Tribocorrosion behavior of bio-functionalized highly porous titanium

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ABSTRACT

Titanium and its alloys are widely used in orthopedic and dental implants, however, some major clinical concerns such as poor wear resistance, lack of bioactivity, and bone resorption due to stress shielding are yet to be overcome. In order to improve these drawbacks, highly porous Ti samples having functionalized surfaces were developed by powder metallurgy with space holder technique followed by anodic treatment. Tribocorrosion tests were performed in 9 g/L NaCl solution using a unidirectional pin-on-disc tribometer under 3 N normal load, 1 Hz frequency and 4 mm track diameter. Open circuit potential (OCP) was measured before, during and after sliding. Worn surfaces investigated by field emission gun scanning electron microscope (FEG-SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Results suggested bio-functionalized highly porous samples presented lower tendency to corrosion under sliding against zirconia pin, mainly due to the load carrying effect given by the hard protruded oxide surfaces formed by the anodic treatment.

1. Introduction

Titanium and its alloys are widely used in orthopedic and dental implants due to their excellent corrosion resistance, high yield strength, good ductility and better biocompatibility (Chen et al., 2009; Guo et al., 2013). However, some major clinical concerns are still valid, namely bone resorption due to stress shielding, lack of bioactivity, and low wear resistance.

Most commercially used Ti-based implant materials exhibit much higher Young's modulus (Commercially pure Ti: 105 GPa, Ti-6Al-4V: 110 GPa) as compared to human bones (varies in a range of 4–30 GPa) (Guo et al., 2013; De Viteri and Fuentes, 2013; Nag and Banerjee, 2012). Studies have shown that implants do not adequately strain the bone that can result in disuse atrophy and bone resorption due to the difference on Young's modulus between implant and bone. This phenomenon known as stress shielding that is one of the major cause of orthopedic implant failures by resulting in bone resorption (Lee et al., 2012).

In order to avoid stress shielding, on one hand, β and near β alloys with lower Young's modulus such as Ti-Nb-Ta-Zr, Ti-Nb-Si, Ti-Mo-Nb, Ti-Zr-Mo are being developed (Guo et al., 2013; Martins and Grandini, 2014; Correa et al., 2014), but on the other hand, porous Ti implants having open-cellular structure are also being developed not just to reduce the biomechanical mismatch, but as well for the possibilities of the new-bone tissue in-growth, or even the transport of the body fluids

and their potential use on drug delivery systems (Goriainov et al., 2014; Amin Yavari et al., 2014; Lee et al., 2014; Jha et al., 2013).

Ti is the most biocompatible metallic material, however, it cannot create a direct bond with bone to promote new bone formation at the early stage after implantation, which is required for the rapid fixation of bone to implant. This leads to the early implant failure particularly for the patient groups with the diseases such as diabetes, osteoporosis, and chronic inflammation (Gosavi et al., 2013; Tanigawa et al., 2013; Hu et al., 2011).

When an implant material attached to the bone, during the cyclic loads, relative movements cause wear (Thomann and Uggowitzer, 2000; Ganesh et al., 2012). Furthermore, implants are surrounded by corrosive body fluids, thus they suffer not only wear, but the simultaneous action of corrosion and wear that is defined as tribocorrosion, being an irreversible process that occurs on the surface causing the deterioration of the material (Marino and Mascaro, 2004; Landolt et al., 2004). It is known that under this simultaneous action, total material loss may be significantly higher than that of the mechanical wear or corrosion, individually (Mischler, 2008).

In addition to hard coatings, surface modifications are also being applied in order to improve the wear resistance of Ti (Hu and Lim, 2010; Wood, 2007; Alves et al., 2013). Among these surface modification techniques, anodic treatment not only leads to better corrosion and tribocorrosion resistance through the formation of porous titanium oxide layers, but also improves the interaction of the implant surface

with host tissue by tailoring Ti surfaces in terms of topography, porosity, and composition leading to a better osteointegration (Alves et al., 2013; Ishizawa and Ogino, 1995; Szesz et al., 2013; Teixeira et al., 2015; Fazel et al., 2015). The technique also allows to incorporate Ca and P with a similar Ca/P ratio to hydroxyapatite (HA) which afterwards can be precipitated as crystals by hydrothermal treatment that leads to increase the bioactivity (Benea et al., 2014). There are some studies in the literature showing that it is also possible to modify highly porous Ti surfaces by anodic treatment (Amin Yavari et al., 2014; Teixeira et al., 2015; Fan et al., 2011).

Most of the studies on highly porous Ti were focused on the mechanical behavior, while there is very limited information on the corrosion or wear behavior. Electrochemical studies showed that porosity can alter the corrosion behavior of materials either by localized corrosion due to the trapping of electrolyte species and the exhaustion of oxygen in the small, isolated pores, or by the differences between the nature and the structure of the oxide film formed on the top surfaces and on the inner pore surfaces (Seah and Chen, 1993; Seah et al., 1998; Li et al., 2002; Menini et al., 2006; Xie et al., 2013; Alves et al., 2016).

