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Enhancement of bonding strength by graded structure at interface between apatite layer and bioactive tantalum metal

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Tantalum metal is a candidate for use as an implant material in high load-bearing bony defects, due to its attractive features such as high fracture toughness and high workability. This metal, however, does not have bone-bonding ability, i.e. bioactivity, and therefore the development of bioactive tantalum metal is highly desirable. It is known that the essential prerequisite for an artificial material to show bioactivity is to form a bonelike apatite layer on its surface in the body environment. The same type of apatite layer is formed in a simulated body fluid (SBF) with inorganic ion concentrations nearly equal to those of human blood plasma. The present authors previously showed that the apatite formation on tantalum metal in SBF was remarkably accelerated by treatment with 0.5 M-NaOH aqueous solution and subsequent firing at 300 °C, while untreated tantalum metal spontaneously formed the same apatite after a long soaking period. In the present study, the bonding strength of the apatite layer to the substrate was quantitatively evaluated in comparison with that to the untreated tantalum metal. Adhesive strength was measured as an estimation of bonding strength, and the surface microstructure of both the substrates was characterized in order to discuss the difference in the bonding strength in terms of surface structure. The apatite layer formed on the NaOH- and heat-treated tantalum metal shows higher adhesive strength than that formed on the untreated metal. The amorphous sodium tantalate layer formed on the tantalum metal by NaOH and heat treatments, has a smooth graded structure where its concentration gradually changes from the surface into the interior metal. Smooth graded structure with complex of apatite is constructed after soaking in SBF. The higher bonding strength of the apatite layer formed on the treated metal is attributed to its smooth graded structure.

1. Introduction

Metallic materials are popularly used as orthopedic implants even in highly loaded areas such as the stem of artificial joints, due to their high mechanical strength and high fracture toughness. Among the metallic biomaterials, tantalum has attractive mechanical properties that enable it to be easily fabricated into complex shapes [1–6]. Tantalum metal, however, does not show bone-bonding ability, i.e. bioactivity. Providing tantalum metal with bioactivity is expected to promote its utilization in both orthopedic and dental fields.

Previous studies reported that the essential requirement for an artificial material to show bioactivity is the formation of a biologically active bonelike apatite layer on its surface when implanted in the body environment [7]. The same type of apatite formation can be observed on bioactive materials even in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma [8, 9]. Thus, the bioactivity of an artificial material can be assessed *in vitro* by examining its apatite-forming ability in SBF.

The present authors revealed that apatite deposition

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was observed on the surface of even mere tantalum metal after soaking in SBF for as a long period as four weeks [10]. This indicates that tantalum metal hardly shows bioactivity, although it has the potential to be bioactive. The rate of the apatite deposition on tantalum metal in SBF is accelerated by chemical treatment with 0.5 M (mol/L)-NaOH aqueous solution at 60 °C for 24 h and subsequent heat treatment at 300 °C for 1 h [10, 11]. The NaOH- and heat-treated tantalum metal formed an apatite layer within four days in SBF. Therefore, the treated tantalum metal has high potential to bone-bonding. In clinical usage, a tight attachment is required between the formed apatite layer and the substrate. However, the bonding strength of the apatite layer to the tantalum substrate has not been identified by means of characterization of the interfacial structure.

In the present study, the bonding strength was quantitatively estimated in terms of the adhesive strength of the apatite layer formed on the NaOH- and heat-treated tantalum metal in SBF to the substrates, in comparison to the untreated tantalum metal. The adhesive strength was measured using a tensile test in which the load is applied perpendicularly to the interface between the apatite layer and the substrate. The difference in the adhesive strength and fracture behavior was discussed in terms of the interfacial structure between the apatite and the substrates, which was characterized by scanning electron microscopic observation, energy dispersive X-ray (EDX) microanalysis and Auger electron spectroscopy (AES).

2. Materials and methods

2.1. Preparation of specimens

Commercially available pure tantalum (Ta > 99.5%, Showa Cabot Super Metal Ltd., Tokyo, Japan) disks, 10 mm in diameter and 2 mm in thickness, were abraded with No. 400 diamond sheet, and then ultrasonically washed with acetone and distilled water. The specimens were soaked in 5.0 mL of 0.5 M-NaOH aqueous solution, and kept at 60 °C. After 24 h, they were removed from the solution and gently washed with distilled water, followed by drying at 40 °C for 24 h in an air atmosphere. The treated metal was heated to 300 °C at a rate of 5 °C/min in a Ni–Cr electrical furnace in an air atmosphere, held for 1 h at 300 °C, and then allowed to cool to room temperature inside the furnace. The treated specimen is hereafter denoted as ''Treated-Ta'', while the tantalum metal without the NaOH and heat treatments will be ''Control-Ta''.

