Photocatalytic Activity of the Oxide Layer Formed on NiTi Surface through Thermal Oxidation Process

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In the present study, we attempted to prepare a photocatalytic titanium dioxide (TiO₂) layer on nickel-titanium (NiTi) alloy surface through a simple thermal oxidation process in air. At 723 K, an amorphous TiO₂ layer including a slight amount of Ni was formed on the surface. Above 873 K, the TiO₂ layer crystallized into a rutile phase. At 1023 K, a complex oxide of NiTiO₃ was also formed. The methylene blue degradation test for evaluating photocatalytic activity showed that the formed TiO₂ layers act as photocatalyst under ultraviolet (UV) light illumination, and its activity is superior to that of the surface layer formed by oxidizing a pure Ti substrate. The adhesion strength of the surface layers formed at 723 K on NiTi alloy was higher than that of a commercially available TiO₂-coating. We conclude that thermal oxidation as a surface modification technique is expected to make NiTi alloys give photocatalytic activity. [doi:10.2320/matertrans.M2014114]

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1. Introduction

A nickel–titanium (NiTi) alloy has been used as a material for dental and medical devices such as root canal files and catheters, due to its shape memory property and super-elasticity.¹⁾ In medical practice, these devices must generally be sterilized in order to remove microorganisms attached on their surfaces, and high-pressure steam or dry-heat treatments have been used as sterilization processes. However, the risk of infectious disease transmission from the devices persists, even after the aforementioned processes. It is considered that this risk can be reduced if the NiTi alloy itself possesses an antimicrobial activity. Thus far, researchers have made efforts to increase the antimicrobial activity of metallic substrates.^{2–6)}

Our research group has focused on photocatalytic TiO₂ as a possible antimicrobial medium. Photocatalytic TiO₂ has excellent antimicrobial activity under ultraviolet light (UV) illumination, and is not modified in the process.^{7–10)} Furthermore, TiO₂ is a chemically stable, nontoxic material. To coat TiO₂ on metallic substrates, chemical and physical deposition techniques such as plasma spraying and sputtering have been used.^{11,12)} However, the adhesion strength of the coating using these techniques is comparatively low, in general. Thus, these processes are not considered suitable for medical devices. Compared to those deposition techniques, the adhesion strength of surface layers formed by oxidizing a metallic surface is high due to its gradual interfacial structure. Anodic oxidation process is possible candidate to prepare TiO₂ layers. Wong *et al.* reported that the oxide layer could be formed on NiTi surfaces through alternating current anodization, resulting in a loose surface layer with large cracks.¹³⁾ Such loose surface layer may injure a human body, causing inflammation. Therefore, this technique is not suitable for medical devices.

A simple thermal oxidation process in an atmosphere including oxygen is suggested to be an alternative technique

for forming TiO₂ layers on these alloys. It is well known that the oxidation reaction's elemental selectivity in the thermal oxidation of an alloy is dominated by the standard free energy for the formation of metallic oxides. For instance, the values at 298 K for TiO₂ and NiO are 889.5 and 211.7 kJ mol^{−1}, respectively. This selectivity implies that the Ti contained within the alloy is preferentially oxidized when heated it in air, resulting in the formation of a TiO₂ layer. Vojtěch *et al.* reported that a TiO₂ layer was formed on NiTi alloy by heating it in air at 803 K,¹⁴⁾ and Wu *et al.* reported that a TiO₂ layer was prepared on NiTi alloy by heating it in air at 723 K.¹⁵⁾ These reports revealed that TiO₂ layers could be formed through heating. However, in those studies, the purpose of the formation of TiO₂ layers was to create brier for Ni ion diffusion to the human body, and the photocatalytic activity of the layers was hardly discussed. In this study, therefore, oxide layers were formed on NiTi surfaces through a thermal oxidation process, and their characteristics were investigated in detail. Furthermore, the photocatalytic activities of surface layer were estimated by using a methylene blue (MB) degradation test.

2. Material and Methods

NiTi disks (55.07 at% Ni, NEC TOKIN, Japan), 15 mm in diameter and 2 mm in thickness, was used as a substrate. The substrate was mechanically polished using emery papers up to #1200, and the disk was then ultrasonically rinsed in ethanol for 600 s. The thermal oxidization was conducted using a conventional electronic furnace (FO-100, Yamato Scientific, Japan) in an ambient atmosphere. The substrate was placed in the furnace, heated at oxidizing temperatures ranging from 573 to 1023 K for 18 ks. Then, the furnace was turned off and allowed to cool to room temperature, with the sample inside.

