Applied Surface Science 290 (2014) 287–294

Contents lists available at ScienceDirect

Applied Surface Science

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

Crystal structure and nanotopographical features on the surface of heat-treated and anodized porous titanium biomaterials produced using selective laser melting

S. Amin Yavari[a,b,*], R. Wauthle[c,d], A.J. Böttger[a], J. Schrooten[e], H. Weinans[a,f], A.A. Zadpoor[a]

[a] Faculty of Mechanical, Maritime, and Materials Engineering, Delft University of Technology (TU Delft), Mekelweg 2, 2628 CD Delft, The Netherlands
[b] FT Innovations BV, Braamsluiper 1, 5831 PW Boxmeer, The Netherlands
[c] KU Leuven, Department of Mechanical Engineering, Section Production Engineering, Machine Design and Automation (PMA), Celestijnenlaan 300B, 3001 Leuven, Belgium
[d] LayerWise NV, Kapeldreef 60, Leuven, Belgium
[e] Department of Metallurgy and Materials Engineering, KU Leuven, Kasteelpark Arenberg 44 PB 2450, 3001 Heverlee, Belgium
[f] Department of Orthopedics and Department of Rheumatology, UMC Utrecht, Heidelberglaan 100, 3584 CX Utrecht, The Netherlands

ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form 1 November 2013
Accepted 17 November 2013
Available online 23 November 2013

Keywords:
Porous biomaterials
Selective laser melting
Anodizing
Nanotubes
Heat treatment

ABSTRACT

Porous titanium biomaterials manufactured using additive manufacturing techniques such as selective laser melting are considered promising materials for orthopedic applications where the biomaterial needs to mimic the properties of bone. Despite their appropriate mechanical properties and the ample pore space they provide for bone ingrowth and osseointegration, porous titanium structures have an intrinsically bioinert surface and need to be subjected to surface bio-functionalizing procedures to enhance their in vivo performance. In this study, we used a specific anodizing process to build a hierarchical oxide layer on the surface of porous titanium structures made by selective laser melting of Ti6Al4V ELI powder. The hierarchical structure included both nanotopographical features (nanotubes) and micro-features (micropits). After anodizing, the biomaterial was heat treated in Argon at different temperatures ranging between 400 and 600 °C for either 1 or 2 h to improve its bioactivity. The effects of applied heat treatment on the crystal structure of TiO_2 nanotubes and the nanotopographical features of the surface were studied using scanning electron microscopy and X-ray diffraction. It was shown that the transition from the initial crystal structure, i.e. anatase, to rutile occurs between 500 and 600 °C and that after 2 h of heat treatment at 600 °C the crystal structure is predominantly rutile. The nanotopographical features of the surface were found to be largely unchanged for heat treatments carried out at 500 °C or below, whereas they were partially or largely disrupted after heat treatment at 600 °C. The possible implications of these findings for the bioactivity of porous titanium structures are discussed.

1. Introduction

Titanium and its alloys are considered biocompatible materials [1–3] and are commonly used for manufacturing of different types of orthopedic implants including the ones used in joint replacement surgeries [4–6] and bone grafting [7,8]. The elastic moduli of solid titanium materials are, however, much higher than that of the bone they replace, resulting in the stress-shielding phenomenon [9,10]. Porous titanium structures are suggested as replacements for solid titanium materials, with their high porosity resulting in much lower overall elastic moduli that are comparable with or even below that of bone [11,12]. In addition to eliminating the stress-shielding phenomenon, porous titanium structures offer other advantages such as ample space for bone ingrowth and simpler handling by surgeons.

Recently developed additive manufacturing techniques such as selective laser melting [13–15] enable manufacturing of regular porous structures with precisely controlled pore shape, pore size, and pore distribution within the biomaterial. It is therefore possible to manufacture biomaterials with arbitrary distributions of mechanical and physical properties. Since bone apposition [16–19], implant performance [20,21], and osseointegration [22,23] are dependent on mechanical loading, the possibility to precisely

* Corresponding author at: Faculty of Mechanical, Maritime, and Materials Engineering, Delft University of Technology (TU Delft), Mekelweg 2, 2628 CD Delft, The Netherlands. Tel.: +31 15 2781859; fax: +31 15 2784717.
E-mail addresses: s.aminyavari@tudelft.nl, saber.aminyavari@gmail.com (S. Amin Yavari).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.11.069

control the distribution of the mechanical properties of biomaterials could be potentially useful for improving the long-term performance of bone-mimicking porous biomaterials.

The surface of biomedical materials is often treated using surface engineering techniques to improve the (biological) performance of the materials [24–27]. Since titanium alloys are bio-inert materials, surface treatments and coatings are often applied to improve their bioactivity [28–32]. Anodizing is one of the surface treatment techniques that have been applied for creating TiO_2 nanotubes and hierarchical structures that have shown to improve the bioactivity of bulk/solid titanium alloys [28,33–35]. In most studies, anodizing has been applied on solid titanium, while one recent study has applied it on porous titanium manufactured using conventional manufacturing techniques such as the space-holder method [36]. However, anodizing has not been applied on selective laser melted titanium alloys.

In this study, we apply anodizing on porous titanium alloy structures manufactured using an additive manufacturing technique, namely selective laser melting (SLM). Despite many advantages that they offer, selective laser melting machines are not currently capable of controlling the surface morphology of the produced biomaterials at the micro-scale [37]. The anodizing process is therefore applied to improve the bioactivity of porous titanium structures for bone grafting applications.

