Materials Science and Engineering C 68 (2016) 383–396

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Application of chemical mechanical polishing process on titanium based implants

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 26 April 2016
Accepted 1 June 2016
Available online 6 June 2016

Keywords:
Implantable biomaterials
Surface structuring
Chemical mechanical polishing
Biocompatibility

ABSTRACT

Modification of the implantable biomaterial surfaces is known to improve the biocompatibility of metallic implants. Particularly, treatments such as etching, sand-blasting or laser treatment are commonly studied to understand the impact of nano/micro roughness on cell attachment. Although, the currently utilized surface modification techniques are known to improve the amount of cell attachment, it is critical to control the level of attachment due to the fact that promotion of bioactivity is needed for prosthetic implants while the cardiac valves, which are also made of titanium, need demotion of cells attachment to be able to function. In this study, a new alternative is proposed to treat the implantable titanium surfaces by chemical mechanical polishing (CMP) technique. It is demonstrated that the application of CMP on the titanium surface helps in modifying the surface roughness of the implant in a controlled manner (inducing nano-scale smoothness or controlled nano/micro roughness). Simultaneously, it is observed that the application of CMP limits the bacteria growth by forming a protective thin surface oxide layer on titanium implants. It is further shown that there is an optimal level of surface roughness where the cell attachment reaches a maximum and the level of roughness is controllable through CMP.

1. Introduction

Biomaterials are commonly used to make implantable structures such as dental prostheses, orthopedic devices, cardiac pacemakers, stents and catheters [1]. The choice of an adequate implant material for a selected application is based on the bio-stability and bio-compatibility of the material once the required mechanical strength and durability is achieved. Commercially, pure titanium and its alloys (most commonly Ti-6Al-4V) are widely used as structural biomaterials due to their extraordinary properties such as high mechanical strength per unit volume in addition to their high corrosion resistance due to their stable passive oxide layer [1–4]. The native oxide layer of titanium that spontaneously forms in air is in nanometer scale (3–10 nm) and it is typically amorphous and stoichiometrically defective [5–6]. To be a protective oxide film, the formed TiO_2 layer has to be continuous, pore free and adhesive. Hence, although the native oxide film of titanium is known to be protective, additional oxidation treatments such as chemical etching [6], thermal treatment [7] and electrochemical anodization [8] of the titanium surface are practiced to grow an oxide layer by controlling the thickness, porosity, crystal structure of the oxide to enhance the wear characteristics as well as the bio-compatibility.

The nano-scale oxide layer of titanium has multiple functionalities in biomaterial implant Spontaneously, when the titanium oxide film is continuous and pore free, it can also prevent the titanium ion dissolution once the implant is implanted applications. First of all, it is known to promote the biocompatibility of the titanium by enhancing cell attachment [9]. It also serves as an adhesion layer between the implant and the bone tissue (commonly simulated with hydroxyapatite-HA) particularly when an anatase crystalline structure is formed [10], which justifies the deposition of the TiO_2 layers on the bare titanium implants [7]. In addition, the formation of a protective oxide film of titanium helps shield the implant surface against corrosion by stopping the oxygen diffusion as shown by electrochemical analyses in detail [4]. As the implants are exposed to aggressive environments such as in body fluids (particularly in the acidic mouth environment when the dental implants are considered) the surface properties of this film becomes more important [4]. Consequently, it is favorable to promote the formation of the protective oxide layer of titanium during its processing for the implant applications.

In addition to the characteristics of the titanium oxide film, the surface topography of the titanium implants has also been studied intensively to analyze the effect of surface roughness on the biocompatibility. There are many processing techniques adopted to modify the implant material surface roughness and concurrently the chemical composition [11]. Gupta and coworkers classified the available surface

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http://dx.doi.org/10.1016/j.msec.2016.06.002
0928-4931/

modification techniques into four main groups including (i) the methods to increase surface roughness, (ii) chemical etching, (iii) various methods of coating and (iv) the surface chemical and chemical topography modifications [8]. Blasting is one of the most commonly practiced techniques to increase surface roughness in which particles of various diameters of mainly alumina (Al_2O_3) and titania (TiO_2) with particle size ranging from small, medium to large grit are used to blast the surfaces of the implant [12,13]. The obtained roughness depends on the particle size, time of blasting, pressure and distance from the source of particle to the implant surface. The created micro-scale roughness allows adhesion, proliferation and differentiation of bone cells (osteoblasts) yet the soft tissue cells (fibroblasts) adhere to the surface with difficulty and hence this method can limit soft tissue proliferation and increase bone formation. However, some particles are commonly left on the surface after blasting which may impair bone formation by a possible competitive action on calcium ions [14]. Chemical etching is another method in which the implant is dipped into an acidic environment and the surface structure changes as a function of acid type, concentration and exposure time. This method has also been observed to promote osteointegration and implemented following the sand blasting on the implant surfaces as well [15]. However, a yellowish, blurry looking film was observed to form on the implant surface after the etch operation [16]. Blasting method is also practiced by using only hydroxyapatite (HA) particles or biphasic calcium phosphate (BCP) particles. BCP is a mixture of the hydroxyapatite and beta-tricalcium phosphate. Implementation of an etch procedure is also common following the BCP treatment. The advantage of BCP is that the surface can be structured at micro-scale due to higher hardness of the BCP particles relative to pure HA. Moreover, even if the HA or BCP particles maybe left on the implant post blasting operation, they do not adversely impact biocompatibility since both of these minerals are known to have similar compositions to the bone tissue and they are commonly utilized to mimic the osteoblast attachment for implant studies [17]. Other than blasting and etching, application of coating on the implant surfaces with HA by using plasma spraying, laser ablation, pulsed laser deposition, sputtering or simply dip coating are also practiced [8]. While these methods help improve the cell attachment, they are also prone to delamination at the implant/coating interface, which may fail the healthy integration of the implant with the surrounding tissue [8,18]. Hydroxyapatite composites with zirconia and alumina were also shown to be good coating materials particularly for dental implants promoting the mechanical properties of the implants in addition to enhanced osteointegration [18]. Finally, the surface chemical and chemical topography modifications involve the treatment of the implant surface by the control of surface chemistry and attachment of proteins and cell adhesion molecules on the surfaces of the implant through electrical double layer interactions [8,19].