The surface morphologies of the oxidized substrates were observed using scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL, Japan), with an acceleration voltage of 10 kV, using secondary electron image. The crystallinity was investigated using X-ray diffractometry (XRD; New D8 ADVANCE, Bruker AXS, Germany) in the Bragg-Brentano

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geometry using Cu K α radiation. The chemical state and depth profile of the surface layers were characterized using X-ray photoelectron spectroscopy (XPS; PHI5000 VersaProbe, ULVAC-PHI, Japan) with monochromatized Al K α radiation ($h\nu = 1486.6$ eV). For the XPS measurements, the diameter of the X-ray probe was approximately 100 nm, and the photoelectron take-off angle was set at 45°. The binding energy was corrected using the C 1s peak corresponding to surface adsorbed hydrocarbon (284.8 eV). Elemental depth profiling was done using an Ar ion gun with an acceleration voltage of 4 kV. The etching rate estimated from the SiO₂ layer was approximately 0.2 nm s⁻¹. The adhesion strength of the surface layers on the substrate was estimated from the critical load to exfoliate the oxide layer using nanolayer scratch tester (CSR-2000, Rhesca, Japan). The surface layers were scratched using a diamond stylus with 200 g mm⁻¹ spring constant and tip radii of 5 μ m. The lateral rate, amplitude and loading rate were 10 μ m s⁻¹, 100 μ m and 2.50 mN s⁻¹, respectively.

The photocatalytic activity of the oxidized substrate was estimated using a methylene blue (MB) degradation test. Prior to the test, the specimens were immersed in a polypropylene vessel containing 5 dm³ of 10 μ mol cm⁻³ MB aqueous solution, after which the vessels were placed in the dark for 86.4 ks, in order to complete the adsorption of MB molecules. The aqueous solution was thereafter refreshed, and irradiated with light of a 370 nm wavelength and an intensity of 1 mW cm⁻² for 10.8 ks, using an LED. The MB concentration was evaluated every 1.2 ks during the illumination by measuring the absorbance of MB at 664 nm, using a UV-vis spectrometer (UV-2400 PC, Shimadzu, Japan). The evaluated concentration was plotted versus the illumination periods, and MB degradation rates (μ mol cm⁻³ s⁻¹) were calculated from the slope of the resulting line.

3. Results and Discussion

3.1 Characteristics of the oxidized NiTi surface

Morphological images of thermally oxidized NiTi alloy surface with various temperatures, observed by SEM, are shown in Fig. 1. An SEM image of an untreated NiTi alloy surface is also shown for comparison. The surface morphology of the alloys oxidized at 573 K (Fig. 1(b)) and 723 K (Fig. 1(c)) are similar to that of the untreated alloy surface (Fig. 1(a)). The formation of the surface layer could not be confirmed from the SEM images. On the other hands, a transition in surface morphology, towards higher granularity (Fig. 1(d)), was observed at oxidation temperatures above 873 K, and the exfoliation of specific areas was observed on the surface after oxidizing at 1023 K (Fig. 1(e)). The grains observed on the surface after oxidizing at 1023 K were much larger than those observed after oxidizing at 873 K.

The XPS spectra of the Ti 2p, O 1s and Ni 2p regions, obtained from NiTi substrates oxidized at 723 and 873 K, are shown in Fig. 2. In both temperatures, the binding energy of the Ni 2p_{3/2} peak is 856.2 eV and small satellite peaks associated with Ni 2p peaks were observed. These characteristics in Ni 2p region agree with those of NiO.¹⁶⁾ Similarly, in the case of O 1s, the spectral shape for 723 K almost coincides with that for 873 K. The binding energy of the O 1s

Fig. 1 SEM images of NiTi alloy substrate without treatment (a), and with thermal oxidation at temperatures of 573 K (b), 723 K (c), 873 K (d), and 1023 K (e).

peak is 530.2 eV, which agrees with that for metallic oxide state.¹⁶⁾ On the other hand, slight chemical shift in Ti 2p spectra was observed between the 723 and 873 K surfaces. The binding energy of the Ti 2p_{3/2} peak for 873 K is 458.5 eV, which almost agrees with that of TiO₂,¹⁶⁾ whereas the energy for 723 K is slightly lower than that for 873 K. The atomic ratio of Ni to Ti ([Ni]/[Ti]) for 723 and 873 K, calculated from the spectral intensity of Ni 2p and Ti 2p, were 1.1 and 0.4, respectively. Wu *et al.* analyzed the binding energy of nanostructured Ti–Ni–O compounds with various [Ni]/[Ti] ratios using XPS, revealed that the energy of Ti 2p_{3/2} was shifted toward low value with the increase of [Ni]/[Ti] ratio.¹⁷⁾ Considering from their report, we concluded that the slight shift of Ti 2p peaks was originated from the difference in the [Ni]/[Ti] ratio in the topmost surface. Combined, these results indicate that the surface chemical state of the oxidized NiTi alloys is composed of TiO₂ with small amounts of NiO.

