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Surface morphology of Zn-containing hydroxyapatite (Zn-HA) deposited electrochemically on Ti–xNb alloys

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ABSTRACT

In this study, the surface morphology of Zn-containing hydroxyapatite (Zn-HA) electrochemically deposited on Ti–xNb alloys was investigated using various experimental techniques. Ti alloys containing from 10 to 50 wt.% Nb were manufactured in a vacuum arc-melting furnace. The Zn-HA layers were grown by electrochemical deposition at 85 °C on the Ti–xNb alloy surface in a solution containing Ca, Zn, and P ions. The microstructures of the Ti–xNb alloys changed from a needle-like structure to an equiaxed structure with increasing Nb content. The phases and morphologies for the Zn-HA layers were influenced by the Zn ion content. The HA and Zn-HA layers formed denser microstructures with increasing Nb content. The nano-scale morphologies of the Zn-HA layers changed from a rod-like structure to a network-like structure.

1. Introduction

Commercially pure titanium and Ti–6Al–4V are widely used for various bone substitute applications, including orthopedic and dental implants [1,2], because they show many advantages, such as generally accepted biocompatibility, excellent corrosion resistance, low elastic modulus, and good mechanical properties [3,4]. However, some investigators are concerned that the Ti–6Al–4V alloy used for implants has the disadvantage of releasing aluminum and vanadium ions that may cause toxicity in the body, leading to undesirable long-term effects. There is further concern about the high elastic modulus of Ti and Ti–6Al–4V compared to bone, although stress-shielding effects have not been reported for dental implants. Therefore, some investigators have focused on the development of Al- and V-free Ti alloys that contain non-toxic element such as Nb, Ta, Zr, and Sn for biomedical applications [5]. In particular, Nb has identified as a non-toxic element that does not cause any adverse reaction in the human body. Accordingly, research has focused on β-Ti alloys, due to their increased biocompatibility and decreased elastic modulus [6].

While it is generally considered that Ti and Ti alloys are bio-inert, these metallic materials cannot bond directly to bone tissue, which is an inorganic/organic (ceramic–polymer) composite. Therefore, various surface modifications have been carried out on Ti implants to improve their bioactivity [7]. Among these surface modifications, hydroxyapatite [HA; $Ca_{10}(PO_4)_6(OH)_2$] has frequently been deposited on Ti implants to improve the cell responses and osteoconductivity because of its similarity in composition and crystal structure to bone minerals, which have been considered to be Ca-deficient apatites with substituted elements [8,9].

Thus, HA coatings has been used on dental implants to encourage the growth of natural bone into the prosthetic devices [10], and these coatings must possess certain important properties. An ideal HA coating should be fully dense and have good interfacial attachment to the underlying Ti/Ti alloy substrate to minimize Ti-body fluid contact [11]. Among the elements that have been incorporated in Ti alloys, zinc (Zn) is considered to have great potential for enhancing the attachment to HA [12].

Zinc plays very important roles in bone formation and immune system regulation, and is also the most abundant trace element in bone [13,14]. It has been demonstrated that titanium surfaces chemically modified with ZnO could significantly reduce the viability of five *streptococcus* bacterial strains [15,16]. Moreover, Zn can also promote bone metabolism and growth, increase bone density and prevent bone loss. Furthermore it has been found that an electrochemical method is capable of incorporating zinc into HA when a zinc salt is added to the electrolyte [17,18].

In this work, the surface morphology of Zn-containing hydroxyapatite (Zn-HA), electrochemically deposited on binary Ti–xNb alloys, was investigated using various experimental techniques.

2. Experimental details

Ti–xNb binary alloys were prepared from pure Ti (G&S Titanium, Grade 4, USA) and 10 to 50 wt.% Nb (Kurt J. Lesker Company, 99.95 wt.% purity, USA). Each alloy was melted six times to improve

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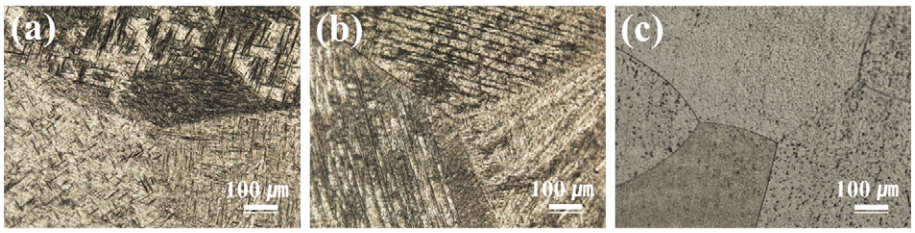

Fig. 1. OM morphologies of Ti–xNb alloys: (a) Ti–10Nb, (b) Ti–30Nb, and (c) Ti–50Nb.

chemical homogeneity using a vacuum arc-melting furnace (SVT, Korea). Heat treatment was carried out at 1000 °C for 2 h in a high-purity argon atmosphere, followed by 0 °C water quenching, to homogenize the alloys. The specimens for electrochemical experiments were prepared by abrasion with 100 grit sandpaper, followed by polishing with 2000 grit sandpaper and 0.3 μm Al_2O_3 slurry. All polished specimens were ultrasonically cleaned in acetone for 10 min and air-dried. The specimens for electrochemical treatment were cut by a diamond saw having a diameter of 10 mm and thickness of 3 mm.

