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HA coating fabricated by electrochemical deposition on modified Ti6Al4V alloy

Dai-Hua He [a,*], Pu Wang [b], Ping Liu [a], Xin-Kuan Liu [a], Feng-Cang Ma [a], Jun Zhao [c]

[a] School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[b] School of Mechanical Engineering, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[c] Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, PR China

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ABSTRACT

In the paper, Ti6Al4V substrates have been pretreated with sodium hydroxide (NaOH) solution. After that, hydroxyapatite (HA) is deposited on the Ti6Al4V surface by electrochemical methods. The aim of this study is to investigate the influences of current density on the coating compositions, microstructure, and bonding strength between coating and substrate. The results show that the composition of the HA coating and the grain size remained relatively unchanged with the variations of current density during electrochemical deposition. When the value of electrochemical deposition current density is 2.5 mA/cm^2, the HA coating has the largest thickness, and the bonding strength is near 18 MPa. The experiments of the samples being immersed into simulated body fluid estimate that the HA coating promotes the deposition of calcium phosphate. The formation mechanism of HA coating on modified Ti6Al4V deposited by electrochemical method is discussed.

1. Introduction

Ti6Al4V has become the primary material of medical implants owing to its excellent biocompatibility and mechanical properties for load bearing orthopedic applications [1]. However, the bioactivity of titanium alloy is poor [2]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) has excellent biocompatibility and has been recognized as osteoconductive [3,4]. Natural hydroxyapatite represents about 70% of the natural human bones. It has been clinically applied in orthopedics and dentistry. HA has an ability to accelerate bone growth and attachment to the surface of implants. Moreover, it can improve the fixation and lifetime of the implants. However, the mechanical strength of HA is too poor to be used in load-bearing applications. Therefore, HA coatings on bio-inert metallic prostheses have been extensively investigated in order to obtain medical implants combining the chemical and biological properties of hydroxyapatite with the mechanical properties of titanium alloy [4–6]. Several methods have been reported to fabricate HA coating on implant surfaces, such as plasma spraying [8,10–12,14], sputtering process [13,14], pulsed laser deposition [15], sol–gel [16], electrophoretic method [17], and electrochemical deposition [18–24].

The electrochemical deposition process has many advantages: highly irregular objects can be coated relatively quickly at low temperatures; the thickness, crystallinity, phase purity and chemical composition of coatings can be well controlled during this process [25]. However, the low bonding strength of pure HA coating fabricated by traditional electrochemical deposition method affects the long-term stability of HA coating and the interface between the bone and the implant [26].

Kim et al. [27] treated pure Ti, Ti–6Al–4V, Ti–6Al–2Nb–Ta and Ti–15Mo–5Zr–3Al substrates with 10 M NaOH aqueous solution at 60 °C for 1–24 h and subsequently heated them at 600 °C. The results suggested that the treated substrates induced the formation of a dense and uniform bonelike apatite layer. Kokubo et al. [28,29] conducted research on alkaline-treated and subsequently heat-treated titanium alloy and then soaked the substrates in simulated body fluid (SBF) to study the apatite formation. They showed that the alkaline and heat treatment could accelerate the formation of a bonelike apatite layer on the titanium alloy surface soaked in SBF.

In the present paper, Ti6Al4V was immersed in 8 M NaOH for 48 h, and then HA coatings were deposited on the modified substrate surface by electrochemical method. The aim of immersing the substrate is to modify the substrate surface. The influences of current density during the electrochemical deposition on the HA coating are investigated. The

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* Corresponding author.
E-mail addresses: hedh21@163.com (D.-H. He), 1017935798@qq.com (P. Wang), liuping@usst.edu.cn (P. Liu), xinkuanliu@usst.edu.cn (X.-K. Liu), mafengcang@163.com (F.-C. Ma), zhaojun@mail.sic.ac.cn (J. Zhao).

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formation mechanism of HA coating deposited by electrochemical method on the special surface is also discussed.

2. Experimental

Commercially available Ti6Al4V alloy with a thickness of 3 mm was used as the substrate. The specimens were cut into pieces of 25 mm × 25 mm by an electric discharge machine. In order to remove the surface oxides, all specimens were polished with sandpaper. The specimens were cleaned with acetone and alcohol, rinsed by distilled water, and air-dried at room temperature. Subsequently, the specimens were immersed in 8 M NaOH solution at 60 °C for 48 h. After alkali treatment, the substrates were washed with distilled water, and dried at 40 °C for 24 h in an air atmosphere.

The electrochemical deposition method was applied to deposit the HA coating. The electrolyte contained 0.042 mol/L $Ca(NO_3)_2 \cdot 4H_2O$, 0.025 mol/L $NH_4H_2PO_4$, and 1.5×10^{-3} mol/L EDTA-2Na. The cathode and anode were the alkali-treated Ti6Al4V plate and a platinum plate, respectively. The electrolyte temperature was 90 °C, and the deposition time was 60 min. The current density values were 1.25 mA/cm^2, 1.87 mA/cm^2, 2.50 mA/cm^2, 3.12 mA/cm^2 and 3.61 mA/cm^2.

A Quanta FEG-450 field emission scanning electron microscope (FESEM) was used to observe the microstructures of the alkali-treated substrate surface and the HA coating deposited by electrochemical deposition method. An X-ray diffractometer (XRD) was used to study the phase content of the coating. The thickness of the HA coating was measured by a step profiler (AMBIOS Technology Inc., XP-1). The bonding strengths between the titanium alloy substrate surface and the HA coatings were tested using the standard tensile adhesion test (ASTM-C633) carried out with a 50 kN universal testing machine. The in vitro bioactivity of the HA coating was estimated by immersing the samples in simulated body fluid (SBF). The tests were carried out in a water bath at 37 °C. The SBF was refreshed every day. The samples were taken out after 3 days, cleaned in deionized water and dried at room temperature before characterization. The microstructures and the content were observed by FESEM, XRD and FT-IR.

