Reduction in nickel content of the surface oxide layer on Ni-Ti alloy by electrolytic treatment

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Abstract

Purpose: Ni-Ti alloy has been increasingly applied to dental and medical devices, however, it contains nickel, which is known to have adverse effects on the human body. The purpose of this study was to form a nickel-free surface oxide layer on Ni-Ti alloy by electrolytic treatment for better biocompatibility.

Methods: Ni-49.15Ti (mol%) alloy was used, and the electrolytic treatment was performed in the electrolytes under 50 V for 30 minutes. The electrolytes were composed of lactic acid, water, and glycerol with different compositions. Surface analysis and characterization of Ni-Ti alloy were carried out by means of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

Results: Results indicated that the outermost surface oxide layer was nickel-free when using an electrolyte comprising 7.1% lactic acid, 57.2% water, and 35.7% glycerol by volume. The composition of this nickel-free surface oxide layer was determined as TiO1.92(OH)1.35·0.43H2O by AES, similar to that of an unalloyed titanium. The thickness of this nickel-free layer was estimated at 6.4 nm by AES.

Conclusion: The nickel-free surface oxide layer produced on Ni-Ti alloy is considered to improve the biocompatibility of medical and dental devices having shape memory effect and/or super-elasticity.

Keywords: electrolytic treatment, nickel-free, Ni-Ti alloy, oxide layer, surface analysis

Introduction

Titanium and titanium alloys are widely applied in the production of dental prostheses due to their excellent biocompatibility, good mechanical properties and castability [1]. Among the titanium alloys, the special properties of shape memory effect and super-elasticity of Ni-Ti alloy allow its use for special dental appliances, including orthodontic wires [2] and root canal files [3], however, the corrosion behavior of Ni-Ti alloy is inferior to that of unalloyed titanium. The thickness of shape memory effect and super-elasticity of Ni-Ti alloy were determined by the reported method [23,24] (n = 2). In order to obtain more information on the compositional change in the surface oxide layer, an angle-resolved technique for XPS was performed at photoelectron take-off angles of 12, 24, 35, 53, and 90° (n = 1).

XPS measurement
An electron spectrometer (SSX100, SSI, Pleasanton, CA, USA) was used for XPS measurement. Spectra acquisition was performed with monochromatized Al Kα radiation under the pressure less than 2.3 × 10−7 Pa, and the thickness and compositions of the surface oxide layer were determined by the reported method [23,24] (n = 2). In order to obtain more information on the compositional change in the surface oxide layer, an angle-resolved technique for XPS was performed at photoelectron take-off angles of 12, 24, 35, 53, and 90° (n = 1).

AES measurement
Depth profiles of the element compositions were investigated by AES measurement with an Auger electron spectroscope (JAMP-7100, JEOL, Tokyo, Japan) with argon ion sputter etching, according to the method in a previous study [19]. The thickness of the oxide layer was calculated using the etching rate for SiO2 film on silicon, 0.08 nm s−1. (Received May 7, 2020; Accepted June 24, 2020)

Results

XPS analysis
Ti 2p XPS spectra of the electron energy region are shown in Fig. 1(a). The Ti 2p spectra included 2p1/2 and 2p3/2 electron peaks. The Ti 2p1/2 region of the MP specimen had four peaks of the valences of Ti0, Ti+, Ti2+, and Ti4+, with binding energies of these valences of 454.2, 455.5, 457.5, and 458.6 eV, respectively. The Ti2+ peak was assigned to the metallic state in the substrate metal. The Ti3+ and Ti4+ peaks were derived from Ti of the oxide state in the surface oxide layer [24]. The intensity of the Ti2+ peak was higher than the other valences. With respect to the specimens with electrolytic treatment (GLW1-5), the Ti 2p3/2 peaks gave only one peak.
according to valance, Ti\(^{4+}\), of which the binding energies were 458.8–458.9 eV. Therefore, Ti\(^{3+}\) in the oxide layer of the MP specimen were oxidized to Ti\(^{4+}\), and Ti in the surface oxide layer became more thermodynamically stable by the electrolytic treatment.

