Cross-sectional analysis of the surface ceramic layer
developed on Ti metal by NaOH-heat treatment
and soaking in SBF

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The surface structure developed on Ti metal after the NaOH and heat treatment and subsequent soaking in SBF was investigated using cross-sectional analysis involving SEM observations and EDX analysis, as well as an outer surface analysis involving SEM observations, thin-film X-ray diffraction, and Raman spectroscopy. A 1 μm-thick layer, which consisted of lathlike sodium hydrogen titanate (Na$x$H$_2$–$x$Ti$_3$O$_7$) elongated perpendicular to the surface, formed on the surface of the Ti metal after the initial NaOH treatment. This layer gradually changed into Ti metal at the boundary. The surface layer was densified by the subsequent heat treatment, accompanied by a transformation of the sodium hydrogen titanate into sodium titanate (Na$_2$Ti$_6$O$_{13}$), rutile, and anatase. The scratch resistance of the surface layer significantly increased after the heat treatment. When this Ti metal with a modified surface was soaked in SBF, apatite began to precipitate in the interior of the surface layer, filled the interspaces of the lathlike phases to integrate with the latter giving a dense composite structure, and grew over the surface layer.

Key-words : Cross section, Alkali-heat, Bioactivity, Titanium, Apatite

1. Introduction

It is known that titanium (Ti) metal spontaneously forms bone-like apatite on its surface in the living body, and bonds to living bone after it has been subjected to NaOH and heat treatments to form sodium titanate on its surface.1,2 This type of bioactive Ti metal was applied to an artificial hip joint, and has been used clinically in Japan since 2007.

However, structural changes on the surface of the Ti metal by the NaOH and heat treatments have only been partially investigated by analysis of the outer surface.1,3–5) In this study, the structural changes on the surface layer of Ti metal due to NaOH and heat treatments have been investigated using cross-sectional analysis employing scanning electron microscopy (SEM) and energy dispersed X-ray (EDX) analysis, as well as outer surface analysis using SEM observation, thin-film X-ray diffraction, and Raman spectroscopy.

The process of apatite formation on NaOH- and heat-treated Ti metal in a simulated body fluid (SBF)6) was investigated using cross-sectional analysis involving SEM observations and EDX analysis, as well as an outer surface analysis involving SEM observations, thin-film X-ray diffraction, and Raman spectroscopy. A 1 μm-thick layer, which consisted of lathlike sodium hydrogen titanate (Na$_x$H$_2$–$x$Ti$_3$O$_7$) elongated perpendicular to the surface, formed on the surface of the Ti metal after the initial NaOH treatment. This layer gradually changed into Ti metal at the boundary. The surface layer was densified by the subsequent heat treatment, accompanied by a transformation of the sodium hydrogen titanate into sodium titanate (Na$_2$Ti$_6$O$_{13}$), rutile, and anatase. The scratch resistance of the surface layer significantly increased after the heat treatment. When this Ti metal with a modified surface was soaked in SBF, apatite began to precipitate in the interior of the surface layer, filled the interspaces of the lathlike phases to integrate with the latter giving a dense composite structure, and grew over the surface layer.

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2. Experimental procedure

2.1 NaOH and heat treatment of Ti metal

Commercial pure titanium (Ti > 99.5%, Nilaco Co.) was cut into rectangular 10 × 10 × 1 mm$^3$ samples, abraded with #400 diamond plates, washed with acetone, 2-propanol, and ultrapure water in ultrasonic cleaner for a period of 30 min, and dried at 40°C. The samples were then soaked in 5 ml of an aqueous 5 M NaOH solution at 60°C for a period of 24 h in an oil bath, and shaken at a speed of 120 strokes/min. After being removed from the solution, the samples were gently rinsed with ultrapure water for a period of 30 s, and dried at 40°C. The samples were subsequently heated to 600°C at a heating rate of 5°C/min in an Fe–Cr–Al electric furnace, kept at 600°C for a period of 1 h, followed by natural cooling in the furnace.

2.2 Soaking in SBF

The NaOH- and heat-treated samples were soaked in 24 ml of SBF having ion concentrations nearly equal to those of human blood plasma at 36.5°C (Na$^+$ = 142.0, K$^+$ = 5.0, Ca$^{2+}$ = 2.5, Mg$^{2+}$ = 1.5, Cl$^-$ = 147.8, HCO$_3$– = 4.2, HPO$_4^{2–}$ = 1.0, and SO$_4^{2–}$ = 0.5 mM). The SBF was prepared by dissolving reagent grade NaCl, NaHCO$_3$, KCl, K$_2$HPO$_4$, MgCl$_2$·6H$_2$O, CaCl$_2$, and Na$_2$SO$_4$ (Nacalai Tesque, Inc.) in ultrapure water and buffered at pH = 7.4 with tri-sodium ethylenediaminetetraacetate (CH$_2$OH)$_3$CNH$_2$ (Nacalai Tesque, Inc.), and 1 M HCl at 36.5°C.6) After soaking in the SBF for various periods, the samples were removed from the SBF, gently rinsed with ultrapure water for a period of 30 s, and dried at 40°C.

