Surface structure of Ti-O films formed on pure titanium by anodic oxidation

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Abstract. The formation of Ti-O thin films on pure titanium was carried out by anodic oxidation, not only to improve the corrosion resistance of the material but also to form stable coating in passive state with the adsorption site for the BMP (Bone Morphogenetic Protein) on the material, aiming at the clinical use of the material as a carrier or a substratum for the BMP. Furthermore the effects of electrolytic voltage ranging from 110V to 220V for the anodic oxidation on the formation of Ti-O films on the pure titanium were investigated by analysing the surface morphology, the layer composition and the structural property. The sparking voltage was about 160V on the pure titanium material. On the treatment below the sparking voltage, the Ti-O films formed by anodic oxidation was thin and optically interferential, while above the sparking voltage, thick Ti-O films having many pin-holes ranging from 0.1 to 0.3 micrometer in diameter as well as fine craters ranging from 2 to 3 micrometer in diameter were formed on the treated surface. According to Auger electron spectroscopy (AES) in-depth profiles, it was found that the Ti-O films formed above the sparking voltage was around 10 times thicker than those formed below the sparking voltage. On the basis of X-ray diffraction (XRD), it was concluded that the titanium oxide of anatase phase was formed in both the films formed by anodizing below and above the sparking voltage.

1. Introduction
Pure titanium material, featuring excellent biocompatibility, is suitable for the application to prostheses or implants in dental or orthopedic field such as denture clasps and artificial dental roots or artificial joints, fixing plates and screws for broken bone [1-4]. However, the pure titanium does not have enough corrosion resistance to be applied to carriers or substrata for BMP (Bone Morphogenetic Protein) [5-7], because in case of this material being implanted to biological tissues, the contamination of the tissues surrounding its carriers or substrata with titanium atoms leaching out may be caused, which prevents more or less the BMP from inducing new bone.

Thus the formation of Ti-O thin films on pure titanium was carried out by anodic oxidation, not only to improve the corrosion resistance of the material but also to form stable coating in passive state with the adsorption site for the BMP on the material, aiming at the clinical use of the material as a carrier or a substratum for the BMP.

Furthermore the effects of electrolytic voltage ranging from 110V to 220V for the anodic oxidation on the formation of Ti-O films on the pure titanium were investigated by analyzing the surface morphology, the layer composition and the structural property.
2. Experimental
Small plates (9×30mm², thickness 0.38mm) of a commercially produced pure titanium were anodized in the electrolytic solution of 3% sulfuric acid–3% phosphoric acid mixture. The schematic outline of the anodising system used in this study is shown in Fig.1. The sparking voltage was about 160V on the pure titanium material in this study. Thus the anodizing below and above the sparking voltage, i.e. at several voltages ranging from 110V to 220V, was carried out for 20min under keeping the solution’s temperature within 27±1°C.

The surface morphology of the obtained films was studied on SEM images and topographic profiles using an Electron probe micro-analyser (EPMA) (JEOL Corp. Type JCXA-733). In-depth profiles of the obtained films were analysed by Auger electron spectroscopy (AES) (JEOL Corp. Type JUMP10-SX) with an ion sputter etching method using argon ion beam. Characterization of the obtained films was accomplished by X-ray diffractometry (XRD) (RIGAKU Corp. Type RAD-1B).

![Fig.1. Schematic outline of the anodizing system.](image)

3. Results and discussion
3.1. Appearance and surface morphology. Under visual observation, the Ti-O films obtained under various voltages appeared to be uniform and adhesive, while their appearance varied with the voltage. On the treatment below the sparking voltage, the Ti-O films formed by anodic oxidation was thin and optically interferential, while the Ti-O films obtained above the sparking voltage looked thick without such optical interference. A typical SEM image of the surface for Ti-O films obtained below the sparking voltage is shown in Fig.2. On the other hand, a typical SEM image and a topographic profile of the surface for Ti-O films obtained above the sparking voltage is shown in Fig.3. Under SEM, it was found that the Ti-O films formed above the sparking voltage had many pin-holes ranging from 0.1 to 0.3 micrometer in diameter as well as fine craters ranging from 2 to 3 micrometer in diameter on the treated surface.
Fig. 2. A SEM image of the surface the Ti-O film formed by anodizing at 110V (below the sparking voltage).

Fig. 3. A SEM image of the surface and a topographic profile of the Ti-O film formed at 220V (above the sparking voltage).

3.2. In depth profiles. Auger electron spectroscopy (AES) in-depth profiles of titanium and oxygen for the both Ti-O films obtained below and above the sparking voltage are shown in Fig.4 and in Fig.5, respectively. In their figures, the horizontal axis indicates the depth from the film surface while the vertical axis indicates the relative concentration (atomic%) of titanium or oxygen. Thus, according to the AES in-depth profiles, it was found that the Ti-O films formed above the sparking voltage was around 10 times thicker than those formed below the sparking voltage.
Fig. 4. AES in-depth profiles of titanium and oxygen for the Ti-O film formed at 110V (below the sparking voltage).

Fig. 5. AES in-depth profiles of titanium and oxygen for the Ti-O film formed at 220V (above the sparking voltage).

3.3. Characterization and structural property. Fig. 6 and Fig. 7 show the X-ray diffraction patterns of the films obtained below and above the sparking voltage, respectively. Several peaks attributed to TiO$_2$(anatase) were detected for the film anodized above the sparking voltage, while some peaks attributed to Ti(titanium) as well as a small peak attributed to TiO$_2$(anatase) were detected for the film.
anodized below the sparking voltage. It was guessed that these peaks attributed to titanium were originated from the pure titanium substrate, due to the small thickness of the anodised Ti-O film. Thus, on the basis of X-ray diffraction (XRD), it was concluded that the titanium oxide of anatase phase was formed in both the films formed by anodizing below and above the sparking voltage.

**Fig. 6.** X-ray diffraction pattern of the Ti-O film formed by anodising at 110V (below the sparking voltage).

**Fig. 7.** X-ray diffraction pattern of the Ti-O film formed by anodising at 220V (above the sparking voltage).
4. Conclusions
Small plates of pure titanium were anodized in the electrolytic solution of 3% sulfuric acid–3% phosphoric acid mixture. The sparking voltage was about 160V on the pure titanium material. On the treatment below the sparking voltage, the Ti-O films formed by anodic oxidation was thin and optically interferential, while above the sparking voltage, thick Ti-O films having many pin-holes ranging from 0.1 to 0.3 micrometer in diameter as well as fine craters ranging from 2 to 3 micrometer in diameter were formed on the treated surface. According to AES in-depth profiles, it was found that the Ti-O films formed above the sparking voltage was around 10 times thicker than those formed below the sparking voltage. On the basis of XRD, it was concluded that the titanium oxide of anatase phase was formed in both the films formed by anodizing below and above the sparking voltage. Therefore the improvement of corrosion resistance and the formation of stable coating in passive state with the adsorption site for the BMP were expected to be accomplished at the same time by anodic oxidation above the sparking voltage.

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