Microstructures of the alloys were examined with an optical microscope (OM; Olympus BM60M, Japan). Specimens for OM observation were etched in Keller's solution consisting of 2 mL HF (1%), 3 mL

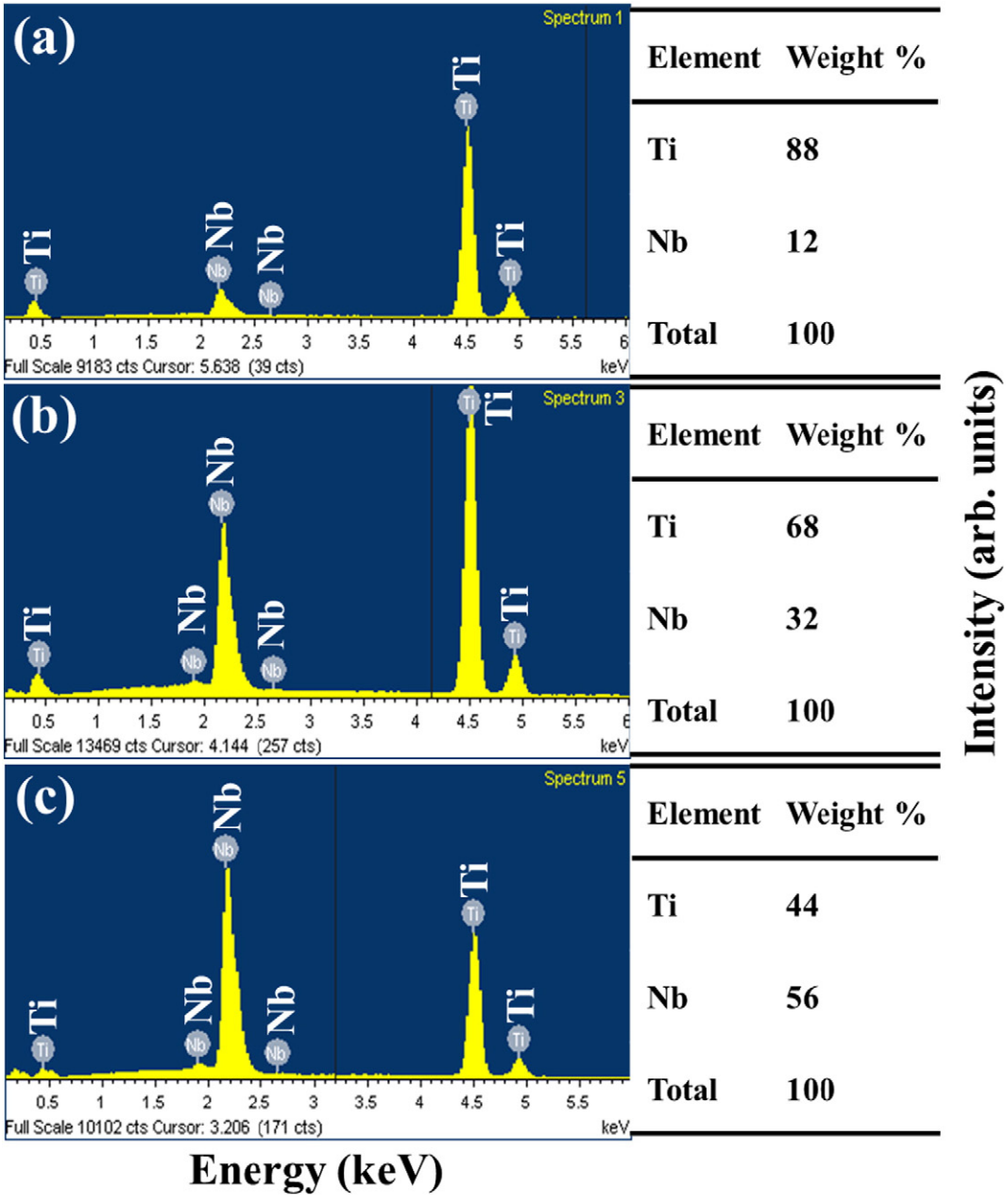

Fig. 2. EDS peaks and compositions of Ti–xNb alloys: (a) Ti–10Nb, (b) Ti–30Nb, and (c) Ti–50Nb.