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2.3 Analysis of the surface and cross sections

The surfaces of the Ti metal samples that were subjected to the NaOH and heat treatments and then soaked in the SBF were analyzed using thin-film X-ray diffraction (TF–XRD, RINT–2500, Rigaku Co.), field emission scanning electron microscopy (FE–SEM, S–4300, Hitachi, Ltd.) and Fourier transform confocal laser Raman spectroscopy (FT–Raman, LabRAM HR800, Horiba Jovin Yvon, France). The TF–XRD measurements were performed using Cu Kα radiation emitted at 50 kV and 200 mA, with a step width = 0.01° using a step rate = 1 step/s. The glancing angle of the surface of the samples was 1° against the incident beam. The FE–SEM observations were conducted on the surfaces coated with Pt/Pd under an accelerating voltage = 15 kV. The FT-Raman measurements were performed using an Ar laser (λ = 514.5 nm).

The scratch resistance of the surface layer formed on the Ti metal after the NaOH and heat treatments was measured using a thin-film scratch tester (CSR–2000, Rhesca Co., Ltd.) using a stylus with a diameter = 5 μm and a spring constant = 200 g/mm. The amplitude, scratch speed, and loading rate were 100 μm, 10 μm/s, and 100 mN/min based on the standard, JIS R–3255.

The Ti metal samples that were subjected to the NaOH and heat treatments and soaked in SBF for various periods were bent using monkey wrenches to produce microcracks on their surfaces, as shown in Fig. 1. Cross sections of these cracks were observed under an FE–SEM and analyzed using energy dispersive X-ray analysis (EDX, EMAX–7000, Horiba, Ltd.) without the samples having been coated on their surfaces under accelerating voltages of 15 and 9 kV for the FE–SEM and EDX, respectively. Then, the samples were coated with Pt/Pd and observed once again in the FE–SEM using the same accelerating voltage to obtain clearer images.

3. Results and discussion

3.1 Surface structural changes on the Ti metal due to the NaOH and heat treatments

Figure 2 shows FE–SEM photographs of the surface of Ti metal samples subjected to NaOH and heat treatments for comparison with that of untreated Ti metal. From Fig. 2, it can be seen that a fine network structure on the nanometer scale had formed on the surface of the Ti metal after the NaOH treatment, and this had essentially not changed with the subsequent heat treatment.

Figure 3 shows TF–XRD and FT-Raman profiles of the surface of Ti metal samples subjected to NaOH and heat treatments for comparison with that of untreated Ti metal. From Fig. 3, it can be seen that sodium hydrogen titanate (Na$_x$H$_{2-x}$Ti$_3$O$_7$) was formed on the surface of the Ti metal by the initial NaOH treatment, and then, this was transformed into sodium titanate (Na$_2$Ti$_6$O$_{13}$), rutile, and anatase by the subsequent heat treatment. In the previous papers,1,3,4 the phase formed by the NaOH treatment was identified as an amorphous or microcrystalline sodium titanate hydrogel. This phase must be corrected to sodium hydrogen titanate (Na$_x$H$_{2-x}$Ti$_3$O$_7$), according to the more precise
present data, and from later publications\textsuperscript{10,11} Weak, broad X-ray peaks of the sodium hydrogen titanate and sodium titanate phases indicate that these crystalline phases took the form of small crystals.

**Figure 4** shows an FE–SEM photograph and an EDX line profile of a cross section of the surface layer of a Ti metal sample subjected to the NaOH treatment. It can be seen from the FE–SEM photograph that a 1 μm-thick layer, which consisted of many lathlike phases elongated perpendicular to the surface, had formed on the surface of the Ti metal by the NaOH treatment. This surface layer increased in density with increasing depth. The EDX line profile shows that the Na and O content gradually decreased with increasing depth, while the Ti content increased near to a depth of 1 μm. This means that the sodium hydrogen titanate gradually changed into Ti metal near the boundary between the surface layer and the Ti substrate.

