Surface Oxide Films on Titanium Alloys Regenerated in Hanks’ Solution

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Titanium and some of its alloys are successfully used for biomaterials. The surface oxide films on these materials play important roles in maintaining corrosion resistance and biocompatibility. In this study, Ti–6Al–4V, Ti–56Ni, and Ti–xZr (x = 0, 25, 50, 60, 75, 100) alloys in mass% were abraded and kept for 300 s in water and Hanks’ solution. The regenerated surface oxide film in Hanks’ solution was characterized using X-ray photoelectron spectroscopy. As a result, phosphate ions were preferentially taken up in the surface oxide film during regeneration. Ions constituting Hanks’ solution other than calcium and phosphate were absent from the surface oxide film. In the case of titanium and Ti–6Al–4V, calcium phosphate was formed on/in the surface oxide film regenerated in Hanks’ solution. However, Ti–56Ni, Ti–Zr, and zirconium did not form calcium phosphate on themselves but formed phosphate without calcium. These results are in good agreement with those for titanium alloys immersed in Hanks’ solution.

Keywords: titanium alloy, surface oxide film, repassivation, surface analysis

1. Introduction

Titanium and some of its alloys are now dominant biomaterials because of their good biocompatibility. The biocompatibility of titanium is associated with the sufficiently large corrosion resistance in biological systems. As is widely known, corrosion resistance is maintained with a surface oxide film consisting of non-stoichiometric TiO₂ with an amorphous or low-crystalline structure.

Calcium, phosphorus, and sulfur are incorporated into the surface film of titanium surgically implanted into the human jaw. Calcium phosphates are formed on titanium and its alloys by immersion in Hanks’ solution and other solutions, resulting in the preferential adsorption of phosphate ions. Hydroxylated phosphate ions are adsorbed by a hydrated titanium oxide surface during the release of protons. Calcium ions are adsorbed by phosphate ions adsorbing on the titanium surface, and eventually calcium phosphate is formed. In this regard, when titanium is immersed in Hanks’ solution containing albumin, a non-uniform and porous apatite-containing albumin is formed. The above phenomena are characteristic in titanium and its alloys. Not only inorganic ions but also proteins are incorporated into the surface film. Calcium phosphate is also formed on Ti–6Al–4V and Ti–56Ni after immersion in Hanks’ solution, but the [Ca]/[P] ratio is smaller than that in titanium. On the other hand, only phosphate without calcium is formed on Ti–Zr alloys that contain over 50 mass%Zr.

The surface film may be scratched and destroyed during insertion and implantation into hard tissue by abrasion with bone and other materials. The destruction of the film also occurs in fretting corrosion. Of course, the surface oxide is immediately regenerated in a biological system when biofluid surrounds the titanium and its alloys. However, the composition and properties of the oxide film regenerated in a biological system may be different from those in water.

In the case of commercially pure titanium, the repassivation rate of titanium in Hanks’ solution is slower than that in saline. The pH of the solution does not influence the repassivation rate within the pH range examined. These results indicate that the repassivation of titanium in biological systems is slower than hitherto predicted when the surface oxide film is destroyed, possibly inducing the dissolution of more titanium ions into bioliquid. Dissolved oxygen does not influence the repassivation. The surface oxide film regenerated in Hanks’ solution contains phosphate ions in the outer layer. Phosphate ions are preferentially taken up in the surface film during repassivation during the regeneration. Calcium ions and phosphate ions are adsorbed to the film after regeneration, and calcium phosphate or calcium titanium phosphate is formed at the outermost surface. In this regard, however, we do not have any information about the surface oxide film on titanium alloys regenerated in biofluid.

In this study, we removed the surface oxide film on titanium alloys in water and Hanks’ solution and characterized the composition of the regenerated film. This information is intended to enhance the understanding of the surface oxide film on titanium alloys in biological systems.

