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Title
Corrosion Mechanism of Ti-Cr Alloys in Solution Containing Fluoride

Authors’ name
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Short Title
Corrosion mechanism of Ti-Cr alloys

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Introduction

The good resistance to corrosion and biocompatibility of titanium and its alloys have led to an increase in their use as restorative and prosthodontic dental materials in clinical dentistry. The passive films of these materials allow them to maintain resistance to corrosion\(^1-^3\). Although titanium and its alloys are well-known for their good corrosion resistance in the body, titanium appliances do occasionally show discoloration or corrosion in an oral environment\(^4,^5\). One reason for this is the presence of fluoride in prophylactic agents used to help prevent dental caries\(^6,^7\). Fluoride has been reported to compromise the passive film in an oral environment\(^8-^13\). Therefore, high resistance to fluoride-induced corrosion would further enhance the suitability of titanium alloys for clinical use.

Recently, in discoloration experiments on titanium alloys, we found that an experimental titanium alloy containing 20 mass% chromium (Ti-20Cr alloy) showed the least discoloration and superior corrosion resistance in a fluoride-containing saline solution\(^14,^15\). This particular alloy has been reported to show greater corrosion resistance in an acidic saline solution containing fluoride than commercially pure titanium\(^16\). Furthermore, the chromium content of Ti-Cr alloy has been suggested to be related to its mechanical properties\(^17\), and resistance to fluoride-induced corrosion. However, how surface reaction to fluoride affects the chromium content of such alloys, and whether the chromium itself is responsible for the enhanced resistance to fluoride-induced corrosion, remains to be clarified. Therefore, it is important to determine the role of chromium in Ti-Cr alloys when discussing surface reaction.

The purpose of the present study was to clarify the corrosion mechanism of Ti-Cr alloys in acidic saline solution containing fluoride by investigating the surface structure
of the oxide films on those Ti-Cr alloys.

Materials and Methods

Specimens

Experimental Ti−5, 10, 15 and 20 mass% Cr alloys (denoted as CR5, CR10, CR15 and CR20, respectively) were made by melting sponge titanium (>99.8%, Sumitomo Titanium, Japan) and pure chromium (99.99% JMC New Materials Inc., Japan) in an argon-arc melting furnace (ACM−01, Daivac Limited, Japan) to produce 30-g button alloys. To make the castings, a sheet-type wax pattern 14 mm in diameter and 1.5 mm in thickness was invested. Each alloy was arc-melted and cast in an alumina-magnesia mold (Titavest CB, J. Morita, Japan) using an argon-arc melting/pressure casting machine (Cyclarc II, J. Morita, Japan). The specimen for XPS measurement was polished with No. 600 silicon carbide paper, and that for AES measurement was finally mirror-polished with buff and colloidal silica. As reference specimens, titanium plates (TI) were cut from a sheet of commercially available pure titanium (TI, grade 2, Kobe Steel, Japan).

The immersion solution contained 0.154 mol NaCl and 0.0476 mol NaF (905 mg F) in 1 L distilled water (NAF solution). The NAF solution was adjusted to a pH of 5.0 using lactic acid at 37°C. The specimens were immersed in 36 mL test solution at 37°C. They were then removed from the solutions after a 3-day immersion and gently rinsed with distilled water.

Dissolution of metal elements

Three specimens of each alloy were prepared for each condition to determine the
amount of dissolved metal. The amount of dissolved metal in the test solution after immersion was determined with an inductively coupled plasma emission spectrometer (ICP; Vista–MPX, SII, Japan). Amount of dissolution was calculated per unit metal area in contact with the solution. Area was determined by the image analysis system HC-2500/OL (Olympus, Japan) and Image-Pro PLUS software (Media Cybernetics Inc., USA). Amount of dissolved metal was statistically analyzed using a one-way analysis of variance (ANOVA) at a significance level of 95%. The specimens were then compared using the Scheffe test at a significance level of 95%.

**XPS analysis**

XPS measurement was performed by means of an SSX–100 photoelectron spectrometer (SSI, USA) with monochromatized Al Kα radiation (1486.6 eV). The take-off angle for photoelectron detection was set at 35° for the specimen surface. The vacuum level of the analyzing chamber during measurement was of the order of 10⁻⁸ Pa. The binding energy was normalized to the C 1s peak (285.0 eV) of hydrocarbon on the specimen. At least 3 specimens of each alloy were prepared. The composition of the surface oxide film was quantitatively calculated according to the method of Asami et al. 18,19. Empirical data 18–22 and theoretically calculated data 23 on the relative photoionization cross-sections were used for quantification.

