Structure of Surface-Modified Layers of Calcium-Ion-Implanted Ti-6Al-4V and Ti-56Ni

Takao Hanawa*, Hidemi Ukai**, Koichi Murakami**
and Kenzo Asaoka*

*Department of Dental Engineering, Tokushima University School of Dentistry,
3-18-15 Kuramoto-cho, Tokushima 770, Japan

**Research Institute, Ishikawajima-Harima Heavy Industries Co., Ltd.,
3-1-15 Toyosu, Koto-ku, Tokyo 135, Japan

The structures of surface-modified layers of calcium-ion (Ca^{2+})-implanted Ti-6 mass%Al-4 mass%V and Ti-56 mass%Ni were characterized using Auger electron spectroscopy with argon-ion-sputtering and X-ray photoelectron spectroscopy. Calcium ions were implanted in Ti-6Al-4V and Ti-56Ni in the amount of 10^{22} ions/ m^2 with an acceleration energy of 2.88 fJ (18 keV). The surface oxide layers of these alloys grew to approximately 12 nm as a result of the Ca^{2+} -implantation. The oxide layers contained hydroxide. The outermost layer of the surface oxide was 3-nm-thick calcium oxy-hydroxide. A large part of the surface-modified layer, existing inside the calcium oxide, consisted of a mixture of titanium oxide, aluminum oxide and calcium oxide in Ca^{2+} -implanted Ti-6Al-4V, and a mixture of titanium oxide, nickel oxide and calcium oxide in Ca^{2+} -implanted Ti-56Ni. In Ca^{2+} -implanted Ti-6Al-4V, Ca^{2+} -free oxide layers existed in the deepest region and this layer consisted of a mixture of titanium oxide with aluminum oxide, whereas this layer was absent in Ca^{2+} -implanted Ti-56Ni.

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I. Introduction

Titanium and some of its alloys are well known to be the best biocompatible metallic materials. In fact, these materials are successfully used for implants for medicine and dentistry. One of the reasons why the materials show good biocompatibility is that calcium phosphate is formed on the materials in electrolyte in the initial stage⁽¹⁾⁻⁽⁴⁾. This property is specific only in titanium and some of its alloys. However, the amount of calcium phosphate formed on the materials is small; the thickness is only a few nm if a uniform film is formed. The surface properties of such a thin calcium phosphate are different from those of the calcium phosphate bulk because the surface of such a thin film is electronically affected by the substrate. In addition, calcium phosphate does not exist at the moment when titanium is implanted in biological tissue. That is, titanium and its alloys do not bond with bone, unlike with some bioactive materials, such as calcium phosphate ceramics and bioactive glass.

Recently, the authors have revealed that calcium phosphate precipitation on titanium in an electrolyte is tremendously accelerated by calcium-ion-implantation⁽⁵⁾. This phenomenon is also observed on calcium-ion-implanted titanium retrieved from canine femur⁽⁶⁾. In addition, osteogenic cells on titanium are activated, and the formation of osteoid tissue by the cells is accelerated, when calcium ions are implanted in titanium⁽⁷⁾. Therefore, calcium-ion-implanted titanium has an interesting property and should be useful as a biomaterial. This

favorable property of the calcium-ion-implanted titanium is caused by the implanted calcium ions. The surface oxide of titanium grows as a result of the ion implantation and implanted calcium ions exist in the oxide⁽⁵⁾. They exist as a calcium oxide and/or calcium titanate⁽⁸⁾. This surface-modified layer works as a substrate improving hard-tissue compatibility.

However, titanium does not have sufficient strength for some purposes as an implant material and Ti-6Al-4V in mass percent is usually used for orthopedic implants, e.g. artificial joints. An interesting point is whether Ti-6Al-4V and other titanium alloys show the same favorable change as titanium when calcium ions are implanted. In this study, we have implanted calcium ions in Ti-6Al-4V and Ti-56Ni (Ti-51Ni in atomic percent: a shape memory alloy) and characterized the surface-modified layers formed by the ion implantation using Auger electron spectroscopy and X-ray photoelectron spectroscopy. The materials investigated in this study will be used for biomaterials. Therefore, the specimens were treated in ambient atmosphere and exposed to air before the analyses. The results were compared with that for calcium-ion-implanted titanium.