2. Experimental Methods

2.1 Materials

Commercial Ti–6 mass%Al–4 mass%V (Ti–10.2 at%Al–3.6 at%V) and Ti–56 mass%Ni (Ti–50 at%Ni) plates were employed in this study. The plates were metallographically polished and finished by polishing with #1500 SiC polishing paper followed by ultrasonic rinsing in acetone and ethanol for 900 s each and drying in a stream of high-purity nitrogen (> 99.999%). The chemical compositions of these alloys are summarized in Table 1. In addition, commercially pure sponge titanium (99.6%) and pure sponge zirconium (99.8%) were mixed, and the resultant mixtures of Ti–25Zr, Ti–50Zr, Ti–60Zr, and Ti–75Zr (in mass%: Ti–18.7 at%, Ti–40.8 at%, Ti–50 at%Zr, and Ti–67.4 at%, respectively) were obtained.
The mixtures were melted in an argon-arc furnace, and alloys of the above compositions were obtained. The alloys were cut into 1-mm-thick plates. Each plate was treated according to the above methods. For comparison, pure titanium (99.8%) and zirconium (99.6%) plates were also prepared.

2.2 Repassivation of materials

We used deionized water (pH 6.9) and Hanks’ solution without organic species and with ion concentrations similar to extracellular fluid. The ion concentrations of the Hanks’ solution are summarized in Table 2. The pH of the solution was 7.4 just after preparation. We examined the effects of inorganic ions in Hanks’ solution on the composition of the surface oxide film regenerated in the solution by repassivation. Hanks’ solution contained ions that may have influenced the composition of the film. Therefore, the carbon detected by XPS can be ascribed to a so-called contaminant carbon. Apart from carbon, only titanium, aluminum, and oxygen, were detected, but other elements contained in the Hanks’ solution were undetected. Therefore, the carbon detected by XPS can be ascribed to a so-called contaminant carbon. Apart from carbon, only titanium, aluminum, and oxygen were detected with XPS in the surface oxide film. This result is in good agreement with that of a previous study. 2, 3) On the other hand, in specimens abraded in water, vanadium was not detected from titanium, aluminum, and oxygen were detected with XPS in the surface oxide film. For comparison, the same manipulation was performed in water.

2.3 Surface analyses

XPS was performed with an electron spectrometer (SSI-SSX100). All binding energies given in this paper are relative to the Fermi level, and all spectra were excited with the monochromatized Al Kα line (1486.61 eV). The spectrometer was calibrated against Au 4f 7/2 (binding energy, 84.07 eV) and Au 4f 5/2 (87.74 eV) of pure gold and Cu 2p 3/2 (932.53 eV), Cu 2p 1/2 (952.35 eV), and Cu Auger L 3M 4N 4 with kinetic energy, 918.65 eV) of pure copper. The energy values were based on published data. 15) In order to estimate the photoelectron peak intensities, the background was subtracted from the measured spectrum according to Shirley’s method. 16)

The compositions of the surface oxide film and the substrate were simultaneously calculated according to the method of one of the authors of this study. 17, 18) Empirical data18–21, 23, 24) and theoretically calculated data22) of the relative photoionization cross-sections were used for the quantification. The relative photoionization cross-sections used in this study are summarized in Table 3, where \( \sigma_{ij}/\sigma_{O1s} \) represents the relative photoionization cross-section of a level \( j \) electron of an element \( i \) to that of O 1s electrons. An angle-resolved technique for XPS was applied to the specimens at a photoelectron take-off angle of 35°, where the take-off angle is defined as the angle between the direction of the photoelectron path to the electron spectrometer and the specimen surface.

3. Experimental Results and Discussion

3.1 Ti–6Al–4V alloy

Carbon was detected on all specimens. From the C 1s spectra, it was concluded that none of the specimens contained carbonate because no peak was detected at an energy region of 289–290 eV, where carbonate should give a C 1s peak. 25) Therefore, the carbon detected by XPS can be ascribed to a so-called contaminant carbon. Apart from carbon, only titanium, aluminum, and oxygen were detected with XPS in specimens abraded in water. Vanadium was not detected from the surface oxide film. This result is in good agreement with that of a previous study. 2, 3) On the other hand, in specimens abraded in Hanks’ solutions, phosphorus and calcium, along with titanium, aluminum, and oxygen, were detected, but other elements contained in the Hanks’ solution were undetected. The relative concentrations of titanium, aluminum, vanadium, oxygen, calcium, and phosphorus in the surface oxide film on Ti–6Al–4V were calculated assuming the gross

Table 1 Chemical composition of Ti–6Al–4V and Ti–56Ni (mass%).

