hyogo, Japan) and pure chromium (99.99%, JMC New Materials Inc., Tokyo, Japan) in an argon-arc melting furnace (ACM-01, Diavac, Chiba, Japan).

All specimens (8 mm in diameter and 1 mm in thickness) were arc-melted and cast using an argon-arc melting/pressure casting machine (Cyclarc II, J. Morita, Kyoto, Japan), as described in the literature20). Each specimen was polished with 0.02-µm colloidal silica particles and ultrasonic washing in acetone and distilled water for 10 min.

Preparation of palatal plate

Ten healthy dentulous volunteers (5 men and 5 women, range 25-35 years, mean age 28.8±2.7 years) were enrolled in the study. Informed consent was obtained from each volunteer in accordance with the guidelines of the Ethics Committee of Tokyo Dental College (#212). Individual palatal plates were made of commercial heat-curing acrylic resin (Acron, GC) for dentures. Four hollows, 10 mm in diameter and 1 mm in thickness,
were made between the first and second premolars and between the first and second molars on each palatal plate to allow attachment of alloy specimens with acrylic resin (Unifast II, GC). Figure 1(a) shows the four alloy specimens. Figure 1(b) shows the palatal plate within the oral environment.

**Exposure to oral environment**
Each volunteer wore one of the prepared palatal plates with attached alloy specimens. During the experimental period, 1) no denture cleansers were used to wash the palatal plate, 2) no fluoride-containing toothpaste or gargle solution was used, 3) food and drink were consumed with the plate in place, and 4) the plate was corrected after 100, 200, and 300 h of wear.

**Evaluation**
Saliva was evaluated by semi-quantitative evaluation of microorganisms and for buffering effect and pH. The Rezazurin Disc test (RD test: Showa Yakuhin, Tokyo, Japan), MSB broth (Mucount: Showa Yakuhin), and microbial culture in specific agar medium (Dentocult LB: Oral Care Inc., Tokyo and CHROMagar™ Candida, Kanto Reagents Ltd., Tokyo, Japan) were used to detect Lactobacillus, Streptococcus mutans, and Candida species. Buffering capacity and pH of saliva were investigated using reagent (Dentobuff Strip™, Oral Care Inc., Tokyo, Japan) and a pH meter (Twin, Horiba, Kyoto, Japan). Measurements were performed according to the manufacturer’s instructions.

The color value of the specimens was determined with a color meter (MCR-A, Luck Office, Tokyo, Japan) at before and after exposure to the oral environment according to the CIE L*a*b* color coordinator system. Specimens were removed from the palatal plate after 100, 200, or 300 h exposure and ultrasonically washed in water. Specimens were re-mounted on the palatal plate with resin after each measurement. An area 6 mm in diameter was used for measurements. 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:

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

where \(L^*_0\), \(a^*_0\) and \(b^*_0\) are values at before exposure to the oral environment and \(L^*_x\), \(a^*_x\) and \(b^*_x\) are values at after exposure, and \(x\) indicates exposure time.

After 300 h, some specimens were analyzed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Surface morphology was determined by observation under a field emission SEM (FE-SEM; ERA-8900FE, Elionix, Tokyo, Japan). Accelerating voltage was 15 kV. The XPS analysis was performed using a photoelectron spectroscope (Axis-Ultra, Kratos-Shimadzu, Kyoto, Japan). The X-ray resource was monochronized Al Ka (filament voltage: 15 kV, emission current: 10 mA), the area of measurement

<table>
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<tr>
<th>Alloy</th>
<th>Composition (mass%)</th>
<th>Brand</th>
<th>Manufacturer</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-20Cr</td>
<td>Ti-20Cr</td>
<td>Experimental</td>
<td>TCR</td>
<td></td>
</tr>
<tr>
<td>Grade2-Ti</td>
<td>Ti&gt;99.5</td>
<td>T-ALLOY M</td>
<td>GC</td>
<td>TI</td>
</tr>
<tr>
<td>Ti-6Al-7Nb</td>
<td>86.5Ti-7Nb-6Al-0.5Bal</td>
<td>T-ALLOY TOUGH</td>
<td>GC</td>
<td>TNB</td>
</tr>
<tr>
<td>Co-Cr-Mo</td>
<td>63Co-29.53Cr-5Mo&lt;2% other</td>
<td>WIRONIUM</td>
<td>BEGO</td>
<td>COCR</td>
</tr>
</tbody>
</table>
was 200×600 µm, and take-off angle of photoelectrons was 90°.

