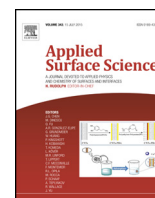




Contents lists available at ScienceDirect

Applied Surface Science

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



Electrochemically designed interfaces: Hydroxyapatite coated macro-mesoporous titania surfaces

F.S. Utku^{a,*}, E. Seckin^b, G. Goller^b, C. Tamerler^c, M. Urgen^b

^a Yeditepe University, Department of Biomedical Engineering, Istanbul, Turkey

^b Department of Metallurgical & Materials Engineering, Istanbul Technical University, Istanbul 06800, Turkey

^c Department of Mechanical Engineering and Bioengineering Research Center, University of Kansas, Lawrence, KS 66045, USA

ARTICLE INFO

Article history:

Received 31 October 2014

Received in revised form 18 April 2015

Accepted 18 April 2015

Available online xxx

Keywords:

Macro-mesoporous titania
Pulsed electrochemical deposition
Hydroxyapatite coating
Dual-acid polishing
Surface functionalization

ABSTRACT

Titanium-based implants are key weight-bearing materials in biomedical engineering due to their excellent bulk mechanical properties and biocompatibility. Designing tissue-material interfaces of titanium implants is essential for an increase in osteointegration of engineered implant materials. Surface morphology is a crucial determinant in the construction of biocompatible and osteointegrative orthopedic and dental implants. Biomimicry of the structural features of bone, specifically its macro-to-mesoporosity, may enable the bone cells to osteointegrate, attain and maintain a physiological strain level. In this study, the surface chemistry and morphology of commercially pure titanium plates were modified using electrochemistry. Titanium oxide substrates were prepared by dual acid polishing and alkaline anodization using 0.1 M KOH in an electrochemical cell with a stainless steel cathode and an anodic voltage of 40 V at 20 °C for 3 min. FE-SEM characterization revealed macro-mesoporous anodized titania surfaces, which were coated by hydroxyapatite using simulated body fluid and pulsed electrochemical deposition at 80 °C, while unprocessed commercially pure titanium surfaces were used as controls. The calcium phosphate deposit on titania plates was characterized as calcium-deficient carbonated hydroxyapatite using XRD, FTIR and FE-SEM, whereas the deposit on non-porous, non-functionalized titanium surfaces was characterized as carbonated apatite. The adhesion strength of the hydroxyapatite coated titania surfaces was 38 ± 10 MPa, implying that these surfaces may be suitable for biological and chemical functionalization of medical implants to tune bioactivity, including delivering drugs.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Titanium and alloys are widely used in the production of biomedical materials due to their high toughness, strength, elastic modulus, corrosion resistance, inertness and biocompatibility [1–3]. Titanium implant surfaces can be modified by physical deposition, thermo-chemical surface treatment, porous surface generation, ceramic coating in order to improve functional properties and osseointegration [2,4–7]. Complemented with the ease of surface microfunctionalization, titanium is used as weight-bearing orthopedic and dental material in the enhancement of osteointegration [8,9].

Successful osteointegration of an implant, the ability of host tissues to interact with the implant without a layer of connective tissue, is a function of its surface topography, morphology, composition, chemistry and roughness [9–14]. With osteointegration, the implant displays increased mechanical stability, biological activity and chemical bonding [11,12]. Surface topography and substrate stiffness affect tissue-implant surface mechanical compatibility by the anisotropic stresses developed on the tissue [15] and dictate cellular attachment [16,17]. According to their phenotype and the nature of the cell adhesion receptor [18], mammalian cells display different cell morphologies and migration patterns [19] based on the wettability, roughness [20] and stiffness of the substrate [18].

