



Corrosion behavior of plasma electrolytically oxidized gamma titanium aluminide alloy in simulated body fluid



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HIGHLIGHTS

- Dense PEO coatings with submicron pores can be formed on γ TiAl.
- The corrosion resistance of PEO treated γ TiAl is considerably higher.
- The PEO treatment also reduces localized corrosion to a great degree.

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ABSTRACT

Plasma electrolytic oxidized (PEO) γ TiAl alloy samples were electrochemically characterized by open circuit potential (OCP), cyclic polarization and electrochemical impedance spectroscopy (EIS) to evaluate their corrosion resistance in simulated body fluid (SBF) in order to gauge their potential for biomedical applications. Experimental results through OCP and cyclic polarization studies demonstrated the protective nature and the beneficial effect of the PEO coatings on γ TiAl. The PEO surface increased corrosion resistance of these surface modified alloys. EIS data indicated the presence of an underlying compact oxide layer with surface pores represented by two domes in the Nyquist plots. Electrical equivalent circuits to describe the EIS results are proposed.

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1. Introduction

Although titanium and its alloys have been extensively used for different types of biomedical applications in the last few years [1,2], biocompatibility issues have been widely reported, promoting the quest for newer materials and innovative manufacturing methods principally within the orthopaedic field [3–6]. Corrosion related problems and wear debris leading to metal ion release into the surrounding tissue have affected the useful long term performance of metallic biomaterials [7,8]. Adverse reactions such as inflammation or cytotoxicity in the surrounding tissue and even systemic side effects due to the accumulation of these metallic ions ranging from hypersensitivity to thrombogenesis have also been reported [9,10] resulting eventually in implant loosening and requiring revision surgery which is painful, expensive and usually resulting in a low success rate [1,3]. Currently, the approach to overcome such

drawbacks has mostly been through the application of coatings which are expected to function as a barrier to the aggressive body environment [11,12]. Nonetheless, most of these coating techniques result in poor adherence to the substrate and heterogeneous composition and structure, eventually causing the aforementioned adverse effects [13,14]. To develop materials with a longer life span, the challenge lies in the development of smart materials that mimic the natural biological structure, while promoting a specific response from the surrounding tissue [6,15,16] and concurrently serving as a functional barrier to degradation of the material in the human body environment.

Plasma electrolytic oxidation (PEO) is a technique which involves the modification of a conventional anodic grown oxide film by the application of an electric field greater than the dielectric breakdown field for the oxide [17]. The resulting plasma-chemical reactions contribute to the growth of the coating while local conditions of heat and pressure sinter and anneal the coating, resulting in superior properties [17,18]. Recently, this technique has been successfully applied to Ti6Al4V alloy. Different studies reveal the

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effect of process variables such as current density and electrolyte composition in coating features such as morphology, surface roughness and composition [19–25]. Moreover, different immersion studies have revealed the significant improvement of corrosion and wear resistance, and the beneficial effect of the PEO coatings in terms of biocompatibility [26–31]. Nevertheless, the increasing concern with regard to the cytotoxicity of vanadium ions in Ti6Al4V [32–34] has encouraged the consideration of new titanium alloys that can perform in the highly aggressive environment of the human body [35]. Gamma titanium aluminide (γ TiAl) is an alloy which had shown potential for implantation in the human body [36–38].

The present study intends to address the effect of PEO treated γ TiAl on corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}) and additionally to investigate interactions of these coatings with simulated body fluid in an attempt to predict their behavior in the human body. For comparison purposes, the effect of PEO treatments on Ti6Al4V alloy will also be tested under similar conditions.

2. Materials and methods

2.1. Sample preparation and coating procedure

Both titanium alloys (γ TiAl and Ti6Al4V) were received in the form of 25 mm diameter rods. Electric discharge machining (EDM) was used to obtain 13 mm diameter rods from which 2 mm thick disk shaped samples were cut using a Buehler[®] Isomet slow speed diamond saw. The nominal composition of the γ TiAl alloy is 48% Ti, 48% Al, 2% Cr and 2% Nb, all in atom percent. The γ TiAl alloy rods were produced by hot isostatic pressing of powder material. The composition of Ti6Al4V alloy in weight percentage is 87.73% Ti, 6.85% Al and 5.42% V (ASTM F136 annealed condition). The disks (with a standard nominal area of 1.32 cm² for all subsequent tests) were ground with silicon carbide paper (up to #1200 grit), cleaned ultrasonically with ethanol, rinsed with distilled water and finally dried with an air gun.

