Journal of Alloys and Compounds 678 (2016) 549–555

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

On the electrocrystallization of pure hydroxyapatite nanowalls on Nitinol alloy using a bipolar pulsed current

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
17 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Nitinol
Electrocrystallization
Hydroxyapatite
Monoclinic phase
Bipolar pulse current

ABSTRACT

In this study a bipolar pulsed current was used for the electrochemical deposition of calcium phosphate coatings on the Nitinol superelastic alloy. The coatings were characterized using FE-SEM, XRD, FTIR, HRTEM, and gas adsorption techniques. Results show that the electrodeposited coating is a crystalline film which is composed of pure hydroxyapatite (HA) nanowalls. According to the FTIR data, the coating is free from other metastable calcium phosphate phases like octacalcium phosphate. It was shown that both monoclinic and hexagonal phases can be detected in HRTEM images and related SAED patterns. The coating, which is deposited at direct and reverse current densities of −3.0 and 0.1 mA/cm^2 respectively, revealed a surface area of 38.5 m^2/g and ultra-fine pores were detected in the surface of the coating plates. Study on the effect of the reverse pulse current revealed that the volume of porosity is increased by increasing in the current density of the reverse pulse. Also in this condition the resulted film was composed of nanosized HA crystals. It seems that the reverse current step can influence the porosity and the structure of the coatings by dissolution of the unstable phases which are formed during direct current step of the bipolar pulse deposition.

1. Introduction

NiTi alloys have been considered as an important biomaterial since several years ago [1,2]. Metallic biomaterials which are used in human body should offer a reasonable biocompatibility especially in mechanical properties. In most other metallic implants, the elastic modulus mismatch between the implant and surrounding tissues restricts the life of implants [3]. The low difference between the elastic modulus of NiTi alloys and the human tissues makes the alloys a suitable candidate as implant materials [4].

Despite the superior properties of Nitinol alloys, there are some problems in the application of these alloys as implants especially because of the high Ni concentration and the bio inert surface of the alloy. It was shown that Ni ions leaching leads to a weak cells proliferation on the NiTi alloy [5,6]. Also, the bio inert surface of the alloy leads to the formation of a bi-film on the implants which could be a reason for the failing of implantations [7–9].

Although Calcium–Phosphate (Ca–P) based compounds offer a good medium for the attachment and growth of living body cells, they cannot be used as bulk materials in implants due to their poor mechanical properties. Using Ca–P based coatings on the surface of metallic implants would be a suitable way to achieve the both advantages of metallic implants and Ca–P compounds [10,11].

The Ca–P compounds generally include a wide range of structures with different Ca/P stoichiometries. Hydroxyapatite (HA) is the most important calcium phosphate as the major mineral in hard tissues. It was shown that hydroxyapatite shows the best biocompatibility among other Ca–P compounds [12,13]. HA can crystallize in two forms of hexagonal and monoclinic. The hexagonal form of HA is the most regular structure which has lattice parameters of $a = b = 9.4225$ (Å), $c = 6.8850$ (Å), and $\gamma = 120°$ [14]. The monoclinic form of HA is the most ordered and the thermodynamically most stable form of HA. The major difference between the monoclinic and the hexagonal HA is the orientations of the hydroxyl groups. In the hexagonal phase, the hydroxyl groups place along the *c*-axis and the adjacent groups point in opposite directions. The hydroxide ions in the monoclinic phase are pointed in the same direction in a given column, and the direction reverses in the next column; accordingly the *b*-axis is doubled in comparison with that of the hexagonal phase [15]. Considering the similar electrical properties in bone and a synthetic monoclinic HA, the

