



Hydroxyapatite based and anodic Titania nanotube biocomposite coatings: Fabrication, characterization and electrochemical behavior



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ABSTRACT

The main challenges of biological implants are suitable strength, adhesion, biocompatibility and corrosion resistance. This paper discusses fabrication, characterization and electrochemical investigation of anodized Ti6Al4V without and with a hydroxyapatite (HA) layer, HA/TiO₂ nanoparticles (NPs) and HA/TiO₂ nanotubes (HA/anodized). X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS) were used to characterize and compare properties of different samples. Dense HA with uniform distribution and 12.8 ± 2 MPa adhesive strength enhanced to 19.2 ± 4 MPa by the addition of TiO₂ nanoparticles and enhanced to 23.1 ± 4 MPa by the deposition of a TNT interlayer was fabricated by an anodic oxidation process. EIS analysis divulged the polarization behavior of various layers formed on a Ti6Al4V substrate. Electrochemical measurements indicated polarization passivation due to incorporation of TiO₂ nanoparticles to HA. Hydroxyapatite on a TNT layer revealed lower corrosion resistance than a HA/TiO₂ nanoparticle sample due to the vacuolar nature of TNT conformation. The passivation current density of the Ti6Al4V alloy coated with a HA/TiO₂ nanocomposite (0.125 μA/cm²) was less than 1% of the bare substrate.

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1. Introduction

Titanium and its alloys have attractive properties like strength, lightness, passivation and biocompatibility [1–5] which introduce them as appropriate materials for biomedical applications. Localized corrosion and ion release, however, are due to their detracting behaviors [6–9]. Because of inadequate bioactivity, most metallic implants need surface modification for the enhancement of bioactivity and hard-tissue osseointegration [10–14].

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is the major inorganic component of natural bone and its presence in biomedical coatings can support hard-tissue ingrowth [15–17]. Hydroxyapatite (HA) is widely used as a coating biomaterial of dental and orthopedic implants [18–22]. Nevertheless, its interfacial adhesion to its substrate is relatively weak [23,24]. Recent studies have indicated that the use of titanium oxide (TiO₂) in the coating structure can improve the adhesion and corrosion behavior of the contacting layer [14,23,25–28]. In some cases, this oxide can stand as an intermediate layer between the hydroxyapatite deposit and the substrate. A TiO₂ layer can form by anodization. Porosity presence in a TiO₂ layer can enhance HA adhesion and produce suitable cell anchorage circumstances [29–31].

Previous researchers have shown substantial improvement by direct addition of TiO₂ nanoparticles into the HA layer [25,28–30]. This has

attracted much attention due to its bonding strength, good adhesion and corrosion resistance [14,23,25,28–30]. Expectation of drastic improvements in multilayer limb behavior by TiO₂ nanoparticle addition to the HA layer has motivated us to run further in-depth research on the subject. Titanium based anodized alloys coated with HA seem beneficial for biomedical applications plus nanoparticle extra returns. In spite of all promising gains, to the best of the authors' knowledge, no comparative study has previously been made available on different HA/TiO₂ configurations deposited on a Ti6Al4V substrate. The purpose of this study is to construct, characterize and compare bioengineering properties of Ti6Al4V alloy with and without various anodization, HA deposition and HA/TiO₂ nanocomposite formation processes. In order to study the electrochemical behavior and adhesion strength, the anodized, HA deposited and HA/TiO₂ nanoparticle combined samples were compared with the untreated samples.

2. Experimental procedure

Prior to electrochemical treatments, the specimens were polished by mechanical grinding from P600 to P2000 by SiC emery paper, 0.3 and 0.05% Al₂O₃ (~200 nm size) suspensions and then diamond paste. Fig. 1 illustrates a scanning electron microscopy image of the polished Ti6Al4V alloy surface. The shiny samples were cleaned by sonication in acetone for 10 min at 60 °C, then cleaned with ethanol in an ultrasonic bath for 5 min and rinsed with deionized water. They finally were dried with a stream of flowing air.

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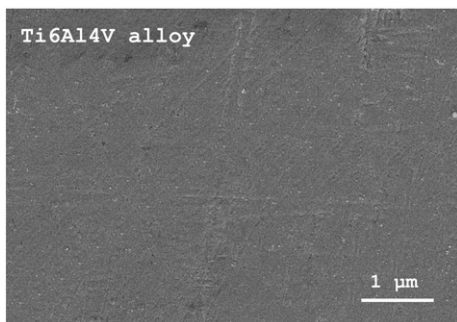


Fig. 1. Scanning electron microscopy images of the polished Ti6Al4V alloy surface.

2.1. TiO₂ nanotube production during electrochemical anodization process

Anodic oxidation was accomplished by using 1 M (NH₄)₂SO₄ electrolyte solution containing 0.5 wt.% NH₄F at the room temperature. The electrochemical setup consisted of a conventional two-electrode configuration with a SS 316L plate with a size of 6 × 2.5 cm and a thickness of 1 mm working as a cathode and a Ti6Al4V strip as anode. The electrochemical process involved a potential ramp from an open circuit potential (OCP) to 25 V with a sweeping rate of 25 mV/s followed by holding at the final potential for 2700 s. The samples were rinsed with deionized water and finally dried in flowing air.