II. Experimental Procedure

1. Preparation of specimens

Commercial Ti-6 mass%Al-4 mass%V and Ti-56 mass%Ni were used as starting materials. The chemical compositions of the alloys and Ti are summarized in

Table 1 Chemical compositions of Ti, Ti-6Al-4V and Ti-56Ni (mass%).

	H	C	N	O	Al	V	Fe	Ni	Si	Ti
Ti	0.001	—	0.01	0.07	—	—	0.04	—	—	balance
Ti-6Al-4V	0.004	0.005	0.003	0.147	6.23	4.12	0.189	—	—	balance
Ti-56Ni	0.0001	0.046	0.004	0.065	<0.002	—	0.017	55.8	<0.01	balance

Table 1. The plates of these materials were metallographically polished and finally polished using diamond paste with 3- μm particles. The materials were ultrasonically washed with acetone and ethanol for 900 s each, and dried with a stream of high purity nitrogen (99.999%). The acetone and ethanol were not degassed and dehydrated. In addition, the specimens were exposed to air during operation.

Calcium ions were implanted into Ti-6Al-4V and Ti-56Ni with an acceleration energy of 2.88 fJ (18 keV) and ion-beam current-density of 0.5 A/m². The assist gas for the implantation was krypton. The pressure in the chamber for the ion implantation was approximately 10⁻⁴ Pa. Calcium ions were uniformly implanted in amounts of 10²² ions/m². After the implantation, the specimens were washed and dried by the method described above. For comparison, calcium ions were also implanted in Ti under the same conditions. The specimens were restored in a desiccator until analyses.

2. Auger electron spectroscopy

An Auger electron spectrometer (AES, JAMP-30, JEOL, Japan) was used for the determination of the depth profiles of elements in the surface-modified layer formed by the ion implantation. The differential Auger spectra were recorded. The KL_{2,3}L_{2,3} transition peaks for carbon, oxygen, aluminum, the L₂M_{2,3}M_{2,3} peak for calcium, the L₃M_{2,3}M_{4,5} peaks for titanium and vanadium, and the L₃M_{4,5}M_{4,5} peak for nickel, were used for the analysis. The acceleration voltage of the electron beam was 10 kV and argon-ion-sputtering (3.0 kV and 47 kA/m² in 3 $\times$ 10⁻⁴ Pa) was performed to obtain the depth profiles. The sputter rate was calibrated using Ti. The sputtering time at which oxygen is undetected in Ti was determined by AES depth profile and the surface oxide thickness was determined by a calculation using the ratio of the integrated intensity of Ti⁰ to that of Ti⁴⁺ obtained by X-ray photoelectron spectroscopy (XPS)⁽⁹⁾. In the calculation, the density of the titanium surface oxide was assumed as 4.0 Mg/m³. The ratio of the photo-ionization cross-section of Ti 2p_{3/2} to that of O 1s for the calculation is summarized in Table 2.

Table 2 Ratios of photo-ionization cross-section of Ti 2p_{3/2} to that of j level of i element.

	Al 2p	Ni 2p _{3/2}	O 1s	Ca 2p _{3/2}
$\sigma_{\text{Ti } 2p_{3/2}} / \sigma_{ij}$	2.69	0.69	1.98	0.78

