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Hydroxyapatite deposition on micropore-formed Ti-Ta-Nb alloys by plasma electrolytic oxidation for dental applications

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ABSTRACT

Hydroxyapatite deposition on micropore-formed Ti-Ta-Nb alloys by plasma electrolytic oxidation for dental applications was investigated. Ti-35Ta-xNb alloys ($x = 0$ and 10 wt.%) were prepared with an arc-melting furnace. Micropores were formed on the Ti-35Ta-xNb alloys in 0.15 M calcium acetate monohydrate + 0.02 M calcium glycerophosphate at 280 V for 3 min. Hydroxyapatite deposition were carried out on the alloy surfaces using cyclic voltammetry in 2.5 mM $Ca(NO_3)_2 \cdot 4H_2O$ + 1.5 mM $NH_4H_2PO_4$ solution with various deposition cycles. Morphology and structure of the alloy surfaces and hydroxyapatite were investigated by field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction.

The microstructure of Ti-35Ta-xNb alloys showed the α'' and β phases, and the XRD peak for the β phase increased with Nb content. For the non-NaOH treated surface, the morphology of HA deposited on Ti-35Ta-xNb alloys showed a plate-like shape, whereas the HA particle shape on the micropore-structured Ti-35Ta-xNb alloys was flower-like. The pore size and thickness of the surface barrier layer increased as the voltage increased. The fraction of rutile also increased as the applied potential increased. The anatase and rutile phases of TiO_2 can be controlled by applied voltage for enhanced biocompatibility.

1. Introduction

Dental materials have been successfully used for a variety of biomaterials and different applications. CP Ti (commercially pure titanium), Ti-6Al-4V, and nickel–titanium shape memory alloys are widely used because of several benefits, including lower elastic modulus, excellent corrosion resistance and enhanced biocompatibility [1,2]. Especially, Ti-6Al-4V is the most widely used dental implant material due to its excellent strength, low modulus of elasticity, and good corrosion resistance in clinical use. However, Ti-6Al-4V has a high elastic modulus compared with that of bone, and potentially adverse stress-shielding of the surrounding bone can occur [3]. Moreover, Ti-6Al-4V may cause serious health problems because the vanadium ions have been found to cause cytotoxic effects and adverse tissue reactions, while the aluminum ions have been associated with neurological disorders [1]. For this reason, new β-type titanium alloys are composed of non-toxic elements such as Nb, Ta, Zr, Hf, and Mo. In particular, Ta and Nb can reduce the modulus of elasticity when alloyed with Ti due to stabilization of the β phase [3–5]. To enhance biocompatibility, surface treatment methods on Ti alloys, such as pulsed laser deposition, plasma spraying, and electrochemical deposition, have been widely used [3,6]. Among the latter methods, plasma electrolytic oxidation (PEO) offers the advantages of quick coating time and controlled coating conditions [6]. The anodized oxide layer and adaptation to a diameter range of Ti alloys promote improvement of cell adhesion [7,8]. Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is widely known as being osteoconductive, namely able to promote bone in-growth and attachment to the surface of the implant during the early stages of the implantation [9,10]. An ideal HA coating should be fully dense and have good adhesion at the coating-Ti interface to minimize Ti-body fluid contact [11].

The motivation for this research for dental applications was to form pores on the titanium implant surface that would enable controlling the morphology of HA precipitation and improving cell adhesion and proliferation for clinical use [1], while maintaining an adequate surface roughness comparable to that achieved by previous surface treatment methods. When considering surface pore dimensions, micron-range diameters can give the greatest potential for fixation between bone and the implant surface [1]. In addition, HA is an excellent biomaterial choice for a dental implant surface because of its similar chemical composition to the adjacent bone. A plate-like shape was previously reported for HA deposited on a pure titanium plate by a hydrothermal–electrochemical process in an electrolyte solution containing calcium and phosphate ions [12]. This earlier study was focused on the HA structure and growth on the bulk surface of the Ti alloy by use of an

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electrochemical method involving cyclic voltammetry [12]. The present study continues our investigation of the surface morphology of HA precipitated on titanium oxide surfaces using cyclic voltammetry after nanotube formation. In this investigation, hydroxyapatite formation on Ti-Ta-Nb alloys for dental applications containing micropores created by plasma electrolytic oxidation was examined in detail.

