Surface Characteristics of Titanium Oxide Films Prepared by Micro-Arc Oxidation: Comparison of Direct Current Electrolysis and Pulse Electrolysis

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Oxide layers formed by micro-arc oxidation (MAO) using direct current electrolysis and pulse electrolysis were characterized by scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy and adhesive strength measurements. Ti oxide films fabricated by pulse electrolysis were found to have a significantly higher adhesive strength than those fabricated by direct current electrolysis. This can be explained by the different interface adhesive strengths between the two Ti oxide layers and the Ti substrate, as revealed by cross-sectional SEM micrographs. In addition, the dependences of the voltage and the current on the electrolysis time were investigated.

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1. Introduction

Pure titanium and its alloys are often used as dental and orthopedic implant materials because of their good mechanical properties and high corrosion resistances.^{1–3)} However, they are not able to induce bone formation due to the bioinertness of the native oxide film.^{4,5)} Surface modifications for enhancing their biocompatibilities have been extensively investigated using physical, chemical, and electrochemical techniques.^{6–9)} Of these techniques, micro-arc oxidation (MAO) has recently attracted considerable interest because newly formed titanium oxide films produced by MAO are highly porous and adhere firmly to titanium.^{10–13)} By controlling the composition and concentration of the electrolyte, Ca- and P-containing ceramics such as hydroxyapatite have been incorporated into the surface layer by us¹⁴⁾ and others.^{15–17)}

There are two kinds of MAO techniques: those that employ direct current electrolysis^{18,19)} and those that use pulse electrolysis.^{20,21)} However, to the best of our knowledge, no studies have compared the surface characteristics (e.g., surface structure, morphology, and composition) of films produced by these two electrochemical methods.

In this study, we investigated the surface characteristics of titanium oxide films fabricated by direct current electrolysis and pulse electrolysis and compared their surface properties, cross sections, and adhesive strengths. In addition, the dependences of the voltage and the current on the electrolysis time of the two electrolyses were studied.

2. Materials and Methods

2.1 Materials

Pure titanium plates (Showa Co., Japan) were used for both the anode and the cathode during MAO. Natural hydroxyapatite (HAp; Eccera Co.) was used without modification.

2.2 Micro-arc oxidation

2.2.1 Fabrication of anodized and HAp-fixed anodized titanium plates

A Ti plate (30 mm × 25 mm × 1.0 mm) was immersed in an electrolyte composed of 0.5 M or 1.0 M NaOH–0.05 M Na₃PO₄–0.05 M H₂O₂ (0.5 M or 1.0 M bath) at a distance of 5.0 cm from both electrodes. It was anodized at a constant current density of 0.2–2 kA/m² in a potential of 150 or 200 V for 1.5–20 min by direct current electrolysis. This procedure produced an anodized titanium (AO–Ti) plate, which was washed with distilled water and dried in air. A HAp-fixed anodized titanium (HAp–AO–Ti) plate was also fabricated by adding 1–10 g/L of HAp to the above electrolyte and performing MAO in the same manner as described above.

2.2.2 Fabrication of pulse anodized and HAp-fixed pulse anodized titanium plates

Using the same electrodes and electrolyte as those described in 2.2.1, MAO was performed at a constant current density of 2 kA/m² in a potential of 200 V for 1.5–20 min by pulse electrolysis. This procedure produced a pulse anodized titanium (pulse–AO–Ti) plate, which was washed with distilled water and dried in air. Square waves with frequencies of 10–150 Hz were used for pulse electrolysis. A HAp-fixed pulse anodized titanium (HAp–pulse–AO–Ti) plate was also fabricated by adding 1–10 g/L of HAp to the above electrolyte and applying the same pulse electrolysis method.

2.3 Characterization of the anodized materials

The microstructure and composition of the oxidized layer were analyzed by scanning electron microscopy (SEM; S-4800 Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDX; EX-420, Horiba, Japan). The cross sectional morphologies were observed with SEM of the samples cut by use of a cross section polisher (IB-09010CP, JEOL, Japan), where the laser light was irradiated for 3 hr at 6.00 kV under Argon gas flow of 1.0–1.2 ml/s. Phase analysis was performed by X-ray diffraction (XRD) (Rinto2500, Rigaku, Japan). The thickness of the oxidized layer was measured by

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Fig. 1 Voltage vs. time in the direct current electrolysis.