3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed using an electron spectrometer (ESCALAB MK-II, Vacuum Generator Scientific, UK). All binding energies given in this paper are relative to the Fermi level and all spectra were obtained with the Mg K α line: energy 200.58 aJ (1253.6 eV), voltage 15 kV, and current 20 mA. The beam-size of the X-ray was 10 mm $\times$ 6 mm in an ellipse. The electron energy analyzer was operated in the constant analyzer energy mode at a pass energy of 3.20 aJ (20 eV). The binding energies measured were calibrated with those of Au 4f_{7/2} (13.44 aJ: 84.0 eV) and Cu 2p_{3/2} (149.23 aJ: 932.7 eV). These values were obtained from a reference⁽¹⁰⁾. Resolution with full width at half-maximum (FWHM) of the Au 4f_{7/2} peak was 0.18 aJ (1.1 eV) under the experimental conditions and the binding energies were measured with an accuracy of 0.016 aJ (0.1 eV). The base pressure was 6 $\times$ 10⁻⁸ Pa during the spectral acquisitions. The escape angle for photoelectron detection was 15° (75° from the surface of the specimen). The quantification was performed using the values summarized in Table 2 according to a reference⁽⁹⁾. Single crystals of TiO₂ made by the Bernoulli method and analytical-grade commercial CaTiO₃, CaO, Al₂O₃, and NiO powders, which were heated at 300°C for 43.2 ks in a pressure of 6 $\times$ 10⁻⁸ Pa to eliminate hydroxyl groups and adsorbed water as large as possible amount, were analyzed using XPS. The data for the oxides were used for the determination of photo-ionization cross-sections and used as references.

III. Results and Discussion

1. Auger electron spectroscopy

The depth profiles of differential intensity of elements in Ti and Ca²⁺-implanted Ti obtained using AES are shown in Figs. 1(A) and (B). The magnitude of intensity of an element does not always represent that of the concentration of the element. The sputtering time at which oxygen is undetected in Ti is approximately 300 s. On the other hand, the thickness of the surface oxide on Ti is determined as 4.0 nm by a calculation using the ratio of the integrated intensity of Ti⁰ to that of Ti⁴⁺ using XPS⁽⁹⁾. Therefore, the sputter rate was determined to be approximately 13.3 pm/s (0.8 nm/min) for titanium oxide film on Ti. The depth profiles of elements in Ti-6Al-4V and Ca²⁺-implanted Ti-6Al-4V obtained using AES are shown in Figs. 2 (A) and (B). For Ti-56Ni and Ca²⁺-implanted Ti-56Ni, the depth profiles are shown in Figs.

Fig. 1 Depth profiles of elements obtained from titanium (A) and Ca^{2+} -implanted titanium (B) using AES.

Fig. 2 Depth profiles of elements obtained from Ti-6Al-4V (A) and Ca^{2+} -implanted Ti-6Al-4V (B) using AES.

3(A) and (B). The thicknesses of the surface oxides of Ti-6Al-4V and Ti-56Ni were estimated as approximately 4.0 nm according to the sputter rate. It seemed that carbon was implanted into Ca^{2+} -implanted Ti and Ca^{2+} -implanted Ti-6Al-4V judging from the depth profile of carbon because the depth profile has a peak somewhat inside the surface like the profile of calcium. However, carbon detected by AES originated from surface contamination and no evidence for the implantation of carbon into the materials as discussed in XPS section. The differential intensities of aluminum and vanadium were much smaller than those of other elements in AES. Therefore, the intensities of aluminum and vanadium were almost constant in the depth profiles when the absolute values of the intensities from aluminum and vanadium were much smaller than those from other elements. In addition, the KLL peaks for oxygen contain the $\text{L}_{3}\text{M}_{2,3}\text{M}_{4,5}$ peaks for vanadium in their energy region, indicating that depth

profile of vanadium was affected by the oxygen profile. The small peak on the depth profile of vanadium in surface oxide layer from Ti-6Al-4V as shown in Fig. 2(B) was possibly caused by this influence. We do not treat vanadium in this section because no vanadium was detected using XPS as explained in the XPS section.

