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Full Length Article

Mn-coatings on the micro-pore formed Ti-29Nb-xHf alloys by RF-magnetron sputtering for dental applications

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ABSTRACT

In this study, Mn-coatings on the micro-pore formed Ti-29Nb-xHf alloys by RF-magnetrons sputtering for dental applications were studied using different experimental techniques. Mn coating films were formed on Ti-29Nb-xHf alloys by a radio frequency magnetron sputtering technique for 0, 1, 3, and 5 min at 45 W. The microstructure, composition, and phase structure of the coated alloys were examined by optical microscopy, field emission scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. The microstructure of Ti-29Nb alloy showed αp̈hase in the needle-like structure and Ti-29Nb-15Hf alloy showed β phase in the equiaxed structure. As the sputtering time increased, the circular particles of Mn coatings on the Ti-29Nb alloy increased at inside and outside surfaces. As the sputtering time increased, [Mn + Ca/P] ratio of the plasma electrolytic oxidized films in Ti- 29Nb-xHf alloys increased. The corrosion potential (E_{corr}) of Mn coatings on the Ti-29Nb alloy showed higher than that of Mn coatings on the Ti-29Nb-15Hf alloy. The passive current density (I_{pass}) of the Mn coating on the Ti-29Nb alloy and Mn coatings on the Ti-29Nb-15Hf alloy was less noble than the non-Mn coated Ti-29Nb and Ti-29Nb-15Hf alloys surface.

1. Introduction

The commercially pure titanium (CP-Ti) and Ti-6Al-4V alloys have the superior corrosion resistance and excellent mechanical properties such as tensile strength, toughness, and low density [1]. However, there are some disadvantages such as releasing of element Al and V with cytotoxicity into the human body in the case of extensively used Ti-6Al-4V alloy, these elements can be played role in undesirable negative effects [1,2]. To overcome these problems, Ti alloys with non-toxic elements such as Nb, Zr, and Hf have been recently developed and studied.

The surface modification has been carried out using various physical and chemical processes on the surface for obtaining the adhesive strength between the bone and surface of implant. In this regard, improved osteointegration has been sought through formation of titanium-based implant surface, using implant surface coating techniques, for example, plasma electrolytic oxidation (PEO) and magnetron sputtering [3–5]. PEO technique can also be used for the surface treatment of dental implant alloys. Using this technique, a dense titanium oxide layer can be grown in situ on the surface of Ti alloy. Nowadays, some researches have focused on the surface structure and morphology of the coatings on the PEO-treated surface and their properties such as corrosion resistance and cell proliferation [5–8].

Hydroxyapatite (HA) coatings on the pore-formed surfaces have been implemented to improve the bioactivity of the implant and enhance osteoblast adhesion on the surface. The morphology of HA on the pore-formed surface can be controlled by varying the applied potential, current density, electrolyte concentration, and temperature for good cell proliferation. Moreover, radio frequency (RF) magnetron sputtering is a good deposition technique for HA and mineral elements in bone that can produce uniform, dense and hard coatings with a thickness <1 μm that are homogeneous in structure and composition [3,4,9].

In the natural bone, bone is mainly composed of Ca and P, additionally, and contained the mineral elements such as Si, Sr, Mn, Mg, and Zn, and so on. Manganese (Mn) of these elements has a variety of stable valence states and increases the ligand-binding affinity of integrins, a quite large family of receptors, which mediate cellular interactions with extra-cellular matrix, and activate cell adhesion. Consequently, the presence of Mn^{2+} in coatings should promote the interaction with the host bone tissue [10–13]. In pre-reported research [14], alkali-treatment for nanomesh-formation was car-

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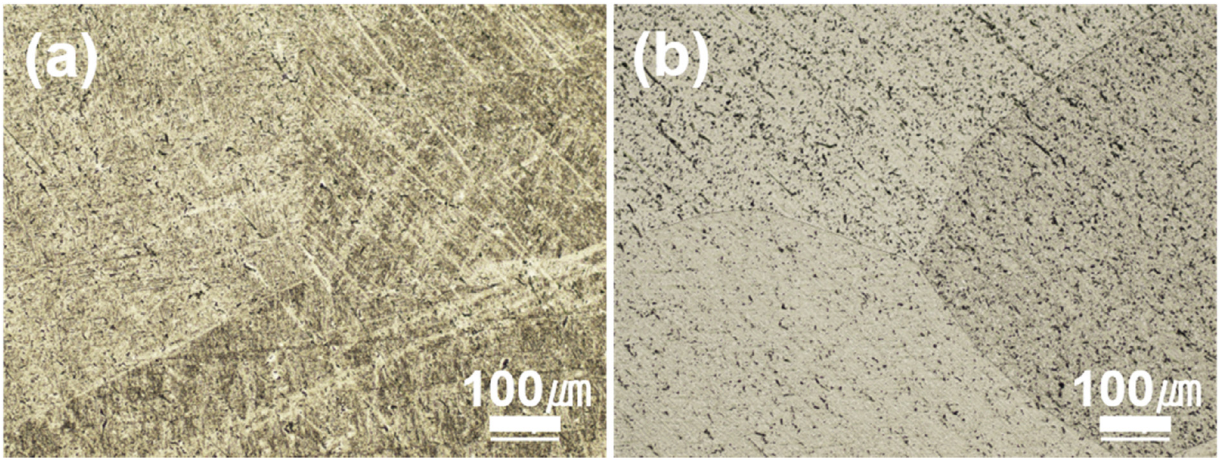

