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Characterization and biostability of HA/Ti6Al4V ACL anchor prepared by simple heat-treatment

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Abstract

Here, we report a simple heat-treatment process to prepare hydroxyapatite (HA)-coated Ti6Al4V anterior cruciate ligament (ACL) anchor that has good hard tissue compatibility and biostability. Heat treatment was carried out for 1.5 h at temperature range of 700–900 °C. Morphological characterization showed rougher surface and larger pore spaces as the heat treatment temperature was increased. The Ti6Al4V heat-treated at 800 °C had the highest diffused titanium phosphide formation, thus making it high in biocompatibility. For in vivo test, the most bone integration ability was obtained for heat-treatment at 800 and 900 °C. Furthermore, the HA/Ti6Al4V ACL anchor heat-treated at 800 °C had the highest amount of new bone formation. The present results suggest that an implant with complex shape like an ACL anchor could be prepared and used with an easy and low-cost technique by simple heat treatment surface modification method after dip-coating with HA.

Keywords: B. Interfaces; B. Surfaces; E. Biomedical applications

1. Introduction

Titanium-based materials are popularly used for implants by virtue of their inertness in biological media. However, when they are exposed to severe loading or shear stress, the oxide film of titanium can deteriorate and dissolve, thereby exposing the unprotected metal to corrosion. When the stable oxide films are removed by corrosion, the body fluids could not regenerate them, which present a problem due to the dissolution of metal ions [1–3]. The amount of released metal ions is reported to increase for prosthesis with rough and porous surfaces. In long term implantation time based from clinical experiments, the accumulation of metal ions in the surrounding tissues could create adverse effects to bone tissue growth [2,4,5]. To address the problem of corrosion and metal ion dissolution, surface treatment of titanium (Ti) alloy is usually employed [1]. A lot of research have been carried out to modify the surface of Ti materials and to produce biomaterials with better compatibility with living tissues. Some of the surface treatment methods include anodic oxidation, pulse raiser deposition, chemical vapor deposition, plasma spraying, ion implantation, electrophoresis precipitation and annealing, and hot isostatic pressing (HiP) [6–9]. Among the materials used for coating, hydroxyapatite (HA) has gained attention as coating material on titanium surfaces because of its close resemblance to the natural minerals of bones and teeth [10], and it minimizes foreign body reaction to the metals, thereby allowing osteoconductive properties for direct bone bonding [11,12]. Significant research activities have been associated with the development of HA coatings.

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Kim and Ducheyne [13] reported that a stable and bone-bonding Ti phosphide (TiP) layer at the HA–Ti interface can be obtained by a vacuum sintering process of electrophoretically deposited HA coating on titanium alloys. One widely accepted method for depositing HA coatings on titanium-based implants is plasma spraying, but it suffers some drawbacks such as high-temperature process and difficulty in coating HA evenly. Furthermore, plasma-sprayed HA coating is reported to have problems in its long term stability due to absorption of the implant [14]. The plasma-spraying technique is also not effective for coating tiny dental implants with a complex shape [15]. To overcome these drawbacks, many HA coating processes have been investigated with the aim of improving the long term hard tissue compatibility and biostability of the HA-coated implant material, and providing a simple and economical coating process that can be used for complex-shape implants.

Here, a low-cost and simple surface modification technique by heat treatment of titanium alloy material was studied in order to achieve stable bone bonding at the interface between bone and titanium alloy implant. In the present study, a new anterior cruciate ligament (ACL) anchor made of titanium alloy (i.e., Ti6Al4V) was investigated for its hard tissue compatibility and biostability. An ACL anchor is a device that is designed for artificial ligament fixation between the femur and tibia as a substitute for an injured and ruptured ligament. The present ACL anchor made of Ti6Al4V was dip-coated with HA paste and was subjected to heat treatment. Ti6Al4V has higher mechanical strength than pure titanium (Ti) but is also known to cause an increase in stress shielding because of its higher modulus of elasticity [16]. In this paper, a dip-coating technique was used to coat the Ti6Al4V ACL anchor with HA paste (referred herein as HA/Ti6Al4V) instead of using HA powder, and was subjected to heat-treatment at different temperatures (i.e., 700–900 °C). The objectives of the present study were to investigate the physico-chemical surface properties of a heat-treated HA/Ti6Al4V ACL anchor, and to determine its hard tissue compatibility and biostability.