XRD patterns of the oxidized NiTi alloys at various temperatures were measured using a Bragg-Brentano geometry, and are shown in Fig. 3. In the case of oxidation temperatures below 723 K, oxides peaks were hardly observed. After oxidizing at 873 K, peaks corresponding to the rutile phase of TiO₂ appeared in the patterns. For oxidizing temperatures between 873 and 1023 K, the intensities of the TiO₂ peaks drastically increased. This change indicates the extensive development of the oxide layer. Furthermore, small peaks corresponding to the

Fig. 2 XPS spectra of Ti 2p, O 1s and Ni 2p regions obtained from the NiTi surface oxidized at 723 and 873 K.

Fig. 3 XRD patterns of the oxidized NiTi alloy substrate measured by using Bragg-Brentano geometry.

complex oxide NiTiO_3 were also found in the pattern after oxidation at 1023 K. The XRD results demonstrated that a crystallized TiO_2 layer can be formed on NiTi alloys through thermal oxidation by heating above 873 K, although the use of too high of a temperature such as 1023 K, results in the formation of a complex oxide. The NiTiO_3 is formed by reacting NiO and TiO_2 , and its standard free energy decreases with increasing temperature.¹⁸⁾ When employing comparatively low temperature, NiO formed in surface layer. The NiO react with TiO_2 when raising the temperature, thereby forming NiTiO_3 .

XRD measurements cannot detect amorphous compounds. Thus, in order to confirm the existence of amorphous TiO_2 on the surface, we measured a depth profile of the oxidized NiTi alloy surface. Elemental depth profiles for NiTi alloys oxidized at 573 and 723 K are shown in Fig. 4. In the case of 573 K, oxygen was detected only in the topmost surface region, and decreased abruptly away from the surface. This result indicates that a distinct TiO_2 layer was not formed on the surface. On the other hand, after heating at 723 K, oxygen diffused into the alloy up to about 100 nm from the surface, and the atomic ratio of O to Ti was approximately 2 to 1 in this region. Concomitantly, a Ni content of approximately 10 at% was found in the shallower region. Firstov *et al.* reported that the inward diffusion of oxygen and the outward diffusion of Ti from the interior occur simultaneously when oxidizing NiTi alloy at the temperature above 673 K.¹⁹⁾ The similar diffusion of Ni also occurs during the oxidation; however, its speed is slower than that of Ti, thereby forming Ti-oxide layer.¹⁹⁾ We considered that the Ni remaining in the surface layer diffused toward both outward and inward directions after forming Ti-oxide because Ni atoms diffuse easily through defective TiO_x .^{19,20)} Consequently, the Ni-rich regions at the topmost surface and beneath the oxide layer formed on NiTi alloy.

3.2 Photocatalytic activity of the oxide layer

The formation of the crystallized or amorphous TiO_2 layer was confirmed on a NiTi alloy oxidized at temperatures above 723 K. This result lets us expect that the oxidized alloy should act as a photocatalyst. The photocatalytic activity under UV light illumination as estimated by the MB degradation test is shown in Fig. 5. Test results obtained using two types of control samples consisting of first, pure Ti oxidized at various temperatures, and second, a TiO_2 layer formed using a commercially available TiO_2 -coating reagent (ST-K211, Ishihara Sangyo, Japan), are also shown in the figure. In the case of the NiTi alloy, the degradation rate of the MB was almost zero at an oxidation temperature of

Fig. 4 The elemental depth profiles of the NiTi surface oxidized at 573 and 723 K.

Fig. 5 MB degradation rate of the NiTi alloy substrates oxidized with various temperatures. This result obtained from commercial-regent TiO_2 coating is also inserted. All error bars are mean $\pm$ S. D.; $n = 3$.