The specimens were then soaked in 30 mL of SBF. The fluid was prepared by dissolving reagents of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 into distilled water to adjust ion concentrations to Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mM, following on from the previous report [12]. It was kept at a temperature of 36.5 °C, and buffered at pH 7.40 with 50 mM of *tris*-hydroxymethylaminomethane ($(CH_2OH)_3CNH_2$) and an appropriate amount of hydrochloric acid (HCl). The soaking period required for initial deposition of apatite on the surfaces of the specimens was four weeks for Control-Ta and one week for Treated-Ta. After soaking for these periods, the fluid was renewed, followed by further soaking of the substrates for one week to grow the apatite crystals into a continuous layer of approximately 10 μm in thickness.

2.2. Measurement of adhesive strength of apatite layer on tantalum metal

The Control-Ta and Treated-Ta were subjected to a tensile test using a modified ASTM C633 method after soaking in SBF for the period described above [13, 14]. Both sides of the Control-Ta and Treated-Ta on which an apatite layer was formed, were attached to cylindrical stainless steel jigs with rapid-type Araldite® glue (Ciba-Geigy Ltd., Switzerland) as illustrated in Fig. 1. The specimens were kept at 36.5 °C for 24 h in order to harden the glue, but further heat treatment was not carried out. The tensile stress was applied perpendicularly to the substrates with an Instron-type material testing machine (DSS-2000, Shimadzu Co., Kyoto, Japan) at a cross-head speed of 1 mm/min until fracture occurred somewhere between the jig and the substrates. The adhesive strength was calculated from the maximum load and geometrical surface area of the specimens. Five specimens were used for each measurement in order to determine the average of the adhesive strength and its standard deviation. The fractured surfaces were analyzed by a scanning electron microscope (SEM; S-2500, Hitachi Co., Tokyo, Japan) attached with an EDX microanalyzer (EDX; EMAX-3700, Horiba Co., Kyoto, Japan). For SEM observation, the surfaces of the specimens were coated with carbon by vacuum deposition. The distribution of Ca, P, and Ta on the fractured surfaces was analyzed by a lateral analytical mode in the EDX.

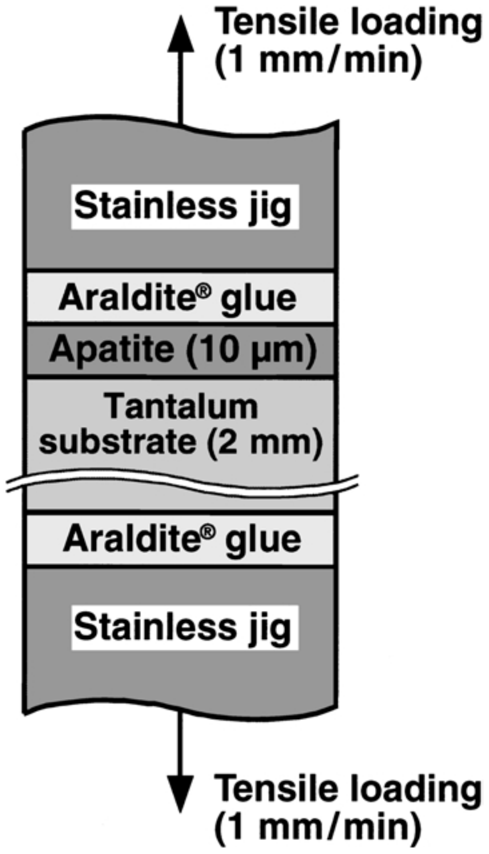

Figure 1 Schematic representation of tensile test.

2.3. Analysis of surface structure of tantalum metal

Both Control-Ta and Treated-Ta, described above, were soaked in SBF with pH 7.40 at 36.5 °C for four days and four weeks, respectively. The surfaces of the metals were then characterized by AES. During AES measurements, the primary electron beam voltage was set at 5 keV and the take-off angle of an incident beam at 45°. Xenon-ion sputtering was carried out at 3 keV to measure the depth profiles. The sputtering rate of the specimen was determined, referred to previous report [15, 16]. A tantalum oxide layer was formed on the tantalum metal by a heat treatment at 300 °C for 1 h and sputtered by Xe^+ ions at 3 keV. The thickness of the tantalum oxide was measured using atomic force microscopy (AFM: Nanoscope III, Digital Instruments Inc., USA) in a tapping mode. The sputtering rate was determined from the measured thickness of the tantalum oxide layer and the sputtering time.