The limited number of studies performed on the wear behavior of porous metals showed that porosity can have positive or negative effects on the wear behavior of metallic materials. First of all, pores result with decreased real contact area between the sliding surfaces thus increase the contact pressure on the metallic surface where higher effective stress and higher possibility of crack nucleation and propagation can increase the material degradation (Mondal et al., 2009; Hamid et al., 2008; Jha et al., 2011). However, during sliding, depending on their fraction and size, the pores can be filled up by the wear debris, furthermore, the debris can be compacted in the pores under the influence of the applied load. In this case, the real contact area will be increased, consequently, the contact pressure will be decreased that may result in increased wear resistance (Mondal et al., 2009; Jha et al., 2011). On the other hand, under lubricated conditions such as body conditions where body fluids can act as lubricant, pores can act as reservoirs for the body fluids and as a result, may lower the coefficient of friction and increase the wear resistance (Salahinejad et al., 2010).

Although these first attempts made valuable insights to the corrosion and wear behavior of the highly porous metals, it is clear that further studies are needed in order to have a better understanding on their degradation mechanisms. Moreover, the combined action of corrosion and wear, and their synergistic interactions are also needed to be evaluated. However, to the best of our knowledge, there is no study available in the literature on the tribocorrosion behavior of these materials. Thus, the present study aimed to be the first insight to the tribocorrosion behavior of as-processed and anodized Ti having closed and open pores.

2. Materials and methods

2.1. Processing

Highly porous cylindrical Ti samples 12 mm in diameter and 3 mm in height were processed by powder metallurgy with space holder technique using angular shaped Ti powders having average size of 25 μm (Grade 2, Alfa Aesar), angular shaped urea space holder particles under 500 μm (Scharlau), and PVA as binder (Sigma Aldrich Chemistry).

Titanium, urea (30 and 50 vol%) and PVA (0.4 vol%) were mixed using a ball mill rotating with alumina balls at 130 rpm during 4 h. Powder blends were uniaxially pressed in a zinc stearate lubricated nitrided stainless steel die under 350 MPa for 2 min. Green compacts were pre-heated under argon atmosphere at 450 °C during 3 h for binder and space holder removal. Afterwards, the samples were heated up to 1100 °C with 5 °C/min heating rate and sintered during 3 h in horizontal tubular furnace under high vacuum ($< 10^{-5}$ mbar). The
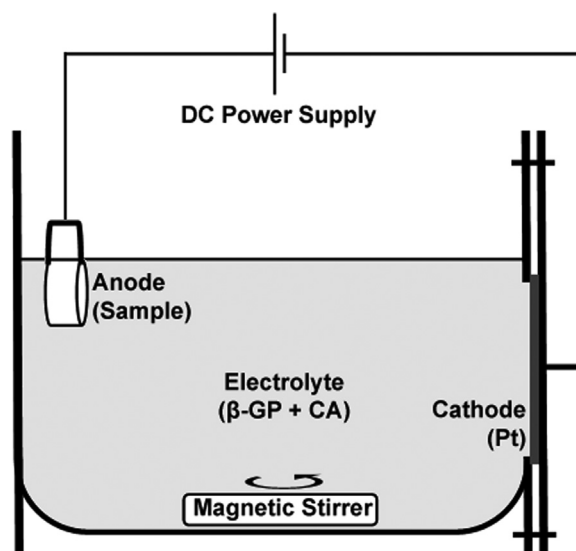

Fig. 1. Schematic representation of the anodic treatment test setup.

binder/space holder removal and sintering temperatures were chosen after differential thermal analysis and thermal gravimetric analysis (DTA/TG), together with dilatometric analysis that had been presented elsewhere (Alves et al., 2016).

2.2. Anodic treatment

The functionalization of the dense and porous samples were realized by anodic treatment using an electrolyte containing 0.02 M of β-glycerophosphate disodium salt pentahydrate (β-GP; Fluka-BioChemika) and 0.35 M of calcium acetate monohydrate (CA; Sigma-Aldrich). This electrolyte was chosen to incorporate bioactive species, namely P (from β-GP) and Ca (from CA). Prior to the treatment, the samples were etched in Kroll's reagent (2 ml HF, 10 ml HNO$_3$, 88 ml H$_2$O) for 1 min. The anodic treatment was performed at room temperature using a DC power supply (GPR-30H10D) under a constant voltage of 300 V during 1 min where all sample (anode) immersed into the electrolyte solution and positioned 8 cm away from a platinum plate that was used as the cathode with an exposed area of 3.39 cm^2. All the anodic treatments were carried out under magnetic stirring at 200 rpm (Fig. 1).

2.3. Tribocorrosion tests

Tribocorrosion tests were performed in a triboelectrochemical cell containing the electrolyte (9 g/L NaCl) and electrodes (Fig. 2). Prior to the tribocorrosion tests, the untreated samples were etched in Kroll's reagent and kept in desiccator for 24 h. For the tribocorrosion tests, the cell was installed on a pin-on-disc tribometer with the working surface area of the samples facing upwards. Zirconia pin 7 mm in diameter having a lower spherical end with 100 mm of radius was used as a counter material and it was mounted vertically above the exposed sample area (1.13 cm^2) where it rotated clockwise over the samples. Open circuit potential (OCP) was monitored before, during and after sliding at room temperature (25 ± 1 °C) using Parstat 2263 potentiostat (Princeton Applied Research). A three-electrode electrochemical cell with an electrolyte volume of 225 ml was used, where a saturated calomel electrode (SCE) was used as the reference electrode, a Pt net was used as the counter electrode, and the samples were used as the working electrode. The OCP was considered stable when ΔE was below 60 mV h^{-1} and the pin was loaded, the sliding started in a unidirectional system with track diameter of 4 mm, frequency of 1 Hz (60 rpm), and total sliding time of 30 min (1800 cycles). The normal load was chosen as 3 N, corresponding to maximum Hertzian contact pressure