In all materials, the thickness of the surface oxide layer was larger than that in unimplanted materials. The thicknesses of the oxides on Ca^{2+} -implanted Ti, Ca^{2+} -implanted Ti-6Al-4V, and Ca^{2+} -implanted Ti-56Ni were all approximately 12 nm while original thicknesses before implantation were 4.0 nm as described above. Calcium ions passed through a mass separator before the implantation. Thus, oxygen was hardly implanted in the substrates. Therefore, the growth of oxide should be caused by surface oxidation because both calcium as implanted ions and titanium as the substrate have large negative free-energies of oxidation. The pressure in the chamber for

Fig. 3 Depth profiles of elements obtained from Ti-56Ni (A) and Ca²⁺-implanted Ti-56Ni (B) using AES.

the ion implantation was approximately 10^{-4} Pa. Two causes for the oxidation are possible. (1) Calcium ions were implanted to both surface oxide and substrate and calcium and titanium existing in the substrate were oxidized when the specimen was exposed to air after the Ca²⁺-implantation. (2) The surface oxide grew during Ca²⁺-implantation because the heat generated by the impacts of calcium ions colliding with the substrates caused the oxidation. In this case, the surface oxides grew during the implantation and implanted calcium ions could not reach the substrates. We could not specify the cause by this study. In any case, the surface oxide was grown by Ca²⁺-implantation and implanted Ca²⁺ existed in the oxide.

The depth profile of the differential intensity of an element obtained using AES is not always coherent with the actual profile of concentration of the element. However, change in relative concentration is reflected in the depth profile in the AES. In all Ca²⁺-implanted materials, elements existing in the substrate, i.e. titanium, aluminum, vanadium, and/or nickel, did not exist at the outermost layer of the surface oxide. That is, only carbon, calcium, and oxygen existed at the outermost layer. Calcium in this layer possibly existed as a calcium oxide and hydroxide. The thickness of this layer was approximately 3 nm in all Ca²⁺-implanted materials. On the other hand, calcium ions were absent in the deepest layer of the surface oxides on Ca²⁺-implanted Ti and Ca²⁺-implanted Ti-6Al-4V, indicating that titanium oxide existed on Ca²⁺-implanted Ti and that titanium oxide and/or aluminum oxides existed on Ca²⁺-implanted Ti-6Al-4V. The thickness of each of these Ca²⁺-free oxide layers was approximately 2 nm. In Ca²⁺-implanted Ti-56Ni, the Ca²⁺-free oxide layer was absent. The intermediate layer between the outermost layer and the deepest layer contained titanium, calcium, and oxygen, as well as aluminum or nickel. This layer consisted of a mixture of the oxides of these elements and/or complex oxide of these elements. The thickness of the intermediate layer on

Ca²⁺-implanted materials was approximately 7 nm in Ca²⁺-implanted Ti and Ca²⁺-implanted Ti-6Al-4V and 9 nm in Ca²⁺-implanted Ti-56Ni. The all layers contained hydroxide as discussed in the XPS section.

2. X-ray photoelectron spectroscopy

(1) Relative concentrations of elements

The detective depth by XPS was smaller than the depth detected by AES with argon-ion-sputtering in this study. In other words, the results obtained by XPS covered only outer surfaces of specimens. Only outer part of surface oxide was detected in Ca²⁺-implanted materials whereas the whole of surface oxide was detected in the unimplanted materials by XPS. C 1s spectra obtained from all specimens did not contain carbonate because no peak was detected at an energy of 46.24–46.4 eV (289–290 eV) that is the energy region of C 1s peak obtained from carbonate⁽¹¹⁾⁽¹²⁾. Carbon detected using AES and XPS was originated from surface contamination from diffusion pump oil. In addition, the binding energy of C 1s peak should be approximately 45.04 eV (281.5 eV)⁽¹¹⁾⁽¹²⁾ if carbon was implanted into Ti and the Ti alloys and TiC was formed. However, no peak was detected at the energy, indicating that carbon was hardly implanted into the materials. Therefore, carbon was not contained in the quantification.