All the surface modification methods mentioned so far tend to form random surface structures on the implant surface ranging from nano to micro scale roughness. The isotropic nature of the surface structures result in equal probability of the cell attachment on the implant surface. To induce anisotropic surface structuring, more recently introduced alternative of implant surface structuring is the utilization of lasers [20–23]. The use of lasers allows the manufacturing of anisotropic surfaces which can help grow the cells in a specific direction. Furthermore, laser structuring can help in controlling cell attachment between the osteoblast which prefer micro-scale roughness and the fibroblast which is preferably better attached on the nano-rough surfaces [22,23]. It is also known that although micro-scale roughness has been studied intensively to promote cell attachment, the cellular events takes place on the nano-scale for cell-substrate interactions as the nano-metric cues have been shown to influence the cell activities [6,22,23]. Therefore, the scale of surface roughness from nano towards micro is critical to control bioactivity by selective promotion or demotion of the cell attachment.

In the present study we introduce chemical mechanical polishing (CMP) technique as an alternative to surface structuring of the biomedical implants [24]. CMP has initially been introduced for glass polishing and extended into the planarization of the interlayer metal connectors and dielectrics in microelectronics manufacturing [25]. In CMP process, the top film surface of the material is exposed to the chemicals in the polishing slurry which is made of submicron size particles and corrosives. This interaction forms a chemically altered top film that is removed by the mechanical action of the slurry abrasive particles. Therefore, it is a different method as compared to the mechanical polishing techniques used for implant surface finishing [26]. The chemically altered top films have to be a protective oxide to enable planarization by stopping chemical corrosion on the recessed metal surfaces while the elevated structures are polished [27]. Titanium CMP is performed in microelectronics to planarize Ti/TiN layers used as barriers to aluminum interconnect diffusion to the dielectric layers [28]. Furthermore, it has been shown by an earlier study that the application of CMP on Ti films has been very successful in terms of creating a titanium oxide film on the surface that might also help promote biocompatibility in addition to helping removal of the reacted and contaminated surface layers [16,29]. The comparison of the electrochemical etch to CMP application on titanium has shown that the titanium surfaces treated by CMP using colloidal silica slurries and an oxidizer concentration of 3 wt% were much clear and compositionally continuous than the yellowish and blurry titanium oxide layers formed by electrochemical etching. Furthermore, in this study CMP is synergistically utilized to induce nano-scale smoothness or nano/micro scale roughness on the bioimplant surface. Particularly, we focus on the dental implants to change the surface roughness in a control manner. Implementation of the CMP process on titanium bio-implants results in a synergy by (i) cleaning the implant surface from potentially contaminated surface layers by removing a nano-scale top layer during the process, (ii) simultaneously creating a non-porous and continuous nano-scale oxide film on the surface to limit any further contamination to minimize risk of infection and prevent corrosion and (iii) inducing controlled surface smoothness/roughness by designing the CMP process variables such as slurry particle size, solids loading as well as the oxidizer type and concentration.

In order to demonstrate the use of CMP on dental implants, both titanium plates and dental implants were processed. The CMP process was carried out by using alumina based slurries and H_2O_2 as an oxidizer on commercially pure (cp) Ti samples with different polishing pads to modify surface topography. CMP characterization was performed by material removal rate, surface roughness by using atomic force microscopy (AFM) and wettability analysis (through contact angle measurements) in addition to the surface topography and elemental composition analyses on the treated surface by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Biological evaluations were performed by cytotoxicity evaluations in addition to bacterial and cell attachment tests and hydroxyapatite adhesion through wet deposition.

2. Materials and methods

2.1. Materials

The original titanium foil sample surface, which is considered as baseline in this experimental study, was annealed. Fig. 1a illustrates the optical micrograph of the anodized titanium plate surface (200X) as well as the SEM cross sectional image illustrating the thick and porous oxide layer with 30–40 μm thickness. Fig. 1b shows the titanium based dental implant used to implement the optimized CMP conditions through hand polishing on a 3-D sample. The dental implants were provided by MODE Medical Company and they were only shaped by machining prior to their exposure to the CMP testing.