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http://dx.doi.org/10.1016/j.jallcom.2016.03.268
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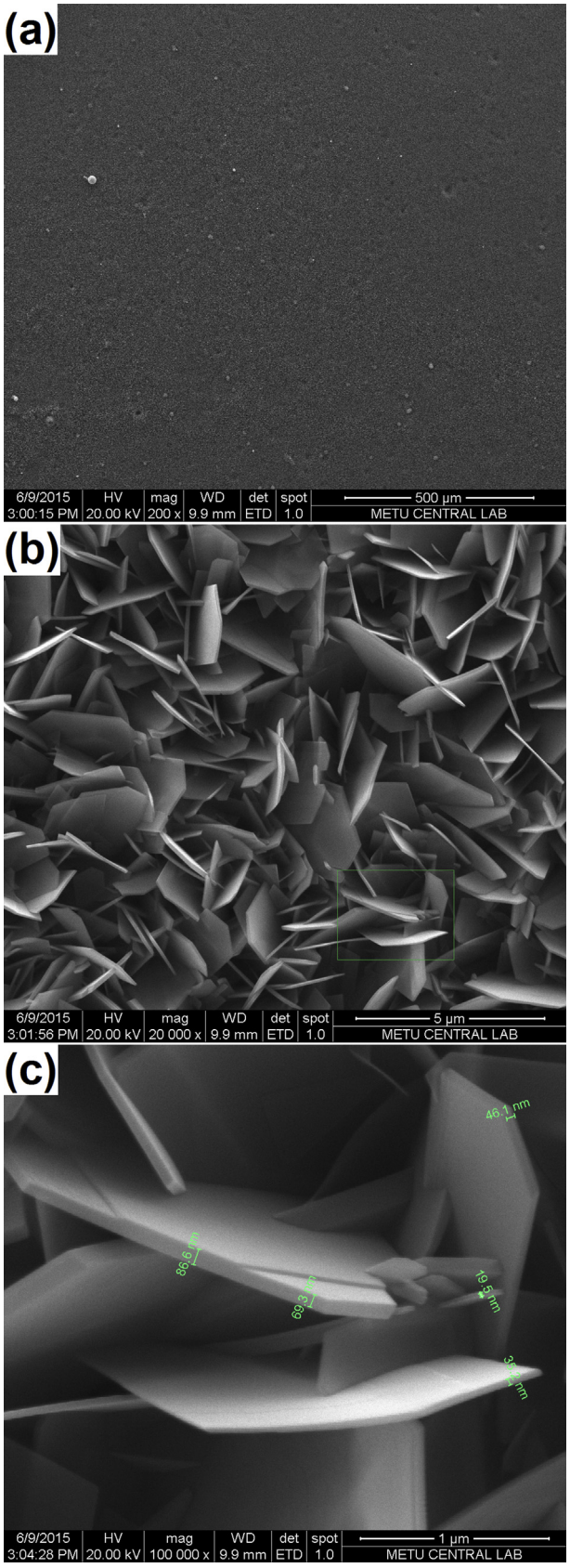

Fig. 1. (a) to (c) FE-SEM micrographs of the pulse deposited sample under direct and reverse pulse current densities of −3 and 0.1 mA/cm^2 respectively.

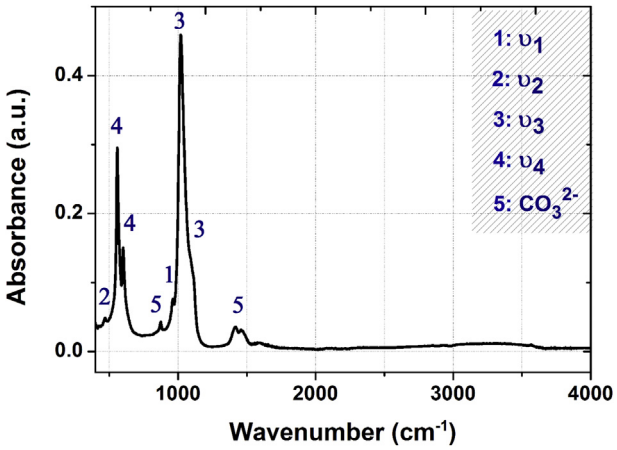

Fig. 2. FTIR spectrum of the pulse deposited sample under direct and reverse pulse current densities of −3 and 0.1 mA/cm^2 respectively.

presence of monoclinic symmetry in biological apatite is predicted [16].

Different methods have been introduced for the precipitation of Ca–P compounds [17–21]. Electrocrystallization is one of the effective methods to deposit these compounds in low temperature with controlled thickness, crystallinity and morphology [21].

It was demonstrated that the unipolar pulsed current deposition gives more stable and crystalline Ca–P coatings as compared to the direct current deposition [21,22]. Gopi et al. [21] studied the effects of a unipolar pulse deposition on the phase, composition, and morphology of Ca–P coatings on surgical grade stainless steel. It was proposed that the off part of the pulse cycle gives sufficient time for the diffusion of ions towards the substrate and favors HA formation. Wang et al. [23] used a bipolar pulsed current in the deposition of Ca–P film onto Mg–Zn–Ca alloy. The reverse current pulse with a high current density of 20 mA/cm^2 is applied to promote HA formation by dissolving Mg from the substrate. The resulted film is Ca-deficient apatite with a Ca/P ratio of 1.3.

While some contributions can be found in the literature on the synthesis of Ca–P compounds onto Nitinol alloys [24–26], pure HA film deposition by the pulse technique are not reported yet. Also, considering all published data on the electrolytic synthesis of HA, the phase analysis of HA and the monoclinic phase formation are not reported so far.

In the current work, a bipolar pulsed current was used for the synthesis of a pure HA film on Nitinol alloy. The crystal structure of the film was analyzed by XRD, selected area electron diffraction (SAED), as well as high resolution transmission electron microscopy (HRTEM). Also the gas adsorption analysis was used to investigate the porosity of coatings.

2. Experimental details

2.1. Preparation of specimens

In this work, NiTi rod with nominal composition of 50.9% Ni was used to make substrates. The rods with the diameter of 13 mm were sliced into 1 mm disks. The surface of samples was abraded with different grades of SiC papers from P80 to P600 grit and then was etched in an acid solution of 1 HF–4 NHO_3–5 H_2O for 4 min, and finally was soaked in distilled boiling water for 20 min. After each step, specimens were cleaned in acetone and then rinsed with deionized water. In order to age hardening of the bulk alloy and stabilizing the surface oxide film [27], the specimens were