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–6Al–4V</td>
<td>0.004</td>
<td>0.005</td>
<td>0.003</td>
<td>0.147</td>
<td>6.23</td>
<td>4.12</td>
<td>0.189</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ti–56Ni</td>
<td>0.0001</td>
<td>0.046</td>
<td>0.004</td>
<td>0.065</td>
<td>&lt;0.002</td>
<td>—</td>
<td>0.017</td>
<td>55.8</td>
<td>&lt;0.01</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2 Ion concentrations of Hanks’ solution.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (kmol m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>1.42 x 10(^{-3})</td>
</tr>
<tr>
<td>K(^+)</td>
<td>5.81 x 10(^{-3})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>8.11 x 10(^{-4})</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.26 x 10(^{-3})</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1.45 x 10(^{-4})</td>
</tr>
<tr>
<td>HPO(_4)^{2-}\</td>
<td>7.78 x 10(^{-4})</td>
</tr>
<tr>
<td>SO(_4)^{2-}\</td>
<td>8.11 x 10(^{-4})</td>
</tr>
<tr>
<td>CO(_3)^{2-}\</td>
<td>4.17 x 10(^{-3})</td>
</tr>
</tbody>
</table>

Table 3 Photoionization cross-sections of level \( j \) of element \( i \) relative to that of the O 1s, \( \sigma_{ij}/\sigma_{O1s} \).

<table>
<thead>
<tr>
<th>Level</th>
<th>Ti 2p(_{3/2})</th>
<th>Al 2p</th>
<th>Ni 2p(_{3/2}) (Oxide)</th>
<th>Ni 2p(_{3/2}) (Metal)</th>
<th>Zr 2p(_{3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{ij} )</td>
<td>1.28</td>
<td>0.19</td>
<td>2.3</td>
<td>7.47</td>
<td>2.4</td>
</tr>
<tr>
<td>Reference</td>
<td>19</td>
<td>20</td>
<td>21</td>
<td>18</td>
<td>22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>Ca 2p</th>
<th>P 2p</th>
<th>C 1s</th>
<th>Na 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{ij} )</td>
<td>2.59</td>
<td>2.6</td>
<td>0.34</td>
<td>2.9</td>
</tr>
<tr>
<td>Reference</td>
<td>23</td>
<td>24</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>
phosphorus exist as a calcium phosphate where phosphate
mered in Hanks’ solution. The binding energy of the Ca
vanadium was never detected from the film. Calcium and
relatively low compared with the nominal composition, and
in the regenerated surface film on Ti–6Al–4V in water and
mole percent. Table 4 presents the concentrations of elements
amount of these elements as detected using XPS was 100
mole percent. Table 4 presents the concentrations of elements
in the regenerated surface film on Ti–6Al–4V in water and
Hanks’ solution. The aluminum concentration in the film was
relatively low compared with the nominal composition, and
vanadium was never detected from the film. Calcium and
phosphorus were detected from the specimen abraded and
immersed in Hanks’ solution. The binding energy of the Ca
2p3/2 electron from the specimen was 347.6 eV, indicating
that calcium exists as Ca2+.26) The binding energy of a P 2p
electron was about 133.4 eV, indicating that phosphorus exists
as a phosphate ion.26) Therefore, it can be said that calcium
and phosphorus preferentially proceeds, and dehydration
during the regeneration of the surface oxide and the oxidation
of the oxide is inhibited by the adsorption.

Table 4 XPS results for relative concentrations of elements in surface oxide
film on Ti–6Al–4V (Ti–10.2 at%Al–3.6 at%V) regenerated in water and
Hanks’ solution during 300-s immersion.

<table>
<thead>
<tr>
<th>Abraded in</th>
<th>Relative concentration (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Water</td>
<td>24.5 (0.9)*</td>
</tr>
<tr>
<td>Hanks</td>
<td>21.4 (0.1)</td>
</tr>
</tbody>
</table>

*Standard deviation

Fig. 1 The ratio of the proportion of the concentration of OH− to that of
O2−, [OH−]/[O2−], and proportion of the cationic fraction of Ti4+ among
titanium species in the surface oxide film on Ti–6Al–4V regenerated in
water and Hanks’ solution estimated from XPS data.