Titanium implant surface can be modified through mechanical, physical and chemical means. Implants can be mechanically produced to have various shapes and surface topography by micro/machining, sand/grit blasting and rough polishing [9]. The physical methods of implant surface modification include atmospheric plasma and vacuum plasma spraying of Ca-P and TiO₂ coatings, sputtering of thin films and ion deposition of titanium

* Corresponding author at: Yeditepe University, Faculty of Engineering, Department of Biomedical Engineering, 26 Agustos Yerlesimi, Inonu Mahallesi, Kayisdagi Caddesi, 34755 Atasehir, Istanbul, Turkey. Tel.: +90 216 5780433; fax: +90 216 5780244.

E-mail address: sermin.utku@yeditepe.edu.tr (F.S. Utku).

implants. Chemical surface modification of titanium alters surface roughness and composition and enhances wettability of the implant [21]. The chemical methods used are hydrogen peroxide treatment, sol–gel treatment, chemical vapor deposition, acidic or alkaline treatment and anodization.

The acid treatment used in this study entails the use of strong acids in order to remove the surface oxide and clean and polish the implant surface, giving a uniform roughness of 0.5–2 μm and increasing not only the surface area, but also the migration and adhesion of osteogenic cells on the implant surface [22–26]. Alkaline treatment involves the use of sodium or potassium hydroxide and formation of a bioactive, rough TiO_2 surface layer with higher biocompatibility, increased cell attachment and proliferation [27]. Anodization is an electrochemical process conducted in acidic or alkaline electrolyte solutions, where oxide films with improved adhesion and bonding are deposited on the titanium implant surface connected to the anodic electrode of an electrochemical cell. The oxide layer thickness can be modulated by altering the parameters of the electrochemical process, such as, current density, electrolyte solution concentration, composition and temperature.

Produced by anodization in fluoride-containing electrolytes, nanotubular titania surfaces, provide a canaliculi-like tubular base for osteoblastic adhesion, leading to an advanced stage of cellular development [13,14,23,28]. The bonding strength of the titania nanotubes to the titanium base may pose a risk factor in biomedical applications, and therefore, must be either improved by annealing at high temperatures [29,30], or replaced by titania surfaces that can dissipate the bonding stress, i.e. macro-mesoporous surfaces with a higher bonding strength [30–32]. Production of a hierarchically organized macro-mesoporosity may overcome these mechanical concerns related to interfacial interactions at the implant-host level [33–35].

Mimicking the natural features of bone and using electrochemical deposition methods, ceramic coated biomaterials with macro- and/or mesoporous topography have been previously developed using acidic/(dual-acidic) and alkaline treatments [9,31]. The aim of this study is to produce a hierarchically organized macro-mesoporous implant surface using nitric-hydrofluoric acid, dual-acidic polishing, alkaline anodization and cathodic ceramic deposition, which, to the extent of our knowledge has not been previously experimented and implemented before. Here, a hierarchically organized topography, with mesoporosity embedded within the macroporosity, was produced at low temperatures using (nitric-hydrofluoric) dual-acid polishing and alkaline electrochemical anodization procedure and cathodically ceramic coated.

2. Materials and method

2.1. Materials

Twelve commercially available pure titanium Grade IV (250 mm \times 500 mm \times 1 mm) plates were metallographically ground and polished using #120 grit down to #1200 grit Emery paper and finally 1 μm diamond paste, washed with distilled water and sonicated in acetone.

2.2. Method

2.2.1. Surface functionalization

Unprocessed titanium plates were used as controls. Titanium plates to be used as samples were dipped in 45% HNO_3 :20% HF (v/v) aqueous solution for 10 min at room temperature and then rinsed in distilled water [8]. Consequently, titanium samples were anodized in 0.1 M KOH, in an electrochemical cell, using a stainless steel cathode electrode at an anodic voltage of 40 V at 20 $^\circ\text{C}$ for 3 min (Fig. 1a).