2. Materials and methods

2.1. Specimen preparation

Cylindrical specimens (Grade 2, ASTM F67, length = 5 mm and diameter = 6 mm) were used for the investigation of the surface properties of commercial grade Ti6Al4V. The cylindrical specimens were mechanically polished in sequence by SiC grit papers (# 1200, # 2000) and then with alumina powder (0.3 μm, 0.05 μm), and then ultrasonically cleaned three times in biotergent and distilled water in accordance with the standard procedures for metallic implant devices [17,18]. The specimens were coated with HA ($Ca_5(OH)(PO_4)_3$, MW = 502.31 g mol^{-1}, Fluka Biochemika Sigma Aldrich, No. 55497) to an approximately 200 μm in thickness by dipping them in an HA paste (mixture of 0.06 g HA and 1 ml distilled water) for 3–5 min and subsequently dried in ambient condition. Heat-treatment of the uncoated and HA-coated specimens was carried out for 1.5 h under protective Argon atmosphere in vacuum (10^{-2} Torr) at different temperatures: 700, 800, 850, and 900 °C. The adhered HA layers on the metal surfaces were then exfoliated with strong water jet spray, and the specimens were dried on a clean bench.

2.2. Characterization and measurement

The surface morphology and structure of the specimens were characterized by scanning electron microscopy (SEM, Hitachi X-650, Japan), atomic force microscopy (AFM, Autoprobe LS, PSI, USA), X-ray diffraction (XRD, Rigaku D/MAX-IIIA, Japan), and scanning Auger electron spectroscopy (SAES, VG Escalab 210, UK). Typical SAES instrument conditions for the interface analysis were: vacuum $< 6 \times 10^{-11}$ Torr, 6 keV electron beam energy, and 0.3 μA/(500 × 500 μm^2) electron beam current density. The tensile strength and hardness of the heat-treated Ti6Al4V specimens ($n = 5$) were measured by Instron mechanical tester and Vicker's hardness tester, respectively.

2.3. In vivo test

In order to evaluate the in vivo behavior of the heat-treated HA/Ti6Al4V samples, the same dip-coating preparation and heat-treatment procedure as stated above were carried out using an ACL anchor specimen (Fig. 1a). The design parameters and initial tests of the present ACL anchor are reported in our previous study [19]. The in vivo test was divided into the bone integration and biological stability tests. For bone integration test, nine adult New Zealand rabbits all aged 9 months old were used for experiments. They were anesthesized with intramuscular injections of Ketamine (10 mg/kg of animal weight) and Rompun (0.15 mg/kg of animal weight). Additionally, 1 ml of 2% Lidocaine (1:100,000 epinephrine) was administered to the cortical bone where the ACL anchor was to be inserted. Four implant specimens were implanted into the cortical bone of each rabbit. The operation was conducted according to the surgical protocol of Branemark's implant system. The round drill, 2.0-mm twist drill, 2.7-mm pilot drill, and 3.0-mm twist drill were used consecutively, including careful drilling with a low rotary drill (never exceeding 2000 rpm) and profused saline cooling. After four weeks of insertion, the rabbits were sacrificed with a fatal amount of pentobarbital injection. Immediately after sacrifice, each specimen was subjected to a removal torque test using a torque gauge instrument (Shinsung Co., Korea).

Moreover, biological stability test was conducted in order to evaluate the cytotoxicity and inflammatory reaction of the heat-treated ACL anchors by implanting them into the cortical bone of the femur of a dog under local anesthesia. Blood tests, which include complete blood count (CBC) and chemistry screening (CS), were conducted for every two weeks and after six weeks, the dog was euthanized by intravenous administration of