Statistical analysis
Statistical analysis of ΔE*ab was performed by a two-way analysis of variance (α=0.05) to determine the effects of exposure time and type of alloy. Comparisons were then made with the Bonferroni test. Statistical significance was set at α=0.05.

RESULTS
Saliva condition in volunteers
Volume of saliva ranged from 0.6 to 2.4 mL/min (average 1.48 mL/min). Salivary bacteria count revealed large numbers of S. mutans, but low activity for Candida and Lactobacilli species. The average pH of the saliva was 8.0, a little on the high side. Saliva showed a high buffering capacity, indicating that the acid generated by bacterial metabolism was being diluted due to salivary buffering capacity.

Change in color
Figure 2 shows the ΔE*ab of each alloy by period of exposure. The ΔE*ab of the TCR specimens ranged from 0.2 to 10.5, and the median value after exposure for 100, 200, and 300 h was 1.7, 1.0, and 1.4, respectively. The ΔE*ab of TI ranged from 0.5 to 9.9. The median value for the TI specimens after exposure for 100, 200, and 300 h was 2.2, 1.5, and 3.5, respectively. The ΔE*ab of the TNB specimen ranged from 0.4 to 12.0, and the median value after exposure for 100, 200, and 300 h was 1.5, 1.3, and 1.0, respectively. The ΔE*ab of the COCR specimens ranged from 0.1 to 8.1, and the median value after exposure for 100, 200, and 300 h was 0.8, 0.6, and 0.8, respectively. No significant difference was observed in the ΔE*ab value for each alloy among exposure periods (p>0.05).

SEM observation
Figure 3 shows typical SEM images of the discolored TCR, TI, TNB, and COCR specimens after exposure to the oral environment for 300 h. No corrosion was observed in any specimen. As shown in Figs. 3(a)–(c), a thin adhesive film appears to have formed on some areas of the titanium alloys. The film had peeled from the alloy surface in some areas. On the other hand, a thinner film was observed in the COCR specimens than in the others, as shown in Fig. 3(d).

Surface composition and chemical state
As shown in Fig. 2, although the median ΔE*ab was less than 3 except for TI for 300 h, some specimens showed discoloration (ΔE*ab>6). Table 2 lists detected elements in those specimens showing little or large amounts of discoloration in comparison with polished alloys as a reference. Elements detected on the polished alloys included elements of those alloys, including carbon, oxygen, and traces of nitrogen. Nitrogen and carbon were strongly detected, as were calcium and phosphorus as trace elements after exposure to the oral environment. Figure 4 shows the Ti2p, Cr2p, C1s, O1s, N1s XPS spectra of the TCR specimens, which were mirror-polished, after exposure for 300 h. The Ti2p peak was decomposed to four doublets of Ti0, Ti2+, Ti3+, and Ti4+, originating from metal and surface oxide (passive film). These four components were confirmed on the mirror-polished, slightly-discolored and discolored TCR specimens. Similarly, the Cr2p peak of the discolored TCR specimen was also decomposed to metal and oxide peaks, as were those of the mirror-polished and slightly-discolored specimens, as shown in Fig. 4(b). These Ti2p and Cr2p spectra suggested that the surface of the TCR was covered with passive film consisting of...
titanium and chromium oxides, regardless of degree of discoloration. Judging from the metal states detected in the Ti2p and Cr2p spectra, the passive film was thin. Decomposition of hydrocarbon (C-C, C-H) was mainly observed, along with hydroxyl and carbonyl carbons (C-OH, C=O) to a lesser degree in the C1s peak shown in Fig. 4(c). In comparison with in mirror-polished TCR, hydroxyl and carbonyl carbons in the slightly-discolored or discolored TCR specimens yielded a large shoulder or peak. A comparison of O1s peaks is shown in Fig. 4(d). The profile of the discolored TCR specimens was quite different from those of the mirror-polished or slightly-discolored specimens. The O1s peaks consist of at least three peaks originating from oxide (O\(^2\)) hydroxide or hydroxyl (OH\(^-\)) or hydrate and/or adsorbed water (H\(_2\)O). Therefore, the discolored TCR specimens had a much higher fraction of OH\(^-\) and H\(_2\)O groups than the others. As shown in Fig. 4(e), the N1s spectra showed that the