**AES analysis**

AES measurement was performed by means of a JAMP-7100 electron spectrometer (JEOL, Japan) with argon-ion-sputter etching. The vacuum level of the analyzing chamber during measurement was of the order of 5 × 10⁻⁷ Pa. The differential Auger
electron spectra were measured, and their peak-to-peak intensities were used for quantification. Argon-ion-sputter 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 oxide layer was determined as the oxygen signal in the oxide at the point halfway between its initial intensity and the background noise²⁴). Two specimens of each alloy were prepared.

**Results**

**Dissolution of metal elements**

Fig. 1 shows the total amounts of dissolved metal from the Ti-Cr alloys in NAF solution following a 3-day immersion. Titanium showed the highest level of dissolution, and the amount of dissolved chromium was around 4 µg/cm². Total amounts of dissolved metal showed a significant decrease with increase in chromium content in the alloys. A significant difference was observed in total amount of elements released from each alloy (p<0.05).

**XPS analysis**

Chemical states

Figs. 2(a) ~ (c) show the typical Ti 2p, Cr 2p and O 1s XPS spectra of CR5 and CR20 before and after immersion in NAF solution. The Ti 2p XPS spectrum before immersion included 2p₁/₂ and 2p₃/₂ electron peaks that decomposed into Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺, indicating the presence of both metal and oxide. Although the Ti⁰ peak was clearly visible in the Ti 2p spectrum of both CR5 and CR20 before immersion in NAF solution, both these specimens showed a smaller peak or shoulder after immersion. In
Fig. 2(b), the Cr 2p XPS spectrum included 2p$_{1/2}$ and 2p$_{3/2}$ electron peaks. The Cr 2p$_{3/2}$ peak decomposed into two peaks, indicating a metallic, Cr$^0$, and oxide, Cr$^{3+}$, state. The Cr$^0$ peak in the Cr 2p$_{3/2}$ spectrum of both CR5 and CR20 decreased with immersion in NAF solution. The O 1s XPS spectra shown in Fig. 2(c) decomposed into three peaks indicating metal oxide, O$^{2-}$, hydroxide or hydroxyl groups, OH$^-$, and hydrate and/or adsorbed water, H$_2$O. The oxide films on all the Ti-Cr alloys consisted of oxide, hydroxide, and hydrate. The decomposed peak, O$^{2-}$, in the CR5 and CR20 spectra after immersion was slightly larger than that before immersion.

Composition

All as-polished Ti-Cr alloys consisted of carbon, oxygen, titanium, chromium, and trace nitrogen. The carbon and nitrogen were removed from the composition calculation because they originated in a contaminant layer. Chromium concentration of as-polished CR5, CR10, CR15, and CR20 was 2.0, 3.3, 3.8, and 4.7 atomic%, respectively, and titanium concentration was 22.7, 22.7, 21.3, and 21.2 in atomic%. Furthermore, oxygen concentration was approximately 74 atomic% and constant in the oxide films, regardless of chromium content. Table 1 lists the composition of the surface oxide films on the Ti-Cr alloys after immersion as determined by XPS. Fluorine was detected on all specimens. An increase in chromium ratio was found in the oxide films with increase in chromium content.

The fraction in Fig. 3 shows the proportion of chromium to chromium and titanium in the surface oxide films of the Ti-Cr alloys before and after immersion. The [Cr]/([Ti]+[Cr]) values in CR5, CR10, CR15, and CR20 before immersion were 0.08, 0.13, 0.16, and 0.19, respectively. These values were close to the nominal values.
After immersion, the \([\text{Cr}] / ([\text{Ti}] + [\text{Cr}])\) value increased with increase in chromium content. Furthermore, the Ti-Cr alloys showed larger \([\text{Cr}] / ([\text{Ti}] + [\text{Cr}])\) values after immersion.

**AES analysis**

Fig. 4 shows the typical AES depth profiles of relative concentration of each element in the surface oxide layer of TI and CR5 before and after immersion. In Fig. 4(a), the AES depth profile of as-polished TI indicated that carbon concentration abruptly decreased, and then remained constant after 30 s Ar\(^+\) etching. Oxygen concentration increased with decrease in carbon concentration, and then abruptly decreased. Titanium concentration increased with decrease in oxygen concentration. Relative concentrations of carbon and oxygen gradually decreased, whereas that of titanium increased after immersion, as seen in Fig. 4(b). The profile of the relative concentration of fluorine showed an abrupt decrease.