Figure 1(b) shows the Ni spectra in the 2p\(^{3/2}\) region. For the MP specimen, the Ni 2p\(^{2/3}\) region had three peaks that originated from Ni\(^0\), Ni\(^{2+}\), and satellite. The main peak had binding energy at 852.4 eV, which was attributed to Ni\(^0\) derived from Ni in the substrate metal. The second peak of binding energy at 855.8 eV was assigned to the Ni\(^{2+}\) state, corresponding to Ni(OH)\(_2\) in the surface oxide layer [25]. The integrated intensity of Ni\(^0\) was higher than Ni\(^{2+}\) for the MP specimen. The Ni 2p\(^{3/2}\) peaks of all electrolyzed specimens showed different peak intensity patterns in comparison with that of MP specimen. The specimens of GLW1, GLW2, GLW3, and GLW5 gave Ni\(^{2+}\) peaks and satellites, without any detectable Ni\(^0\) peaks. This could be explained by the fact that the photoelectrons of Ni\(^0\) in the substrate metal could not be detected because the thickness of the oxide layer exceeded the effective photoelectron escape depth at a 35° take-off angle, which is the detectable limit of photoelectrons. Furthermore, in the Ni 2p\(^{3/2}\) peak from the GLW4 specimen, the Ni\(^0\) and Ni\(^{2+}\) peaks could not be detected at all, implying that the oxide layer of GLW4 does not contain nickel element within the escape depth of photoelectrons.

Figure 1(c) shows the O 1s spectra, in which three peaks are observed. The peaks at 530.2 and 531.7 eV were assigned to O\(^{2-}\) and OH\(^-\) respectively, and the peak at 533.2 eV was attributed to absorbed and bound water [26].

Figure 2 shows Ni\(^{2+}\) concentration as a function of sine of photoelectron take-off angle. When the sine of photoelectron take-off angle is 1.0, the effective escape depth of photoelectron reaches a maximum, which is equal to the average mean free path of Ni 2p\(^{3/2}\) photoelectron. The Ni\(^{2+}\) concentration was almost constant at each photoelectron take-off angle for the GLW1 specimen, while it was lower in the outmost layer than in the inside layer for the GLW3 and GLW4 specimens. The nickel-free oxide layer of the GLW4 specimen was observed in the surface layer until a depth of 0.6 of the average mean free path.

The thickness and composition of the surface oxide layer calculated with integrated intensity are shown in Table 2. The thickness of the oxide layer of MP specimens was 2.2 ± 1.3 nm. Since the photoelectrons of substrate metals were not detected for the specimens with electrolytic treatment, the thickness of the oxide layers was thicker than the escape depth of photoelectrons.

The composition of the surface oxide layer was measured at a 35° take-off angle. The dominant element of the surface oxide layer was oxygen for all specimens. The Ti concentration of the surface oxide layer was increased, whereas the Ni concentration was decreased by electrolytic treatment. These changes varied with the electrolyte composition, i.e. the

| Code   | Composition (vol%) |
|--------|--------------------|
|        | Lactic acid | Water | Glycerol |
| GLW1   | 57.2       | 7.1   | 35.7    |
| GLW2   | 42.9       | 21.4  | 35.7    |
| GLW3   | 14.3       | 50.0  | 35.7    |
| GLW4   | 7.1        | 57.2  | 35.7    |
| GLW5   | 0.1        | 64.2  | 35.7    |

Lactic acid: 85.0–92.0% (Guaranteed reagent, Kanto Chemical, Tokyo, Japan). Glycerol: 84.0–87.0% (Japanese Pharmacopoeia, Kozakai Pharmaceutical, Tokyo, Japan).
ratio of lactic acid to water. No nickel was detected in the surface oxide layer when the ratio was $1.2 \times 10^{-1}$ (GLW4).

AES analysis

The depth profiles of the relative concentration of the elements in the surface region of the specimens are shown in Fig. 3. The concentrations of Ti and Ni increased in a similar manner with increasing depth for the MP specimen. For the electrolyzed specimens (GLW1, GLW3, and GLW4), however, the Ni concentrations increased gradually from a lower value than that for Ti. With respect to the GLW4 specimen, the Ni concentration in the outmost region of the surface oxide layer, within 80 s of sputtering time, was as low as the noise level.

Discussion

In this study, oxidization of the surface oxide layer of Ni-Ti alloy was promoted by electrolytic treatment. Ti$^{2+}$ and Ti$^{3+}$ in the surface oxide layer of the MP specimen was oxidized to Ti$^{4+}$, by the electrolytic treatment. 

$$\text{Ti}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{TiO(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \quad \text{(oxidation to tetravalence)}$$

$$2\text{TiO(OH)}_2 \rightarrow 2\text{TiO}_2 + 2\text{H}_2\text{O} \quad \text{(dehydration)}$$

TiO$_2$ is thermo-dynamically stable in the presence of aqueous solution. In this study, the valence of Ni in the surface oxide layer of electrolyzed specimens was only Ni$^{2+}$, which corresponds to Ni(OH)$_2$ [25], a thermodynamically stable substance in the presence of neutral or slightly alkaline solutions. On the other hand, Ni(OH)$_2$ dissolves in acid easily with the formation of nickel ions Ni$^{2+}$, and dissolves in very alkaline solution as nickelite ions HNiO$^-$  (Deltombe E, de Zoubov N, Pourbaix M. Atlas of electrochemical equilibria in aqueous solution, 2nd ed, National Association of Corrosion Engineers, Houston, 1974, 331-342). The pH of the electrolytes used in this study ranged from 0.63 to 2.7. Therefore, it is suggested that Ni(OH)$_2$ selectively dissolves from the outmost layer into electrolytes by the electrolytic treatment. Therefore, Ni concentration in the outmost surface oxide layer became lower for the electrolyzed specimens compared with that of the MP specimen.