3. Results

Fig. 2 shows the nominal adhesive strength of the apatite layer to the tantalum substrates. The adhesive strength of the apatite layer on Control-Ta and Treated-Ta was 9.08 ± 1.38 and 14.79 ± 2.74 MPa, respectively. The adhesive strength of Treated-Ta was significantly higher

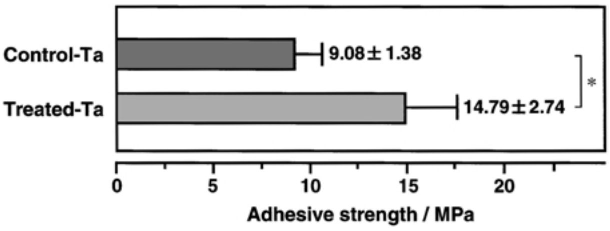

Figure 2 Nominal adhesive strength of apatite layer formed on Control-Ta and Treated-Ta to the substrate. The values are analyzed by ANOVA. Asterisk (*) means $p < 0.01$.

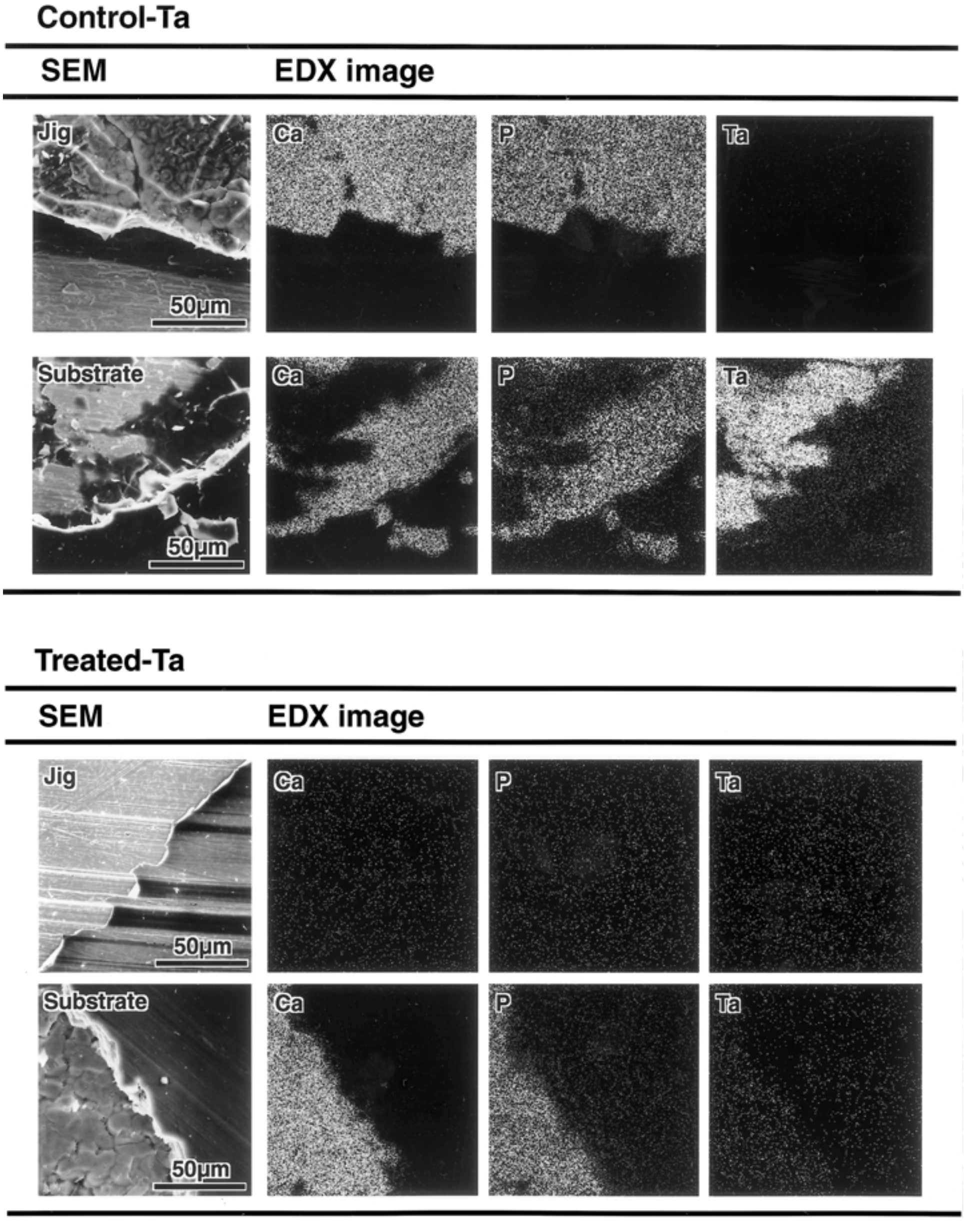

Figure 3 SEM photographs and EDX images of fractured surfaces of Control-Ta and Treated-Ta.