### Table 2 Detected elements on mirror-polished, slightly- discolored, and much discolored specimens at before and after exposure to oral environment for 300 h

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<tr>
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<th>TCR</th>
<th>TI</th>
<th>TNB</th>
<th>COCR</th>
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<tbody>
<tr>
<td>Mirror polished</td>
<td>Ti, Cr(\text{O, C, N^t})</td>
<td>Ti(\text{O, C, N^t})</td>
<td>Ti, Al, Nb(\text{O, C, N^t})</td>
<td>Co, Cr, Mo(\text{O, C, N^t})</td>
</tr>
<tr>
<td>Slight discolored</td>
<td>Ti, Cr(\text{O, C, N, Ca, P})</td>
<td>Ti(\text{O, C, N, Ca, P})</td>
<td>Ti, Al, Nb(\text{O, C, N, Ca, P})</td>
<td>Co, Cr, Mo(\text{O, C, N, Ca, P})</td>
</tr>
<tr>
<td>Much discolored</td>
<td>Ti, Cr(\text{O, C, N, Ca^t, P^t})</td>
<td>Ti(\text{O, C, N, Ca^t, P^t})</td>
<td>Ti, Nb(\text{O, C, N})</td>
<td>Co(^t), Cr(^t), Mo(^t)</td>
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T: Trace detection
slightly-discolored and discolored TCR specimens had larger peaks than the mirror-polished ones. These peaks originated in amino and amide groups in proteins or amino acids.

Analysis of the constituent elements is important in determining the level of corrosion in an alloy. Figures 5 and 6 show the XPS spectra of the component elements of the TNB and COCR specimens, respectively, which were mirror-polished and exposed for 300 h. The Ti2p, Nb3d, Al2p, Co2p, Cr2p, Mo3d XPS spectra for mirror-polished specimens showed the largest peak assigned to metal oxides, respectively, and a small peak at low binding energy assigned to metals, respectively, indicating that passive film on the mirror-polished specimen was thin. On the other hand, the discolored specimens showed markedly smaller metal peaks in comparison with noise signals. The Ti2p spectra for TNB were similar to those for TCR and TI (data not shown), confirming the formation of a thin passive film on the discolored specimens. Although the metal state in Al2p and Nb3d in the discolored TNB specimen could hardly be detected, that in the Co2p, Cr2p, and Mo3d spectra for the COCR specimen was clear. Therefore, the small signal of this metal peak may have been caused by protein adsorption and formation of a thick passive film.

**DISCUSSION**

Color differences were classified into six ranks: $\Delta E^{*ab}=0–0.5$, trace; $\Delta E^{*ab}=0.5–1.5$, slight; $\Delta E^{*ab}=1.5–3.0$, noticeable; $\Delta E^{*ab}=3.0–6.0$, appreciable; $\Delta E^{*ab}=6.0–12.0$, much; and $\Delta E^{*ab}=12.0–$, very much. Difference in the degree of discoloration of specimens after exposure to the oral environment was large between individuals and between the exposure periods. The box plot of change in color is shown in Fig. 2. The median value of $\Delta E^{*ab}$ in TI in this study was 3.5 after 300 h exposure to the oral environment, indicating appreciable
discoloration. The median value of $\Delta E^{*ab}$ in TCR, TNB, and COCR was less than 1.5, indicating slight discoloration. No significant difference was observed in $\Delta E^{*ab}$ value with length of exposure. Thus, change in color in TCR was equivalent to that in commercially available Ti or cobalt-chromium-molybdenum alloys. However, a few specimens of each type of alloy showed $\Delta E^{*ab}$ value of over 6. The cause for this change, however, remains to be determined.

To evaluate the influence of the oral environment, including saliva, food, and drink, on corrosion resistance in Ti or Ti alloys, use of fluoride-contained toothpaste and peroxide-contained denture cleanser was excluded as much as possible in this study. Moreover, the specimens were mirror-polished and the volunteers all less than 35 years old. Maximum exposure was kept to 300 h. This meant that the saliva had high buffering capacity and that there was only a low risk of caries in the volunteers. Furthermore, the discoloration test was performed over a short period of time. If the patients, however, had worn the palatal plate for 10 h per day, this would correspond to one month of exposure. In spite of the test period, few of the Ti alloys showed discoloration.