The change in Ni concentration according to depth from the surface of the electrolyzed Ni-Ti alloy specimens was analyzed by an angle-resolved technique for XPS, as shown in Fig. 2. When the photoelectron take-off angles were 12, 24, 35, 53, or 90°, its sine value was 0.2, 0.4, 0.6, 0.8, or 1.0, respectively. For the GLW3 and GLW4 specimens, the Ni concentration was low at a small take-off angle and increased with increasing take-off angle, indicating that Ni concentration was low in the outmost surface oxide layer and increased with increasing depth. When the average mean free path of photoelectron is hypothetically set at 10 nm [27], the thickness of the nickel-free surface oxide layer of the GLW4 specimen can be estimated at 6 nm or slightly more.

In Table 2, the thickness of the nickel-free surface oxide layer of the GLW4 specimen was estimated at 6.4 nm, given that 80

| Code | Relative concentration (mol%) | Composition |
|------|-----------------------------|-------------|
| GLW1 | 19.0 ± 0.5 | 3.0 ± 0.2 | TiNi$_{0.16}$O$_{1.87}$(OH)$_{1.59}$·0.65H$_2$O |
| GLW2 | 15.0 ± 3.7 | 1.8 ± 0.9 | 84.3 ± 0.7 | TiNi$_{0.13}$O$_{1.94}$(OH)$_{2.73}$·1.18H$_2$O |
| GLW3 | 22.0 ± 0.2 | 1.4 ± 0.4 | 76.7 ± 0.2 | TiNi$_{0.06}$O$_{1.92}$(OH)$_{1.20}$·0.37H$_2$O |
| GLW4 | 21.1 ± 0.3 | 0.0 ± 0.0 | 78.9 ± 0.3 | TiO$_{1.92}$(OH)$_{1.35}$·0.43H$_2$O |
| GLW5 | 18.5 ± 0.1 | 3.1 ± 0.5 | 78.4 ± 0.5 | TiNi$_{0.17}$O$_{1.70}$(OH)$_{1.78}$·0.73H$_2$O |
| MP  | 13.3 ± 1.4 | 9.9 ± 1.2 | 76.8 ± 2.6 | TiNi$_{0.74}$O$_{2.43}$(OH)$_{2.32}$·1.07H$_2$O |

\( n=2; \text{Mean} \pm \text{SD} \)

Fig. 3 AES depth profiles of relative concentrations of elements in the surface oxide layer of Ni-Ti alloy. Specimens were mechanically polished (MP) and electrolyzed (GLW). (a) GLW1; (b) GLW3; (c) GLW4; and (d) MP specimens.
s of sputtering time was required to remove the layer. This nickel-free surface oxide layer consisted of Ti, O\(^{2-}\), OH\(^-\), and the adsorbed and/or bound water. The ratio of oxygen to titanium in this layer was calculated as 1.92 (Table 2) and, therefore, this surface layer is considered to be similar to the nonstoichiometric TiO\(_2\) layer on unalloyed titanium surface (Uhlig HH, Revie RW. Corrosion and corrosion control – An introduction to corrosion science and engineering, 3rd ed., John Wiley & Sons, New York, 1985, 375-388). A previous study [26] using the same XPS analysis as in the present study reported that the surface oxide layer thickness of unalloyed titanium was 3.7 nm. Therefore, the nickel-free oxide layer of the GLW4 specimen in the present study was approximately 1.7-fold thicker than that of unalloyed titanium.

In conclusion, the oxidation of the surface oxide layer of Ni-Ti alloy progressed, and the thickness of the surface oxide layer increased by the electrolytic treatment with the GLW electrolyte. The Ti concentration in the layer increased, while the Ni concentration decreased by the electrolytic treatment, and no nickel was detected when the ratio of lactic acid to water was 1.2 \times 10^{-4} (GLW4). The thickness of this nickel-free surface oxide layer was estimated at 6.4 nm, which was thicker than that of unalloyed titanium. The nickel-free oxide layer produced on Ni-Ti alloy is considered to effectively improve the corrosion resistance, thus allowing the production of biocompatible medical and dental devices having shape memory effect and/or super-elasticity. Since the medical and dental devices made of Ni-Ti alloy utilize the special mechanical performance derived from super-elasticity and/or shape memory effect, the stability of the improved surface layer should be investigated in order to ensure the biocompatibility.

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Conflict of interest
None of the authors has any conflict of interest regarding this article.

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