2. Experimental details

Ti-35Ta-xNb alloys (x = 0 and 10 wt.%) were prepared using a vacuum arc-melting furnace. All ingots were melted 6 times, and the cast alloys were heat treated at 1000 °C for 12 h in an Ar atmosphere and water-quenched at 0 °C to ensure homogenization. Samples for study were initially cut to 2.5 mm thickness using a high-speed diamond cutting machine (Accutom-5, Struers, Denmark) with 2000 rpm speed. Polishing was carried out using SiC paper of different grades ranging from 100 to 2000, ending with an alumina slurry (1 μm particle size). Lastly, the polished samples were ultrasonically cleaned in deionized water and dried in flowing nitrogen.

The formation of micropores on the titanium alloy surfaces was achieved by an electrochemical method. A three-electrode configuration employed a platinum electrode and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The electrolyte was 0.15 M calcium acetate monohydrate + 0.02 M calcium glycerophosphate at room temperature. Electrochemical anodization was carried out at constant voltage (280 V) for 3 min (KDP-1500, Korea).

Precipitation of hydroxyapatite (HA) was performed on the alumina-polished and micropore-treated Ti–35Ta-xNb alloy surfaces after alkali treatment in 5 M NaOH solution at 60 °C for 12 h for control of the nanostructure and buffer surface, using a potentiostat (PARSTAT 2273, Princeton Applied Research, USA). The electrochemical setup for HA deposition again consisted of a three-electrode configuration with a platinum electrode and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The electrolyte for HA deposition was composed of 2.5 mM $Ca(NO_3)_2{\cdot}4H_2O$ + 1.5 M $NH_4H_2PO_4$ in distilled water, yielding a 1.67 Ca/P ratio for the electrolyte. A single voltammetry cycle was composed of a 2 s deposition time (t_d) with potential E range between −1.5 V and 0.3 V (vs. SCE electrode) and scan rate of 500 mV/s followed by a break time (t_b) of 2 s. Three different numbers of cycles (5, 30, and 50) were employed for electrochemical HA deposition, which was performed at 80 °C.

Microstructures of the alloys were observed using optical microscopy (OM, Olympus BM60M, Japan) and field-emission scanning electron microscopy (FE-SEM, Hitachi 4800, Japan) after etching with Keller's solution (2 mL HF, 3 mL HCl, 5 mL HNO_3 and 190 mL H_2O). The phases were identified by X-ray diffraction (XRD) (X'pert Pro Diffractometer, Philips), utilizing Cu Kα radiation ($\lambda = 0.15406$ nm), with steps of 0.03 degree in the diffraction angle (2θ) and comparing peak positions to selected atomic planes in the JCPDS files for appropriate powder standards. The surface morphology and chemical composition of the Ti-35Ta-xNb alloys and coatings were investigated with the FE-SEM and an energy-dispersive X-ray spectrometer (EDS, Oxford ISIS 310, England) coupled to the SEM.

3. Results and discussion

Fig. 1 shows the microstructures of the Ti-35Ta-xNb alloys with different Nb content (0 and 10 wt.%) after heat treatment at 1000 °C for 12 h in an Ar atmosphere. The microstructure of the Ti-35Ta alloy contained the needle-like α″ phase, as shown in Fig. 1 (a) and (b). The Ti-35Ta-10Nb alloy also presented a microstructure containing a needle-like α″ phase, as shown in Fig. 1 (c) and (d), but this microstructure had a more equiaxed character for the β-phase matrix. It is assumed that the needle-like α″ martensite plates were transformed to equiaxed β phase with increased Nb content and homogenization treatment at 1000 °C for 12 h, followed by ice water quenching. The elements Ta and Nb are known β-phase stabilizers [13–15]. The EDS results indicated that the compositions of the prepared alloys were in good agreement with the starting proportions of the component elements.