Several studies have reported that discoloration of dental gold- or silver-based alloys in the oral environment was caused by corrosion products such as sulfide and oxide. Endo et al. reported that corrosion products differed depending on the composition of the alloy: Au-based alloys had metal sulfide and silver-based alloy restorations had oxides of non-precious elements such as In$_2$O$_3$, ZnO, and SnO$_2$. Komoriyama et al. investigated commercially pure Ti and silver-palladium-copper-gold alloy in dentures in the elderly over 6 months, and found that the surface of the alloys showed evidence of corrosion products such as sulfide. Although silver-palladium-copper-gold alloy showed discoloration with exposure to vapor sulfur compounds, Ti or cobalt-chromium alloys did not. Denture plates made from Ti-6Al-4V alloy showed discoloration after exposure for three years. These studies indicate that discoloration of alloys in the oral environment differs depending on type of alloy, age of patient, and periods of use.

Generally, Ti and its alloys have good corrosion resistance and biocompatibility, with formation of thin passive films composed of calcium phosphate on the alloys. However, corrosion of these alloys has been observed with exposure to fluoride-containing prophylactic agents, macrophage-generated peroxides, or sulfide under specific conditions. On soaking in denture cleanser, Ti alloy denture bases blacken, suggesting that alkaline and peroxides contained in these cleansers induce a change in color in Ti alloys. Noguchi et al. suggested that Ti-20Cr alloy shows greater resistance to corrosion in fluoride- or peroxide-containing solutions among seven kinds of Ti alloy. Takemoto et al. suggested that resistance to fluoride-induced corrosion is correlated with chromium-rich oxide film on titanium alloys. One cause of discoloration of Ti alloys is the development of an oxide film, increase in thickness of this film causes change in interaction with light, resulting in change in color. This indicates that an increase in the thickness of the oxide film results in the generation of corrosion products and subsequent discoloration.

In this study, observation of the adhered thin film on the Ti alloys after exposure to the oral environment revealed no bacteria. The XPS analysis revealed that the outermost surface of the alloys consisted of carbon, oxygen, and nitrogen. Change in color ($\Delta E^{*ab}$) increased or decreased, regardless of length of exposure. Equilibrium of serum proteins such as albumin and fibrinogen in the human body is achieved by repeated cycles of adsorption and desorption. A 0.2–0.5-µm layer of adhesive substances was observed on Ti surfaces after exposure to the oral environment. In the present study, the volunteers consumed food and drink with the palatal plate in position during the experimental period. Consequently, residue from the food may have remained on the alloys. Therefore, biomolecules such as protein originating from saliva or food were adsorbed and desorbed on the Ti alloys, and aggregation of this material may have contributed to the formation of a thin film.

Koike and Fujii reported marked discoloration of Ti in formulaic acid solution and the formation of an oxide film. Burstein et al. observed slight nucleation of pits on Ti exposed to saline solution containing serum proteins. Our previous study suggested that adsorbed albumin film on Ti delayed fluoride-induced corrosion. Thus, in rare cases, proteins or organic acid may either corrode or protect titanium alloys. In the present study, even where biomolecules had adsorbed to the Ti alloys, small metal peaks were observed, as shown in Fig. 4. In other words, exposure to the oral environment did not result in corrosion due to the production of corrosion products by bacteria or oxidation.

In an in vivo discoloration test, differences in change in color of three Ti alloys or cobalt-chromium-molybdenum alloys were not significant. Moreover, Ti-Cr alloys were shown to possess the mechanical properties required for use in prosthetic devices such as denture bases and fixed bridges. This indicates that Ti-20Cr alloy could be applied to prosthetic devices such as denture bases, crowns, bridges, and dental implants.

CONCLUSIONS

To compare commercially available Ti and cobalt-chromium-molybdenum alloys, the resistance of Ti-20Cr alloy to discoloration and corrosion was investigated in an oral environment over a short period. The results revealed the following:

1. No significant difference was observed in change in color in Ti-20Cr, commercially pure Ti, Ti-6Al-7Nb, or Co-29Cr-5Mo alloy with exposure to an oral environment for 300 h.

2. The XPS analysis revealed carbon, oxygen, and nitrogen originating from saliva, food, and drink, regardless of type of alloy, in specimens showing discoloration. Although a thin film was
observed on the specimens, there appeared to be no adhesive bacteria or corrosion.

3. The degree of discoloration in experimental Ti-20Cr alloy may be similar to that of other commercially available Ti and Co-29Cr-5Mo alloys.

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