Table 5 XPS results for relative concentrations of elements in surface oxide
film on Ti–56Ni (Ti–50 at%Ni) regenerated in water and Hanks’ solution
during 300-s immersion.

<table>
<thead>
<tr>
<th>Abraded in</th>
<th>Relative concentration (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Water</td>
<td>23.4 (0.1)*</td>
</tr>
<tr>
<td>Hanks</td>
<td>24.0 (0.4)</td>
</tr>
</tbody>
</table>

*Standard deviation
**Trace amount

oxide possibly contains hydroxyl radicals. On the other hand,
the proportion of Ti4+ in titanium ions in the oxide regener-
ated in water was larger than that in Hanks’ solution, indicat-
ing that the surface oxide film regenerated in Hanks’ solution
was more oxidized. Therefore, the surface oxide film is less
hydrated and more oxidized when regenerated in Hanks’ solu-
tion than when regenerated in water. The adsorption of cal-
cium and phosphate preferentially proceeds, and dehydration
during the regeneration of the surface oxide and the oxidation
of the oxide is inhibited by the adsorption.

3.2 Ti–56Ni alloy

The relative concentrations of titanium, nickel, oxygen, calcium, and phosphorus in specimens were calculated assum-
ing the gross amount of these elements as detected using XPS was 100 atomic percent. The results of the quantification
are summarized in Table 5. In the case of Ti–56Ni, the nickel
concentration in the surface oxide film was relatively lower
than the nominal composition. That is, titanium was pref-
entially oxidized. Calcium was slightly detected, but the
resultant concentration by quantification in XPS was almost
zero. Phosphorus was detected as phosphate ions because
the binding energies of the peak of P 2p spectra were 133.5–
133.6 eV.26) Therefore, phosphate forms titanium phosphate
and/or nickel phosphate in or on the surface oxide film.

The ratios of the proportion of OH− to that of O2−,
[OH−]/[O2−], and the proportion of Ti4+ among
Ti2+, Ti3+, and Ti4+ in the surface film did not differ between solutions
in the case of Ni–56Ni. Therefore, the ratio of the integrated
intensity of the spectrum originating from metallic-state ti-
nium to that from oxide-state titanium, [TiMe]/[TiOx], and
the ratio in nickel, [NiMe]/[NiOx], were calculated as shown
in Fig. 2. In both solutions, [NiMe]/[NiOx] was much larger
than [TiMe]/[TiOx], indicating that a large amount of metallic
nickel exists in the surface layer with the depth of the XPS
detection limit. The free energy of oxidation of titanium is
much lower than that of nickel, implying that a concentrated
layer of metallic nickel is formed. This phenomenon is usu-
ally observed.33) On the other hand, these ratios were larger
in Hanks’ solution than in water, indicating that the oxida-
tion was delayed in Hanks’ solution. One cause of the de-
lay was the adsorption of phosphate ions during regeneration
of the surface oxide film. Similar results were obtained with
titanium.14)
Surface Oxide Films on Titanium Alloys Regenerated in Hanks’ Solution

3.3 Ti–Zr alloy

Relative concentrations of titanium, zirconium, and Ti–Zr alloys are summarized in Table 6. Calcium was not detected, but phosphorus was detected in the surface oxide film on zirconium and Ti–Zr alloys regenerated and immersed in Hanks’ solution. Phosphorus exists as phosphate according to the binding energy of P 2p peak, which is similar to other alloys mentioned above. Titanium phosphate and/or zirconium phosphate are formed on and/or in the oxide. The cation fraction, the gross fraction of titanium and zirconium, in the oxide film was lower in zirconium and Ti–Zr alloys in Hanks’ solution than in water because of the incorporation of phosphate ions into the oxide. The titanium fraction was larger and the zirconium fraction was smaller in the surface oxide than the fractions in the nominal compositions.

The ratios of the proportion of OH\(^-\) to that of O\(^2-\), \([\text{OH}^-]/[\text{O}^{2-}]\), in the surface oxide film on titanium, zirconium, and Ti–Zr alloys after being regenerated in water and Hanks’ solution as a function of zirconium content are shown in Fig. 3. The ratio in Hanks’ solution was larger than that in water, indicating that the regenerated oxide film in Hanks’ solution was more hydrated than that in water. The formation of phosphate may be related to the increase in the hydroxide or hydroxyl ion. In addition, the ratio increased with the increase of the zirconium content in Hanks’ solution. Zirconium in the surface oxide regenerated in Hanks’ solution plays an important role in the hydration of the oxide.