The AES depth profiles for CR5 and CR10 were similar to that for TI; that is, the relative concentrations of titanium and chromium increased with decrease in carbon and oxygen concentrations, as shown in Figs. 4(c), (d), (e) and (f). Furthermore, fluorine concentration in CR5 after immersion indicated a decrease with 100 s Ar\(^+\) etching, as shown in Fig. 4(d). The thickness of oxide film in as-polished TI was 30 nm, whereas that in CR5 was about 15 nm. After immersion in acidic fluoride-containing saline solution, TI and CR5 showed a thicker oxide layer than as-polished alloys. Furthermore, higher chromium content in the Ti-Cr alloy, as shown in Figs. 4(e) and (f), yielded a thinner oxide layer on the alloy after immersion.
Discussion

Titanium and its alloys were corroded by fluoride in solutions\(^8,10,25\). It was suggested that sodium fluoride and monofluoro phosphoric acid in prophylactic agents electrically dissociate, with subsequent generation of fluoride ions, and that the degree to which these electrical-dissociated fluoride ions become hydrofluoric acid partially depends on the pH of the solution\(^{10,25}\). It was also found that hydrofluoric acid attacked the passive film on the titanium surface, with subsequent formation of corrosion products, titanium-fluorine compounds, which were degraded in solution as follows:

\[
\begin{align*}
    \text{Ti}_2\text{O}_3 + 6\text{HF} & \rightarrow 2\text{TiF}_3 + 3\text{H}_2\text{O} \\
    \text{TiO}_2 + 4\text{HF} & \rightarrow \text{TiF}_4 + 2\text{H}_2\text{O} \\
    \text{TiO}_2 + 2\text{HF} & \rightarrow \text{TiOF}_2 + \text{H}_2\text{O}.
\end{align*}
\]

In this study, too, the metal elements of Ti-Cr alloys showed dissolution after immersion in an acidic saline solution containing fluoride. This dissolution of titanium and chromium was confirmed in all the Ti-Cr alloys tested. However, the amount of chromium dissolved was small, and showed no correlation with chromium content. On the other hand, amount of titanium dissolved was lower than that in Ti, with rate of dissolution decreasing with increase in chromium content in all alloys. These results agree with those of earlier studies showing greater corrosion resistance to fluoride and lower discoloration in fluoride-containing saline solution in Ti-20Cr alloy than in commercially pure titanium\(^{14-16}\).

Chromium oxide films on cobalt-chromium alloys and stainless steel on dental alloys show consistently good corrosion resistance in an oral environment\(^{26-29}\). According to the electrochemical corrosion test, cobalt-chromium alloys in an acidic
saline solution containing 0.1% sodium fluoride were reported to show good corrosion resistance, equal to that exhibited by gold alloys\(^{26}\). Furthermore, stainless steel wire was found to show low reactivity, low discoloration, and low dissolution in fluoride-containing solutions\(^{27,28}\). This suggests that chromium oxide has good resistance to fluoride-induced corrosion, and that corrosion resistance to fluoride differs between titanium oxide and chromium oxide, with corrosion occurring in titanium oxide, but being resisted in chromium oxide.

The \([\text{Cr}]/([\text{Ti}]+[\text{Cr}])\) values in the oxide films reflected the compositional rate of the as-polished Ti-Cr alloys. Also, the chemical state in O 1s XPS spectra suggested that the titanium and chromium oxides consisted of oxide, hydroxide, and hydrate, indicating that the titanic and chromic species in oxide films were contained. After immersion, the Ti-Cr alloys mainly consisted of \(\text{Ti}^{4+}\) and \(\text{Cr}^{3+}\), indicating progression in oxidation of the titanium and chromium and subsequent increase in thickness of the oxide film. Furthermore, the oxide films on the Ti-Cr alloys showed larger \([\text{Cr}]/([\text{Ti}]+[\text{Cr}])\) values after immersion. These results suggest selective fluoride-induced corrosion of the titanium oxide in the oxide film, although both titanium and chromium were repassivated in the solutions. This selective dissolution of titanium oxide indicated microscopic localized corrosion. This corrosion induced a rough surface on the alloys, after which, the alloys were repassivated by greater exposure to access by water. Viewed from the outermost surface, a thick oxide film appeared to have formed.

The thickness of oxide films on alloys as determined by AES analysis depends on the \(\text{Ar}^+\) etching rate, which depends on the elements of those alloys. Therefore, difference in thickness among alloys can not be discussed within this context.
However, increase or decrease in thickness of oxide films on alloys before and after immersion in solution can be. AES analysis indicated that the thicknesses of the oxide films on TI and CR5 were approximately 30 and 15 nm (calculated from SiO$_2$ on Si), respectively, before immersion in saline solution. After immersion, the thicknesses of the oxide films on TI and CR5 showed an increase. These findings agreed with the XPS results indicating an increase in the thickness of the oxide films after immersion in fluoride-containing solution. Furthermore, the oxide film in CR5 was thinner than that in TI, indicating that titanium alloy containing chromium exhibited lower oxidation in fluoride-containing solution than commercially pure titanium. On the other hand, the profiles of TI and CR5 revealed fluorine on the outermost surface of the oxide films. These data suggest that corrosion resulted from contact between fluoride and the outermost surface of the specimens.