Fig. 2 Voltage vs. time in the pulse electrolysis.

Fig. 3 Surface SEM micrographs of AO-Ti anodized by 5 kA/m^2 of current density in 0.5 M NaOH bath. (a) 5 min, 0.5 kA/m^2 , 0.5 M NaOH bath (b) 10 min, 0.5 kA/m^2 , 0.5 M NaOH bath (c) 20 min, 5 kA/m^2 , 0.5 M NaOH bath (d) 5 min, 0.5 kA/m^2 , 1.0 M NaOH bath.

a coating thickness meter (Isoscope MP3, Hanami, Japan; EDY-1000, Sanko, Japan).

The adhesive strength was measured by bonding samples to the adhesion strength measurement system (BA-450D, Marubishi, Japan) using cyanoacrylate adhesive (#31701, Toagosei, Japan).

The voltage and current variation with electrolysis time was measured using an oscilloscope (8835-01, Hioki, Japan).

3. Results and Discussion

3.1 Voltage vs. electrolysis time for anodic oxidation

Figure 1 shows the voltage–time characteristics for direct current electrolysis at a current density of 2 kA/m^2 for 90 s in the electrolyte containing 0.5 M NaOH. The voltage increases sharply for about 17 s from the commencement of MAO with no added HAp and the titanium substrate surface is oxidized to produce a TiO_2 layer without sparking. The

TiO_2 layer becomes denser and thicker with increasing voltage. At a voltage of 80 V, spark discharge starts to occur due to dielectric breakdown and the voltage remains almost constant with time, although it fluctuates slightly.^{16,18)} When HAp is added to the electrolyte, the spark discharge voltage is attained after about 10 s, suggesting that either dielectric breakdown occurs due to the increase in the conductivity caused by adding HAp or a film with sufficient thickness for spark discharge is formed faster.

Figure 2 shows the voltage vs. time characteristics for pulse electrolysis without HAp with a current density of 2 kA/m^2 and a frequency of 100 Hz; the voltages were taken at maximum points of square waves. Similar to the direct current electrolysis, the voltage rises up sharply to 110 V during 18 s, and then spark discharge initiates and the voltage increases very slowly with small fluctuation. The resulting voltage was also confirmed to be independent of the current density ($1.4\text{--}2 \text{ kA/m}^2$) and the frequency (100–150 Hz).

Fig. 4 Surface SEM micrographs of AO-Ti anodized for 3 min. (a) 0.8 kA/m² (b) 1.1 kA/m² (c) 1.4 kA/m².

Fig. 5 Surface SEM micrographs of HAp-AO-Ti prepared with (a) 0.5 M NaOH or (b) 1.0 M NaOH bath.

3.2 Surface SEM micrographs

MAO was initially performed at a constant current density of 0.5 kA/m² in the electrolyte consisting of 0.5 M NaOH–0.05 M Na₃PO₄–0.05 M H₂O₂ using direct current electrolysis. Figure 3 shows SEM micrographs of AO-Ti surfaces obtained after performing MAO for 5, 10, and 15 min. The SEM micrographs reveal many pores with diameters of 1–10 μm and very rough surfaces. The roughness increases with increasing MAO time. Next, MAO was performed at current densities of 0.8, 1.1, and 1.4 kA/m² for 3 min (Fig. 4). The smoothness increased with increasing current density, indicating that increasing increase of travel distance of the spark discharge by increasing the current density produces more uniform and flatter oxide layers. When 1.0 M NaOH was used as the electrolyte rather than 0.5 M NaOH, the surface roughness increased; this is probably due to more vigorous spark discharge by the increase in the conductivity of the electrolyte, as shown in Fig. 3(d).¹⁸⁾ Figure 5 shows surface SEM micrographs of a HAp-AO-Ti plate fabricated by adding HAp particles

(10 g/L) to the above electrolyte. Many HAp particles were deposited on the surface, reducing the smoothness and uniformity of the surface. The oxidized layer of the HAp-AO-Ti plate was 12.0 μm thick, whereas the AO-Ti layer was 8.2 μm thick. This increase in thickness is probably because HAp particles were incorporated on and in the oxidized layer.