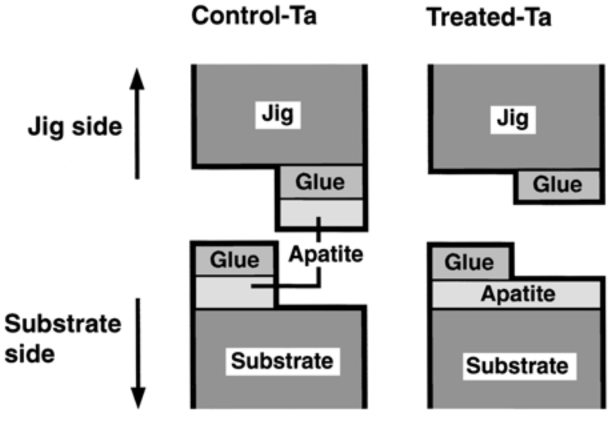

Figure 4 Schematic representation of fracture modes of Control-Ta and Treated-Ta under tensile stress.

than that of Control-Ta, on the basis of a one-way analysis of variance (ANOVA) ($p < 0.01$).

Fig. 3 shows the SEM photographs and EDX images of the fractured surfaces of Control-Ta, Treated-Ta, and the attached jigs. One part of the fractured specimen attached with tantalum substrate was denoted as, ''Substrate side'', and the other part was denoted as, ''Jig side''. In the case of Control-Ta, EDX images showed the distinct existence of Ca and P corresponding to apatite on both Substrate and Jig sides, while Ta corresponding to the tantalum substrate, was detected on Substrate side only. This indicates that the facture occurred at the interface between the substrate and the apatite layer as well as the interface between the glue and the jig. On the other hand, in the case of Treated-Ta, Ca, and P were distinctly detected on Substrate side, and none of the elements among Ca, P, and Ta appeared on Jig side. This indicates that the apatite layer did not peel off from the substrate at the maximum tensile stress and that the fracture occurred mainly at the interface between the glue and the apatite layer. These fracture modes on Control-Ta and Treated-Ta are schematically represented in Fig. 4.

Fig. 5 shows AES depth profiles of the surfaces of Control-Ta and Treated-Ta before and after soaking in SBF. The depth of the specimens was determined on the basis of the measured sputtering rate. Control-Ta has O distributed on the top surface less than 100 nm in depth, before soaking in SBF. The O concentration sharply decreased with increasing depth from the top, while the Ta concentration steeply increased. On the other hand, Treated-Ta has an O distribution extending down to 1500 nm, before soaking in SBF. Furthermore Na distribution to a depth of about 1500 nm was observed. Both the O and Na concentrations gradually decreased with increasing depth from the top surface, while the Ta concentration gradually increased. After soaking in SBF, both specimens showed Ca and P distributions corresponding to apatite, which was formed on the surface of the tantalum metal. A Na distribution was hardly observed for both specimens. Treated-Ta had larger regions of the graded structure, where Ca, P, and O concentrations decreased and the Ta concentration increased.

4. Discussion

It is obvious from Fig. 2 that the adhesive strength of the apatite layer formed on the tantalum metal to the substrate is significantly improved by the prior NaOH and heat treatments. Control-Ta shows that the fracture occurs at the interface between the substrate and the apatite layer as well as at the interface between the jig and glue. In contrast, Treated-Ta shows that the fracture occurs mainly at the interface between the glue and the apatite layer, neither inside the apatite layer nor at the interface between the substrate and the apatite layer. This means that the actual adhesive strength of the apatite layer formed on Treated-Ta with the substrate can reach a higher value than the measured value. It should be noted that the NaOH and heat treatments improve not only bonding strength of the apatite layer to the substrate, but also fracture mode at the interface between the apatite layer and the substrate.