The relative concentrations of titanium, aluminum, vanadium, nickel, oxygen, and/or calcium in Ti, Ti-6Al-4V, and Ti-56Ni before and after Ca²⁺-implantation, assuming the gross amount of these elements detected using XPS was 100 atomic percent, are summarized in Table 3. The peak locating at an energy of V 2p was eliminated by the subtraction of O1s satellite peaks excited by K $\alpha_{3,4}$ and K $\alpha_{5,6}$ lines of the X-ray source. Therefore, no vanadium was detected from Ti-6Al-4V in the experiment. When comparing the amount of oxygen with those of other elements on the assumption that the surface oxide layers are stoichiometric, the amount of oxygen is more than enough. That is, the oxides must contain

Table 3 Relative concentrations in surfaces of Ti, Ti-6Al-4V and Ti-56Ni before and after calcium-ion-implantation obtained using XPS (at.%).

Specimen	Calcium ion	Ti	Al	V	Ni	O	Ca
Ti	Implanted	17.4	—	—	—	79.9	2.7
	Unimplanted	31.6	—	—	—	68.4	0.0
Ti-6Al-4V	Implanted	18.6	1.2	0.0	—	74.5	5.8
	Unimplanted	26.0	2.3	0.0	—	71.7	0.0
Ti-56Ni	Implanted	12.9	—	—	8.0	67.5	11.5
	Unimplanted	23.8	—	—	3.8	72.4	0.0

Fig. 4 The ratio of the concentration of titanium to that of aluminum obtained from Ti-6Al-4V, [Ti]/[Al], and the ratio of the concentration of titanium to that of nickel obtained from Ti-56Ni, [Ti]/[Ni], before and after Ca^{2+} -implantation.

hydroxide, hydrate, and adsorbed water. Titanium in all materials and aluminum in Ti-6Al-4V decreased and nickel in Ti-56Ni increased after Ca^{2+} -implantation. Changes in the ratio of the concentrations of titanium to those of aluminum and nickel, [Ti]/[Al] and [Ti]/[Ni], before and after Ca^{2+} -implantation, are shown in Fig. 4. Aluminum decreased and nickel increased in relation to titanium after Ca^{2+} -implantation. These phenomena may have been caused by the difference in the sputter efficiency of Ca^{2+} -implantation or in the free energy of oxidation between aluminum and nickel. In addition, the concentration of calcium in Ca^{2+} -implanted material was larger in this order: Ti-56Ni, Ti-6Al-4V, and Ti. That is, the larger the amount of the alloying element was, the larger concentration of calcium was.

(2) Ti 2p spectra

Ti 2p spectra obtained from Ti, Ti-6Al-4V, and Ti-56Ni before and after Ca^{2+} -implantation are shown in Fig. 5. The metallic titanium peak at about 72.61 aJ (453.8 eV), as shown by Traces A, C, and E in Fig. 5, was eliminated after the Ca^{2+} -implantation (Traces B, D, and F) and only the Ti^{4+} peak was detected, indicating that the surface oxide film on Ti, Ti-6Al-4V, and Ti-56Ni grew after the ion implantation and that the films were thick enough to hide XPS signals from the substrates. This result is in accord with that of AES analysis. There-

Fig. 5 Ti 2p XPS spectra obtained from titanium (A), Ca^{2+} -implanted Ti (B), Ti-6Al-4V (C), Ca^{2+} -implanted Ti-6Al-4V (D), Ti-56Ni (E), and Ca^{2+} -implanted Ti-56Ni (F).

fore, only outer part of surface oxide was detected by XPS in Ca^{2+} -implanted materials whereas the whole of surface oxides was detected in the unimplanted materials as described above.