573 K. The rate drastically increased for oxidation temperatures greater than 723 K, and the highest value was observed for an oxidation temperature of 873 K. The rate decreases if the sample is oxidized above 1023 K. These results show that NiTi alloys oxidized above 723 K act as a photocatalyst under UV light illumination, although the activities are lower than that of a coating formed using a commercially available reagent. It should be noted that the value at 873 K is slightly higher than that of 723 K. This difference is probably due to the crystallinity of the oxide layer. Furthermore, the usage of too high temperature deteriorates this activity because the peeling off of the layer occurs.²¹⁾

Photocatalytic activity was also observed on the oxidized pure Ti substrate (Fig. 5). However, for oxidation temperatures above 723 K, the rates are lower than those for

oxidized NiTi alloy surfaces. We conjectured that this surprising result originates from the NiO present on the topmost surface. Sreethawong *et al.* reported that the loading of NiO enhances the photocatalytic activity of TiO_2 because Ni^{2+} oxidation state in NiO can trap photo-generated electrons, thereby suppressing the recombination of the photo-generated electrons-hole pairs.²²⁾ The trapped electron is released immediately; therefore, the activity is not deteriorated. Consequently, we consider that the Ni^{2+} present in the TiO_2 layer enhanced the photocatalytic activity of the oxidized NiTi surface. On the other hand, it is well-known that Ni ion released from a metallic surface causes allergic reaction and cytotoxicity. This effect makes us hesitate to use oxidized NiTi as medical devices, although NiO in the topmost surface is beneficial in the view from photocatalytic activity. However, the concentration of Ni existing in the topmost surface was below 20 at%, which was lower than that of Ni contained within NiTi alloy. Furthermore, we consider that a NiTi alloy with photocatalytic activity would be used in medical devices that are repeatedly used clinically, such as root canal files and catheters. In these applications, the amount of Ni ion released from the surface would be trivial because these devices are not implanted for a long time in a human body. On the basis of these considerations, we concluded that the harmful effect from the NiO present in topmost surface is negligible.

3.3 The adhesion strength of the oxide layer on the NiTi

A merit of thermal oxidation process is the ability to form surface layers having high adhesion strength. To confirm this, we estimated the adhesion strength of the oxide layer on the NiTi alloys using a nanolayer scratch tester. The critical loads of the oxide layer for oxidation temperature of 723 and 873 K are compared with that of commercial-regent TiO_2 -coating in Fig. 6. We couldn't measure the strength of the layer oxidized at 1023 K because the layer had already exfoliated after the oxidation (Fig. 1(e)). The critical load of

Fig. 6 The critical load of the oxide layer formed by oxidizing NiTi alloy. This result obtained from commercial-reagent TiO₂-coating is also inserted for comparison. All error bars are mean $\pm$ S. D.; $n = 3$.

the layer oxidized at 723 K is higher than that oxidized at 873 K, which is more than double of the commercial-reagent TiO₂-coating. From the XPS profile (Fig. 4), the thickness of oxide layer formed at 723 K is about 100 nm, and the layer thickness probably increases with the increase of the temperature. Kim *et al.* reported that the oxide layer of 1.2 μ m in thickness was formed on NiTi alloy when heating it at 873 K.²³⁾ We therefore considered that the difference of the adhesion strength depending on the temperature is due to the thickness of the oxide layer.²⁴⁾ The surface layer of the sample oxidized at 723 K showed a notable advantage in its adhesion strength although its photocatalytic activity was inferior to that of commercial-reagent TiO₂-coating (Fig. 6). In medical practice, the peeling off of the surface layer is directly linked to the risk of the failure in medical operation; accordingly, the adhesion strength is the most significant property. Consequently, we believe that thermal oxidation using a temperature of 723 K is the optimum treatment procedure for medical safety to give NiTi alloys photocatalytic properties.

4. Conclusions

We prepared photocatalytic TiO₂ layers on NiTi alloy surfaces through a simple thermal oxidation process. The TiO₂ layers were formed by heating NiTi alloys in air at temperatures above 723 K, and the crystallinity of oxide varied from amorphous to rutile with the oxidation temperature. The prepared layers included small amounts of Ni in the topmost surface regions, in a NiO chemical state. The oxidized surface acted as a photocatalyst under UV light illumination, and its activity was higher than that of oxidized pure Ti substrates. The adhesion strength of the surface layer for a 723 K oxidation temperature was notably higher than that of TiO₂ layers produced using a commercially available

reagent. In conclusion, thermal oxidation using a temperature of 723 K is an excellent technique to produce photocatalytic surface layers having high adhesion strengths on NiTi alloy surfaces, and this technique is promising for use in medical practice.

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