Acta Biomaterialia 6 (2010) 1584–1590

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Nanohydroxyapatite coating on a titanium–niobium alloy by a hydrothermal process

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ARTICLE INFO

Article history:
Received 29 June 2009
Received in revised form 16 September 2009
Accepted 9 October 2009
Available online 14 October 2009

Keywords:
Titanium–niobium alloy
Nanohydroxyapatite
Coating
Hydrothermal process

ABSTRACT

A novel one-step hydrothermal coating process was used to produce nanohydroxyapatite (nano-HA) coating on a titanium–niobium (TiNb) alloy substrate in a newly designed solution containing calcium and phosphate ions. The morphology of the coating was studied using scanning electron microscopy. The phase identification of the coating was carried out using X-ray diffraction, attenuated total reflectance Fourier transform infrared spectroscopy and transmission electron microscopy. The reaction between the surface of TiNb alloy and the solution during the hydrothermal process was studied by X-ray photoelectron spectroscopy. Results show that the coating formed on the surface of TiNb alloy was composed of nano-HA particles. During the hydrothermal process, TiO_2 and Nb_2O_5 formed on the TiNb alloy surface and hydrated to $Ti(OH)_4$ and $Nb(OH)_5$, respectively. Calcium phosphate nucleated and grew into a layer of nano-HA particles on the surface of TiNb alloy under the hydrothermal conditions. The crystallinity of the nano-HA coating was improved with the increase in hydrothermal treatment temperature and time duration. Nano-HA coating with good crystallinity was produced on the TiNb alloy via the hydrothermal process at a temperature of 200 °C for 12 h.

1. Introduction

Titanium and its alloys are widely used as load-bearing dental and orthopaedic implant materials due to their superior biocompatibility, appropriate mechanical properties and high corrosion resistance in physiological environment [1,2]. In particular, among the Ti alloys, Ti-based shape memory alloys (SMAs) are fascinating materials for implant applications as their unique shape memory property and superelasticity provide the possibility of preparing self-expanding, self-compressing and other functional implants [3]. Although a relatively wide variety of alloys exhibit shape memory properties, Ni-free Ti-based SMAs with transformation temperatures near the human body temperature (~37 °C), such as Ti–26Nb (at.%), Ti–22Nb–6Zr (at.%) [4] and Ti–24Nb–2Zr–7.5Sn (wt.%) [5], are favourable materials for implant applications because these alloys avoid Ni hypersensitivity and have the potential to activate their shape memory properties at body temperature.

Ti alloys are generally recognized as bioinert materials due to the lack of direct chemical bonding to the host bone tissues after implantation [6]. To overcome this drawback, hydroxyapatite (HA) has been applied as a coating material on Ti alloy implants for hard tissue applications because of its chemical similarity to the inorganic component of human bone, capability of conducting bone formation and strong affinity to the surrounding bone tissues [7–10].

Recent studies have shown that cells in the human body are predisposed to interact with nanostructured surfaces, such as surfaces of nanoscale roughness [11] and surfaces with immobilized nanoparticles [12]. Thus nanostructures on implant surfaces, e.g. a coating composed of nano-HA particles on Ti and Ti alloys, have aroused increasing research interest in the biomedical field.

Among the current coating techniques, sputtering [13], the sol–gel process [14], the electrophoretic method [15], E-beam deposition [16] and the biomimetic process [17–19] are used to produce nano-HA coatings on the surface of metallic implants. Sputtering method exhibits low effectiveness and high operating cost [20]. In the cases of the sol–gel process, the electrophoretic method and E-beam deposition, a subsequent heat treatment process is necessary to crystallize the HA coatings at a temperature usually higher than 500 °C [14–16]. Because of the differences in the thermal properties between the coatings and the substrates, the heat treatment process usually causes thermal stress, which leads to cracking within the coating layer [21]. Furthermore, the heat treatment process may disturb the microstructures and mechanical properties of the metallic substrates, especially SMAs, which are sensitive to heat treatment [22]. The biomimetic method is based on the nucleation and growth of calcium phosphate on a substrate soaked in simulated body fluid (SBF). SBF solutions are prepared with the aim of simulating the ion concentrations in the human blood plasma. Besides Ca^{2+} and HPO_4^{2-}

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1742-7061/$ - see front matter
doi:10.1016/j.actbio.2009.10.016

ions, several other kinds of ions, i.e. Na^+, K^+, Mg^{2+}, Cl^-, HCO_3^-, CO_3^{2-} and SO_4^{2-} ions, are present in SBF. Usually, the biomimetic method requires several weeks to form an HA layer on the surface of an implant [17–19]. In other words, this method is extremely time-consuming. On the other hand, chemical pre-treatments of the substrate, such as acid treatment, alkali-heat treatment and peroxide treatment [23–25], are needed to produce hydroxyl groups (–OH) on the surface, thus inducing the formation of HA on the substrate surface.

In the present study, a novel Ca/P solution with an ionic composition much simpler than that of SBF was designed and a one-step quick hydrothermal process was attempted for the surface coating of an Ni-free titanium–niobium (TiNb) SMA. Since low-temperature treatment is an essential requirement for the surface modification of Ti-based SMA implants and a significant number of chemical systems in the form of powders and films can be synthesized at a treatment temperature not higher than 200 °C [26], the upper temperature limit of the hydrothermal treatment in this study was set at 200 °C. TiNb alloy samples without chemical pre-treatment were subjected to the hydrothermal process to produce a nano-HA coating on the alloy surface. The parameters used in the hydrothermal process and the resultant surface coating were investigated.