It has been shown that the anodized titanium structures need to be heat-treated in order to stabilize the oxide layer [36]. Choosing the correct combination of heat-treatment temperature and duration is important. On the one hand, the heat-treatment temperature should be high enough and the duration long enough to allow stabilization of the oxide layer. On the other hand, if the temperature is too high and/or if the heat treatment takes too long, an increasing amount of the initial crystal structure of the oxide layer, namely anatase, may convert to rutile [38–40]. Since the phase composition of the oxide layer, i.e. the ratio of anatase to rutile phase, regulates the rate of apatite formation and, thus, bioactivity of the biomaterial [41–44], it is important to choose the optimal heat treatment parameters. Even though there are some guidelines in the literature regarding the effects of temperature on the crystal structure of TiO_2 applied on the surface of solid titanium material [40], there are no such guidelines for porous titanium alloy structures particularly the ones manufactured using selective laser melting. The highly porous build of porous structures and their high surface to volume ratio means that the heat transfer dynamics and air flow through their pores and the structure of the formed oxide layers are different from those of solid titanium alloy materials. It is therefore important to study how different combinations of heat treatment temperature and duration influence the crystal structure of TiO_2 nanotubes created on the surface of porous titanium alloy structures.

In this study, we first optimized the anodizing process to obtain a consistent hierarchical oxide layer throughout the selective laser melted porous titanium structures. Then, the anodized porous structures were heat treated at three different temperatures, namely 400, 500, and 600 °C, for two different durations, namely 1 and 2 h. The crystal structures of the resulting oxide layers were characterized using scanning electron microscopy and X-ray diffraction.

2. Materials and methods

Selective laser melting technique was used for manufacturing of porous titanium alloy structures (Layerwise NV, Belgium). The architecture of the porous structures was closely controlled and was based on a dodecahedron unit cell. Spherical pre-alloyed Ti6Al4V ELI powder according to ASTM B348, grade 23 was used. The design (nominal) values of the micro-architectural dimensions were as follows: strut size = 120 μm, pore size = 500 μm, porosity = 88%. The samples were produced in an inert atmosphere and were built on top of a solid titanium alloy substrate. Subsequently, the samples were removed from the substrate using wire electro-discharge machining (EDM). The specimens were fabricated in the shape of disks (Ø8 mm × L3 mm). The actual-as-manufactured micro-architecture of the samples was characterized using micro-computed tomography (μ-CT). The μ-CT images were subsequently segmented using a global threshold for detecting the titanium structure. The morphometric parameters of the porous structure including pore size, strut size, and the average structure porosity were then determined using the segmented μ-CT images and 3D morphometry algorithms using an algorithm describe elsewhere [45].

Prior to surface treatment, the samples were immersed in an acidic mixture (2 mL 48% HF, 3 mL 70% HNO_3 (both Sigma–Aldrich) and 100 mL distilled water) for 5 min to remove the naturally formed oxide layer.

The titanium alloy structures served as anode in the anodizing process, while an inert platinum mesh was used as cathode. Copper wires connected the anode and cathode, respectively, to the positive and negative ports of a 60 V/20A power supply (CPX400SP; Aim TTI). During the anodizing process, the anode and cathode were kept in parallel with a separation distance of about 3 cm, while being submerged in an electrolytic solution in a Teflon beaker (VWR). A dilute 0.5 wt% HF (Sigma–Aldrich) solution was used as the electrolyte.

Since porous titanium structures have a very distinct internal geometry from solid titanium materials, the anodizing parameters that are reported in the literature for solid titanium samples could not be used for anodizing porous titanium samples. In the most general case, the parameters of the anodizing process could be different even for different designs of porous titanium alloys. We therefore needed to optimize the parameters of the anodizing process for every new porous titanium structure. In this study, we kept the anodizing voltage constant at 20 V while using different anodizing times, namely 30 s, 1 min, 2 min, 5 min, 30 min, 45 min, 60 min, 90 min, 120 min, and 240 min. The structure of the oxide layers resulting from the different sets of parameters were examined using scanning electron microscopy and the optimum structure in appearance (60 min) was chosen for the remainder of the study. The selection was based on obtaining an ordered hierarchical structure (both micro- and nano-features) throughout the surface of the specimens. A number of samples were anodized using the optimized anodizing parameters and were used for heat treatment. The morphometric parameters of the anodized samples were measured using μ-CT with a procedure similar to the one explained above.

The anodized samples were heat treated at three different temperatures, namely 400, 500 and 600 °C, and for two different durations, namely 1 and 2 h. The heat treatment was carried out in an Argon furnace with a pressure of 100 mm Hg. The furnace was heated at a rate of 10 °C/min to the annealing temperature and was kept at the annealing temperature for the duration of heat treatment. Afterwards, the furnace was turned off and the samples were allowed to cool down in the furnace.

The surface structure of samples was observed using a JEOL (JSM-6500F, Japan) scanning electron microscope (SEM). The heat-treated samples were mounted and etched using an etching reagent (98 ml saturated oxalic acid in H_2O + 2 ml HF) and were subsequently observed using an optical microscope (Olympus BX60M) equipped with polarization facility (U-DICR prism UMPL LMPL).

Phase analysis of the heat-treated samples was carried out to characterize the crystal structure of TiO_2 nanotubes. The phase analysis was carried out by X-ray diffraction (XRD) using a Bruker D5005 diffractometer equipped with Huber