This phenomena can be explained in terms of the larger graded structure that is formed at the interface than on the tantalum substrate without the treatments. The present authors reported that the NaOH and heat

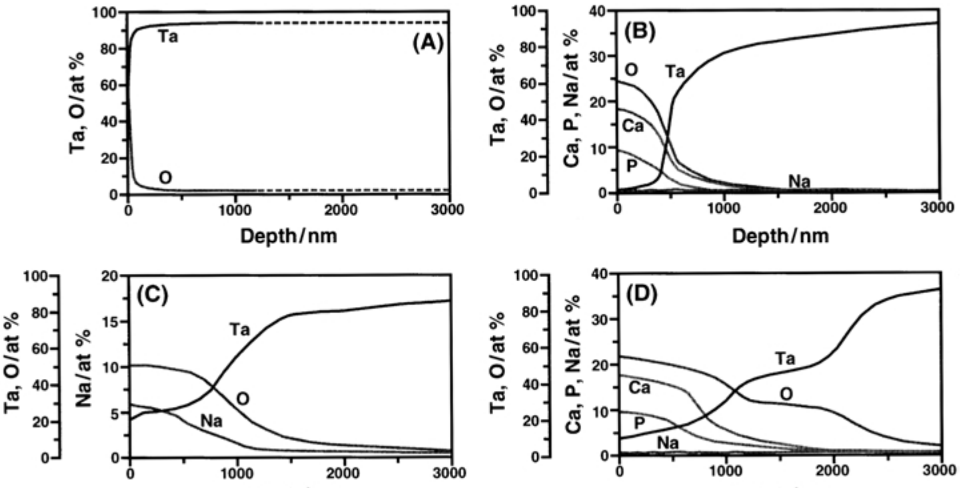

Figure 5 AES depth profiles of the surfaces of Control-Ta before (A) and after (B) soaking in SBF for four weeks, and Treated-Ta before (C) and after (D) soaking in SBF for four days. The dotted line represents the assumed profiles.

treatments allow for the formation of an amorphous sodium tantalate layer on the surface of tantalum metal [11]. AES spectra of the treated tantalum metal in Fig. 5 shows the continuous changes in concentration of Na, O, and Ta from the top surface to the interior metal. This indicates that the amorphous sodium tantalate layer formed on the tantalum metal has a smooth graded structure from the amorphous sodium tantalate to the tantalum metal. The amorphous sodium tantalite layer has apatite-forming ability, based on similar mechanisms on other types of bioactive materials such as $CaO–SiO_2$ glass [17] and NaOH- and heat-treated titanium metal [18]. When the treated tantalum is exposed to SBF, the sodium tantalate exchanges its Na^+ ion with H_3O^+ ion in the SBF to form many Ta-OH groups on its surface [19]. The formed Ta-OH groups induce heterogeneous nucleation of the apatite on its surface. In addition, the released Na^+ ion accelerates the apatite nucleation by increasing the degree of supersaturation of SBF with respect to the apatite. The nuclei of the apatite spontaneously grow into a continuous layer by consuming the calcium and phosphate ions in SBF which is already supersaturated with respect to the apatite. Accordingly, the graded structure formed on the tantalum metal by the NaOH and heat treatments, remains after soaking in SBF and causes integration of a complex graded structure over a large region, where the concentration of the apatite gradually changes from the top surface into the interior metal. Such a smooth graded structure may avoid a concentration of stress at the interface between the substrate and the apatite layer, when a tensile stress is applied. By contrast, a tantalum substrate alone can form the apatite layer on its surface by the existence of Ta-OH groups after soaking in SBF [19]. The Ta-OH groups are formed by hydration of a thin tantalum oxide passive layer which originally covers mere tantalum substrate. The passive layer of tantalum oxide has a narrower region of a steeply graded structure than the sodium tantalate layer. The steep graded structure on only a tantalum substrate allows for stress concentrations at the interface between the substrate and the apatite layer. Consequently, the apatite layer formed on the NaOH- and heat-treated tantalum, bonds more tightly to the substrate than that on a tantalum alone does.

It can be said that the NaOH and heat treatments give sodium tantalate layer with a smooth graded structure on the surface of tantalum metal. The smooth graded structure not only accelerates the formation of apatite layer on its surface, but also improves the bonding strength of the apatite layer to the tantalum substrate. These findings based on *in vitro* experiments strongly support the result that the NaOH- and heat-treated tantalum metal can accomplish a tight bond to living bone *in vivo* [20]. The potential of tantalum based materials for clinical applications can be broadened by the NaOH and heat treatments since a graded structure is introduced.

5. Conclusions

The apatite layer formed on the surface of the NaOH- and heat-treated tantalum metal in SBF, showed an adhesive strength higher than that formed on the surface of the untreated tantalum metal. The tight bonding of the apatite layer to the tantalum substrate is attributed to a graded surface structure, where the apatite gradually changes from the surface to the interior metal.

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