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Influence of the microstructure and topography on the barrier properties of oxide scales generated on blasted Ti6Al4V surfaces

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ABSTRACT

The long-term interfacial bond between an implant and bone may be improved by creating a rough surface on the implant in order to increase the surface area available for bone/implant apposition. A natural consequence of surface roughening is an increase in metal ion release, which is itself a surface dominated process. Based on this fact, the aim of this work is to study the influence of the microstructure and topography on the barrier properties of oxide scales thermally generated at 700 °C for 1 h on Ti6Al4V surfaces after blasting with Al_2O_3 particles (coarse) or SiO_2 and ZrO_2 particles (fine). The microstructural and topographical characterization of the thermally treated blasted surfaces has been studied by means of scanning electron microscopy coupled with energy dispersive X-ray analysis, contact profilometry and X-ray diffraction. The barrier properties and corrosion behaviour of the oxide layers have been studied by means of electrochemical impedance spectroscopy (EIS) in Hank's solution. Thermal treatment at 700 °C for 1 h promotes the formation of oxide scales with different morphologies and crystalline structures depending on the degree of deformation of the blasted surface. The oxide scale grown on the finely blasted sample has a pine needle-like morphology which is mainly formed of anatase TiO_2. In contrast, the oxide scale grown on the coarsely blasted sample has a globular morphology formed mainly of rutile TiO_2. The differences in morphology, i.e. fine or coarse, of the oxide scales influence the corrosion response of the blasted thermally treated samples in Hank's solution. The EIS results permit evaluation of the different oxide scales from the capacitance and resistance values obtained in the high-frequency region and show a good correlation between the morphology and barrier properties. Oxidation treatment at 700 °C for 1 h of Ti6Al4V samples coarsely blasted with Al_2O_3 improves the corrosion behaviour due to an increase in the thickness of a compact, ordered and more structurally stable oxide scale. This is due to the globular morphology of the rutile (TiO_2) structure maintaining an average surface roughness suitable for optimal osseo-integration with long-term interfacial bonding between the implant and bone.

1. Introduction

When metallic materials are implanted in the human body possible consequences of in vivo degradation are metal ion release from the surface of the implanted material and harmful effects of the metal ions released, which could escape into the surrounding tissues [1]. Thus, the best implant material will be one exhibiting minimum ion release of low-toxicity ions. Titanium and its alloys in aqueous solution simultaneously have, according to passivity theory, both active and passive surfaces and undergo a continuous process of partial dissolution and repasivation [1,2]. The composition of the Ti oxide film is, from outside to inside, $TiO_2 \rightarrow Ti_2O_3 \rightarrow$ - $TiO \rightarrow Ti$ [3]. The passive film composition and properties may change with time depending on the in vivo environment, by reacting with ions and molecules and reconstructing the surface oxide film. This stability and the ability to regenerate the passive film are crucial for lower ion release and, consequently, good biocompatibility. On the other hand, the long-term interfacial bond between an implant and bone may be improved by creating a rough or porous surface coating on the implant in order to increase the surface area available for bone/implant apposition [4]. There are a large number of methods to create a rough surface on an implant surface [5]. Among these, blasting is used as an effective method to increase the surface roughness of metallic biomaterials and enhance osseo-integration. The natural consequence of surface roughening is an increase in metal ion release. The new surface generated after the blasting process displays abrasive pollution and contains peaks and valleys that can act as active sites promoting corrosion [6,7]. Blasting of Ti6Al4V alloy has been considered a

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cost-effective method to increase roughness. However, this change in the implant surface also implies an increase in the effective area, and thus in the release of Ti and Al ions.

The study of new roughened surfaces is increasingly important because of the need to decrease ion release and consequently improve biocompatibility and long-term stability. The role of the oxide layer has been discussed in the literature [8,9] and its has been shown that ageing treatments (aged in boiling deionized water for 10 h) result in a more resistant surface oxide, as compared with standard nitric acid passivation treatments. Furthermore, a number of researchers have shown that dissolution of the oxide layer occurs during nitric acid passivation treatment, resulting in a thinner, less stable oxide layer [10–12]. To solve this problem, thermal oxidation is an alternative surface treatment to improve the biocompatibility and corrosion resistance of blasted alloys. In vivo evidence indicates that thermal oxidation (800 °C for 2 h) of blasted commercial purity Ti implants increases the percentage bone–implant contact by the oxidized surface [13]. Results from our group have shown that thermal oxidation of polished Ti6Al4V (500 °C for 1 h) enhances initial cell attachment and cytoskeleton reorganization while slightly increasing several markers of osteoblast proliferation and differentiation [14]. Oxidation treatment at 500 °C for 1 h of a polished surface releases less Ti and Al metal ions into cell culture medium over 5 weeks than from the natural passive film on a Ti64 alloy [15] and results in the formation of an outer thin ceramic layer that improves osteoblast behaviour and also decreases Ti and Al ion release from Ti6Al4V alloy. In a previous work the in vitro biocompatibility of Ti6Al4V alloy blasted with Al_2O_3 and thermally treated (500 °C for 1 h) was also assessed. The in vitro results indicate that thermal oxidation of alumina blasted Ti6Al4V alloy may favour successful osseo-integration by promoting early interaction of osteoblastic cells with the modified alloy surface [16].