2.2. Pulse electrodeposition of calcium phosphate

For electrochemical coating, both anodized and bare Ti6Al4V plates were placed in the cathode position (as substrate of HA/anodized Ti6Al4V and HA coatings, respectively) with a SS 316L plate functioning as the counter electrode. The electrolyte contained 0.042 M Ca(NO₃)₂, 0.025 M (NH₄)₂HPO₄, 0.1 M NaNO₃ and 2000 ppm H₂O₂. NaNO₃ was added to the electrolyte for the improvement of the ionic strength and H₂O₂ was added to suppress the H₂ evolution for dense deposit formation. The electrolyte pH was adjusted in the range of 5.5 to 6.5 by the addition of sodium hydroxide (NaOH) and nitric acid (HNO₃) at 60 °C.

To fabricate a HA/TiO₂ nanocomposite, 10 g/L TiO₂ powder with an irregular shape in the range of 80–120 nm (Merck Co. Ltd.) was also added to the electrolyte solution. In order to achieve a uniform and adherent deposition, a current density of $J_{\text{on}} = 1 \text{ mA/cm}^2$ was applied for 2 s (t_{on}), a resting time of $t_{\text{off}} = 5 \text{ s}$ ($J_{\text{off}} = 0 \text{ mA/cm}^2$) was implemented and the procedure was periodically repeated. The electrolyte temperature was adjusted at 60 °C, total procedure time was 60 min, and deposition process was done using a potentiostat/galvanostat pulsing current produced by a pulse rectifier (SL 2/25 PCS, I.R. Iran) as illustrated

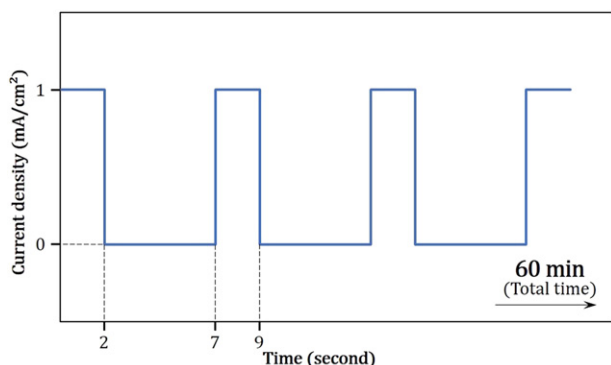


Fig. 2. Pulsating regime for electrodeposition of hydroxyapatite. Deposition at current density of $J_{\text{on}} = 1 \text{ mA/cm}^2$ for $t_{\text{on}} = 2 \text{ s}$ followed by breaking time of $t_{\text{off}} = 5 \text{ s}$ at $J_{\text{off}} = 0 \text{ mA/cm}^2$ for a total period of 60 min.

in Fig. 2. It should be noted that the prepared solution was dispersed by ultrasonic microwaves for 2 h in order to achieve a homogeneous suspension and stirred during the electrodeposition process in order to fabricate uniform layers and homogeneous deposition of TiO₂ nanoparticles into the hydroxyapatite matrix.

At the end of deposition, the sample was dried and then heated up to 120 °C by a 3 °C/min temperature rate. It was held at 120 °C for 2 h and then at 480 °C for 2 h, again. The purpose of heat treatment was the enhancement of calcium phosphate crystallinity and phase transformation of TiO₂ from amorphous to anatase configuration [32–35].

2.3. Bonding strength

The bonding strength of a deposit with substrate was measured according to ASTM F1044-05 standard. The uniaxial tensile load was applied to the deposit which was bonded to the substrate surface with the epoxy resin using an electromechanical testing system (Model 5565, Instron Co.) at a crosshead speed of 10 mm/min. The size of the samples used for the bonding strength tests was 30 × 30 × 1 mm. Five measurements were done for each deposit and the mean value was reported to determine the bonding strength.

2.4. Electrochemical behavior in body-simulated fluid (SBF) solution

Potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) tests were carried out by a potentiostat apparatus (Autolab, PGSTAT302N) and EG&G (model 273A) respectively having a conventional three-electrode cell (saturated calomel electrode as reference, graphite plate (30 × 20 × 2 mm in size) as counter electrode and test specimen as the working electrode) for determination of the electrochemical behavior of the samples with and without surface modification. The working electrode consisted of a disk having an active surface area of 1 cm² and all other areas being isolated by an electrolyte-proof ring.

Potentiodynamic polarization tests were performed in the potential range of −0.8 to 1.2 V (vs. Ag/AgCl) at a scan rate of 1 mV/s. EIS studies were carried out in the frequency range of 10^{−2}–10⁵ Hz by using a 10 mV peak-to-peak sinusoidal potential amplitude. For acquiring spectra at the OCP, seven points per frequency decade was recorded. The data was analyzed by CorrView and ZSimpWin V3.40 software. Reproducibility check was done by three times repetition of the experiments. The test electrolyte was simulated body fluid (SBF) having pH = 7.4 and chemical composition indicated in Table 1. Prior to the electrochemical measurement, each sample was immersed into SBF for 30 min in order for OCP establishment.

2.5. Morphology and phase structure characterizations

Morphologies of the surface coatings were inspected by high vacuum FE-SEM model SIGMA/VP ZEISS. Before FE-SEM observation, Au was sputtered on the surface of the specimens. For each coating, three FE-SEM images were taken. Thickness measurements were done at four

Table 1

Chemical composition of the simulated body fluid (SBF) used in the electrochemical tests.

Component	Concentration (g/L)
NaCl	8.035
(CH ₂ OH) ₃ CNH ₂ (Tris)	6.118
NaHCO ₃	0.355
MgCl ₂ ·2H ₂ O	0.311
CaCl ₂	0.292
K ₂ HPO ₄ ·3H ₂ O	0.231
KCl	0.225
Na ₂ SO ₄	0.072
HCl (1 M)	39 mL/L

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