Figure 6 shows surface SEM micrographs of pulse-AO-Ti plates fabricated by pulse electrolysis in the electrolyte consisting of 0.5 M NaOH–0.05 M Na₃PO₄–0.05 M H₂O₂; the current density, pulse frequency, and the electrolysis time were set to 1.4–2 kA/m², 100 Hz, and 10 min, respectively. In pulse electrolysis, dielectric breakdown occurred uniformly over the whole surface and small spark discharge was generated. These things can explain that compared to the direct current electrolysis, the surface was very smooth, on which many small pores with the diameter of 0.2–1.0 μm were observed. The oxide layer thickness and the pore diameter both increased with increasing current density. Next, the frequency was increased from 10 to 150 Hz at a

Fig. 6 Surface SEM micrographs of Pulse-AO-Ti. (a) $0 \pm 14 \text{ kA/m}^2$ (b) $0 \pm 17 \text{ kA/m}^2$ (c) $0 \pm 20 \text{ kA/m}^2$.

Fig. 7 Surface SEM micrographs of Pulse-AO-Ti. (a) 10 Hz (b) 50 Hz (c) 100 Hz (d) 150 Hz.

constant current density of 2 kA/m^2 for an electrolysis time of 10 min (see Fig. 7). The surface anodized at 10 Hz had a similar roughness to the AO-Ti plate, indicating that pulse electrolysis at low frequencies has a similar effect as direct current electrolysis. An oxide layer containing many small pores was formed at high frequencies. Spark discharge did not occur above 150 Hz, probably because the pulse energy is too low to generate dielectric breakdown.

Figure 8 shows SEM micrographs of a HAp-pulse-AO-Ti plate obtained by the addition of HAp 1.0–14.0 g/L; the current density, pulse frequency, and electrolysis time

were set to 2 kA/m^2 , 100 Hz, and 10 min, respectively. The amount of HAp deposited on the surface increased with increasing amount of added HAp.

3.3 EDX measurements

Figure 9 shows an EDX spectrum of the HAp-AO-Ti plate made by direct current electrolysis at a current density of 0.5 kA/m^2 for 5 min in the 0.5 M NaOH bath that contains 10 g/L HAp. It reveals that the surface has high levels of Ca and P, indicating that HAp particles were included in the oxidized film. In addition, the Ca brightness increased with

Fig. 8 Surface SEM micrographs of HAp-Pulse-AO-Ti. (a) HAp 1 g/L (b) HAp 4 g/L (c) HAp 10 g/L (d) HAp 14 g/L.

Fig. 9 EDX Spectra and 2D mapping of Ti, O, Ca and P for surface of HAp-AO-Ti anodized for 5 min.

Fig. 10 EDX Spectra and 2D mapping of Ti, O, Ca and P for surface of HAp-Pulse-AO-Ti anodized at current density of 2 kA/m^2 and frequency of 100 Hz.

increasing current density and electrolysis time. Thus, increased biocompatibility is expected due to the uptake of HAp particles onto the film. Similarly, the EDX spectrum of the HAp-pulse-AO-Ti plate fabricated by pulse electrolysis shown in Fig. 10 reveals that Ca and P are present on the surface due to HAp fixation.

3.4 XRD measurements

Figure 11 shows XRD patterns of HAp-AO-Ti plates fabricated at various current densities and electrolysis times. Anatase TiO_2 and rutile TiO_2 were formed in almost equal amounts, which indicate that the heat generated by MAO with a direct current is insufficient to form highly crystalline rutile TiO_2 . However, some studies have indicated that anatase is preferable for artificial bone.^{20,21)} The XRD peaks for HAp particles reveal that HAp particles are incorporated in the oxide film with no loss of crystallinity. Interestingly, CaTiO_3 , which is known to play a key role in the induction of bone-like apatite through the formation of Ti-OH ,^{19,22,23)} was detected as clear peaks. CaTiO_3 is considered to be produced by Ca^{2+} ions from HAp being incorporated in Ti substrates by the spark discharge energy.

Fig. 11 XRD patterns of HAp-AO-Ti. Current density and anodic oxidation time (a) 2 kA/m^2 , 90 s, HAp 10 g/L (b) 0.5 kA/m^2 , 5 min, HAp 10 g/L, A: Anatase, R: Rutile, T: Titanium, CT: Calcium titanate, H: Hydroxy apatite.

Figure 12 shows XRD patterns of a HAp-pulse-AO-Ti plate formed using a current density of $0 \pm 20 \text{ kA/m}^2$ and a frequency of 100 Hz. These XRD patterns contain anatase and rutile peaks, just as for the samples fabricated by direct current electrolysis. Although CaTiO_3 was observed in the presence of HAp, just as for direct current electrolysis, the CaTiO_3 peaks are considerably smaller, suggesting that many HAp particles are incorporated in the oxide layer.