Thus, the main aim of this work is to study the influence of microstructure and topography on the barrier properties of oxide scales generated on the Ti6Al4V surface after the blasting process (coarse and fine). On blasted surfaces characteristics such as plastic deformation, macro- and micro-roughness, surface chemistry and blasting contamination will all determine the uniformity, continuity, thickness, porosity, morphology and chemistry of the oxide scales formed. To achieve the main aim of this work a deep topographical, morphological, compositional and electrochemical characterization of blasted Ti6Al4V surfaces after thermal treatment has been carried out. The protective effect of oxide scales generated by thermal oxidation on the electrochemical properties and, specifically, on the corrosion behaviour of the blasted surfaces in simulated human body fluids has been studied.

2. Materials and methods

2.1. Sample preparation

The experiments were carried out on Ti6Al4V (wt.%) alloy supplied by IQL (Biomet Spain Orthopaedics SL) in the form of 2.5 × 2.5 cm squares of 0.5 cm thickness. Three types of surface condition were studied. Polished surfaces, hereafter termed Ti64-P, were prepared by abrading the sample surface with successively finer silicon carbide papers and then mechanically polishing with 1 μm diamond paste to a mirror-like finish. Two types of standard blasted rough surfaces were prepared by the implant manufacturer under industrial particle blasting conditions. The two blasting treatments were:

- Ti64-FB, finely blasted with SiO_2 and ZrO_2 particles with mean sizes of 240 ± 60 and 185 ± 65 μm, respectively.
- Ti64-CB, coarsely blasted with Al_2O_3 particles with a mean size of 500 ± 60 μm.

The oxidized blasted surfaces were prepared by oxidation of Ti64-FB and Ti64-CB discs at 700 °C for 1 h in air and then cooling at room temperature outside the furnace. The samples were washed in running water and ultrasonically cleaned with ethanol.

2.2. Surface roughness

The surface roughness was determined before and after surface modification using a Mitutoyo Surftest 401 profilometer. A diamond stylus was used, which is reported by the manufacturer to have a tip radius of 5 μm on a 90° cone and a contact force of 4 mN. Original tracings of 4 mm length were performed and a high-pass filter with a cut-off of 0.8 mm was selected. The roughness parameters were obtained from five line profiles starting from a common origin line and spaced 5 mm apart. The roughness values were evaluated following the norm DIN 4768, in which R_a is the arithmetic average of the absolute values of all points of the profile, R_{zDIN} is the arithmetic average of the maximum peak to valley height roughness values, R_q is the root mean square of the values of all points of the profile and R_{maxDIN} is the maximum individual roughness depth encountered when determining R_{zDIN}. The surface roughness is given as the average surface roughness (R_a) in micrometres at a sensitivity setting of 0.01 μm.

2.3. Morphology characterization

Characterization of the surface morphology of selected specimens was carried out by scanning electron microscopy (SEM) using a JEOL-6500F scanning electron microscope equipped with a field emission gun (FEG) and coupled with an energy dispersive X-ray analysis (EDX) system for chemical analysis. The samples were examined at acceleration voltages of 7 and 15 keV. Thermally treated samples were coated with graphite to avoid charging due to the non- or semi-conductive oxide scale formed on the surface of the sample.

2.4. X-ray diffraction

The different phases present in the oxide scale were identified from the X-ray diffraction (XRD) patterns obtained using a Siemens D5000 diffractometer employing Cu K_α radiation and running at 40 kV, 30 mA in the 2θ range 1–70° with a step size of 0.05°.

2.5. Electrochemical impedance spectroscopy (EIS)

All the samples were exposed to Hank's solution oxygenated by direct contact with the laboratory atmosphere. The chemical composition of Hank's solution, which simulates human body physiological fluids, is given in Table 1. The pH of the solution was 7.4 ± 0.1 over the testing period. The measurements were carried out with the electrolyte at rest (without external stirring). The electrochemical cell was prepared by fixing a glass cylinder onto a metallic sheet and filling it with Hank's solution. The tested area of the sample surface was 0.196 cm^2. The electrochemical cell was designed with a saturated calomel electrode (SCE) as the reference electrode, a sheet of platinized titanium as the counter electrode and the samples under study as the working electrode. Prior to beginning the electrochemical measurements the specimens were maintained for 1 h in Hank's solution in order to obtain a stable corrosion potential. The electrochemical behaviour was studied by means of EIS. To carry out the impedance measurements a PAR 273A potentiostat was connected to a 1250 Solartron frequency response analyzer. EIS was performed by applying a