Fig. 1. OM micrographs of homogenized Ti-29Nb-xHf alloys: (a) Ti-29Nb and (b) Ti-29Nb-15Hf.

ried out on the Ti-29Nb-xHf alloys in 5 M NaOH solution and then Ca and P were precipitated on nanomesh-treated surface, finally, Mn coating was carried out using sputtering. From the results of pre-research, it was suggested that nanomesh structure was affected on the structure of sputtered Mn coatings. Therefore, it was needed to investigate the effect of micro-pore formed surface on the structure of sputtered Mn coatings for dental implant.

In this study, Mn-coatings on the micro-pore formed Ti-29Nb-xHf alloys by RF-magnetrons sputtering for dental applications were studied using different experimental techniques.

2. Experimental

2.1. Materials preparation

The Ti-29Nb-xHf(x = 0, 15 wt%) alloy was manufactured using a vacuum arc-melting furnace (SVT, Korea) and was melted five times to improve the chemical homogeneity. Each alloy was homogenized under an argon atmosphere at 1050 °C using a tube furnace (MSTF-1650, MS ENG, Korea) for 12 h, followed by quenching in water at 0 °C. The ingots were cut using a diamond wheel (Accutom-5, Struers, Denmark) into disk specimens having a diameter of 10 mm and thickness of 3 mm. Each alloy was polished using SiC paper (100–2000 grit size). Al_2O_3 slurry (0.3 μm) was used for final polishing, and then all the samples were washed in an ultrasonic bath with acetone and distilled water.

2.2. PEO treatment

The samples for PEO treatment were prepared by polishing with 100–2000 grit sandpaper and finally with a 0.3 m Al_2O_3 slurry. The polished disk were washed thoroughly with distilled water and ultrasonicated for 10 min in ethyl alcohol and used as a control group. The samples were used as anodes, and a Pt rod was used as the cathode in equivalent electrolytic baths and electrolytes. A pulsed direct-current power supply was employed. The applied voltage and PEO treatment time were selected to be 270 V and 3 min, respectively. The electrolyte for PEO was prepared by mixing with 0.15 M calcium acetate and 0.02 M calcium glycerophosphate. The temperature of the electrolyte was maintained below 25 °C by a cooling system. The PEO films formed on samples were flushed with water after the PEO treatment and then dried in warm air.

2.3. Mn thin film coating

The Mn thin film was coated using a RF-magnetron sputtering system (A-Tech system Co., Korea). The distance between the substrate and the target was 80 mm, and a diameter of 4 inch was used for sputtering. The pressure in the chamber was initially set to less than 10^{-6} Torr. A mass flow controller was used to generate a 40-sccm Ar gas flow into the chamber. The coating processing pressure of the Ar gas atmosphere was maintained at $2–4 \times 10^{-2}$ Torr, and a RF power of 45W was applied for 0, 1, 3, and 5 min, which led to the formation of plasma. Prior to coating, pre-sputtering was carried out with Ar gas using a shield to protect the sample for 5 min.

2.4. Analysis

The microstructure of each alloy was observed by optical microscopy (OM, Olympus BM60 M, Japan). Samples for OM examination were etched in Keller's solution consisting of 2 mL Hf, 3 mL HCl, 5 mL HNO_3, and 190 mL H_2O. Morphologies of the Mn coatings on the micro-pore formed Ti-29Nb-xHf surface were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi 4800, Japan). In order to identify the phases, composition, and structures, the Mn-sputtered Ti-29Nb-xHf alloys were characterized by X-ray diffraction (XRD, X′pert Pro Diffractometer, Philips) and energy-dispersive X-ray spectroscopy (EDS, Oxford ISIS 310, England). Electrochemical studies were performed via potentiodynamic polarization test in 0.9% NaCl solution at 36.5 ± 1.0 °C with a scan rate of 1.667 mV s^{-1} was performed from −1500 to 2000 mV.

3. Results and discussion

Fig. 1 presents the microstructure of the homogenized new alloy surfaces for Ti-29Nb and Ti-29Nb-15Hf alloys. The Fig. 1a is Ti-29Nb alloy and Fig. 1b is Ti-29Nb-15Hf alloy, respectively. The microstructure of Ti-29Nb alloy showed αp̈hase in the needle-like structure and Ti-29Nb-15Hf alloy showed β phase in the equiaxed structure. The needle-like structure changed to equiaxed structure with increasing Hf content as shown in Fig. 1. These results can be explained that the Ti–29Nb alloy can suppress the formation of the metastable α″ phase when an appropriate amount of Hf is added, which acts as a β-phase stabilizer [2,15].

Fig. 2 shows the XRD patterns of the Ti-29Nb and Ti-29Nb-15Hf alloys. In Fig. 2a, Ti-29Nb alloy showed the α″-titanium; (020) and (101) peaks. From Fig. 2b, Ti-29Nb-15Hf alloy showed the β-titanium; (110), (220), and (221) peaks. As shown in Fig. 2, it is assumed that the addition of Hf to the Ti–25Nb alloy suppressed the

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