2. Materials and methods

2.1. Materials

TiNb alloy samples were prepared by powder metallurgy [27–29]. Commercially available elemental metal powders of Ti (purity 99.7%, particle size 325 mesh) and Nb (purity 99.8%, particle size 325 mesh) were used as starting materials. The powder handling was conducted in argon gas atmosphere. Ti and Nb powders with a nominal composition of Ti–26Nb (at.%) were blended together using a planetary ball-milling machine (Retsch PM400) at 100 rpm for 2 h. The weight ratio of ball to powder was 2:1. TiNb discs with a diameter of 10 mm and a thickness of 2 mm were prepared by consolidating the metal powder mixture at 200 MPa and sintering at 1200 °C for 5 h in a vacuum of 10^{-5}–10^{-6} Torr (CAMCo G-VAC 12). The surfaces of the sintered TiNb discs were ground using silicon carbide papers to a 1200 grit finish and subsequently cleaned ultrasonically in acetone, ethanol and distilled water for 10 min at each step.

2.2. Hydrothermal processing

A buffer solution was first prepared using reagent grade chemicals. This was done by dissolving 2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid (HEPES, purity 99.5%) in a 0.2 M NaOH aqueous solution. After that, K_2HPO_4 (purity 99%) and $CaCl_2$ (purity 99.9%) were successively dissolved in the buffer solution. Thus a solution containing Ca^{2+} ions and HPO_4^{2-} ions (Ca/P solution) was obtained. The Ca^{2+} and HPO_4^{2-} ion concentrations in the Ca/P solution were 1.67 and 1.00 mM, respectively. The pH value of the Ca/P solution was adjusted to 7.4 by titrating 1.0 M NaOH aqueous solution. The Ca/P solution was supersaturated with respect to HA [30].

The TiNb alloy discs were put into a 100 ml Teflon container and 70 ml of Ca/P solution was added. The Teflon container was then sealed in a stainless steel cell and the TiNb alloy samples were hydrothermally treated in the Ca/P solution at 80, 120, 160 and 200 °C for 5, 8 and 12 h.

2.3. Characterization of hydrothermally processed TiNb samples

The hydrothermally treated samples were ultrasonically washed in distilled water for 5 min, then dried at 50 °C for 24 h for further characterization. The morphology and phase structure of the coating were analysed using scanning electron microscopy (SEM), X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and transmission electron microscopy (TEM). SEM examinations were carried out using a scanning electron microscope with a voltage of 5 kV and a working distance of 5 mm (Zeiss Gemini Supra 55 VP). XRD analysis was done using a X-ray diffractometer with Cu K_α incident radiation (1.542 Å) at 40 kV and 30 mA (Philips PW1729). The diffraction patterns were collected at room temperature over the 2θ range of 20–55° with a step size of 0.01° and an acquisition time of 1 s per step. ATR-FTIR spectra of the coatings were measured on an FTIR spectrometer using a single reflection horizontal ATR accessory (Bruker Vertex 70). Each spectrum was collected in the range of 1300–500 cm^{-1} by cumulating 32 scans at a resolution of 4 cm^{-1}. The baseline was corrected for all spectra using the Bruker software. TEM studies were carried out on a JEOL JEM-2100 transmission electron microscope operated at 200 kV. The reaction between the surface of the TiNb alloy and the solution during the hydrothermal process was studied by X-ray photoelectron spectroscopy (XPS) using a spectroscope equipped with a non-monochromatic Mg K_α (1253.6 eV) X-ray source and a hemispherical electron energy analyser (VG Microlab 310F). All the regional XPS spectra were calibrated with the binding energy of the adventitious C 1s peak (284.6 eV), and a Shirley-type background was subtracted.

3. Results

Surface observation revealed that the temperature of the hydrothermal process played a critical role in the coating formation. No deposit was observed on the surfaces of TiNb alloy after hydrothermal treatment at 80 and 120 °C for a time from 5 to 12 h. Some particles started to form on the surface of TiNb alloy after hydrothermal treatment at the temperature of 160 °C for 5 h, and the number of the particles increased with time. Fig. 1 shows the SEM images of the surface morphologies of the TiNb alloy samples after hydrothermal treatment at 160 and 200 °C for 5, 8 and 12 h. It can be seen from Fig. 1(a) and (b) that a few scattered particles formed on the TiNb surface after hydrothermal treatments at 160 °C for 5 and 8 h. A dense layer of the particles formed on the surface of the TiNb alloy after hydrothermal treatment at 160 °C for 12 h, as shown in Fig. 1(c). Increasing the temperature to 200 °C, dense layers of particles formed on all the TiNb alloy samples hydrothermally treated for 5, 8 and 12 h, as shown in Fig. 1(d)–(f).

The particles exhibited polygonal shapes. Determined from the SEM micrographs, the mean sizes of the particles formed after hydrothermal treatment at 160 °C for 12 h and at 200 °C for 5, 8 and 12 h were 42, 40, 43 and 45 nm, respectively. In other words, there was no obvious change in the particle size with increasing hydrothermal treatment temperature and time duration. Fig. 2 shows the thickness of the HA coating formed on the surface of the TiNb alloy after hydrothermal treatment at 200 °C for 12 h. It can be seen that the thickness of the coating was in the range of 50–200 nm.

The XRD patterns of the coatings formed on the surfaces of the TiNb alloy after hydrothermal treatments at 160 °C for 12 h and 200 °C for 5, 8 and 12 h are shown in Fig. 3. The weak and broad reflection peaks are attributable to HA (designed as H in Fig. 3); the strong peaks belong to the TiNb alloy substrate (designed as S in Fig. 3). No obvious change in the intensity of the HA peaks was observed.

Fig. 4 shows the ATR-FTIR spectra of the coatings formed after the hydrothermal treatments at 160 and 200 °C for 12 h. The