Corrosion resistance to fluoride has been reported in Ti-Cr alloys. As-polished Ti-Cr alloys exhibited chromium and titanium oxide films with a thickness of less than 3 nm. With immersion in an acidic saline solution containing fluoride, the surface oxide films of these alloys was attacked by hydrofluoric acid partially arising from fluoride ions$^{8,10,25}$. Titanium oxide film was selectively dissolved in solution, with a chromium oxide film remaining due to greater resistance to fluoride. On exposure of titanium or chromium by dissolution of oxide film, these metals are then rapidly repassivated by contact with H$_2$O. In this study, rate of chromium oxide formation increased as chromium content increased, with subsequent formation of a chromium oxide-rich layer in the Ti-Cr alloys. Increase in chromium oxide on Ti-Cr alloys would decrease the potential for contact between titanium oxide and fluoride in the solution. This suggests that addition of chromium to titanium is effective in enhancing resistance
to corrosion by fluoride.

**Conclusion**

Four Ti-Cr alloys were characterized in terms of corrosion resistance in fluoride-containing saline solution and surface structure. Amount of chromium oxide in the oxide films was correlated with chromium content in the Ti-Cr alloys, with increase in chromium oxide depending on chromium content of the alloy. Formation of a chromium oxide-rich surface film improved corrosion resistance to fluoride in Ti-Cr alloys.

**Acknowledgements**

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References


Figure and Table Caption

Figure 1  Total amount of dissolved elements (chromium and titanium) from Ti and Ti-Cr casting alloys immersed in acidic saline solution containing fluoride for 3 days.

Figure 2  Typical XPS spectra of CR5 and CR20 before and after immersion in acidic saline solution containing fluoride.  (a) Ti 2p, (b) Cr 2p, (c) O 1s

Figure 3 Fraction showing proportion of chromium to constituted metals (chromium and titanium) in surface oxide films on Ti-Cr casting alloys before and after immersion in acidic saline solution containing fluoride.  "Nominal" indicates composition when making of ingot.

Figure 4 AES depth profiles of the relative concentrations of elements at the surface oxide of TI, CR5 and CR10 before and after immersion in an acidic saline solution containing fluoride.  The horizontal axis of TI indicates twice that of CR5 and CR10.

  (a) TI before immersion, (b) TI after immersion in NAF, (c) CR5 before immersion, (d) CR5 after immersion in NAF, (e) CR10 before immersion, (f) CR10 after immersion NAF

Table 1 Composition of surface oxide films on Ti-Cr casting alloys after immersion in acidic fluoride-containing saline solution determined by XPS (n=3)
Figure 1 Total amount of dissolved elements (chromium and titanium) from Ti and Ti-Cr casting alloys immersed in an acidic saline solution containing fluoride for 3 days.
Figure 2  Typical XPS spectra of CR5 and CR20 before and after immersion in an acidic saline solution containing fluoride. (a) Ti 2p, (b) Cr 2p, (c) O 1s
Figure 3 Fraction of proportional chromium to constituted metals (chromium and titanium) in the surface oxide films on Ti-Cr casting alloys before and after immersion in an acidic saline solution containing fluoride. “Nominal” indicates the composition when making of an ingot.
Figure 4  AES depth profiles of the relative concentrations of elements at the surface oxide of Ti, CR5 and CR10 before and after immersion in an acidic saline solution containing fluoride. The horizontal axis of Ti indicates twice that of CR5 and CR10.

(a) Ti before immersion, (b) Ti after immersion in NAF, (c) CR5 before immersion, (d) CR5 after immersion in NAF, (e) CR10 before immersion, (f) CR10 after immersion NAF

Fig. 4
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Table 1  Composition of surface oxide films on Ti-Cr casting alloys after immersion in acidic fluoride-containing saline solution determined by XPS (n=3)

<table>
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<th>Specimen</th>
<th>Composition (atomic%)</th>
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<tr>
<td></td>
<td>Ti</td>
<td>Cr</td>
<td>O</td>
<td>F</td>
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<tr>
<td>CR5</td>
<td>26.0 ± 0.2</td>
<td>5.8 ± 0.9</td>
<td>63.9 ± 2.4</td>
<td>4.2 ± 2.2</td>
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<td>CR10</td>
<td>22.1 ± 0.8</td>
<td>7.9 ± 1.1</td>
<td>63.7 ± 2.1</td>
<td>6.4 ± 1.7</td>
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<tr>
<td>CR15</td>
<td>18.7 ± 0.2</td>
<td>9.2 ± 1.0</td>
<td>65.6 ± 1.7</td>
<td>6.5 ± 1.4</td>
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<tr>
<td>CR20</td>
<td>16.8 ± 0.8</td>
<td>11.6 ± 0.5</td>
<td>67.4 ± 0.6</td>
<td>4.3 ± 0.2</td>
</tr>
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Average ± Standard deviation