For the PEO treatment of the γ TiAl and Ti6Al4V samples, a DC power supply (Hoeffler PS-300, Cambridge, MA) was operated galvanostatically. A stainless steel beaker was used as solution container and cathode while the titanium alloy sample was placed as the anode in the electrolytic cell. The specimen holder was designed to allow complete exposure of the sample to the electrolyte. A calcium and phosphorous rich simulated body fluid (SBF) was used as the electrolyte and prepared as described elsewhere [18], by dissolving high purity reactants Na₂-EDTA (0.12 M), calcium acetate Ca(CH₃COO)₂ (0.075 M), and Ca(H₂PO₄)₂·H₂O (0.025 M) in distilled water. The composition of the electrolyte is given in Table 1. After some preliminary testing to determine the effectiveness of the PEO treatment on the titanium alloys used in this study, current densities and time periods for the PEO process noted in Table 2 were used. In the PEO process, the initial stage corresponds to anodization and as the voltage is increased the oxide layer breaks down and microarcing is observed at which time the PEO process is initiated. At this point, time periods varying from 2 to 5 min were selected to accomplish the PEO process.

Table 1
Chemical composition of Calcium/Phosphorous rich electrolyte.

Reactant	Quantity
Na ₂ -EDTA	44.67 g/L
Calcium acetate Ca(CH ₃ COO) ₂	12.76 g/L
Calcium dihydrogen phosphate Ca(H ₂ PO ₄) ₂ ·H ₂ O	6.3 g/L

2.2. Composition and morphology of PEO coatings

The coatings obtained by PEO were imaged using an SEM (JEOL JSM-5410) to visualize the effect of the process variables on the coating morphology (structure, pore size, etc). Image J software[®] was used to determine average pore diameter for each coating condition. EDS measurements were also carried out to identify the elements present in the oxide layers using the EDAX DX-4 attachment of a JEOL JSM 5800 LV SEM.

2.3. Electrochemical characterization

To evaluate the effect of the process parameters on the electrochemical behavior of the PEO treated titanium alloy substrates, both DC and AC electrochemical techniques were employed. Tests were performed using a GAMRY potentiostat/galvanostat using a three electrode cell (K cell) with a saturated calomel electrode (SCE) as reference in contact with the solution through a bridge tube. Two graphite rods symmetrically positioned with respect to the working electrode were used as counter electrodes. In order to simulate the physiological conditions of human body, SBF solution [36] was used as the electrolyte for all corrosion studies. Prior to the beginning of all electrochemical measurements, the samples were kept in contact with the SBF for 30 min to allow for stabilization of the open circuit potential. Potentiodynamic polarization scans were carried out at a reverse/forward scan rate of 1 mV/s comprising the range from –750 mV to 1500 mV versus open circuit potential.

For electrochemical impedance spectroscopy (EIS) experiments, a sinusoidal potential variation with 10 mV amplitude with respect to the open circuit potential was applied for frequencies ranging from 100 kHz to 1 mHz. A data density of seven points per decade was used. Impedance spectra were represented in both complex impedance diagram (Nyquist plot) and Bode amplitude and phase angle plots. The analysis of the EIS was performed using the Gamry EChem Analyst Software[®], using a simplex fit method to obtain the equivalent electrical circuit model for the substrate–electrolyte during the exposure time. To obtain consistent results, all electrochemical measurements were carried out in triplicate using fresh solution for each experiment.

3. Results

3.1. Characterization of PEO coating

Figs. 1 and 2 correspond to the SEM micrographs of the coatings obtained on γ TiAl and Ti6Al4V respectively. Although the coatings obtained in both alloys exhibit a porous morphology, differences in the pore size diameter are remarkable. In the case of coatings obtained on Ti6Al4V, the pore size measured was between 1.5 and 4 μ m, which is in agreement with previous results for PEO coatings on the same alloy [21,22]. On the other hand, the pores on the γ TiAl coatings are much smaller and range between 250 and 500 nm. In addition, morphological and topographical features were specific for each alloy, as well as for the process parameters used for each treatment. The micrographs obtained for γ TiAl shows a compact layer structure in contrast with the more porous Ti6Al4V samples. Although pore size for each current–time combination for this material also varies, the effect on its distribution through the γ TiAl sample is less evident compared to the results obtained for Ti6Al4V. Details are reported elsewhere [39]. EDS spectra of the coatings formed on γ TiAl and Ti6Al4V (Figs. 3 and 4) display the characteristic peaks of calcium and phosphorous thus implying the feasibility of this technique (under the process parameters applied) to incorporate these elements in the growing oxide matrix of both alloys.

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