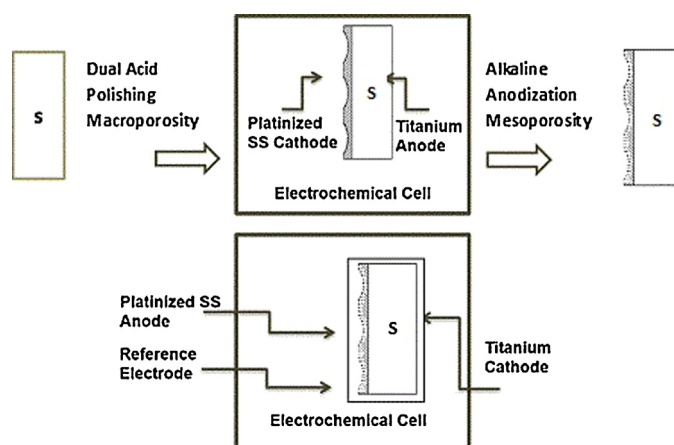


Fig. 1. Schematic representation of titanium surface preparation using (a) acidic polishing and alkaline anodization and (b) cathodization methods. Acidic polishing of titanium produces macroporosity on the surface, while alkaline anodization introduces mesoporosity within the macroporous surface.

The surface morphology of the specimen was characterized using field emission scanning electron microscopy (FE-SEM) (JEOL JSM 7000F FEI).

2.2.2. Calcium phosphate coating

All titanium plates were bioactivated by immersion in 0.5 M NaOH for 2 min at 50 $^\circ\text{C}$ followed by rinsing in deionized water [36] prior to electrochemical deposition, which allows Ca-P coating of implants of any size and shape from an electrolyte solution [8,29]. Since the chemistry of calcium phosphate coating can be modulated by controlling certain parameters, such as current density, potential, length of cathodic and anodic deposition cycles, temperature and the type of solution, in this study, parameters were adjusted to enable deposition of hydroxyapatite [8,30,37–39]. Ca-P deposition was conducted using a modified simulated body fluid (SBF), containing reagent grade 0.15 M NaCl, 1.67 mM K_2HPO_4 and 2.50 mM CaCl_2 , pH buffered at 7.2 with the addition of 0.05 M tris(hydroxyl aminomethane) (pH 7.4) and hydrochloric acid [29]. A typical three-electrode electrochemical cell, with the titanium substrate as the working electrode, a standard silver–silver chloride electrode (Ag/AgCl in saturated KCl) as the reference electrode and the platinized stainless steel as the counter electrode, was used. At 80 $^\circ\text{C}$, surfaces were coated by pulsing the current density between -10 mA/cm^2 for 0.2 s and $10 \mu\text{A/cm}^2$ for 10 s for 100 pulsing cycles and then by maintaining a constant cathodic current density of -10 mA/cm^2 for 60 min (Fig. 1b) [29].

2.2.3. Characterization of calcium phosphate coating

Samples were oven-dried at 100 $^\circ\text{C}$ for 1 h and characterized using XRD, FT-IR and FE-SEM. A glancing X-ray diffractometer (Philips PW 3710), at the grazing angle of 1 $^\circ$, and at the range of scattering angle from 20 up to 80 2θ , at a step size of 0.2 2θ was used to determine the XRD spectrum. FT-IR spectrometer (Perkin Elmer, Spectrum One) with the attenuated total reflectance (ATR) technique over a frequency range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} was used to examine molecular bonding. Sample cross-sections were prepared by breaking the samples after immersion in liquid nitrogen for 15 s. The calcium and phosphorus ratios, surface and cross-sectional images of the coated titania plates were determined by field emission scanning electron microscope with an EDS spectrometer addition (FE-SEM) (JEOL JSM 7000F FEI). As a further analysis, the calcium and phosphorus content of the samples was determined respectively by atomic absorption spectrophotometer (AAS) (Perkin Elmer, Analyst 800) and by colorimetric

Download English Version:

<https://daneshyari.com/en/article/5349171>

Download Persian Version:

<https://daneshyari.com/article/5349171>

[Daneshyari.com](https://daneshyari.com)