Fig. 2 shows the FE-SEM images of micropores formed on the Ti-35Ta-xNb alloys in 0.15 M calcium acetate monohydrate + 0.02 M calcium glycerophosphate at 280 V for 3 min. Fig. 2 (a) shows NaOH-treated Ti-35Ta; Fig. 2(b) shows a nano-mesh structure formed in the matrix of Fig. 2(a); Fig. 2 (c) shows a nano-mesh structure formed in the micropores of Fig. 2(a), and Fig. 2 (d) shows the surface of NaOH-treated Ti-35Ta-10Nb. The process of NaOH treatment was performed in 5 M NaOH solution for 10 min. These observations established that the NaOH-treated Ti-35Ta-xNb alloys have a rougher micropore surface and that a nano-mesh structure was formed inside the micropores as

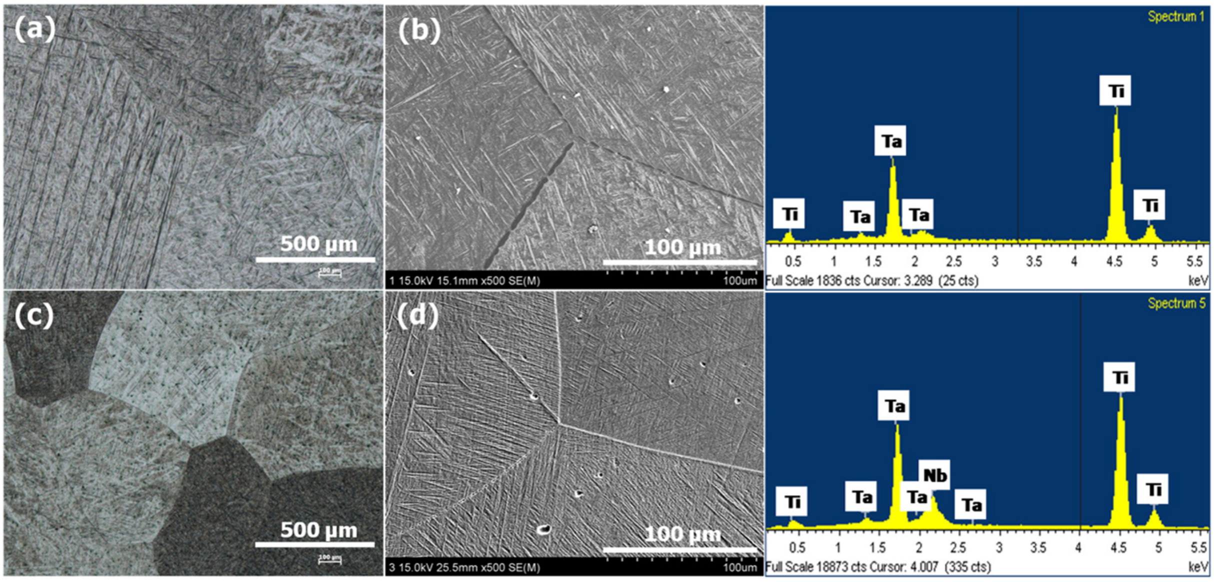

Fig. 1. OM and FE-SEM images, and EDS analyses, of Ti-35Ta-xNb alloys after heat treatment at 1000 °C for 12 h in Ar atmosphere, followed by 0 °C water quenching: (a) OM image of Ti-35Ta alloy (b) FE-SEM image of Ti-35Ta alloy (c) OM image of Ti-35Ta-10Nb alloy (d) FE-SEM image of Ti-35Ta-10Nb alloy.