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Synthesis of TiO_2 nanopore arrays by pulsed laser treatment and anodic oxidation

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ABSTRACT

Functionalization of the Ti6Al4V alloy by combining laser texturing and anodizing has been performed. The laser texturing was carried out with a Q-switched Nd:YAG laser using 1064 nm and an energy of 90 mJ/pulse. After the laser treatment, nanostructured titanium anodic oxide layers have been grown in an aqueous electrolyte ($H_2SO_4 + HF$). The topography and the surface morphology of the laser textured alloy without and after anodizing were characterized using an optical imaging profiler and a scanning electron microscopy (SEM), respectively. Changes in wettability and the electrochemical stability of the modified surfaces have been also analyzed.

The results show that the consecutive use of both processes allows changing the topological pattern thus developing a micro-nano topography that could selectively promote tissue cell attachment. While laser texturing promotes an important increase in the roughness due to the generation of dimples on the surface, the anodizing process fabricates a homogeneous nanoporous titanium oxide layer that it turns the surface hydrophilic. Moreover, corrosion resistance of the laser textured surface can also be improved due to the better chemical stability of the nanostructured oxide layer formed on the surface.

1. Introduction

As is well-known, titanium alloys are widely used in advanced applications such as aerospace engineering, biomedical devices, marine technologies and jet engines, because of their high strength-to-weight ratio, excellent corrosion resistance and biocompatibility [1,2]. Besides these properties, titanium alloys can be easily functionalized through different surface modification techniques in order to improve their behavior [3–6]. In the field of biomaterials, modified titanium surfaces are being extensively used due to their unique properties, combined with the possibility of easy nanostructuring. TiO_2 can in fact be synthesized by a wide spectrum of techniques, including sol–gel methods, template-assisted methods, hydro/solvothermal approaches, as well as by electrochemical methods, and shaped into a broad range of nanoscale morphologies [7].

It is well known that TiO_2 nanotubes are corrosion-resistant, possess ionic and electronic properties, and can significantly accelerate osteoblast adhesion enhancing bone mineralization, as well as cellular proliferation at the biomaterial/tissue interface [8]. Among other techniques, the anodizing process easily allows the growth of a titanium oxide layer. By controlling the anodizing conditions (current density and/or anodization voltage, pH, temperature and electrolyte composition) it is possible to fabricate titanium oxide layers with different thickness and nanostructures. In previous papers, the authors have demonstrated the growth of TiO_2 F-doped nanopores and nanotubes with antibacterial and osteointegration properties [9–11].

More recently, laser texturing has emerged as an attractive alternative since it presents competitive advantages such as easy automation, localized treated area, three-dimensional treatments and great flexibility [12]. Surface patterning of the Ti alloy can be done by modulating the most important laser parameters (focal spot diameter, power on sample, scan rate, spot spacing, and repetition rate and pulse length), thus improving its mechanical and corrosion properties. In addition, it is possible to enhance its osseointegration. For instance, Erdogan and coworkers [13] used low-cost fiber laser for surface texturing of Ti biomedical implant surfaces. Ulerich et al. [14] improved the growth and adhesion of cells by means of a pulsed frequency tripled Nd:YVO_4 laser (355 nm). Mukherjee et al. using a 2-kW Yb fiber laser (1080 nm) created surface textures which were able to promote cell attachment and differentiation [15]. Lastly –among other papers- Mirhosseini [16] used a 35 W Nd:YAG laser (1064 nm) for the surface patterning of small holes on Ti6Al4V, observed an increase in 2 T3 osteoblast cell growth on laser treated surfaces.

Although the fabrication of anodic alumina film templates has been carried out by anodizing laser textured aluminium surfaces [17], few research papers are found in the literature combining the advantages of laser texturing and anodizing process to functionalize surfaces with advanced properties. Kim et al. [18] characterized the nanotubes formed on the femtosecond laser textured Ti-35Nb-x Hf alloys in order to enhance osseointegration and cell adhesion. More recently, Parsikia et al. have showed that low-energy laser processing of Ti6Al4V samples

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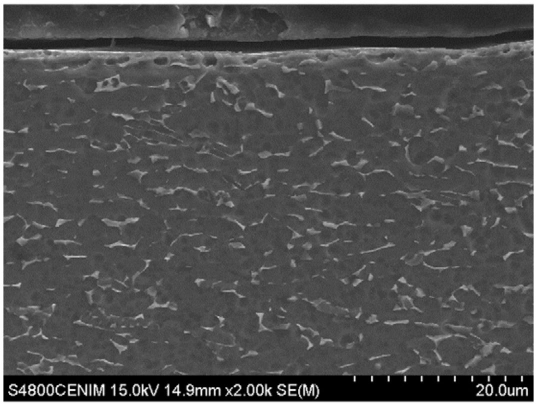

Fig. 1. Microstructure of Ti–6Al–4 V alloy showing dispersed β-phase particles on an α matrix.

followed by grit blasting and anodizing, showed a higher bioactivity and presented considerable amounts of bioactive compounds in comparison to pristine Ti6Al4V samples [19].