**Figure 5** shows an FE–SEM photograph and an EDX line profile of a cross section of the surface layer of Ti metal after the subsequent heat treatment. From Fig. 5, it can be seen that the surface layer had densified after the heat treatment without any appreciable change in the morphology. The scratch resistance of the surface of the Ti metal was as low as 5 mN for a sample treated with the NaOH solution, but this increased markedly to about 50 mN after the subsequent heat treatment. Based on these analyses, the structural changes of the surface of Ti metal due to the NaOH and heat treatments are shown schematically in Fig. 6.

### 3.2 Process of apatite formation on Ti metal

**Figure 7** shows FE–SEM photographs of the surfaces of NaOH- and heat-treated Ti metal samples that were soaked in SBF for different periods from 6 h to 72 h. It can be seen from Fig. 7 that spherical particles began to deposit on the surface of the Ti metal after soaking in the SBF for a period of 12 h, and these increased in number to cover the entire surface after soaking for a period of 24 h in the SBF. Each spherical particle consisted of many tiny particles, which were identified as being crystalline apatite by TF–XRD.

**Figure 8** shows FE–SEM photographs and EDX line profiles of cross sections of the surface layers of NaOH- and heat-treated Ti metal samples that were soaked in SBF for different periods. No significant structural changes were observed in the lathlike
surface structure within a period of 6 h after soaking in the SBF. After a period of 12 h, the interspaces of the lathlike phases in the surface layer were filled with material, and their grain boundaries became indistinct, as seen in the second photograph on the left-hand side. The Ca and P content began to be detectable in the interior of the surface layer after a period of 12 h. This indicates that apatite had begun to precipitate in the interspaces of the lathlike phases in the surface layer within a period of 12 h in the SBF. After a period of 18 h, apatite had filled all the interspaces of the lathlike phases, integrated with the latter, and had begun to grow over the surface. After a period of 24 h, the integration of the apatite with the lathlike phases had progressed to form a uniform densified composite structure, and the apatite continued to grow to form a thick and dense apatite layer on the surface. After a period of 72 h, the apatite was fully integrated with the lathlike phases so that they could not be distinguished from each other, even under higher magnification.

Based on these analyses, the process of apatite formation on Ti metal subjected to NaOH and heat treatments in SBF is shown schematically in Fig. 9. As previously reported by Takadama et al. and Kim et al., the apatite formation on NaOH- and heat-treated Ti metal is caused by the sodium titanate of the lathlike phases in the surface layer. It releases Na⁺ ions via exchange with H₃O⁺ ions in the surrounding fluid. The released Na⁺ ions are enriched in the interspaces of the lathlike phases, especially in the deep region of the surface layer, to increase the local pH of the surrounding fluid (Fig. 9(a)). The Ti–OH groups formed on the titanate by this ion exchange are negatively charged in the high pH fluid, and combine with positively charged calcium ions and then the negatively charged phosphate ions. As a result, apatite begins to precipitate in the interspaces of the lathlike phases in the deep region of the surface layer (Fig. 9(b)). The apatite formed fills the interspaces of the lathlike phases and integrates with the latter to give a dense uniform composite structure (Fig. 9(c)). Then, the apatite continues to grow over the surface layer (Fig. 9(d)).

It is expected that NaOH- and heat-treated Ti metal can form apatite on its surface by a similar process, even in the living body, and bond to living bone through this apatite layer. It has already been conformed from animal experiments that NaOH- and heat-treated Ti metal can form so tight a bond in a rabbit femur that fractures do not form at the boundary between the metal and the bone under shearing stress, but in the bone itself. The surface structure of the lathlike phase densely integrated with apatite on Ti metal may form an important contribution to a strong bond with Ti metal with living bone.

4. Summary

The surface structures developed on Ti metal after NaOH and heat treatments and subsequent soaking in SBF were investigated using cross-sectional analysis employing SEM observations and EDX analysis, as well as outer-surface analysis employing SEM observations, thin-film X-ray diffraction, and Raman spectros-
A layer 1 μm thick, which consisted of lathlike sodium hydrogen titanate (Na$_{x}$H$_{2-x}$Ti$_{3}$O$_{7}$) elongated perpendicular to the surface, formed on the surface of the Ti metal after the initial NaOH treatment. This gradually changed into Ti metal at the boundary. The surface layer was densified by the subsequent heat treatment, accompanied by a transformation of the sodium hydrogen titanate into sodium titanate (Na$_{2}$Ti$_{6}$O$_{13}$), rutile, and anatase. The scratch resistance of the surface layer was significantly increased by the heat treatment. When Ti metal with such a modified surface was soaked in SBF, apatite began to precipitate in the interior of the surface layer, filled the interspaces of the lathlike phases to integrate with the latter, giving a dense structure, and grew over the entire surface layer.

References