The $\text{Ti}2p_{3/2}$ electron binding energy values for unimplanted Ti, Ti-6Al-4V and Ti-56Ni, are almost the same (458.5–458.6 eV), and the data show that titanium existed as Ti^{4+} . In addition, FWHMs were relatively small, 0.24–0.256 aJ (1.5–1.6 eV), indicating that the surfaces of these materials contained only Ti^{4+} . Therefore, these materials were essentially covered by a thin TiO_2 film⁽¹⁾⁽³⁾⁽¹³⁾⁽¹⁴⁾. The binding energies of Ti $2p_{3/2}$ in Ti and Ti-6Al-4V seemed to be almost the same (77.68 aJ: 485.5 eV), but that in Ca^{2+} -implanted Ti-56Ni decreased (73.3 aJ: 458.2 eV) after Ca^{2+} -implantation. This indicates that the chemical state in the oxide on Ti-56Ni was changed by Ca^{2+} -implantation. This change may correspond to the decrease of [Ti]/[Ni] and the large amount of calcium. The surface oxides of Ti-6Al-4V and Ti-56Ni apparently contained oxide-states of aluminum and nickel, respectively, in addition to titanium oxide, as shown by a previous study⁽²⁾.

(3) Al 2p, Ni 2p, and Ca 2p spectra

The binding energy of Al 2p (11.84–11.87 aJ: 74.0–74.2 eV) was in the range of that of aluminum oxides before and after Ca^{2+} -implantation.

The spectrum of Ni $2p_{3/2}$ contained two peaks, a metallic state and an oxide state as shown in Fig. 6. The binding energies of both peaks did not change before and after Ca^{2+} -implantation. The energy of 136.37 aJ (852.3

Fig. 6 Ni 2p XPS spectra obtained from Ti-56Ni (A) and Ca^{2+} -implanted Ti-56Ni (B).

eV) is the metallic state and that of 136.88 aJ (855.5 eV) or 136.90 aJ (855.6 eV) is the oxide state. The peaks in Ni $2p_{3/2}$ obtained from Ca^{2+} -implanted Ti-56Ni were sharper and the relative intensities of nickel peaks to those of titanium peaks were larger than those from Ti-56Ni, causing the $[\text{Ti}]/[\text{Ni}]$ value smaller after Ca^{2+} -implantation.

In addition, the binding energies of Ca $2p_{3/2}$ was larger in this order: Ti-56Ni (55.58 aJ: 347.4 eV), Ti-6Al-4V (55.57 aJ: 347.3 eV), and Ti (55.54 aJ: 347.1 eV). The chemical state of calcium changed according to the substrate.

(4) O 1s spectra

O 1s spectra obtained from Ti-6Al-4V before and after Ca^{2+} -implantation are shown in Fig. 7. The peaks located on the low-energy side (approximately 84.80 aJ: 530 eV) in both spectra are originated from titanium oxide because the binding energies of O 1s spectra obtained from TiO_2 was 84.83 aJ (530.2 eV) in this study. The small peaks on the higher-energy side on unimplanted Ti-6Al-4V (trace B in Fig. 7) originated from aluminum oxide⁽¹⁵⁾, hydroxyl groups and adsorbed water. After the Ca^{2+} -implantation, a large shoulder appeared on the higher-energy side (trace A). This spectrum originated from calcium oxide. That is, the chemical state of calcium oxide appeared in addition to titanium oxide and aluminum oxide in Ti-6Al-4V after Ca^{2+} -implantation.

On the other hand, O 1s spectra obtained from Ti-56Ni before and after Ca^{2+} -implantation are shown in Fig. 8. In this study, the binding energies of O 1s spectra obtained from NiO was 84.91 aJ (530.7 eV). Therefore, the peaks located on the low-energy side (approximately 84.80 aJ: 530 eV) in both spectra are mainly originated from titanium oxide and nickel oxide in divalent form (NiO). Small peak that exist on the higher-energy side on unimplanted Ti-56Ni (trace B in Fig. 8) originated from

Fig. 7 O 1s XPS spectra obtained from Ca^{2+} -implanted Ti-6Al-4V (A) and Ti-6Al-4V (B).

Fig. 8 O 1s XPS spectra obtained from Ca^{2+} -implanted Ti-56Ni (A) and Ti-56Ni (B).

hydroxyl groups and adsorbed water. After the Ca^{2+} -implantation, a large shoulder appeared on the higher-energy side (trace A). The spectrum is originated from calcium oxide, hydroxyl groups, and adsorbed water. That is, the chemical state of calcium oxide appeared in addition to titanium oxide in Ti-56Ni after Ca^{2+} -implantation. As described above, the surface oxide layer contained hydroxide before and after Ca^{2+} -implantation, indicating that surface oxide layer is oxy-hydroxide.