Thus, the present paper aims to establish a technique for functionalization of Ti6Al4V alloy for biomedical applications based on a double surface modification process. First, the alloy is textured to form dimples on its surface in order to create varying degrees of roughness on the Ti6Al4V. Then, the textured surfaces are anodized in order to obtain a well-arranged nanofilm of TiO_2 with tunable length and diameter.

The main goal of this duplex treatment is to obtain surfaces with multiple functionalities; this implies a change in the topological patterns which could selectively act on tissue cell attachment onto F-doped anodic layer of enhanced anti bacterial properties and improved corrosion resistance.

2. Experimental

The material under study was ELI grade $\alpha + \beta$ Ti6Al4V alloy in accordance with the ASTM F136-02 standard supplied by SURGIVAL. The alloy was machined into rectangles of 15x50 mm in diameter and 2 mm thickness. Before the laser treatments, the specimens were ground via successive grades of SiC paper up to 1200 grade, degreased with a detergent and rinsed in tap water followed by deionised water. Fig. 1 shows the typical morphology of the Ti6Al4V V alloy with dispersed 2–3 μm long β-phase irregular shapes particles.

Laser treatment was carried out in air atmosphere, at normal incidence, with a Q-switched Nd:YAG laser (Lotis TII, LS-2147, pulse duration of 15 ns full width half maximum) at a repetition rate of 2 Hz. A first harmonic at 1064 nm was used for texturing. The energy per pulse was 90 mJ. The beam was focused by way of a cylindrical plano-convex quartz lens with focal length of 150 mm. The sample was placed perpendicular to the beam path and its movement was controlled by a CNC motion stage. The x-y table scan speed was 1 mm/s.

Surface topographies were examined and roughness Ra values were obtained using an optical imaging profiler PLμ2300 (SENSOFAR) operated at 20x. The profiles combine confocal and interferometry techniques with a sub-nanometer resolution. The cited Ra values are an average of 5 measurements with standard error of the mean <5 %. For the purposes of the analysis of a wider area, roughness measurements were also made using a Mitutoyo stylus instrument (SurfTest 401) with a cut-off length of 2.5 mm and a total measurement length of 12.5 mm. The average value of the surface profile roughness Ra was determined from these results.

The morphology and the chemical composition of anodic films was examined by a JEOL JSM – 6500 field emission gun scanning electron microscopy (FEG-SEM) and energy dispersive X-ray (EDX) spectroscopy at 15 keV for EDS analysis, as well as 7 keV for secondary electron imaging.

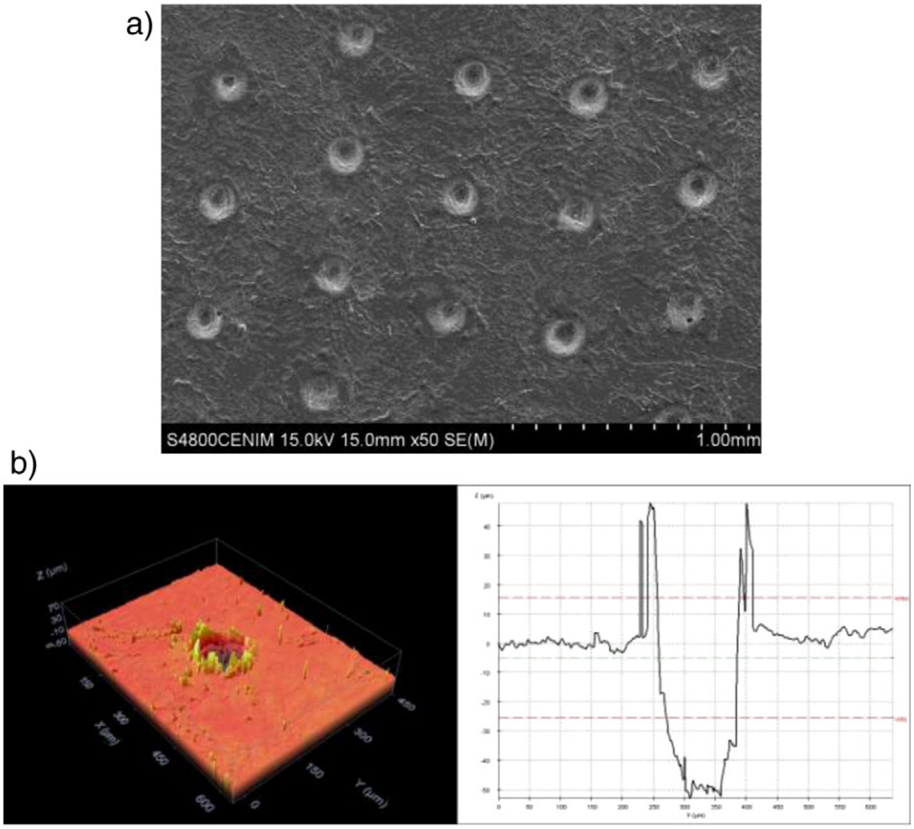

Fig. 2. a) SEM image of the sample after laser treatment. b) Confocal image and profile of the dimple.