3. Results

Fig. 1 shows the SEM micrographs of Ti6Al4V alloy surfaces before and after immersion in 8 mol/L NaOH for 48 h. The surfaces reveal a porous microstructure, consisting of a three-dimensional network of tangled nanotubes or nanofibers.

Fig. 2 demonstrates the surface morphology of HA coatings deposited by electrochemical method for 60 min at different current densities. The temperature of the electrolyte was 90 °C. The results indicate that the hydroxyapatite coatings are lamellar when the current density is in the range of 1.25–3.61 mA/cm^2. HA crystals have uniform size at the same current density. The crystal size changes little with increasing current density. The crystal structures change from porous to dense and then back to porous with increasing current density. The reasons may be that the larger current density increases the cathodic hydrogen evolution reaction, and the escaping hydrogen gas leads to the broken and porous structures of the HA layer. When the current density is 2.50 mA/cm^2, the structure is much more dense.

The specimens were hydrothermally treated at 160 °C before XRD analyses [30]. Fig. 3 shows the XRD pattern of HA coatings deposited by electrochemical method with different current densities. The XRD pattern indicates that HA crystals were successfully fabricated by electrochemical deposition on the modified substrates according to JCPDS card for HA (JCPDS 09-0432). The intensities of the HA peaks are similar when the coatings were processed at 160 °C. The results show that the preferable growth face of HA crystals is (002).

Fig. 4 represents the dependence of the HA coating thickness on the depositing current density. The thickness increases first, and then decreases with increasing current density. The maximum thickness is 21.8 μm at the current density of 2.50 mA/cm^2.

Fig. 5 shows the bonding strengths between HA coatings and the substrates. The results indicate that the maximum bonding strength value is about 18 MPa when the current density is 2.5 mA/cm^2. The bonding strength will be reduced when the current density exceeds 2.5 mA/cm^2.

The SEM images of samples after the immersing test in SBF are shown in Fig. 6. It can be that the plate-like crystallites become round owing to precipitation in varying degrees by newly grown secondary HA. The phenomenon suggests that the HA coating deposited on the modified titanium surface may possess promising bioactivity. The HA coating with large spherical cauliflower-like structure appeared on the samples deposited at the current density of 2.5 mA/cm^2, which suggested that the HA coating fabricated in the parameter had better inductivity. Fig. 7 shows the XRD patterns of the sample deposited with 2.5 mA/cm^2 current density. The results indicate that the phase contents are hydroxyapatite and calcium oxalate hydrate according to the JCPDS cards (JCPDS 09-0432 and JCPDS 20-0233). Fig. 8 is the FT-IR spectra of the sample deposited with 2.5 mA/cm^2 current density. The absorption band characteristics for HA have been largely reported in the literature [31]. The internal modes corresponding to PO_4^{3-} groups occur at: 603 cm^{-1} and 562 cm^{-1} (ν_4), 470 cm^{-1} (ν_2), 1078 cm^{-1} and 1028 cm^{-1} (ν_3). The stretching and bending modes of the OH^- groups appears at: 3571 cm^{-1} and 1641 cm^{-1}. CO_3^{2-} presents typical bands in the region 1500–1400 cm^{-1}. So the bands at 1463 cm^{-1} and 1420 cm^{-1} are the CO_3^{2-} groups. The low intensity centered around 871 cm^{-1} is the CO_3^{2-} group [32,33]. Refer to the literature [34], the

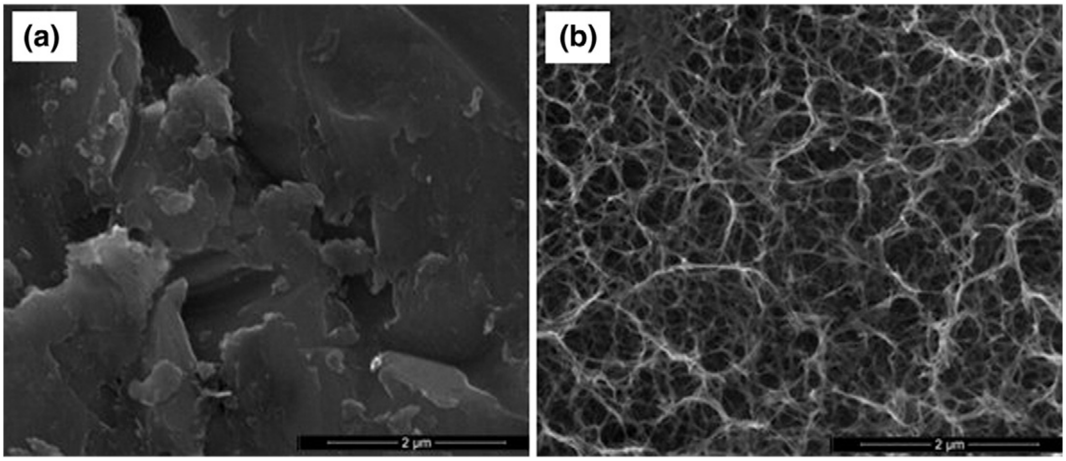

Fig. 1. SEM micrographs of Ti6Al4V surfaces before and after NaOH immersion. a—before immersion, b—after immersion.