3. Structure of surface-modified layer

According to the above results obtained from AES and XPS analyses, the structures of surface-modified layers

calcium oxide	calcium oxide	calcium oxide
calcium titanate	titanium oxide	titanium oxide
titanium oxide	aluminum oxide	nickel oxide
calcium oxide	calcium oxide	calcium oxide
titanium oxide	titanium oxide Aluminum oxide	
Ti	Ti-6Al-4V	Ti-56Ni
(A)	(B)	(C)

Fig. 9 Schematic illustration of the structures of surface-modified layers of Ca^{2+} -implanted Ti (A), Ca^{2+} -implanted Ti-6Al-4V (B), and Ca^{2+} -implanted Ti-56Ni (C).

of Ca^{2+} -implanted Ti, Ca^{2+} -implanted Ti-6Al-4V, and Ca^{2+} -implanted Ti-56Ni, are illustrated in Fig. 9. The outermost layers of Ca^{2+} -implanted materials consist of calcium oxy-hydroxide whose thickness is approximately 3 nm. A large part of the surface-modified layer, existing inside the calcium oxide, consists of a mixture of titanium oxide, aluminum oxide, and calcium oxide in Ca^{2+} -implanted Ti-6Al-4V, and a mixture of titanium oxide, nickel oxide, and calcium oxide in Ca^{2+} -implanted Ti-56Ni, while that in Ca^{2+} -implanted Ti consists of calcium titanate, titanium oxide, and calcium oxide. In Ca^{2+} -implanted Ti-6Al-4V as well as Ca^{2+} -implanted Ti, Ca^{2+} -free oxide layers exist at the deepest site whose thickness are approximately 2 nm. That is, this layer consists of a mixture of titanium oxide and aluminum oxide in Ca^{2+} -implanted Ti-6Al-4V and titanium oxide in Ca^{2+} -implanted Ti. This layer is absent in Ca^{2+} -implanted Ti-56Ni. In any case, the surface-modified layer consists of oxides and these oxide layers contain hydroxide.

No vanadium was detected using XPS in this study as shown in the previous studies⁽²⁾⁽¹⁴⁾. In other words, no vanadium was contained in the surface layer of Ti-6Al-4V and surface-modified layer of Ca^{2+} -implanted Ti-6Al-4V. In addition, the dissolution of vanadium to artificial bioliquid is little⁽¹⁶⁾. Therefore, the toxicity of vanadium in Ti-6Al-4V and Ca^{2+} -implanted Ti-6Al-4V is negligible unless the abrasion occurs under non-oxidizing atmosphere.

IV. Conclusions

The surface oxide layers of Ti, Ti-6Al-4V, and Ti-56Ni grew by Ca^{2+} -implantation. The thicknesses of these oxide layers were approximately 4 nm and 12 nm before and after Ca^{2+} -implantation, respectively. Implanted Ca^{2+} did not exist in substrates but exist in the surface oxide layer. The oxide layer contained hydroxide. The outermost layers of Ca^{2+} -implanted materials consist of calcium oxy-hydroxide whose thickness is approximately 3 nm. A large part of the surface-modified layer, existing inside the calcium oxide, consists of a mixture of titanium oxide, aluminum oxide, and calcium oxide in Ca^{2+} -

implanted Ti-6Al-4V, and a mixture of titanium oxide, nickel oxide, and calcium oxide in Ca^{2+} -implanted Ti-56Ni. The deepest layer consists of a mixture of titanium oxide and aluminum oxide in Ca^{2+} -implanted Ti-6Al-4V and titanium oxide in Ca^{2+} -implanted Ti. This layer is absent in Ca^{2+} -implanted Ti-56Ni.

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