The proportion of Ti\(^{4+}\) among Ti\(^{2+}\), Ti\(^{3+}\), and Ti\(^{4+}\) in the surface film is shown in Fig. 4. Only Zr\(^{4+}\)-state zirconium was detected from the Zr 3d peak. In zirconium and Ti–Zr alloys, the value in Hanks’ solution was larger in water. That is, the titanium atom was more oxidized in Hanks’ solution than in water while the surface oxide was more oxidized in Hanks’ solution than in water, as mentioned above. Therefore, more zirconium atoms than titanium atoms formed hydroxide in the oxide film. The ratio increased as the zirconium content increased. Again, the hydration of the zirconium atom in the surface oxide was revealed.

3.4 Phosphate formation

Only calcium and phosphate reacted with titanium alloys during the regeneration of the surface oxide films except the water molecule. The composition of the surface oxide film

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**Table 6** XPS results for relative concentrations of elements in surface oxide film on titanium, zirconium, and Ti–Zr alloys regenerated in water (top values) and Hanks’ solution (bottom values) during 300-s immersion.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Zr</th>
<th>O</th>
<th>Ca</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>29.6</td>
<td>0.0</td>
<td>70.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ti</td>
<td>28.6</td>
<td>0.0</td>
<td>70.5</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Ti–mass 25Zr</td>
<td>29.4</td>
<td>4.7</td>
<td>65.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(18.7 at%Zr)</td>
<td>24.1</td>
<td>4.0</td>
<td>70.2</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Ti–mass 50Zr</td>
<td>23.7</td>
<td>12.0</td>
<td>64.3</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(40.8 at%Zr)</td>
<td>18.2</td>
<td>9.1</td>
<td>70.8</td>
<td>0.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Ti–mass 60Zr</td>
<td>18.6</td>
<td>15.5</td>
<td>65.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(50 at%Zr)</td>
<td>16.1</td>
<td>11.8</td>
<td>70.4</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Ti–mass 75Zr</td>
<td>12.7</td>
<td>20.9</td>
<td>66.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(67.4 at%Zr)</td>
<td>10.0</td>
<td>15.5</td>
<td>72.4</td>
<td>0.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Zr</td>
<td>0.0</td>
<td>32.1</td>
<td>67.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Zr</td>
<td>0.0</td>
<td>20.6</td>
<td>77.5</td>
<td>0.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>
on titanium alloys regenerated in Hanks’ solution was different from that in water. The phosphate ion in Hanks’ solution was incorporated into the surface oxide film of all alloys and formed metallic phosphate. However, calcium was incorporated only by titanium, Ti–6Al–4V, and Ti–56Ni to form calcium phosphate. Only a slight amount of calcium was incorporated by Ti–56Ni. These results are in good agreement with those for titanium materials immersed in Hanks’ solution. Calcium phosphate was formed on titanium and Ti–6Al–4V when these were immersed in Hanks’ solution. The amount of calcium phosphate is large in this order: titanium, Ti–6Al–4V, and Ti–56Ni. In the case of Ti–Zr alloys, the amount of incorporated calcium decreases as the zirconium content in the alloys increases. The difference in the composition of the surface oxide film regenerated in Hanks’ solution among the alloys depends on the alloy elements and their amounts. The alloying elements are contained in the surface oxide film, while the cation fraction is not the same as that in nominal composition. The ability of titanium surface oxide to form calcium phosphate may be inhibited by the alloying element in the oxide.

4. Conclusions

Ions constituting Hanks’ solution other than calcium and phosphate were absent from the surface oxide. In the case of titanium and Ti–6Al–4V, calcium phosphate was formed on/in the surface oxide film regenerated in Hanks’ solution. However, Ti–56Ni and Ti–Zr alloys did not form calcium phosphate on themselves but formed phosphate. These results are in good agreement with those in titanium alloys immersed in Hanks’ solution.

REFERENCES