Fig. 12 XRD patterns of HAp-Pulse-AO-Ti. (a) HAp 10.0 g/L (b) HAp 4.0 g/L (c) HAp 2.0 g/L, A: Anatase, R: Rutile, T: Titanium, CT: Calcium titanate, H: Hydroxy apatite.

Fig. 14 Adhesive strength of AO-Ti, Pulse-AO-Ti and HAp-Pulse-AO-Ti plates.

Fig. 13 Cross-section SEM micrograph of (a) AO-Ti and (b) Cross-section SEM micrograph of Pulse-AO-Ti.

3.5 Cross-sectional SEM micrographs

Figure 13(a) shows a cross-sectional SEM micrograph of an AO-Ti plate fabricated at a current density of 0.4 kA/m^2 for 10 min. It shows that the oxide layer is about $5 \mu\text{m}$ thick and that many pores on the surface are interconnected and extend to the Ti substrate. Based on this, the pores are expected to be useful for fabricating a scaffold suitable for forming new bone. On the other hand, a small gap was observed between the TiO_2 layer and the Ti substrate. In direct current electrolysis, spark discharge is generated locally and moves continuously in a line as well as being generated in the gas near the anode. The heterogeneous movement of spark discharge and the gaseous emission may be responsible for the gap at the interface.

Figure 13(b) shows a cross-sectional SEM micrograph of the pulse-AO-Ti plate shown in Fig. 6(c). Unlike the AO-Ti plate, TiO_2 was closely attached to the Ti substrate, with no gap at the interface. High temperatures are generated locally at places where spark discharge occurs. As mentioned above, spark discharge is generated locally along a line in direct current electrolysis. This may result in local heat generation, which may produce the gap due to the different thermal expansion coefficients of TiO_2 and Ti. In contrast, smaller spark discharges are generated over the whole Ti plate in pulse electrolysis. This reduces the destruction of the TiO_2 and Ti interface due to their different thermal expansion coefficients. In addition, many small interconnected pores with diameters of $0.2\text{--}1.0 \mu\text{m}$ were observed in the Ti substrate.

3.6 Adhesive strength

Figure 14 shows the adhesive strength measurement results for AO-Ti, pulse-AO-Ti, and HAp-pulse-AO-Ti; AO-Ti was fabricated at 0.5 kA/m^2 using pulse electrolysis with a current density of 2 kA/m^2 , a frequency of $10\text{--}100 \text{ Hz}$, an electrolysis time of 20 min, and 10 g/L HAp. This figure shows that pulse-AO-Ti plate has a greater adhesive strength than the AO-Ti plate ($5\text{--}6 \text{ MPa}$) and that the adhesive strength increases with increasing frequency. In addition, the HAp-pulse-AO-Ti plate has an almost identical adhesive strength as the pulse-AO-Ti plate, indicating that HAp has little effect on the adhesive strength. For the AO-Ti plate, the small gap between the Ti substrate and the TiO_2 layer is considered to reduce the adhesive strength at the interface, as shown in Fig. 13(a). In contrast, the pulse-AO-Ti plate has no gap at the interface, as shown in Fig. 13(b). These observations can explain the higher adhesive strength of the pulse-AO-Ti plate than the AO-Ti plate. We confirmed that in the adhesive strength measurements for the HAp-AO-Ti and HAp-pulse-AO-Ti plates, the interface between the TiO_2 layer/Ti substrate and between the TiO_2 layer/adhesive detached, respectively.

4. Conclusion

The pulse-AO-Ti plate had a smoother and more uniform surface than the AO-Ti plate. Cross-sectional SEM micrographs revealed that while there are small gaps between Ti and TiO_2 in AO-Ti, TiO_2 adheres closely to Ti with no gap in

the pulse–AO–Ti plate. In addition, the pulse–AO–Ti plate had a significantly higher adhesive strength than the AO–Ti, which can be explained by it not having an interface gap. Thus, pulse electrolysis was demonstrated to be superior to direct current electrolysis for modifying surfaces of implant materials. In particular, HAp–pulse–AO–Ti plates with CaTiO_3 and many interconnected pores in the surface film are promising for producing artificial bones.

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